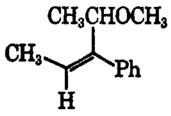
et al., and reinvestigated their configurations. Their reassignments are consistent with our experimental results.

Interestingly, when **1a** was stirred with methanolic silver nitrate at reflux for 12 hr, a mixture of **2a** and what has tentatively been assigned structure **2b** was obtained in a 5:1 ratio.[7] This result would imply



2b

that ionization of **1a** is for the most part a nonconcerted process.

Experimental Section[8]

1-Phenyl-1-chloro-*cis*-2,3-dimethylcyclopropane (1a + 1b).[9]—To a solution of 320 ml (3.76 mol) of *cis*-2-butene and 75.8 g (0.47 mol) of benzal chloride in 500 ml of tetrahydrofuran (THF) was added dropwise with stirring and under a nitrogen atmosphere 0.54 mol of *n*-butyllithium in hexane. The reaction mixture was kept at −80° while the addition took place and then stirred for 1 hr at this temperature. After warming to room temperature the THF was removed by vacuum distillation. Water and ether were added and the organic layer was separated. The aqueous layer was extracted with four 20-ml portions of ether. The ether extracts were combined with the organic layer, dried (magnesium sulfate), and concentrated. Fractional distillation afforded 42.3 g (50%) of **1a** and **1b**, bp 70–72° (1.25 mm) [lit.[2] bp 50–53° (0.3 mm)]. An nmr spectrum of the product exhibits multiplets at 0.8, 1.2, and 7.3 ppm. The relative intensities of high-field/low-field absorption was 8:5. The isomer ratio of **1a**:**1b**, determined by integrating the multiplets at 0.8 (**1a**) and 1.2 ppm (**1b**), was found to be 3:1. The infrared spectrum of the product was consistent with the desired structure. A vpc of the product on column a[8] at 150° gave one major peak which was collected. An nmr spectrum showed that **1a** and **1b** were present in the collected sample.

Sodium-Liquid Ammonia Reduction of *anti*-1-Phenyl-1-chloro-*cis*-2,3-dimethylcyclopropane (1a).—A solution of 1.580 g (69 mg-atoms) sodium in 100 ml of liquid ammonia and 0.112 g (0.63 mmol) of **1a** were added dropwise and simultaneously to 250 ml of liquid ammonia. The reaction mixture was then stirred for 1 hr. Ammonium chloride was added until the solution became white, and the excess ammonia was evaporated. The reaction mixture was worked up in the usual manner. Analysis of the product mixture on column c[8] showed >99% **3a** and <1% **3b** to be present in a 63% yield.[10]

Sodium-Liquid Ammonia Reduction of 1a and 1b (3:1).—The reduction was carried out as described previously. Compounds **3a** and **3b** were obtained in a 60% yield (13:1 ratio).

Reaction of 1-Phenyl-1-chloro-*cis*-2,3-dimethylcyclopropane (1a + 1b) with Silver Nitrate.—To a solution of 10 g (0.056 mol) of **1a** + **1b** in 20 ml of reagent grade methyl alcohol was added with stirring 3.2 g (19 mmol) of silver nitrate. The reaction mixture was stirred for 10 hr at room temperature. Water and ether were added and the organic layer was separated. The reaction mixture was worked up in the usual manner. Compound **1a** was separated from **2a** by column chromatography on silica gel and elution with ligroin. A 50% yield (5 g) of **1a** was obtained after distillation. *cis*-3-Phenyl-4-methoxy-2-pentene (**2a**) was eluted from the column with benzene. A mass spectrum of **2a** exhibits a molecular ion peak of *m/e* 176.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.76; H, 9.24.

An nmr spectrum of **1a** exhibits multiplets centered at 1.2 and 7.3 ppm. The infrared spectrum of **1a** differs from that of the mixture of **1a** and **1b** in that absorbance at 1179 and 939 cm^{-1} is absent. An ultraviolet spectrum of **1a** measured in hexane exhibits absorption maxima at 252 mμ (ε 1600) and 220 (7700).

Registry No.—Ammonia, 7664-41-7; **1a**, 13154-00-2; **2a**, 18744-16-6.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administrated by the American Chemical Society, for support of this research, and to the University of Vermont for making its nmr facilities available to us.

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[7] The structure of **2b** is assigned on the basis of a correct elemental analysis and nmr measurements made on the mixture, and a mass spectrum of pure **2b**.

[8] Infrared spectra (ir) were determined with a Perkin-Elmer Model 137 recording spectrophotometer. All spectra were measured in carbon tetrachloride unless otherwise stated. Ultraviolet spectra were determined on a Bausch and Lomb spectrophotometer, Model 505. The nmr spectra were determined at 60 Mc with a Varian Model A-60 spectrometer using tetramethylsilane (TMS) as the internal reference. Carbon–hydrogen analyses were carried out by C. F. Geiger, Ontario, Calif. Columns used for gas chromatography (vpc) were (a) 10% Carbowax 20M column, 6 ft × 0.25 in. glass tubing, (b) 10% Carbowax 20M column, 6 ft × 0.25 in. aluminum tubing, and (c) a 25% DC QF-1 column, 6 × 0.25 in. glass tubing. All yields were determined by gas chromatography.

[9] Prepared according to the procedure of D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4417 (1965).

[10] The retention times of both **3a** and **3b** were identical with those of authentic samples prepared by independent means.[5]

The Acid-Catalyzed Cyclization of 2-Substituted 3,3-Diphenylacrylophenones

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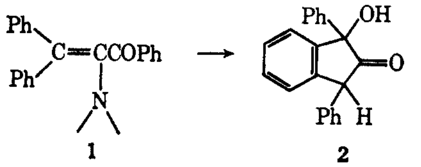
Received August 2, 1968

The cyclization of 2-substituted 3,3-diphenylacrylophenones to substituted 1,3-diphenylindenones, or their tautomers, under the influence of Brønsted acids, and some related cyclizations, were first described by Kohler and coworkers.[2,3] A previous publication from this laboratory[4] has described the cyclization of 2-amino-3,3-diphenylacrylophenones (**1**) to 1,3-diphenyl-1-hydroxyindan-2-one (**2**) with aqueous sulfuric acid. In this Note we present additional evidence for the course of this reaction and correlate this and some similar cyclizations with a general reaction mechanism.



1 **2**

Barré and Kohler[2] obtained 2,3-dibromo-1,3-diphenylindene (**4**) by treating 2-bromo-3,3-diphenylacrylophenone (**3**) with hydrogen bromide in refluxing acetic acid, and also as a by-product of the bromination of 3,3-diphenylacrylophenone (**14**) in chloroform at room temperature. The major product of the latter reaction is 2-bromo-3,3-diphenylacrylophenone (**3**) which is formed exclusively when the reaction is done in refluxing chloroform. Kohler and Weiner[3] obtained 1-chloro-1,3-diphenylindan-2-one (**5**) by treating 3,3-

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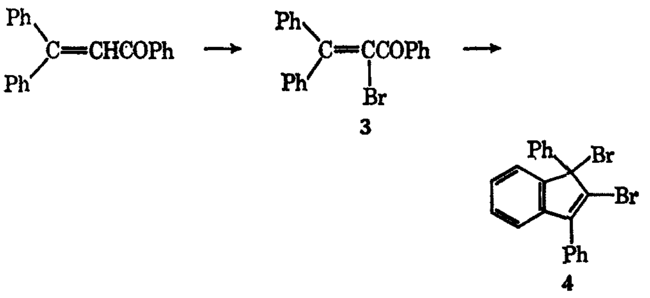
[1] To whom all inquires should be addressed.

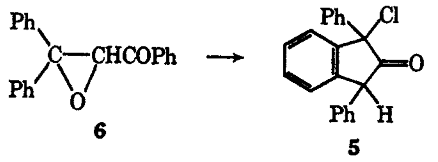
[2] R. Barré and E. P. Kohler, *J. Amer. Chem. Soc.*, **50**, 2036 (1928).

[3] E. P. Kohler and N. Weiner, *ibid.*, **56**, 434 (1934).

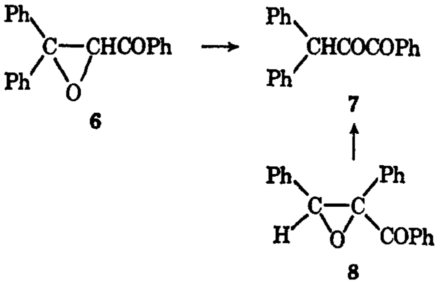
[4] N. H. Cromwell and M. C. McMaster, *J. Org. Chem.*, **32**, 2145 (1967).

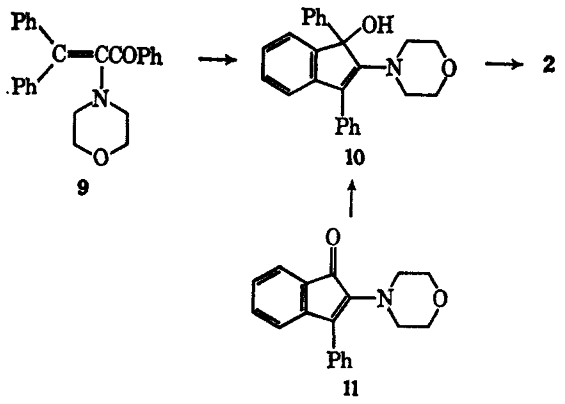


diphenyl-2,3-epoxypropiophenone (6) with hydrogen chloride in glacial acetic acid at −10°.

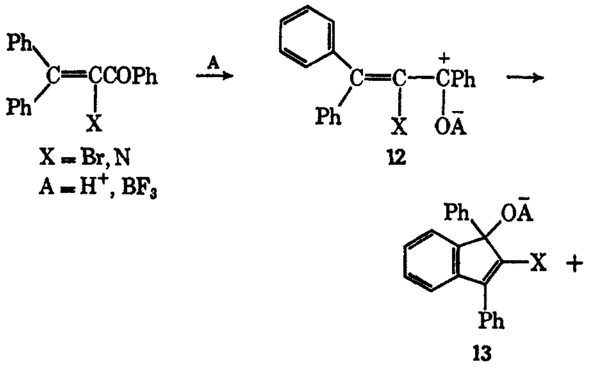


As earlier reported,[4] treatment of 2-amino-3,3-diphenylacrylophenones (1) with refluxing 20% sulfuric acid provides 1,3-diphenyl-1-hydroxyindan-2-one (2) in good yields, the product resulting from both hydrolysis and cyclization of the α-amino-α,β-unsaturated ketone. If hydrolysis was the initial reaction, the intermediate should be the known 1,3,3-triphenylpropane-1,2-dione (7).[3,5] However, it has been shown[4] that 7 is recovered unchanged and is not cyclized after prolonged treatment with hot 20% sulfuric acid.[6] Addition of a cosolvent, dioxane, to produce a homogeneous reaction mixture, gave the same result. In addition, House[5,7] obtained diketone 7, and not the cyclized compound 2, on treating α,β-diphenylacrylophenone oxide (8) with boron trifluoride. It thus appeared desirable to attempt the cyclization under anhydrous conditions in order to obtain the other possible intermediate, a 2-amino-1,3-diphenyl-3-hydroxyindene. We now wish to report the formation and isolation of such a compound by the Lewis acid catalyzed cyclization of 3,3-diphenyl-2-morpholinoacrylophenone (9). Treatment of compound 9 in benzene with 1 equiv of boron trifluoride etherate at room temperature provided 1,3-diphenyl-3-hydroxy-2-morpholinoindene (10). This same compound was also prepared by the action of phenyllithium on 2-morpholino-3-phenylindenone (11). Treatment of 10 with hot 20% sulfuric acid easily hydrolyzed it to 1,3-diphenyl-1-hydroxyindan-2-one (2).





Thus cyclization preceeds hydrolysis and the following mechanism is proposed to account for the course of this and related cyclizations. Protonation, or coordination, of the carbonyl oxygen atom by the acid provides a carbonium ion (12) which undergoes an intramolecular electrophilic substitution to form indene **13**. Subsequent hydrolysis of the Lewis Acid complex **13** or substitution of the hydroxyl group by, *e.g.*, bromine,[2] provides the observed products.



The ease with which substituents in the 3 position of substituted 1,3-diphenylindenes undergo nucleophilic displacement has been demonstrated by several workers.[2,3,8] We have converted 2,3-dibromo-1,3-diphenylindene (4) into the 3-methoxy derivative by refluxing in methanol, and into the known 3-acetoxy derivative[8] by treatment with sodium acetate in refluxing acetic anhydride.

Experimental Section[9]

1,3-Diphenyl-3-hydroxy-2-morpholinoindene (10). A. From 2-Morpholino-3-phenylindenone (11).—To a stirred solution of phenyllithium (0.0172 mol) in 16 ml of benzene and 7 ml of ether, at 0°, was added dropwise a solution of 2.50 g (0.00859 mol) of 11[4] in 10 ml of benzene and 10 ml of ether. The mixture was stirred at 0° for 30 min and then 25 ml of iced water was added. On stirring, a white solid appeared in the organic layer. The mixture was transferred to a separatory funnel and the solid was dissolved by the addition of 250 ml of benzene. The organic layer was washed twice with water and dried ($MgSO_4$). Evaporation of the solvents under reduced pressure left a white solid which was collected, washed with hexane, and dried. The crude product 10, 2.55 g (81%), mp 192–193.5°, was twice recrystallized from ethanol to provide pure 10 as white needles, mp 198–199°. The infrared spectrum (Fluorolube mull) showed broad

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[5] H. O. House and D. J. Reif, *J. Amer. Chem. Soc.*, **77**, 6525 (1955).

[6] 2 is obtained in small yield as a by-product of the rearrangement of 1,3-diphenyl-2,3-epoxyacrylophenone (6) by alkoxide.[4] Acidification of the basic reaction mixture with sulfuric acid produced the main product, 1,2 diketone 7, together with about 7% 2.

[7] H. O. House, *ibid.*, **76**, 1235 (1954).

[8] R. Weiss and S. Luft, *Monatsh.*, **48**, 337 (1927).

[9] Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. Nmr spectra, reported in units of τ, were determined with a Varian A-60 spectrometer, with tetramethylsilane as an internal standard (τ 10.00 ppm).

hydroxyl absorption at 3250–3325 cm^{-1} and no carbonyl absorption: $\lambda_{max}^{CH_3CN}$ 242 mμ (ε 20,5000), 312 (14,400), 358 (5110).

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.26; H, 6.28; N, 3.79. Found: C, 81.09; H, 6.36; N, 3.85.

B. From 3,3-Diphenyl-2-morpholinoacrylophenone (9).—To a solution of 0.70 g (0.0019 mol) of 9[4] in 30 ml of anhydrous benzene was added 0.25 ml (0.002 mol) of boron trifluoride etherate. The solution was stirred for 2 hr at room temperature and then the solvents were distilled off under reduced pressure. The off-white solid residue was collected, washed once with 1% sodium hydroxide solution, twice with water, and twice with cold ethanol. Recrystallization (charcoal) from ethanol provided white crystals, 0.25 g (36%), of 10, mp 198–199°. A mixture melting point with a sample of 10 prepared from 11 and phenyllithium was undepressed, and the infrared spectrum of the product was superimposable on that of 10 prepared by procedure A above.

2-Bromo-1,3-diphenyl-3-methoxyindene.—A solution of 1.00 g (0.0024 mol) of 4 in 20 ml of methanol was refluxed for 10 min. On cooling, 2-bromo-1,3-diphenyl-3-methoxyindene precipitated as large, colorless crystals, 0.80 g (95%), mp 96–96.5°. The nmr spectrum ($CDCl_3$) showed a complex multiplet at τ 2.35–2.95 (14 aromatic H) and a singlet at 6.88 (3 methyl H); uv $\lambda_{max}^{CH_3OH}$ 234 mμ (ε 31,300), 293 (5600), and 309 sh (4000).

Anal. Calcd for $C_{22}H_{17}BrO$: C, 69.87; H, 4.51; Br, 21.19; OCH_3, 7.69. Found: C, 69.72; H, 4.53; Br, 21.17; OCH_3, 8.12.

3-Acetoxy-2-bromo-1,3-diphenylindene.—A mixture of 2.0 g (0.0047 mol) of 4, 0.772 g of anhydrous sodium acetate and 10 ml of acetic anhydride was heated under reflux for 1.5 hr. After cooling, the solution was poured into 150 ml of water and extracted with ether. The ether extract was washed with water and dried ($CaSO_4$). Evaporation of the solvent left a brown oil that was crystallized by triturating with petroleum ether (bp 60–70°). Recrystallization from petroleum ether provided 1.37 g (72%) of 3-acetoxy-2-bromo-1,3-diphenylindene, mp 117–118° (lit.[8] mp 115–117°). This compound was identical (mixture melting point, infrared spectra) with a sample prepared according to the procedure of Weiss and Luft[8] by the action of phenylmagnesium bromide on 2-bromo-1-phenyl-indenone and treatment of the crude 2-bromo-1,3-diphenyl-3-hydroxyindene with sodium acetate and acetic anhydride.

Registry No.—**9,** 13118-12-2; **10,** 18742-06-8; 2-bromo-1,3-diphenyl-3-methoxyindene, 18742-07-9.

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Nuclear Magnetic Resonance Spectra of Exocyclic Methylene Epoxides

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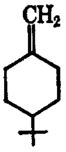
Received July 23, 1968

Carlson and Behn have reported[2] nmr data for epimeric epoxides derived from olefins I–IV. While no correlation was found between the chemical shift of the epoxide methylene protons and the pseudoaxial or pseudoequatorial character of the methylene group, the half band width of the methylene signal (singlet) was shown to be larger (1.23–1.61 *vs.* 0.14–0.16 cps) for the pseudoaxial methylene epoxides. This difference in half band width was ascribed to the long-range coupling of the epoxide methylene groups with the immediately adjacent methylene protons of the cyclohexane ring, the theoretical coupling constants[3] for pairs of epoxides being in accord with the observed half band widths.



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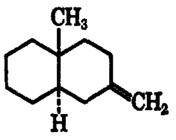

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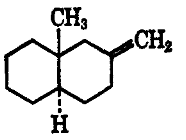
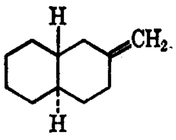


III



IV

We wish to report the nmr data for a series of exocyclic methylene epoxides in the steroid series (see Table I). For the epoxides[4] derived from 3-methylenecholestane, in which the environment of the epoxide function is similar to the limited range of structures examined by Carlson and Behn, the same correlation of large half band width and pseudoaxial epoxide methylene group was observed. However, for epoxides where the cyclohexane ring environment was less symmetrical, namely for the epoxides[4] derived from 3β-acetoxy-6,6′-methylenecholestane, 3β-acetoxy-7,7′-methylenecholestane and 3β-acetoxy-12,12′-methylenetigogenin, the pattern of data was significantly more complicated. For these epoxides the epoxide methylene protons gave rise to an AB quartet, although for the 12α,12′ epoxide the central components of the quartet were not completely separated. Again there was no correlation between the chemical shift of the epoxide methylene proton signals and the pseudoaxial or pseudoequatorial character of the methylene group. A marked pattern was discernible in the half band widths of the components of the AB quartet and the orientation of the epoxide methylene group. While the half band widths of the upfield pair of signals of the AB quartet were within the range 0.81–1.41 cps (tending to the upper limit for pseudoaxial cases, and to the lower limit for pseudoequatorial epoxide–methylene groups), the half bands widths of the downfield pair of signals were markedly dependent upon the orientation of the methylene epoxide protons. For compounds with a pseudoequatorial methylene group the downfield pair of signals had half band widths within the range 0.94–1.46 cps, in contrast to the pseudoaxial methylene groups which gave downfield signals with half band widths over the wide range 2.14–3.50 cps.

It seems probable that this marked increase in half band widths for the downfield proton *only* of a pseudoaxial epoxide methylene group must reflect long-range coupling of the downfield proton additional to that considered by Carlson and Behn, in accounting for the difference between pseudoaxial and pseudoequatorial methylene groups in the systems which they examined. It should be noted for the upfield proton no simple pattern of half band widths is discernible in terms of the pseudoaxial or pseudoequatorial nature of the group.

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(1) To whom correspondence should be addressed.

(2) R. G. Carlson and N. S. Behn, *J. Org. Chem.*, **32**, 1363 (1967).

(3) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

(4) B. N. Blackett, J. M. Coxon, M. P. Hartshorn, B. L. J. Jackson, and C. N. Muir, submitted for publication.