

# Organosodium and Organopotassium Compounds

## Part II: Preparation and Synthetic Applications [1]

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*A selection of well established procedures for the preparation of the most common organosodium and organopotassium compounds is given. The wide synthetic applicability of organoalkali-metal compounds is shown by means of examples. Unlike Part I, Part II deals not only with "true" organoalkali compounds, but also with salt-like compounds such as sodium acetylides and sodiocarboxylic esters, since these possess considerable preparative value.*

### A. Preparative Methods

1. From metal derivatives
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  - b) Metalation with alkali amides
  - c) Other methods
2. Reactions with metals
  - a) Metal-metal exchange
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- c) Halogen-metal exchange
- d) Cleavage of ethers
- e) Cleavage of carbon-carbon bonds
- f) Addition of metals to multiple bonds

### B. Experimental procedures

1. Alkali metals
2. Organoalkali-metal compounds
3. Syntheses using organoalkali-metal compounds

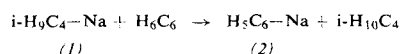
### A. Preparative Methods

A distinction is to be drawn between methods which lead to the creation of new organometallic bonds by the action of elemental alkali metals, and those which merely effect transfer of the organometallic bond from one organic residue to another. We shall first consider the latter type, in which a readily accessible organometallic compound, or occasionally an alkali metal amide or alkoxide, is used for the preparation of an organometallic reagent.

#### 1. From Metal Derivatives

##### a) Transmetalation

By analogy with an acid-base reaction, the weaker organometallic base may be obtained from the corresponding hydrocarbon and a more strongly basic organometallic compound. The first transmetalation of this type was observed by Schorigin [2] [(1) → (2)]. Tables 1 and 2 list examples of such transmetalations.



[1] Part I: Properties and Reactions: *M. Schlosser*, *Angew. Chem.* 76, 124 (1964); *Angew. Chem. internat. Edit.* 3, 287 (1964).

[\*] Present address.

[2] *P. Schorigin*, *Ber. dtsh. chem. Ges.* 41. 2711, 2717, 2723 (1908).

[3] *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).

[4] *A. A. Morton, M. L. Brown, M. E. T. Holden, R. L. Letsinger, and E. E. Magat*, *J. Amer. chem. Soc.* 67, 2224 (1945).

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

Table 1. Metalation of hydrocarbons.

Hydrocarbon to be metalated	Metalating agent [a]	Ref.	New compound	Yield [%] [b]
Ethylene	(3)	[3]	Vinylsodium	[c]
Propene	(3)	[4, 5]	Allylsodium	69[d]
1-Butene	(3)	[4, 5]	Crotylsodium	62[d]
2-Butene	(3)	[4, 5]		
Isobutene	(4)	[6]	2-Methylallylpotassium	63
Benzene	(3)	[7]	Phenylsodium	78
Benzene	(5)	[8]		[c]
Benzene	(6)	[9]	Phenylpotassium	45
Benzene	(7)	[8, 10, 11]		83
Cyclohexene	(3)	[12]	Δ <sup>2</sup> -Cyclohexenylsodium	38-84
Toluene	(3)	[7]	Benzylsodium	40
Toluene	(2)	[13, 14]		99
Toluene	(7)	[8]	Benzylpotassium	44
Toluene	(4)	[6]		70
Indene	(8)	[15]	Δ <sup>2</sup> -Indenylsodium	50
Acenaphthene	(3)	[16, 17]	1,5-Acenaphthylenedisodium	50
Fluorene	(3)	[16, 18]	9-Fluorenylsodium	100
Fluorene	(8)	[15]		40-70
Diphenylmethane	(3)	[7, 16]	Diphenylmethylsodium	92
1,2-Diphenylethane	(3)	[16]	1,2-Diphenylethylenedisodium	70
Triphenylmethane	(3)	[16]	Triphenylmethylsodium	93
Triphenylmethane	(4)	[19]	Triphenylmethylpotassium	[c]
Tri- <i>o</i> -tolylmethane	(4)	[20]	Tris-( <i>o</i> -potassio- <i>o</i> -tolyl)methane	40

[a] (3): n-Amylsodium (6): Ethylpotassium  
(4): Phenylisopropylpotassium (7): n-Butylpotassium  
(5): n-Butylsodium (8): Triphenylmethylsodium

[b] The yields given should be regarded as minimum values, since they almost all refer to the carboxylic acids prepared for characterization purposes.

[c] Exact values not given.

[d] The products isolated from the carboxylation were the isomeric carboxylic acids

R-CH=CH-CH<sub>2</sub>-COOH and H<sub>2</sub>C=CH-CHR-COOH, together with small amounts of the α,β-unsaturated acid R-CH<sub>2</sub>-CH=CH-COOH and dicarboxylic acids.

Ferrocene readily undergoes double metalation by reaction with (2) or (3) to give (13) in yields of 47 and 68 %, respectively [30a].

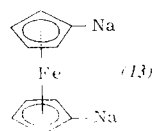


Table 2. Metalation of ethers and thioethers.

Ether or thioether	Metalating agent [a]	Ref.	New compound	Yield [%] [b]
Furan	(9)	[21]	2-Furylsodium	58
Thiophene	(2)	[22]	2-Thienylsodium	89
Thiophene	(3)	[23]	2,5-Thienylenedisodium	50
2,3-Dihydrofuran	(3)	[24]	2,3-Dihydro-5-furylsodium	58
Anisole	(2)	[25]	<i>o</i> -Anisylsodium	64
Anisole	(10)	[26]	<i>o</i> -Anisylsodium and -lithium	71
Anisole	(11)	[27]	<i>o</i> -Anisylpotassium	60
Dibenzofuran	(9)	[28]	4,6-Dibenzofurylenedisodium	80
	(12)	[28]		88
Dibenzothiophene	(3)	[25]	4-Dibenzothiénylenesodium	37
Diphenyl ether	(2)	[29]	<i>o</i> -Phenoxyphenylsodium	10
Diphenyl ether	(10)	[30]	<i>o</i> -Phenoxyphenylsodium and -lithium (together with <i>o,o'</i> -dimetalated derivative)	50
Diphenyl sulfide	(2)	[25]	<i>o</i> -Thiophenoxyphenylsodium	56

[a] See footnote [a] of Table 1. In addition:

(9): Benzylsodium (11): Phenylpotassium  
 (10): Diphenyl-lithium-sodium (12): *p*-Tolylsodium

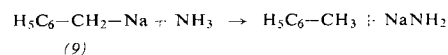
[b] See footnote [b] of Table 1.

- [6] K. Ziegler and H. Dislich, Chem. Ber. 90, 1107 (1957).  
 [7] A. A. Morton and I. Hechenbleikner, J. Amer. chem. Soc. 58, 2599 (1936).  
 [8] H. Gilman and J. C. Bailie, J. org. Chemistry 2, 84 (1937).  
 [9] H. Gilman and R. H. Kirby, J. Amer. chem. Soc. 58, 2074 (1936).  
 [10] H. Gilman, A. L. Jacoby, and H. Ludeman, J. Amer. chem. Soc. 60, 2336 (1938).  
 [11] D. Bryce-Smith and E. E. Turner, J. chem. Soc. (London) 1953, 861.  
 [12] A. A. Morton and R. A. Finnegan, J. Polymer Sci. 38, 19 (1959).  
 [13] J. F. Nobis and L. F. Moormeier, Ind. Engng. Chem., analyt. Edit. 46, 539 (1954).  
 [14] H. Gilman, H. A. Pacevitz, and O. Baine, J. Amer. chem. Soc. 62, 1514 (1940).  
 [15] J. B. Conant and G. W. Wheland, J. Amer. chem. Soc. 54, 1212 (1932).  
 [16] A. A. Morton and E. L. Little, J. Amer. chem. Soc. 71, 487 (1949).  
 [17] 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).  
 [18] A. A. Morton and F. Fallwell, J. Amer. chem. Soc. 60, 1924 (1938).  
 [19] K. Ziegler, Angew. Chem. 49, 459 (1936).  
 [20] P. D. Bartlett and J. E. Jones, J. Amer. chem. Soc. 64, 1837 (1942).  
 [21] H. Gilman and F. Breuer, J. Amer. chem. Soc. 56, 1123 (1934).  
 [22] J. W. Schick and H. D. Hartough, J. Amer. chem. Soc. 70, 286 (1948).  
 [23] A. A. Morton and C. E. Claff, J. Amer. chem. Soc. 76, 4935 (1954).  
 [24] R. Paul and S. Tchelitcheff, C. R. hebdom. Séances Acad. Sci. 235, 1226 (1952).  
 [25] H. Gilman and R. L. Bebb, J. Amer. chem. Soc. 61, 109 (1939).  
 [26] G. Wittig and E. Benz, Chem. Ber. 91, 874 (1958).  
 [27] A. A. Morton and E. J. Lanpher, J. org. Chemistry 23, 1639 (1958).  
 [28] H. Gilman, F. W. Moore, and O. Baine, J. Amer. chem. Soc. 63, 2479 (1941).

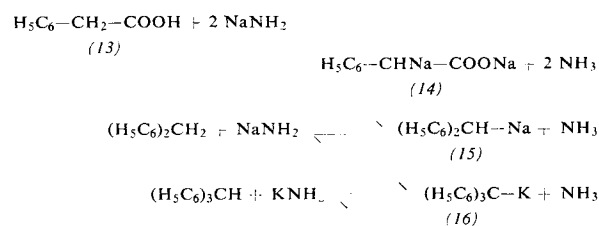
## b) Metalation with Alkali Amides

True organometallic compounds are not required for the anionization of ketones, nitriles, esters, sulfoxides, and other compounds containing activated hydrogens. The exchange of hydrogen for metal may be accomplished with even relatively weak proton acceptors such as sodium dispersions, potassium hydroxide, sodium

hydride, sodium ethoxide, or potassium *t*-butoxide. Sodamide or potassamide in liquid ammonia are even more effective. However, these amides are too weakly basic to metalate purely aliphatic or monophenylated hydrocarbons [31]. On the other hand, alkali-metal benzyls, *e.g.* (9), are rapidly ammonolyzed with decolorization by liquid ammonia.



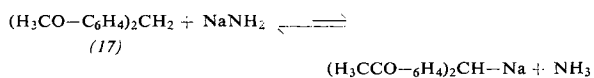
The reactive hydrogens in acetylene [31a] or fluorene [32] are readily metalated by alkali-metal amides. As a rule, alkali-metal benzyls such as (15) and (16) are obtained smoothly with these amides if at least one additional activating group is present besides one aryl



- [29] A. Lüttringhaus and G. v. Sääf, Angew. Chem. 52, 578 (1939); Liebigs Ann. Chem. 542, 241 (1939); 557, 25 (1947).  
 [30] G. Wittig and L. Pohmer, Chem. Ber. 89, 1334 (1956).  
 [30a] A. N. Nesmeyanov and E. G. Perevalova, Dokl. Akad. Nauk SSSR 112, 439 (1957); *ibid.* 120, 1263 (1958); S. I. Goldberg, D. W. Mayo, M. Vogel, H. Rosenberg, and M. Rausch, J. org. Chemistry 24, 824 (1959); E. O. Fischer and H. Brunner, Z. Naturforsch. 16b, 406 (1961).  
 [31] C. B. Wooster and J. F. Ryan, J. Amer. chem. Soc. 54, 2419 (1932).  
 [31a] R. A. Raphael: Acetylenic Compounds in Organic Synthesis. Butterworths, London 1955, pp. 192-196.  
 [32] R. S. Yost and C. R. Hauser, J. Amer. chem. Soc. 69, 2325 (1947).

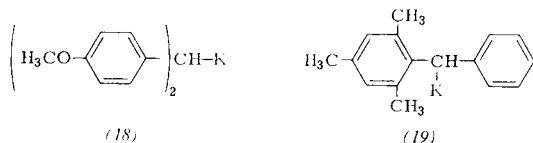
residue. This is illustrated by the preparation of sodium  $\alpha$ -sodio- $\alpha$ -phenylacetate (14) [33], diphenylmethylsodium (15) [31], and triphenylmethylpotassium (16) [34].

These transformations are equilibrium reactions. In the case of di-*p*-anisylmethane (17) [35], the equilibrium lies more to the left.



With diphenyl- and triphenylmethane, it is only in the ammonia solution that the equilibrium seems to be shifted completely towards the organometallic compound. Even on careful (vacuum) removal of the ammonia from a solution of triphenylmethylsodium, the residue is simply a mixture of triphenylmethane and sodamide. Addition of an organic solvent before the removal of the ammonia does not prevent the aminolysis [36a, 36b]. In contrast to diphenyl- and triphenylmethylsodium, the corresponding potassium derivatives may be isolated from their ammonia solutions with no difficulty, immaterial of whether the ammonia is evaporated off directly or whether an organic phase is first admixed [36a, 36b]. The fact that here the reversion to the hydrocarbon is suppressed does not necessarily imply that the organopotassium compound is more stable; the phenomenon could also be due to extremely slow attainment of the aminolysis-equilibrium in the case of the organopotassium derivative [37].

Di-*p*-anisylmethylpotassium (18) and mesitylphenylmethylpotassium (19) are stronger bases. If the attempt is made to isolate them from ammonia solution, they are protonated to regenerate the hydrocarbon just like the organosodium compounds [36a, 36b].



### c) Other Methods

New organosodium and organopotassium reagents may also be prepared by the reactions of organosodium and -potassium compounds with olefins (20) (addition), with halides (21) (halogen-metal interconversion), and with organometallic compounds, particularly those of mercury (22) (metal-metal interconversion). None of these reactions is of major preparative significance.

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

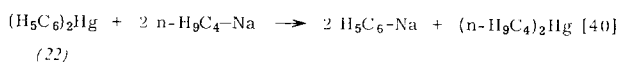
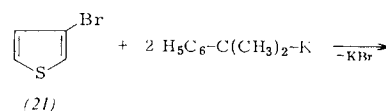
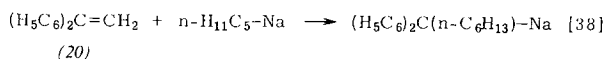
[34] C. A. Kraus and R. Rosen, *J. Amer. chem. Soc.* 47, 2739 (1925).

[35] C. R. Hauser and P. J. Hamrick, *J. Amer. chem. Soc.* 79, 3142 (1957).

[36a] R. Levine, E. Baumgarten, and C. R. Hauser, *J. Amer. chem. Soc.* 66, 1230 (1944).

[36b] C. R. Hauser, D. S. Hoffenberg, W. H. Puterbaugh, and F. C. Frostik, *J. org. Chemistry* 20, 1531 (1955)

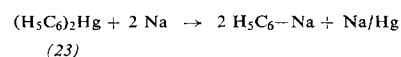
[37] Cf. G. Wittig, *Experientia* 14, 392 (1958).



## 2. Reactions with Metals [\*]

### a) Metal-Metal Exchange

The first organoalkali-metal compounds were prepared from organomercury compounds [(23) and Table 3] and sodium [2, 41, 42], and were even isolated [43].



Lithium and potassium derivatives may be obtained analogously. Since these are equilibrium reactions, the

Table 3. Organosodium and organopotassium compounds obtained from the corresponding mercury derivatives.

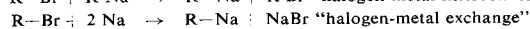
Organic residue of mercury compound	Reference	
	Na derivative	K derivative
Methyl	[43, 44]	[43, 45]
Ethyl	[2, 9, 43, 45, 46]	[9]
n-Propyl	[46]	--
n-Butyl	[8] [d]	[8, 14] [d]
i-Amyl	[2] [d]	--
n-Octyl	[43]	--
Phenyl	[14, 43]	[47]
o-Tolyl	[14] [d]	--
m-Tolyl	[14] [d]	--
p-Tolyl	[14] [d]	[14] [d]

[d] Under the reaction conditions used, these organoalkali-metal compounds occur only as intermediates.

[38] A. A. Morton and H. C. Wohlers, *J. Amer. chem. Soc.* 69, 167 (1947).

[39] G. Wittig and V. Wahl, unpublished data.

[\*] In Anglo-American literature, a distinction is made between exchange reactions between organic halides and organoalkali-metal compounds, and those involving alkali metals, *e.g.*



See R. G. Jones and H. Gilman in R. Adams: *Organic Reactions*, Wiley, New York 1951, Vol. 6, p. 339; *Chem. Reviews* 54, 835 (1954).

[40] H. Gilman, W. Langham, and A. L. Jacoby, *J. Amer. chem. Soc.* 61, 109 (1939).

[41] F. S. Acree, *Amer. Chem. J.* 29, 588 (1903).

[42] G. Buckton, *Liebigs Ann. Chem.* 112, 222 (1859).

[43] W. Schlenk and J. Holtz, *Ber. dtsch. chem. Ges.* 50, 262 (1917).

[43a] W. Schlenk and J. Holtz, [43], pp. 265 et seq.; cf. H. Gilman and T. C. Wu, *J. org. Chemistry* 18, 759 (1953).

[44] W. H. Carothers and D. D. Coffman, *J. Amer. chem. Soc.* 52, 1254 (1930).

[45] W. H. Carothers and D. D. Coffman, *J. Amer. chem. Soc.* 51, 588 (1929).

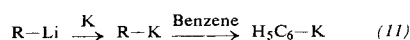
[46] F. C. Whitmore and H. D. Zook, *J. Amer. chem. Soc.* 64, 1783 (1942).

[47] A. A. Morton and R. L. Letsinger, *J. Amer. chem. Soc.* 69, 172 (1947).

alkali metal is always introduced in great excess. Often no attempt is made to separate the resulting organo-alkali-metal compound from the unused alkali metal and the amalgam, although the separation procedure is a simple one [43a].

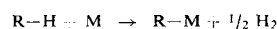
Although many organomercury compounds are easily prepared, this method soon fell out of favor, since it is not suitable for the preparation of large quantities of organo-alkali compounds. The insidious toxicity of liquid mercury derivatives is a further serious disadvantage. Nowadays the mercury/alkali metal exchange is used only for the preparation of limited amounts of salt-free organosodium or organopotassium compounds when drastic conditions must be avoided.

The displacement method can be applied to other organometallic compounds, provided that the metal to be displaced is more electronegative than sodium. Alkylpotassium compounds are thus obtained elegantly from lithium alkyls and potassium metal in hydrocarbons [48]; transmetalation in benzene leads directly to phenylpotassium (11) in 86 % yield [11]:



#### b) Direct Metalation

The direct replacement of hydrogen by the elemental metal provides the simplest means of access to organo-alkali compounds.



The controlling factors in direct metalation are the acidity of the hydrocarbon, the electropositivity and particle size of the metal used, and the nature of the solvent. The conversion of triphenylmethane into triphenylmethylpotassium by means of molten potassium, which reacts with the hydrocarbon above 200 °C, is accompanied by side reactions [49]. Metalation may be accomplished quite easily, however, with the blue solution of potassium in liquid ammonia [50], or with the corresponding solution of sodium [51]; the latter, however, reacts more sluggishly. Sodium dispersions (see Section B.1) and sodium aromatic complexes [52] are far superior to solid sodium in the anionization of carboxylic esters and aliphatic nitriles. Potassium reacts more vigorously with thiophene [22] than sodium does, and metallic cesium displaces even the hydrogen atoms of paraffins [53]. Table 4 gives a list of some organosodium and organopotassium compounds obtained by hydrogen-metal exchange. The displaced hydrogen is not always liberated as gas. With acetylene

[48] D. Bryce-Smith, J. chem. Soc. (London) 1954, 1079.

[49] M. Hanriot and O. Saint-Pierre, Bull. Soc. chim. France [3], 1, 775 (1889); A. Werner and A. Grob, Ber. dtsh. chem. Ges. 37, 2898 (1904).

[50] C. B. Wooster and N. W. Mitchell, J. Amer. chem. Soc. 52, 688 (1930).

[51] C. A. Kraus and T. Kawamura, J. Amer. chem. Soc. 45, 2756 (1923).

[52] L. Horner and H. Güsten, Liebigs Ann. Chem. 652, 99 (1962).

[53] E. Marcus, unpublished data; cited by W. Schlenk in Houben-Weyl: Die Methoden der organischen Chemie. 2nd Edit. Thieme-Verlag, Leipzig 1924, Vol. IV, p. 946.

[54], fluorene [55], and triphenylmethane [56], the reaction mixtures contain hydrogenation products as well as the appropriate organometallic base. The metalation of toluene to give benzylpotassium (24) in the presence of sodium oxide is especially noteworthy in this respect [57].

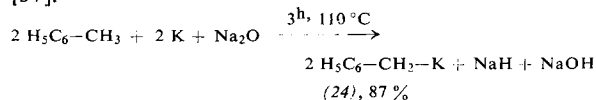


Table 4. Organosodium and organopotassium compounds obtained by hydrogen-metal exchange.

Organic residue	Reference	
	Na derivative	K derivative
Ethynyl	[58, 59, 59b]	[59]
Ethynylene	[60]	—
Phenylethynyl	[61]	[61]
Pentaphenylcyclopentadienyl	—	[62]
Indenyl	[63, 64]	—
9-Fluorenyl	[64]	—
9-Fluorenylidene	[c]	[65] [e]
Triphenylmethyl	[50]	[49, 50, 55]
Diphenylmethylene	—	[66] [e]
Benzyl	—	[56]
2-Furyl	—	[21]
5-Methyl-2-furyl	—	[21]
2-Thienyl	—	[67]
5-Chloro-2-thienyl	[22]	—
5-Bromo-2-thienyl	[22]	—
5-Iodo-2-thienyl	[22]	—

[c] Apparently the geminally dimetalated derivatives are formed.

The hydrogen atoms bound to the metalloids in germane GeH<sub>4</sub>, triphenylgermane (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeH, and triphenylstannane (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnH are metalated with particular ease by sodium or potassium in liquid ammonia, but not by sodamide [68–70].

#### c) Halogen-Metal Exchange

Derivatives of heavier alkali metals can be prepared in a manner analogous to the synthesis of organomagnesium

[54] R. A. Raphael: Acetylenic Compounds in Organic Synthesis. Butterworths, London 1955, p. 1.

[55] J. J. Eisch and W. C. Kaska, J. org. Chemistry 27, 3745 (1962).

[56] H. O. House and V. Kramar, J. org. Chemistry 27, 4146 (1962).

[57] C. E. Claff and A. A. Morton, J. org. Chemistry 20, 440 (1955).

[58] K. Heß and M. Munderloh, Ber. dtsh. chem. Ges. 51, 377 (1918).

[59a] T. H. Vaughn, G. F. Hennion, R. R. Vogt, and J. A. Nieuwland, J. org. Chemistry 2, 1 (1937).

[59b] R. A. Raphael: Acetylenic Compounds in Organic Synthesis. Butterworths, London 1955, pp. 192–196.

[60] C. Matignon, C. R. hebd. Séances Acad. Sci. 124, 775 (1897).

[61] H. Gilman and R. V. Young, J. org. Chemistry 1, 315 (1936).

[62] K. Ziegler and L. Ewald, Liebigs Ann. Chem. 473, 163 (1929).

[63] R. Weißgerber, Ber. dtsh. chem. Ges. 41, 2913 (1908); 42, 569 (1909).

[64] U.S.-Pat. 2 171 867 (Sept. 5th, 1939), inventors: N. S. Scott, J. F. Walker and V. L. Hansley.

[65] G. W. H. Scherf and R. K. Brown, Canad. J. Chem. 38, 697 (1960).

[66] O. Saint-Pierre, Bull. Soc. chim. France [3] 6, 292 (1891).

[67] Cf. K. Ziegler [87], pp. 1745 et seq.

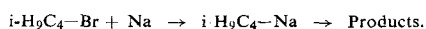
[68] C. A. Kraus and E. S. Carney, J. Amer. chem. Soc. 56, 765 (1934).

[69] G. K. Teal and C. A. Kraus, J. Amer. chem. Soc. 72, 4705 (1950).

[70] C. A. Kraus and W. H. Kahler, J. Amer. chem. Soc. 55, 3537 (1933).

and organolithium compounds, *i.e.* by the action of the metal on organic halides.

Many years ago, *Schorigin* [2] postulated the occurrence of the alkylsodium compounds (1), which were supposed to be formed by halogen-metal exchange, as intermediates in the Wurtz synthesis and in certain addition reactions:



(1)

Nevertheless, it was a long time before this procedure became a standard method, surpassing in importance all other preparations of organosodium and organopotassium compounds. The high reactivity of the organometallic compounds at first frustrated any attempts at their isolation; instead, they were consumed by subsequent reactions with the solvent or with unreacted halide.

It was only after the studies of *Morton* [72–75] that it became possible to suppress secondary processes such as transmetalation, elimination, and Wurtz condensation. The use of finely divided sodium, high-speed stirring, and effective temperature control permit the preparation of numerous organosodium compounds in quantitative yield. Thus, a continuous unit [71] is capable of handling more than 1 kg of sodium powder per hour to give phenylsodium in 75% yield [71].

The greater reactivity of sodium and potassium derivatives, relative to the Grignard and lithium compounds used previously, extends the scope of organometallic reagents in preparative reactions. Furthermore, organometallic compounds may now be prepared economically from sodium and alkyl or aryl chlorides, using cheap solvents, and are thus suitable for industrial applications. Grignard compounds are mostly obtained from expensive bromides or iodides, whereas all of the organoalkali-metal derivatives in Table 5, with but a single exception [84], are derived from chlorides.

*E. Müller* [85] described some interesting exchange reactions of the disodium adduct of tetraphenylethylene, which behaves like dissolved sodium. Thus, *o*-bromofluorobenzene is converted by it into *o*-fluorophenylsodium at  $-70^\circ\text{C}$  in tetrahydrofuran; treatment of this with benzophenone leads to a 65% yield of *o*-fluorophenyldiphenylmethanol. Under the same conditions, *o*-bromophenylsodium, which is obtained similarly from *o*-dibromobenzene, is unstable, dehydrobenzene derived from its decomposition can be trapped with furan in 15–36% yield.

[71] *H. Ruschig, R. Fugmann, and W. Meixner, Angew. Chem. 70, 71 (1958).*

[72] *A. A. Morton, G. M. Richardson, and A. T. Hallowell, J. Amer. chem. Soc. 63, 327 (1941).*

[73] *A. A. Morton, J. B. Davidson, and H. A. Newey, J. Amer. chem. Soc. 64, 2240 (1942).*

[74] *A. A. Morton and H. A. Newey, J. Amer. chem. Soc. 64, 2248 (1942).*

[75] *A. A. Morton, J. B. Davidson, and R. J. Best, J. Amer. chem. Soc. 64, 2239 (1942).*

Table 5. Organosodium and organopotassium compounds obtained by halogen-metal exchange.

Organic residue	Na derivative		K derivative	
	Ref.	Yield [%] [b]	Ref.	Yield [%] [b]
n-1-Propyl	[72]	26	—	—
n-1-Butyl	[73]	42	—	—
n-1-Amyl	[3, 74]	72–80	[4]	35
n-1-Octyl	[75]	64	—	—
n-1-Decyl	[75]	31	—	—
n-1-Dodecyl	[76]	20	[76]	10
n-2-Butyl	[73]	2	—	—
n-2-Amyl	[73]	2	—	—
Cyclohexyl	[77]	8	—	—
Triphenylmethyl	[43, 78, 79]	95–100	—	—
Vinyl	[80]	90	[80, 81]	73
1-Cyclohexenyl	[80]	60	—	—
$\alpha$ -Styryl	[80]	21	—	—
Phenyl	[13, 14, 82]	100	[27]	55
<i>p</i> -Tolyl	[14, 19]	80	—	—
<i>p</i> -Biphenyl	[77]	78	—	—
1-Naphthyl	[83]	90	—	—
3-Pyrenyl	[83]	80	—	—
9-Anthryl	[83]	55	—	—
9-Phenanthryl	[83]	35	—	—
2-Furyl	[77]	[c]	—	—
3-Furyl	—	—	[84]	0.5
2-Thienyl	[22]	84	—	—

[b], [c]: See corresponding footnotes in Table 1.

#### d) Cleavage of Ethers

The cleavage of ethers by alkali metals [86–88] is formally analogous to the halogen-metal exchange, but differs from it in one significant respect: purely aliphatic ethers are stable toward metals below  $200^\circ\text{C}$ . Only aryl and benzyl ethers are cleaved; with mixed aryl ethers (25), the oxygen remains attached to the aromatic residue, while the alkyl residue becomes part of the organometallic compound. Benzyl aryl ethers (26) are decomposed to the more weakly basic benzylalkali-metal compound and alkali phenoxide.

[76] *R. N. Meals, J. org. Chemistry 9, 211 (1944).*

[77] *A. A. Morton, G. H. Patterson, J. J. Donovan, and E. L. Little, J. Amer. chem. Soc. 68, 93 (1946).*

[78] *W. B. Renfrow and C. R. Hauser in Organic Syntheses, Wiley, New York 1943, Coll. Vol. II, p. 607.*

[79] *H. E. Zimmermann and F. J. Smentowski, J. Amer. chem. Soc. 79, 5455 (1957).*

[80] *Brit. Pat. 886980 (Oct. 2nd, 1959), Union Carbide Corporation, inventor: D. J. Foster.*

[81] *R. G. Anderson, M. B. Silverman, and D. M. Ritter, J. org. Chemistry 23, 750 (1958).*

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

[83] *French Pat. 1236912 (June 13th, 1960), Union Carbide Corporation, inventor: D. J. Foster.*

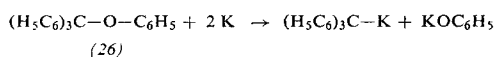
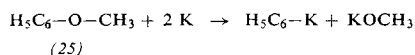
[84] *H. Gilman and G. F. Wright, J. Amer. chem. Soc. 55, 2893 (1933).*

[85] *E. Müller and G. Röscheisen, Chem. Ber. 90, 543 (1957).*

[86] *P. Schorigin, Ber. dtsh. chem. Ges. 56, 176 (1923).*

[87] *K. Ziegler and F. Thielmann, Ber. dtsh. chem. Ges. 56, 1740 (1923).*

[88] *A. Lüttringhaus in Houben-Weyl: Die Methoden der Organischen Chemie, 2nd Edit., Thieme-Verlag, Leipzig 1924, Vol. II, p. 424.*



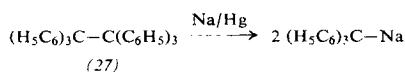
A convenient source of metal is a liquid Na/K alloy [87], an excess being used. Cleavage is generally quantitative (see Table 6, K derivatives). Only a few very labile ethers react at low temperatures with pulverized or solid sodium (see Table 6, Na derivatives). Ether cleavage provides a means of degrading complex ethers and thioethers [88,94]. Acetals are cleaved with particular ease. The resulting  $\alpha$ -metalated ethers sometimes undergo Wittig rearrangement [91].

Table 6. Organosodium and organopotassium compounds obtained by ether cleavage.

Organic residue	Reference	
	Na derivative	K derivative
Phenyl	—	[27]
Allyl	[89]	[93]
Phenylisopropyl	—	[6,90]
Dibenzylphenylmethyl	—	[90]
Diphenylmethyl	—	[87]
1,1-Diphenylethyl	—	[90]
1,1,2-Triphenylethyl	—	[90]
Triphenylpropynyl	—	[90]
1,1,3,3-Tetraphenylprop-2-yl	—	[90]
Methoxydiphenylmethyl	[91]	[87,91]
9-Fluorenyl	[92]	—
9-Phenyl-9-fluorenyl	[57]	—
9-Methoxy-9-fluorenyl	[57]	—

### e) Cleavage of Carbon-Carbon Bonds

Polyarylethanes (27) are reported by Schlenk [95] to be cleaved by alkali metals at their weakened central C-C bond, giving two molecules of organometallic compound.



With sodium powder, hexaphenylethane (27) is largely irreversibly isomerized to *p*-diphenylmethylphenyltriphenylmethane.

The tendency of the ethane derivatives to dissociate may be roughly estimated from the nature of the metal required for cleavage. Hexaphenylethane reacts even with 1% sodium amalgam, 9,9'-dimethylbixanthyl requires 40% sodium amalgam [96], while 1,1,2,2-tetraphenylethane [87] is cleaved only with liquid Na/K alloy to yield diphenylmethylpotassium. Table 7 gives a

[89] R. L. Letsinger and J. G. Traynham, J. Amer. chem. Soc. 70, 3342 (1948).

[90] K. Ziegler and B. Schnell, Liebigs Ann. Chem. 437, 227 (1924).

[91] G. Wittig and W. Happe, Liebigs Ann. Chem. 557, 205 (1947).

[92] A. Kliegl, Ber. dtsh. chem. Ges. 62, 1327 (1929).

[93] A. A. Morton, E. E. Magat, and R. L. Letsinger, J. Amer. chem. Soc. 69, 959 (1947).

[94] R. L. Burwell, Chem. Reviews 54, 673 (1954); D. S. Tarbell and D. P. Harnish, ibid. 49, 1 (p. 38 et seq.) (1951); W. E. Truce, D. P. Tate, and D. N. Burdge, J. Amer. chem. Soc. 82, 2872 (1960).

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

[96] J. B. Conant and B. S. Garvey, J. Amer. chem. Soc. 49, 2599 (1927).

survey of the organosodium and organopotassium compounds obtained from symmetrical ethanes by such cleavage reactions. The cleavage of unsymmetrical hydrocarbons such as pentaphenylethane [95] and 1,1,1,2-tetraphenylethane [87] is also possible. In this case, mixtures of two organometallic compounds are obtained.

Table 7. Organosodium and organopotassium compounds obtained by cleavage of symmetrical ethanes.

Organic residue	Reference	
	Na derivative	K derivative
Triphenylmethyl	[95]	—
Di- <i>p</i> -biphenyl- $\alpha$ -naphthylmethyl	[95]	—
Xanthyl	[96]	[96]
9-Methyl-9-xanthyl	[96]	[96]
Diphenylmethyl	—	[96]
(H <sub>5</sub> C <sub>6</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> O)C—	[97]	[97]
(H <sub>5</sub> C <sub>6</sub> ) <sub>2</sub> (H <sub>5</sub> C <sub>6</sub> -C $\equiv$ C)C—	[98]	—
<i>p</i> -Biphenylmethyl	—	[99]
(H <sub>5</sub> C <sub>6</sub> ) <sub>2</sub> C=CH-CH <sub>2</sub> —	—	[99]
(H <sub>3</sub> C) <sub>3</sub> C-C $\equiv$ C—	—	[100]

The preparation of triphenylmethylsodium [43] from triphenylmethyl chloride and Na/Hg certainly involves hexaphenylethane as an intermediate. The latter is then cleaved by excess metal to give triphenylmethylsodium. Benzyl chloride does not react with sodium to give benzylsodium, since condensation occurs instantaneously to give 1,2-diphenylethane, which cannot be cleaved [96, 99].

Polyarylated disilanes, digermanes, distannanes, and diplumbanes react with alkali metals in a manner similar to the polyarylethanes. They are cleaved in ether (or, preferably, in liquid ammonia) to give "quasi-organometallic" compounds. For example, hexaphenyldisilane is converted into triphenylsodium [101] and diphenylsilylpotassium [101, 102]. Other preparations of this type include (CH<sub>3</sub>)<sub>3</sub>GeNa [103-106], (CH<sub>3</sub>)<sub>3</sub>SnNa [107], (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNa [108], and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbNa [109]. The triaryl derivatives are chemically very similar to the triaryl-methylalkali-metal compounds.

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

[98] J. G. Stampfli and C. S. Marvel, J. Amer. chem. Soc. 53, 4057 (1931).

[99] G. Wittig and M. Leo, Ber. dtsh. chem. Ges. 63, 943 (1930).

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

[101] A. G. Brook and H. Gilman, J. Amer. chem. Soc. 76, 278 (1954).

[102] H. Gilman and T. C. Wu, J. org. Chemistry 18, 753 (1953).

[103] C. A. Kraus and L. S. Foster, J. Amer. chem. Soc. 49, 457 (1927).

[104] C. A. Kraus and H. S. Nutting, J. Amer. chem. Soc. 54, 1622 (1932).

[105] C. A. Kraus and C. S. Sherman, J. Amer. chem. Soc. 55, 4694 (1933).

[106] F. B. Smith and C. A. Kraus, J. Amer. chem. Soc. 74, 1418 (1952).

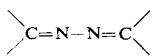
[107] C. A. Kraus and W. V. Session, J. Amer. chem. Soc. 47, 2361 (1925).

[108] R. F. Chambers and P. C. Scherer, J. Amer. chem. Soc. 48, 1054 (1926).

[109] H. Gilman and J. C. Bailie, J. Amer. chem. Soc. 61, 731 (1939).

f) Addition of Metals to Multiple Bonds

*Beckman* [110a] was the first to observe that a solution of benzophenone in dry ether acquires a deep blue-violet color when it is shaken with sodium powder or when boiled with sodium wire. A brief induction period precedes the reaction, in which the sodium ketyl (29) is formed. The reaction has been studied extensively by *Schlenk* [110b]. Later, numerous other intensely colored metal adducts became known including those of ketones, nitriles, Schiff bases, hydrazones, azo compounds, ketazines



nitrogen heterocycles, and derivatives of styrene, stilbene and tolane (diphenylacetylene), as well as of allenes and polycyclic aromatics [111, 112].

Most of these unsaturated systems also add on organometallic reagents readily. However, a few aromatic hydrocarbons, such as naphthalene, appear to add on only the elemental metals.

The ability of such compounds to undergo addition reactions increases with the number of their double bonds. Thus, sodium adds much more rapidly onto anthracene than onto naphthalene, while it does not add onto benzene at all at 80 °C. Strong electropositivity of the metal likewise facilitates the reaction. Benzene probably forms an adduct with potassium under drastic conditions [113], but no adduct is obtained with sodium; ethylene will not react with potassium, but it does react with cesium to yield ethylenedicesium [114].

Lithium appears superior to the heavier alkali metals in additions to triple bonds; for example, it is taken up by tolane much faster than other metals [115]; (it is also the only metal which reacts with molecular nitrogen at room temperature to form a nitride [116]).

Depending on the composition of the products obtained, one can distinguish between

- 1:1 adducts (radical anions)
- 2:1 adducts, and
- 2:2 adducts (dimeric adducts).

[110a] *E. Beckmann* and *Th. Paul*, *Liebigs Ann. Chem.* 266, 1 (1891).

[110b] *W. Schlenk* and *T. Weickel*, *Ber. dtsh. chem. Ges.* 44, 1182 (1911); *W. Schlenk* and *A. Thal*, *ibid.* 46, 2840 (1913).

[111] Reviewed by *C. B. Wooster*, *Chem. Reviews* 11, 37, 48 (1932).

[112] *B. J. Morantz* and *E. Warhurst*, *Trans. Faraday Soc.* 51, 1375 (1955); *A. Mathias* and *E. Warhurst*, *ibid.* 58, 942, 948 (1962); *D. G. Powell* and *E. Warhurst*, *ibid.* 58, 953 (1962).

[113] *H. Abeljanz*, *Ber. dtsh. chem. Ges.* 5, 1027 (1872); 9, 10 (1876); cf. *W. Schlenk* and *H. Meyer*, *ibid.* 46, 4060 (1913); cf. *A. A. Morton* and *E. J. Lanpher*, *J. org. Chemistry* 23, 1640 (1958).

[114] *L. Hackspill* and *R. Rohmer*, *C. R. hebd. Séances Acad. Sci.* 217, 152 (1943).

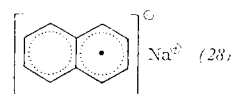
[115] *W. Schlenk* and *E. Bergmann*, *Liebigs Ann. Chem.* 463, 71 (1928).

[116] *F. W. Dafert* and *R. Miklauz*, *Mh. Chem.* 31, 981 (1910).

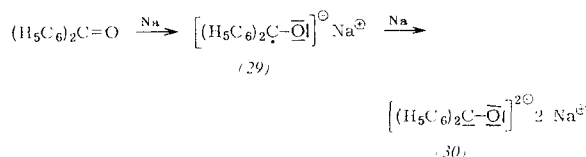
[117a] *N. D. Scott*, *J. F. Walker* and *V. L. Hansley*, *J. Amer. chem. Soc.* 58, 2442 (1936).

[117b] *W. Hüchel*, *Z. Elektrochem., Ber. Bunsenges. physik. Chem.* 43, 838 (1937).

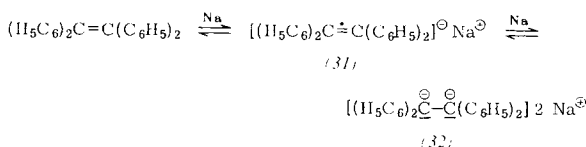
A typical 1:1 complex is naphthalenesodium [51, 117a], which exists as the undissociated ion pair (28) [112, 117b].



The 1:1 adducts can take up additional atoms of metal, particularly at high temperature. Thus, the blue-violet sodium ketyl (29) affords red-violet benzophenone-disodium (30) [118a, 118b].

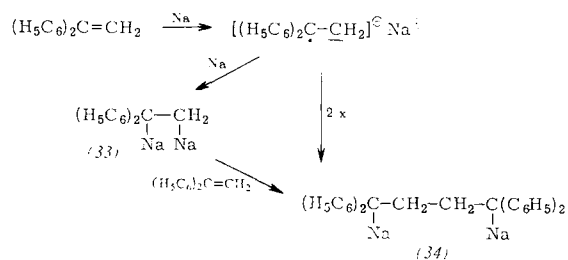


In the case of tetraphenylethylene in ether, the 2:1 adduct (32) is so favored that none of the 1:1 adduct (31) can be detected, no matter how much olefin is present. It is only when the equilibrium between (31) and (32) is shifted by changing the solvent (*e.g.* by replacing ether with 1,2-dimethoxyethane) that the radical anion (31) can be detected by its ESR signal [119].



Many hydrocarbons can bind metal atoms to go beyond the 2:1 adduct, giving highly metalated products such as anthracenedecasodium [120].

With 1,1-diphenylethylenes, adduct formation proceeds by a fundamentally different process. Here, in a formal sense, two radical anions combine to form a dimer that is substituted with metal at the 1- and 4-positions. In this process, however, the 2:2 adduct (34) does not appear to be generated by coupling of two radicals, as *Schlenk* assumed [118a, 121], but rather by addition of the organometallic 2:1 complex (33) onto a second molecule of olefin, as proposed by *Ziegler* [122].



[118a] *W. Schlenk*, *J. Appendoit*, *A. Michael*, and *A. Thal*, *Ber. dtsh. chem. Ges.* 47, 473 (1914).

[118b] *W. Schlenk* and *E. Bergmann*, *Liebigs Ann. Chem.* 464, 22 (1928).

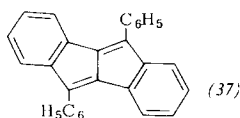
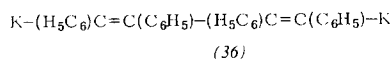
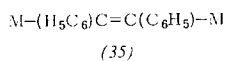
[119] *J. F. Garst* and *R. S. Cole*, *J. Amer. chem. Soc.* 84, 4352 (1962).

[120] U.S.-Pat. 2948762 (August 9th, 1960), *Snia Viscosa*, Milano, inventors: *W. Muench*, *L. Notarbartolo*, *G. Selvestri*, and *V. Ruoti*.

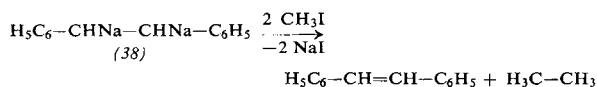
[121] *W. Schlenk* and *E. Bergmann*, *Liebigs Ann. Chem.* 463, 1 (1928).

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

The normally high readiness of a methylene-sodium bond to undergo addition reactions should be even further increased in the adduct (33) by the neighboring diphenylmethyl anion. The increase in reactivity due to directly neighboring organometallic bonds [123] may also be responsible for adduct formation in the case of tolane. Compounds (35) derived from the monomer presumably appear as intermediates, which promptly take up a second molecule of tolane. In ether, lithium adds smoothly onto tolane, giving tetraphenylbutadiene-1,4-dilithium. The analogous greenish-blue adduct (36) is formed with Na/K alloy in dioxan. Its hydrolysis yields, besides tolane (35%), 1% diphenyldibenzopentalene (37), 2% *cis,trans*-1,2,3,4-tetraphenylbutadiene, and 5% 1-benzyl-2,3-diphenylindane [124].



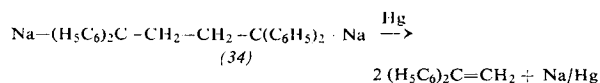
The chemical behavior of most of the 1:1 and 2:1 adducts based on the monomeric hydrocarbons is similar to that of a solution of the appropriate alkali metal in an organic solvent. Thus, when stilbene disodium (38) is treated with methyl iodide, benzyl chloride, aryl halides, oxygen, sulfur, or arsenic(III) chloride, the original hydrocarbon is always regenerated [121, 125a-125c].



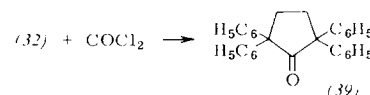
In other cases, stilbene disodium (38) reacts like an organometallic compound. For example, it reacts with proton donors to give diphenylethane, with dimethyl sulfate to give racemic and *meso*-2,3-diphenylbutane, and with carbon dioxide to give *meso*-2,3-diphenylsuccinic acid (together with some racemate) [125a-125c].

Unlike the 1:1 and 2:1 adducts, the dimeric (2:2) adducts find many preparative applications, since they only rarely revert to the parent hydrocarbon; for example, 1,1,4,4-tetraphenylbutylene-1,4-disodium (34) may be cleaved with mercury [121, 126], and the ana-

logous dipotassium compound is cleaved with iodine, methylene iodide, or tetramethylethylene dibromide [127], reverting to 1,1-diphenylethylene.

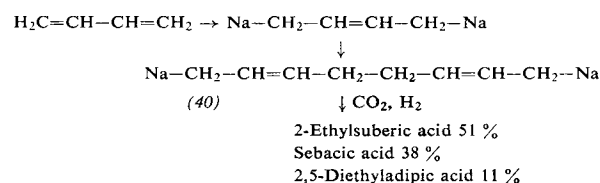


The other reactions of the 2:2 adducts, including those with alkyl and acyl halides, esters, aldehydes, or nitrosyl chloride, give the corresponding 1,4-disubstituted derivatives, e.g. (39) [121].



Under mild conditions, 2:2 adducts of butadiene [128], styrene [129], and  $\alpha$ -methylstyrene [129] may also be obtained. To inhibit polymerization, polar ethers such as dimethyl ether, tetrahydrofuran, or dimethoxyethane are used as solvents. In these media, adduct formation occurs with sufficient rapidity even at  $-30^\circ\text{C}$ . A small amount of *o*-terphenyl serves as a carrier for the dispersed sodium. The metal is transferred to the olefin via the aromatic sodium complex initially formed.

The dimeric adduct of butadiene (40) and sodium is now being produced on an industrial scale. The mixture of unsaturated  $\text{C}_{10}$  dicarboxylic acids which results from carboxylation of (40) is sold commercially in the hydrogenated form [128, 130].



The alkali metal adducts are important in many reactions, in which they act as intermediates that cannot be isolated. The chief examples are the Birch-Hückel-Ziegler [131] and Bouveault-Blanc [132, 133] reductions using the elemental metals in the presence of proton donors. Related to these is a convenient method for the preparation of diphenylmethyl-type organosodium and organopotassium compounds, in which the metal is added onto derivatives of 1,1-diphenylethylene in liquid ammonia. All the alkali-metal atoms attached to an

[123] This principle was formulated by K. Ziegler et al. [Liebigs Ann. Chem. 511, 64 (1934)] to explain the fact that 2,3 dimethylbutadiene dimerizes - but does not polymerize - in the presence of lithium metal. 1,4-Dilithium-2,3-dimethyl-2-butene,  $\text{Li}-\text{CH}_2-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{CH}_2-\text{Li}$ , an adduct with two vinylogously vicinal organolithium bonds, does indeed add more rapidly onto 2,3-dimethylbutadiene than the subsequent products  $\text{Li}-\text{CH}_2-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{CH}_2-\text{R}$ , in which the organometallic bond is isolated.

[124] C. Hoogzand, personal communication.

[125a] G. F. Wright, J. Amer. chem. Soc. 61, 2106 (1939).

[125b] G. S. Myers, H. H. Richmond, and G. F. Wright, J. Amer. chem. Soc. 69, 710 (1947).

[125c] A. G. Brook, H. L. Cohen, and G. F. Wright, J. org. Chemistry 168, 447 (1953).

[126] E. Bergmann, Ber. dtsh. chem. Ges. 63, 1617 (1930); K. Ziegler, Ber. dtsh. chem. Ges. 64, 445 (1931).

[127] G. Wittig and F. v. Lupin, Ber. dtsh. chem. Ges. 61, 1633 (1928).

[128] C. E. Frank and W. E. Foster, J. org. Chemistry 26, 303 (1961).

[129] C. E. Frank, J. R. Leebrick, L. F. Moormeier, J. A. Scheben, and O. Homberg, J. org. Chemistry 26, 307 (1961).

[130] U.S.-Pat. 2816916 (Dec. 17th, 1957), U.S. Industrial Chemical Co., inventors: C. E. Frank and W. E. Foster.

[131] K. Ziegler, L. Jakob, H. Wollthan, and A. Wenz, Liebigs Ann. Chem. 511, 64 (1934); W. Hückel and H. Bretschneider, ibid. 540, 157 (1939); A. J. Birch, Quart. Rev. (chem. Soc., London) 4, 69 (1950); G. W. Watt, Chem. Reviews 46, 317 (1950); D. H. R. Barton and C. H. Robinson, J. chem. Soc. (London) 1954, 3045; E. A. Benkeser, G. Schroll, and D. M. Sauve, J. Amer. chem. Soc. 77, 3378 (1955); A. J. Birch and H. Smith, Quart. Rev. 12, 17 (1958).

[132] L. Bouveault and G. Blanc, C. R. hebd. Séances Acad. Sci. 136, 1676 (1903); 137, 60, 328 (1903).

[133] V. L. Hansley, Ind. Engng. Chem. 39, 55 (1947).



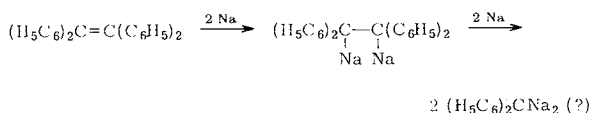
alkyl or benzyl group of the intermediate 2:1 adduct are immediately replaced by hydrogen, while organometallic bonds with two neighboring aryl groups are resistant to the aminolysis. Examples are given in Table 8.

Table 8. End-products of the reaction of olefins with sodium in liquid ammonia.

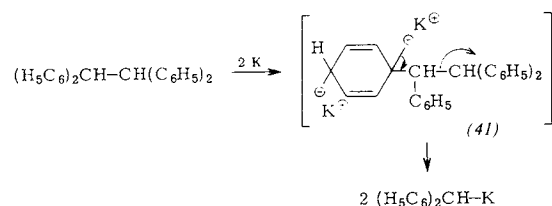
Olefin	Na derivative	Ref.
$(\text{H}_5\text{C}_6)_2\text{C}=\text{CH}_2$	$(\text{H}_5\text{C}_6)_2\text{C}(\text{CH}_3)-\text{Na}$	[134, 135]
$(\text{H}_5\text{C}_6)_2\text{C}=\text{CH}-\text{CH}_3$	$(\text{H}_5\text{C}_6)_2\text{C}(\text{C}_2\text{H}_5)-\text{Na}$	[135]
$(\text{H}_5\text{C}_6)_2\text{C}=\text{CH}-\text{C}_6\text{H}_5$	$(\text{H}_5\text{C}_6)_2\text{C}(\text{CH}_2-\text{C}_6\text{H}_5)-\text{Na}$	[135]
$(\text{H}_5\text{C}_6)_2\text{C}=\text{CH}-\text{CH}(\text{C}_6\text{H}_5)_2$	$(\text{H}_5\text{C}_6)_2\text{CNa}-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)_2$	[135]
$(\text{H}_5\text{C}_6)_2\text{C}=\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$	$\text{Na}-(\text{H}_5\text{C}_6)_2\text{C}-\text{CH}_2-\text{C}(\text{C}_6\text{H}_5)_2-\text{Na}$	[135]

Addition of the intermediate 1,1-diphenylethylenedisodium onto unreacted 1,1-diphenylethylene resulting in a 10–30 % yield of 1,4-disodium-1,1,4,4-tetraphenylbutane competes with its ammonolysis [135].

Liquid ammonia promotes the addition of metal to an extraordinary degree. Thus, 1,1-diphenyl-1-propene reacts smoothly with sodium in ammonia, although it forms no sodium adduct in ether [121, 125c]. Moreover, tetraphenylethylenedisodium, which is otherwise stable, seems to be cleaved at the central C–C bond by excess sodium in liquid ammonia [135, 136].



It may be presumed that alkali metal/hydrocarbon adducts play a decisive role in the cleavage of carbon-carbon bonds and in the cleavage of ethers. Of course, the reaction of hexaphenylethane with sodium to form triphenylmethylenedisodium may also be formulated as a dissociation equilibrium producing triphenylmethyl radicals, which are then trapped by the metal (cf. *Paneth's* demonstration of methyl radicals [137]). However, no corresponding radical mechanism can be postulated for the cleavage of tetraphenylethane or of 1,2-di-*p*-biphenylethane, since here there is no evidence for a dissociation equilibrium at room temperature. None the less, it may well be that in the first of the above cases a potassium adduct (41) occurs as an intermediate from which the two halves of the molecule are separated to form the final product.



In a similar manner, the cleavage of ethers by alkali metals [137a] may be considered as the result of adduct formation (42).

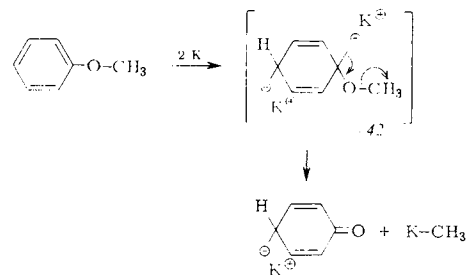
[134] *K. Ziegler, H. Colonius, and O. Schäfer*, *Liebigs Ann. Chem.* 473, 36 (1929).

[135] *C. B. Wooster and J. F. Ryan*, *J. Amer. chem. Soc.* 56, 1133 (1934).

[136] The analogous cleavage of *N,N'*-disodiohydrazobenzene at the N–N bond, to yield *N,N'*-disodioaniline, is known [*W. Schlenk and J. Holtz*, *Ber. dtsh. chem. Ges.* 50, 274 (1917)].

[137] *J. H. Simons and M. F. Dull*, *J. Amer. chem. Soc.* 55, 2696 (1933); cf. *F. O. Rice and K. Rice*: *The Aliphatic Free Radicals*. J. Hopkins Press, Baltimore 1935, p. 58.

[137a] *R. L. Burwell*, *Chem. Reviews* 54, 672 (1954).



On the other hand, the exchange processes, in which a chlorine, bromine, or iodine atom bound to an organic residue is replaced by a metal, may be completely explained by a nucleophilic attack on the halogen, which is capable of enlargement to an electron decet; this is the reason that aliphatic halides can also react in this way. However, alkali metal adducts must again be assumed as intermediates in the exchange of halogen by metal in fluorinated aromatics [138], in the Emde degradation of ammonium salts [139], and in the analogous cleavage of phosphonium salts [140].

## B. Experimental Procedures

### 1. Alkali Metals

It is advantageous to use sodium in solution in ammonia, as an ether-soluble aromatic/sodium adduct, or as a dispersion [141, 142]. Thirty and fifty per cent sodium stock dispersions are available as mobile suspensions, generally stabilized against sedimentation by small amounts of additives [149]. The preparation of sodium dispersions is described in Procedures 2β and 2δ. The average size of the sodium particles in Procedure 2δ is 2–3 μ. Metallic potassium is generally used as a fine powder or in the form of the readily prepared liquid alloy with sodium [90, 102, 143].

### 2. Organoalkali-Metal Compounds

#### α) Methylsodium [43]

A Schlenk tube is charged under nitrogen with 60 ml of dry ligroin (b.p. ca. 80 °C), fine chips of sodium, and 3.0 g (13 moles) of dimethylmercury. The sodium should be present in four-fold excess [9], although still covered by the liquid. The Schlenk tube is sealed and kept for several days in a drying oven at 65 °C. The tube is then placed in an ice-salt mixture, after which it is shaken vigorously to loosen the yellowish incrustations of methylsodium from the unreacted sodium and sodium amalgam. The methylsodium is thus obtained as powder and flakes. The light particles of methylsodium can be decanted off with the ligroin and are washed with petroleum ether [144]. The corresponding preparations of ethylsodium, higher sodium alkyls, and phenylsodium proceeds much more rapidly; the reaction is completed within a few hours at room temperature.

[138] *H. Gilman and T. S. Soddy*, *J. org. Chemistry* 22, 1121 (1957).

[139] *H. Emde*, *Ber. dtsh. chem. Ges.* 42, 2590 (1909).

[140] *L. Horner, P. Beck, and H. Hoffmann*, *Chem. Ber.* 92, 2088 (1959).

[141] *V. L. Hansley*, *Ind. Engng. Chem., analyt. Edit.* 43, 1760 (1951).

[142] Sodium Dispersions, brochure obtainable from U.S. Industrial Chemical Co., Division of National Distillers and Chemical Corp. (1957).

[143] *H. Lecher*, *Ber. dtsh. chem. Ges.* 48, 527 (1915).

[144] It is often possible to omit this rather bothersome separation step, since the presence of sodium and sodium amalgam has no deleterious effect on many of the reactions of sodium alkyls.

### β) n-Amylsodium [3,5,73,145]:

A 1-liter three-necked flask with two creases (Morton flask [146a]) is charged under nitrogen with 23 g (1 gram-atom) of sodium, which is then covered with about 300 ml of olefin-free n-octane. This mixture is heated to 110 °C and stirred for at least one minute with a propeller-type agitator (10000 rpm). After cooling, the "sodium sand" (average particle size 25 μ) is allowed to settle, the octane is siphoned off under nitrogen, and the sodium washed several times with dry n-pentane. Such a sodium dispersion in about 200 ml of pentane or octane is mixed with 53.2 g (0.5 mole) of n-amylochloride, which is added dropwise at -10 °C over a period of one hour while stirring is continued at approx. 5000 rpm [146b]. The mixture usually becomes blue. Finally it is stirred for further 30 min at -10 °C. The yield of n-amylochloride is 80%. As a safety precaution, it is inadvisable to use more than one gram-atom of sodium at a time.

### γ) Phenylsodium/Phenyl-lithium Solution [147]:

Diphenylmercury (0.9 g = 2.5 mmoles) in 15 ml of absolute ether is mixed in a Schlenk tube with 1 g (43.5 mmoles) of sodium wire and 5 ml of a 1 N phenyl-lithium solution prepared from diphenylmercury and lithium chips in ether; glass fragments are added, and the tube is sealed and shaken for 3 h. The solution is decanted from the greyish white precipitate and the lump of amalgam into a storage burette, where it is diluted with 40 ml of absolute ether. The solution decomposes slowly by reacting with the ether.

Variations of this method include the action of Li/Na alloy on diphenylmercury and the combination of phenyl-lithium with phenylsodium. Ether suspensions with higher phenylsodium/phenyl-lithium mole ratios (e.g. 5:1) have also been described [147].

### δ) Phenylsodium [13,42]:

A Premier Mill laboratory dispersion unit [148,142] (high-speed stirrer with a dispersing head) is filled with nitrogen, and 150 g of dry toluene and 27 g (1.17 gram-atom) of sodium are introduced [149]. The sodium melts when the temperature is raised to 105 °C. The stirrer is then gradually brought to maximum speed (15000-18000 rpm) and maintained there for 5-15 min; the grey mixture is then cooled to room temperature [150]. A mixture of 56.3 g (0.5 mole) of chlorobenzene and 50 g of toluene is then prepared in a dropping funnel and 10-15 ml of it is rapidly added to the sodium mixture with gentle stirring. As a rule, reaction begins suddenly within a few minutes, with a noticeable increase in temperature and the appearance of black particles of phenylsodium. Otherwise the reaction may be initiated with 2 ml of amyl alcohol. The remainder of the chlorobenzene is then added dropwise over 20-30 min, but precaution must be taken to maintain the reaction temperature at 30-35 °C. The yield of phenylsodium is 99-100%.

### ε) Benzylsodium [13]:

A suspension of phenylsodium in toluene is heated for 2 hours under reflux in a nitrogen atmosphere. Benzylsodium

[145] A. A. Morton and J. Hechenbleikner, J. Amer. chem. Soc. 58, 1697 (1936).

[146a] A. A. Morton, Ind. Engng. Chem., analyt. Edit. 11, 170 (1939); A. A. Morton and D. M. Knott, *ibid.* 13, 650 (1939).

[146b] A. A. Morton and L. M. Redman, Ind. Engng. Chem., analyt. Edit. 40, 1190 (1948).

[147] G. Wittig, R. Ludwig, and R. Polster, Chem. Ber. 88, 294 (1955).

[148] Premier Mill Co., Geneva, N.Y. (U.S.A.).

[149] It often happens that the dispersion cannot be used at once in further reactions, or must be prepared in benzene or an alkane rather than in toluene. In these cases, it is advisable to introduce 1% oleic acid (based on the weight of sodium) or another additive before making the dispersion.

[150] O. D. Frampton and J. F. Nobis, Ind. Engng. Chem., analyt. Edit. 45, 404 (1953).

is thus obtained in 99-100% yield. A modification of this procedure is applied for the preparation of benzylsodium in the n-butylbenzene synthesis (cf. Procedure 3 γ).

### ζ) Triphenylmethylsodium [78]:

A 1% sodium amalgam is prepared under nitrogen in a 1 liter Schlenk tube by introducing 5.53 g (0.25 gram-atom) of sodium as small pieces speared on the end of a pointed glass rod into 575 g of pure mercury; (this operation must be performed in a hood). After cooling, 750 ml of absolute ether are added, followed by 31.5 g (0.113 mole) of triphenylmethyl chloride [m.p. 112-113 °C; recrystallized from a 10:1 ligroin (b.p. 100 °C)/acetyl chloride mixture]. The Schlenk tube is sealed off and shaken vigorously, whereupon the solution becomes deep orange. The exothermic reaction is moderated by cooling the tube with wet cloths, or by occasional immersion in ice water. The reaction is largely complete after fifteen minutes' shaking; to obtain total conversion, the tube is shaken for three hours on a horizontal mechanical shaker. After the sodium chloride produced has settled out, the tube is opened under nitrogen, and the organometallic solution is transferred to a storage burette through polyethylene tubing, into which a plug of glass wool has been loosely inserted. The yield is practically quantitative, as shown by titration of a sample with 0.1 N acid. If the mercury is not objectionable, the triphenylmethylsodium can be prepared more simply in a three-necked flask, and then used directly for further reaction [79].

### η) Sodium Acetylide [59b,151]:

A one-liter flask is fitted with a glass or Hershberg stirrer (with mercury seal) and a dry-ice condenser (or a freezing mixture at -35 °C). Anhydrous liquid ammonia (300 ml) is added. Acetylene gas is passed through a cold trap at -70 °C and two wash bottles containing conc. sulfuric acid and is bubbled through the liquid. Simultaneously 5.5 g (0.24 gram-atom) of sodium are added slowly in small pieces so that the blue color disappears before the next piece is added. As soon as all of the sodium has been introduced and the solution has lost color, the flow of acetylene is discontinued. This method can be used with only minor variations to produce large quantities of sodium acetylide (13 moles in 6 l of ammonia) [59a,59b]. Large amounts can also be obtained with sodamide in liquid ammonia [152]. The excess acetylene in solution, inevitable in these preparations, generally causes no difficulty in further use.

### θ) Sodium Phenylacetylide [61]:

A mixture of 3.06 g (30 mmoles) of phenylacetylene, 0.46 g (20 mmoles) of finely divided sodium, and 30 ml of absolute ether is stirred at room temperature. After about 8 h all of the metal is consumed; this is shown by absence of hydrogen evolution when a few drops of the suspension are hydrolysed. The corresponding reaction with potassium, which yields potassium phenylacetylide, usually requires 48 h.

### κ) p-Tolylpotassium [48]:

A solution of p-tolyl-lithium (95 mmoles) in ether is evaporated *in vacuo* (at the end for 30 min at 60 °C) to remove the solvent completely. Dry benzene (45 ml) and an alloy of 7.8 g (0.2 gram-atom) of potassium with 2 g (0.087 gram-atom) of sodium are now added, and the mixture is stirred for 10 h at 20 °C. An aliquot of the dark brown mixture is withdrawn and filtered. A small alkali content of the filtrate indicates that the reaction has been almost quantitative. The preparations of ethyl-, n-propyl-, n-butyl-, s-butyl-, and t-butylpotassium and other potassium alkyls are analogous [11,48].

[151] A. I. Vogel: Practical Organic Chemistry. 3rd Edit., Longmans, London 1961, p. 898.

[152] K. W. Greenly and A. L. Henne in Inorganic Syntheses. Wiley, New York 1946, Vol. 2, pp. 75, 79, 128; T. L. Jacobs in Organic Syntheses. Wiley, New York 1949, Vol. 5, pp. 25-40.

### λ.) $\alpha$ -Phenylisopropylpotassium [6, 153]:

A mixture of  $\alpha$ -methylstyrene and methanol in a molar ratio of 1:2 is treated with 0.05 % of its weight of 70 % perchloric acid solution and allowed to stand for 48 h at 50 °C. Aqueous sodium hydroxide is then added, the methanol completely extracted from the oil layer with water, and the oil layer dried with  $\text{CaCl}_2$ . Fractional distillation *in vacuo* yields 26 % unreacted  $\alpha$ -methylstyrene (b.p. 64–65 °C/23 mm,  $n_D^{20} = 1.5372$ ) and 62 % methyl  $\alpha$ -phenylisopropyl ether (b.p. 83–84 °C/23 mm,  $n_D^{20} = 1.4956$ ) [6]. Methyl  $\alpha$ -phenylisopropyl ether (5.0 g, 33 moles), 6 g of potassium-sodium alloy (5:1), and 400 ml of absolute ether are filled into a large Schlenk tube under nitrogen. The tube is sealed off and shaken vigorously. The intense red color of the organopotassium compound develops within two minutes. The reaction is complete after two days' shaking. The tube is opened under nitrogen and the solution transferred to a storage burette through a polyethylene tube containing a plug of glass wool [153]. Phenylisopropylpotassium may also be obtained as a suspension in hydrocarbons or, free of by-products, in solid form [6].

### μ.) Diphenylmethylpotassium [154]:

A two-liter 3-necked flask, fitted with a dry-ice condenser and a Hershberg stirrer (with a mercury seal), is filled with 800 ml of liquid ammonia, and 21.5 g (0.55 gram-atom) of potassium are added in small pieces with thorough mixing. The deep blue solution is decolorized within two hours, this indicating the formation of potassium amide [155]. A solution of 84.0 g (0.5 mole) of diphenylmethane in 800 ml anhydrous ether is added, and, after the dry-ice condenser has been replaced by a water-cooled condenser, the ammonia is evaporated off on a water bath. Sufficient ether is added to bring the total volume up to 800 ml, and the mixture is refluxed for further two hours. Carboxylation of the orange-red solution gives a 90 % yield of diphenylacetic acid. Alkylation, acylation, and other reactions may also be carried out in the ammonia-ether medium before the ammonia is evaporated off [154]; with diphenylmethylsodium, it is essential that these reactions be performed before evaporation [35].

## 3. Syntheses Using Organoalkali-Metal Compounds

### α) Vinylacetic Acid [156]:

A Morton flask is charged under nitrogen with 5.8 g (0.25 gram-atom) of "sodium sand" (see Procedure 2β). The octane is replaced by hexane, and 14.7 g (0.15 mole) of diallyl ether dissolved in an equal volume of hexane are added dropwise over a period of one hour, the mixture being stirred at 5000 rpm and an average temperature of 35 °C being maintained. After further 30 min, the purely white, moderately viscous reaction mixture is transferred from the flask by pressure (via an outlet tube) onto solid carbon dioxide. After addition of 200 ml of water and extraction with ether, 8.3 g of vinylacetic acid (b.p. 61–62 °C/3 mm,  $n_D^{20} = 1.4220$ ) are isolated (77 % yield based on sodium).

### β) Phenylmalonic Acid [13]:

A suspension of benzylnsodium in toluene, prepared by Procedure 2ε [13] using 112.6 g (1 mole) of chlorobenzene, is carboxylated by introducing carbon dioxide gas with stirring at 30–60 °C. In this operation about half of the theoretical quantity of gas is added during the first ten minutes,

[153] K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, *Liebigs Ann. Chem.* 473, 20 (1929).

[154] R. S. Yost and C. R. Hauser, *J. Amer. chem. Soc.* 69, 2325 (1947).

[155] C. R. Hauser and T. M. Harris, *J. Amer. chem. Soc.* 80, 636 (1958).

[156] R. L. Letsinger and J. G. Traynham, *J. Amer. chem. Soc.* 70, 3342 (1948).

stirring is continued for 30 min, and more carbon dioxide is introduced during 80 min to complete the carboxylation slowly. The excess sodium is now destroyed with steam in a hydrolysis apparatus, the aqueous phase removed and decolorized with animal charcoal, and then neutralized with hydrochloric acid at 0 °C [157]. Large quantities of phenylmalonic acid are precipitated. Additional product is obtained by extraction of the mother liquor with ether [157]. The total yield of acid, m.p. 145–148 °C, is 67 % (based on chlorobenzene). The phenylacetic acid (28 %) present as a by-product is previously removed by benzene extraction.

### γ) n-Butylbenzene [158]:

A 1-liter three-necked flask is charged under nitrogen with 300 ml of toluene and 27.5 g (1.2 gram-atom) of sodium wire. Over a period of two hours, 68 g (0.6 mole) of chlorobenzene are added dropwise at 30–35 °C with vigorous stirring (blade-type stirrer, mercury seal). The reaction begins quickly. The mixture is then refluxed for 35 min, the heating bath is removed, and 49 g (0.4 mole) of n-propyl bromide are added dropwise to the benzylnsodium suspension at 103–105 °C over a period of 20 min. After cooling, any benzylnsodium remaining is destroyed with a stream of carbon dioxide, and the excess sodium with water. The toluene layer is separated off, dried, and fractionally distilled twice; 40 g of pure n-butylbenzene (b.p. 181–181.5 °C,  $n_D^{20} = 1.4898$ ) is obtained (74 % yield based on n-propyl bromide). In contrast, the condensation of phenylsodium and n-butyl bromide gives only a 44 % yield of n-butylbenzene.

### δ) 1-Chloro-5-nonyne [59b]:

A solution of sodium acetylide in ammonia is prepared from 5.5 g (0.24 gram-atom) of sodium, and 41 g (0.24 mole) of n-propyl iodide are added to it slowly, stirring being continued for four hours. A solution of 0.25 gram-atom of sodamide (prepared from 5.8 g of sodium) in 150 ml of liquid ammonia [59b] is then added in portions to the thoroughly cooled mixture, which is stirred for another hour. Next 41 g (0.24 mole) of 1-chloro-4-bromobutane are slowly added dropwise, and the cooled reaction mixture is stirred for further 12 h. Then 15 g (0.28 mole) of ammonium chloride are added, the ammonia is evaporated off, and the residue is extracted with water and ether. Distillation of the dried organic phase gives 5.3 g (13 %) of unreacted 1-chloro-4-bromobutane and 24.2 g (64 %) of 1-chloro-5-nonyne (b.p. 83–84 °C/13 mm,  $n_D^{18} = 1.4620$ ).

### ε) 1,8-Cyclotetradecadiyne [159]:

$\alpha,\omega$ -Nonadiyne (0.1 mole) is added with stirring to a solution of 0.2 mole of sodamide [59b] in 1 liter of liquid ammonia. After one hour, 0.1 mole of  $\alpha,\omega$ -dibromopentane is added, again with agitation. Stirring under a condenser cooled with dry ice is continued for four days, and the ammonia is then removed by evaporation. Water is added, the mixture is extracted with ether, the ether extracts are dried, the ether is evaporated off, and the residue is distilled at 100–110 °C and 10<sup>-3</sup> mm Hg. The diyne thus obtained is crystallized from alcohol and melts at 97–98 °C. The yield (56 %) may be increased to more than 70 % by working in more dilute solution.

### ζ) p-Nitrophenyl Phenethyl Ketone [160]:

A solution of 1.2 g (4 mmoles) of di-t-butyl benzylnsodium in 25 ml of dry benzene is stirred gently in a three-necked flask under slight reflux and treated with 0.15 g (6 mmoles) of

[157] Above 30 °C decarboxylation may occur.

[158] D. Bryce-Smith and E. E. Turner, *J. chem. Soc. (London)* 1950, 1975.

[159] J. Dale, A. J. Hubert, and G. S. D. King, *J. chem. Soc. (London)* 1963, 73.

[160] G. S. Fonken and W. S. Johnson, *J. Amer. chem. Soc.* 74, 831 (1952).

sodium hydride. As soon as the evolution of gas has ceased (after about 2.5 h), 0.75 g (4 mmoles) of *p*-nitrobenzoyl chloride is added without interrupting the stirring or reflux. One hour later the mixture is cooled, and the excess sodium hydride is decomposed with 0.35 g (2 mmoles) of anhydrous *p*-toluenesulfonic acid. The salts precipitated are filtered off, the benzene is distilled off, and the residual oil is refluxed for one hour with a mixture of 0.1 g of *p*-toluenesulfonic acid in 25 ml of glacial acetic acid containing about 2% (by volume) of acetic anhydride. The evolution of gas ceases after about 45 min. The mixture is poured onto ice, neutralized with dilute alkali, and the white precipitate is filtered off (0.83 g; 81% yield). After recrystallization from ethanol, colorless leaflets are obtained which melt at 74.5–75°C.

#### 7) Diphenylenephosphine [161]:

A Schlenk tube is charged under nitrogen with 21.6 g (83 moles) of triphenylphosphine and a suspension of phenylsodium (prepared from 8.5 g of chlorobenzene and 3.5 g of sodium) in 40 ml of benzene, then sealed and shaken for 10 h at 20°C and for 30 h at 70°C. After decomposition of unreacted starting material with methanol and addition of water, the benzene layer is dried, the solvent is evaporated, and the residue distilled. Thirteen grams of distillate are collected at 0.05 mm Hg and 155–160°C. This is mullied

[161] G. Wittig and G. Geissler, *Liebigs Ann. Chem.* 580, 50 (1953).

with aqueous HCl (2 parts conc. HCl, 1 part H<sub>2</sub>O) to extract 10.2 g of triphenylphosphine. After recrystallization from methanol, the residue melts at 93–94°C. The yield varies from 8 to 15%. For reasons of safety, larger-scale preparations should be carried out in a three-necked flask with thorough mixing (Vibrator).

#### 8) Tetraphenylgermane [162]:

A mixture of 10 g (47 mmoles) of germanium tetrachloride, 100 ml of toluene, 9 g (39 mg-atom) of sodium and 30 g (190 mmoles) of bromobenzene is carefully heated. As soon as the reaction has begun, cooling must be applied. When the reaction has subsided, the mixture is refluxed for another hour. The hot solution is hydrolyzed with hydrochloric acid. Additional 100 ml of warm toluene are added, and the toluene layer is separated off, filtered, and concentrated to a small volume. The dark colored solution yields a precipitate of 9.6 g of purely white crystals (53% yield).

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[162] D. E. Worrall, *J. Amer. chem. Soc.* 62, 3267 (1940).

## COMMUNICATIONS

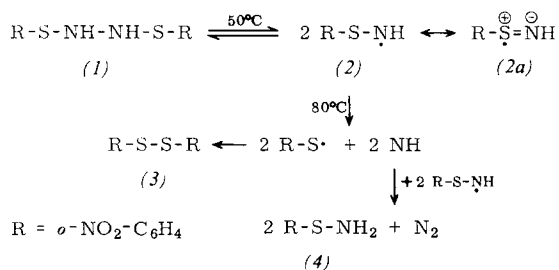
### The *o*-Nitrophenylsulfenylimine Radical [1]

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Di(*o*-nitrophenylsulfenyl)hydrazine (1) dissociates in toluene at about 50°C into *o*-nitrophenylsulfenylimine radicals (2). The ESR spectrum shows three lines of equal intensity which indicates a spin density at the nitrogen. As the equidistant line-spacing is only about half as great (11 Gauss) as in the spectrum of diphenylpicrylhydrazyl (DPPH), one must assume a high spin density at an atom without nuclear spin, in this case at the sulfur [formula (2a)]. Also, the high *g*-factor (2.0076) which lies in the region of the values found for sulfur radical ions ( $\text{CH}_3\text{OC}_6\text{H}_4-\overset{\ominus}{\text{S}}-\text{C}_6\text{H}_4\text{OCH}_3$ ;  $g = 2.0079$  [2]) and away from the *g*-values of *N*-radicals (DPPH:  $g = 2.0036$ ) indicates an important participation of resonance structures with radical sulfur.

On cooling, the signal dies away and appears on reheating, indicating a reversible dissociation. Above 80°C in toluene, nitrogen is evolved from (1). The sulfenylimine radical (2) probably decomposes into a sulfur radical, which recombines to give the disulfide (3), and into imene which reduces the



sulfenylimine radical (2) to sulfenylamine (4). Compounds (3) and (4) were identified. Dry decomposition of (1) gave rise to (3), N<sub>2</sub>, and NH<sub>3</sub>. Decomposition of (1) in acrylonitrile resulted in polymerisation.

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Publication deferred until now at the authors' request  
German version: *Angew. Chem.* 76, 376 (1964)

[1] Communication No. 7 on Organic Sulfur Radicals. – Communication No. 6: U. Schmidt, A. Müller, and K. Markau, *Chem. Ber.* 97, 405 (1964).

[2] U. Schmidt, K. H. Kabitzke, and K. Markau, *Liebigs Ann. Chem.*, in the press.

### Formation of Bis-( $\beta$ -chloro- $\beta$ -alkoxyethyl) Sulfoxides by Addition of Thionyl Chloride onto Alkyl Vinyl Ethers

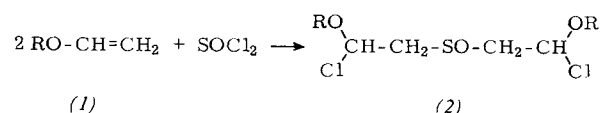
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*Dedicated to Professor H. Bredereck on the occasion of his 60th birthday*

2-Chloro-2-ethoxyethanesulfinyl chloride has been described [1] as the unstable product of the addition of thionyl chloride onto ethyl vinyl ether.

The reaction of thionyl chloride and alkyl vinyl ethers (1) in a molar ratio of 1:3 has now yielded bis-( $\beta$ -chloro- $\beta$ -alkoxyethyl) sulfoxides (2).



When absolute ether was used as solvent, the sulfoxides (2) crystallized directly as colorless compounds that are readily