Reductive Cleavage of Polycyclic Oxetanes

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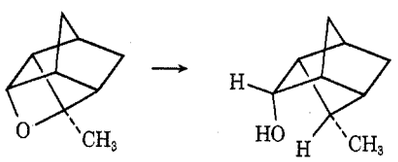
The action of hydrogen and catalysts, lithium–ethylenediamine, lithium–ammonia, and alane on several polycyclic oxetanes is reported. In general, ring cleavages were effected which produced several novel alcohols.

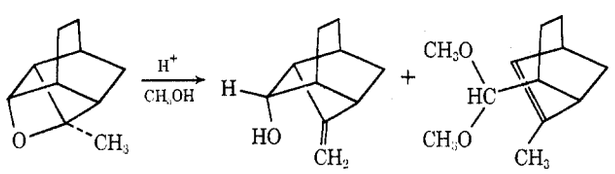
In previous publications[1] we have emphasized the synthetic utility of polycyclic oxetanes.[2] For example, oxetane **1** can be cleaved by lithium aluminum hydride in refluxing *N*-ethylmorpholine to form alcohol **2**.



1 **2**

This mode of cleavage was unexpected,[3] since it has the characteristics of an electrophilic rather than a nucleophilic ring opening. Significantly, certain oxiranes undergo cationic-type rearrangements on treatment with lithium aluminum hydride.[4]

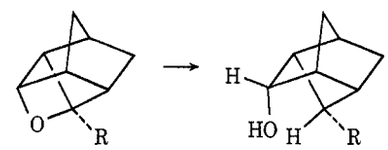
By contrast, acid-catalyzed ring openings may result in two-bond cleavages, as shown by the example below.[1b] In fact, many of these oxetanes are so sensitive to acid that they cannot be readily handled as such; in these cases they may be routinely converted to unsaturated dinitrophenylhydrazones on treatment with acidic 2,4-dinitrophenylhydrazine.[1b,c]



In this report we wish to detail and expand our results on the synthesis and cleavage reactions of polycyclic oxetanes. In particular, the cleavage of oxetanes with hydrogen and metal catalysts, lithium–amine combinations, and alane are discussed.

Results and Discussion

Catalytic Hydrogenolyses.—Aromatic oxetanes which contain the Ar–CO linkage may be smoothly hydrogenolyzed with hydrogen and Raney nickel[1b] but not with palladium on charcoal. It is believed that the cleavages proceed with retention of configuration on the basis of chemical-shift data and by analogy with similar cleavages.[5] Thus, oxetanes **3a** and **3b** are converted to tricyclic alcohols **4a** and **4b** on treatment with hydrogen and nickel. The stereochemical assignments are based on the chemical shifts of the benzylic and naphthylic protons (δ 4.12 and 4.75 ppm, respectively). The deshielding[6] of these protons is attributed to steric interactions with syn hydroxyl groups, a well-documented effect.[7]

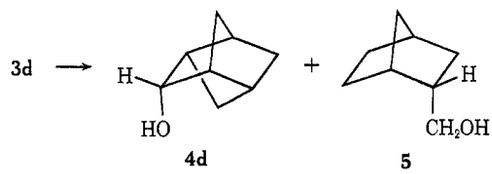


3 **4**

a, R = C_6H_5
b, R = α-$C_{10}H_7$
c, R = $C_6H_5CH_2$
d, R = H

The most interesting result in this series of experiments was observed on reduction of the benzyl oxetane **3c**. In view of the examples provided by Bonner[8] it was anticipated that hydrogenolysis would be accompanied by debenzylation. In fact, only hydrogenolysis was observed: **3c** → **4c**. Relief of ring strain provides added driving force for the hydrogenolysis pathway, but the presence of the aromatic ring was shown to be necessary since the methyl analog **1** proved to be stable to the same reaction conditions.

Lithium–Amine Reductions.—Reduction of an oxetane with a metal–amine combination had been reported only once previously.[9] This procedure appeared promising as a general method for reductive cleavage of oxetanes under relatively mild conditions. The first case studied was the symmetrical system **3d**. On treatment with lithium in ethylenediamine (EDA)[10] the oxetane was reduced to a mixture of two alcohols in the ratio 25:75. The major product was identified as tricyclo[3.3.0.$0^{3,7}$]octan-2-ol (**4d**). The minor prod-



4d **5**

(1) (a) R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 79 (1969); (b) R. R. Sauers and J. A. Whittle, *J. Org. Chem.*, **34**, 3579 (1969); (c) R. R. Sauers and K. W. Kelly, *ibid.*, **35**, 498 (1970); (d) R. R. Sauers, K. W. Kelly, and B. R. Sickles, *ibid.*, **37**, 537 (1972).

(2) S. Searles, Jr., in "Heterocyclic Compounds with Three- and Four-membered Rings," Part II, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, Chapter IX.

(3) S. Searles, E. F. Lutz, and M. Tamres, *J. Amer. Chem. Soc.*, **82**, 2932 (1960); C. Schaal and J. Seyden-Penne, *C. R. Acad. Sci., Ser. C*, **266**, 217 (1968).

(4) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); J. P. Monthéard and Y. Chrétien-Bessière, *Bull. Soc. Chim. Fr.*, 336 (1968); H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

(5) For an example which involves a tetrahydrofuran, see S. Mitsui, Y. Senda, and K. Konno, *Chem. Ind. (London)*, 1354 (1963); for an example which involves an oxirane, see S. Mitsui and Y. Nagahisa, *ibid.*, 1975 (1965).

(6) The analogous protons in phenylcycloalkanes are found at δ 3.4–2.7; *cf.* A. M. Khan, F. J. McQuillin, and I. Jardine, *J. Chem. Soc. C*, 136 (1967).

(7) S. Winstein, P. Carter, F. A. R. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5247 (1965).

(8) W. A. Bonner, *ibid.*, **82**, 1382 (1960); nearly equivalent amounts of cleavage to toluene and ethylbenzene were observed on hydrogenolysis of β-phenylethanol.

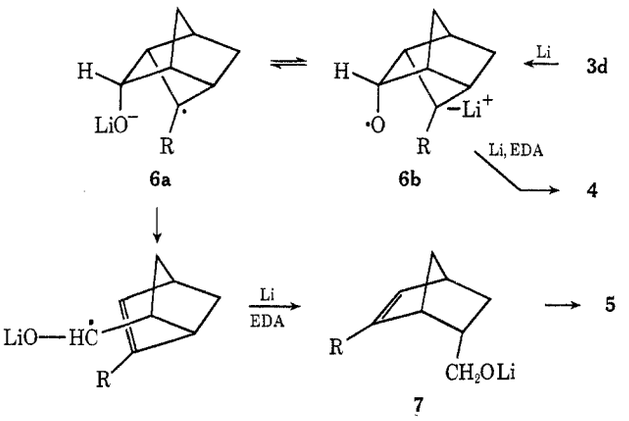
(9) A. S. Hallsworth and H. B. Henbest, *J. Chem. Soc.*, 3571 (1960).

(10) This procedure was patterned after that used for epoxide reductions: H. C. Brown, S. Ikegami, and J. H. Kawakami, *J. Org. Chem.*, **35**, 3243 (1970).

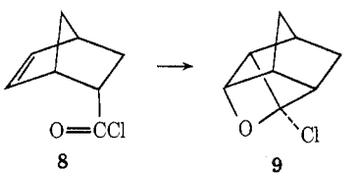
uct proved to be *endo*-2-norbornylmethanol (**5**) by direct comparison of infrared and nuclear magnetic resonance data.

A reasonable, if incomplete, mechanistic picture of the course of these reactions is presented in Scheme I. The exact timing of the electron and proton transfers cannot be specified, but it seems likely that the unsaturated carbinol salt **7** (R = H) is an intermediate. Krapcho and Nadel[11] had shown that norbornene can be reduced by lithium in amines, an important analogy in this context.

SCHEME I



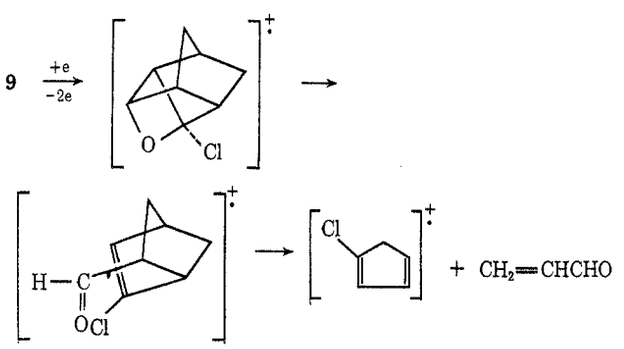
These results proved useful in providing chemical evidence for the structure of the photocyclization product of acid chloride **8**.[12] The photoproduct proved to be an isomer of **8** as shown by elemental analyses and mass spectral data. Interestingly, no significant peak could be detected in the molecular ion region, but a prominent pair of peaks in the ratio of *ca.* 3:1 did appear at *m/e* 100 and 102, respectively. We interpret this data in terms of structure **9** for the photoproduct in view of the fact that the methyloxetane (**1**) likewise undergoes cleavage of acrolein in the mass spectrometer. These cleavages seem best rationalized in terms of initial ring openings followed by reverse Diels–Alder reactions (Scheme II).

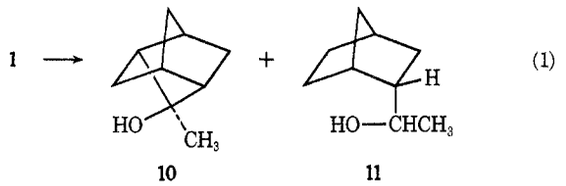


Although oxetane **9** was inert toward ethanolic silver nitrate solution, it was smoothly reduced by lithium in EDA to an identical mixture of **4d** and **5** as was obtained from **3d**. In all likelihood, **9** was initially reduced to **3d**, and thence to **4d** and **5**.

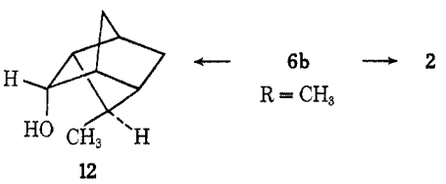
A mixture of five products was obtained on extension of the lithium–EDA reduction to the methyloxetane **1**. Three of the products were identified by spectral comparisons and are shown in eq 1. The

SCHEME II

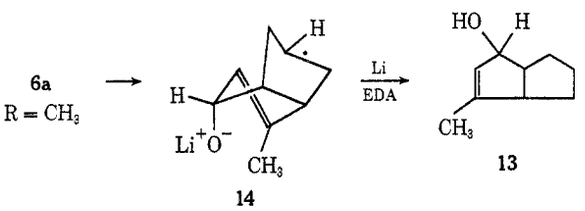




other two products were identified tentatively and were assigned structures **12** and **13**. Compound **12**



is a reasonable product to be expected from protonation of **6b** (R = CH_3). Product **13** is best explained *via* cleavage of **6a** (R = CH_3) to form radical **14**,



which is further reduced. This mode of cleavage has precedent in the behavior of the unsubstituted radical.[1c]

Under milder reaction conditions (lithium in liquid ammonia) unreacted oxetane **1** was recovered along with compound **2** (81%) and smaller amounts of **10** and **12**. On the other hand, the phenyloxetane **3a** was reduced completely and gave mainly alcohol **4a** under these conditions.

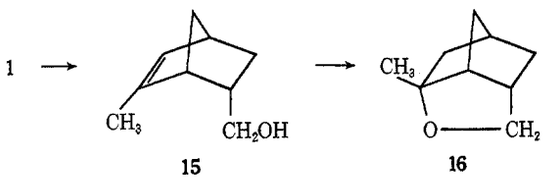
The usefulness of these reductions is restricted by the lack of high selectivity in the direction of cleavage of unsymmetrical oxetanes.[9] A similar lack of selectivity was observed in reductions of epoxides by amine–lithium systems,[10] and the direction of cleavage is apparently a function of structure of the oxide and of the rates of electron transfer.

Alane Reduction.—In an effort to circumvent the vigorous conditions required (*vide supra*) for lithium hydride reductions of these polycyclic oxetanes, the

(11) A. P. Krapcho and M. E. Nadel, *J. Amer. Chem. Soc.*, **86**, 1096 (1964).

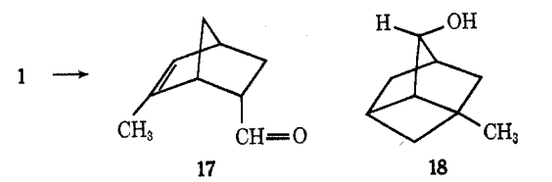
(12) This case represents the first example of an intramolecular photocyclization of an acid chloride. For intermolecular examples, see D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

use of alane was investigated.[13] Oxetane **1** was cleanly reduced under mild conditions (refluxing ether) with the formation of an 80:20 mixture of products. The major product was assigned structure **15**, since the nmr spectrum indicated a primary alcohol, one olefinic proton, and a methyl bonded to a double bond. This material rapidly and spontaneously cyclized on standing and the new material is believed to be the ether **16**.[14]



15 **16**

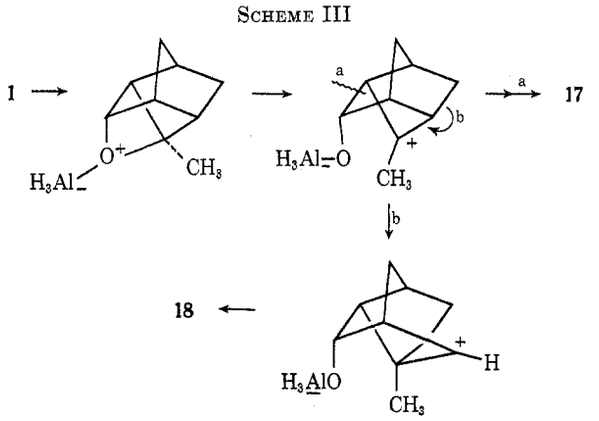
Presumably, the oxetane rearranges first to aldehyde **17**, which ultimately undergoes reduction to the carbinol. The minor product was a tricyclic secondary alcohol, and the methyl resonance was unsplit in the nmr spectrum. Although several possibilities exist, the most likely structure for this product is **18**. Thus,



17 **18**

the reduction proceeds *via* initial complexation followed by rearrangements, as shown in Scheme III.

SCHEME III



The aldehyde **17** is formed as a complex and most likely undergoes reduction directly. The tricyclic alcohol could arise by path b, a sequence which has precedent in the behavior of the deoxy derivative.[1d]

Summary and Conclusions.—Several new reactions of polycyclic oxetanes have been reported, including catalytic hydrogenolysis, metal amine reductions, and reduction with alane. In general, these reactions represent useful synthetic transformations and further extend the usefulness of oxetanes as synthetic intermediates.

(13) (a) P. T. Lansbury, D. J. Scharf, and V. A. Pattison, *J. Org. Chem.*, **32**, 1748 (1967); (b) E. L. Eliel, L. A. Pilato, and V. G. Badding, *J. Amer. Chem. Soc.*, **84**, 2377 (1962).

(14) The corresponding demethyl analog undergoes a similar cyclization in the presence of acid; see H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959).

Experimental Section

Nuclear magnetic resonance (nmr) data was obtained from a Varian Model T-60 spectrometer in carbon tetrachloride solutions using tetramethylsilane as an internal standard. Infrared spectra (ir) were determined on a Perkin-Elmer Model 137 spectrometer. Gas chromatograms (gc) were obtained on a Varian Aerograph Model A-90-P chromatograph using the following columns: A, 18% Carbowax 20M (5 ft × 0.25 in.); B, 10% Carbowax 20M (5 ft × 0.25 in.). Mass spectra were determined at 70 eV on an Hitachi RMU 7 mass spectrometer.

5-Norbornen-2-yl Phenyl Ketone.—A solution of 24.7 g (0.20 mol) of norbornene-5-carboxaldehyde[15] (*ca.* 90% endo) in 15 ml of anhydrous ether was added over 1 hr to the Grignard reagent prepared from 34.1 g (0.20 mol) of bromobenzene and magnesium (6.0 g, 0.24 g-atom) in 50 ml of ether. The reaction mixture was heated at reflux for 0.5 hr, after which time it was quenched with 200 ml of water and 150 ml of 10% hydrochloric acid. The mixture of alcohols was extracted into ether, which was washed with sodium bicarbonate solution and saturated salt solution. The dried extracts were evaporated to give 21.5 g (54%) of a white solid, mp 66–68° (lit.[16] mp 66–67°) after crystallization from pentane.

The alcohols were oxidized to 5-norbornen-2-yl phenyl ketone using Jones[17] reagent. The yield of ketone was 67% (12 g) and the nmr spectrum was identical with that of a sample isolated (alumina chromatography) from a commercial mixture of the endo and exo isomers (Aldrich Chemical Co.).

5-Norbornen-2-yl Benzyl Ketone.—The above sequence was repeated using benzylmagnesium chloride and 98% *endo*-5-norbornene-2-carboxaldehyde. A 65% yield of carbinols was isolated, bp 160–162° (12 mm).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.16; H, 8.60.

Oxidation with Jones reagent[18] gave a 52% yield of ketone: bp 156–161° (12 mm); nmr δ 7.25 (s, 5 H, ArH), 5.85 (octet, 2 H, HC=); ir (film) 5.85 μ (s, C=O).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.17; H, 7.88.

5-Norbornen-2-yl 1-Naphthyl Ketone.—1-Naphthylmagnesium bromide was treated with 90% *endo*-5-norbornene-2-carboxaldehyde to yield a mixture of carbinols in 34% yield, mp 101–102° after crystallization from methanol and hexane.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.24. Found: C, 86.22; H, 6.93.

Oxidation with Jones[17] reagent gave the ketone in 55% yield as a colorless solid: mp 78–79° after crystallization from methanol; nmr δ 7.68 (m, 7 H, ArH), 5.90 (octet, 2 H, HC=); ir (Nujol) 6.22 μ (s, C=O).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found:[19] C, 86.93; H, 6.52.

Preparation of Oxetanes. General.—The ketones were photocyclized in an immersion apparatus with the light from a 450-W Hanovia lamp. Filters and solvents are indicated for each compound. A slow nitrogen stream was passed through the solutions during irradiation. The reactions were monitored by ir or gc and were carried to >95% completion.

3-Phenyl-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (3a).—Irradiation of 6 g of ketone in 220 ml of hexane with a Pyrex filter gave an oil which was washed with potassium permanganate solution and chromatographed on basic alumina to yield 4.2 g (70%) of oxetane **3a**, nmr δ 7.27 (s, 5 H, ArH), 4.62 (q, 1 H, HCO).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.38; H, 7.34.

3-Benzyl-4-oxatetracyclo[4.2.1.0^{2,5}0.^{3,7}]nonane (3c).—A solution of 8.05 g of ketone and 3.40 g of piperylene in 450 ml of spectral grade benzene was irradiated (Corex filter). After removal of solvents the residue was distilled to give 4.26 g (53%) of oxetane **3c**: bp 89–91° (0.75 mm); nmr δ 7.22 (s, 5 H, ArH), 4.44 (q, 1 H, HCO); ir 10.23 (s), 14.30 μ (s).

(15) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 117 (1928).

(16) F. Kasper and H. G. Muller, *J. Prakt. Chem.*, **34**, 283 (1966).

(17) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(18) The procedure of C. Djerassi, R. R. Engle, and A. Bowers [*J. Org. Chem.*, **21**, 1547 (1956)] was followed.

(19) We are indebted to A. Rousseau for the preparation and purification of this sample.

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.15; H, 7.74.

3-(1-Naphthyl)-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (3b).—A solution of 6.0 g of ketone in 210 ml of hexane was irradiated using a Pyrex filter. A viscous oil was obtained which was washed with potassium permanganate solution and chromatographed on basic alumina to yield 3.27 g (55%) of a viscous oil, nmr δ 8.57–7.0 (m, 7 H, ArH), 4.72 (q, 1 H, HCO).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.62; H, 6.62.

3-Chloro-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (9).—A sample of 5-norbornene-2-carbonyl chloride was prepared by addition of acryloyl chloride to cyclopentadiene. A solution of the chloride (149 g, 1.65 mol) in 150 ml of anhydrous ether was added to 104.5 g (1.58 mol) of cyclopentadiene in 325 ml of ether over 1 hr. The resulting solution was stirred at 25° for 19 hr, after which the volatile materials were evaporated. The residue was distilled at 63.5° (4.5 mm) to give 158 g (64%) of the adduct. The exo–endo ratio (5:95) was estimated from the relative amounts of methyl esters produced on methanolysis.

A solution of 15 g (0.096 mol) of the acid chloride in 1.2 l. of dry benzene was purged with dry nitrogen and irradiated with the unfiltered light from a 450-W Hanovia lamp. The total irradiation time was 14 days and the lamp well was cleaned every other day. The solution was washed vigorously with an aqueous solution of potassium hydroxide (40 g in 200 ml). The benzene layer was dried over potassium carbonate, after which the solvents were removed *in vacuo*. The residue was distilled to yield 1.5 g (10%) of an oil: bp 44° (0.025 mm); nmr δ 4.62 (q, J = 2, 4 Hz, 1 H, HCO), 2.72 (m, 1 H), 2.48 (m, 1 H), 2.14 (m, 2 H), 1.58 (m, 3 H); ir 9.10 (s), 9.30 (s), 9.92 (s), and 11.35 μ (s).

Anal. Calcd for C_8H_9ClO: C, 61.35; H, 5.79; Cl, 22.64. Found: C, 61.30; H, 5.96; Cl, 22.64.

2-*syn*-Hydroxy-4-*anti*-phenyltricyclo[3.3.0.0^{3,7}]octane (4a).—A slurry of **3a** (0.90 g, 0.0045 mol) and *ca.* 1 g of Raney nickel (W. R. Grace Co., #28 in water) in 25 ml of ethanol was pressured to 40 psi with hydrogen. After 2 hr the catalyst was removed by filtration and the solvents were evaporated, giving 0.88 g (98%) of a white solid, mp 77–81°. Crystallization from petroleum ether–methylene chloride gave colorless needles: mp 88–89°; nmr δ 7.05 (t, 5 H, ArH), 4.12 (s, 1 H, HCO), 3.81 (d, J = 3 Hz); ir (Nujol) 3.11 μ (br, OH).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.06. Found: C, 83.72; H, 8.04.

The same product was obtained on refluxing a slurry of 1 g of catalyst and 1.0 g of **3a** in 25 ml of ethanol which contained 4.0 ml of 100% hydrazine hydrate.[20] The oxetane was inert to the action of 10% palladium on charcoal with hydrogen in ethanol.

2-*syn*-Hydroxy-4-*anti*-(1-naphthyl)tricyclo[3.3.0.0^{3,7}]octane (4b).—A slurry of oxetane **3b** (0.70 g, 0.0028 mol) and *ca.* 1 g of Raney nickel (W. R. Grace Co., #28 in water) in 25 ml of ethanol was pressured to 14 psi with hydrogen. After 17 hr the catalyst was removed and the solvents were evaporated. A white solid was obtained which was triturated with pentane. The insoluble material (0.49 g) was crystallized from benzene–hexane: mp 174–175°; nmr δ 8.60–6.90 (m, 7 H, ArH), 4.75 (s, 1 H, HCO), 3.97 (d, J = 3 Hz, 1 H); ir (Nujol) 3.11 μ (br, OH).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.24. Found: C, 86.39; H, 6.98.

2-*syn*-Hydroxy-4-*anti*-benzyltricyclo[3.3.0.0^{3,7}]octane (4c).—A slurry of 10 g of damp Raney nickel[21] was stirred at reflux in a solution of 1.07 g of **3c** in 30 ml of ethanol. After 4 hr the reaction was stirred overnight at 25°. Water (150 ml) was added and the product was extracted into pentane. The extracts were washed with water and dried (Na_2SO_4) prior to evaporation. An oil was obtained which was distilled in a molecular still at 26 mm (block temperature 175–180°): yield 0.96 g (89%); nmr δ 7.11 (s, 5 H, ArH), 3.62 (d, J = 3 Hz, HCO), 3.12 (t, J = 7.5 Hz), 2.55 (d, J = 7.5 Hz, CH_2Ar); ir 2.95 μ (br, OH).

A 2,4-dinitrobenzoate derivative was prepared, mp 113.5–114.5°.

Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.46; H, 5.19; N, 6.66.

Reduction of 3d with Lithium in EDA.—A solution of 8.5 g (0.07 mol) of **3d** in 35 ml of pentane was added to 45 ml of ethylenediamine in a flask equipped with a magnetic stirrer and condenser. The flask was placed in an 80° bath and lithium wire (1.9 g, 0.28 g-atom) was added over 0.5 hr with vigorous stirring. The reaction mixture was stirred for an additional 6 hr and subsequently hydrolyzed. The products were extracted into pentane and ether, and the combined extracts were washed with water and dried (Na_2SO_4). Evaporation of the extracts and sublimation of the residue gave 4.8 g (55%) of a white solid. Gc analysis (B, 150°) revealed two components in a 25:75 ratio. The minor product was identified as *endo*-2-norbornylmethanol[22] (**5**) by ir and nmr comparisons. The major component was shown to be tricyclo[3.3.0.0^{3,7}]octan-2-ol (**4d**) by comparative ir and nmr spectra.[1]

Reduction of 9 with Lithium in EDA.—Similar treatment of chlorooxetane **9** gave a 70% yield of alcohols. Gc analysis showed two products in a ratio of 73:27. The two components were isolated and identified as **4d** and **5**, respectively, by comparative ir and nmr spectra.

Reduction of 1. A. Lithium in EDA.—Similarly, oxetane **1** gave an 81% yield of alcohols. Gc separation (A, 160°) revealed five components in the following relative amounts: **11** (10%), **10** (18%), **13** (10%), **12** (7%), and **2** (55%). The three known compounds were separated by preparative gc and identified by comparisons of their ir spectra with those of authentic samples.[23]

The nmr spectrum of **13** showed the following absorbances: δ 5.26 (m, 1 H, HC=), 4.18 (m, 1 H, HCO), 2.99 (br m, 1 H), 2.44 (s, 1 H, OH), 1.65 (d, J = 1 Hz, CH_3); ir 3.00 (s, OH), 9.92 (s, CO), 6.06 μ (w, C=C); mass spectrum (70 eV) molecular ion m/e 138, base peaks at m/e 91 and 92, $M^+ - H_2O$ at m/e 120.

Compound **12** showed the following nmr absorbances: δ 4.05 (m, HCO), 2.27 (m), 1.93 (m), 1.27 (d, J = 6 Hz); ir 9.14 (m), 9.37 μ (m); mass spectrum (70 eV) molecular ion m/e 138, base peak m/e 66, prominent ion at m/e 105 ($M^+ - H_2O - CH_3$).

B. Lithium in Ammonia.—Oxetane **1** (0.20 g, 1.47 mmol) in 75 ml of ether and 25 ml of liquid ammonia was allowed to react with 0.29 g (42 mg-atoms) of lithium for 4 hr at reflux. The solvents were allowed to evaporate at room temperature, and the residue was treated with water. Ether extraction followed by gc analysis revealed the following components: **1** (26%), **10** (4%), **12** (10%), **2** (60%).

Reduction of 3a with Lithium in Ammonia.—To a stirred solution of 0.46 g (2.3 mmol) of **3a** in 25 ml of liquid ammonia and 5 ml of pentane was added 0.126 g (18 mg-atoms) of lithium wire. The reaction mixture was stirred at reflux for 1.5 hr, after which the ammonia was evaporated. Water (10 ml) was added to the residue and the products were extracted into ether. Gc analysis (B, 180°) revealed three minor components (10% total) and one major component. The retention time and nmr spectrum of the major product were virtually identical with those of authentic **4a** as prepared above.

Reduction of 1 with Alane.—A solution of alane was prepared by slow addition of 1.20 g (0.032 mol) of powdered lithium aluminum hydride to an ice-cold solution of 1.42 g (0.011 mol) of freshly sublimed aluminum chloride in 100 ml of dry ether. After the resulting mixture was stirred for an additional 1 hr at 25°, a solution of 2.86 g (0.021 mol) of oxetane **1** in 100 ml of ether was added over 15 min. The reaction mixture was then refluxed for 9 hr, after which water was cautiously added until no further reaction was observed. The salts were removed by filtration and the ether was dried (Na_2SO_4) and evaporated. A simple distillation served to remove nonvolatile materials and yielded 2.65 g of an oil. Gas chromatographic analysis on a 15-ft 10% Carbowax 20M column (170°) revealed two components in an 80:20 ratio. On standing, the major component disappeared and a new product with shorter retention time appeared.

The unstable major component **15** was isolated and characterized by its nmr spectrum: δ 5.57 (s, 1 H, HC=), 1.77 (d, J = 1.8 Hz, CH_3), 0.5 (octet, 1 H, 5 endo).[24] The volatile transformation product **16** was isolated as an oil: nmr δ 3.56 (m, 2 H, (CH_2O), 1.22 (s, 3 H, CH_3); ir (film) 9.65 (s), 10.00 μ (s).

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(24) The 5-endo proton in norbornene derivatives frequently appears as an octet at high fields. For examples and references see R. V. Moen and H. S. Makowski, *Anal. Chem.*, **43**, 1629 (1971); E. Pretsch, H. Immer, C. Pascual, K. Schaffner, and W. Simon, *Helv. Chim. Acta*, **50**, 105 (1967).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.98; H, 10.43.

The minor component had mp 99.5–101.5° and was assigned structure **18** on the basis of spectral data: nmr δ 3.99 (br s, 1 H, HCO), 1.11 (s, 3 H, CH_3); ir (Nujol) 3.00 (br, OH), 9.30 (s), 9.45 μ (s).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.92; H, 10.43.

Registry No.—**1**, 22398-67-0; **3a**, 22398-69-2; **3b**, 22398-43-2; **3c**, 22398-41-0; **3d**, 22398-42-1; **4a**, 22398-47-6; **4b**, 22398-48-7; **4c**, 22398-46-5; **4c** 2,4-dinitrobenzoate, 37750-49-5; *endo*-**8**, 37750-50-8; *exo*-**8**, 34733-86-3; **9**, 37750-52-0; **12**, 37750-53-1; **13**, 37750-54-2; **15**, 37750-55-3; **16**, 37750-56-4; **18**, 37750-57-5; 5-norbornen-2-yl phenyl ketone, 37750-58-6; *endo*-norbornene-5-carboxaldehyde, 19926-90-0; bromobenzene, 108-86-1; 5-norbornen-2-ylphenylcarbinol, 13305-26-5; 5-norbornen-2-ylbenzyl ketone, 37750-61-1; benzylmagnesium chloride, 6921-34-2; 5-norbornen-2-ylbenzylcarbinol, 13305-27-6; 5-norbornen-2-yl-1-naphthyl ketone, 36171-23-0; 1-naphthylmagnesium bromide, 703-55-9; 5-norbornen-2-yl-1-naphthylcarbinol, 37750-66-6; cyclopentadiene, 542-92-7.

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Ring Contraction of Bicyclo[2.2.1]heptanes[1]

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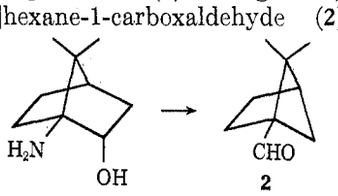
A convenient synthesis of 1-substituted bicyclo[2.1.1]hexanes by ring contraction of 1-substituted bicyclo[2.2.1]heptan-2-ols has been achieved. This method is highly efficient for the synthesis of 5,5-dimethylbicyclo[2.1.1]hexane-1-methanol and 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylic acid from camphor.

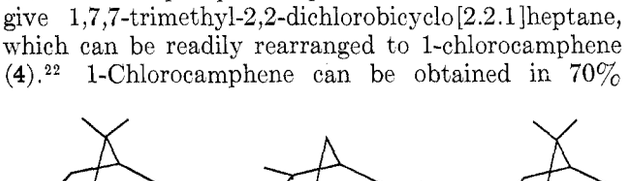
Ring contraction of bicyclo[2.2.1]heptanes has been achieved by deamination of 1-amino-3,3-dimethylbicyclo[2.2.1]heptan-2-ol (**1**)[3] to give 5,5-dimethylbicyclo[2.2.1]hexane-1-carboxaldehyde (**2**) and by



1 **2**

Favorskii rearrangement of 1-bromo-7,7-dimethylnorbornanone[4] to give 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylic acid. Other methods of synthesis of bicyclo[2.1.1]hexanes are known,[5] including the photochemical ring contraction of α-diazo ketones of bicyclo[2.2.1]heptanes and bicyclo[3.1.1]heptanes,[6-9] photolytic cycloaddition of olefins,[10-12] ketone decomposition,[13] solvolysis,[14] intramolecular alkylations,[15-17] and carbene ring contraction.[18] Bicyclo[3.1.1]heptane glycol monotosylates have been rearranged to 2-substituted bicyclo[2.1.1]hexanes and complements this work.[19,20] Many of the above procedures are not synthetically useful if large quantities of materials are desired. We have a procedure by which large quantities of 5,5-dimethylbicyclo[2.1.1]hexane-1-methanol or -1-carboxylic acid can be made in a few steps and in high yield.[21] The sequence utilizes *d*-camphor as the starting material so that all of the products in the sequence are optically active.

Treatment of *d*-camphor (**3**) with phosphorus trichloride and phosphorus pentachloride is known to give 1,7,7-trimethyl-2,2-dichlorobicyclo[2.2.1]heptane, which can be readily rearranged to 1-chlorocamphene (**4**).[22] 1-Chlorocamphene can be obtained in 70%



3 **4**

yield in one step if the by-product, 1,7,7-trimethyl-2-chlorobicyclo[2.2.1]hept-2-ene, obtained in 25% yield, is removed by spinning band distillation. Ozonolysis in methanol[23] at −78° and decomposition of the ozonide with dimethyl sulfide[24] gave 1-chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-one (**5**). Reduction of **5** or the

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