benzyne itself. Stabilization through conjugation of the tetraphenylbenzyne is not deemed likely in view of probability that the adjacent phenyl rings are not coplanar with the central ring. A comparison of the relative reactivities of tetraphenylbenzyne and the structurally related 9,10-phenanthryne toward a diene or of phenyllithium and lithium piperidide toward tetraphenylbenzyne[2b] should shed more light on this question.

Experimental

Preparation of 1,4-Dihydro-5,6,7,8-tetraphenylnaphthalene 1,4-Endoxide.—Lithium amalgam was prepared[2] from 45 g. (0.225 g.-atom) of mercury and 0.12 g. (0.018 g.-atom) of lithium in a Schlenk tube under argon. To the amalgam then was added 3.2 g. (5.3 mmoles) of 1,2-dibromotetraphenylbenzene, 35 ml. of dry diethyl ether, and 35 ml. of dry furan. The resulting suspension (maintained under an argon atmosphere) was shaken using a mechanical shaker for 6 days at room temperature. During this time the liquid phase became light yellow in color.

The Schlenk tube was cooled and opened, and benzene and methylene chloride were added to effect solution of all organic components. The filtered, yellow organic solution was evaporated at reduced pressure, leaving 2.8 g. of crystalline residue, m.p. 78–86°. The latter was recrystallized from carbon tetrachloride–petroleum ether to give a solid with m.p. 182–184°. Further recrystallization gave 1.9 g. (66%) of the desired product, m.p. 214–217° (decomposition with gas evolution).

Anal.[3] Calcd. for $C_{34}H_{24}O$: C, 91.04; H, 5.39; O, 3.57. Found: C, 90.44; H, 5.41; O, 3.52.

The n.m.r. spectrum[4] showed a triplet at 5.55 and a singlet at 6.75 followed by a multiplet from 6.9–7.2 p.p.m. The integrated area ratio of the triplet to the singlet plus multiplet was 1:11. The triplet is assigned to the bridgehead protons at the 1,4-positions, and the olefinic protons appear to overlap with the aromatic protons. A similar situation has been observed in the case of benzonorbornadiene.[5]

Attempted purification of the product by column chromatography (Woelm alumina, neutral) was unsuccessful. Green-violet coloration was observed, and elution with 1:1 benzene–cyclohexane gave a product which did not contain oxygen. Its m.p. 203–205° and its analysis suggest that it is 1,2,3,4-tetraphenylnaphthalene (lit.[6] m.p. 201–203°,[6a] 198–200°[6b]).

Anal. Calcd. for $C_{34}H_{24}$: C, 94.41; H, 5.59. Found: C, 94.28; H, 5.90.

Analysis of the crude product of the tetraphenylbenzyne–furan reaction by thin layer chromatography showed that tetraphenylnaphthalene was not present.

(3) Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

(4) Measured in carbon tetrachloride solution using a Varian Associates A60 n.m.r. spectrometer. Chemical shifts are given in parts per million downfield from tetramethylsilane.

(5) H. Menzel, Dissertation, Universität Heidelberg, 1963.

(6) (a) W. Herwig, W. Metlesics, and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 6203 (1959); (b) H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 1596 (1964).

The Chemistry of Carbanions. VIII. The Intramolecular Alkylation of Ketyl Radical Anions[1]

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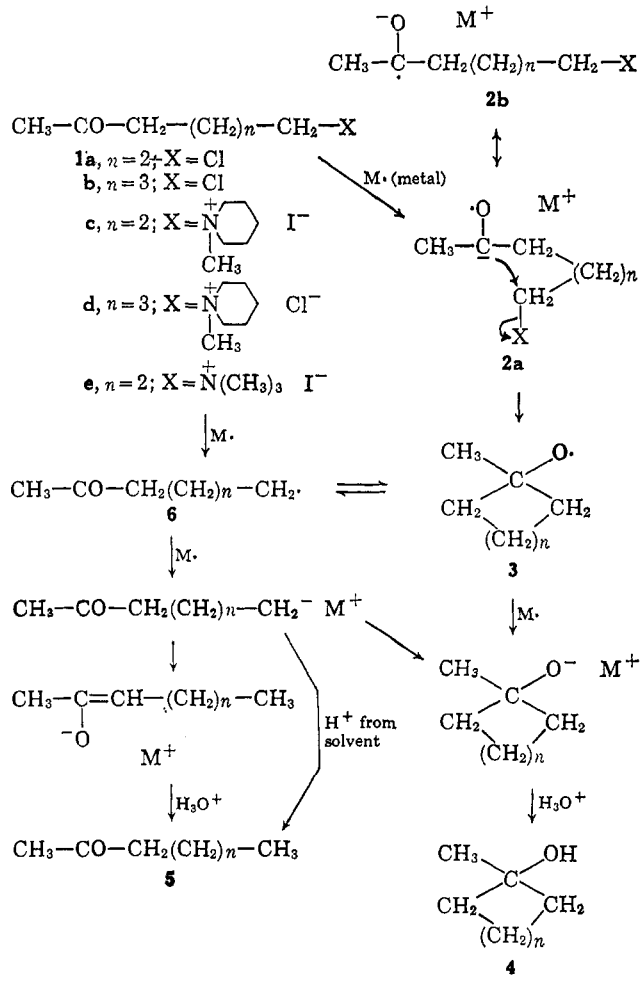
Several alkylation reactions have been described[2] which presumably involve either the intramolecular or the intermolecular alkylation of an intermediate radical anion. These intermediate radical anions have been derived from reduction of either aromatic nuclei or α,β-unsaturated ketones with metals. We wished to learn whether a comparable intramolecular alkylation of a simple ketyl anion radical might be effected since such a procedure might offer a useful synthetic route to bridgehead tertiary alcohols.[3] The accompanying equations illustrate the reaction of interest, namely **1** → **2** → **3** → **4** (see Scheme I).

SCHEME I



To examine this possibility the reactions of the ω-chloro ketones **1a** and **1b** with lithium in liquid ammonia, with the sodium–phenanthrene and sodium–naphthalene radical anions, and with chromium(II) ion [Cr(II)][4] were examined. Although treatment of the chloro ketone **1a** with chromium(II) acetate led to recovery of the starting material, the other two reducing systems did convert the chloro ketones **1a** and **1b** to mixtures of the desired cyclic carbinols **4**

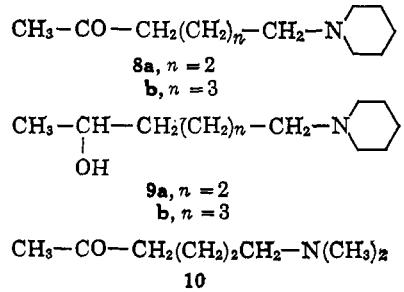
(1) This research has been supported by Grant No. AF-AFOSR-573-64 from the U. S. Air Force Office of Scientific Research.

(2) (a) G. Stork and J. Tsuji, *J. Am. Chem. Soc.*, **83**, 2783 (1961); (b) S. Rakhit and M. Gut, *ibid.*, **86**, 1432 (1964); (c) J. Wiemann and F. Weisback, *Compt. rend.*, **257**, 1486 (1963); (d) D. R. Weyenberg and L. H. Torporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962); (e) D. Lipkin, F. R. Galiano, and R. W. Jordan, *Chem. Ind.* (London), 1657 (1963).

(3) The acylation of anion radicals derived from saturated carbonyl functions is exemplified by the acyloin reaction and by the cyclization of certain δ-keto esters. See C. D. Gutsche and I. Y. C. Tao, *J. Org. Chem.*, **28**, 883 (1963).

(4) The use of the chromium(II) ion was prompted by the observation of an intramolecular alkylation reaction when a suitably substituted α,β-unsaturated δ-bromo ketone was treated with chromium(II) chloride. D. H. R. Barton and C. H. Robinson, U. S. Patent 3,026,337 (March 20, 1962); *Chem. Abstr.*, **57**, 3532 (1962).

and the corresponding saturated, acyclic ketones **5**. The secondary alcohols corresponding to ketones **5** were also formed in reductions with lithium in liquid ammonia, presumably by further reduction of the ketones **5**. Unfortunately, the desired cyclization products **4** composed only 7% (lithium–liquid ammonia) to 28–33% (sodium–phenanthrene or naphthalene) of the volatile, neutral products, the major products being the ketones **5**. In an effort to suppress formation of that portion of the acylic product **5** which might be derived by direct cleavage of the carbon–chlorine bond (*i.e.*, **1** → **6** → **5**), we examined the reductions of the quaternary ammonium salts **1c**, **1d**, and **1e**. These salts were examined as displaceable functions because half-wave potential measurements[5] of alkyl halides and the corresponding tetraalkylammonium salts suggested that the ammonium salts would be less easily reduced. However, the only products isolated from these reductions were the corresponding amines **8**, **9**, and **10** resulting from cleavage of a methyl group from the quaternary ammonium salts.[6]



8a, $n = 2$
b, $n = 3$

9a, $n = 2$
b, $n = 3$

10

Consequently, we have been unable to find reaction conditions which permit the desired cyclization reaction (*i.e.*, **1** → **4**) to predominate over bond cleavage to form acyclic products (*e.g.*, **1** → **5**). Since available half-wave potential measurements[5] suggest that formation of the ketyl **2** should be energetically favored over direct carbon–chlorine bond cleavage (*i.e.*, **1a** or **1b** → **6**), our results imply that the acyclic products **5** isolated have been derived, at least in part, by opening of the intermediate alkoxy radical **3** to form **6** followed by further reduction. However, the symmetry of the reactants we have employed does not provide any direct evidence for this implication since cleavage of either of two carbon–carbon bonds in the alkoxy radical **3** would lead to the same carbon radical **6**.

Experimental[7]

Preparation of the ω-Halo Ketones.—1-Methylcyclopentanol and 1-methylcyclohexanol were each converted to their hypochlorites and decomposed by previously described procedures.[8] The resulting chloro ketones were isolated by distillation and their purity was established by gas chromatography.[9] **7-Chloro-2-heptanone** (**1b**) was isolated (55–77% yield) as a colorless liquid: b.p. 101–102° (13 mm.); $n^{25}D$ 1.4459 [lit.[8a] b.p. 107–108° (17 mm.), $n^{25}D$ 1.4435]; 2,4-dinitrophenylhydrazone m.p. 94.5–95° (lit.[8a] m.p. 95–96°); infrared absorption[10] at 1720 cm.$^{-1}$ (C=O); ultraviolet maximum[11] at 274 mμ (ε 23.5); and n.m.r. peaks[10] at δ 3.65 (2H triplet, J = 7 c.p.s., $-CH_2-Cl$), 2.49 (2H, triplet, J = 7 c.p.s., $-CH_2-CO-$), and 2.15 (3H singlet, CH_3-CO-). **6-Chloro-2-hexanone** (**1a**), isolated (77–79% yield) as a colorless liquid, b.p. 83–84° (10 mm.), $n^{25}D$ 1.4424 [lit.[8a,12] b.p. 52.5–54° (2.3 mm.), 85.5–86.5° (16 mm.), $n^{25}D$ 1.4414], has infrared absorption[10] at 1720 cm.$^{-1}$ (C=O), an ultraviolet maximum at 264 mμ (ε 39.3), and n.m.r. peaks[10] at δ 3.52 (2H triplet, J = 6 c.p.s., $-CH_2-Cl$), 2.43 (2H triplet, J = 7 c.p.s., $-CH_2-CO-$), and 2.07 (3H singlet, CH_3-CO-).

After a solution of 13.43 g. (0.10 mole) of 6-chloro-2-hexanone (**1a**) and 12.3 g. (0.15 mole) of sodium acetate in 60 ml. of acetic acid had been refluxed for 48 hr., the reaction mixture was poured into saturated, aqueous sodium chloride and extracted with ether. The ethereal extract was dried, concentrated, and distilled to separate 10.232 g. (65%) of pure[13] **6-acetoxy-2-hexanone** as a colorless liquid: b.p. 82–83° (2.9 mm.); $n^{25}D$ 1.4266; infrared absorption[10] at 1725 (C=O) and 1740 cm.$^{-1}$ (ester C=O); an ultraviolet maximum[11] at 275 mμ (ε 21.3); and n.m.r. peaks[10] at δ 3.98 (2H triplet, $J \sim 6$ c.p.s., $-CH_2-OAc$) and 2.43 (2H triplet, $J \sim 6$ c.p.s., $-CH_2-CO-$) as well as two singlets (each 3H) at 2.07 and 1.97 (CH_3-CO- and $CH_3-CO-O-$).

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.81; H, 8.83.

After reaction of 13.43 g. (0.10 mole) of 6-chloro-2-hexanone with 18 g. (0.12 mole) of sodium iodide in 50 ml. of refluxing acetone for 18 hr., the reaction mixture was poured into saturated, aqueous sodium chloride and extracted with ether. The ethereal extract was washed with aqueous sodium thiosulfate, dried, and distilled to separate 17.18 g. (76%) of **6-iodo-2-hexanone** as a colorless liquid, b.p. 51–53° (0.1 mm.), $n^{25}D$ 1.5118 [lit.[14] b.p. 117° (14 mm.)], which turned brown on standing. The product has infrared absorption[10] at 1715 cm.$^{-1}$ (C=O) with n.m.r. peaks[10] at δ 3.16 (2H triplet, J = 7 c.p.s., $-CH_2-I$), 2.40 (2H triplet, J = 6 c.p.s., $-CH_2-CO-$), and 2.07 (3H singlet, CH_3-CO-). Application of the same reaction procedure to 14.86 g. (0.10 mole) of 7-chloro-2-heptanone (**1b**) yielded 16.12 g. (67%) of **7-iodo-2-heptanone** as a colorless liquid: b.p. 61–64° (0.1 mm.); $n^{25}D$ 1.5064; infrared absorption[10] at 1720 cm.$^{-1}$ (C=O); and n.m.r. peaks[10] at δ 3.16 (2H triplet, J = 7 c.p.s., $-CH_2-I$), 2.37 (2H triplet, J = 7 c.p.s., $-CH_2-CO-$), and 2.05 (3H singlet, CH_3-CO-). Since this compound decomposed on standing to liberate iodine, no further characterization was attempted.

Preparation of the Amino Ketones and Their Derivatives.—After a solution of 5.62 g. (0.025 mole) of 6-iodo-2-hexanone and 3 g. (0.03 mole) of N-methylpiperidine in 40 ml. of absolute ethanol had been refluxed for 48 hr., the solution was concentrated under reduced pressure and diluted with ethyl acetate to precipitate 5.949 g. of crude quaternary ammonium salt. Repeated recrystallization from mixtures of absolute ethanol and ethyl acetate afforded 5.606 g. (69%) of the pure **methiodide of 6-(1-piperidino)-2-hexanone** (**1c**) as white prisms, m.p. 82–82.5°, which exhibited a single spot on thin layer chromatography.[15] The product has infrared absorption[16] at 1715 cm.$^{-1}$ (C=O) with n.m.r. peaks[17] at δ 3.33 (3H singlet, $CH_3-N\lessdot^{+}$), 2.67 (2H triplet, J = 6 c.p.s., $-CH_2-CO$), and 2.18 (3H singlet, CH_3-CO-) as well as broad absorption in the regions 3.5–4.0 and 1.6–2.1.

Anal. Calcd. for $C_{12}H_{24}INO$: C, 44.31; H, 7.44; I, 39.01; N, 4.31. Found: C, 44.39; H, 7.70; I, 39.25; N, 4.15.

Application of the same reaction and isolation procedure to 16 g. (0.066 mole) of 7-iodo-2-heptanone and 10 g. (0.1 mole) of N-methylpiperidine in 40 ml. of absolute ethanol yielded 14.452 g. (64.5%) of the pure[15] **methiodide of 7-(1-piperidino)-2-heptanone**

(5) P. Zuman, *Collection Czech. Chem. Commun.*, **15**, 1107 (1950).

(6) H. Smith, "Chemistry in Nonaqueous Ionizing Solvents," Vol. 1, Part 2, "Organic Reactions in Liquid," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 187–190.

(7) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated, magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The n.m.r. spectra were determined at 60 Mc. with a Varian Model A-60 n.m.r. spectrometer. The mass spectra were obtained with a CEC Model 21-130 mass spectrometer. The microanalyses were performed by the Scandinavian Microanalytical Laboratory.

(8) (a) J. W. Wilt and J. W. Hill, *J. Org. Chem.*, **26**, 3523 (1961); (b) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *ibid.*, **28**, 55 (1963).

(9) A column packed with Carbowax 20M on Chromosorb W was employed.

(10) Determined as a solution in carbon tetrachloride.

(11) Determined as a solution in 95% ethanol.

(12) T. L. Cairns and B. E. Englund, *J. Org. Chem.*, **21**, 140 (1956).

(13) A gas chromatography column packed with Versamid 900 on Chromosorb was employed for this analysis.

(14) N. Zelinsky and A. Moser, *Ber.*, **35**, 2684 (1902).

(15) A silica gel thin layer adsorbent was used with an eluent composed of chloroform–methanol–concentrated hydrochloric acid (6:6:1 by volume).

(16) Determined as a solution in chloroform.

(17) Determined as a solution in deuteriochloroform.

as white prisms: m.p. 69–69.5°; infrared absorption[16] at 1710 cm.$^{-1}$ (C=O); and n.m.r. peaks[17] at δ 3.37 (3H singlet, CH_3–N$\leqslant^+$), 2.54 (2H triplet, J = 6 c.p.s., –CH_2–CO), and 2.18 (3H singlet, CH_3–CO–) as well as broad absorption in the regions 1.5–2.1 and 3.5–3.9.

Anal. Calcd. for $C_{13}H_{26}INO$: C, 46.02; H, 7.73; I, 37.40; N, 4.13. Found: C, 46.05; H, 7.90; I, 37.60; N, 3.85.

After a solution of 0.743 g. (5.0 mmoles) of 7-chloro-2-heptanone and 0.70 g. (7 mmoles) of N-methylpiperidine in 10 ml. of *n*-butyl alcohol had been refluxed for 48 hr., the mixture was concentrated under reduced pressure. Recrystallization from an absolute ethanol–ethyl acetate mixture separated 0.661 g. (53%) of the pure[15] **methochloride of 7-(1-piperidino)-2-heptanone (1d)** as white needles: m.p. 130.5–131°; infrared absorption[16] at 1720 cm.$^{-1}$ (C=O); and n.m.r. peaks[17] at δ 3.33 (3H singlet, CH_3–N$\leqslant^+$), 2.47 (2H triplet, J = 6 c.p.s., –CH_2–CO–), and 2.13 (3H singlet, CH_3–CO–).

Anal. Calcd. for $C_{13}H_{26}ClNO$: C, 62.80; H, 10.48; N, 5.64. Found: C, 62.64; H, 10.71; N, 5.84.

A solution of 13.43 g. (0.10 mole) of 6-chloro-2 hexanone (**1a**) and 21.3 g. (0.25 mole) of piperidine in 50 ml. of absolute ethanol was refluxed for 12 hr. and then cooled and diluted with ether. After the precipitate of piperidine hydrochloride had been separated and washed with ether, the combined ethereal solutions were concentrated, and the residue was distilled. Pure[13] **6-(1-piperidino)-2-hexanone (8a**, yield, 13.738 g. or 75%) was collected as a colorless liquid: b.p. 58–61° (0.03 mm.); n^{25}D 1.4639; infrared absorption[10] at 1725 cm.$^{-1}$ (C=O); ultraviolet maximum[11] 275.5 mμ (ϵ 24.4); and an n.m.r. peak[10] at δ 2.03 (3H singlet, CH_3–CO–) as well as complex absorption in the regions 2.1–2.5 and 1.3–1.7.

Anal. Calcd. for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64; mol. wt., 183. Found: C, 72.03; H, 11.63; N, 7.58; mol. wt., 183 (mass spectrum).

Application of the same reaction and isolation procedure to 14.86 g. (0.10 mole) of 7-chloro-2-heptanone (**1b**) yielded 14.872 g. (75.5%) of pure[13] **7-(1-piperidino)-2-heptanone (8b)** as a colorless liquid: b.p. 81–84° (0.05 mm.); n^{25}D 1.4640; infrared absorption[10] at 1720 cm.$^{-1}$ (C=O); an ultraviolet maximum[11] at 277 mμ (ϵ 24.4); and an n.m.r. peak[10] at δ 2.04 (3H singlet, CH_3–CO) as well as complex absorption in the regions 2.1–2.5 and 1.2–1.7.

Anal. Calcd. for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10; mol. wt., 197. Found: 73.03; H, 11.81; N, 7.03; mol. wt., 197 (mass spectrum).

A solution of 4.58 g. (25 mmoles) of the amino ketone **8a** in 20 ml. of ether was added to 260 mg. (6.8 mmoles) of lithium aluminum hydride in 30 ml. of ether. The resulting mixture was stirred for 15 min., treated with 0.11 ml. of water to precipitate the aluminum salts, and filtered. After the ethereal filtrate had been dried, distillation separated 3.607 g. (78%) of pure[13] **6-(1-piperidino)-2-hexanol (9a)** as a colorless liquid, b.p. 81–84° (0.04 mm.), n^{25}D 1.4751. The amino alcohol has infrared absorption[10] at 3630 and 3400 (broad) cm.$^{-1}$ (unassocd. and assocd. O–H) with an n.m.r. peak[10] at δ 3.93 (1H singlet, O–H) as well as a broad multiplet centered at 3.68 (1H, CH–O–), a doublet (J = 6 c.p.s.) centered at 1.11 (3H, CH_3–), and complex absorption in the regions 2.0–2.5 and 1.2–1.7.

Anal. Calcd. for $C_{11}H_{23}NO$: C, 71.30; H, 12.51; N, 7.56; mol. wt., 185. Found: C, 71.04; H, 12.57; N, 7.58; mol. wt., 185 (mass spectrum).

Reduction of 4.75 g. (25 mmoles) of the amino ketone **1b** by the same procedure yielded 3.835 g. (77%) of pure[13] **7-(1-piperidino)-2-heptanol (9b)** as a colorless liquid: b.p. 87–91° (0.1 mm.); n^{25}D 1.4749; infrared absorption[10] at 3610 and 3380 (broad) cm.$^{-1}$ (unassocd. and assocd. O–H); and an n.m.r.[10] singlet at δ 3.55 superimposed on a multiplet (2H, CH–OH), a doublet (J = 6 c.p.s.) centered at 1.08 (3H, CH_3–), and complex absorption in the regions 2.0–2.5 and 1.1–1.7.

Anal. Calcd. for $C_{12}H_{25}NO$: C, 72.30; H, 12.64; N, 7.03; mol. wt., 199. Found: C, 72.36; H, 12.71; N, 6.93; mol. wt., 199 (mass spectrum).

The sodium enolate of ethyl acetoacetate was alkylated with 3-(N,N-dimethylamino)propyl chloride[18] and the crude product was hydrolyzed and decarboxylated following the general procedure described previously.[19] Distillation separated pure[20] **6-(N,N-dimethylamino)-2-hexanone (10**, yield 41.5%) as a colorless liquid: b.p. 80–81° (10 mm.); n^{25}D 1.4295 [lit.[21] b.p. 194–195° (720 mm.)]; infrared absorption[10] at 1720 cm.$^{-1}$ (C=O); an ultraviolet maximum[11] at 274 mμ (ϵ 22.7); and n.m.r.[10] singlets at δ 2.14 (6H, CH_3–N–) and 2.07 (3H, CH_3–CO–) as well as complex absorption in the regions 2.0–2.5 and 1.2–1.8. A solution of 3.635 g. (0.026 mole) of this amino ketone **10** and 4.34 g. (0.031 mole) of methyl iodide in 50 ml. of acetone was allowed to stand overnight and then concentrated under reduced pressure. Recrystallization of the residual salt from an absolute ethanol–ethyl acetate mixture separated 4.434 g. (60%) of the pure[15] **methiodide of 6-(N,N-dimethylamino)-2-hexanone (1e)** as white needles: m.p. 88.5–89°; infrared absorption[16] at 1710 cm.$^{-1}$ (C=O); and n.m.r. peaks[22] at δ 3.16 (9H singlet, CH_3–N$\leqslant^+$), 2.69 (2H triplet, J = 7 c.p.s., –CH_2–CO–), and 2.24 (3H singlet, CH_3–CO) as well as unresolved absorption of the regions 3.1–3.5 and 1.4–1.9.

Anal. Calcd. for $C_9H_{20}INO$: C, 37.91; H, 7.08; I, 44.51; N, 4.91. Found: C, 38.57; H, 7.58; I, 44.90; N, 4.65.

Reduction of 7-Chloro-2-heptanone (1b). A. With Lithium in Liquid Ammonia.—A solution of 3.55 g. (24 mmoles) of the chloro ketone **1b** in 300 ml. of ether was added, dropwise and with stirring over a 3-hr. period, to a solution of 378 mg. (54 mg.-atoms) of lithium in 400 ml. of liquid ammonia and 200 ml. of ether. The addition was interrupted at the end of 2 hr. to add an additional 90 mg. (13 mg.-atom) of lithium. After the addition was complete, the reaction mixture was stirred for 1 hr. and then the excess lithium was destroyed by the addition of 1 ml. of methanol. The ammonia was allowed to evaporate through a 90-cm. Vigreux column and the remaining ethereal solution was washed successively with aqueous hydrochloric acid, aqueous sodium bicarbonate, and water. After the ether solution had been dried and concentrated, the volatile portion of the residual neutral fraction was analyzed by gas chromatography[9] and found to contain, apart from ether and ethanol, 2-heptanone (**5**, n = 3, 67%, first eluted), 2-heptanol (26%, second eluted), and 1-methylcyclohexanol (**4**, n = 3, 7%, third eluted). The products from a comparable reduction were identified both by comparison of retention times and by comparison of the infrared and mass spectra of collected samples with spectra of authentic samples.

B. With the Sodium–Naphthalene Radical Anion.—The chloro ketone **1b** (743 mg. or 5 mmoles) was added to a solution prepared from 460 mg. (20 mg.-atoms) of sodium and 1.921 g. (15 mmoles) of naphthalene in 80 ml. of 1,2-dimethoxyethane. An additional small portion of sodium was added to the solution to maintain the green color of the naphthalene radical anion. The resulting mixture was concentrated under reduced pressure and then mixed with saturated, aqueous ammonium chloride and extracted with ether. The ethereal extract was washed successively with aqueous hydrochloric acid, aqueous sodium bicarbonate, and water and then dried and concentrated. Analysis[9] of the volatile portion of the crude, neutral product indicated the presence of 2-heptanone (**5**, n = 3, 72%) and 1-methylcyclohexanol (**4**, n = 3, 28%).

Attempts to reduce the chloro ketone **1b** with chromium(II) chloride in aqueous acetone resulted in recovery of the starting chloride, and no 1-methylcyclohexanol (**4**, n = 3) was detected in the crude neutral product obtained by reduction of the chloro ketone **1b** with sodium and isopropyl alcohol.

Reduction of 6-Chloro-2-hexanone (1a).—The chloro ketone **1a** (581 mg. or 4.3 mmoles) was added, dropwise and with stirring, to a solution prepared from 345 mg. (15 mg.-atoms) of sodium, 1.335 g. (7.5 mmoles) of phenanthrene, and 40 ml. of 1,2-dimethoxyethane until the dark green color of the radical anion was just discharged. The crude, neutral product was isolated as in the previous experiment. The volatile portion of this product contained[9] four components, A (2%), B (60%), C (33%), and D (5%), listed in order of increasing retention time. Components B and C were identified as 2-hexanone (**5**, n = 2) and 1-methylcyclopentanol (**4**, n = 2), respectively. For a comparable reduction employing **6-iodo-2-hexanone** the volatile portion of the crude, neutral product contained[9], in order of elution, an uniden-

(18) R. Marechal and J. Bagot, *Ann. pharm. franc.*, **4**, 172 (1946); *Chem. Abstr.*, **41**, 5099 (1947).

(19) D. S. Breslow, R. S. Yost, H. G. Walker, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1921 (1944).

(20) A gas chromatography column packed with silicone gum, No. SE-30, suspended on Chromosorb W was employed for this analysis.

(21) A. Lipp, *Ann.*, **289**, 249 (1896).

(22) Determined as a solution in deuterium oxide.

tified component (1%), 2-hexanone (31%), 2-hexanol (5%), 1-methylcyclopentanol (22%), and cyclohexanone (41%).

Reduction of the Methochloride of 7-(1-Piperidino)-2-heptanone (1d).—Lithium (158 mg. or 23 mg.-atoms) was added, portionwise with stirring, to a solution of 2.275 g. (9.2 mmoles) of the salt **1d** in 600 ml. of liquid ammonia until the solution maintained a blue color (indicative of excess lithium) for 15 min. Then the excess lithium was destroyed by the addition of methanol and the ammonia was allowed to evaporate through a 90-cm. Vigreux column. The residue was mixed with saturated, aqueous sodium chloride and extracted with ether. After the ethereal extract had been washed with water, dried, and concentrated, the residual oil (1.132 g.) was found to contain[13] three volatile components: an unidentified component (4%, first eluted), 7-(1-piperidino)-2-heptanone (**8b**, 34%, second eluted), and 7-(1-piperidino)-2-heptanol (**9b**, 62%, third eluted). The latter two samples were identified both by retention times and by comparison of the infrared and mass spectra of collected samples with the spectra of authentic samples.

Reduction of the Methiodide of 6-(1-Piperidino)-2-hexanone (1c).—The preceding experimental procedure was applied to 1.882 g. (5.6 mmoles) of the salt **1c**, 134 mg. (19 mg.-atoms) of lithium and 400 ml. of liquid ammonia being employed. The crude basic fraction, 875 mg. of liquid, contained[13] the following volatile components: an unidentified product (7%, first eluted), 6-(1-piperidino)-2-hexanone (**8a**, 34%, second eluted), and 6-(1-piperidino)-2-hexanol (**9a**, 59%, third eluted). As in the previous case, the products were identified by comparison of retention times, infrared spectra, and mass spectra.

Reduction of the Methiodide of 6-(N,N-Dimethylamino)-2-hexanone (1e).—The previously described reaction and isolation procedure was followed with 2.121 g. (7.5 mmoles) of the salt **1e**, 181 mg. (26 mg.-atoms) of lithium, and 500 ml. of liquid ammonia. The crude, basic product, 784 mg. of liquid, contained[13] three volatile components: A (5%, first eluted), B (17%, second eluted), and C (78%, third eluted). Product B was identified as 6-(N,N-dimethylamino)-2-hexanone (**10**) by comparison of the infrared spectrum of a collected sample with the spectrum of an authentic sample and from its mass spectrum with peaks at *m/e* 143 (M^+), 58 [abundant, $(CH_3)_2N^+{=}CH_2$ and $CH_3(OH)C{=}CH_2^+$], and 43 ($CH_3C{\equiv}O^+$). Component C was tentatively identified as 6-(N,N-dimethylamino)-2-hexanol from the following spectral characteristics of a collected sample. The material has infrared absorption[10] at 3620 and 3400 (broad) cm.$^{-1}$ (unassocd. and assocd. O–H) with n.m.r.[10] singlets at δ 2.62 (1H, OH) and 2.15 (6H, CH_3–N) as well as a doublet (J = 6 c.p.s.) centered at 1.10 (3H, CH_3–) and broad absorption in the regions 3.5–3.9, 2.1–2.4, and 1.3–1.6. The mass spectrum has peaks at *m/e* 145 (M^+), 130 (M^+-CH_3), 58 [abundant, $(CH_3)_2N^+{=}CH_2$], 45 ($CH_3CH{=}O^+H$), and 44 ($CH_3N^+H{=}CH_2$).

Essential Oils and Their Constituents. XXVI.[1] Rearrangement of Caryophyllene Oxide during Gas Chromatography

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The application of chemical and instrumental methods of analysis to essential oils and their constituents requires discriminating interpretation of experimental results. In a previous paper the authors reported the transformation of humulene monoxide, a constituent of oil of wild ginger, to the corresponding alcohol during column chromatography over grade I alumina.[2] It is the purpose of this communication to describe an interesting rearrangement taking place during gas chromatography of caryophyllene oxide, a terpenoid occurring in a number of commercially important essential oils.

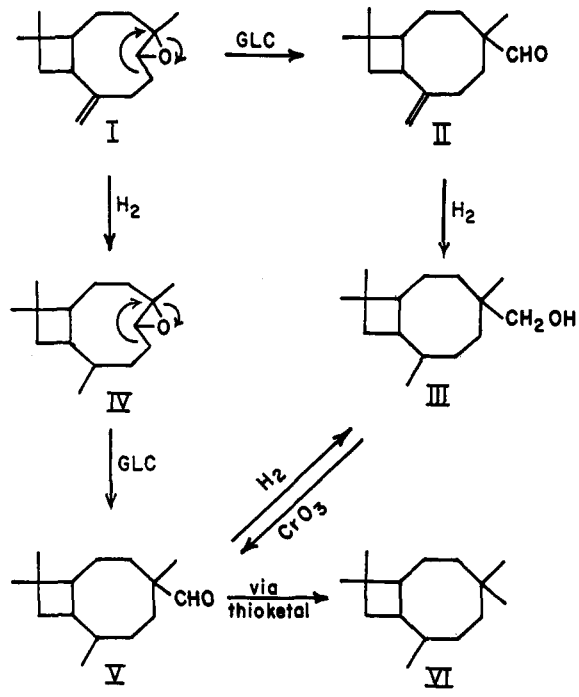

Figure 1.—Rearrangements and transformations of caryophyllene oxide and dihydrocaryophyllene oxide.

The transformation of caryophyllene oxide to compounds possessing novel carbon skeletons has been the subject of a number of investigations.[3,4] The authors found that the epoxide I decomposed completely when subjected to gas–liquid chromatography through a column of Reoplex 400 (10% on acid-washed Chromosorb W). Infrared and n.m.r. examination proved the major degradation product (62%) to be an unsaturated aldehyde II with infrared absorption bands at 3080, 1632, and 885 cm.$^{-1}$ (>C=CH_2) and 2688 and 1726 cm.$^{-1}$ (—CHO) and n.m.r. peaks at 9.30 (—CHO), 4.40, and 4.61 p.p.m. (>C=CH_2) (tetramethylsilane = 0). Catalytic hydrogenation of the aldehyde ($C_{15}H_{24}O$) showed the presence of one double bond. Chromic acid oxidation of the saturated alcohol (III) obtained yielded the corresponding saturated aldehyde V having infrared absorption bands at 2698 and 1726 cm.$^{-1}$ and n.m.r. peak at 9.26 p.p.m. This aldehyde was also formed when subjecting dihydrocaryophyllene oxide (IV) to gas chromatography under the experimental conditions. The saturated aldehyde V was, in turn, converted *via* desulfurization of its thioketal with Raney nickel to the corresponding saturated hydrocarbon VI. Gas chromatographic and infrared characteristics of this hydrocarbon were different from those displayed by caryophyllane. These observations suggested that a rearrangement of the caryophyllane carbon framework had taken place. Quantitative analysis of the n.m.r. spectra of aldehydes II and V established the presence of three and four methyl groups, respectively. Since during the rearrangement reaction the number of

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