

Organosodium and Organopotassium Compounds

Part I: Properties and Reactions [1]

BY DR. M. SCHLOSSER

UNION CARBIDE EUROPEAN RESEARCH ASSOCIATES, BRUSSELS (BELGIUM), AND
ORGANISCH-CHEMISCHES INSTITUT DER UNIVERSITÄT HEIDELBERG (GERMANY) [*]

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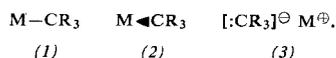
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A. Properties

1. Bond and Polarity

The typical organometallic bond links a saturated, non-polar hydrocarbon residue to a strongly electropositive alkali or alkaline earth metal. The limiting structures (1) and (3) represent the two possible extremes of the state of the bond.



[*] Present address.

[1] For earlier reviews see [1a-1g].

[1a] C. B. Wooster, *Chem. Reviews* 11, 1 (1932).

[1b] G. Wittig, *Angew. Chem.* 53, 241 (1940).

[1c] A. A. Morton, *Chem. Reviews* 35, 1 (1944).

[1d] F. Runge: *Organometall-Verbindungen*. Wissenschaftl. Verlagsgesellschaft, Stuttgart 1944.

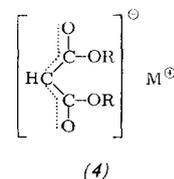
[1e] H. Gilman in: *Organic Reactions (The Metalation Reactions with Organolithium Compounds)*. Wiley, New York 1954, Vol. VIII, p. 258.

[1f] E. G. Rochow, D. T. Hurd, and R. N. Lewis: *The Chemistry of Organometallic Compounds*. Wiley, New York 1957.

[1g] R. A. Benkeser, D. J. Foster, D. M. Sauve, and J. F. Nobis, *Chem. Reviews* 57, 867 (1957).

The actual state (2) of the metal-carbon bond in metal alkyls lies between these two limiting structures. This representation of a covalent, but more or less polarized, bond is intended to indicate that the negative charge is concentrated in the vicinity of the carbon atom.

Two factors contribute to this strong polarization of the bond. One is the high electropositivity of the metal, and the other is the stabilization of the electron pair on the carbon atom which occurs as a result of inductive and mesomeric effects. The mesomeric effects are the more pronounced. Organometallic compounds capable of forming a resonance-stabilized carbanion are mostly present as ion pairs - e.g. malonic ester derivatives (4) - and thus react only with strong electrophiles. The corresponding hydrogenated compounds behave as Brönsted acids.



The incompatibility of carbon and an alkali metal as components of a bond is the reason for the extraordinary reactivity and the unusual reactions exhibited by or-

organoalkali compounds. This incompatibility exists when the organic residue cannot stabilize the negative charge sufficiently. The dependence of the properties of organometallic compounds on the nature of the alkali metal is particularly strong for those with covalent bond character. The increase in electropositivity observed on going from lithium to sodium to potassium is clearly reflected in a striking increase in reactivity. In ionic organometallic compounds, on the other hand, the metal cation does not play an active part [2].

The reactivity is not necessarily directly related to the bond polarity, as indicated by the fact that the electropositivity of the metal, which tends to increase the basicity, and the resonance stabilization of the carbanion, which tends to reduce it, both exert polarizing effects. For example, amylpotassium is more polar and more reactive than amyl-lithium which, in turn, is far more reactive than sodiomalonic ester which is fully ionized.

Although unequivocal, sharp differentiation between true and salt-like organoalkali-metal compounds is not possible, differences in their chemical and physical behavior allow them to be grouped as follows [3]:

Group A: 1. Alkyl-, vinyl-, and aryl-lithium derivatives; 2. Alkyl, vinyl, and aryl derivatives of higher alkali metals.

Group B: 1. Benzylalkali-metal compounds; 2. Alkali-metal derivatives of acidic and highly acidic hydrocarbons; 3. Alkali metal-aromatic complexes and ketyls.

Group C: 1. Metal salts of allylic and cyclopentadienyl compounds; 2. Metal salts of ketones, esters, and nitriles; 3. Metal salts of acetylenes and hydrogen cyanide.

On the basis on this classification, we shall now consider in detail the bond character in organoalkali-metal compounds.

Group A: On passing from organolithium to organic compounds of the higher alkali metals, there are immense changes in properties, even though the electropositivity and the atomic radii increase continuously from lithium to cesium. This unusual behavior is obviously due to the great tendency of lithium compounds to undergo association [4].

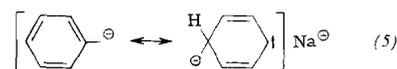
Lithium derivatives are colorless, crystallizable substances that are volatile *in vacuo*. Their solutions in ether are stable at 0°C. Lithium alkyls, with the exception of methyl-lithium, are readily soluble in hydrocarbons. Derivatives of higher alkali metals are also colorless but are not volatile and possess no definite melting points. They are practically insoluble in hydrocarbons and are rapidly decomposed by ethers.

[2] In its ionic form, the alkali metal can, however, also affect the course of reaction. For example, because of its complex-forming cation, lithium hydroxide is a more effective catalyst of the benzilic acid rearrangement than other alkali hydroxides [*W. H. Putterbaugh and W. S. Gaugh, J. org. Chemistry* 26, 3513 (1961)].

[3] Based on a classification used by *K. Ziegler* [*K. Ziegler et al., Liebigs Ann. Chem.* 473, 1 (1929)].

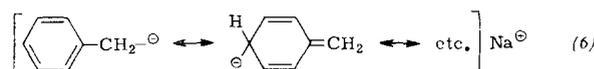
[4] *F. Hein and H. Schramm, Z. physik. Chem. A* 151, 234 (1930); *G. Wittig, F. J. Meyer, and G. Lange, Liebigs Ann. Chem.* 571, 167 (1951); *M. T. Rogers and R. L. Brown, J. physik. Chem.* 61, 366 (1957); *R. West and W. Glaze, J. Amer. chem. Soc.* 83, 3580 (1961); *T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, ibid.* 84, 1371 (1962); *P. A. Fowell and C. T. Mortimer, J. chem. Soc. (London)* 1961, 3793.

This diversity in behavior is often interpreted as indicating that the bond between lithium and an alkyl or aryl group is polarized, yet covalent, whereas all organosodium and organopotassium compounds [*e.g.* the ion pair (5)] are salt-like [5].



This assumption is not consistent with the observation that amylpotassium is more reactive than amylsodium [6]. Dipole measurements cannot be used to investigate the bond character here, because the lithium alkyls and aryls tend to associate [7], and the corresponding sodium and potassium derivatives are insoluble. It is to be hoped that infrared and nuclear resonance spectroscopy will soon provide further insight into the polarity of the organometallic bond.

Group B: All intensely colored alkali derivatives belong to this group. It is apparent that the benzyl group, sometimes substituted, is a common structural characteristic of these derivatives. The gain in energy due to mesomerism according to (6) is so great that the metal-carbon bond is cleaved.



As will be shown below, it appears that all benzylalkali-metal compounds exist as ion pairs. As a result, variation of either the alkali metal (triphenylmethyl-lithium, -sodium, -potassium) or the substituent (benzyl-, dimethylphenyl-, triphenylmethyl-sodium) produces no drastic alterations in properties but rather a series of gradual difference from compound to compound. The decrease in basicity in going from sodium alkyls to benzylsodium is much more pronounced than that resulting from the introduction of a second or third phenyl group capable of resonance. All benzylalkali compounds are soluble and rather stable in ether, although the monophenyl derivatives, in contrast to the polyphenyl compounds [8], are not entirely stable, but cause slow decomposition of the ether [9].

The high dipole moment of triphenylmethylsodium ($\mu = 7.11$ D in dioxan) [10] supports its formulation as an ion pair. The tetramethylammonium salts (7) and (8) possess completely free anions [11].



Any enlargement of the resonance system results in further decrease in basic strength of the anions; the acidity of the corresponding acids increases corre-

[5] *A. A. Morton, Chem. Reviews* 35, 2 (1944).

[6] *H. Gilman and R. V. Young, J. org. Chemistry* 1, 315 (1936); *H. Gilman in: Organic Chemistry*, 2nd Ed., Wiley, New York 1943, Vol. I, p. 520.

[7] *T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, J. Amer. chem. Soc.* 84, 1371 (1962).

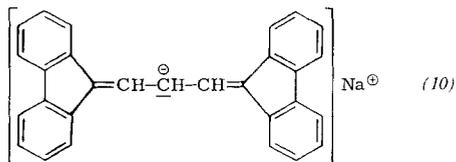
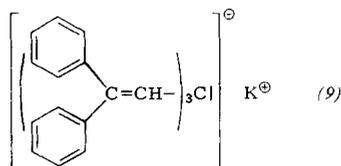
[8] Diphenylmethylsodium is stable towards ether [*W. Schlenk and E. Bergmann, Liebigs Ann. Chem.* 464, 1 (1928)].

[9] *K. Ziegler and O. Schäfer, Liebigs Ann. Chem.* 479, 150 (1930).

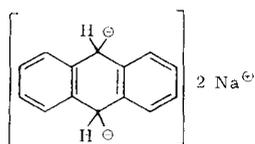
[10] *L. M. Nazarova, Zh. fiz. Khim.* 28, 36 (1954); *Chem. Abstr.* 48, 10396g (1954).

[11] *W. Schlenk and J. Holtz, Ber. dtsch. chem. Ges.* 50, 274 (1917).

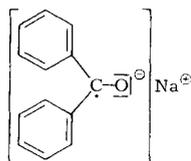
spondingly [12]. Compounds (9) [13] and (10) [14] are salts of acidic and highly acidic hydrocarbons.



The adducts resulting from the addition of an alkali metal onto aromatic compounds, olefins, carbonyl compounds, or azomethines, *e.g.* anthracenedisodium (11) or the sodium ketyl of benzophenone (12), do not possess the reactivity of organometallic compounds [15].



(11)



(12)

Group C: The members of this group, although colorless, have ionic structures similar to that of the benzylic derivatives. Because of the complete delocalization of its free electron pair, the allylic anion (13) shows high resonance stabilization and is similar in this respect to the triphenylmethyl anion.



The anions of enols, esters, and nitriles have considerably less energy because the negative charge encompasses the electronegative hetero-atoms as well. On the other hand, the stability of acetylides and cyanides is not due to mesomerism but to the intrinsic acidity of hydrogens on *sp*-hybridized carbon atoms. Acetylides and cyanides are too weakly basic to be considered as true organometallic compounds.

2. Color and Spectra

No unequivocal correlation has yet been established between the color and the structure of organoalkali compounds. The rule of thumb that benzylic anions are

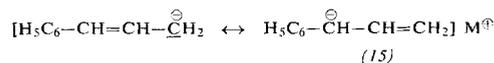
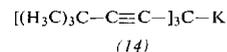
[12] *G. W. Wheland* [J. chem. Physics 2, 474 (1934)] represents the acidity as a linear function of the difference between the energy of conjugation of the hydrocarbon and that of its carbanion.

[13] *G. Wittig* and *H. Kosack*, *Liebigs Ann. Chem.* 529, 167 (1937).

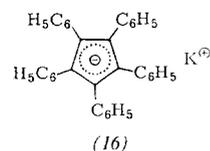
[14] *R. Kuhn*, *Herbert Fischer*, *F. A. Neugebauer*, and *Hans Fischer*, *Liebigs Ann. Chem.* 654, 64 (1962).

[15] *C. B. Wooster*, *Chem. Reviews* 11, 37 (1932); *D. J. Morantz*, and *E. Warhurst*, *Trans. Faraday Soc.* 51, 1375 (1955); *R. O. C. Norman*, *G. A. Thompson*, and *W. A. Waters*, *J. chem. Soc. (London)* 1958, 175.

colored is not without exception. Tris-(3,3-dimethyl-1-butynyl)methylpotassium (14) [16,17] is bright red; metal derivatives of alkyl-substituted styrenes (15) are colorless.

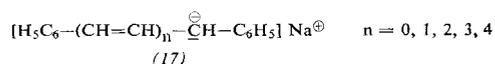


The color phenomena observed are consistent with the following hypothesis: The chromophore is an anion delocalized by resonance. The π -electron system with which the carbanion is in resonance must belong to a hydrocarbon with multiple unsaturation, preferably an aromatic compound. A vinyl group is not sufficient as is indicated by the fact that allylmetal compounds do not absorb in the visible region. An appreciable portion of the negative charge must be transferred to the resonance system. Compound (15) and pentaphenylcyclopentadienylpotassium (16) [18] are colorless, because the probability of residence of the free electron pair in the benzene rings is too low.

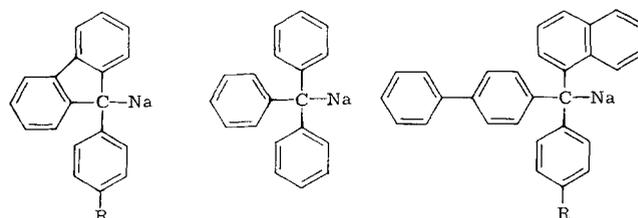


(16)

Any increase in the size of the resonance system causes a shift in absorption toward longer wavelengths. In the case of the polymethine carbanion (17) [19], this shift amounts to 33 $m\mu$ per vinylene group.



The effect of aryl substituents on color was visually established for derivatives (18) through (22) [20].



(18) (orange-red), R = H (20) (red) (21) (blue-purple), R = H
(19) (red), R = OCH₃ (22) (dark-purple), R = C₆H₅

If, as suspected, the color arises from the free resonating carbanion, then the light absorption should be independent of the cation [21]. Identical spectra were in

[16] *W. Schlenk* and *E. Bergmann*, *Liebigs Ann. Chem.* 463, 1 (1928).

[17] *P. L. Salzberg* and *C. S. Marvel*, *J. Amer. chem. Soc.* 50, 1737 (1928).

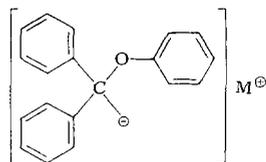
[18] *K. Ziegler* and *L. Ewald*, *Liebigs Ann. Chem.* 473, 163 (1929), p. 192; cf. the purple color of the heptaphenylcycloheptatriene anion [*R. Breslow* and *H. W. Chang*, *J. Amer. chem. Soc.* 84, 1484 (1962)].

[19] *K. Hafner* and *K. Goliash*, *Angew. Chem.* 74, 118 (1962); *Angew. Chem. internat. Edit.* 1, 114 (1962).

[20] *W. Schlenk* and *E. Marcus*, *Ber. dtsh. chem. Ges.* 47, 1664 (1914).

[21] The lighter color of benzyl-lithium compared to benzyl sodium and its greater stability towards ether may be due to a partially covalent C-Li bond.

fact obtained for the lithium-, sodium-, and potassium-substituted benzhydryl ethers (23). The Lambert-Beer law is satisfied [22].

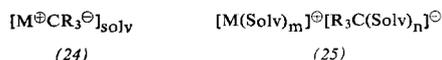


(23), M = Li, Na, K

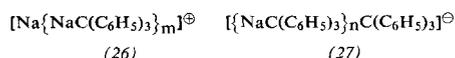
The infrared absorption of allylic anions [23] and the electron-spin resonance of benzophenone ketyls [24] are also independent of the alkali metal. On the other hand, the infrared spectra of phenyl-lithium, phenylsodium, and phenylpotassium show not only common bands but also bands whose positions depend on the alkali metal [25, 26]. One of these groups of bands was tentatively assigned to the carbon-metal bond [26]; for another [25], a linear dependence on the reduced mass of the metal atom was established. These infrared spectroscopic data provide support for the argument that strongly polarized, yet still covalent, organometallic bonds exist in compounds of group A.

3. Electrical Conductivity and Electrolysis

Because of their small dielectric constants, ordinary nonpolar solvents do not separate a salt into individual ions. This can be demonstrated, for example, by measurements of the electrical conductivity. Thus, in ether, the carbon-metal bond in group B and group C compounds is fully ionized as the internal ion pair (24), but by no means dissociated into a solvent-separated ion pair (25). In (24), the alkali cation and the carbanion are held together by electrostatic attraction and are surrounded by a common solvent shell. Not even benzophenone ketyls are dissociated in 1,2-dimethoxyethane, as is indicated by ESR measurements [24].



Triphenylmethylsodium has a low conductivity which vanishes with decreasing concentration [20]. A 0.005 M solution of triphenylmethylpotassium in ether is essentially non-conducting [27]. This phenomenon is plausibly explained by the following transport mechanism [20]: Free cations and anions, incapable of existing in ether, add on triphenylmethylsodium affording the complex ions (26) and (27). The conductivity of lithium iodide in ether is also very low and that of the sodium salt of acetophenone is immeasurably small [27].



In strongly solvating media such as ammonia, pyridine, or dimethyl sulfoxide, triphenylsodium and triphenylmethyl-

[22] G. Wittig and E. Stahnecker, *Liebigs Ann. Chem.* 605, 69 (1957).

[23] E. J. Lanpher, *J. Amer. chem. Soc.* 79, 5578 (1957).

[24] P. B. Ayscough and R. Wilson, *Proc. chem. Soc. (London)* 1962, 229.

[25] M. Margoshes and V. A. Fassel, *Spectrochim. Acta* 7, 14 (1955).

[26] E. J. Lanpher, *J. org. Chemistry* 21, 830 (1956).

[27] D. C. Hill, J. Burkus, S. M. Luck, and C. R. Hauser, *J. Amer. chem. Soc.* 81, 2787 (1959).

potassium have identical equivalent conductivities, which are inversely proportional to the concentration, and are as large as those of strong inorganic electrolytes [28].

Organoalkali-metal compounds of group A are apparently all non-conductors [29]. Earlier statements to the contrary are, without exception, based on electrolyses in which a zinc dialkyl was used as solvent. Under these conditions, however, the conductivity is due to the formation of a complex $M(\text{ZnR}_3)$ [30].

Ziegler [31] recently worked out an industrially interesting synthesis of tetraethyl-lead which is based on the electrolysis of such an $M(\text{ZnR}_3)$ complex. Sodium tetraethylaluminum, which behaves chemically as a mixture of ethylsodium and triethylaluminum, is subjected to electrolysis with a mercury cathode and a lead anode, the latter reacting with the ethyl radicals. Tetraethyl-lead distills off along with triethylaluminum. The ethylsodium consumed is regenerated by the reaction of the sodium liberated at the cathode with hydrogen and ethylene; the overall reaction is thus as follows:

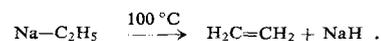


4. Configurational and Structural Stability

Until now, the studies carried out on optically active lithium alkyls [32], lithium cyclopropyl derivatives [33], and geometrically isomeric vinyl-lithium derivatives [34] have not been extended to the corresponding sodium and potassium derivatives.

Optically active carbanions have been detected as short-lived intermediates in base catalysed deprotonations of hydrocarbons and sulfones, in the cleavage of secondary alkoxides and in the decarboxylation of carboxylic acids. Neutralization proceeds with retention, inversion, or racemization, depending on the protonating solvent applied [35].

Organometallic compounds with β -hydrogens undergo thermal decomposition with particular ease. Ethylsodium [36] decomposes mainly as follows:



Higher homologues *e.g.* propylsodium [37] and amylsodium [38], also decompose gradually at room temperature, and rapidly between 50 and 100°C. In addition to the olefin, this process usually yields the saturated hydrocarbon as a by-product; in some instances it even becomes the major product. An interpretation of this thermal decomposition in terms of a free-radical

[28] K. Ziegler and H. Wollschitt, *Liebigs Ann. Chem.* 470, 123 (1930).

[29] For example, fused ethyl-lithium is not electrically conductive (G. E. Coates: *Organo-Metallic Compounds*, Wiley, New York 1956, p. 7).

[30] G. Wittig, F. J. Meyer, and G. Lange, *Liebigs Ann. Chem.* 571, 167 (1951); G. Wittig, *Angew. Chem.* 70, 65 (1958).

[31] K. Ziegler, *Angew. Chem.* 72, 565 (1960).

[32] R. L. Letsinger, *J. Amer. chem. Soc.* 72, 4842 (1950).

[33] H. M. Walborsky and F. J. Impastato, *J. Amer. chem. Soc.* 81, 5835 (1959); D. E. Applequist and A. H. Peterson, *ibid.* 83, 863 (1961).

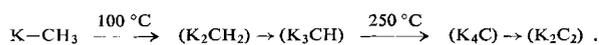
[34] D. Y. Curtin and W. J. Koehl, *J. Amer. chem. Soc.* 84, 1967 (1962).

[35] Review: G. Köbrich, *Angew. Chem.* 74, 453 (1962); *Angew. Chem. internat. Edit.* 1, 382 (1962).

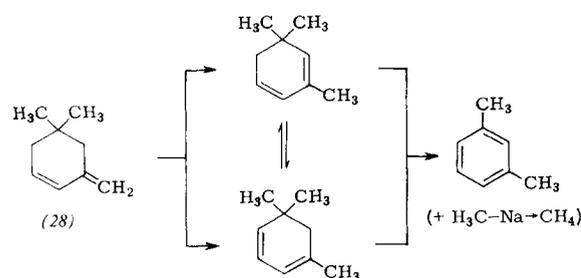
[36] W. H. Carothers and D. D. Coffman, *J. Amer. chem. Soc.* 51, 588 (1929); 52, 1254 (1930).

[37] R. L. Letsinger and D. F. Pollart, *J. Amer. chem. Soc.* 78, 6079 (1956).

reaction [38] was proved by *Bryce-Smith* [39] to be incorrect. For example, decomposition in the presence of cumene affords no 2,3-diphenyl-2,3-dimethylbutane. It is possible that the alkane formation is due to a disproportionating autometalation [36] of the alkylsodium [40]. Methylsodium decomposes at 200 °C into methane, sodium, and sodium carbide. The thermolysis of methylpotassium, although vigorous at 100 °C, goes to completion only at 250 °C. This suggests the formation of thermally more stable intermediates [36,41]:



Neopentylsodium is also devoid of β -hydrogens. Its decomposition at 144 °C gives, in addition to resins, 17% neopentane, 8% methane, 45% methylsodium, and 0.5% *i*-butenylsodium [42]. Obviously, a β -elimination of methylsodium is involved, as was observed for the base-catalysed rearrangement of 1,1,3-trimethylcyclohexadienes (28) to *m*-xylene [43].



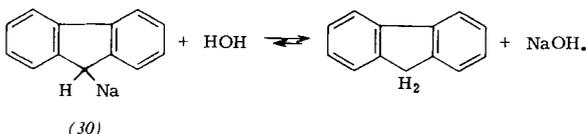
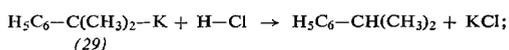
B. Replacement of the Metal by Hydrogen

1. Neutralization with Compounds Containing Active Hydrogen

Suitable coreactants for organoalkali compounds, regardless of their bond polarity, are X-Y compounds in which Y can become an anion and X is capable of neutralizing the latent or free carbanion by the formation of a stable, covalent bond.



In the simplest case, X is hydrogen and Y an acid anion:



[38] *A. A. Morton and E. J. Lampher, J. org. Chemistry* 21, 93 (1936).

[39] *D. Bryce-Smith, J. chem. Soc. (London)* 1955, 1712.

[40] On the other hand, the photolytic decomposition of organoalkali-metal compounds seems to proceed by a radical process [cf. [22]] as well as *H. Linschitz, M. G. Berry, and D. Schweitzer, J. Amer. chem. Soc.* 76, 5833 (1954).

[41] The isolation of methylenedilithium, Li_2CH_2 , after mild thermolysis of methyl-lithium has been accomplished [*K. Ziegler, K. Nagel, and M. Patheiger, Z. anorg. allg. Chem.* 282, 345 (1955); *Chem. Abstr.* 52, 1203h (1958)].

[42] *R. A. Finnegan, Chem. and Ind.* 1962, 895.

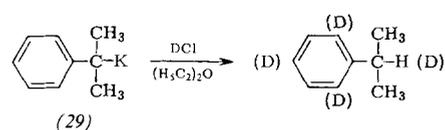
[43] *H. Pines and H. E. Eschinazi, J. Amer. chem. Soc.* 78, 5950 (1956).

In the third example, the neutralization of a weak organometallic base (30) with a weak proton donor (H_2O), an equilibrium is observed that is shifted to the right [44].

2. Neutralization with Compounds Containing Active Deuterium

On neutralization with heavy water, the metal is replaced by deuterium; thus, a hydrocarbon labelled in a specific position is obtained.

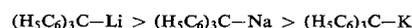
This selectivity is not observed with carbanions with delocalized negative charge. Phenylisopropylpotassium (29) reacts with deuterium chloride in ether to afford cumene in which 69% of the α -, 5% of the *ortho*-, and 15% of the *para*-positions are substituted by deuterium. Mass spectrograms indicate that 58% of the product are monodeuterated, 14% dideuterated, and 1% tri-deuterated; 14% contain no deuterium [45].



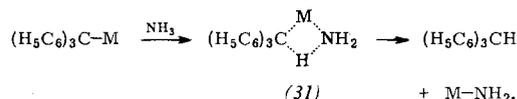
Heavy water [45], carbon dioxide, and dimethyl sulfate [46], on the other hand, attack (29) exclusively at the α -position. Even deuterium chloride effects only α -substitution when the more polar solvent 1,2-dimethoxyethane or pentane (in heterogeneous phase) is used instead of ether [45].

3. Aminolysis

A "reverse" order of reactivity has been established for the reactions of triphenylmethylalkali-metal compounds with ammonia or piperidine yielding triphenylmethane and alkali amide [47,48]:



This may be due to the greater tendency of the lower alkali metals to form complexes, which might promote the formation of an intermediate (31) [48].



4. Hydrogenolysis

Molecular hydrogen cleaves organometallic compounds into hydrocarbons and metal hydrides. Whereas the hydrogenolysis of organolithium compounds [49] pro-

[44] *R. Weissgerber, Ber. dtsh. chem. Ges.* 34, 1659 (1901).

[45] *G. A. Russell, J. Amer. chem. Soc.* 81, 2017 (1959).

[46] *K. Ziegler and B. Schnell, Liebigs Ann. Chem.* 437, 227 (1934).

[47] *C. R. Hauser, D. S. Hoffenberg, W. H. Putterbaugh, and F. C. Frostick, J. org. Chemistry* 20, 1531 (1955).

[48] *G. Wittig, Experientia* 14, 389 (1958).

[49] *H. Gilman, A. L. Jacoby, and H. Ludeman, J. Amer. chem. Soc.* 60, 2336 (1938).

ceeds smoothly only under pressure, potassium derivatives [50] react quite readily even under normal conditions. For example:



5. Metalations

Pure hydrocarbons also act as proton donors for organometallic compounds. Reactions in which a new organometallic base is produced by replacement of organic hydrogen with a metal atom from another organometallic base are called "metalations" [51]; the term "anionization" denotes proton abstraction from distinctly acidic reactants such as inorganic acids, alcohols, enols, esters, or nitriles. In metalations, as in other acid-base reactions, the weaker organometallic base and the less acidic hydrocarbon are generally produced:



For sodium and potassium compounds, the differences in acidity can be rather small. Thus, phenyl-lithium is a poor metalating agent even for triphenylmethane, whereas phenylpotassium reacts readily with toluene.

Table 1 gives a list of several representative hydrocarbons, and Table 2 of a few amines and alcohols, arranged according to their acidic strengths [52a–52d].

Table 1. Acid strengths of acidic hydrocarbons.

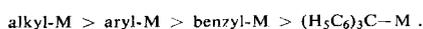
Proton donor	pK _a
R ₃ CH (R=H, alkyl)	40 [*]
H ₂ C=CH ₂	39 [*]
C ₆ H ₆	39 [*]
H ₃ C-CH(CH ₃) ₂	37
H ₃ C-CH ₃	37
H ₂ C=CH-CH ₃	37 [*]
(H ₅ C ₂) ₂ CH ₂	35
(H ₅ C ₆) ₃ CH	33
Fluorene	25
Indene	21
H ₃ C ₆ -C≡C-H	21

[*] Extrapolated values.

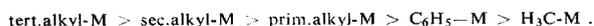
Table 2. Acid strength of amines and alcohols.

Proton donor	pK _a
NH ₃	36
H ₃ C-NH ₂	27
(H ₅ C ₆) ₂ NH	23
(H ₅ C ₃)COH	19
H ₃ COH	16

In accordance with experimental results, the following order of basic strengths for organosodium and organopotassium compounds can be derived from Table 1:



The more subtle differences established for organolithium compounds are probably also applicable to the higher alkali metals:



[50] K. Clauss and H. Bestian, *Liebigs Ann. Chem.* 654, 8 (1962).

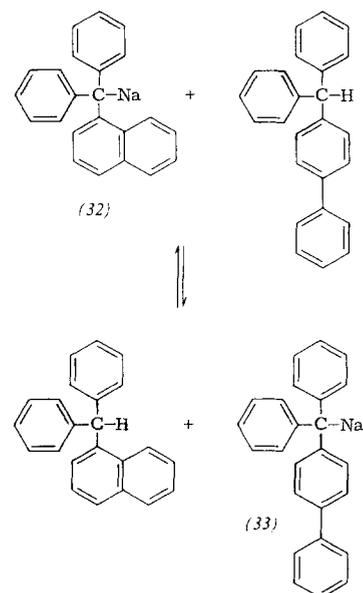
[51] H. Gilman and G. F. Wright, *Chem. Reviews* 11, 1323 (1932). – It is not possible to differentiate sharply between metalation and anionization, in view of the gradual transition from strong to weak organometallic bases.

[52a] J. B. Conant and G. W. Wheland, *J. Amer. chem. Soc.* 54, 1212 (1932).

[52b] W. K. McEwen, *J. Amer. chem. Soc.* 58, 1124 (1936).

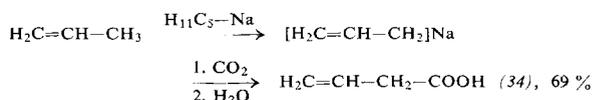
[52c] A. Streitwieser, *Tetrahedron Letters* 1960, No. 6, 23.

If the hydrocarbons involved in an acid-base reaction are nearly equal in acidity, an equilibrium will result which for potassium derivatives is attained within a few hours and for sodium derivatives [(32) ⇌ (33)] only after one month [52a].

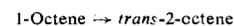
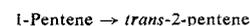


a) Allylic Compounds

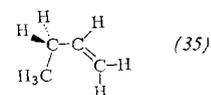
Propylene reacts readily with amylsodium to afford the allyl anion, which can be characterized by carboxylation to give vinylacetic acid (34); in addition, 15% of a dicarboxylic acid formed by dimetalation is obtained [53].



The isomerization of olefins discovered by Morton [54] is promoted by catalytic amounts of organometallic compounds and proceeds by way of such allylic anions:



The double-bond shift can be followed readily in reactions catalyzed with potassium *t*-butoxide in dimethyl sulfoxide [55]. Thus 1-butene first yields mainly *cis*-2-butene, which then slowly rearranges to the thermodynamically more stable isomer *trans*-2-butene. Apparently, the removal of a proton from a conformation such as (35), resulting in a *cis*-anion and a *cis*-olefin, is particularly easy.



[52d] Cf. the new, more extensive list of pK_a values compiled by D. J. Cram, *Chem. Engng. News* 41, No. 33, p. 93 (1963).

[53] A. A. Morton and M. E. T. Holden, *J. Amer. chem. Soc.* 69, 1675 (1947).

[54] A. A. Morton and E. J. Lanpher, *J. org. Chemistry* 20, 839 (1955).

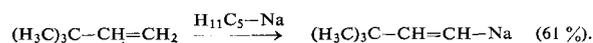
[55] A. Schriesheim and C. A. Rowe, *Tetrahedron Letters* 1962, 405.

b) Benzylic Compounds

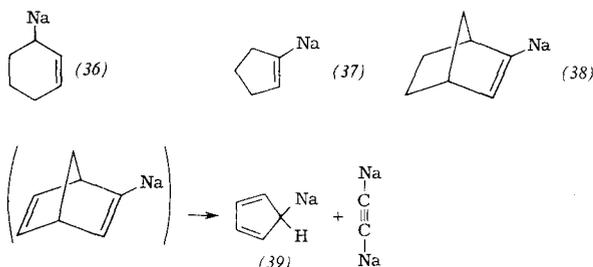
Amylsodium metalates toluene instantaneously to give benzylsodium [56]. Phenylsodium is less basic and therefore reacts quantitatively with toluene only on prolonged boiling, whereas the reaction with diphenyl- and triphenylmethane occurs in the cold. The reaction of amylsodium with ethylbenzene is slower than that with toluene. In the reaction of amylsodium with cumene substitution no longer takes place at the sterically protected α -position but instead, preferentially at the more readily available ring hydrogens (55% *meta*, 42% *para*). Benkeser [57] differentiates between kinetically and thermodynamically controlled reactions. Thus, after 3 hours' treatment with amylopotassium, cumene gives 42% α -, 39% *meta*-, and 19% *para*-metalated product; however, a 20 hour reaction period affords exclusively phenylisopropylpotassium.

c) Olefins

The acidity of a C-H bond increases with increasing s-character ($sp > sp^2 > sp^3$) [58]. Accordingly, alkali alkyls replace an olefinic hydrogen by a metal atom, provided that, as in ethylene [59] or 3,3-dimethyl-1-butene [59], more readily metalated allylic hydrogens are absent.



Ring strain also enhances the s-character of exocyclic bonds. Whereas cyclohexene and amyloxy sodium interact to form an allylic anion (36), cyclopentene [60], norbornene [61], and norbornadiene [62] undergo metalation with increasing ease to the derivatives (37), (38), and (39), respectively [63a,63b], with ring opening in the last case.



[56] A. A. Morton and I. Hechenbleikner, J. Amer. chem. Soc. 58, 2599 (1936).

[57] R. A. Benkeser and T. V. Liston, J. Amer. chem. Soc. 82, 3221 (1960).

[58] Cf. F. Bohlmann, Angew. Chem. 69, 82 (1957).

[59] A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, J. Amer. chem. Soc. 72, 3785 (1950).

[60] A. A. Morton and R. A. Finnegan, J. Polymer Sci. 38, 19 (1959).

[61] R. A. Finnegan and R. S. McNees, Chem. and Ind. 1961, 1450.

[62] R. A. Finnegan and R. S. McNees, Tetrahedron Letters 1962, 755.

[63a] Cf. A. Streitwieser and R. A. Caldwell, J. org. Chemistry 27, 3360 (1962).

[63b] G. Schröder, personal communication; studies on base-catalysed deuterium exchange have confirmed the cited increase in acidity.

The olefinic hydrogen in 2,3,3-trimethyl-1-cyclopropene [64] is nearly as active as the hydrogen in acetylene; hence, it is replaced even with methyl-lithium. Cyclopropane [65] reportedly reacts with amyloxy sodium to give cyclopropylsodium [66].

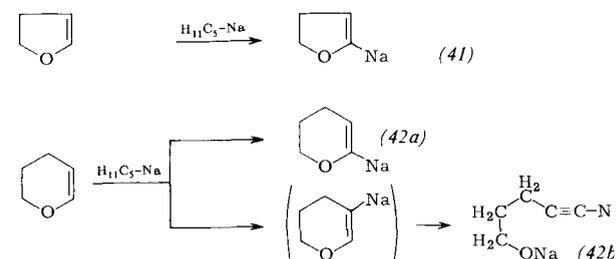
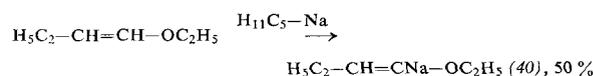
d) Aromatic Compounds

Benzene hardly reacts with n-butyl-lithium [67] but is metalated by amyloxy sodium at elevated temperatures to give a 90% yield of phenylsodium; a small amount of phenylenedisodium is formed as by-product. *m*-Phenylenedisodium is reportedly obtained in 85% yield if benzene is used in less than the stoichiometric amount [68].

The acidity of polyphenyls and naphthalene differs only slightly from that of benzene. These hydrocarbons, therefore, cannot be metalated at all or only to a slight extent [69,70]. The reaction of naphthalene with amyloxy sodium produces a mixture of the α - and β -isomers of mono-, di-, and trimetalated products [71].

e) Heterosubstituted Olefins and Heterocycles

Because of the electron attraction of the hetero-atom, metalation of vinyl ethers involves the alpha rather than the allylic hydrogen, leading for example, to (40), (41), (42a), and (42b) [72].



In the case of dihydropyran, the formation of the stable α -metalated derivative is accompanied by a ring opening promoted by β -metalation. The pseudoaromatic furan

[64] G. L. Closs and L. E. Closs, J. Amer. chem. Soc. 83, 1003 (1961).

[65] For information concerning the unsaturated character of cyclopropane, see H. A. Staab: Einführung in die theoretische organische Chemie. Verlag Chemie, Weinheim 1959, p. 54; and E. Vogel, Fortschr. chem. Forsch. 3, 430 (1955).

[66] E. J. Lanpher, L. M. Redmen, and A. A. Morton, J. org. Chemistry 23, 1370 (1958).

[67] R. V. Young, Iowa State Coll. J. Sci. 12, 177 (1937); quoted from H. Gilman and J. W. Morton in: Organic Reactions. Wiley, New York 1954, Vol. VIII, p. 265.

[68] A. A. Morton, E. L. Little, and W. O. Strong, J. Amer. chem. Soc. 65, 1339 (1943); cf. D. Bryce-Smith and E. E. Turner, J. chem. Soc. (London) 1953, 861.

[69] A. A. Morton, J. T. Massengale, and G. M. Richardson, J. Amer. chem. Soc. 62, 126 (1940).

[70] H. Gilman and R. L. Bebb, J. Amer. chem. Soc. 61, 109 (1939).

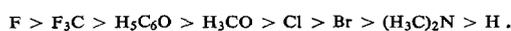
[71] A. A. Morton, J. B. Davidson, T. R. P. Gibb, E. L. Little, E. W. Clarke, and A. G. Green, J. Amer. chem. Soc. 64, 2250 (1942).

[73, 74] and thiophene [75] undergo substitution of the α -hydrogens by metal with surprising ease. With excess amylsodium, both heterocycles give the 2,5-dimetallated derivatives, thiophene reacting more readily than furan [76].

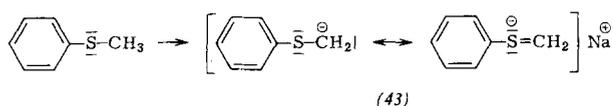
f) Heterosubstituted Aromatic Compounds

More remote hydrogens can also be activated by electronegative hetero-atoms, albeit to a lesser extent. This activation accounts for the ease of metalation of *ortho*-hydrogens in aryl halides, aryl ethers, and benzotri-fluoride [77].

The ability of ring hydrogens to undergo metalation is strongly enhanced by hetero-atoms of the first period which obey the octet rule, indicating inductive effects. Substituents can be arranged in the order of their acidifying effect, as follows:

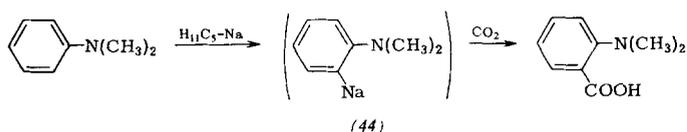


Anisole [56, 70], diphenyl ether [78], and diphenyl sulfide [70] are metalated in the *ortho*-position. With methyl phenyl sulfide, the side chain is more reactive because the d-orbitals of the sulfur participate in the resonance (43) [79].



The behavior of dibenzothiophene is similar to that of the acyclic diphenyl sulfide, *i.e.* it is metalated by strong organometallic compounds in one of the two *ortho*-positions [70]. The *ortho*-positions in dibenzofuran are far more activated. This compound is attacked even by methyl-lithium, and benzylsodium, a relatively weak base, converts it into the *o,o'*-disodio derivative in 80 % yield [80].

Aniline [81] and its derivatives [56, 70, 82] are also metalated in the *ortho*-position [*e.g.* (44)].



[72] R. Paul and S. Tchelitcheff, C. R. hebd. Séances Acad. Sci. 235, 1226 (1952); Bull. Soc. chim. France, Documentat. 19, 808 (1952).

[73] H. Gilman and F. Breuer, J. Amer. chem. Soc. 56, 1123 (1934).

[74] A. A. Morton and J. T. Massengale, J. Amer. chem. Soc. 65, 1346 (1943).

[75] J. W. Schick and H. D. Hartough, J. Amer. chem. Soc. 70, 286 (1948).

[76] A. A. Morton and C. E. Claff, J. Amer. chem. Soc. 76, 4935 (1954).

[77] J. D. Roberts and D. Y. Curtin, J. Amer. chem. Soc. 68, 1658 (1946).

[78] A. Lüttringhaus and G. v. Sääf, Angew. Chem. 52, 578 (1939); Liebigs Ann. Chem. 542, 241 (1939).

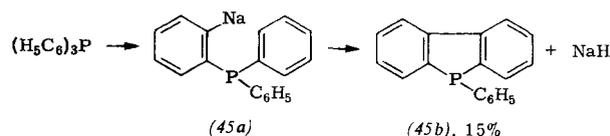
[79] H. Gilman and F. J. Webb, J. Amer. chem. Soc. 71, 4062 (1949).

[80] H. Gilman, F. W. Moore, and O. Baine, J. Amer. chem. Soc. 63, 2479 (1941).

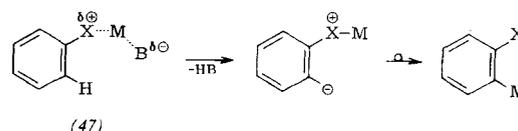
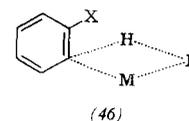
[81] A. A. Morton and R. L. Letsinger, unpublished data; taken from [1c]; cf. also [82].

[82] H. Gilman, G. E. Brown, F. J. Webb, and S. M. Spatz, J. Amer. chem. Soc. 62, 977 (1940).

Under drastic conditions, *n*-butyl-lithium slowly attacks triphenylamine [83], triphenylphosphine [84], and triphenylarsine [85] at the *meta*-position. At 70 °C, phenylsodium converts triphenylphosphine into diphenylenephenylphosphine (45b) [86] presumably by intramolecular elimination of sodium hydride from the *ortho*-metalated form (45a). The *meta*-metalated compound formed undergoes subsequent hydrolytic decomposition.



The seeming randomness with which organometallic bases bring about metal-hydrogen exchange – sometimes in the *ortho*- and sometimes in the *meta*-position – has prompted extensive discussions of the underlying mechanism. The interpretation of metalation as an electrophilic reaction [87] or as a free-radical process [88] is obsolete. It is now known that the reaction occurs by a nucleophilic, or more correctly, a protophilic [89], attack by the base. According to the concept developed by Huisgen [90], the process has a concerted mechanism (F 2) involving a four-centered transition state (46) and does not entail an associated precursor (47) [77].



g) Eliminations Leading to Arynes

Studies involving trapping and symmetrizing reactions have demonstrated the striking readiness with which *ortho*-metalated aryl halides [91–93] release the oppositely polarized substituent and thus afford arynes such as dehydrobenzene (48), which cannot be isolated as such.

[83] H. Gilman and G. E. Brown, J. Amer. chem. Soc. 62, 3208 (1940).

[84] H. Gilman and G. E. Brown, J. Amer. chem. Soc. 67, 824 (1945).

[85] H. Gilman and C. G. Stuckwisch, J. Amer. chem. Soc. 63, 3532 (1941).

[86] G. Wittig and G. Geissler, Liebigs Ann. Chem. 580, 50 (1953). An analogous ring closure leading to dibenzothiophene had been accomplished previously by A. Lüttringhaus, G. Wagner, G. v. Sääf, E. Sucker, and G. Borth, Liebigs Ann. Chem. 557, 54 (1947).

[87] A. A. Morton, Chem. Reviews 35, 23 et seq. (1944); J. Amer. chem. Soc. 69, 969 (1947).

[88] A. A. Morton, C. E. Claff, and F. W. Collins, J. org. Chemistry 20, 428 (1955).

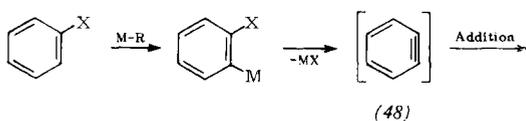
[89] D. Bryce-Smith, J. chem. Soc. (London) 1954, 1079; D. Bryce-Smith, V. Gold, and D. P. N. Satchell, *ibid.* 1954, 2743.

[90] R. Huisgen, Angew. Chem. 72, 100 (1960).

[91] G. Wittig, Naturwissenschaften 30, 699 (1942); Angew. Chem. 69, 245 (1957).

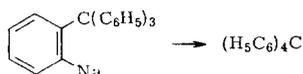
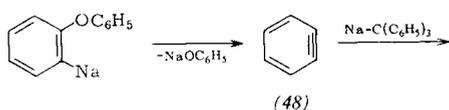
[92] E. F. Jenny, M. C. Caserio, and J. D. Roberts, Experientia 14, 349 (1958).

[93] R. Huisgen in H. Zeiss: Organometallic Chemistry. Reinhold Publ. Corp., New York 1960, p. 36 et seq.



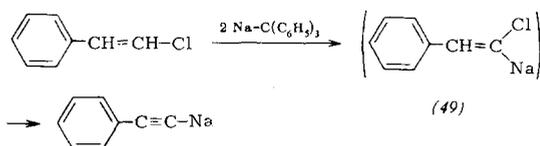
The metalating agents most frequently used in investigations of arynes were organolithium reagents and lithium amide [94]. However, intermediate formation of *o*-phenylene in the reaction of amylsodium with chlorobenzene was already discussed by *Morton* [95] in order to explain the formation of triphenylene and amylbenzene.

o-Halogenophenylalkali-metal compounds lose alkali halide even below -50°C . *ortho*-Metalated diarylethers eliminate phenoxide ion only on heating, because of the stronger bond between the aryloxy group and the ring. The elimination of this group as an anion is facilitated by a high electron density at the adjacent position. For this reason, *o*-phenoxyphenylsodium decomposes at 60°C faster than *o*-phenoxyphenyl-lithium [96,97]. The dehydrobenzene (48) formed can be trapped *in situ* with triphenylmethylsodium [96].



h) Eliminations Leading to Acetylenes

Acyclic acetylenes are lower in energy than the arynes which have a strained triple bond [98]. Accordingly, metalated intermediates could not yet be detected in the dehydrohalogenation of vinyl chlorides with organosodium reagents [99]. The analogous metalation of vinyl ethers and model reactions [100], however, suggest primary attack on the α -hydrogen with formation of (49).



i) Eliminations Leading to Carbenes

The carbenes [101], like the arynes, are short-lived electrophiles that are extremely rich in energy and can

[94] Particular attention is called to the studies of *R. Huisgen* et al., *Chem. Ber.* 92, 192 (1959); 93, 412 (1960).

[95] *A. A. Morton, J. B. Davidson, and B. L. Hakon*, *J. Amer. chem. Soc.* 64, 2242 (1942).

[96] *A. Lüttringhaus and K. Schubert*, *Naturwissenschaften* 42, 17 (1955); *A. Lüttringhaus and H. Schuster*, *Angew. Chem.* 70, 438 (1958).

[97] *G. Wittig and L. Pohmer*, *Chem. Ber.* 89, 1334 (1956).

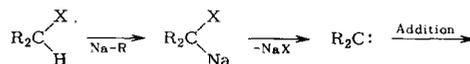
[98] With regard to the nature of the aryne bond see *R. Huisgen*, *Angew. Chem.* 72, 107 (1960).

[99] *G. Wittig and H. Witt*, *Ber. dtsch. chem. Ges.* 74, 1474 (1941); *G. Wittig and G. Harborth*, *ibid.* 77 B, 306, 315 (1944); *G. Wittig and M. Schlosser*, unpublished work.

[100] *S. J. Cristol and R. S. Bly*, *J. Amer. chem. Soc.* 83, 4027 (1961).

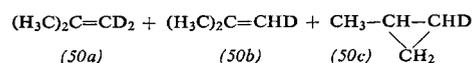
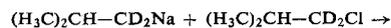
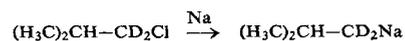
[101] Reviews: *W. Kirmse*, *Angew. Chem.* 71, 537 (1959); 73, 161 (1961).

hence be detected only by means of trapping reactions. The organometallic precursors of the carbenes are obtained by α -metalation of heterofunctional aliphatics and bear on the same carbon oppositely polarized substituents which are released by α -elimination.



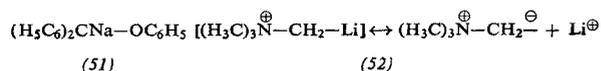
Haloforms [102] and α -chloroalkyl thioethers [103] are sufficiently acidic to be metalated even by alkoxides. On the other hand, the introduction of a metal into α -chloroalkyl ethers [104], dihalogenomethanes [105], and particularly alkyl halides requires the strongest organometallic bases. Thus, methylene is reported to be formed by action of phenylsodium on methyl chloride and to add on in the nascent state to cyclohexene affording norcaradiene in 1% yield [106].

Kirmse and *Doering* [107] used isotope techniques and collected valuable information concerning the reaction of sodium with primary, secondary, or tertiary butyl halides. Following α -elimination, the carbene is stabilized by either a hydride shift (50b) or cyclopropane ring closure (50c); β -elimination to yield (50a) also occurs, but no γ -elimination.



α -Elimination increases when potassium is used in place of sodium but is negligibly small with lithium.

Carbene precursors with sodium and chlorine on the same carbon are unstable even at very low temperatures. Replacement of the halogen by a poorer leaving group makes it possible to trap the metalated carbene precursor, for example (51) and (52).



In tetrahydrofuran or 1,2-dimethoxyethane, (51) undergoes isomerization to triphenylmethoxide (Wittig rearrangement). In ether or petroleum ether, decomposition to diphenylcarbene and phenoxide seems to occur [22, 108].

[102] *J. Hine, J. Amer. chem. Soc.* 72, 2438 (1950); *J. Hine, R. C. Peck, and B. D. Oakes*, *ibid.* 76, 827 (1954); *W. v. E. Doering and A. K. Hoffmann*, *ibid.* 76, 6162 (1954).

[103] *U. Schöllkopf and G. J. Lehmann*, *Tetrahedron Letters* 1962, 165.

[104] *U. Schöllkopf, A. Lerch, and W. Pitteroff*, *Tetrahedron Letters* 1962, 241.

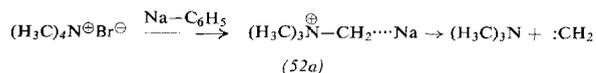
[105] *G. L. Closs and L. E. Closs*, *J. Amer. chem. Soc.* 81, 4996 (1959).

[106] *L. Friedman and J. G. Berger*, *J. Amer. chem. Soc.* 82, 5758 (1960).

[107] *W. Kirmse and W. v. E. Doering*, *Tetrahedron* 11, 266 (1960); cf. *L. Friedman and J. G. Berger*, *J. Amer. chem. Soc.* 83, 492, 500 (1961); *P. S. Skell and A. P. Krapcho*, *ibid.* 83, 754 (1961); and [95].

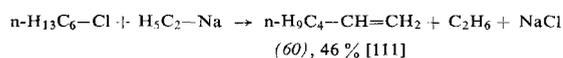
[108] Cf. *U. Schöllkopf and M. Eisert*, *Angew. Chem.* 72, 349 (1960).

The function of the organometallic bond as an electron reservoir becomes manifest in the cleavage of nitrogen ylides (52). Ylides prepared with phenyl-lithium or in the presence of lithium salts are stable [109]; more electropositive metals, *e.g.* Na (52a), promote cleavage of the ylides into amine and carbene [109a]. Sulfonium ylides are unstable and decompose similarly [110a, 110b].



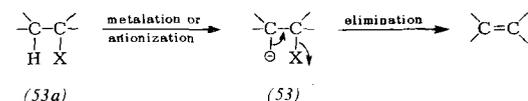
k) Eliminations Leading to Olefins

The reaction of organometallic compounds with alkyl halides yields carbenes or, as will be discussed later, results in either halogen-metal exchange or condensations leading to hydrocarbons. If the prerequisites for one of these three types of reaction are not entirely satisfied, concurrent β -elimination occurs and may often become the main reaction, *e.g.* as with (60).

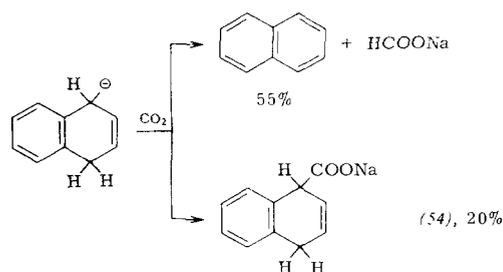


β -Eliminations [112] take place by either the carbanion or the concerted mechanism.

The characteristic of the carbanion mechanism (E 1cB) is an anionic intermediate (53) formed by loss of an acidic hydrogen from (53a). The electronegative substituent X is eliminated in a second, rate-determining step.



The elimination of hydrogen chloride from β -chloro sulfones [113] has been explained on the basis of this mechanism. If the substituent to be removed as an anion, *e.g.* a hydride ion, is not a good leaving group, then the anionic intermediate (53) can be secured. Thus, 1,4-cyclohexadiene reacts with amylsodium affording a diallyl anion which reacts with carbon dioxide to form



[109] G. Wittig and M. H. Weterling, *Liebigs Ann. Chem.* 557, 201 (1944).

[109a] V. Franzen and G. Wittig, *Angew. Chem.* 72, 417 (1960); G. Wittig and S. Krauß, unpublished work.

[110a] V. Franzen, H. J. Joschek, and C. Mertz, *Liebigs Ann. Chem.* 654, 82 (1962).

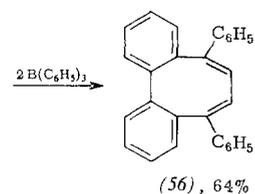
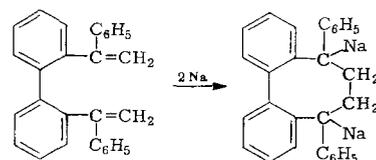
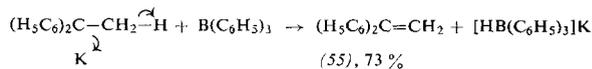
[110b] V. J. Hruby and A. W. Johnson, *J. Amer. chem. Soc.* 84, 3586 (1962).

[111] F. C. Whitmore and H. D. Zook, *J. Amer. chem. Soc.* 64, 1783 (1942).

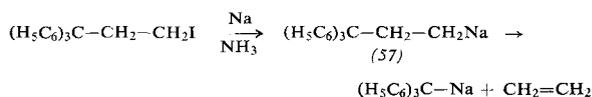
[112] Review: J. Hine: *Physical Organic Chemistry*. McGraw-Hill, New York 1956; J. F. Bunnett, *Angew. Chem.* 74, 731 (1962); *Angew. Chem. internat. Edit.* 1, 225 (1962).

benzene and sodium formate. Carboxylation of the corresponding metalation product obtained from 1,4-dihydronaphthalene affords naphthalene and 1,4-dihydro-1-naphthoic acid (54) [114].

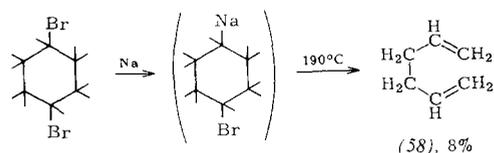
If aromatization is precluded, as with (55) and (56), elimination of alkali-metal hydride is possible only in the presence of hydride acceptors such as triphenylborane [115].



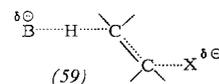
Sometimes the leaving anion is a carbanion. 3,3,3-Triphenyl-n-propylsodium (57) [116] evolves ethylene even in liquid ammonia, whereas the analogous decomposition of 3,3-dimethyl-3-phenyl-n-propylpotassium takes



place only in boiling cyclohexane [117]. The 1,4-elimination leading from 4-bromocyclohexylsodium to diallyl (58) must be effected in boiling decalin.



Eliminations involving a concerted mechanism (E 2) are much more frequent. The simultaneous bond cleavage and formation circumvents the formation of the high-energy intermediate (53) and leads directly to the stable olefinic end product via the transition state (59) which is similarly favorable as the transition state occurring in S_N2 processes [118].



[113] H. L. Goering, D. L. Town, and B. Dittmar, *J. org. Chemistry* 27, 736 (1962).

[114] R. Paul and S. Tchelitcheff, *C. R. hebdom. Séances Acad. Sci.* 239, 1222 (1954).

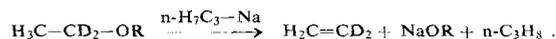
[115] G. Wittig and W. Stilz, *Liebigs Ann. Chem.* 598, 85, 93 (1956).

[116] C. B. Wooster and R. A. Morse, *J. Amer. chem. Soc.* 56, 1735 (1934).

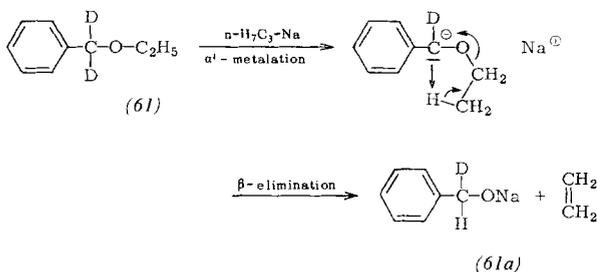
[117] H. Pines and L. Schaaf, *J. Amer. chem. Soc.* 80, 4379 (1958).

Strictly speaking, such concerted eliminations should not be considered as metalation reactions, because, in contrast to all the eliminations discussed so far, metalated, even if short-lived, intermediates are no longer formed.

The cleavage of aliphatic ethers by strong organometallic reagents mentioned above also proceeds by β -elimination [119].



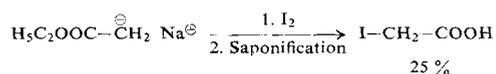
Benzyl ethers (61) [119], ammonium salts [120], and sulfonium salts [121] are degraded to olefins via α' , β -elimination. The organometallic base attacks the more acidic α' -hydrogens, and the resulting carbanions then undergo a rapid intramolecular β -elimination to form the more stable end product, e.g. (61a).



C. Replacement of Metal by Halogen

1. Halogenolysis

Donors of positive halogen, like active-proton compounds, are capable of heterolysing the organometallic bond. In the chemistry of organolithium compounds, for example, iodolysis has found wide application in both analysis and synthesis [122]. There are no reports that true organosodium and organopotassium derivatives undergo analogous reactions, although the reaction of iodine with the sodio derivative of ethyl acetate is known [123]:



2. Halogen-Metal Interconversion

The reaction of an organic halide with an organometallic compound effecting metathesis of the substituents is referred to as halogen-metal interconversion. If R'H is a stronger acid than RH, the reaction proceeds from left to right:



[118] C. Ingold, Proc. chem. Soc. (London) 1962, 265.

[119] R. L. Letsinger, Angew. Chem. 70, 154 (1958).

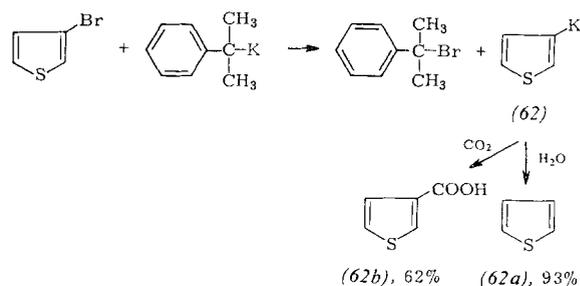
[120] F. Weygand, H. Daniel, and H. Simon, Chem. Ber. 91, 1691 (1958); Liebigs Ann. Chem. 654, 111 (1962).

[121] V. Franzen and C. Mertz, Chem. Ber. 93, 2819 (1960).

[122] G. Wittig, D. Hellwinkel, and G. Klar, unpublished work; H. Gilman and J. F. Nobis, J. Amer. chem. Soc. 67, 1479 (1945); E. H. Braye, W. Hübel, and I. Caplier, *ibid.* 83, 4406 (1961); S. Gronowitz and R. Håkansson, Ark. Kemi 16, 309 (1961).

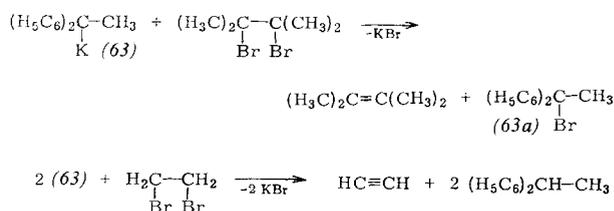
[123] E. Müller, H. Gawlick, and W. Kreuzmann, Liebigs Ann. Chem. 515, 109 (1934).

Halogen-metal interconversion is characteristic of organolithium compounds [124] since their associating power is strong enough to give rise to the intermediate complex [125], which is probably responsible for the reaction. Only a few metathesis reactions involving compounds of the higher alkali metals are known; these include *n*-butylsodium/1-bromonaphthalene [80]; amylsodium/*o*-bromotoluene, bromobenzene, 1-bromonaphthalene [126]; and amylsodium/methyl iodide [95].



The reaction of 3-bromothiophene with phenylisopropylpotassium to give 3-thienylpotassium (62) is surprisingly smooth; (62) can then be hydrolysed to thiophene (62a) or can be carboxylated to 3-thiophene-carboxylic acid; the phenylisopropyl bromide formed as by-product reacts with excess phenylisopropylpotassium to give 2,3-diphenyl-2,3-dimethyl-*n*-butane [127].

2,3-Dibromo-2,3-dimethylbutane is a very effective brominating agent. It converts 1,1-diphenylethylpotassium (63) into the corresponding bromide (63a) which, in turn, reacts with excess (63), to yield 70% 2,2,3,3-tetraphenyl-*n*-butane. The reaction of (63) with 1,2-dibromoethane, on the other hand, occurs predominantly with elimination [46].



D. Replacement of the Metal by Carbon and Other Non-Metals

1. Alkyl and Aryl Halides

a) Condensations [128]

The organometallic bond reacts not only with acidic hydrogen or positively charged halogen but also with the positive carbon of organic halides. This C-C coupling proceeds satisfactorily only with alkyl deri-

[124] R. G. Jones and H. Gilman in: Organic Reactions (The Halogen-Metal-Interconversion Reaction with Organolithium Compounds), Wiley, New York 1951, Vol. VI, p. 339.

[125] G. Wittig and U. Schöllkopf, Tetrahedron 3, 91 (1958).

[126] A. G. Lindstone and I. A. Morris, Chem. and Ind. 1958, 560.

[127] G. Wittig and V. Wahl, unpublished work.

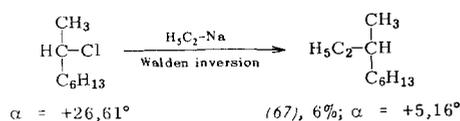
[128] Condensation generally implies a union of two reactants with loss of an electropositive substituent from the one and of an electronegative substituent from the other. The concept of coupling should be restricted to use in the chemistry of dyes.

Table 3. Condensation of organometallic compounds R-M with (-)-2-bromooctane (R'-Br).

R-M	R-R' [%]	Racemate [%]	Ref.
Benzylmagnesium bromide			
H ₂ C=CH-CH ₂ -Na	83	13 [*]	[143]
H ₂ C=CH-CH ₂ -MgBr	78	13 [*]	[143]
H ₅ C ₆ -CH ₂ -Na	81	30 [*]	[144]
H ₅ C ₆ -CH ₂ -MgBr	17	91 [*]	[143]
H ₅ C ₂ -Na	25	97 [*]	[145]
n-Butylsodium	35	100	[144]
2-Octylsodium	—	100	[145]

[*] The configuration of the remainder of R-R' is opposite to that of R'-Br.

activity, whereas the latter is preserved in condensations with the analogous alkyl chlorides, although inversion takes place. Thus, the reaction of (+)-2-chlorooctane with ethylsodium affords (+)-3-methylnonane (67) with only 20 % racemization.



Two hypotheses have been advanced to explain the racemization observed in the case of alkyl bromides. According to the one theory, the sodium ion causes the alkyl bromide to dissociate into a carbonium ion [146a, 146b], while in the other, the racemization is supposed to be preceded by a rapid halogen-metal interconversion and to proceed by way of a carbanion [119].

2. Non-Metal Halides

Phenylsodium condenses with boron trichloride to give triphenylborane (50 %) or with silicon tetrachloride at -40 °C to form a mixture of trichlorophenylsilane (38 %), dichlorodiphenylsilane (14 %), and tetraphenylsilane (35 %). Phosphorus trichloride reacts with phenylsodium to give triphenylphosphine, and with benzylsodium to give tribenzylphosphine (84 %) [147]. Silane [148a] and triarylsilanes [148b] condense with organoalkali-metal compounds resulting in elimination of alkali-metal hydride.

[143] R. L. Letsinger and J. G. Traynham, J. Amer. chem. Soc. 72, 849 (1950).

[144] R. L. Letsinger, J. Amer. chem. Soc. 70, 406 (1948).

[145] N. G. Brink, J. F. Lane, and E. S. Wallis, J. Amer. chem. Soc. 65, 943 (1943).

[146a] S. E. Ulrich, F. H. Gentes, J. F. Lane, and E. S. Wallis, J. Amer. chem. Soc. 72, 5127 (1950).

[146b] J. F. Lane and S. E. Ulrich, J. Amer. chem. Soc. 72, 5132 (1950).

[147] J. F. Nobis, L. F. Moormeier, and R. E. Robinson: Organosodium Compounds for Preparation of Other Carbon-Metal Bonds in Metalorganic Compounds. Advances in Chemistry Series, No. 23, published by the Amer. Chem. Soc., Washington D.C. 1959, p. 63 et seq.

[148a] J. S. Peake, W. H. Nebergall, and Y. T. Chen, J. Amer. chem. Soc. 47, 1526 (1925).

[148b] R. A. Benkeser and F. J. Riel, J. Amer. chem. Soc. 73, 3472 (1951).

E. Replacement of the Metal by Another Metal

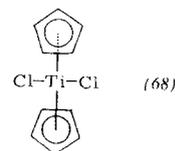
1. Reactions with Metal Halides [149]

The substitution of an alkali-metal atom in an organometallic compound by another less electropositive one occurs quantitatively with inorganic salts. This represents a convenient and effective method for preparing Grignard reagents in hydrocarbon solution [150].



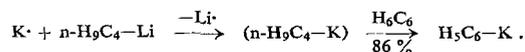
Similarly, lithium halides or alkoxides transform phenylsodium into phenyl-lithium, and the reaction of aluminum trichloride with butylsodium yields dibutylaluminum chloride [147].

The synthesis of π -complexes from the weak base cyclopentadienylsodium and transition metal salts falls into the same category as these reactions. Ferrocene can be synthesized in this way [151] from ferrous chloride, and titanocene (68) [152] from titanium(IV) chloride, both in 90 % yield.



2. Reactions with Metals

When the substituting metal is used in elemental form, the nobler (*i.e.* less electronegative) metal separates out also in elemental form. This phenomenon is applied for the preparation of potassium derivatives from organolithium or organosodium compounds [153].



F. Addition Reactions

In all the reactions discussed so far, the residue Y in polarizable compounds X-Y was displaced by a carbanion (cryptoanion):



The reactions dealt with in the following all have the common feature that the organoalkali compound adds onto an electron-deficiency site (69) or across a multiple bond (70).

[149] These reactions could also be considered as condensations of metal halides with organoalkali-metal compounds.

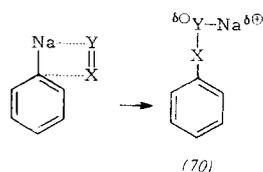
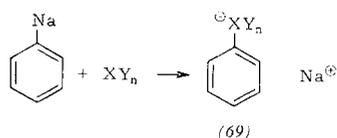
[150] US.-Pat. 2795626 (June 11th, 1957) and 2914578 (Nov. 24th, 1959) National Distillers and Chem. Corp., inventors: J. F. Nobis and R. E. Robinson; cf. Chem. Abstr. 54, 15318h (1960).

[151] W. F. Little, R. C. Koestler, and R. Eisenthal, J. org. Chemistry 25, 1435 (1960).

[152] G. Wilkinson and J. M. Birmingham, J. Amer. chem. Soc. 76, 4281 (1954).

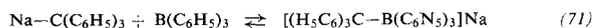
[153] D. Bryce-Smith and E. E. Turner, J. chem. Soc. (London) 1953, 861.

These reactions, too, can be interpreted in terms of the broad concept of charge neutralization. The driving force behind the reaction is provided by the tendency of the carbon to transmit its negative charge to a more electronegative atom or another, less basic, carbon.

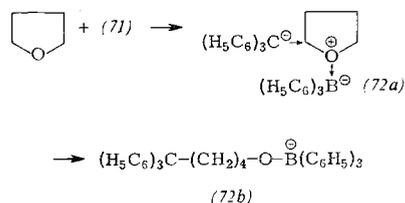


1. Lewis Acids

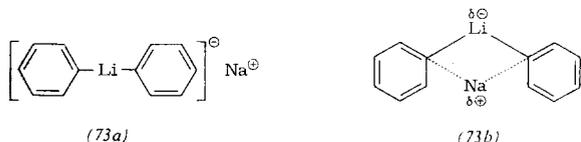
Phenylsodium combines with triphenylborane to form sodium tetraphenylborate (Kalignost[®]), a useful analytical reagent that is not affected by water or alcohol [154]. Phenylisopropylpotassium also gives a corresponding borate complex [114], and the bulky base triphenylmethylsodium gives adducts (71) that are in equilibrium with their components [155].



Solutions of such antagonist pairs exhibit simultaneous electrophilic and nucleophilic reactivity resulting, for example, in the formation of (72a) and (72b) [156].



Organic derivatives of many elements from different groups of the periodic system (Be, Mg, Zn, B, Al, Si, Sb) undergo addition with organoalkali compounds. Surprisingly, even organolithium bases can act as Lewis acids for other organoalkali compounds. Phenyl-lithium gives a 1:1 complex [(73a) or (73b)] with phenylsodium which can be crystallized from ether.



This complex (73a) \leftrightarrow (73b) reacts vigorously with butyl iodide until the phenylsodium is completely consumed; the

[154] G. Wittig and P. Raff, *Liebigs Ann. Chem.* 573, 195 (1951).

[155] G. Wittig, H. G. Reppe, and T. Eicher, *Liebigs Ann. Chem.* 643, 47 (1961).

[156] G. Wittig and O. Bub, *Liebigs Ann. Chem.* 566, 113 (1950); G. Wittig and G. Kolb, *Chem. Ber.* 93, 1469 (1960).

residual phenyl-lithium continues to react slowly, with a half-life of 9 hours [157].

The addition of even a few per cent of phenyl-lithium to a suspension of phenylsodium (or phenylpotassium, phenylrubidium, or phenylcesium) stabilizes the latter towards ether [158]. Small amounts of phenyl-lithium are evidently sufficient to complex the entire amount of dissolved phenylsodium. Phenylsodium that is moderated in this manner is less active than the lithium-free reagent prepared in hydrocarbons; however, this loss in activity is compensated by the polarity of the ether (see Table 4).

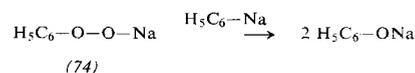
Table 4. Metalation of anisole with phenylalkali-metal compounds at about 20 °C.

R-M	Solvent	Reaction time [hrs]	Metalation [%]	Ref.
H ₅ C ₆ -Li + LiBr	Ether	20	0	[159]
H ₅ C ₆ -Li	Ether	20	17	[159]
[H ₅ C ₆ -Li-C ₆ H ₅]Na	Ether	20	71	[159]
H ₅ C ₆ -Na	Benzene	24	44	[70]
H ₅ C ₆ -Na	Benzene	48	64	[70]

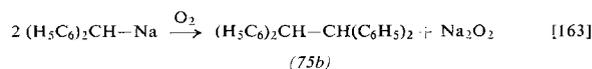
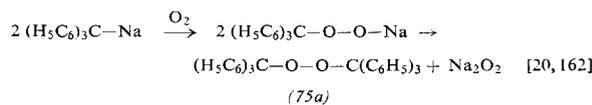
Because of their electron-sextet, carbenes are extremely active Lewis acids. Until now, their reaction with organic derivatives of the higher alkali metals have been reported only sporadically [160]. This reaction is analogous to the frequently observed insertion of carbenes into carbon-lithium bonds [101].

2. Oxygen and Sulfur Functions

Molecular oxygen cleaves organoalkali-metal compounds with formation of a peroxide, e.g. (74), which in turn, oxidizes a second molecule of the organometallic



compound [161]. Peroxides of resonance-stabilized organoalkali-metal compounds decompose with elimination of alkali peroxide, for example, to give (75a) and (75b).



The reactions of sulfur and sulfur compounds with organoalkali-metal compounds have not yet been systematically studied. The reaction of triphenylmethylsodium with sulfur

[157] G. Wittig, R. Ludwig, and R. Polster, *Chem. Ber.* 88, 294 (1955); German Pat. 955 596 (Jan. 3rd, 1957) BASF, Ludwigshafen/Rh., inventor: G. Wittig; *Chem. Abstr.* 53, 13 108h, 16064b (1959).

[158] G. Wittig, *Angew. Chem.* 70, 65 (1958).

[159] G. Wittig and E. Benz, *Chem. Ber.* 91, 874 (1958).

[160] A. P. Krapcho, P. S. Huyffer, and I. Starer, *J. org. Chemistry* 27, 3096 (1962).

[161] H. Hock and H. Kropf, *Angew. Chem.* 69, 315, 317 (1957).

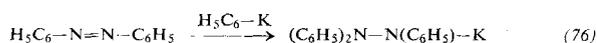
[162] C. A. Kraus and R. Rosen, *J. Amer. chem. Soc.* 47, 2739 (1925).

[163] According to C. B. Wooster, *Chem. Reviews* 11, 14 (1932).

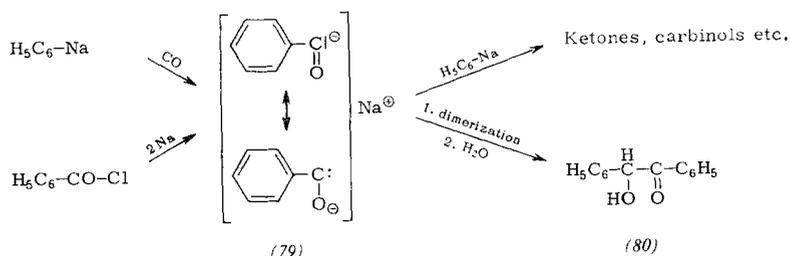
dioxide affords triphenylmethyl sulfinate [163], and that with diphenyl sulfoxide gives a red-violet adduct [164]. Phenylsodium and diphenyl sulfoxide give diphenylene sulfide [165]. The reaction of sultones with organosodium reagents takes place with ring-opening and leads to sulfonates [166].

3. Nitrogen Functions

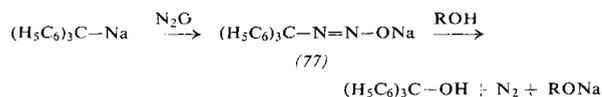
The $N \equiv N$ triple bond of molecular nitrogen does not react with organometallic compounds. However, phenylpotassium does add onto the $N=N$ double bond of azobenzene to give (76).



Phenylcalcium iodide also adds onto azobenzene, whereas phenylsodium, phenyl-lithium, and phenyl-magnesium bromide act predominantly as reducing agents yielding, respectively, 25%, 52%, and 62% hydrazobenzene [167].



Nitroso and nitro compounds and most nitrogen oxides react with organometallic compounds so vigorously and give reaction products of such high reactivity that the reaction is uncontrollable; for preparative purposes, less reactive organometallic compounds are therefore used [168]. Nitrous oxide reacts only with organoalkali bases, *e.g.* with triphenylmethylsodium, to yield a diazotate (77) which liberates nitrogen on hydrolysis [136].



4. Carbon Functions

a) Carbon Oxides

Carboxylation converts organometallic compounds smoothly into carboxylates (77) [169]. However, a local excess of the organometallic compound can cause transmetalation and consequent formation of dicarb-

[164] K. Fuchs and P. Gross, Ber. dtsh. chem. Ges. 63, 1009 (1930).

[165] K. Fuchs, Mh. Chem. 53/54, 443 (1929).

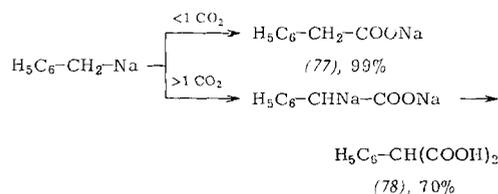
[166] German Pat. 895598 (Oct. 22nd, 1953), Böhme Fettchemie GmbH., inventor: J. H. Helberger and R. W. F. Heyden; Chem. Abstr. 48, 4234f (1954).

[167] H. Gilman and J. C. Bailie, J. org. Chemistry 2, 84 (1937).

[168] Cf., for example, the preparation of nitroso compounds from nitrosyl chloride and organomercury halides [L. I. Smith and F. L. Taylor, J. Amer. chem. Soc. 57, 2460 (1935)].

[169] J. F. Nobis and L. F. Moormeier, Ind. Engng. Chem. 46, 539 (1954).

oxylic acids (78) [170]; under suitable conditions, the latter can be obtained in high yields [171].



Prolonged treatment of phenylsodium suspensions with carbon monoxide leads to the acyl anion (79) and thence to benzophenone, triphenylmethanol, and benzoic acid [172, 173]. A mechanism involving the same anion (79) has been postulated to explain the formation of acyls (80) in the reaction of sodium-aromatic complexes with acid chlorides [174].

The lower resonance structure predicts the properties of a nucleophilic carbene for the acyl anion (79) [175]; however, it does not add onto olefins or acetylene derivatives [176].

Free triphenylmethylsodium does not react with carbon monoxide [20], but does form a dark-colored adduct with it in the presence of triphenylborane [177].

b) Carbonyl and Carboxylic Compounds

Sodium alkyls and sodium aryls combine with aldehydes or ketones with extreme rapidity. Triphenylmethylsodium undergoes normal addition onto benzaldehyde [20], phenyl isocyanate [178], and phenyl isothiocyanate

[170] Cf., for example, H. Gilman and H. A. Pacevitz, J. Amer. chem. Soc. 62, 1301 (1940).

[171] J. F. Nobis and L. F. Moormeier, Ind. Engng. Chem. 46, 539 (1954).

[172] H. H. Schlubach, Ber. dtsh. chem. Ges. 52, 1910 (1919). Participation of organomercury compounds cannot be excluded in view of the method by which phenylsodium is prepared [cf. W. Schoeller, W. Schrauth, and W. Essers, Ber. dtsh. chem. Ges. 53, 62 (1920)].

[173] For corresponding reactions of carbon monoxide with organolithium compounds, see G. Wittig, Angew. Chem. 53, 241 (1940) (footnote [58]); for reactions with Grignard compounds, see F. G. Fischer and O. Stoffers, Liebigs Ann. Chem. 500, 253 (1933).

[174] W. Schlenk and E. Bergmann, Liebigs Ann. Chem. 463, 19 (1928).

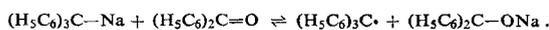
[175] H. W. Wanzlick, Angew. Chem. 74, 129 (1962); Angew. Chem. internat. Edit. 1, 75 (1962).

[176] M. Schlosser, unpublished work.

[177] G. Wittig and H. Vogel; G. Wittig and L. Gonsior, unpublished work.

[178] W. Schlenk and E. Bergmann, Liebigs Ann. Chem. 464, 1 (1928).

[178]; the reaction with benzophenone, however, involves an unusual radical formation [179].



The attack of organoalkali-metal compounds on enolizable aldehydes and ketones is also influenced by steric factors. Secondary and tertiary alkoxide formation from bulky bases [180], particularly from triphenylmethylsodium [181], is suppressed in favor of enolate formation. The dependence of the enolate/alkoxide ratio on the nature of the metal has been investigated by *Hauser* [182]. Lithium and magnesium, which undergo complex formation, promote addition [\rightarrow (82)] via a concerted mechanism with a four-centered transition state [183]; sodium and potassium, on the other hand, favor deprotonation [\rightarrow (81)] (Table 5).

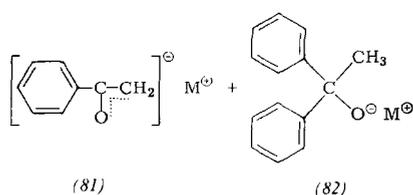


Table 5. Effect of the metal in the phenylmetal compound on the formation of (81) and (82) from acetophenone.

M	Enolate: carbinolate
K	10:1
Na	2:1
Li	1:23
BrMg	1:∞

Nonpolar solvents such as benzene impair metalation and thus promote carbinolate formation [182].

α,β -Unsaturated compounds react as 1,2- or 1,4-dipolar structures with organometallic compounds; the type of addition (1,2- or 1,4-) occurring depends on the metal [182, 184]. Magnesium promotes 1,4-addition via a chelate; other metals give predominantly 1,2-addition (Table 6).

Table 6. 1:1-Addition of C_6H_5-M onto β -benzoylstyrene ($H_5C_6CH=CHCO_2C_6H_5$).

C_6H_5-M	1,2-Adduct [%]	1,4-Adduct [%]
+ H_5C_6-K	67	—
+ H_5C_6-Na	60	14
+ H_5C_6-Li	75	14
+ H_5C_6-MgBr	—	94

[179] *W. Schlenk* and *R. Ochs*, *Ber. dtsh. chem. Ges.* 49, 608 (1916).

[180] *B. F. Landrum* and *C. T. Lester*, *J. Amer. chem. Soc.* 76, 5797 (1954).

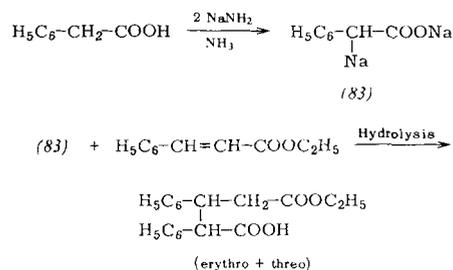
[181] *E. Müller*, *H. Gawlick*, and *W. Kreutzmann*, *Liebigs Ann. Chem.* 515, 97 (1934).

[182] *W. I. O'Sullivan*, *F. W. Swamer*, *W. J. Humphlett*, and *C. R. Hauser*, *J. org. Chemistry* 26, 2306 (1961).

[183] *J. Mathieu*, *A. Allais*, and *J. Valls*, *Angew. Chem.* 72, 74 (1960).

[184] *P. G. Stevens* et al., *J. Amer. chem. Soc.* 57, 1112 (1935); *C. F. Koelsch* and *R. H. Rosenwald*, *ibid.* 59, 2166 (1937); *H. Gilman* and *R. H. Kirby*, *ibid.* 63, 2046 (1941); *A. Lüttringhaus* et al., *Liebigs Ann. Chem.* 557, 70 (1947); *G. Wittig* and *O. Bub*, *ibid.* 566, 121 (1950).

Benzylsodium derivatives (83) undergo exclusively 1,4-addition onto α,β -unsaturated esters [185, 186].



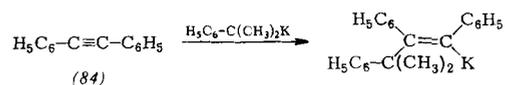
The reactions of organoalkali-metal compounds with carboxylic acids [187], carbonyl chlorides, anhydrides, and esters proceed in the manner of a normal Grignard reaction.

c) CN Multiple Bonds

Azomethines (Schiff bases) react with organoalkali compounds in the same way as the isoelectronic carbonyl compounds, and isonitriles behave like carbon monoxide. Heterocyclic compounds containing CN double bonds, *e.g.* pyridine, undergo a variety of organometallic addition and substitution reactions resulting in numerous different products [188]. The reaction of nitriles with organometallic compounds represents a useful ketone synthesis [189]. For practical purposes, the readily available Grignard or organolithium compounds are mostly used. In contrast to phenyl-lithium, phenylsodium does not add onto butyronitrile, but produces the anion instead [189a].

d) CC Multiple Bonds

The highly strained triple bond in arynes and lower cycloalkynes is not the only one capable of undergoing nucleophilic additions [190]. Organometallic compounds also add onto linear acetylenes, although not quite as smoothly.



Methylphenylacetylene behaves like toluene (84). Purely aliphatic acetylenes with a non-terminal triple bond undergo isomerization to 1-alkynes [191] instead.

The addition of organoalkali compounds onto conjugated double bonds was discovered and studied ex-

[185] *C. R. Hauser* and *M. T. Tetenbaum*, *J. org. Chemistry* 23, 1146 (1958).

[186] *R. B. Meyer* and *C. R. Hauser*, *J. org. Chemistry* 26, 3183 (1961).

[187] *J. F. Nobis*, unpublished work; quoted from *R. A. Benkeser* et al., *Chem. Reviews* 57, 867 (1957), p. 891 et seq.

[188] Review: *R. Gaertner*, *Chem. Reviews* 45, 493 (1949).

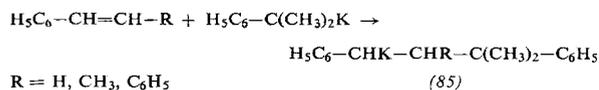
[189] *C. Moureu* and *G. Mignonac*, *C. R. hebd. Séances Acad. Sci.* 156, 1801 (1913).

[189a] U.S.-Pat. 2012372 (Aug. 27th, 1935), *Winthrop Chem. Co.*, inventor: *M. Bockmühl* and *G. Ehrhart*.

[190] Review: *G. Wittig*, *Angew. Chem.* 74, 479 (1962); *Angew. Chem. internat. Edit.* 1, 415 (1962).

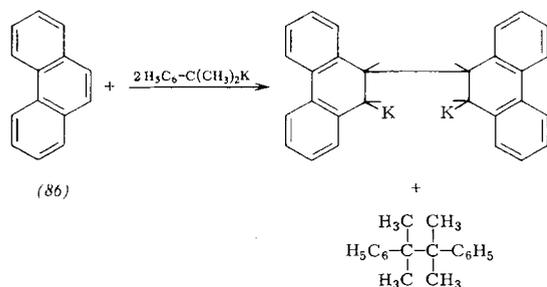
[191] *K. Ziegler* and *H. Dislich*, *Chem. Ber.* 90, 1107 (1957).

tensively using phenylisopropylpotassium by Ziegler [192a–192c].



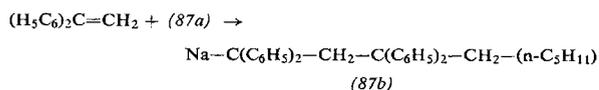
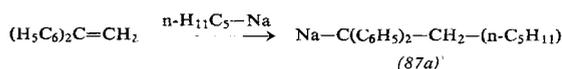
Phenylisopropylpotassium reacts with styrene, β-methylstyrene, stilbene, α-methylstyrene, 1,1-diphenylethylene, and several fulvenes. Other olefins are metalated to allylic derivatives. These include ethylene derivatives with only alkyl substituents, styrenes that are doubly substituted with alkyl groups, α-methylstilbene, and 2-methyl-1,1-diphenylethylene. Monosubstituted styrenes seem to represent the dividing line between predominant addition and predominant metalation. In pentane, the more active reagent amylsodium gives 85 % hydrogen-metal interconversion with α-methylstyrene and 29 % with β-methylstyrene [193]. Substitution of the methyl group with long-chain alkyl groups causes a further increase in metalation at the expense of addition.

A third, free-radical reaction of multiple CC bonds has been observed with phenanthrene (86) [192a, 192b].



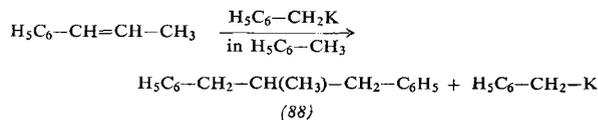
Although phenylsodium [194] and vinylsodium [59] do not react with 1,1-diphenylethylene in nonpolar solvents, both benzylsodium [194], which is less basic, and the alkali-metal amyls, which are more basic, do (relative reaction rates for amyl-lithium, amylsodium, and amylpotassium = 0.03:1:3 [194]).

Addition of a second molecule of olefin onto the addition product (87a) obtained from the olefin and amylsodium affords (87b) [194].



Additions can often be accomplished with catalytic amounts of organometallic compounds; the resulting adducts, e.g. (88), give rise in turn to new addends by hydrogen-metal interconversion [195].

- [192a] K. Ziegler and K. Bähr, Ber. dtsch. chem. Ges. 61, 253 (1928).
 [192b] Electron transfer to unsaturated systems via organoalkali-metal compounds has been observed in several other cases [G. Wittig and D. Wittenberg, Liebigs Ann. Chem. 606, 8 (1957); K. Ziegler and H. Kleiner, ibid. 473, 70 (1929)].
 [192c] K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, Liebigs Ann. Chem. 473, 1 (1929).
 [193] A. A. Morton and E. Grovenstein, J. Amer. chem. Soc. 74, 5437 (1952).
 [194] A. A. Morton and H. C. Wohlers, J. Amer. chem. Soc. 69, 167 (1947).
 [195] J. Shabtai, E. M. Lewicki, and H. Pines, J. org. Chemistry 27, 2618 (1962).



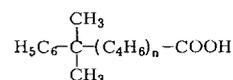
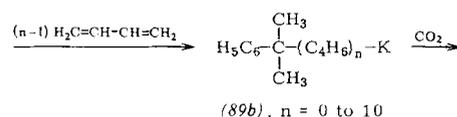
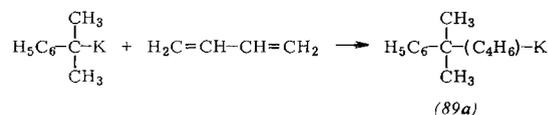
Organoalkali-metal compounds also add onto cycloheptatriene [196] and cyclooctatetraene [197]. Butadiene adds on amylsodium and benzylsodium but not phenylsodium [198]. Phenylpotassium seems to add even onto benzene [198a].

Tri- and tetraarylethylenes do not add on organoalkali compounds. With this exception, obviously due to steric hindrance, additions proceed smoothly whenever a weaker base is formed from a stronger one. For example, the reaction of phenylisopropylpotassium with 1,1-diphenylethylene produces a more highly resonance-stabilized benzhydrylpotassium derivative.

On the other hand, when ethylene reacts with benzylsodium, a stronger base, 3-phenylpropylsodium, results, from which propylbenzene (36 %) and 3-phenyl-n-pentane (37 %) are produced [199]. This reaction requires heat and pressure (100 °C, 200 atm) in contrast to the additions of isopropyl-lithium or *t*-butyl-lithium onto ethylene, which take place even at -60 °C, because they lead to weaker bases [200].

e) Polymerizations [201a–203]

The study of addition reactions provided the key to an understanding of anionic polymerization, recognized by Ziegler [201a] to be “an organometallic synthesis on the largest scale”. In this polymerization, an organometallic compound adds onto a butadiene- or styrene-type olefin giving rise to another organometallic compound which, in turn, can add on further molecules of olefin. Thus, chain growth (89b) takes place by recurring additions of butadiene onto the allylpotassium end-group of the butadiene-isopropylpotassium adduct (89a). After all the monomer is consumed, the reactive

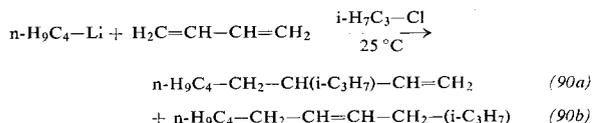


- [196] K. Hafner and W. Rellensmann, Angew. Chem. 72, 918 (1960).
 [197] A. C. Cope and M. R. Kinter, J. Amer. chem. Soc. 73, 3424 (1951).
 [198] A. A. Morton, G. H. Patterson, J. J. Donovan, and E. L. Little, J. Amer. chem. Soc. 68, 93 (1946).
 [198a] A. A. Morton and E. J. Lanpher, J. org. Chemistry 23, 1639 (1958).
 [199] US.-Pat. 2548 803 (April 10th, 1951), du Pont de Nemours, inventor: E. L. Little; H. Pines, J. A. Vesely, and V. N. Ipatieff, J. Amer. chem. Soc. 77, 554 (1955).
 [200] P. D. Bartlett, S. Friedman, and S. Stiles, J. Amer. chem. Soc. 75, 1771 (1953).
 [201a] K. Ziegler, Angew. Chem. 49, 499 (1936).
 [201b] C. E. H. Bawn and A. Ledwith, Quart. Rev. 16, 386 (1962).
 [202] K. Ziegler and H. Kleiner, Liebigs Ann. Chem. 473, 57 (1929).
 [203] K. Ziegler, E. Eimers, W. Hechelhammer, and H. Wilms, Liebigs Ann. Chem. 567, 43 (1949).

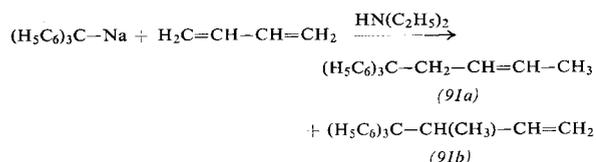
chain ends remain intact, provided hydrolytic agents are excluded. Subsequent introduction of dienes results in avid absorption and addition (living polymers).

The reaction can be stopped at an early stage by using low monomer concentrations [202] or scavengers [203] that are inert toward the chain-initiating organoalkali-metal compounds. The products of the initial addition (99b) have been isolated and confirm the postulated mode of chain growth.

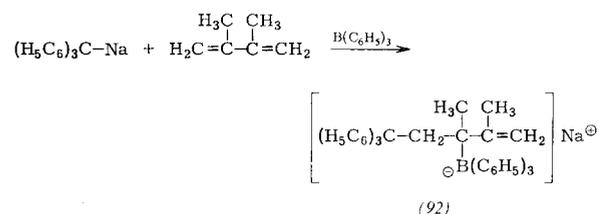
In the polymerization of butadiene with *n*-butyl-lithium, (90a) and (90b) were identified as the products of the second addition step.



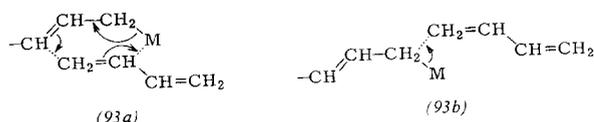
The mechanism of the polymerization of butadiene or styrene initiated by phenylsodium or triphenylmethylsodium was revealed by an elegant, effective scavenging method using diethylamine and yielding (91a) and (91b).



The initiators appear to act as true catalysts, since they are not detectably consumed; but here, too, organometallic addition is the actual initiating step; however, this process is extremely slow in comparison to the rate of chain growth. Polymers of high molecular weight can be obtained by preventing chain termination [202, 203]. Occasionally the scavenger increases the reactivity of the olefin by complex formation. Thus, 2,3-dimethylbutadiene adds onto triphenylmethylsodium only in the presence of triphenylborane and with exclusive formation of the 1,2-adduct [204].



The polymerization of butadiene does not give stereochemically uniform chains. 1,2-Addition predominates at low temperature (90% at -70°C) almost independently of the nature of the organometallic initiator and the solvent, whereas at high temperature, 1,4-linked polymers are primarily produced (85% at 110°C). These results possibly reflect the competition between abnormal (93a) and normal (93b) allylic addition [203].



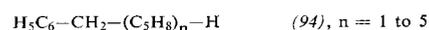
[204] G. Wittig and H. Schloeder, *Liebigs Ann. Chem.* 592, 38 (1955).

The stereochemistry of isoprene polymerization depends on both the solvent and the alkali-metal initiator. In polymerizations carried out in hydrocarbons, lithium behaves differently from the other alkali metals. This difference disappears with increasing polarity of the solvent (Table 7) [205].

Table 7. Isoprene polymerization with alkali metals or their organometallic derivatives.

Solvent	Metal	Polymer [%]			
		1,2	3,4	<i>cis</i> -1,4	<i>trans</i> -1,4
<i>n</i> -Heptane	Li	—	6	94	—
<i>n</i> -Heptane	Na	10	42	—	48
<i>n</i> -Heptane	K	7	35	—	58
THF	Li	14	52	—	34
THF	Na	15	51	—	34
THF	K	17	35	—	48

In practice, it is immaterial whether the metal is used in elemental form or as the alkyl, aryl, or benzyl derivative, since polymerization is effected identically in all cases. Thus, with isoprene, sodium gives the disodium adduct and then isoprenylsodium, which is the actual chain initiator. In the presence of toluene, benzylsodium is the initiator, as indicated by the hydrocarbon (94) isolated after premature hydrolysis [206].



The details of the polymerization of butadiene with sodium are not entirely clarified. In contrast to the known rules of organometallic polymerization, the structure of the Buna rubber polymer is fairly independent of the temperature of polymerization. On the other hand, its structure is quite different from that of the polymer obtained by the free-radical process using azobisbutyronitrile [203].

Polymerizations promoted by alfin catalysts [59, 207] or Ziegler catalysts [208] cannot be discussed here.

G. Rearrangements

Intramolecular rearrangements provide another route for the conversion of organoalkali-metal compounds into less basic, and hence more stable compounds.

1. Charge Transfer to Nitrogen

The Stevens rearrangement (95) [209] effectively "short-circuits" the charges condensed in the ylides of nitrogen, arsenic, and antimony. The corresponding high energy

[205] A. V. Tobolsky and C. E. Rogers, *J. Polymer Sci.* 40, 73 (1959).

[206] R. E. Robertson and L. Marion, *Canad. J. Res. Sect. B* 26, 627 (1948).

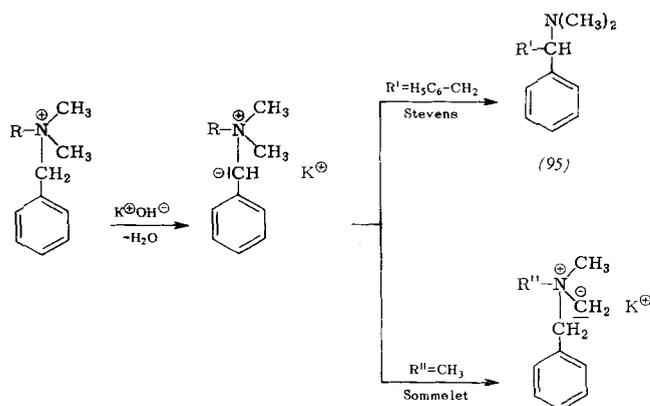
[207] A. A. Morton, E. E. Magat, and R. L. Letsinger, *J. Amer. chem. Soc.* 69, 950 (1947).

[208] C. D. Nenitzescu, C. Huch, and A. Huch, *Angew. Chem.* 68, 438 (1956); *Rev. Chim. (Bucaresti)* 7, 573 (1956); cf. K. Ziegler, *Angew. Chem.* 68, 581 (1956).

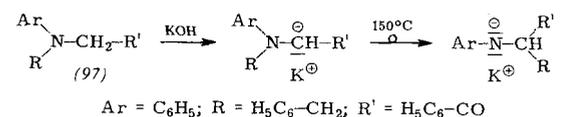
[209] Reviews: G. Wittig, *Angew. Chem.* 63, 15 (1951); 66, 10 (1954); *Acta chim. Acad. Sci. hung.* 12, 347 (1957); G. Köbrich, *Angew. Chem.* 74, 453 (1962); *Angew. Chem. internat. Edit.* 1, 382 (1962).

gain also promotes the competing Sommelet rearrangement (96) [209,210].

In the base-promoted isomerization of tertiary amines (97), also studied by Stevens [211], the negative charge is transferred to a previously uncharged nitrogen atom.

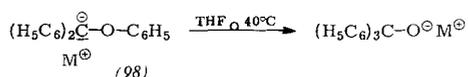


Consequently, here the tendency towards rearrangement is less pronounced, and higher temperatures are required.



2. Charge Transfer to Oxygen

The Wittig rearrangement [22,48,212] of metalated ethers is analogous to the above rearrangement of tertiary amines. This rearrangement generally takes place in the cold; strongly resonance-stabilized metalates, e.g. (98), require slight heating to effect isomerization.



Although the alkali metal M is bound only electrostatically, it exerts an effect on the rate of rearrangement. The kinetic data obtained were measured with relatively concentrated solutions, and, hence, the decrease in reactivity Li > Na, K [22] may be due to a salt effect. The alternative cleavage of metalated ethers in non-polar solvents leading to carbenes has been discussed above.

According to a mechanism postulated by Schöllkopf [213a, 213b] for s-alkyl benzyl ethers, the Wittig rearrangement proceeds in two steps, but chiefly by an intramolecular process via an internal ion pair. Competition experiments [213b] show that intermolecular rearrangement is still negligible at -56°C. t-Alkyl benzyl ethers possibly react according to an S_Ni mechanism [214].

[210] F. N. Jones and C. R. Hauser, *J. org. Chemistry* 26, 2979 (1961).

[211] W. F. Cockburn, R. A. W. Johnstone, and T. S. Stevens, *J. chem. Soc. (London)* 1960, 3340; R. A. W. Johnstone and T. S. Stevens, *ibid.* 1960, 3346.

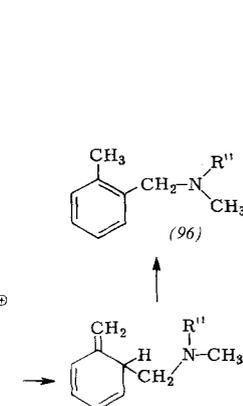
[212] G. Wittig and L. Löhmann, *Liebigs Ann. Chem.* 550, 260 (1942); G. Wittig and H. Schlör, *Suomen Kemistilehti B* 31, 2 (1958).

[213a] U. Schöllkopf and W. Fabian, *Liebigs Ann. Chem.* 642, 1 (1961).

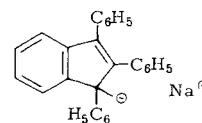
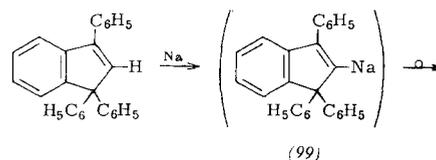
[213b] U. Schöllkopf and D. Walter, *Liebigs Ann. Chem.* 654, 72 (1962).

3. Charge Transfer to Another Carbon Atom

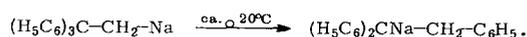
The isomerization of a metalated hydrocarbon (99) was observed thirty-five years ago by both Schlenk [215] and Ziegler [216].



The rearrangements of β-substituted di- and triaryl-ethylalkali-metal compounds have been investigated recently [135,217,218].



The ease with which the organometallic bond can shift within hydrocarbon molecules is surprising in view of what is known about the nitrogen- and oxygen-containing compounds. The isomerization is initiated by a



weakening of the metal-carbon bond, as indicated by the effect of the metal M on this phenomenon (K > Na > Li ≫ Mg, Hg). When several residues are available for migration, the course of the rearrangement depends more on their tendency to migrate than on the stability of the final product. The following order of decreasing mobility has been observed [217,218]: R = benzyl > phenyl > p-tolyl > methyl.

For example, 2,2-diphenyl-n-propylpotassium [R = CH₃; M = K] does not afford the more stable isomer 1,1-

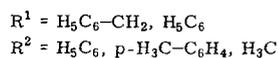
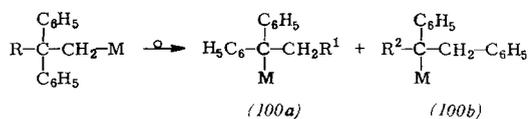
[214] P. T. Lansbury and V. A. Pattison, *J. org. Chemistry* 27, 1933 (1962).

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diphenyl-*n*-propylpotassium (100a); instead, 1,2-diphenylisopropylpotassium (100b) is produced [217]. However, these rearrangements, too, reflect the tenden-

cy of more strongly basic organoalkali-metal compounds to undergo conversion into less basic ones, thus satisfying a principle established for the chemistry of organosodium and organopotassium compounds.

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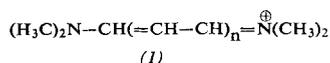
COMMUNICATIONS

Hindered Internal Rotation in Cyanine Dyes

By Prof. Dr. G. Scheibe, Doz. Dr. C. Jutz, Dr. W. Seiffert, and Dipl.-Chem. D. Grosse

Physikalisch-Chemisches Institut and Organisch-Chemisches Institut der Technischen Hochschule München (Germany)

The proton magnetic resonance of the chain chromophores of *N,N*-dimethylaminoproenylylidene- (1a), *N,N*-dimethylaminopentadienylylidene- (1b), and *N,N*-dimethylaminohaptatrienylylidene-dimethylammonium perchlorates (1c) corresponds to the AX₂, A₂X₂Y, or AB₂X₂Y₂ type, respectively. It is the *all-trans*-configuration that occurs in the ground state [1].



(1a), (1b), (1c): n = 1, 2, or 3

At room temperature in neutral medium, the methyl groups of the auxochromes of (1a) and (1b) each supply two signals

Table 1. Proton magnetic resonance signals ($\delta \equiv$ chemical shift), coupling constants (J), and activation energies (E_a) of dimethylaminopolyenylylidenedimethylammonium perchlorates. External standard: tetramethylsilane.

	(1a)	(1b)	(1c)
δ_α [ppm] [*] conc./solvent	-7.49; doublet 0.5 M/D ₂ O	-7.17; doublet 0.1 M/CD ₃ COCD ₃	-7.16; doublet 0.05 M/CD ₃ COCD ₃
J _{αβ} [cps]	11.8	11.8	11.8
δ_β [ppm] conc./solvent	-5.19; triplet 0.5 M/D ₂ O	-5.33; quartet 0.1 M/CD ₃ COCD ₃	-5.31; quartet 0.05 M/CD ₃ COCD ₃
J _{βγ} [cps]		12.7	12.7
δ_γ [ppm] conc./solvent		-7.0; triplet 0.1 M/CD ₃ COCD ₃	-6.88; quartet 0.05 M/CD ₃ COCD ₃
J _{γδ} [cps]			12.6
δ_δ [ppm] conc./solvent			-5.69; triplet 0.05 M/CD ₃ COCD ₃
δ_{CH_3} [ppm] conc./solvent	-3.23 and -3.03 0.5 M/D ₂ O	-2.79 and -2.59 0.1 M/CD ₃ COCD ₃	-2.7 0.05 M/CD ₃ COCD ₃
E _a [kcal/mole] solvent	17 (C ₆ H ₅) ₂ CO	10 (C ₆ H ₅) ₂ CO	7 CH ₃ CN/CCl ₄
T ₂ [sec/rad] [**]	0.227	0.274	0.227

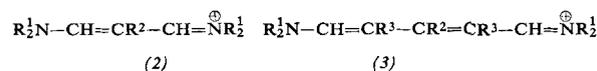
[*] The carbon atoms of the chain are designated according to their positions relative to the nitrogen atoms as $\alpha, \beta, \gamma, \delta$.

[**] T₂ is the transverse relaxation time in seconds/radian and is estimated from the linear width $\Delta\omega_{1,2}$.

of equal intensity (see Table 1). This splitting of the methyl signals is independent of temperature and is an approximately linear function of the field strength, e.g. for (1a) in CHCl₃: 11.75 cps at 60 Mcps; 4.4 cps at 25 Mcps. It is largely independent of the nature of the solvent in neutral medium. Any external ions added have no influence on the splitting. These results imply that the internal rotation of the *N,N*-dimethylamino groups around the N=C(α) bond is hindered [2, 3], a phenomenon described by Gutowsky et al. [4] for carbonyl compounds of the type R-CO-N(CH₃)₂. Like all *cis-trans*-rearrangements, the internal rotation is acid-catalysed. When the rotation of the *N,N*-dimethylamino groups is inhibited, the protons of the two freely rotating methyl-groups lie in fields of different intensities. The height of the energy barrier E_a to rotation around the N=C(α) bond was estimated by the method of Gutowsky [4] (see Table 1). E_a and T_{coin} (i.e. the temperature at which the two methyl signals coincide) decrease with increasing chain length, e.g. (1c) shows only one methyl-group signal at room temperature (see Table 1).

Addition of acid lowers the activation energy for reorientation, (0.11 % by vol. of H₂SO₄ in 0.2 M aqueous solution reduced E_a for (1a) from 17 to 8.6 kcal/mole). The NMR spectrum of the protons of the chain carbons remains unchanged, i.e. the *trans*-linkage of the cyanine chain is retained. However, proton exchange in β-position of the cyanine chain does take place. In D₂O with addition of about 0.1 % by vol. of D₂SO₄ it is slow enough that its kinetics can be examined. The β-position becomes occupied by deuterium; and a singlet replaces the α-doublet. The rate constant in 0.04 N D₂SO₄ is k ≈ 2 × 10⁻⁴ sec⁻¹.

Hindered rotation of *N,N*-dialkylamino groups was also observed in compounds of types (2) and (3).



(2a): R₂¹ = -(CH₂)_n-; R² = H

(2b): R¹ = CH₃, C₂H₅; R² = H, CH₃, CH=overset{oplus}{N}(CH₃)₂

(3): substituents as in (2b); R₂³ = H + H, o-C₆H₄

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