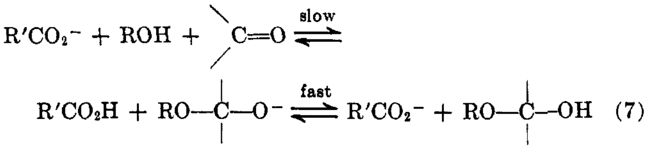

$$R'CO_2^- + ROH + \rangle C{=}O \overset{\text{slow}}{\rightleftharpoons} R'CO_2H + RO{-}\overset{|}{\underset{|}{C}}{-}O^- \overset{\text{fast}}{\rightleftharpoons} R'CO_2^- + RO{-}\overset{|}{\underset{|}{C}}{-}OH \quad (7)$$

and general base (eq 7) catalysis rather than other kinetic equivalents.[28] However, it seems reasonable that concerted catalysis, which combines both processes, would occur much more rapidly (in the absence of the entropy disadvantage), especially since carboxylate acids and bases are very approximately equally effective as catalysts in these reactions.

Although our results strongly suggest that the mechanisms by which the polycarboxylic acid-bases used in this study catalyze the reactions are the ones for general acid and general base catalysis, it is possible that in some of the cases the rate constant for the concerted catalysis mechanism is of the same magnitude as that predicted for the summation of general acid and general base catalysis. In such cases, reaction proceeds in part by concerted catalysis.

Registry No.—Acetaldehyde, 75-07-0; acetone, 67-64-1.

Acknowledgment.—This work was supported in part by a grant (GB4848) from the National Science Foundation.

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[28] W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964).

Some Chemistry of the Dimethyl-1-norbornylcarbinyl System

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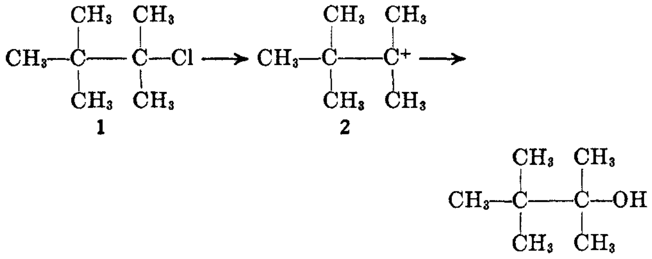
School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey

Solvolysis of dimethyl-1-norbornylcarbinyl chloride proceeds without appreciable anchimeric assistance and leads to the corresponding alcohol under buffered conditions. Treatment with the Lucas reagent leads to a mixture of ring-expanded products, **9** and **10**. The rearranged chlorides lead to alcohol **6** on reaction with silver nitrate.

The gross features of solvolytic reactions of simple aliphatic tertiary systems are well-established. The classic studies of Roberts[1] and Brown[2] and their collaborators serve as "calibration points"[3] for classical ion behavior. For example, the pentamethylethyl cation[2] is generated at an unexceptional rate from the corresponding chloride and is captured by solvent without rearrangement. Under conditions whereby the ion is generated repeatedly, complete scrambling of the methyl groups ensues.

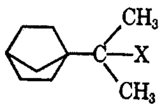


$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl \longrightarrow CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{CH_3}{\underset{CH_3}{C^+}} \longrightarrow CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH$$

1 **2** **3**

On the other hand, incorporation of tertiary centers into highly strained bicyclic systems has led to results which have been interpreted by some workers in terms of bridged intermediates.[4,5]

As an intermediary case, it seemed of interest to investigate the behavior of a tertiary cation generated adjacent to a bridgehead of a bicyclic system. The dimethyl-1-norbornylcarbinyl system **4** seemed ideally suited for this purpose. Solvolysis rates in this system should be uncomplicated by torsional and nonbonded interactions of the type found in norbornyl systems.[4] Carbon skeletal rearrangements would be expected to parallel those observed in the norbornylcarbinyl system,[6] *i.e.*, simple ring expansion.

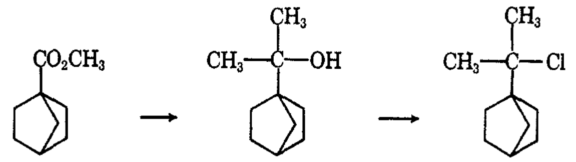


4

(4a, X=Cl)

Results and Discussion

Syntheses.—The desired chloride **4a** could be readily prepared by reaction of dimethyl-1-norbornylcarbinol (**6**) with hydrochloric acid. The alcohol was prepared by treatment of the known ester **5**[7] with methylmagnesium iodide. The structure of alcohol **6** follows from the method of synthesis and the spectral data. The nmr spectrum displayed a single, broad peak at 2.2 ppm and a sharp singlet at 1.2 ppm due to absorption of the six equivalent methyl protons.



5 **6** **4a**

The chloride **4a** likewise exhibited a sharp singlet for the methyl protons. The downfield shift to 1.6 ppm is

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[1] J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, **77**, 5558 (1955).

[2] H. C. Brown and I. Moritani, *ibid.*, **77**, 3623 (1955).

[3] P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 154.

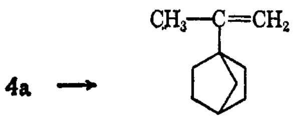
[4] For a lucid summary, see G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

[5] For the opposing point of view, see M. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).

[6] K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963); W. P. Whelan, Jr., Ph.D. Thesis, Columbia University, 1952.

[7] W. R. Boehme, *J. Am. Chem. Soc.*, **81**, 2762 (1959); H. Kwart and G. Null, *ibid.*, **81**, 2765 (1959).

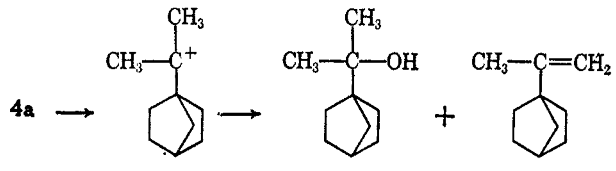
analogous to the shift observed for the methyl protons between *t*-butyl alcohol (1.22 ppm) and *t*-butyl chloride (1.58 ppm).[8] Chemical evidence was furnished by the observation that a 1,1-disubstituted olefin was formed on treatment of **4a** with potassium butoxide. The most reasonable structure for this material is that of structure **7** as evidenced by a strong band at 11.43 μ in the infrared spectrum and the integrated nmr spectrum which showed two olefinic protons as a multiplet at 4.7 ppm. Also in agreement with this structure are the position (1.7 ppm) and appearance of the methyl protons in this spectrum.[8]



7

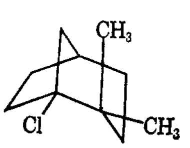
Kinetics.—The rate of solvolysis of chloride **4a** was determined in aqueous ethanol at 35° and compared to the rate of solvolysis of *t*-butyl chloride under identical conditions. The calculated first-order rate constants were 0.280 hr^{-1} (**4a**) and 0.175 hr^{-1} (C_4H_9Cl). The relative rates on this basis are 1.6:1. For comparison, the rate ratio for pentamethylethyl chloride/*t*-butyl chloride is 1.2 (25°).[2] Clearly, anchimeric assistance to ionization is not an important factor in these solvolyses.

Product Studies.—The products of the solvolysis were determined in an experiment in which buffered, aqueous acetone was used as the reaction medium. There was obtained a 75:25 mixture of alcohol **6** and olefin **7**. These products most logically arise from addition and elimination reactions of the classical intermediate **8**.

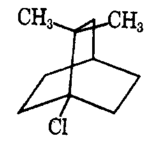


Treatment of chloride **4a** with Lucas reagent was expected to generate ion **8** reversibly. This reaction was found to lead to rapid consumption of starting material with formation of two new products. The ratio of these (2:1) was essentially invarient with time. Preparative separation of these products could not be achieved by gas chromatography although a partial separation was possible by capillary gas chromatography.

These materials appeared to be bicyclic as evidenced by the absence of any absorptions attributable to olefins in either the infrared or the nmr spectrum. Also absent was any indication of a H–C–Cl grouping. All of the methyl peaks (three) in the nmr spectrum were at high field (*ca.* 1.0 ppm), and from the relative intensities it is suggested that two components are present in a 2:1 ratio. These data and mechanistic considerations strongly suggest that the two products in question are 1-chloro-2,2-dimethylbicyclo[3.2.1]octane (**9**) and 1-chloro-2,2-dimethylbicyclo[2.2.2]octane (**10**), respectively.

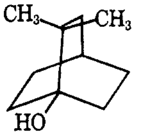


9

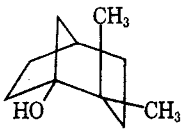


10

Treatment of the alcohol **6** with anhydrous formic acid at room temperature effected an analogous transformation. As before, the isomeric products appeared to be formed in a constant ratio (*ca.* 2:1) throughout the course of the reaction. In this case, the products, as alcohols, could be examined separately for identification purposes. The major component showed two sharp methyl resonance peaks near 1.0 ppm in the nmr spectrum and no H–C–O absorption. The minor component exhibited a sharp singlet near 1.0 ppm. Thus, the major product would appear to be 2,2-dimethylbicyclo[3.2.1]octan-1-ol (**12**) and the minor one 2,2-dimethylbicyclo[2.2.2]octan-1-ol (**11**).



11



12

Significantly, the separate alcohols **11** and **12** were not interconverted under the reaction conditions. On the other hand, treatment of either **11** or **12** with the Lucas reagent produced the same 2:1 mixture of **9** and **10**.

A rational conclusion to be drawn from these results would be that ion **8** is rapidly destroyed by solvent under buffered conditions, but under reversible conditions rearrangement to the thermodynamically more stable ring-expansion products occurs. The fact that formic acid yields the same ratio of the rearranged products as the Lucas reactions suggests that the ions **13** and **14** are equilibrating faster than they are attacked by nucleophiles.[9]

Scheme I outlines a reasonable representation of the kinds of intermediates which are involved in these equilibrations. Since no unrearranged products are obtained from the Lucas and formic acid reactions, ion **8** serves only as a mechanistic bridge between **13** and **14**.

The relative stabilities of the ions implied in Scheme I are based on semiquantitative calculations involving the relative stabilities of the ions *vs.* the relative stabilities of the ring systems. The bicyclo[2.2.1]heptyl system is believed to be *ca.* 6–7 kcal/mole more strained than the bicyclo[2.2.2]octyl system.[10] Substituted bicyclo[3.2.1]octyl systems are probably of comparable stability to bicyclo[2.2.2]octyl systems.[11] These dif-

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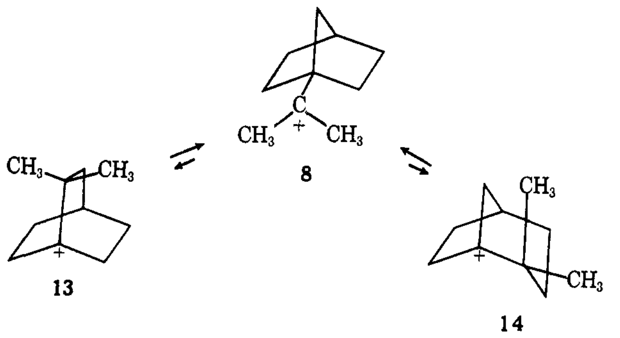
[8] Data of G. V. D. Tiers, quoted in J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1966, p 1115.

[9] Since the stability of the chlorides to the Lucas reagent was not unambiguously demonstrated, the fact that the ratio of **9**/**10** was the same as the ratio of **12**/**11**, might simply reflect a coincidence of the product stabilities and the relative rates of formation of the two systems. Whether the equilibration is complete or only partial cannot be determined from the available data.

[10] E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 302.

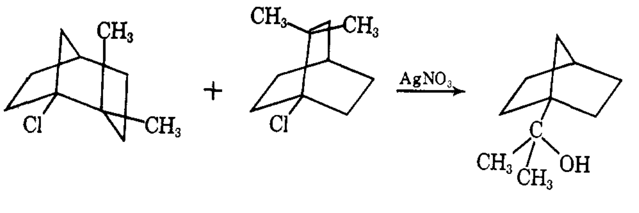
[11] P. von R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Am. Chem. Soc.*, **85**, 1358 (1963); H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961).

Scheme I



ferences are more than compensated for by the greater stability of the cation **8**, probably by a factor of 8–9 kcal/mole.[12]

As a confirmatory test of the above hypothesis, it was of interest to generate ions **13** and **14** under conditions expected to lead irreversibly to products. If, indeed, equilibration of the ionic intermediates is rapid relative to solvent collapse, one would expect the products to be derived mainly from the dimethylnorbornylcarbinyl ion **8**. Acetolysis of the mixture of chlorides in buffered medium led to a mixture of the acetates of all three alcohols **6**, **11**, and **12**, with **6** predominating. The reaction conditions, however, were fairly vigorous and the stability of **6** under these conditions is suspect. More definitive results were obtained on treatment of the chlorides **9** and **10** with silver nitrate solution. The only product of this reaction was dimethyl-1-norbornylcarbonol (**6**).



Thus, all of the results are internally consistent with the picture of equilibrating ions outlined in Scheme I.[13] It is interesting that the product distribution in the formic acid reaction does not result from predominant migration of the more strained C_1–C_7–C_4 bond as is the case in the unsubstituted system.[6] Strain relief alone is not sufficient to overcome the adverse electronic effects in this rearrangement and the product distribution is also affected by the relative stabilities of the ring systems.[14]

Experimental Section

Analyses are by W. Manser, Herliberg, Switzerland. The infrared spectra were determined on a Beckman Model 5A spectrophotometer. Nuclear magnetic resonance spectra were determined on a Varian Model A-60 spectrometer in carbon tetrachloride using tetramethylsilane as an internal standard. Chemical shifts are reported as parts per million (ppm). Gas chromatograms were obtained on a Model A-90P Aerograph instrument in the preparative work. All columns were 0.25-in. o.d. aluminum tubing packed with Chromosorb G and the indicated liquid phases. Capillary gas chromatograms were determined on a Barber-Colman, Model 5000 system using a hydrogen flame ionization detector. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

Dimethyl-1-norbornylcarbinol (**6**).—Alcohol **6** was prepared according to the procedure of Greene, *et al.*,[15] and had mp 66–68° (lit.[15] mp 67–68°).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 73.56, 74.16; H, 11.41, 11.16.

The low carbon analyses probably result from hydrate formation. The calculated values for a hemihydrate are C, 73.63; H, 11.62.

The nmr spectrum of this product in CCl_4 showed a sharp singlet at 1.2 ppm (*ca.* 6 H), a broad peak (1 H) at 2.2 ppm, and other multiplets which overlapped with the methyl resonance peaks (*ca.* 11 H).

Dimethyl-1-norbornylcarbinyl Chloride (**4a**) **Synthesis. In Acetic Acid.**—To a solution of 2.8 g (0.016 mole) of alcohol **6** in 3.0 ml of glacial acetic acid was added 20 ml of concentrated hydrochloric acid. A white solid formed almost immediately which was removed by filtration after 20 min. The solid was dissolved in ether and the solution was washed with water and sodium bicarbonate solution. After drying over magnesium sulfate, the ether was evaporated to yield 2.5 g (79%) of a white solid, mp 40–42°.

Careful gas chromatographic analysis on a 150 ft × 0.01 in. column of Ucon 50 HB-2000 revealed that the crude project was a mixture of three components in the ratio 83:12:5.

Sublimation of the crude solid raised the melting point to 41–42°. The analytical sample was prepared by collection of the major component from the effluent of a 9-ft Carbowax 20 M column at 120°.

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.60; H, 9.85; Cl, 20.55. Found: C, 69.62; H, 9.76; Cl, 20.29.

The nmr spectrum of this material displayed a sharp singlet (*ca.* 6 H) at 1.6 ppm which overlapped a complex multiplet (*ca.* 10 H). A broad absorption (1 H) also appeared at 2.2 ppm. The infrared spectrum showed medium absorptions at 6.93, 7.37, 8.24, 8.96, and 15.57 μ.

In Methylene Chloride.—A solution of 1.3 g (0.0084 mole) of alcohol **6** in 15 ml of methylene chloride was cooled to 0°. A stream of dry hydrogen chloride was passed into the solution for 0.5 hr. The solution was allowed to warm to room temperature after which the gas was bubbled through the solution for 1 hr. The resulting solution was washed with water, sodium carbonate solution, and water. After drying over magnesium sulfate, the solvent was carefully evaporated to give 0.8 g (55%) of chloride **4a**. The retention time of this material on the Carbowax column coincided with that for the major product prepared in the above experiment. Again, a peak caused by a small amount of other components was seen, presumably the unresolved rearranged chlorides **9** and **10**.

Reaction of 4a with Lucas Reagent.—The Lucas reagent was prepared by the addition of 9.6 g of anhydrous zinc chloride to 6 ml of concentrated hydrochloric acid. To this solution was added 300 mg of chloride **4a** in 1.5 ml of methylene chloride. The reaction was allowed to run for 3 hr at which time the layers were separated. The aqueous phase was extracted twice with methylene chloride and the combined extracts were washed with sodium bicarbonate solution and water. The dried extracts were evaporated to give 190 mg (63%) of a waxy solid, mp 147–148°. Repeated sublimation raised the melting point to 154–155° (sealed capillary). Gas chromatographic analysis on Carbowax 20 M, Apiezon L, Silicones FS 1265, and TCEP columns failed to resolve this mixture. The Ucon capillary column (see above)

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(12) Estimated from solvolytic and other data; see P. von R. Schleyer in "Advances in Alicyclic Chemistry," Vol. I, H. Hart and G. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, p 299; see also J. L. Franklin and F. H. Field, *J. Chem. Phys.*, **21**, 550 (1953). Recent results by R. S. Bly and E. K. Quinn (153rd National Meeting of the American Chemical Society, Miami, Fla., 1967, Abstract O-91) also suggest a similar stability for **13** and **14**.

(13) It is recognized that the products of these reactions are also dependent on the relative rates of collapse of the ions with nucleophiles. The bridgehead ions **13** and **14** would presumably react faster than **8**, but no quantitative estimate can be made for this partitioning.

(14) Similar interpretation can be applied in the case of the dimethylcyclopropylcarbinyl system; see P. Bruylants and A. Dewael, *Bull. Classe Sci., Acad. Roy. Belg.*, **14**, 140 (1928). Kinetically controlled conditions lead to ring-closed products *via* the stable, tertiary ion. Thermodynamically controlled reactions lead to methylpentenyl derivatives, allowing relief of the cyclopropyl ring strain. The dimethylcyclobutylcarbinyl system is more complex in that the ring-expansion step is irreversible; see C. F. Wilcox, Jr., and M. E. Mesirov, *J. Am. Chem. Soc.*, **84**, 2757 (1962).

(15) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

gave a partial separation into a *ca.* 2:1 mixture and about 1% of third component.

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.60; H, 9.85; Cl, 20.55. Found: C, 69.73; H, 10.20; Cl, 20.69.

The nmr spectrum of this mixture could also be interpreted on the basis of a 2:1 mixture if it is assumed that the minor component possesses the singlet methyl peak at 1.15 ppm and the major component is responsible for the pair of singlets of 1.1 and 1.0 ppm. The tentative structures assigned to these materials are 9 and 10 for the major and minor products, respectively.

The same reaction was repeated with reaction times of 40 min and 40 hr. In both cases the ratios of the rearranged products were the same as that found in the 3-hr experiment, namely, 2:1. Appreciable starting material was still present in the 40-min experiment.

Hydrolysis of 4a. Product Study.—A solution of 1.0 g of the chloride **4a** in 15 ml of an 80% acetone–20% water mixture which also contained 1.0 g of potassium bicarbonate was stirred at 26° for 60 hr. Addition of 20 ml of saturated ammonium chloride solution produced two layers. The organic phase was separated and dried over magnesium sulfate. Gas chromatographic analysis of this product on a 9-ft Carbowax 20 M column (150°) revealed two major components. Samples of these were collected for spectral determinations. It was concluded from infrared and nmr comparisons that the component with the shorter retention time was olefin **7** and the other product was alcohol **6**, mp 63–65°. The weight ratio of these two was calculated by peak 23:77, respectively. The molar ratio on this basis was 25:75.

Kinetic Study.[4]—The solvolytic rate constants for chloride **4a** and *t*-butyl chloride were determined in 80% ethanol by titration of the liberated hydrogen chloride with 0.060 *N* sodium hydroxide solution. The bath temperature was held at 35 ± 0.05° and methyl red was the indicator. The calculated first-order rate constants were 0.280 for **4a** and 0.175 hr^{-1} for *t*-butyl chloride.

2-(1-Norbornyl)propene (7).—A solution of potassium *t*-butoxide in *t*-butyl alcohol was prepared by the reaction of 0.34 g of potassium with 30 ml of dry alcohol. Chloride **4a** (1 g, 0.0058 mole) was added and the mixture was heated at reflux for 5 hr. Most of the alcohol was removed by careful distillation. The residue was treated with ether to remove the olefin. The ether was washed with water, dried over magnesium sulfate, and evaporated to give the olefin, $n^{25}D$ 1.474.

A pure sample was obtained by gas chromatography on Apiezon L. The infrared spectrum of this material showed bands at 3.32 (w), 6.08 (m), 9.06 (w), and 11.43 (s) μ. The nmr spectrum showed a complex multiplet centered at 4.7 (2 H), a broad singlet at 2.2 (1 H), and complex absorptions extending from 1.7 to 1.2 ppm (13 H). The strong sharp doublet at 1.7 ppm was undoubtedly due to the methyl group. The infrared data matches that given for **7** in ref 15.

Treatment of Alcohol 6 with Formic Acid.—A solution of 1.0 g of alcohol **6** in 5 ml of anhydrous formic acid was allowed to stand at 25° for 2 days. Gas chromatographic analysis (Carbowax 20 M) revealed the presence of two alcohols and two formate esters. The solution was diluted with 50 ml of water and extracted with three 10-ml portions of ether. The combined extracts were washed with water, sodium bicarbonate solution, and water. The solution was dried over magnesium sulfate and added to a slurry of 4 g of lithium aluminum hydride in 200 ml of ether. After 2 hr, enough water was added to decompose the excess hydride and form a dense precipitate. The clear ether solution was separated by filtration and the precipitate was washed thoroughly with ether. The combined extracts were dried and evaporated to give 0.65 g (65%) of a white solid. Gas chromatography of this material on either a 15-ft Carbowax column or a 150 ft × 0.01 in. Castorwax column revealed three components in the ratio 66:30:4. The two major components were collected by preparative gas chromatography. The major product was assigned the structure 2,2-dimethylbicyclo[3.2.1]-octan-1-ol and the second isolable component was assigned the structure 2,2-dimethylbicyclo[2.2.2]octan-1-ol on the basis of the following evidence.

The infrared spectrum of the major component (**12**) showed peaks at 2.9 (w), 7.27 (m), 7.37 (m), 9.27 (s), and 10.66 (m) μ. The nmr spectrum of this product displayed complex absorption from 1.0 to 2.2 ppm (12 H). A sharp doublet of relative area 6 was centered at 0.9 ppm.

The other component (**11**) showed infrared absorptions at 2.9 (w), 7.29 (m), 7.39 (m), 9.28 (s), 10.38 (m), and 10.69 (m) μ. This material showed a singlet at 1.0 (6 H) and complex absorption between 2.1 and 1.1 ppm (12 H) in the nmr spectrum. Elemental analyses were carried out on a sublimed sample of the mixture of products.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.74; H, 12.13.

Control Experiment.—Formic acid solutions of the separated alcohols were allowed to stand at room temperature for several hours. Gas chromatographic analysis revealed little or no interconversions of the alcohols and formates in the two cases.

Treatment of Alcohols 11 and 12 with Lucas Reagent.—Solutions of 100 mg of either alcohol **11** or **12** in 3 ml of methylene chloride were stirred at room temperature for 48 hr with 1 g of Lucas reagent. At the end of this period, the layers were separated and the organic phase was washed with water, sodium bicarbonate solution, and water. The dried extracts were evaporated to give the same mixtures of chlorides as shown by gas chromatography on a 150 ft × 0.01 in. Apiezon L column. The nmr spectra of these products were identical with each other and identical with those of the samples of **9** and **10** prepared above from **4a**.

Treatment of Chlorides 9 and 10 with Silver Nitrate.—A solution of 500 mg (3 mmoles) of silver nitrate and 100 mg (0.6 mmole) of chlorides **9** and **10** in 10 ml of 80 % aqueous acetone was stirred at 25° for 3 days. The excess silver nitrate was destroyed by addition of sodium chloride and the resulting solution was filtered to remove the silver chloride.

The organic products were removed by addition of saturated ammonium chloride solution to the filtrate followed by ether extraction. The extracts were dried over magnesium sulfate and evaporated. Gas chromatography on a 15-ft Carbowax column or a 150 ft × 0.01 in. Castorwax column revealed one main component (>98%) with the same retention time as that of alcohol **6**. The infrared and nmr spectra of this material were identical with those of **6**.

Acetolysis of Chlorides 9 and 10.—To a solution of 15 ml of glacial acetic acid containing 0.02 mole of sodium acetate was added 2.0 g (0.011 mole) of the mixture of chlorides **9** and **10**. The solution was heated at reflux for 1 week after which the mixture was quenched with water and extracted with ether. The dried extracts were treated with lithium aluminum hydride followed by hydrolysis to give a crude mixture which was analyzed directly by gas chromatography on a 15-ft Carbowax column. The major component (*ca.* 60%) was unreacted starting material. Also present were dimethyl-1-norbornylcarbinol (24%), alcohol **12** (7%), alcohol **11** (4%), and an unidentified peak (5%).

Registry No.—**4a,** 10498-92-7; **6,** 10498-93-8; **7,** 10498-94-9; **9,** 10498-95-0; **10,** 10498-96-1; **11,** 10588-74-6; **12,** 10561-80-5.

Acknowledgments.—We wish to acknowledge the generous financial support of the National Institutes of Health (GM-8701). We are also grateful to Professor J. Wilt for unpublished data.