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Cyclopropanes. XXX. Reductive Cleavage of Cyclopropane Rings[1]

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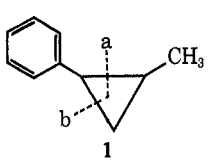
1,1-Biphenylene-2-methylcyclopropane (**5**) was synthesized and subjected to reductive cleavage with sodium and lithium in liquid ammonia, sodium in glyme, sodium naphthalide in glyme, and by controlled potential electrolysis in acetonitrile at a mercury cathode. The reductive cleavage of **5** yielded under all conditions a mixture of 9-propylfluorene (**6**) and 9-isopropylfluorene (**7**) with the isomer ratio of **6**:**7** varying from 96:4 to 81:19. The cleavage of the cyclopropane ring is in the direction of the more substituted carbon (less thermodynamically stable carbanion), and the change in isomer ratio is ascribed to a solvent effect.

The reductive cleavage of the cyclopropyl ring system by solutions of alkali metals in liquid ammonia has been receiving a great deal of current interest. It has been shown, originally by Boord and coworkers[2] and more recently by Norin,[3] Dauben,[4] and Fraisse-Jullien,[5] that a carbonyl group attached to the ring was necessary to observe the ring opening. House[6] extended this to cyclopropylcarboxylic esters. More recently it was demonstrated that a phenyl substituent[7] would also cause the cyclopropyl ring to undergo reductive cleavage.

As data accumulated it became apparent that a number of factors controlled the direction of ring opening, among them being the ability of the π orbital of the carbonyl or phenyl group to overlap with an adjacent cyclopropyl bond.[3,4] This postulate accounts well for the regiospecific mode of ring opening in fused bicyclic systems.[3,4] Other factors that are considered to be important are electronic and steric[4a,6,7b,d] in nature and have been shown to be significant factors in systems in which dynamic conformational isomers are involved.[4b,7d] For example, in the cases studied by Staley,[7d] the geometric isomers, *cis*- and *trans*-1-methyl-2-phenylcyclopropane (**1**), yielded different ratios of cleavage product



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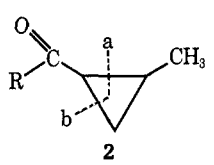

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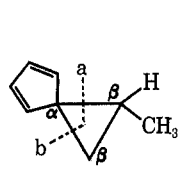
with the trans isomer giving mainly cleavage of bond b and the cis isomer giving predominant cleavage of bond a. A similar observation was made by Dauben[4b] for *cis*- and *trans*-alkyl-2-methylcyclopropyl ketones (**2**). Both groups of workers rationalized their results on the bases of steric and electronic factors.

Of particular interest were the results of the reduction of 1-methylspiro[2.4]hepta-4,6-diene (**3**) in which the cleavage of bond b is favored by a ratio of 5:1.[7d] Due



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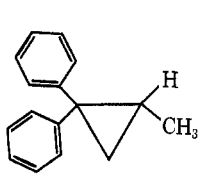

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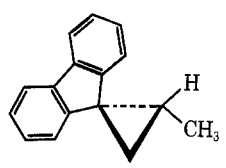

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to the rigidity of the structure there are no preferential conformational isomers possible (*vide supra*). The preference for bond b cleavage was taken as further support of the electronic influence on the reaction in which negative charge is believed to accumulate on the β carbon in the activated complex and with the methyl group exerting a destabilizing effect.

In our work[7a] on the reductive cleavage of 1-methyl-2,2-diphenylcyclopropane (**4**) it was shown that bond a was cleaved in preference to b by a factor of *ca.* 5. This result was rationalized on the basis, *inter alia*, that a methyl group would stabilize the ion-radical intermediate which has radical character at the β carbon atom and the anion localized on the diphenylcarbinyl atom. It was pointed out[7d] that steric factors are also playing an important role in the reduction of **4**. In order to help evaluate the role of steric factors, the electronically analogous system, 1,1-biphenylene-2-methylcyclopropane (**5**), was chosen for investigation. This system not only has the phenyl groups frozen but they are in the preferred bisecting conformation[8] as well.

Syntheses and Reactions.—The synthesis of **5** was accomplished by standard procedures. The addition of 9-diazofluorene to methyl acrylate produced methyl 2,2-biphenylenecyclopropanecarboxylate in 65% yield. Reduction with lithium aluminum hydride produced the corresponding carbinol (88%) which was converted to the tosylate (98%), and the tosylate was reduced to **5** in 78% yield with lithium aluminum hydride.

(1) Support of this work by grants from the Petroleum Research Fund of the American Chemical Society and the National Science Foundation is gratefully acknowledged.

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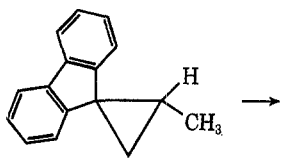
The reduction of **5** was carried out on a vacuum line using a slight excess of sodium in liquid ammonia (~0.3% solution). Initially, after addition of hexane to the reaction mixture, the ammonia was allowed to evaporate and the red hexane solution was filtered through a sintered glass funnel. The filtrate was colorless and glpc analysis indicated two products. One product was shown to be a mixture of the expected 9-



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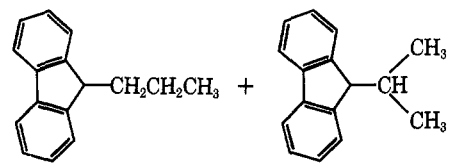
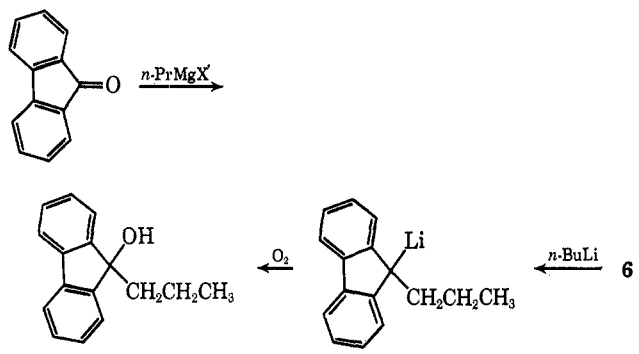


6 **7**

propylfluorene (**6**) and 9-isopropylfluorene and the other product the unexpected 9-propyl-9-fluorenol (**8**) which was identified by spectral data and by synthesis from the addition of *n*-propylmagnesium bromide to fluorenone.



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A clue to the mode of formation of **8** was provided by the observation that the red hexane solution became colorless on exposure to air during the filtration of the solution (*vide supra*). This suggested that the hexane solution may have contained the 9-propyl-9-fluorenyl anion formed as a result of the reduction and that rapid air oxidation produced **8**. The reasonableness of this hypothesis was demonstrated by the treatment of **6** with *n*-butyllithium to generate the 9-*n*-propyl-9-fluorenyl anion, and the red solution was almost instantaneously decolorized by bubbling dry oxygen through the solution. The alcohol **8** was isolated in 70% yield. In order to obviate the formation of **8** in the reduction reaction, the ammonia solution was quenched with ammonium chloride prior to the addition of hexane.

Discussion

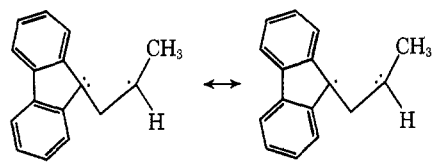
The results of the reduction of **5** are summarized in Table I. The isomer distribution shows that cleavage of bond a in **5** is preferred even more than in **4**. The steric interaction between the methyl group and the aromatic ring in **5** is considerably less than in **4** due to the rigidity and planarity of the fluorenyl moiety.

TABLE I

REDUCTIVE CLEAVAGE OF 1,1-BIPHENYLENE-2-METHYLCYCLOPROPANE (**5**)

Reducting agent	Solvent (temp, °C)	% conversion	% **6**	% **7**
Sodium	Ammonia (−28)	90	95	5
Sodium	Ammonia-*tert*-BuOH (−28)	90	96	4
Lithium	Ammonia (−78)	100	96	4
Electrolysis	Acetonitrile (25)	100	93	7
Sodium	Glyme (25)	22	82	18
Sodium naphthalide	Glyme (25)	100	81	19
Sodium naphthalide	Glyme (−78)	21	83	17

Steric considerations in **5** do not seem to be so important as electronic considerations. The direction of cleavage of the cyclopropane ring is determined by the stability of the two anion radicals **9** and **10** which we believe are intermediates in the reduction.[7a] The intermediates **9** and **10** have most of the negative charge residing on the 9-fluorenyl carbon and thereby giving



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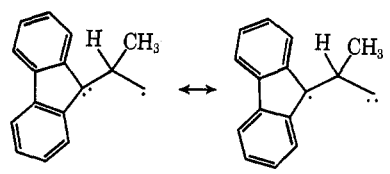

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more radical character the cyclopropyl ring cleavage carbon. As **9** is a secondary and **10** a primary radical, the former is of lower energy and the cleavage proceeds largely in that direction. Subsequent events such as addition of the second electron and proton resulting in a red solution of the 9-*n*-propyl- and 9-isopropylfluorenyl anion is identical with that previously described for the reduction of **4**.[7a]

A variety of reducing agents were used to ascertain whether or not the source of electrons would have any effect on the mode of ring opening. Table I lists the reducing agents dissolving metals and electrolysis and the conditions (solvent, temperature) used. It can be seen that the isomer ratio varies from 95:5 to 81:19 with the cleavage of bond a being favored. The change in isomer ratio under the different conditions used is small but significant and could be accounted for by either a solvent effect or a temperature effect. The latter seems unlikely in view of our observation that using sodium naphthalide in glyme at 25 and −78° there is less than a 2% change in isomer ratio. Our results indicate that solvation best accounts for the change with solvents of high dielectric giving rise to the higher ratio.

Experimental Section

Methyl 2,2-Biphenylenecyclopropanecarboxylate.—Methyl acrylate (40.4 g, 0.47 mol) was heated to reflux and a benzene

solution of 9-diazofluorene[9] (45 g, 0.24 mol) was slowly added over a period of 4.5 hr. The excess acrylate and solvent was removed *in vacuo* leaving an orange oil which was triturated with methanol to yield an orange solid. Recrystallization from ether gave 37.6 g (65% yield) of white solid, mp 95–97°.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.63. Found: C, 81.52; H, 5.41.

2,2-Biphenylenecyclopropylcarbinol.—To a solution of lithium aluminum hydride (20 g, 0.53 mol) in 500 ml of tetrahydrofuran was added dropwise a solution of methyl 2,2-biphenylenecyclopropanecarboxylate (37.6 g, 0.15 mol) dissolved in 500 ml of tetrahydrofuran. The reaction mixture was refluxed for 1 hr, cooled, and hydrolyzed with a saturated solution of ammonium chloride. The work-up was done in the usual manner to yield an oil which upon trituration with low boiling petroleum ether gave 29 g (88%) of a white solid, mp 90–92°.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.48; H, 6.58.

1-Methyl-2,2-biphenylenecyclopropane (5).—To a cooled mixture 61.6 g (0.32 mol) of *p*-toluenesulfonyl chloride and 250 ml of dry 2,6-lutidine was added a solution of 35 g (0.16 mol) of 2,2-biphenylenecyclopropylcarbinol dissolved in 250 ml of 2,6-lutidine. The reaction mixture was allowed to come to ambient temperature and to remain there for 4 hr. The reaction mixture was hydrolyzed with water and extracted with ether. The ether extracted was washed successively with water, 5% hydrochloric acid, water, 5% sodium hydroxide, and water and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to yield 58.5 g (98%) of an oil which showed characteristic absorption at 7.3 and 8.5 μ for the tosylate.

The crude tosylate dissolved in 500 ml of tetrahydrofuran was added to a solution of lithium aluminum hydride (15 g, 0.39 mol) in 500 ml of tetrahydrofuran. The reaction mixture was stirred overnight and then hydrolyzed with a saturated solution of ammonium chloride and worked up in the usual manner to yield, after recrystallization from methanol, a white solid (25 g, 78%), mp 90–91°.

An infrared spectrum (CCl_4) showed absorptions at 3.18 (w), 3.25 (s), 3.32 (s), 3.35 (s), 3.39 (s), 3.42 (s), 5.15 (m), 5.25 (m), 5.35 (m), 5.45 (m), 5.55 (m), 5.71 (w), 5.80 (w), 5.92 (w), 6.21 (m), 6.78 (s), 6.92 (s), 7.20 (m), 7.30 (m), 7.48 (s), 7.75 (s), 8.20 (s), 8.61 (m), 8.67 (m), 9.05 (s), 9.39 (s), 9.72 (s), 9.92 (m), 10.20 (m), 10.70 (s), 11.25 (s), and 11.50 μ (s). The nmr spectrum (CCl_4) showed a broad doublet of 1.30 ppm, a broad singlet at 1.77 ppm, a complex multiplet centered at 7.10 ppm, and a multiplet centered at 7.66 ppm (integration 4:2:6:2, respectively). A mass spectrum showed large fragment peaks at *m/e* 206, 191, 178, and 165.

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.37; H, 6.89.

9-Propylfluorene was prepared by the procedure of Schoen and Becker[10] in 90% yield: bp 108–110° (0.35 mm); ir (film) 3.25, 3.40, 6.25, 6.90, 13.8 μ; nmr (CCl_4) δ 0.65–1.50 (complex, 5 H), 1.60–1.80 (complex, 2 H), 3.75 (t, 1 H), 6.85–7.75 (complex, 8 H); mass spectrum *m/e* 208, 180, 164, 152.

9-Isopropylfluorene was prepared by the method of Brown and Bluestein:[11] ir (CCl_4) 3.28, 3.38, 3.42, 6.25, 6.90, 7.22, 7.30, 7.70 μ; nmr (CCl_4) δ 0.80 (d, 6 H, J = 7 Hz), 2.20–2.8; (complex, 1 H), 3.83 (d, 1 H, J = 3.2 Hz) 7.18–7.80 (complex, 8 H); mass spectrum *m/e* 208, 193, 178, 165, 152, 139.

Reduction of 5 with Sodium in Liquid Ammonia.—This reaction and all the subsequent reduction reactions were performed on a vacuum system which is described as follows. The vacuum line is connected to two glass vessels, one of which as a sidearm and stopcock. The vacuum line terminates in a long vertical glass tube which dips under the level of a flask containing mercury (thereby acting as a manometer). Another connection to the vacuum line is to a two-way stopcock which is in turn connected to an oil bubbler and a tank of argon. The vacuum source is a standard mechanical pump. The entire system was operated *in vacuo* at 0.005 mm routinely. The procedure that follows should be considered representative of all of the reduction reactions. The vacuum line was set up as above and pumped down to 0.005 mm.

The system was pressurized with argon. A small chunk of sodium was placed in the vessel with side arm and stopcock. The chamber will be used to dry the ammonium prior to reaction. The other vessel has two 14/20 female ground glass joints and a glass covered magnetic stirring bar. To these are attached two solid addition arms, one containing **5** (0.2045 g, 0.00099 mol) and the other containing sodium metal (0.0790 g, 0.0035 g-atom). Both of the addition arms were flushed with argon and stoppered. The transfer and weighing of the reactants was done under a vigorous argon flow, thereby excluding atmosphere moisture and oxygen. The system was pumped down, pressurized with argon, and then pumped down again while simultaneously flaming out the entire system. This process was repeated three times and the final pressure was brought to 0.005 mm. A dewar flask containing Dry Ice and acetone was placed under the drying chamber, the pump was shut off, and the liquid nitrogen trap was isolated from the system by closing a one-way stopcock. Liquid ammonia was admitted to the system through the side arm of the drying vessel. The volume of the ammonia that was collected and dried was determined by a scratch mark on the drying chamber. After 25 ml of anhydrous ammonia (dark blue solution) was collected, the stopcock on the side arm was closed and the Dry Ice–acetone bath was transferred to the reaction chamber. The sodium was added to the ammonia and the ensuing dark blue solution was stirred for 30 min. At that time, **5** was added in one portion. The reaction was allowed to proceed for 4.25 hr. The solution had a reddish tinge but was still a dark blue in color. At that time, the system was pressurized with argon and the two-way stopcock was opened to the oil bubbler and the ammonia evaporated off through the bubbler without exposing the solution to air. Hexane (100 ml) was added and the Dry Ice–acetone bath was removed. After approximately 2 hr, all of the ammonia had evaporated. The ensuing red solution was filtered through a sintered glass funnel to remove small traces of sodium. Upon passing through the funnel the solution turned clear. Removal of the solvent *in vacuo* left approximately 0.27 g of a semisolid residue. Glpc analysis (4-ft SE-30, helium flow rate 120 ml/min, 200°) indicated a major peak (retention time 5.9 min) and a minor peak (retention time 11.4 min). The major peak constituted 70% of the sample and was successfully augmented with a sample of 9-propylfluorene and 9-isopropylfluorene. Thin layer chromatography of the sample (in benzene) afforded 0.03 g of the unknown compound. The nmr, infrared, and mass spectra indicated that this compound was 9-propyl-9-fluorenol (confirmed with an authentic sample).

9-Propyl-9-fluorenol was prepared by the addition of propylmagnesium bromide, prepared by the reaction of *n*-propyl bromide (10 g) with 2 g of magnesium, to 9-fluorenone (14 g). 9-Propyl-9-fluorenol was obtained in 82% yield and gave mp and mmp 119–121° with alcohol isolated from preceding reaction: ir (CCl_4) 2.78, 3.30, 3.40, 6.25, 6.90, 9.75 μ; nmr (CCl_4) δ 0.68–0.85 (complex, 5 H), 1.68–2.0 (complex, 2 H), 2.35 (s, 1 H), 7.10–7.60 (complex, 8 H); mass spectra *m/e* 224, 206, 181, 165, 152.

Reaction of 9-Propylfluorene with *n*-Butyllithium Followed by Reaction with Oxygen.—To a cooled solution of (1.0 g, 0.005 mol) 9-propylfluorene in 100 ml of anhydrous tetrahydrofuran was added a solution of 1.6 g (0.025 mol) of *n*-butyllithium in hexane. The solution turned deep red and after stirring for 20 min, dry oxygen was bubbled through the solution and the red color was discharged leaving a yellow solution. Hydrolysis followed by usual work-up yielded a solid (69%), mp 119–121°.

Reduction of 5 with Sodium Metal in Liquid Ammonia in the Presence of *tert*-Butyl Alcohol.—The standard apparatus was used. The reagents used were **5** (0.206 g, 0.001 mol), sodium metal (0.069 g, 0.003 g-atom), and *tert*-butyl alcohol (0.141 g, 0.0019 mol). The reaction time was 5 hr. The standard work-up procedure was used. Glpc analysis (4-ft SE-30, helium flow rate 120 ml/min, 200°) indicated a major peak (retention time 5.9 min) and a minor peak (retention time 8.4 min). The major peak constituted 90% of the total chromatogram and was successfully augmented with a mixture of 9-propyl- and 9-isopropylfluorene. The minor peak constituted 10% of the total chromatogram and was augmented with **5**. Glpc analysis (1.5-ft EGIP, helium flow rate 100 ml/min, 145°) indicated a major peak (retention time 14.9 min) and a minor peak (retention time 11.2 min). The major peak constituted 96.3% of the total chromatogram and was successfully augmented with 9-propylfluorene. The minor peak constituted 3.7% of the total chromatogram and was successfully augmented with 9-isopropylfluorene.

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(10) K. Schoen and E. Becker, *J. Amer. Chem. Soc.*, **77**, 6030 (1955).
(11) W. Brown and B. Bluestein, *ibid.*, **65**, 1082 (1943).

Reduction of 5 with Sodium Metal in Liquid Ammonia Followed by Ammonium Chloride.—The procedure used was the same as described previously. The reagents used were **5** (0.206, 0.001 mol) and sodium metal (0.0730 g, 0.0031 g-atom). The reaction time was 5 hr. After the system was pressurized with argon, ammonium chloride (0.200 g, 0.0037 mol) was added. The blue color of the solution changed to red and then was discharged to a yellow solution. Addition of hexane and evaporation of the ammonia through an oil bubbler followed by filtration of the hexane solution led to a yellow oil which weighed 0.208 g. Glpc analysis (4-ft SE-30, helium flow rate 120 ml/min, 200°) indicated a major peak (retention time 5.7 min) and a minor peak (retention time 8.3 min). The major peak constituted 90% of the total chromatogram and was successfully augmented with a sample of 9-propylfluorene and 9-isopropylfluorene. The minor peak constituted 10% of the total chromatogram and was successfully augmented with 1,1-biphenylene-2-methylcyclopropane. Glpc analysis (4-ft EGIP, helium flow rate 120 ml/min, 215°) indicated a major peak (retention time 10.2 min) and a minor peak (retention time 8.9 min). The major peak constituted 95.4% of the total chromatogram and was successfully augmented with a sample of 9-propylfluorene. The minor peak constituted 4.6% of the total chromatogram and was successfully augmented with a sample of 9-isopropylfluorene.

Reduction of 5 by Lithium Metal in Liquid Ammonia Followed by Ammonium Chloride.—The reagents used were **5** (0.209, 0.001 mol) and lithium metal (0.0210 g, 0.003 g-atom). The reaction time was 5 hr. After the system was pressurized with argon, ammonium chloride (0.200 g, 0.0037 mol) was added. The blue color of the solution changed to red and then was discharged to a yellow solution. Addition of hexane and evaporation of the ammonia through an oil bubbler followed by filtration of the hexane solution led to a yellow oil which weighed 0.21 g. Glpc analysis (4'SE-30, helium flow rate 120 ml/min, 200°) indicated one peak (retention time 5.9 min). The peak was successfully augmented with a mixture of 9-propylfluorene and 9-isopropylfluorene. A trace peak was also observed (retention time 7.5 min) and was successfully augmented with **5**. Glpc analysis (4-ft EGIP, helium flow rate 120 ml/min, 215°) indicated a major peak (retention time 9.1 min) and a minor peak (retention time 7.9 min). The major peak constituted 96.4% of the total chromatogram and was successfully augmented with a sample of 9-propylfluorene. The minor peak constituted 3.6% of the total chromatogram and was successfully augmented with 9-isopropylfluorene.

Electrolytic Reduction of 5 in Acetonitrile.—A standard electrolytic reduction cell was used. The working electrode was a mercury pool, the reference electrode was silver/silver nitrate, and the supporting electrolyte was tetraethylammonium bromide (0.25 *M* solution). The solvent used was 8 ml of dry and degassed acetonitrile. The solvent and supporting electrolyte were added to the cell under a partial vacuum. The cell was then pressurized with nitrogen and sealed. A prelectrolysis was carried out at −3.0 V down to a current of 400 mA, and then **5** (0.0832 g, 0.0004 mol) was added and the electrolysis begun at −3.0 V. The initial current obtained was 17 mA. The solution immediately turned a bright red. The electrolysis was run for 1 hr at which time the current had dropped to 1.5 mA.

A coulometer, using hydrazine sulfate, indicated that the electrolysis was a two-electron transfer. The cell was removed and the contents of the cell were transferred in air into a stoppered flask. Glpc analysis (4-ft SE-30, helium flow rate 120 ml/mm, 200°) indicated a major peak (retention time 11.1 min) and a minor peak (retention time 6.1 min). The major peak constituted 65% of the total chromatogram and was successfully agumented with 9-propyl-9-fluorenol. The minor peak constituted 35% of the total chromatogram and was successfully agumented with a mixture of 9-propylfluorene and 9-isopropylfluorene. Glpc analysis (4-ft EGIP, helium flow rate 120 ml/min, 215°) indicated a major peak (retention time 8.3 min) and a minor peak (retention time 7.2 min). The major peak constituted 92.5% of the total chromatogram and was successfully augmented with 9-propylfluorene. The minor peak constituted 7.5% of the total chromatogram and was successfully augmented with 9-isopropylfluorene.

Reduction of 5 with Sodium Metal in Glyme.—The reagents used were **5** (0.206 g, 0.001 mol) and sodium metal (0.072 g, 0.0031 g-atom). The glyme (45 ml) was degassed twice and was then distilled onto a sodium mirror. The glyme was then distilled into the reaction vessel and the temperature maintained at −50°. The sodium had been melted to a sodium mirror in the reaction vessel prior to the distillation of the glyme. No color change was observed in the solution. The reaction mixture was stirred for 30 min at which time the reaction vessel was allowed to warm to room temperature. After 30 min **5** was added. There was no apparent color change but the sodium mirror began to dissolve slowly and after 20 min the solution turned a light yellow. After 32 min the reaction vessel was allowed to warm to room temperature and after 3 hr the reaction was a light pink in color. The reaction was halted after 7 hr, at which time the solution was a deep red. Addition of 10 ml of anhydrous methanol discharged the red color, and the reaction mixture was diluted with ether and washed with water several times and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*, and the residue, which weighed 0.21 g, was added to benzene, and the benzene was distilled to dry the solution. Glpc analysis (4-ft SE-30, helium flow rate 120 ml/min, 215°) indicated a major peak (retention time 8.6 min) and a minor peak (retention time 5.9 min). The major peak constituted 78% of the total chromatogram and was augmented with 1,1-biphenylene-2-methylcyclopropane. The minor peak constituted 22% of the total chromatogram and was augmented with a mixture of 9-propyl- and 9-isopropylfluorene. Glpc analysis (4-ft EGIP, helium flow rate 120 ml/min, 210°) indicated a major peak (retention time 10.1 min) and a minor peak (retention time 8.7 min). The major peak constituted 81.5% of the total chromatogram and was augmented with 9-propylfluorene. The minor peak constituted 18.5% of the total chromatogram and was augmented with 9-isopropylfluorene.

Reduction of 5 with Sodium Naphthalide in Glyme at Room Temperature.—The reagents used were **5** (0.206 g, 0.001 mol), sodium metal (0.071 g, 0.003 g-atom), naphthalene (0.575 g, 0.005 mol), and glyme (45 ml). The glyme was degassed two times and distilled into the drying chamber. After letting the glyme (melted) stand over the sodium mirror for several minutes, the glyme was distilled into the reaction chamber and allowed to warm to −50°. The naphthalene was added followed by the sodium metal. No coloration occurred and after 10 min the reaction mixture was allowed to warm to room temperature. After 45 min the solution began to darken and after 80 min **5** was added. The color of the solution was a brownish green. After 7 hr, anhydrous methanol (10 ml) was added. The color was quickly discharged. The ensuing yellow solution was washed with water and extracted with ether, and the ethereal extracts were separated and dried. The solvent was removed *in vacuo* leaving a residue, 0.779 g. Glpc analysis (4-ft SE-30, helium flow rate 120 ml/min, 200°) indicated one peak (retention time 5.5 min). The peak was successfully augmented with a mixture of 9-propyl- and 9-isopropylfluorene. Glpc analysis (4-ft EGIP, helium flow rate 120 ml/min, 210°) indicated a major peak (retention time 10 min) and a minor peak (retention time 8.7 min). The major peak constituted 81.1% of the total chromatogram and was successfully augmented with 9-propylfluorene. The minor peak constituted 18.9% of the total chromatogram and was successfully augmented with 9-isopropylfluorene.

Reduction of 5 with Sodium Naphthalide in Glyme at Low Temperature.—The reagents used were **5** (0.206 g, 0.001 mol), sodium metal (0.073 g, 0.0032 g-atom), naphthalene (0.587 g, 0.0045 mol), and glyme (45 ml). The glyme was degassed two times and was distilled into the drying chamber. After the glyme (melted) was allowed to stand over the sodium mirror for several minutes, the glyme was distilled into the reaction flask (which was coated with a sodium mirror). The glyme was allowed to warm to room temperature at which time the naphthalene was added. The green solution was stirred for 15 min at room temperature and was then cooled to −78°. After 15 min at −78° **5** was added and the reaction was run at −78° for 7 hr at which time water (10 ml) was added. The color of the solution was rapidly discharged and the clear solution was extracted into ether. The solvent was removed *in vacuo*, the residue was added to benzene, and the benzene was distilled off to dry the solution. The residue weighed 0.784 g. Glpc analyses (4-ft SE-30, helium flow rate 120 ml/min, 200°) indicated a major peak (retention time 8.5 min) and a minor peak (retention time 6.0 min). The major peak constituted 21% of the total chromatogram and was successfully augmented with a mixture of 9-propyl- and 9-isopropylfluorene. Glpc analysis (1.5-ft EGIP, helium flow rate 100 ml/min, 145°) indicated a major peak (retention time 15.5 min) and a minor peak (retention time 12.4 min). The major peak constituted 82.8% of the total chromatogram and was success-

fully augmented with 9-propylfluorene. The minor peak constituted 17.2% of the total chromatogram and was successfully augmented with 9-isopropylfluorene.

Registry No.—5, 27971-70-6; methyl 2,2-biphenylenecyclopropanecarboxylate, 27921-38-6; 2,2-biphenylenecyclopropylcarbinol, 27921-39-7.

New Friedel–Crafts Chemistry. XXIV.[1] On the Mechanism of Cyclidehydration of Primary Phenylalkanols to Indans[2]

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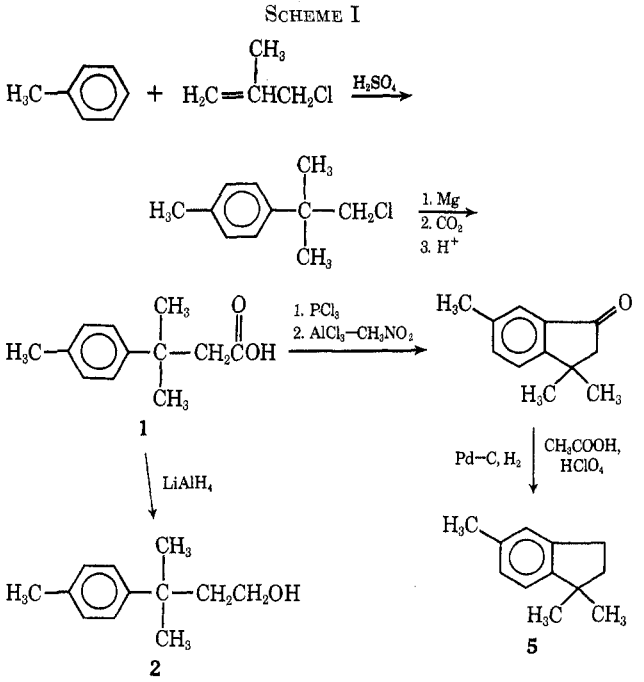
The mechanism of acid-catalyzed cyclidehydration of primary alcohols to five-membered ring compounds was explored by determining the products obtained by subjecting 3-methyl-3-(*p*-tolyl)-1-butanol (**2**) to acid-catalyzed dehydration. These products were found to be a mixture of the expected open-chain rearranged products, 2-methyl-3-(*p*-tolyl)-2-butene (**21**) and 2-methyl-3-(*p*-tolyl)butane (**22**), together with rearranged and nonrearranged cyclidehydration products. The cyclized compounds (*ca.* 55% of the total product) were a mixture of 1,1,4-, 1,1,5-, 1,1,6-, and 1,1,7-trimethylindan isomers in a ratio of 55:17:23:5, respectively. A mechanism invoking anchimerically assisted ionization through Ar_1-4 and Ar_2-5 participations in combination with the usual Wagner–Meerwein type shifts is suggested to account for the cyclized products. On the basis of product composition, the overall ratio of Ar_1-4 to Ar_2-5 participation may be at least 3.5 to 1.

In a previous paper of this series[1] we reported among other things that the treatment of 3-methyl-3-phenyl-1-butanol with phosphoric acid at 230° resulted in some cyclization to 1,1-dimethylindan. On the other hand, similar treatment of 3-phenyl-1-propanol with phosphoric acid produced no detectable amounts of the expected cyclic product, indan. To account for the role of the *gem*-methyls in the above compound, as well as for the role of the keto group in α-alkyl-β-hydroxypropiophenones in promoting ring closure of such primary alcohols to five-membered ring products, we proposed a mechanism[4] involving Ar_1-4 participation and 1,3-phenyl migration to yield intermediates capable of cyclizing to five-membered ring compounds. However, at the time we suggested our mechanism, there were no available experimental data to support it or to distinguish it from a similar likely mechanism that involves Ar_2-5 rather than Ar_1-4 type participation.

The present work was designed to determine the nature and the extent of contribution of the various intermediates responsible for the cyclization of such primary alcohols to five-membered ring compounds by subjecting the methyl-labeled derivative, 3-methyl-3-(*p*-tolyl)-1-butanol (**2**), to the same cyclization conditions and by studying the cyclized products obtained.

Synthesis of Starting Material and Products.—Since a number of isomeric trimethylindans were expected to result from the phosphoric acid induced cyclization of 3-methyl-3-(*p*-tolyl)-1-butanol (**2**), we developed methods to obtain them separately. Unequivocal syntheses of some of the materials needed are outlined in Schemes I and II. Scheme I describes the synthesis of the starting alcohol **2** and 1,1,5-trimethylindan (**5**) from the acid precursor **1**. Scheme II outlines the general steps used for the synthesis of the three isomeric trimethylindans, **4**, **6**, and **7**. Starting with *o*-tolualdehyde (**3**, R = *o*-CH_3), *p*-tolualdehyde (**3**, R = *p*-CH_3), and *m*-tolualdehyde (**3**, R = *m*-CH_3), this procedure gave 1,1,4-trimethylindan (**4**), 1,1,6-trimethylindan (**6**), and a mixture of 1,1,5-trimethylindan (**5**) and 1,1,7-trimethylindan (**7**), respectively. The components of the latter mixture were separated by preparative gas chromatography.

SCHEME I



Results and Discussion

The treatment of 3-methyl-3-(*p*-tolyl)-1-butanol (**2**) with phosphoric acid was carried out under conditions similar to those applied previously for 3-methyl-3-phenyl-1-butanol.[1,4–6] The products of this treatment were analyzed before and after subjection to catalytic hydrogenation and the results of this analysis are given in Table I.

(1) Part XIX: A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **34**, 3571 (1969).

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(4) See Schemes I and II of ref 1.

(5) M. T. Bogert and D. Davidson, *J. Amer. Chem. Soc.*, **56**, 185 (1934).

(6) R. O. Roblin, Jr., D. Davidson, and M. T. Bogert, *ibid.*, **57**, 151 (1935).