[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Reactions of Organometallic Compounds. III. The Reactions of Phenyllithium with Some Epoxides[1,2]

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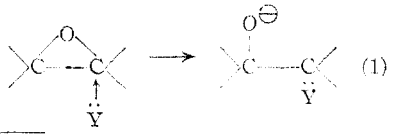
In the course of our work on displacement reactions involving organolithium compounds, it was of interest to study reactions with epoxides. When an organometallic compound is allowed to react with an unsymmetrically substituted ethylene oxide, two alcohols are possible, depending on the direction of ring opening. If the metal is magnesium (and if the addition is not preceded by isomerization of the epoxide to a carbonyl compound), the product is generally found to be the more highly substituted alcohol,[4] that is, involves addition of the organic residue to the less substituted carbon atom, although exceptions involving styrene oxide have been observed.[5,6]

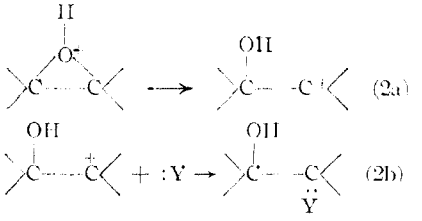
Gilman and Abbott[7] have found that methyllithium reacts with 1,1,1-trichloro-2,3-epoxypropane to give the secondary alcohol 1,1,1-trichloro-2-butanol rather than the isomeric primary alcohol 3,3,3-trichloro-2-methyl-1-propanol. We have studied the reactions of phenyllithium with propylene oxide, styrene oxide and 1,1-diphenylethylene oxide and have obtained the more highly substituted of the two possible alcohols in each case, the products being phenylmethylcarbinol, phenylbenzylcarbinol and diphenylbenzylcarbinol. The presence of the isomeric primary alcohols could not be demonstrated, even by fractionation on activated alumina columns (attempted in the last two cases), the products isolated being the secondary or tertiary alcohols and the olefins derived from them by dehydration.

Discussion.—The first stage of the reaction of the organolithium compound may be assumed to involve coördination to form a complex having a dative bond from the epoxide oxygen to the lithium atom, similar to that observed with ethyl ether and carbonyl compounds.[8] This complex could then react with the anionoid portion of another phenyllithium molecule, or decompose unimolecularly, to give the lithium salt of one or more of the possible alcohol products. Oxides are presumed[9] to react with nucleophilic reagents by processes involving direct displacement mechanisms as



(1)

or by carbonium ion mechanisms (generally involving acid catalysis) as



(2a)

(2b)

When the ring opening involves a direct displacement process, then the reagent generally attacks the less substituted carbon atom, resulting in the more highly substituted alcohol.[10] On the other hand, when the carbonium-ion process is involved, the more stable carbonium ion will be formed, generally resulting in attachment of the nucleophilic group Y on the more highly substituted carbon atom and formation of the less highly substituted alcohol.[11]

On the assumption that coördination of the lithium atom with the epoxy atom might tend to aid in carbonium-ion formation, the organolithium compound being a Lewis acid,[12] and as we have shown that phenyllithium promotes carbonium-ion formation with α- and γ-methylallyl chlorides,[1] we expected to observe products from a mechanism equivalent to equation (2) in these reactions. No such products were observed, even with diphenylethylene oxide, a compound which would give a tertiary carbonium ion, and it must therefore be concluded that the carbonium-ion process is apparently not generally available for the reaction of epoxides with organolithium compounds. Instead the results are consistent with a mechanism involving a direct nucleophilic attack by the phenyl group of a phenyllithium molecule on the carbon atoms of the epoxide ring, with the steric bulk of the alkyl or aryl groups directing that attack to the less substituted carbon atom. Our data give no evidence in favor of or against preliminary coördination of the epoxide atom with the lithium atom of a phenyllithium molecule, but this seems to be a likely intermediate.

Experimental

Materials.—The organolithium solutions were prepared in anhydrous ethyl ether according to previously described methods.[13,14] Propylene oxide and styrene oxide were redistilled from the commercial products before use; 1,1-diphenylethylene oxide was prepared by the synthesis described below. All of the reactions with organolithium compounds were carried out under dry nitrogen atmospheres in a 3-necked flask of suitable size fitted with a mercury-sealed stirrer, reflux condenser and dropping funnel. The quantity of phenyllithium used in each reaction was determined by a simple titration of the base with standard acid.

(1) Previous paper in series: Cristol, Overhults and Meek, THIS JOURNAL, **73**, 813 (1951).

(2) This work was presented before the Division of Organic Chemistry at the April, 1950, Meeting of the American Chemical Society at Philadelphia, Pa.

(3) American Cyanamid Fellow, 1949–1950.

(4) For a review of these reactions, see Gaylord and Becker, *J. Org. Chem.*, **15**, 305 (1950).

(5) Kharasch and Clapp, *ibid.*, **3**, 355 (1938).

(6) Golumbic and Cottle, THIS JOURNAL, **61**, 996 (1939).

(7) Gilman and Abbott, *J. Org. Chem.*, **8**, 224 (1943).

(8) Swain and Kent, THIS JOURNAL, **72**, 518 (1950).

(9) For a discussion of the mechanisms of ring openings of oxide rings, see Winstein and Henderson in Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1950, pp. 27-39.

(10) Ref. 9, p. 33.

(11) Ref. 9, p. 37.

(12) Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(13) Gilman, Langham and Moore, THIS JOURNAL, **62**, 2327 (1940).

(14) Kharasch, Lewis and Reynolds, *ibid.*, **65**, 498 (1943).

Propylene Oxide and Phenyllithium.—An excess of propylene oxide (5.75 g., 0.099 mole) was added to a stirred, ice-cooled solution of 0.094 mole of phenyllithium in 200 ml. of dry ether. When the addition was completed, the cold solution gave a positive test for organometallic compounds,[15] but the test was negative after the reaction mixture had been allowed to stand at room temperature overnight. The mixture was then hydrolyzed, and the ether layer was dried over anhydrous magnesium sulfate. Distillation yielded 7.4 g. (58%) of a liquid, b.p. 95–97.5° (12 mm.), reported 92–93° (8 mm.),[6] which gave only derivatives of methylbenzylcarbinol: hydrogen phthalate, m.p. 113–113.5°, and α-naphthylurethan, m.p. 90–90.5°, reported 113–114°[16] and 88–89.8°,[17] respectively. The isomer expected from ring opening in the other direction, 2-phenyl-1-propanol, is reported to give a hydrogen phthalate of m.p. 79°[18] and an α-naphthylurethan of m.p. 100–101°.[6] No materials of melting points approaching these were observed when the derivatives were prepared.

Styrene Oxide and Phenyllithium.—An excess of styrene oxide (11.15 g., 0.093 mole in an equal volume of ether) was added to a cooled phenyllithium solution (0.085 mole in 170 ml. of ether) and the reaction was brought to completion, as determined by the color test,[15] either by heating at reflux for 15 minutes or by allowing the reaction mixture to stand overnight at room temperature. Fractionation of the reaction product on activated alumina showed a yield of 2–4% (0.39–0.59 g.) of stilbene and 70–72% (11.8–12.1 g.) of phenylbenzylcarbinol. Stilbene was identified through its m.p., 119–122°, and mixed m.p. of 119.5–121.5° with an authentic sample. The carbinol, recrystallized from petroleum ether, had an m.p. of 64.8–65.0° (reported 66–67°)[19] and gave stilbene, m.p. 118–120°, when distilled at 15–18 mm.[5] Attempts to prepare the phenylurethan were not successful. In a preliminary investigation, oily fractions of carbinol were obtained which, when heated with anhydrous oxalic acid, gave only stilbene (m.p. 120–121°) and none of the ester (m.p. 160.5°)[5] which 2,2-diphenylethanol (m.p. 62°)[20] is reported to give under these conditions.

1,1-Diphenyl-2-bromoethanol.—This compound was prepared by the addition of a solution of 32 g. (0.21 mole) of N-bromoacetamide monohydrate in 100 ml. of *t*-butyl alcohol and 50 ml. of water to a rapidly stirred suspension of 36 g. (0.20 mole) of 1,1-diphenylethylene in 85 ml. of *t*-butyl alcohol and 35 ml. of water at 0°.[21] Three-quarters of an hour was required for the addition. The product precipitated from the reaction mixture after two hours in the cold. Filtration of the cold mixture yielded 27.4 g. (49% yield) of a solid of m.p. 71–72°, while 16.1 g. (m.p. 66–69°) were recovered upon working up the mother liquors. The crude yield was 43.5 g. or 78%. After several recrystallizations the melting point remained constant at 73.0–73.5°.

Anal. Calcd. for $C_{14}H_{13}OBr$: C, 60.66; H, 4.73. Found: C, 60.77; H, 4.48.

1,1-Diphenylethylene Oxide and Phenyllithium.—1,1-Diphenylethylene oxide was prepared by adding, with stirring, a solution of 36.1 g. (0.13 mole) of 1,1-diphenylethylene bromohydrin, m.p. 69–72°, in 75 ml. of methanol to a solution of 9.0 g. (0.16 mole) of potassium hydroxide in 60 ml. of methanol at room temperature. The solution was then cooled in an ice-salt-bath and filtered while cold. The solid material was extracted with ether and 14.5 g. of product obtained by recrystallization from that solvent, while concentration of the methanol solution yielded an additional 6.8 g. of product, so that the total yield was 21.3 g. (0.11 mole, 83% yield) of 1,1-diphenylethylene oxide, m.p. 54–56°. The material melted at 55.5–56.0° after recrystallization from petroleum ether. This compound, m.p. 56°, had been previously prepared from the chlorohydrin.[22] An excess of the purified epoxide (4.32 g., 0.022 mole) in 50 ml. of dry ether was added to a solution of phenyllithium (0.019 mole) in 25 ml. of ether at room temperature. After standing for 2.5 hours at room temperature the reaction mixture still contained organometallic material, but the color test was negative the next day. A previous run with twice as much material had shown complete reaction within 2 hours when the solution was held at reflux during that period of time. Hydrolysis was carried out with 50 ml. of water, after which the ether layer was separated, washed with 50 ml. of water and dried over anhydrous magnesium sulfate. The dry solution was transferred to a 250-ml. volumetric flask. The magnesium sulfate cake was washed with several portions of ether which were then used to make up the solution to the mark. Trial fractionation of a 50-ml. aliquot on activated alumina proved unsatisfactory since the ether carried the less adsorbed material through without any separation being effected. The solution was then made up to the mark again, using petroleum ether. A successful fractionation was obtained when the ether was removed from a 50-ml. aliquot before fractionation was attempted, a solution in petroleum ether, b.p. 50–60°, being used instead. Five major fractions were obtained when the material was eluted successively with petroleum ether, a mixture of carbon tetrachloride and benzene in a ratio of one to one by volume, and a mixture of chloroform and carbon tetrachloride in a ratio of one to one by volume. In order of appearance the fractions were:

(1) **Triphenylethylene**, 240 mg., m.p. 68.3–69.3°, dibromide, m.p. 90.8–91.5°; reported 70°,[23] 92°.[24] This is the expected dehydration product of diphenylbenzylcarbinol. Although it would also be formed upon dehydration of 2,2,2-triphenylethanol by a Wagner–Meerwein rearrangement,[25] it seems unlikely that the primary alcohol would be dehydrated under the mild reaction conditions employed.

(2) **Desoxybenzoin**, 87 mg., m.p. 53.5–54.5°; reported m.p. 55–56°.[26] This material, as well as the next fraction, appears to represent unreacted diphenylethylene oxide which had been isomerized by the activated alumina.

(3) **Diphenylacetaldehyde**, 111 mg.; semicarbazone m.p. 163–164°, reported 162°.[27]

(4) **Diphenylbenzylcarbinol**, 301 mg.; m.p. 86.5–87.5°; reported 87–88°.[28] The material did not depress the melting point of authentic diphenylbenzylcarbinol, and the dehydration with sulfuric acid gave triphenylethylene, m.p. 65–66°.

(5) **An oil**, 231 mg. This material was quite intractable, but gave a small amount of diphenylbenzylcarbinol. No 2,2,2-triphenylethanol (m.p. 106–107°)[29] could be found.

The yield of diphenylbenzylcarbinol and triphenylethylene, the products related to the attachment of the phenyl group to the less substituted carbon atom, was 48–67% in several experiments.

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Summary

The reactions of phenyllithium with three unsymmetrically substituted epoxides have been shown to yield the more highly substituted alcohols. Propylene oxide gave methylbenzylcarbinol, styrene oxide gave phenylbenzylcarbinol,

(15) Schulze and Gilman, THIS JOURNAL, **47**, 2002 (1925).

(16) Pickard and Kenyon, *J. Chem. Soc.*, **105**, 1124 (1914).

(17) Huston and Bostwick, *J. Org. Chem.*, **13**, 331 (1948).

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

(19) Hell, *Ber.*, **37**, 453 (1904).

(20) Ramart and Amagat, *Ann. chim.*, [10] **8**, 263 (1927).

(21) This procedure is essentially that used by Reich and Reichstein, *Helv. Chim. Acta*, **26**, 562 (1943), for bromohydroxylation of steroid olefins.

(22) Klages and Kessler, *Ber.*, **39**, 1754 (1906).

(23) Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 503.

(24) Klages and Heilmann, *Ber.*, **37**, 1455 (1904).

(25) *Cf.* the formation of 1,1,2-triphenylethane upon reduction of 2,2,2-triphenylethanol with phosphorus and hydriodic acid—Danislov, *J. Russ. Phys.-Chem. Soc.*, **51**, 97 (1919); *Chem. Zentr.*, **94**, II, 761 (1923).

(26) Allen and Barker in Blatt, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 157.

(27) Stoermer, *Ber.*, **39**, 2288 (1906).

(28) Hellerman and Garner, THIS JOURNAL, **57**, 142 (1935).

(29) Jones and Seymour, *ibid.*, **50**, 1150 (1928).

and 1,1-diphenylethylene oxide gave diphenylbenzylcarbinol and its dehydration product. These results have been interpreted in terms of a reaction mechanism for the opening of the 1,2-epoxide ring with organolithium compounds.

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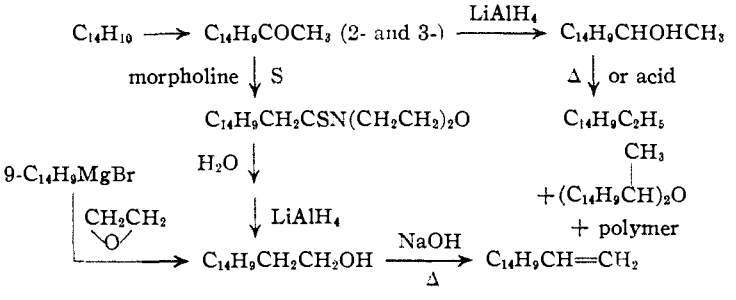
2-, 3- and 9-Vinylphenanthrenes[1a]

BY CHARLES C. PRICE AND BENJAMIN D. HALPERN[1b]

The synthesis of 2-, 3 and 9-vinylphenanthrenes has been accomplished most successfully through alkaline dehydration of the corresponding β-phenanthrylethanols. The β-(2- and β-(3-phenanthryl)-ethanols were prepared by Willgerodt transformation on the 2- and 3-acetyl derivatives, followed by hydrolysis of the thioamides and lithium hydride reduction of the corresponding phenanthrylacetic acids. Physical properties, including ultraviolet absorption data, are reported for many of the intermediates, products and their derivatives.

In order to extend the knowledge of arylethylenes, of potential interest as monomers in vinyl polymerization, the preparation and characterization of three isomeric vinylphenanthrenes have been investigated. Attempts to dehydrate the α-phenanthrylethanols from reduction of 2- and 3-acetylphenanthrene by thermal or catalytic procedures were unpromising. Apparently the desired vinyl compounds were too sensitive to polymerization. From these experiments some ethylphenanthrene and some ether of the reactant alcohol were isolated. 2- and 3-acetylphenanthrene



were successfully converted to the vinyl compounds through Willgerodt transformation, hydrolysis to the phenanthrylacetic acids, lithium aluminum hydride reduction and dehydration of the β-phenanthrylethanols over alkali. β-(9-Phenanthryl)-ethanol was prepared by reaction of the Grignard reagent of 9-bromophenanthrene with ethylene oxide and was also successfully dehydrated over alkali. Most of the compounds prepared have been characterized as their complex with 2,4,7-trinitrofluorenone (T.N.F.).[2]

Results of the investigation of the copolymerization properties of these three arylethylenes will be reported elsewhere.

Incidental to the work, tests were made on the plant growth activity of the intermediate phenanthrylacetic acids. These acids were apparently less effective than β-indolylacetic acid, with the 3-isomer slightly the more effective.[3]

(1) (a) Abstracted from a portion of the Ph.D. thesis submitted to the Graduate School by Benjamin D. Halpern. (b) General Tire and Rubber Co. Fellow, 1947–1948; Socony-Vacuum Oil Co. Fellow, 1948–1949.

(2) Available from Dajac Laboratories, 3430 W. Henderson St., Chicago, Ill.

(3) We are indebted to Professor Albert D. DeLisle, Department of Biology, University of Notre Dame, for this information.

Experimental[4]

2- and 3-Acetylphenanthrenes.—Especially purified phenanthrene (Reilly) was recrystallized once from ethanol, m.p. 98–98.5°. Color reaction with hot and cold concentrated sulfuric acid indicated a high degree of purity.[5] Acetylation, separation and purification were carried out according to Mosettig and van de Kamp[6] to yield 19% of 2-acetylphenanthrene, m.p. 144° (lit. 143°, 15%) and 66.5% of 3-acetylphenanthrene, m.p. 71° (lit. 72°, 63.5%).

2,4,7-Trinitrofluorenone complexes[7] were prepared by mixing hot equimolar benzene solutions of the reagent and the reactant. The yellow to orange precipitates were recrystallized from ethanol. The melting points and analyses are summarized in Table I.

α-2- and α-3-(Phenanthryl)-ethanols.—Reductions of the acetylphenanthrenes were found to proceed more smoothly and in better yield with lithium aluminum hydride than with aluminum isopropoxide. Using essentially the procedure of Nystrom and Brown,[8] 75 g. of 2-acetylphenanthrene (m.p. 135–139°, 0.34 mole) was treated with 6.0 g. of lithium aluminum hydride in 800 ml. of ether. Washing and evaporation left 72 g. (95%) of the carbinol. After precipitation from benzene by Skellysolve "F" it melted at 128.5–130.8° (lit., 131–131.5°,[9] 134–135°[10]). Similar reduction of 140 g. of 3-acetylphenanthrene (m.p. 68–69°) with 19 g. of lithium aluminum hydride in 400 ml. of ether yielded 126 g. (96.5%) of the carbinol, m.p. 76–78° (lit. 79–81°,[11] 83–83.5°[10]).

The acetate of α-2-(phenanthryl)-ethanol was prepared from 20 g. of the alcohol in 200 ml. of pyridine by heating with 80 g. of acetic anhydride. The crude white product, 23 g., m.p. 61–63°, was recrystallized from ethanol to yield 17 g., m.p. 66.8–67.6°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.10. Found: C, 81.76; H, 6.45.

The acetate of the 3-isomer was obtained as a viscous oil, b.p. 171–172° (0.03 mm.). Reaction with bromine (bromine no.,[12] 3.4; calcd. for vinylphenanthrene, 78.8), with permanganate, and saponification equivalent (calcd., 263; found 276) indicated contamination with approximately 5% of the vinylphenanthrene. The **picrate** prepared from this oil could be successfully crystallized from ethanol saturated with picric acid as dense clusters of yellow needles, m.p. 82.4–85.6°. The melting range and analysis indicate some contamination with excess picric acid.

Anal. Calcd. for $C_{24}H_{19}O_9N_3$: C, 58.42; H, 3.88; N, 8.51. Found: C, 57.23; H, 3.81; N, 8.82.

(4) Analyses by Micro Tech Laboratories, Skokie, Illinois.

(5) Price, THIS JOURNAL, **60**, 2839 (1938).

(6) Mosettig and van de Kamp, *ibid.*, **52**, 3704 (1930).

(7) Orchin and Woolfolk, *ibid.*, **68**, 1727 (1946).

(8) Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

(9) Bachmann and Struve, *J. Org. Chem.*, **5**, 420 (1940).

(10) Mosettig and van de Kamp, THIS JOURNAL, **55**, 3442 (1933).

(11) Bachmann and Chemerda, *J. Org. Chem.*, **6**, 36 (1941).

(12) Uhrig and Levin, *Ind. Eng. Chem. Anal. Ed.*, **18**, 90 (1941).