15.85 g. (41%) of 1-methylcyclohexene, b.p. 109–109.5°, n^{25}_{D} 1.4509 (lit.[32] 109.5°, n^{20}_{D} 1.4505). Extraction of the olefin was not quantitative as shown in a blank experiment; authentic 1-methylcyclohexene (Aldrich, distilled), subjected to the same isolation procedure, was recovered in 70% yield.

Reduction of 2α-Bromocholestanone.—To a 100-ml. three-necked flask containing a magnetic stirrer and attached through a condenser to a gas buret were added 13 ml. (0.4 mole) of hydrazine hydrate, 2 g. (20 mmoles) of potassium acetate, and 10 ml. of cyclohexene. The flask was heated until the cyclohexene boiled, and a solution of 2.004 g. (4.3 mmoles) of 2α-bromocholestanone in 30 ml. of cyclohexene was added dropwise over 10 min. while maintaining stirring and boiling. Heating was continued for 30 min. The light yellow mixture was cooled, extracted with ether–water, dried, evaporated, dissolved in hexane, and percolated through a column of acid-washed alumina (Merck). Evaporation of the filtrate yielded 995 mg. (64%) of 2-cholestene, m.p. 72–74°, $[\alpha]_D$ +64°. Recrystallization from ether–ethanol (2:1) gave white needles of 2-cholestene in 95% yield, m.p. 73–75°, $[\alpha]_D$ +65°.

Poorer results were obtained if the reagents were all mixed before heating. Thus a mixture of 2.009 g. of 2α-bromocholestanone, 13 ml. of hydrazine hydrate, 2 g. of potassium acetate, and 13 ml. of cyclohexene heated to reflux yielded a darker reaction mixture and only 269 mg. (19%) of 2-cholestene, m.p. 72–74°.

2α,3β-Dibromocholestane.—To a solution of 109 mg. (0.29 mmole) of 2-cholestene, m.p. 73–75°, in 2 ml. of ether was added dropwise a solution of bromine in acetic acid until a slight excess of bromine was present. Evaporation of solvent and crystallization of the residue from ether–ethanol gave 76 mg. (49%) of white plates of 2α,3β-dibromocholestane, m.p. 123–124°, lit.[28] m.p. 125°.

Hydrogenation of 2-Cholestene.—Microhydrogenation of 40.6 mg. (0.11 mmole) of 2-cholestene, m.p. 72–74°, in acetic acid using 10% palladium on carbon as catalyst, led to the slow (*ca.* 6 hr.) uptake of 1.00 equivalent of hydrogen. Work-up of the solution gave a light yellow residue which was dissolved in hexane and percolated through a short alumina column. Evaporation of the filtrate yielded 34 mg. (85%) of crude cholestane, m.p. 75–80°. The melting point was raised to 79–80°, lit.[28] m.p. 80°, by crystallization from ether–ethanol.

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[32] G. Egloff, "Physical Constants of Hydrocarbons," Vol. 2, Reinhold Publishing Corp., New York, N. Y., 1940, p. 326.

Tropone. Selenium Dioxide Oxidation of 1,3,5-Cycloheptatriene

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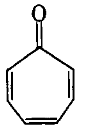
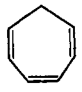
There are several methods known for the preparation of tropone (2,4,6-cycloheptatrien-1-one, I).[1–5] They range in scope from the degradation of tropinone[4] to produce I, to the formation of bis-2,4,6-cycloheptatrien-1-yl ether (III) from the hydrolysis of tropilium salts and subsequent disproportionation of the ether to give I and 1,3,5-cycloheptatriene (II).[2,3]


I


II

We have observed a direct oxidation of II by selenium dioxide in buffered aqueous dioxane to give I in about 25% yield. This reaction, though not high in yield, affords a simple one-step preparation of I from commercially available starting materials. The reaction can readily be adapted to large scale, and the inorganic product, selenium, can be recovered and reoxidized to selenium dioxide if desirable.[6]

Experimental

Preparation of Tropone.—To a solution of potassium dihydrogenphosphate (13.5 g., 0.1 mole) in water (33 ml.) was added 1,4-dioxane (330 ml.), 1,3,5-cycloheptatriene (43.0 g., 0.46 mole, Shell Chemical Corp., contained 6% toluene), and selenium dioxide (53.0 g., 0.48 mole, Matheson, Coleman and Bell). The mixture was warmed on the steam bath (90°) for 15 hr., allowed to cool to room temperature, and then filtered. The filtrate was poured into water (750 ml.) and extracted three times with 250-ml. portions of methylene chloride. The organic extract was washed with 10% sodium bicarbonate, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* to a dark brown liquid. Distillation of this liquid gave 12.8 g. (25%) of pale yellow tropone, b.p. 91–92° at 4 mm., n^{23}_{D} 1.6152. The infrared spectrum of this material was identical with that reported by Doering.[5]

Acknowledgment.—The author wishes to thank Shell Chemical Corporation for its generous supply of 1,3,5-cycloheptatriene.

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[1] J. Birch, M. Graves, and F. Stansfield, *Proc. Chem. Soc.*, 282 (1962).

[2] T. Nozoe, T. Ikemi, and H. Sugiyama, *Chem. Ind.* (London), 932 (1960).

[3] A. P. ter Borg, *Helv. Chim. Acta*, **43**, 457 (1960).

[4] J. Meinwald, S. Emerman, N. Yang, and G. Büchii, *J. Am. Chem. Soc.*, **77**, 4401 (1955).

[5] M. von E. Doering and F. Detert, *ibid.*, **73**, 877 (1951).

[6] N. Rabjon, "Organic Reactions," Coll. Vol. V, R. Adams, Ed., John Wiley and Sons, New York, N. Y., 1949, p. 345.

The Reaction of Chlorocarbene with Styrene

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Received August 29, 1963

A number of carbenes or "carbene-like" species have been added to styrene to give substituted phenylcyclopropanes.[1] Closs and co-workers[2] have generated chlorocarbene from methylene chloride and methyl- or *n*-butyllithium and added it to various olefins to give substituted chlorocyclopropanes. The work which is now reported was undertaken to study the addition of chlorocarbene to styrene.

When ethereal *n*-butyllithium, prepared from *n*-butyl bromide and lithium, was allowed to react with methylene chloride in the presence of excess styrene, two stereoisomeric 1-chloro-2-phenylcyclopropanes were isolated in low yields in addition to several gaseous products. The yields of **1** (4.1%) and **2** (4.9%) are based on distilled material, assuming equal thermal conductivities on gas chromatographic (g.c.) analysis. The structural

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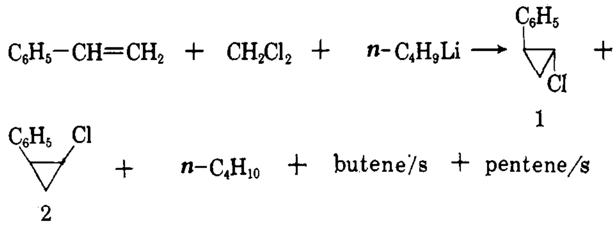
[1] (a) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); (b) W. J. Dale and P. E. Swartzentruber, *J. Org. Chem.*, **24**, 955 (1959); (c) A. Nagasaka and R. Oda, *Kogyo Kagaku Zasshi*, **59**, 1024 (1956); (d) H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961); (e) A. Burger and W. L. Yost, *ibid.*, **70**, 2198 (1948); (f) R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957); (g) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959); (h) G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961).

[2] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960), and subsequent papers.



assignments are based primarily on the nuclear magnetic resonance (n.m.r.) spectra and to a lesser extent on their physical properties. The n.m.r. spectrum (CCl_4) of **1** showed a broad multiplet centered at δ -7.07[3] (5.00)[4] for the aromatic protons, an octet at -3.07 (1.00) for the proton on the chlorine-bearing carbon, an octet at -2.28 (1.00) for the benzylic proton, and at least eight peaks at -1.35 (2.50) for the two remaining cyclopropyl protons. Isomer **2** also showed four sets of peaks at δ -7.20 (5.00, singlet), -3.28 (1.00), -2.27 (1.08), and -1.28 (2.10), respectively. The high resolution n.m.r. spectra of the proton, H_A, on the chlorine-bearing carbon and the benzylic proton, H_B, for the two isomers are shown in Fig. 1 and 2. Analysis of these spectra show the coupling constants between H_A and H_B to be 3.3 c.p.s. for the isomer assigned the *trans* structure and 7.7 c.p.s. for the other isomer. It has been fairly well-established that *cis* protons on a cyclopropane ring have a larger coupling constant than do *trans* protons.[5] The relative chemical shifts for H_A of the two isomers also are consistent with the assigned structures, since the proton on the chlorine-bearing carbon of the *cis* isomer is usually found at a lower field.[5b,c,6] The relative boiling points and refractive indices of **1** and **2** are also in agreement with the assigned structures. A number of cases have been reported in which the *cis* cyclopropyl compounds had the higher values for both of these physical properties.[2,5b,c,6,7]

The slight predominance of the *cis* isomer isolated is in accord with the findings of Closs and co-workers[2,5b] who also found a preference for the *cis* isomers. However, this result may be fortuitous, since the yields are quite low and may only reflect the product distribution after a portion of the primary product has reacted further. An indication that the latter may have occurred was found in the isolation of a high-boiling liquid which contained cyclopropyl protons as shown by n.m.r. spectroscopy. The origins of the n-butane, butene/s, and pentene/s in this type of reaction have been discussed elsewhere.[2,8]

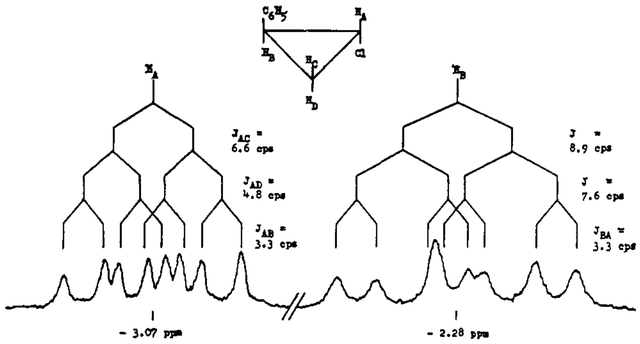


Fig. 1.—Partial n.m.r. spectrum of *trans*-1-chloro-2-phenylcyclopropane (**1**).

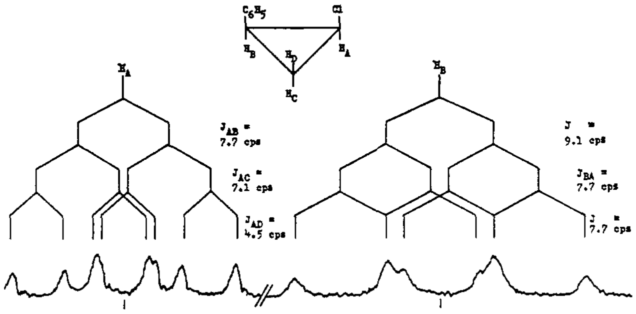
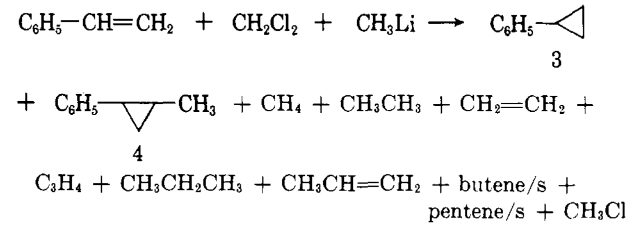


Fig. 2.—Partial n.m.r. spectrum of *cis*-1-chloro-2-phenylcyclopropane (**2**).

In contrast to the above results utilizing n-butyllithium, the reaction of methyllithium, prepared from methyl iodide and lithium, with methylene chloride and styrene in ether at either 5–10° or −70° led to the formation of phenylcyclopropane (**3**, 10%) and 1-methyl-2-phenylcyclopropane (**4**, 20%) in addition to a complex mixture of gases. No **1** or **2** could be detected. The identity of the cyclopropanes was based on elemental analyses, spectral data, and comparison of the physical properties with the literature values.



The mechanism of the latter reaction has not been determined, but several possible reaction paths could be visualized. Initial formation of a complexed carbene ($:CH_2$)[9] could give use to **3**. The presence of lithium iodide could account for the formation of this complexed carbene in a manner analogous as that described by Schöllkopf and Paust[10] for the formation of alkoxy carbenes. Formation of methylcarbene[11] could lead to **4**. Alternatively, various combinations of halogen–metal exchange, alkylation, and hydrolysis of **1** or **2** could give **3** and **4**.[12] The gaseous products probably arose from interaction of methyllithium, methylene chloride, and chlorocarbene. Reactions between methylene halides and organometallic compounds to give products analogous to some of those reported here have been described.[13]

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(3) δ in p.p.m. from tetramethylsilane used as an internal reference.

(4) Integrated area.

(5) (a) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962); (b) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962); (c) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(6) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **82**, 2372 (1960).

(7) R. G. Kelso, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **77**, 1751 (1955).

(8) (a) J. F. Eastham and G. W. Gibson, *J. Org. Chem.*, **28**, 280 (1963); (b) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); (c) G. L. Closs, *ibid.*, **84**, 809 (1962).

(9) For possible related reactions, see (a) W. T. Miller, Jr. and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959); (b) L. Friedman and J. G. Berger, *ibid.*, **82**, 5758 (1960); (c) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1962, p. 500.

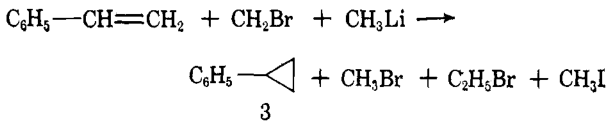
(10) U. Schöllkopf and J. Paust, *Angew. Chem.*, **75**, 670 (1963).

(11) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **No. 10**, 38 (1960).

(12) For pertinent references, see (a) H. M. Walborsky, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **23**, 75 (1962); (b) H. M. Walborsky and F. J. Impastato, *J. Am. Chem. Soc.*, **81**, 5835 (1959), ref. 6.

(13) (a) A. A. Morton and F. Fallwell, Jr., *ibid.*, **60**, 1429 (1938); (b) G. Wittig and H. Witt, *Chem. Ber.*, **74B**, 1474 (1941).

Reaction of methylene bromide with methyllithium and styrene gave **3** as the only identifiable cyclopropyl derivative (1.3%). The formation of **3** is analogous to the results obtained by Miller and Kim with cyclohexene.[9a,14]



Experimental[15]

Reaction of Styrene with Methylene Chloride and *n*-Butyllithium. Preparation of *trans*- (1) and *cis*-1-Chloro-2-phenylcyclopropane (2).—A solution of *n*-butyllithium was prepared according to the method of Gilman and co-workers[16] from *n*-butyl bromide (68.5 g., 0.50 mole) and lithium (7.7 g., 1.11 g.-atoms) in 325 ml. of dry ether. The butyllithium solution was added under an atmosphere of dry helium over a period of 1.5 hr. to a stirred solution of inhibitor-free styrene (208.2 g., 2.00 moles) and methylene chloride (84.9 g., 1.00 mole) held at 5–10°. After the addition was complete, the mixture was stirred at 10–22° for 2 hr. After washing with water and drying ($CaCl_2$), the solution was distilled to give a fraction, b.p. 5–7°, consisting of *n*-butane (4.6 g.), butene/s (0.04 g.), and pentene/s (0.13 g.) by mass spectral analysis. Continued distillation gave a mixture, b.p. 34–49° (1 atm.–22 mm.), shown by g.c. to be ether, methylene chloride (72% recovery), styrene (94% recovery), and a component which was probably benzoic acid, *ca.* 0.1 g. (see following experiment). A third fraction, b.p. 47–51° (0.7 mm.), 1.84 g., was separated by preparative g.c. ($^3/_{16}$ in. × 20 ft. silicone gum rubber column, 190°, helium flow rate 60 ml./min.). The first component eluted was **1**, b.p. *ca.* 47° (0.7 mm.), $n^{25}\text{D}$ 1.5390; $\lambda_{\max}^{\text{neat}}$ 3.31 (m), 3.43 (w), 6.27 (m), 6.70 (s), 6.90 (m), 7.30 (w), 7.98 (s), 8.26 (w), 9.10 (w), 9.36 (m), 9.62 (m), 9.71 (m), 9.99 (w), 10.09 (m), 10.62 (m), 10.92 (w), 11.28 (m), 11.58 (w), 13.12 (s), 14.31 (s), and 14.73 (s) μ.

Anal. Calcd. for C_9H_9Cl: C, 70.83; H, 5.94; Cl, 23.23; mol. wt., 152.6. Found: C, 71.60, 71.80; H, 6.16; 6.39; Cl, 22.37, 22.48; mol. wt., 152 (mass spectrometry).[17]

The second compartment eluted was **2**, b.p. *ca.* 51° (0.7 mm.), $n^{25}\text{D}$ 1.5506; $\lambda_{\max}^{\text{neat}}$ 3.31 (m), 6.28 (m), 6.71 (s), 6.91 (m), 7.39 (w), 7.81 (s), 8.15 (w), 8.61 (w), 9.12 (w), 9.29 (m), 9.62 (m), 9.71 (m), 9.87 (m), 10.79 (m), 10.90 (m), 12.29 (m), 13.03 (s), 13.70 (s), and 14.30 (s) μ.

Anal. Calcd. for C_9H_9Cl: C, 70.83; H, 5.94; Cl, 23.23; mol. wt., 152.6. *Found:* C, *71.35, 71.43;* H, *6.02, 6.09;* Cl, 23.17; 23.29; mol. wt., 152 (mass spectrometry).[17]

The distillation residue, 3.8 g., was dissolved in 50 ml. of carbon tetrachloride, and slow addition of 300 ml. of methanol precipitated polystyrene. Filtration and evaporation of the filtrate gave 0.90 g. of dark brown oil which was distilled, b.p. 140–200° (0.2 mm.). Preparative g.c. gave crude separation of one major component from several minor ones. The component separated had an n.m.r. spectrum which showed a multiplet centered at δ −7.1 (1.00) and two partially resolved multiplets centered at −1.2 and −0.9 (1.35).

Reaction of Styrene with Methylene Chloride and Methyllithium. Reaction at 5–10°.—A solution of methyllithium was prepared according to the method of Gilman and co-workers[18] from methyl iodide (71.0 g., 0.50 mole) and lithium (7.7 g., 1.11 g.-atoms) in 325 ml. of dry ether. The methyllithium solution was added dropwise under dry nitrogen over a period of 1 hr. to a stirred solution of styrene (208.2 g., 2.00 moles) and methylene chloride (84.9 g., 1.00 mole) held at 5–10°. After stirring at room temperature for 2 hr., the reaction mixture was poured into 500 ml. of water and shaken, and the organic layer was separated. The aqueous layer was extracted with methylene chloride, and the combined organic solutions were washed with water and dried. After distillation of the ether, methylene chloride, and styrene (88% recovery), a mixture of products, b.p. 70–97° (50 mm.), and 44.6 g. of residue were *obtained. The mixture was separated by preparative g.c.* into three components. The first component eluted was identified as benzoic acid by mixture melting point and infrared spectroscopy.

The second component eluted was identified as phenylcyclopropane (**3**), $n^{25}\text{D}$ 1.5310, lit.[19] b.p. 90–91° (52 mm.), lit.[1g] $n^{25}\text{D}$ 1.5309; n.m.r. spectrum (CCl_4): a multiplet centered at δ −7.05 (5.00) for aromatic protons, a multiplet at −1.85 (1.07) for the benzylic proton, and a multiplet at −0.80 (3.95) for the remaining cyclopropyl protons. The n.m.r. spectrum is in fair agreement with that given by Bumgardner.[19] The infrared spectrum was identical with that given by Dale and Swartzentruber.[1b]

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53; mol. wt., 118. *Found:* C, 91.09, 91.48; H, 8.04, 8.31; mol. wt., 118 (mass spectrometry).

The third component eluted was identified as 1-methyl-2-phenylcyclopropane (**4**), $n^{25}\text{D}$ 1.5205, lit.[1g] b.p. 78–79° (20 mm.), lit.[1g] $n^{25}\text{D}$ 1.5204; $\lambda_{\max}^{\text{neat}}$ 3.29, 3.37, 6.21, 6.68, 6.89, 9.70, 13.11, 13.38, 13.69, and 14.26 μ; n.m.r. spectrum (CCl_4): a singlet at δ −7.12 (5.00) for the aromatic protons, a sextet at −2.05 (0.95) (J = 6.1, 8.5, and 8.5 c.p.s.) for the benzylic proton, and a multiplet at −0.83 (6.38) for the methyl and the remaining cyclopropyl protons.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15; mol. wt., 132. Found: C, 90.83, 90.90; H, 8.90, 9.04; mol. wt., 132 (mass spectrometry).

The isolated **4** was analyzed by g.c. (Apiezon L column) and shown to consist of two components. The larger component made up 98–99% of the material. These may be the *cis* and *trans* isomers.

Reaction at −70 to −65°.—The preceding reaction was repeated using the same amounts of methyllithium and styrene and a larger amount of methylene chloride (425 g., 5.00 moles). The methyllithium was added over a period of 2 hr. at such a rate that the reaction mixture was maintained at −70 to −65°. After the addition was completed, the mixture was allowed to come to room temperature with stirring over a period of 15 hr. Mass spectral analysis of the gaseous products showed the presence of major amounts of methane, ethylene, propylene, propane, and butene/s. Minor amounts of ethane, methyl chloride, pentene/s, and a C_3H_4 component were present also. Work-up of the reaction mixture as before gave styrene (84% recovery), **3** (0.04%), **4** (1.5%), a trace of benzoic acid, and 13.5 g. of distillation residue. Analysis of the residue by n.m.r. spectroscopy indicated it to be mainly polystyrene.

Reaction of Styrene with Methylene Bromide and Methyllithium.—A solution of methyllithium prepared in the usual manner from methyl iodide (71.0 g., 0.50 mole) and lithium (7.7 g., 1.11 g.-atoms) in 325 ml. of ether was added under dry helium over a period of 1.5 hr. to a stirred solution of styrene (208.2 g., 2.00 moles) and methylene bromide (173.9 g., 1.00 mole) held at 5–10°. After completion of the addition, the reaction mixture was stirred at 10–23° for 2 hr. Mass spectral analysis of the gaseous reaction products showed a trace of methane (*ca.* 0.008 g.) and ethylene (*ca.* 0.01 g.). The reaction mixture was washed with water and dried. Distillation gave a mixture, b.p. 32–21° (1 atm.–0.9 mm.). Mass spectral and g.c. analyses showed the following composition: methyl bromide (3.7 g.), ethyl bromide (7.4 g.), methyl iodide (9.8 g.), methylene bromide (62% recovery), styrene (80% recovery), benzoic acid (0.2 g.), and **3** (5.9 g.). No **4** or any higher boiling materials such as 1-bromo-2-phenylcyclopropane could be detected by

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[14] See also W. Kirmse and B. G. v. Wedel, *Ann.*, **666**, 1 (1963).

[15] Boiling points were uncorrected. Elemental microanalyses were determined by Mr. L. E. Swim and co-workers. Infrared spectra were obtained by Dr. R. D. Moss and co-workers with a Perkin-Elmer Model 137 Infracord. The n.m.r. spectra were obtained by Dr. J. P. Heeschen and co-workers with a Varian A-60 spectrometer operating at 60 Mc./sec. The chemical shifts are reported as δ in p.p.m. *from tetramethylsilane which* was used as an internal reference. Relative areas are given in parentheses. Mass spectral gas analyses were determined by Mr. E. O. Camehl, and molecular weight determinations by mass spectroscopy were by Mrs. W. L. Dilling. G.c. analyses were determined with an F & M Model 500 programmed temperature gas chromatograph. Preparative g.c. separations were carried out by Mr. H. W. Moll and co-workers.

[16] R. G. Jones and H. Gilman, "Organic Reactions," Coll. Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.

[17] The mass spectra of **1** and **2** were nearly identical. The isotopic abundance ratio at the parent peaks verified the presence of one chlorine atom per molecule. Therefore, the formula of each compound was C_9H_9Cl.

[18] H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **55**, 1252 (1933).

[19] C. L. Bumgardner, *ibid.*, **83**, 4420 (1961).

g.c. The distillation residue, 28.6 g., was dissolved in 200 ml. of carbon tetrachloride, and the polystyrene was precipitated by the slow addition of 600 ml. of methanol. Evaporation of the filtrate gave 1.90 g. of dark brown liquid. Distillation of the liquid, b.p. 160–200° (0.1 mm.), and g.c. analysis showed the presence of at least four components. The n.m.r. spectrum of this fraction showed two multiplets centered at $\delta -1.2$ (1.75) and -0.9 (1.00).

Acknowledgment.—The author wishes to thank Dr. J. C. Little and Dr. Y. Chang for many helpful discussions during this work.

Reactions of 1-(Chloromethyl)naphthalenes

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Received September 23, 1963

In a previous study of the reactions of methyl substituted 1,4-epoxy-1,4-dihydronaphthalenes,[1] two alkyl substituted 1-(chloromethyl)naphthalenes were obtained readily by reaction of the epoxides with dry hydrogen chloride in methanol. In view of the potential synthetic value of the (chloromethyl)naphthalenes, and also because some of their reactions appeared to be somewhat unusual, it was desired to study their behavior more fully. For this purpose three alkyl-substituted 1-(chloromethyl)naphthalenes were prepared and used, namely, 4-methyl-,[2] 2,3,4-trimethyl-,[1] and 4-methyl-2,3-diethyl-.[1] Some reactions of the second compound were reported previously.[1]

The Wurtz reaction with sodium, in octane as reaction medium, gave the expected products, one of which, 1,2-bis(4-methyl-1-naphthyl)ethane (I), had been described before.[3] *n*-Octane was chosen as solvent since its boiling temperature is high enough to liquify the sodium metal for efficient reaction. Apparently the reaction is not rapid under these conditions, since in some cases unreacted chloro compound was recovered. No attempt was made to improve the yields, but it is likely that a higher-boiling inert liquid should be more effective.

Hydrolysis of the (chloromethyl)naphthalenes failed in all cases to give the corresponding alcohols, but invariably gave the ethers. Although it has been reported[4] that 1-(hydroxymethyl)-4-methylnaphthalene was obtained in this way in very low yield together with much of the ether, we were not able to confirm this. Similarly, 1-(chloromethyl)-2,3,4-trimethylnaphthalene gave only bis(2,3,4-trimethyl-1-naphthyl methyl) ether,[1] and 1-(chloromethyl)-4-methyl-2,3-diethylnaphthalene gave a 78% yield of bis(4-methyl-2,3-diethyl-1-naphthyl methyl) ether (VI).

Displacement of the chlorine by methoxyl was readily accomplished by boiling methanol or sodium methoxide in methanol. It is interesting to note that, whereas 1-(methoxymethyl)-2,3,4-trimethylnaphthalene[1] is a solid, its homolog, 1-(methoxymethyl)-4-methyl-2,3-diethylnaphthalene (III), is a liquid which failed to solidify after cooling several hours at −40°. It is also worth noting that, when the chloromethyl compound is boiled with methanol containing a little aqueous hydrochloric acid, the product is the ether. Thus, 1-(chloromethyl)-4-methyl-2,3-diethylnaphthalene gave a 45% yield of the ether VI.

1-Methoxymethyl)-4-methyl-2,3-diethylnaphthalene (III) was subjected to a Zeisel methoxyl analysis[5] and the residue was worked up to see if it contained some of the alcohol. However, the product proved to be the hydrocarbon, 1,4-dimethyl-2,3-diethylnaphthalene (IV), apparently the result of complete reduction by the hydriodic acid. The identity of this product was confirmed by reducing 1-(chloromethyl)-4-methyl-2,3-diethylnaphthalene with zinc and acid to obtain the same compound (IV).

Several attempts were made to make the Grignard reagent of the (chloromethyl)naphthalenes. Success was achieved only in the case of 1-(chloromethyl)naphthalene, whose Grignard was converted to 1-naphthylacetic acid (VII).[6] It had been reported[7] that this reaction goes to 88–92% completion. In several attempts it was found impossible to obtain any Grignard reaction with the 1-(chloromethyl)naphthalenes substituted by methyl groups in the 4-, or 2-, 3-, and 4-positions, or by methyl in the 4-, and ethyl groups in the 2- and 3-positions. In ether as solvent, catalysts such as iodine, ethylene bromide, and methyl iodide were tried, but no reaction took place even after 2 hr. at reflux temperature followed by 24 hr. at room temperature. In every case the starting material was recovered nearly quantitatively.

Experimental[8]

1,2-Bis(4-methyl-1-naphthyl)ethane (I).—1-(Chloromethyl)-4-methylnaphthalene (0.400 g., m.p. 61–62°) was dissolved in 20 ml. of *n*-octane, sodium (1 g.) was added, and the mixture refluxed for 3 hr. at 110–115°. The warm mixture was filtered then thoroughly cooled at 0–10°, and the crystalline product was filtered and washed with cold hexane. The yield was 0.160 g. (50%), m.p. 154–155°, lit.[3] m.p. 152–153°. The ultraviolet spectrum in cyclohexane, λ_{max} mμ (log ϵ), showed absorption at 213 sh (4.78), 230 (5.03), 269 sh (3.87), 283 (4.11), 292.5 (4.23), 303 (4.13), and 316 (3.34); lit.[3] 228 (5.05), 292 (4.2), and 302 (4.1).

1,2-Bis(2,3,4-trimethyl-1-naphthyl)ethane (II).—1-(Chloromethyl)-2,3,4-trimethylnaphthalene[1] (0.200 g.) was dissolved in 10 ml. of *n*-octane, sodium (0.5 g.) was added, and the mixture refluxed for 4 hr. On cooling the filtered solution, the product did not crystallize. The solvent was removed under vacuum; the residue was taken up in hexane and chromatographed on a column of neutral alumina. The first fraction consisted of some starting material, while the second yielded 0.12 g. (72%) of the product, m.p. 195–200°. Recrystallization from hexane gave m.p. 207.8–209°. The ultraviolet spectrum in cyclohexane, λ_{max} mμ (log ϵ), showed absorption at 219 sh (4.82), 233 sh (5.07), 235 (5.09), 275 sh (3.88), 2.87 (4.07), 298 (4.18), 311 (4.08), and 323 (3.32).

Anal. Calcd. for $C_{28}H_{30}$ (366.5): C, 91.80; H, 8.20. Found: C, 91.67; H, 8.36.

1-(Methoxymethyl)-4-methyl-2,3-diethylnaphthalene (III).—

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(8) Melting points are corrected. The authors are grateful to Dr. G. Slomp and his staff at the Upjohn Co., Kalamazoo, Mich., for determining the ultraviolet spectra which were run on a Cary Model 15 spectrophotometer.