

sis shows the nitro compound to be a trinitroethyl-dimethylbenzene.

Anal. Calcd. for $C_{10}H_{11}O_6N_3$: C, 44.6; H, 4.1; N, 15.6. Found: C, 44.3; H, 4.5; N, 15.9.

The substance is not, however, either of the two trinitroethyl-dimethylbenzenes described in this paper, nor is it trinitroethyl-*p*-xylene. Mixtures of the 123° nitro compound with trinitro-4-ethyl-*m*-xylene (129°), and with trinitroethyl-*p*-xylene (127–128°), melted at 96–100° and 98–110°, respectively. Trinitro-2-ethyl-*m*-xylene, the other trinitro compound available, melts at 181°. The substance may possibly be 3,5,6-trinitro-4-ethyl-*o*-xylene, reported by Stahl^{12a} to melt at 121°.

4,6-Diaminoethylmesitylene.—The dinitro compound (1 g., m. p. 110°) was dissolved in hot acetic acid (5 cc.) and to the solution there was added stannous chloride (8 g.) dissolved in hot hydrochloric acid. The vigorous reaction soon subsided, after which the mixture was boiled for ten minutes. The stannichloride separated on cooling, but it dissolved completely when washed with alcohol. The alcoholic solution was combined with the acid filtrate from the stannichloride and an excess of concd. sodium hydroxide was added. The white gelatinous precipitate was removed and crystallized from alcohol (2 cc.) and ligroin (2 cc.). The product formed long white needles which melted at 79–80°.

Anal. Calcd. for $C_{11}H_{13}N_2$: C, 74.15; H, 10.11; N, 15.74. Found: C, 74.30; H, 9.91; N, 15.79.

Ethyl-*p*-xylene was prepared from *p*-xylene by the method described in the previous paper.⁶ *p*-Xylene (41.8 g.) was converted to aceto-*p*-xylene (40 g.). The crude product was not purified, but was reduced directly by the Clemmensen method. Ethyl-*p*-xylene (15 g., 28% over-all yield from *p*-xylene) was obtained as an oil, b. p. 81–83° under 25 mm., n_D^{20} 1.5020.¹⁵

Nitration of the hydrocarbon (1 g.) as described for the other ethyldimethylbenzenes gave the trinitro compound,

(15) (a) See ref. 10, where n_D^{15} is given as 1.5026; (b) Jacobsen, *Ber.*, **19**, 2516 (1886), gives the b. p. as 185° under atmospheric pressure.

which after crystallization twice from alcohol (10 cc.) weighed 0.5 g. and melted at 127–128°.¹⁶

The authors are greatly indebted to Dr. Miles A. Dahlen and E. I. du Pont de Nemours and Company for a generous gift of *m*-xylene which was used in the work described in this and the previous paper.

Summary

1. When subjected to the conditions of the Jacobsen reaction, 5-ethylpseudocumene and ethylmesitylene rearrange, while 3-ethylpseudocumene does not.

2. The two hydrocarbons which rearrange give 3-ethylpseudocumene as the main product, in analogy with the rearrangements of durene and isodurene, all of which rearrange to a 1,2,3,4-tetraalkylbenzene.

3. From 5-ethylpseudocumene, prehnitene, 4-ethyl-*m*-xylene, and pseudocumene were also obtained; from ethylmesitylene, prehnitene, 2-ethyl-*m*-xylene, and mesitylene were also obtained.

4. No hexaalkylbenzenes were identified as rearrangement products, although they may have been formed in small amounts.

5. The formation of a tetramethylbenzene, prehnitene, from ethyltrimethylbenzenes represents a new type of rearrangement.

6. Several derivatives of the starting materials and products are described.

7. Several examples are cited in which mixtures of derivatives of polyalkyl benzenes show little or no depression in melting point.

(16) Jacobsen^{15b} gives the m. p. as 129°.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Reaction of Styrene Oxide with Methylmagnesium Iodide

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The suggestion that ethylene oxide rearrangements in Grignard reactions are caused by an oxide-magnesium halide bond reaction was made by Bartlett and Berry² to account for the formation of methylcyclopentylcarbinol observed by Bedos³ in reactions of 1,2-epoxycyclohexane and 2-chloro-1-cyclohexanol with methylmagnesium iodide. This explanation served to predict the

formation of 3-methyl-3-pentanol in the reaction of 3-bromo-2-butanol with ethylmagnesium bromide⁴ inasmuch as Henry⁵ had found that 2,3-epoxybutane reacted with methylmagnesium bromide to produce *t*-amyl alcohol.

Although Fournneau and Tiffeneau⁶ found that methyl- and ethylmagnesium bromides reacted with styrene oxide as if it were phenylacetaldehyde, it is impossible to use the explanation in its

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(2) Bartlett and Berry, *THIS JOURNAL*, **56**, 2683 (1934).

(3) Bedos, *Compt. rend.*, **189**, 255 (1929).

(4) Cottle and Powell, *THIS JOURNAL*, **58**, 2267 (1936).

(5) L. Henry, *Compt. rend.*, **145**, 406 (1907).

(6) Fournneau and Tiffeneau, *ibid.*, **146**, 698 (1908).

present form in order to predict the course of the reaction of styrene halohydrins with Grignard reagents since two products are structurally possible as a result of the reaction of the magnesium halide bond with the oxide.

The work of Tiffeneau and others⁷ indicates that styrene and hypiodous acid yield iodohydrin I⁸ and that the isomeric product II, which melts at 78°, is formed by the action of hydriodic acid upon styrene oxide. It seemed reasonable



to assume that the magnesium iodide bond of an alkylmagnesium iodide would add to styrene oxide to produce a magnesium derivative of iodohydrin II.⁹ In support of this assumption we found that styrene oxide and iodohydrin II reacted with methylmagnesium iodide in the same manner. Distillation of the ether from the respective reaction mixtures produced no explosive reactions such as Grignard observed¹⁰ on similarly treating ethylene oxide with ethylmagnesium bromide. Moreover, iodohydrin II also was prepared by hydrolysis of the product obtained by treating an ether-benzene solution of magnesium iodide with styrene oxide.

It was found previously⁴ that 3-bromo-2-butanol reacted with ethylmagnesium bromide to give appreciable yields of 3-methyl-3-pentanol without the application of heat. Consequently, the absence of the explosive reaction in the present experiments is attributed to the reaction of the secondary iodine atom at temperatures below those reached by removal of the ether on the water-bath. This supposition is supported by experiments in which styrene oxide and iodohydrin II reacted with methylmagnesium iodide without the application of heat and in which 3-bromo-2-butanol failed to react violently when the ether was distilled from the ethylmagnesium bromide reaction mixture according to the technique originally employed by Grignard.

(7) Tiffeneau and Fourneau, *Bull. soc. chim.*, [4] **13**, 977, 978, 980, 981 (1913); [4] **15**, 278, 280 (1914); Tiffeneau, *Ann. chim. phys.*, [8] **10**, 348 (1907); cf. Lestrangé and Levy, *Bull. Sci. Pharmacol.*, **36**, 356, 357, 364 (1929).

(8) In the present work I was obtained crystalline and melted at 34°.

(9) This reaction mechanism appeared in a Doctor's dissertation submitted by the senior author at The Ohio State University in 1930. The research was done under Professor C. E. Boord and we are grateful to him for encouraging us to continue the work.

(10) This phenomenon was interpreted by Grignard [*Bull. soc. chim.*, [3] **29**, 944 (1903)] as due to the cleavage of the oxide ring. We attribute it, as did Ribas and Tapia [*Anal. soc. españ. fis. quim.*, **30**, 944 (1932)], to a Wurtz-type reaction of the alkylmagnesium bond with the organic halogen of the halohydrin derivative.

When iodohydrin I was treated with methylmagnesium iodide without the application of heat, 80 to 85% of the iodohydrin was recovered whereas under the same conditions 6.4% of iodohydrin II was unchanged. Styrene oxide, which according to the theory forms a magnesium derivative of iodohydrin II, was treated in a like manner and 4.1% of the iodohydrin was unattacked. The magnesium derivative of iodohydrin I reacted vigorously with methylmagnesium iodide when the solvent was distilled on a boiling water-bath.

Styrene oxide reacted with one mole of methylmagnesium iodide, without the application of heat, to give 1-phenyl-2-propanol in 51% yield, but under comparable conditions, except that two moles of the Grignard reagent were used, iodohydrin II gave only 9.8% of the alcohol. This discrepancy disappeared largely when the conditions were made more nearly identical and upon adding the oxide to magnesium iodide before treatment with the Grignard reagent the yield decreased to 15%.

Although we were able to predict that styrene oxide and iodohydrin II would react at lower temperatures than iodohydrin I and that styrene oxide and iodohydrin II would yield 1-phenyl-2-propanol, it was impossible to foresee that iodohydrin I also would yield the same alcohol. Inasmuch as the product of experiments in which ether was distilled from reaction mixtures of iodohydrin I and II gave the phenylurethan of phenethyl alcohol instead of 1-phenyl-2-propanol, tests with hydrochloric acid-zinc chloride solution were used to demonstrate the presence of the secondary alcohol. However, the phenylurethan of 1-phenyl-2-propanol was obtained without difficulty from products of two similar, preliminary experiments (9 and 10 in Table I) in which the conditions differed in detail from those of the series of experiments discussed above.

The reaction of styrene oxide and hydriodic acid results in a primary alcohol whereas 1,2-epoxypropane with hydrochloric acid yields a secondary alcohol as the major product.¹¹ Inasmuch as Norton and Hass¹² found as a result of treating several epoxyalkanes with magnesium-diethyl that, "when there is a difference between

(11) Michael and Leighton, *J. prakt. Chem.*, [2] **60**, 423 (1899); [2] **64**, 108 (1901); *Ber.*, **39**, 2785 (1906); Henry, *Rec. trav. chim.*, **22**, 339 (1903); *Nef, Ann.*, **335**, 204 (1904); L. Smith, *Z. physik. Chem.*, **93**, 72 (1918).

(12) Norton and Hass, *THIS JOURNAL*, **58**, 2147 (1936).

the two carbon valences holding the epoxy oxygen atom, the primary valence breaks rather than the secondary or tertiary and the secondary rather than the tertiary" it was of interest to ascertain the course of the reaction of a magnesiumdialkyl with styrene oxide. The reaction with magnesiumdimethyl produced 2-phenyl-1-propanol. The difference in the mode of cleavage is probably not due to the smaller size of the methyl group as compared to the ethyl of the magnesiumdiethyl used by Norton and Hass since we found that 1,2-epoxypropane and magnesiumdimethyl produced 2-butanol. Kharasch and Clapp¹³ also obtained primary alcohols in the reaction of styrene oxide with phenyl- and *p*-anisylmagnesium bromides. It is worth noting that styrene oxide on reduction yields a primary alcohol⁶ whereas 1,2-epoxypropane yields a secondary alcohol.¹⁴

The possibility of hypohalogen acids reacting with a double bond through the primary formation of an oxide which immediately reacts with the halogen acid set free was discussed by Michael.¹⁵ Frahm¹⁶ explained the reaction of hypochlorous acid with ethylene in the presence of copper, cobalt and ferric salts in this way since these salts are known to catalyze the decomposition of hypohalogen acids to oxygen and halogen hydracids.¹⁷ Also Pogorzelski¹⁸ had reported that 1,2-epoxy-2-methylpropane was formed by the action of an aqueous iodine-potassium iodide solution upon 2-methylpropene. Although Frahm does not give sufficient experimental data to afford a critical examination of the theory, it is evident that it cannot be applied without modification to the reaction of styrene with hypiodous acid. Inasmuch as iodohydrin I was prepared according to Tiffeneau's directions from styrene, iodine and yellow mercuric oxide in wet ether and iodohydrin II from styrene oxide and hydriodic acid in water, it seemed possible that the difference in the solvents was responsible for the formation of the two isomers. However, iodohydrin II was obtained by treating an ether solution of hydriodic acid with styrene oxide. Moreover, magnesium iodide in an ether-benzene solution

with the oxide gave iodohydrin II and Detoef¹⁹ prepared 1-phenyl-2-chloro-1-ethanol from styrene and chlorourea in water.

Experimental

The Preparation of Styrene Oxide.—When prepared from styrene and benzoyl hydrogen peroxide, prepared according to the method of Brooks and Brooks,²⁰ the oxide always contained aldehyde but treatment of 2-iodo-1-phenyl-1-ethanol with potassium hydroxide gave an oxide which gave no test for aldehyde with Tollens' reagent, formed no precipitate with sodium bisulfite and only slowly gave a coloration with Schiff's reagent.

Powdered iodine (1.2 moles) was added, during four to five hours, to a mechanically shaken mixture of 0.6 mole of yellow mercuric oxide and 1200 cc. of a water-saturated ether solution of 1.2 moles of styrene. The mixture was filtered, the filtrate washed with dilute sodium bisulfite and potassium iodide solutions and dried. Finely powdered potassium hydroxide (3 moles) was added, during one to two hours, to the ice-cooled and mechanically stirred ether solution; finally the ice-bath was removed and stirring was continued for one and one-half days. The ether solution was decanted, the residue washed with ether, the solvent distilled from the combined, dried solutions and the residue distilled.²¹ The yield of oxide was 51%, b. p. 87–88° (23 mm.); n_D^{25} 1.5331; d_4^{25} 1.0541.

The Preparation of 2-Iodo-2-phenyl-1-ethanol.—Tiffeneau²² prepared this compound by the action of hydriodic acid on styrene oxide but gave no experimental directions. Hydriodic acid (119 g. of 50%), added dropwise to a stirred solution of 55.5 g. of styrene oxide in 120 cc. of ice-cooled petroleum ether, gave a white crystalline precipitate, which, after purification by treatment with water, dilute sodium bisulfite solution and petroleum ether, gave 60 to 85% yields of the iodohydrin, m. p. 77.5°. After precipitation from alcohol by the addition of water it melted at 78.5°. A 34% yield, m. p. 72–74°, was obtained using 200 cc. of ether, 0.0071 mole of constant-boiling hydriodic acid and 0.0092 mole of styrene oxide. On standing this iodohydrin soon decomposed with the liberation of iodine.

The same iodohydrin was obtained by treating an ice-cold solution of 0.15 mole of magnesium iodide²³ in 50 cc. of dry ether and 75 cc. of benzene with 0.05 mole of styrene oxide. The resulting solution was immediately hydrolyzed with an ice-cold solution of ammonium chloride, the ether-benzene solution washed with water, dried and the solvents distilled *in vacuo*. The yield was 65% of iodohydrin, m. p. 68–70°; the melting point was 78.5° after one recrystallization from petroleum ether and one precipitation from alcohol by dilution with water.

The Isolation of 2-Iodo-1-phenyl-1-ethanol.—Whereas this compound²⁴ was described as a liquid which decom-

(13) Kharasch and Clapp, *J. Org. Chem.*, **3**, 355 (1938).

(14) Beilstein's "Handbuch der organischen Chemie," 4th edition, Vol. XVII, p. 6.

(15) Michael and Leighton, *J. prakt. Chem.*, [2] **60**, 464 (1899); cf. Michael and Carlson, *THIS JOURNAL*, **57**, 1268 (1935), footnote 4.

(16) Frahm, *Rec. trav. chim.*, **50**, 261 (1931).

(17) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., New York, 1922, p. 253.

(18) Pogorzelski, *Chem. Centr.*, **77**, I, 331 (1906).

(19) Detoef, *Bull. soc. chim.*, [4] **31**, 177 (1922).

(20) Brooks and Brooks, *THIS JOURNAL*, **55**, 4309 (1933).

(21) These directions are similar to the less specific descriptions given by Fourneau and Tiffeneau for the preparation of the iodohydrin [*Compt. rend.*, **145**, 811 (1907); *Ann. chim. phys.*, [8] **10**, 347, 348 (1907); *Bull. soc. chim.*, [4] **13**, 975 (1913)] and oxide [*Compt. rend.*, **140**, 1595 (1905)].

(22) Tiffeneau, *Ann. chim. phys.*, [8] **10**, 347, 348 (1907).

(23) Gomberg and Bachman, *THIS JOURNAL*, **49**, 241 (1927).

(24) Tiffeneau, *Compt. rend.*, **145**, 811 (1907).

TABLE I

THE REACTION OF STYRENE OXIDE, STYRENE IODOHYDRINS AND 3-BROMO-2-BUTANOL WITH METHYLMAGNESIUM IODIDE

Expt. ^a	Compound treated with MeMgI	Et ₂ O distd. on b. water-bath	Products	Yield, %	% of unchanged iodohydrin
1	PhCHCH ₂ O	Yes	PhCH ₂ CHOHCH ₃	53	...
2	PhCHICH ₂ OH	Yes	Ph(CH ₂) ₂ OH and a <i>s</i> -alcohol	13 ^b	Trace
3	PhCHCH ₂ O	No	PhCH ₂ CHOHCH ₃	51	4.1
4	PhCHICH ₂ OH	No	PhCH ₂ CHOHCH ₃	9.8	6.4
5	CH ₃ CHBrCHOHCH ₃	Yes	Hexene	13	...
6	PhCHOHCH ₂ I	No	"	"	85 ^d
7	PhCHOHCH ₂ I	Yes	Ph(CH ₂) ₂ OH and a <i>s</i> -alcohol	15 ^b	Trace
8	PhCHCH ₂ O + MgI ₂	...	PhCH ₂ CHOHCH ₃	15	4.9
9	PhCHICH ₂ OH	Yes	PhCH ₂ CHOHCH ₃	56	...
10	PhCHOHCH ₂ I	Yes	PhCH ₂ CHOHCH ₃	42	...

^a These experiments are in the order in which they are discussed in the theoretical part. ^b The yield is calculated as though it were pure 1-phenyl-2-propanol. ^c Of the iodohydrin 80% was recovered which melted at 34°. ^d This value was obtained by hydrolysis of an aliquot portion of the ether extract with potassium hydroxide.

posed to acetophenone during distillation *in vacuo* the crystalline iodohydrin was obtained in fair yield by the following procedure.

The ether solution of 2-iodo-1-phenyl-1-ethanol, prepared by treating a mixture of 1.2 moles of yellow mercuric oxide and 1200 cc. of a water-saturated ether solution of 1 mole of styrene with 1 mole of iodine, was washed with sodium bisulfite and potassium iodide solutions, dried and the solvent removed *in vacuo*. The crude product was recrystallized twice from 2.5 liters of hot petroleum ether and gave a 48% yield of white acicular crystals melting at 34°. (*Anal.* Calcd. for C₉H₉O: I, 51.18. Found: I, 51.32, 51.08.) When covered with petroleum ether and stored in an ice-chest for several months the product did not decompose appreciably. A mixture of this iodohydrin with that prepared from styrene oxide and hydriodic acid was partially liquid at room temperature and completely liquefied at 30°.

The Reaction of Styrene Oxide, Styrene Iodohydrins and 3-Bromo-2-butanol with Methylmagnesium Iodide.—Solutions of one mole of methylmagnesium iodide in 350 cc. of ether, analyzed by Gilman's titration method,²⁵ were used in each of the experiments reported in Table I with the exception of expt. 8. The molar ratio of Grignard reagent to the oxide was 1:1 and to the halohydrin, 2:1. The moles of compound treated with methylmagnesium iodide varied from 0.18 to 0.37, with the exception of expt. 6, in which 0.05 mole of iodohydrin was used. In expts. 1-7, the oxide or halohydrin, without solvent, but diluted with ether in expts. 9 and 10, was added to the well-stirred and ice-cooled Grignard reagent. The results are summarized in Table I.

In expt. 8, 0.2 mole of the oxide was added to 0.2 mole of magnesium iodide in 80 cc. of ether and 35 cc. of benzene, a solution of 0.2 mole of methylmagnesium iodide in 40 cc. of ether was added and 30 cc. of solvent was distilled.

Soon after reaching room temperature, the reaction mixtures boiled spontaneously in every experiment, except

expts. 6, 7 and 10. No external source of heat was used in expts. 3, 4 and 6. In expts. 1, 2, 5, 7, 9 and 10, most of the ether was distilled on a water-bath; the mixtures reacted violently in expts. 7 and 10.

The reaction mixtures, with the exception of expts. 6, 9 and 10, were hydrolyzed, extracted with ether and the ether extracts steam distilled from 30% potassium hydroxide solutions. This separated the alcohol from the resin that was formed in all experiments, with the exception of 6, and converted the halogen in the unchanged halohydrin to halide ion, which was determined and is reported as percentage of unchanged iodohydrin. The resin in expt. 8, extracted from the alkaline mixture with chloroform, weighed 13.8 g.

The alcohol from all experiments, with the exception of nos. 6, 9 and 10, was extracted from the steam distillate with ether, the ether extract dried over potassium carbonate, distilled and the alcohol fractionated through a 3- or 6-bulb Snyder column under reduced pressure. The products from expts. 9 and 10 were not steam distilled.

Identification of the Products in Table I.—The hexene from expt. 5 was identified by its reaction with bromine and potassium permanganate solutions and by its boiling point which was 69-70°. Phenethyl alcohol and 1-phenyl-2-propanol were identified by the melting points of their phenylurethans and mixed melting points with the respective derivatives from Eastman phenethyl alcohol and 1-phenyl-2-propanol (b. p. 92-93° at 8 mm.; *n*_D²⁰ 1.5210; *d*₄²⁰ 0.997) which was prepared in 56% yield from phenylacetaldehyde and methylmagnesium iodide. Whereas this phenylpropanol gave a phenylurethan melting at 86.5-87°, uncorr. (*Anal.* Calcd. for C₁₆H₁₇O₂N: N, 5.49. Found: N, 5.58, 5.47), the melting point has been reported previously at 92°²⁶ and 94°.²⁷ The α -naphthylurethan melted at 91-92° but was not analyzed.

The presence of a secondary alcohol in the products from expts. 2 and 7 was shown by tests with hydrochloric acid saturated with zinc chloride. An oily layer was produced in thirty minutes when 1 cc. of the product from

(25) Gilman, Wilkinson, Fishel and Meyers, *THIS JOURNAL*, **45**, 156 (1923).

(26) Tiffeneau and Fourneau, *Compt. rend.*, **146**, 699 (1906).

(27) *Ref. 22*, p. 356.

no. 2 was treated with 8.2 cc. of the hydrochloric acid-zinc chloride mixture. The oily layer did not appear as soon when the product from no. 7 was treated similarly but did appear within two hours. Control tests with pure phenethyl alcohol showed no layer until after standing for twenty-four hours. The results of control tests with known 1-phenyl-2-propanol and with mixtures of phenethyl alcohol and 1-phenyl-2-propanol were similar to the results obtained with the products from expts. 2 and 7.

The Reaction of Styrene Oxide with Magnesiumdimethyl.—A solution of 0.13 mole of magnesiumdimethyl in 430 cc. of ether, prepared from methylmagnesium iodide and dioxane at 100°,²⁸ was treated with 0.25 mole of styrene oxide. The reaction mixture was boiled for five hours and allowed to stand tightly stoppered for one week. The product, isolated in the usual manner, gave, as the only volatile material, a 60% yield of 2-phenyl-1-propanol²⁹ (b. p. 108–109° at 14 mm., n_D^{25} 1.5221, d_4^{25} 1.0036) and a residue of 4.3 g. of resin.

The phenylpropanol was identified by the preparation of its *p*-nitrobenzoate, acid phthalate and acid 3-nitrophthalate, the melting points of which were within 1° of those given by Cohen, Marshall and Woodman.³⁰ The phenylthiourethan melted at 69–70° whereas Cohen, Marshall and Woodman reported it as melting at 156°. However, their derivative was not analyzed and it seems probable that it was diphenylthiourea which melts at 154°. *Anal.* Calcd. for C₁₆H₁₇ONS: S, 11.82. Found: S, 12.09, 12.27.³¹

The α -naphthylurethan, which apparently has not been prepared before (*Anal.* Calcd. for C₂₀H₁₉O₂N: N, 4.58. Found: N, 4.31, 4.35), melted at 100–101°; a mixture of this urethan with the α -naphthylurethan of 1-phenyl-1-propanol (m. p. 102°³²) melted at 80–85°.

The Reaction of 1,2-Epoxypropane with Magnesiumdimethyl.—A solution of 0.4 mole of 1,2-epoxypropane and 0.17 mole of magnesiumdimethyl in 700 cc. of ether

was warmed and the reaction initiated boiled the mixture gently for one-half hour; heating was continued for another thirty minutes and the mixture, hydrolyzed with ice and ammonium chloride, gave 7 g. (28% yield) of 2-butanol, b. p. 98–100°. The melting point of the 3,5-dinitrobenzoate was 73° and this was not lowered when the compound was mixed with an authentic specimen.

Summary

1. Methylmagnesium iodide reacted spontaneously with styrene oxide and with 2-iodo-2-phenyl-1-ethanol. When the ether was distilled from the products, formed by the action of methylmagnesium iodide upon styrene oxide, 2-iodo-2-phenyl-1-ethanol and 3-bromo-2-butanol, no violent reactions occurred, such as is observed with ethylene oxide as the reactant.

2. 2-Iodo-1-phenyl-1-ethanol reacted with methylmagnesium iodide only on the application of heat.

3. 1-Phenyl-2-propanol was a product of the action of methylmagnesium iodide upon styrene oxide, 2-iodo-2-phenyl-1-ethanol and 2-iodo-1-phenyl-1-ethanol.

4. With magnesiumdimethyl, styrene oxide yielded 2-phenyl-1-propanol and 1,2-epoxypropane gave 2-butanol.

5. 2-Iodo-1-phenyl-1-ethanol was obtained crystalline; it was obtained by the action of iodine upon a mixture of mercuric oxide and a wet ether solution of styrene. Hydriodic acid acted upon styrene oxide, in water and in ether solution, to yield 2-iodo-2-phenyl-1-ethanol.

6. The theoretical significance of the above results is discussed.

7. The investigation of the mechanism of the reaction of Grignard reagents upon ethylene oxides is being continued.

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(28) Cope, *THIS JOURNAL*, **57**, 2238 (1935).

(29) This alcohol has been prepared since in good yields by treating an unfiltered mixture of methylmagnesium iodide and dioxane with styrene oxide (Thomas S. Reid, Master's Dissertation, 1938, Rutgers University).

(30) Cohen, Marshall and Woodman, *J. Chem. Soc.*, **107**, 899 (1915).

(31) We are indebted to Mr. Farris Swackhamer for this analysis.

(32) Bickel and French, *THIS JOURNAL*, **48**, 749 (1926).