2-Nitronorbornane.—The general oxidation procedure performed on a 20-mmol scale gave a yellow-green liquid (1.95 g). Chromatography on silicic acid (60 g) using chloroform–hexane mixtures increasing from 10 to 30% chloroform was followed by tlc. Fractions 47–113 were combined and concentrated giving crude 2-nitronorbornane (0.86 g, 31%). Short-path distillation (0.08 mm) gave a solid: mp 64–68°, softening from 45° (lit.[13] mp 64–67° for >90% *endo*-2-nitronorbornane-3-^{14}C; nmr δ 4.84 (quintet, <1 H, J = 5.0 Hz, *exo* $-CHNO_2$) and 4.39 (m, <<1 H, *endo* $-CHNO_2$) (lit.[14] δ 4.73 for *exo* $-CHNO_2$). The nmr spectrum was integrated by planimetry and indicated 91% *endo*-2-nitronorbornane and 9% *exo*-2-nitronorbornane.

Isomerization of 2-Nitronorbornane.—The method of Roberts[13] gave after distillation a liquid: nmr δ 4.8 (m, <<1 H, *exo* $-CHNO_2$) and 4.39 (m, <1 H, *endo* $-CHNO_2$). Integration of the peaks at δ 4.8 and 4.39 ppm indicated that the product was at least 72% *exo* isomer. Roberts[13] estimated the composition as 70–80% *exo* by another method.

Attempted Oxidation of Camphor Oxime.—The general procedure was applied to *anti*-camphor oxime, but the yield of material showing nitro absorption was <5%. Camphor was recovered and identified.

Registry No.—**1c**, 17448-49-6; **1d**, 17448-51-0; **2a**, 17448-50-9; **2b**, 17448-52-1; **2c**, 17448-53-2; **2d**, 17448-54-3; **3a**, 17448-55-4; **3b**, 17448-56-5; **3c**, 17448-57-6; **3d**, 17448-46-3; **6d**, 10343-99-4; **7d**, 767-92-0.

Cyclopropanes. XXV. Cleavage of Cyclopropane Rings by Solutions of Sodium in Liquid Ammonia[1]

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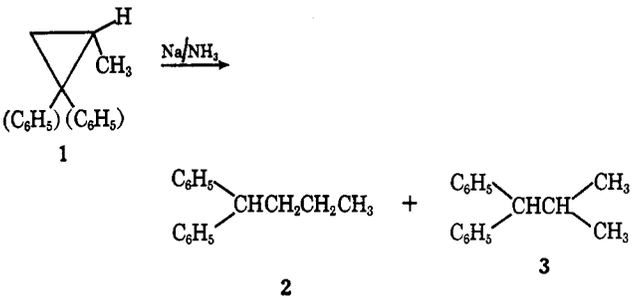
Reduction of 1-methyl-2,2-diphenylcyclopropane (**1**) in sodium and liquid ammonia led to ring cleavage with the formation of 1,1-diphenylbutane (**2**) and 1,1-diphenyl-2-methylpropane (**3**). Under similar conditions (−)-(*R*)-1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane and (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid yielded racemic 1,1-diphenyl-3-methyloctane and 4,4-diphenyl-2-methylbutanoic acid, respectively. A mechanism for this reductive cleavage, involving ion-radical intermediates, is presented.

It has been known for some time that alkali metals in liquid ammonia solutions in the presence of a suitable acid (*i.e.*, NH_4X^-) causes cleavage of the cyclopropane ring in α-cyclopropyl ketones. Thus Van Volkenburg and coworkers[2] have found that the ring in cyclopropyl methyl ketone is opened to give a mixture of methyl propyl ketone and 2-pentanol by reaction with sodium and liquid ammonia in the presence of ammonium sulfate. Similarly, in some recent studies, Norin[3] and Dauben[4] have observed that solutions of lithium in liquid ammonia bring about a stereospecific opening of the cyclopropane ring in such a manner that the bond cleaved is the one possessing the maximum overlap with the π orbital of the carbonyl group. It has also been demonstrated that cyclopropyl esters[5] (but not acids) will undergo an analogous cleavage. On the other hand it has been shown that the cyclopropane ring in 2-cyclopropylpent-1-ene is not opened by sodium in liquid ammonia alone nor in the presence of ammonium bromide.[6] In the presence of methanol the double bond is reduced but the ring remains intact. Nefedov[7] has reported that the sodium–liquid ammonium reduction of 1,1-dichloro-2-phenylcyclopropane produced, besides the expected phenylcyclopropane, a 17% yield of propylbenzene.

During our studies on the reduction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane with solutions of sodium in liquid ammonia[8] we found that the primary reduction product, 1-methyl-2,2-diphenylcyclopropane (**1**), was further reduced under the reaction conditions to give a mixture of 1,1-diphenylbutane (**2**) and 1,1-diphenyl-2-methylpropane (**3**). This observation has led us to study the cleavage of such compounds by sodium in liquid ammonia in more detail, and we now wish to report our results.



The yields of **2** and **3** produced by reduction of **1** have been found to vary with the concentration of the sodium in liquid ammonia solution used as reducing agent. In particular, when solutions of sodium in liquid ammonia of above 8% are used no reaction occurs over a 2-hr period; at concentrations of from 1 to 8% a mixture of **2**, **3**, and recovered **1** is produced; and at concentrations of less than 1% only **2** and **3** are formed. The yields of the two products and of recovered starting material are shown in Table I as a function of the concentration of the sodium in liquid ammonia reducing solutions. The yields shown represent the relative yields of each product as determined by gas chromatography of the reaction mixture. The total yield of these products was always greater than 90%. It will be noted that the ratio of the yields of **2** and **3**, when they are produced, remains fairly constant over

(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.

(2) R. Van Volkenburgh, K. M. Greenlee, J. W. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, **71**, 3595 (1949).

(3) T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965).

(4) M. G. Dauben and E. I. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

(5) H. O. House and C. J. Blankley, *ibid.*, **33**, 47 (1968).

(6) H. Greenfield, R. A. Friedel, and W. Orchin, *J. Amer. Chem. Soc.*, **76**, 1258 (1954).

(7) O. W. Nefedov, N. N. Novitskaya, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **152**, 629 (1963).

(8) H. M. Walborsky, F. P. Johnson, and J. B. Pierce, *J. Amer. Chem. Soc.*, **90**, 5222 (1968).

TABLE I

REDUCTION OF 1-METHYL-2,2-DIPHENYLCYCLOPROPANE WITH SODIUM IN LIQUID AMMONIA

Na, g/100 m	Yield of 1, %	Yield of 2, %	Yield of 3, %	2/3
12.2[a]	100			
12.0	100			
5.2[a]	57.0	35.8	7.2	5.0
3.1	22.0	66.0	12.0	5.5
1.3	15.0	72.1	12.6	5.7
0.05	0.00	79.6	14.1	5.7

[a] Optically active material was used and recovered with the same optical purity.

a wide concentration range. This suggests that these two substances are probably produced from a common intermediate.

In view of the known ability of phenyl groups to accept electrons from sodium in liquid ammonia solutions[9] we propose that a plausible mechanism for the opening of the cyclopropane ring in this and other phenyl-substituted cyclopropanes is as shown in Figure 1.[10] It is noted that, because of the reported comparable acidities ($pK_a \sim 35$) of ammonia and diphenylmethane, the diphenyl carbanions **7** and **8** produced as a result of the ring opening are not expected to be completely protonated in liquid ammonia.[11] Indeed these reductions are always accompanied by the production of deep red solutions which presumably contain anions **7** and **8** in equilibrium with amide ions and the corresponding hydrocarbon. We have been able to trap the predominant carbanion **8** by alkylation with benzyl chloride, a method used previously by Hauser and Hamrick.[12]

In support of the mechanism proposed in Figure 1 we have found that at least one phenyl group attached to the cyclopropane ring is a necessary condition for the ring to be opened by sodium in liquid ammonia solution. Whereas the cyclopropane rings of the sodium salts of 2,2-diphenylcyclopropanecarboxylic acid and *trans*-2-phenylcyclopropanecarboxylic acid are opened by sodium in liquid ammonia solutions to yield 4,4-diphenylbutanoic acid and 4-phenylbutanoic acid, respectively, the rings in 2,2-dimethylcyclopropanecarboxylic acid and cyclopropanecarboxylic acid are not opened under similar conditions. The role of the phenyl group in our case or the carbonyl[3,4] and carbethoxy groups[5] in previously reported cases is to accept an initial electron from the sodium in liquid ammonia to form the short-lived anion-radical species (**4**) or it may simply stabilize the resulting carbanion when ring cleavage does occur and promote the reaction in this way. This latter explanation, however, would seem less likely in view of the previous observation that 2-cyclopropylpent-1-ene does not react with sodium in liquid ammonia.[6]

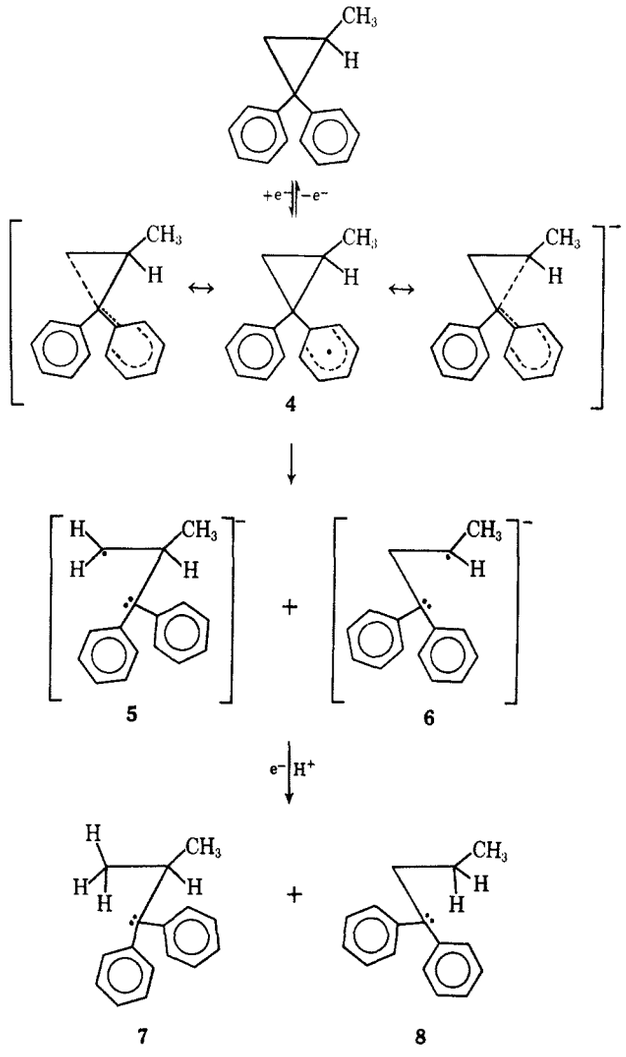


Figure 1.—Mechanisms for the sodium in liquid ammonia reduction of 1-methyl-2,2-diphenylcyclopropane.

In connection with the possibility of anion radicals such as **4**–**6** being involved in these reactions we were interested in attempting to observe them by esr spectroscopy. However, esr spectra of these red solutions (when less than 1 equiv of sodium is used) do not show the presence of any paramagnetic species. This does not mean that **4** cannot be an intermediate, but does indicate that if it is produced it must rapidly open to form **5** and **6** which themselves must quickly add another electron to form a dianion which is protonated by the solvent. Moreover, the ring opening of **4** to **5** and **6** is an irreversible reaction, since, when optically active **1** is used in the reaction, it is recovered without loss of optical activity (Table I). Intermediates such as **6** would be expected to cause at least some loss of optical activity. Indeed, (−)-(*R*)-1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane (**9**)[13] which upon reduction should lead to ion radical **11** (R = *n*-pentyl) did in fact result in the formation of racemic **12** (R = *n*-pentyl). This was also the case when **10** was reduced under similar conditions. We interpret these results to mean that the species formed by the opening of the cyclopropane ring is such that rapid racemization can occur at the optically active center and is consistent with this species being **11**.

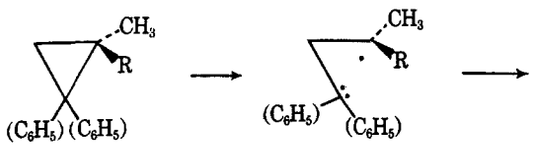
(9) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959).

(10) In a sense, our reaction is somewhat of a modified Birch reduction. An electron adds, but, since there is no proton donor (*i.e.*, ethanol), this step is reversible.

(11) H. Smith in "Chemistry in Non Aqueous Ionizing Solvents," Vol. 1, part 2, Interscience Publishers, New York, N. Y., 1963, p 254.

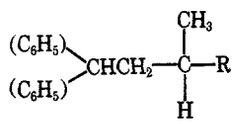
(12) C. R. Hauser and P. J. Hamrick, Jr., *J. Amer. Chem. Soc.*, **79**, 3142 (1957). Based on the amount of stilbene formed (60%) and using the arguments presented by these workers, one would conclude that the equilibrium lies largely in favor of the carbanion and therefore the pK_a of the conjugate hydrocarbon acid is lower than that of ammonia by somewhere between 1 and 2 pK_a units.

(13) J. B. Pierce and H. M. Walborsky, *J. Org. Chem.*, **33**, 1962 (1968).



9, R = *n*-pentyl
10, R = COO^-Na^+

11



12

Furthermore, it should be noted that the reduction of 1-methyl-2,2-diphenylcyclopropane (**1**) results in the cleavage of both 1,2 and 2,3 bonds of the cyclopropane ring. The predominant product, however, is that resulting from 1,2 cleavage as might be expected on the basis of the fact that anion radical **6** would be predicted to be more stable than **5**.

There remains to comment on what we believe to be the reason for the variation in the yields of **2** and **3** with changes in concentration of the sodium in liquid ammonia reducing solution in the reduction of **1**. It is felt that this variation is connected with the solubility of **1** in these solutions. The sodium salt of 2,2-diphenylcyclopropanecarboxylic acid, which is moderately soluble in liquid ammonia, is reduced to 4,4-diphenylbutanoic acid at all concentrations. On the other hand, 1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane (**9**) which appears to be insoluble in liquid ammonia is not reduced at any concentration of sodium in liquid ammonia at −33° and for similar reaction times. In order to realize the reduction of **9** it was necessary to carry out the reaction in a sealed tube at room temperature over a period of about 15 hr. These observations suggest that 1-methyl-2,2-diphenylcyclopropane presents an intermediate case in which the solubility is such that reaction can occur at a reasonable rate in dilute solutions but not in the highly metallic concentrated solutions.

Experimental Section

The reductions were carried out in apparatus that has been previously described.[8] The composition of the reaction mixtures produced by the reduction of 1-methyl-2,2-diphenylcyclopropane at various concentrations was determined by gas chromatography at 200° on a 6-ft column of 15% Carbowax on acid-washed Chromosorb P. The products 1,1-diphenylbutane (**2**) and 1,1-diphenyl-2-methylpropane (**3**) were identified in a manner previously described.[8]

Trapping the Carbanion Involved in the Reduction of 1-Methyl-2,2-diphenylcyclopropane.—A solution containing the anions **7** and **8** was prepared by the reaction of 230 mg (0.00110 mol, an excess) of 1-methyl-2,2-diphenylcyclopropane (**1**) with 48 mg (0.00104 g-atom) of sodium in 40 ml of liquid ammonia. After stirring for 1 hr there was added dropwise, *via* a syringe, 0.240 ml (0.264 g, 0.00208 mol) of benzyl chloride to the red solution. After stirring an additional 5 min hexane was added and the ammonia was allowed to evaporate. The sodium salts were then removed from the hexane solution by filtration, and after removal of the hexane the residue was crystallized from 95% ethanol. Gas chromatography showed that the mother liquors consisted mainly of 1,1-diphenylbutane (**2**) and 1,1-diphenyl-2-methylpropane along with recovered 1-methyl-2,2-diphenylcyclopropane. Infrared and nmr spectra and gas chromatography of the crystalline material indicated that it consisted of a mixture of stilbene and 1,2,2-triphenylpentane. A total of 224 mg of this material was obtained and the gas chromatogram on a 4-ft column of SF-96 at 275° indicated that about one-half of it was stilbene. The yield of stilbene is hence calculated to be about 60%. The stilbene was removed from the desired 1,2,2-triphenylpentane by dissolving the crystalline material in 3.5 ml of acetic acid and adding 0.160 g of pyridinium perbromide; the precipitated stilbene dibromide was then filtered off and recrystallized from methanol, mp 228–234°. Most of the acetic acid was then removed from the filtrate by heating on a steam bath with a stream of air blowing over the solution. Water was then added, and the residue was extracted with hexane. The hexane layer was washed once with sodium bisulphite solution and water and finally was dried with sodium sulfate. Removal of the solvent gave a residue which was crystallized from methanol: mp 110–111°. On analysis, nmr and ir spectra were consistent with this material being 1,2,2-triphenylpentane: nmr (CCl_4) δ 7.05 (10 H, singlet, *gem*-diphenyl), phenyl attached to –CH– (5 H, complex multiplet),[14] 3.2 (1.8 H, singlet), 2.1–1.86 (1.8 H, complex multiplet), 1.4–0.8 (5.3 H, complex multiplet, CH_2CH_3).

Anal. Calcd for $C_{23}H_{24}$: C, 91.94; H, 8.06. Found: C, 91.87; H, 8.12.

Reduction of the Sodium Salt of 2,2-Diphenylcyclopropanecarboxylic Acid.—A solution consisting of 78.0 mg (0.00339 g-atom) of sodium in 37 ml of predried liquid ammonia was prepared using the usual vacuum apparatus,[8] and then 0.282 g (0.00108 mol) of sodium 2,2-diphenylcyclopropanecarboxylate was added. After stirring for 0.5 hr near −33°, dry hexane was added to the red solution and the ammonia was allowed to evaporate. Water was then added, and the hexane layer was separated. The hexane layer was washed once with dilute base, and this aqueous layer was combined with the previous one. After drying the solvent was removed from the hexane layer, but nothing remained. The aqueous layers were acidified with HCl and then extracted with ether. The ether layers were dried, and the solvent was removed to leave a residue which was crystallized from hexane to give 0.227 g (81%) of 4,4-diphenylbutanoic acid, mp 104–105°. Infrared and nmr spectra were identical with those of authentic material.[15] A similar experiment performed at a much higher concentration of sodium in liquid ammonia (11 g/100 ml) gave essentially the same result as that above.

Reduction of the Sodium Salt of 1-Methyl-2,2-diphenylcyclopropanecarboxylic Acid.—The sodium salt of racemic 1-methyl-2,2-diphenylcyclopropanecarboxylic acid was prepared from the corresponding acid in a manner analogous to that described above for the preparation of the sodium salt of 2,2-diphenylcyclopropanecarboxylic acid. A solution consisting of 56.4 mg (0.00245 g-atom) of sodium dissolved in 50 ml of predried ammonia was prepared, and then 0.200 g (0.000730 mol) of the solid sodium salt was added. Work-up in the manner described above gave 0.189 g (94%) of 4,4-diphenyl-2-methylbutanoic acid, mp 101–102°. Infrared and nmr spectra were identical with those of the authentic material.[16] A second reaction was performed using the sodium salt prepared from optically active (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, $[\alpha]_{Hg}$ +40.3°. The resulting 4,4-diphenyl-2-methylbutanoic acid was found to be completely racemic.

Reduction of the Sodium Salt of *trans*-2-Phenylcyclopropanecarboxylic Acid.—A solution consisting of 72 mg (0.00314 g-atom) of sodium dissolved in 50 ml of ammonia was prepared in the usual manner, and then 0.229 g (0.00141 mol) of sodium *trans*-2-phenylcyclopropanecarboxylate was added. In this case the solution did not turn red. After the usual work-up the residue was crystallized from cold hexane to give 0.164 g (72%) of 4-phenylbutanoic acid, mp 50–51°. Infrared and nmr spectra were identical with those of the authentic material.[17]

Reduction of Sodium 2,2-Dimethylcyclopropanecarboxylate.—A solution consisting of 81 mg (0.00352 g-atom) of sodium dissolved in 31 ml of ammonia was prepared in the usual manner, and then 150 mg (0.00132 mol) of sodium 2,2-dimethylcyclopropanecarboxylate was added. The solid salt dissolved, and the solution was allowed to stand for 0.5 hr. The reaction was worked up in the usual manner to yield 100 mg (84%) of the free acid. The acid was converted into the methyl ester by reaction

(14) *ortho* protons produce a quadruplet centered at 6.4 ppm and the *meta,para* protons form a multiplet centered at 6.4 ppm.

(15) S. Wawzonek and J. Kozikowski, *J. Amer. Chem. Soc.*, **76**, 1641, (1954).

(16) Prepared by J. L. Webb, unpublished results.

(17) Purchased from Aldrich Chemical Co., Milwaukee, Wis.

with diazomethane and was analyzed by vpc (EGIP column) and nmr which showed the sample to be pure and uncontaminated with acyclic esters.

Reduction of Sodium Cyclopropanecarboxylate.—A solution consisting of 80 mg (0.00348 g-atom) of sodium dissolved in 34 ml of ammonia was prepared in the usual manner; then 150 mg (0.00167 mol) of sodium cyclopropanecarboxylate was added; and the solution was stirred for 45 min. The reaction mixture was worked up in the usual manner to yield 0.087 g (73%) of the free acid. The acid was converted into the methyl ester by reaction with diazomethane, was analyzed by vpc (PEDS column) and nmr, and was shown to be pure and uncontaminated by methyl butyrate or methyl isobutyrate.

Reduction of 1-*n*-Pentyl-1-methyl-2,2-diphenylcyclopropane.—A solution consisting of 24 mg (0.00104 g-atom) of sodium in 35 ml of predried liquid ammonia was prepared in the usual manner, and then 0.0919 g (0.000331 mol) of crystalline 1-pentyl-1-methyl-2,2-diphenylcyclopropane was added. This material was seen to float on the surface of the solution and did not appear to dissolve. The solution was stirred for 3 hr near −33°; then dry hexane was added; and the ammonia was allowed to evaporate. The hexane solution was then filtered to remove the remaining sodium, and the solvent was then removed. The residue crystallized on standing, mp 55–56.5°. Recovered was 85 mg (94%) of the starting material.

A result similar to that above was obtained when the reduction was carried out in a much more concentrated sodium in liquid ammonia solution (3.78 g in 37 ml).

In one part of a modified U tube, made from thick-walled tubing, was placed 80.0 mg (2.9×10^{-4} mol) of the hydrocarbon, $[\alpha]^{30}_{546}$ −43.3°, and in the other part was placed 24 mg (9.6×10^{-4} g-atom) of sodium. The tube was then connected to the vacuum system and evacuated. Predried ammonia (25 ml) was distilled into the part of the tube containing the sodium, and the tube was then sealed and allowed to come to room temperature. The solid hydrocarbon was then tipped into the ammonia solution. The crystals did not dissolve but turned red at the surface. The mixture was allowed to remain at room temperature for about 15 hr. The reaction mixture was worked up in the usual manner. The residue was shown by vpc to consist of two components with the minor component being only 2–3% of the mixture. Since the residue was completely racemic, we did not attempt to isolate the components in the pure state. The nmr spectrum was consistent with the major components being 1,1-diphenyl-3-methyloctane: nmr (CCl_4) δ 7.05 (10 N, singlet), 3.95 (1 H, J = 8 cps), 2.35–0.75 (18.2 H, complex).

Registry No.—Sodium, 7440-23-5; ammonia, 7664-41-7; 1,2,2-triphenylpentane, 6393-07-3; 4,4-diphenylbutanoic acid, 14578-67-7; 4-phenylbutanoic acid, 1821-12-1; 4,4-diphenyl-2-methylbutanoic acid, 17413-46-6; 1,1-diphenyl-3-methyloctane, 17413-47-7; **1**, 17413-48-8.

Acknowledgment.—We wish to express our appreciation to Dr. B. Garrett for the esr spectra. Thanks are also due to Dr. G. Davis for repeating several experiments.

Oxymercuration–Demercuration of 7-Substituted Norbornenes and Norbornadienes

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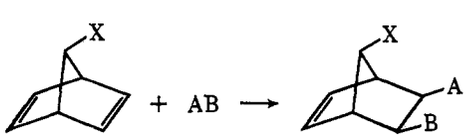
Received April 30, 1968

The oxymercuration–demercuration of *syn*- and *anti*-7-hydroxy- and -acetoxynorbornenes gave high yields of *exo,syn*- and *exo,anti*-2,7-dihydroxynorbornanes, respectively. 7-Acetoxynorbornadiene was converted into a mixture of *exo,syn*-2,7-dihydroxynorbornene-5 and *endo,endo*-3,5-dihydroxynortricyclene. 7-Hydroxynorbornadiene experienced an oxidative rearrangement to yield benzaldehyde as the sole reaction product. The synthetic utility and mechanistic implications of these reactions are discussed.

Recent papers from these[1,2] and other laboratories[3,4] have described the marked propensity for certain 7-substituted norbornenes and norbornadienes to react with electrophilic reagents through the *syn* double bond (eq 1). The stereochemistry of the resultant



(1)

X = OH, $OOCCH_3$, $OC(CH_3)_3$

syn adduct is generally *exo,cis* although in some cases concomitant *endo,cis* addition to the *syn* double bond has been noted.[3,4] The tendency of these mono- and diolefins to experience preferential reaction of the *syn* double bond in spite of the potentially adverse steric factors presented by the 7 substituent was unanticipated.[5] The observed selectivity for *syn* addition has been rationalized by the proposition that apparently adverse steric factors were overcome by a strong electronic effect.[1,3,4] While the nature of this electronic effect was vague, it seemed likely that stabilization of the *syn* transition state by coordination of the attacking electrophile by both the double bond and the oxygen-bearing 7 substituent was an important feature of these reactions.[1,6,7]

Brown and coworkers have recently described the oxymercuration–demercuration of olefins as a convenient synthetic route to Markovnikov-oriented alcohols.[8] Particularly pertinent results described by

(1) Diimide reduction: W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Amer. Chem. Soc.*, **89**, 410 (1967).

(2) Silver nitrate complexation: B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967).

(3) Peroxidation, alkyllithium, carbene additions: G. W. Klumpp, A. H. Veefkind, W. L. deGraaf, and F. Bickelhaupt, *Ann.*, **706**, 47 (1967).

(4) Diazomethane addition: J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

(5) For example, calculations based on molecular models indicated that the diimide reduction of 7-acetoxy- or *t*-butoxynorbornadiene would favor the *anti* double bond by a factor of 24:1. See ref 1.

(6) A chelated structure has been suggested to account for the remarkable stability of the silver nitrate–*syn*-7-acetoxynorbornene complex.[2] This complex has been isolated from ethanolic solution as a stable, crystalline compound, mp 146–149° dec. W. C. Baird, Jr., and J. H. Surridge, unpublished results.

(7) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963), discuss the directive effects of the hydroxyl group on the Simmons–Smith reaction. See also ref 4.

(8) (a) H. C. Brown and P. Geoghegan, Jr., *ibid.*, **89**, 1522 (1967); (b) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967); (c) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).