B.—Attempted iodo lactonization of Ib with iodine in aqueous bicarbonate solution[15] also resulted only in recovery of 88% of the starting material.

Hunsdiecker Reaction[6b] of 14α,17α-Etheno-16α-carboxypregn-5-en-3β-ol-20-one Acetate (Ib).—A slurry of 210 mg of Ib and 203 mg of mercuric oxide in 25 ml of carbon tetrachloride was stirred and heated to reflux for 1 hr in the dark. Then 132 mg of solid iodine was added and stirring and heating were continued for an additional 105 min. The mixture was then cooled and filtered. The filtrate was extracted with aqueous sodium bicarbonate (9 mg of Ib was recovered on work-up of the aqueous phase). The organic phase was washed with aqueous sodium thiosulfate, dried over anhydrous magnesium sulfate, and evaporated to dryness under reduced pressure to give 251 mg of crude product. Crystallization from acetone–hexane gave iodo lactone IX in a yield of 142 mg (54.5%) as white crystals: mp 227–228°; ν^{Nujol} 1789, 1733, 1704 cm^{-1}; the nmr spectrum (100 Mc) showed singlets at 1.05 (18-CH_3 and 19-CH_3), 2.03 (acetate), and 2.29 (21-CH_3) quartets at 4.73 (CH bearing O of lactone) and 5.14 (CH bearing iodine), and multiplets at 3.17 (CH bearing of C=O lactone), and 5.40 (C-6—H).

Anal. Calcd for $C_{26}H_{33}IO_5$: C, 56.53; H, 6.02. Found: C, 56.80; H, 6.04.

The mother liquors on tlc examination (25% ethyl acetate in benzene on silica gel plates) showed two main components and trace amounts of two other substances. The major components on the basis of their R_f values seemed to be IX and the anhydride XI, described below. As the fastest moving spot was that of the anhydride, the presence of normal Hunsdiecker products was precluded. The infrared and nmr spectra of the mother liquors were consistent with their being a mixture of IX and anhydride XI, the composition estimated by nmr being three parts of IX to one part of XI. Attempted chromatogaphy of the mother liquors on silica gel led to detection of iodine color in the first eluted fractions. The column was therefore rapidly eluted with ethyl acetate and the eluate was partitioned between aqueous sodium bicarbonate and ethyl acetate. The aqueous layr afforded 33.5 mg of impure starting acid (nmr) while the neutral fraction consisted mainly of a 2:1 mixture of the iodo lactone IX to anhydride XI (nmr and tlc). Chromatography was again attempted on the recovered neutral fraction with similar results, 17.5 mg of acid and 39 mg of neutral fraction being recovered. It was subsequently demonstrated that stirring pure iodo lactone IX with silica gel in ethyl acetate leads to slow partial decomposition to form a carboxylic acid.

Anhydride of 14α,17α-Etheno-16α-carboxypregn-5-en-3β-ol-20-one Acetate (XI).—After a solution of 0.54 g of Ib in 2.0 ml of acetic anhydride had been left at room temperature overnight, the acetic anhydride was distilled under reduced pressure. The residue was crystallized twice from acetone to give XI, in a yield of 255 mg: mp 211–213°; ν^{Nujol} 1820, 1745 (sh), 1735, 1690 cm^{-1}; the nmr spectrum showed singlets at 2.03 (methyl of acetate) and 2.23 (21-CH_3), a quartet at 3.88 (CH bearing anhydride), a multiplet at 5.46 (vinyl hydrogen at C-6), and a pair of doublets at 6.22 and 6.34 (J = 6.3 cps, vinyl hydrogens at C-15 and C-16).

Anal. Calcd for $C_{52}H_{60}O_9$: C, 74.71; H, 7.89. Found: C, 74.52; H, 7.93.

Hunsdiecker Reaction[6b] of 2-Norbornene-5-carboxylic Acids.—A mixture of *endo-* and *exo*-2-norbornene-5-carboxylic acids (Aldrich Chemical Co.) was analyzed by nmr spectroscopy and found to consist of 69% *endo* isomer and 31% *exo*. Iodo lactonization[14,15] led to the isolation of 26% *exo* acid and of iodo lactone corresponding to the presence of 67% *endo* acid.

A slurry of *endo*-2-norbornene-5-carboxylic acid (regenerated[18] from the iodo lactone prepared above[15,16]) and 483 mg of mercuric oxide in 20 ml of carbon tetrachloride was stirred and refluxed for 45 min in the dark. Then 584 mg of solid iodine was added to the mixture and refluxing was resumed for 1 hr. After the reaction mixture had cooled, it was filtered, and the filtrate was extracted with cold, aqueous sodium bicarbonate. (Work-up of the aqueous extract failed to reveal the presence of any carboxylic acid.) The carbon tetrachloride solution was washed with aqueous sodium thiosulfate, dried over anhydrous magnesium sulfate, filtered, and then evaporated to dryness under reduced pressure to afford 583 mg of crude iodo lactone X. Crystallization from ether–hexane solution gave X, identical with the iodo lactone prepared above, in a yield of 384 mg (64%): mp 56–58°; ν^{CHCl_3} 1790 cm^{-1}; the nmr spectrum showed a doublet at 3.94 (CH bearing I), and a broad doublet at 5.08 (CH bearing O of lactone).[19]

The nmr spectrum of the mother liquors (186 mg) indicated that at least 80% of this material was also iodo lactone X.

Registry No.—Ia, 5498-14-6; Ib, 7732-49-2; IX, 7732-47-0; X, 7732-50-5; XI, 7771-28-0.

Acknowledgments.—We are deeply grateful to Dr. J. Colson of the Hooker Chemical Co. for the 100-Mc nmr spectra and spin decoupling experiments.

[18] J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4083 (1959).

[19] NOTE ADDED IN PROOF.—After this manuscript was submitted, a detailed study of the nmr spectrum of X was published. See R. M. Moriarty, H. Gopal, H. G. Walsh, K. C. Ramey, and D. C. Lini, *Tetrahedron Letters*, 4555 (1966).

Carbonium Ion Reactions of 3-Nortricyclylcarbinyl Systems

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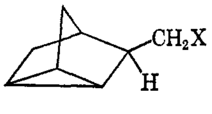
Products of several carbonium ion reactions of 3-nortricyclylcarbinyl systems have been examined. In all cases, *exo,exo*-tricyclo[3.2.1.0^{2,4}]octan-6-ol was a major product, along with unrearranged nortricyclylcarbinol and bicyclo[3.2.1]oct-2-en-7-ol. Experiments bearing on these interconversions are reported.

As an outgrowth of our studies on ring-expansion reactions of polycyclic systems[1] and as a result of an inherent interest in the chemistry of cyclopropylethyl systems,[2] we initiated studies of reactions involving cationic intermediates in the 3-nortricyclylcarbinyl system (**1**).[3,4] In addition to the many interesting possibilities for rearrangements in this system, this study offered promise of providing information concerning the stereoelectronic requirements involved in participation of cyclopropyl groups in solvolysis reactions of β-cyclopropylethyl systems.[5] At the inception of



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[1] (a) R. R. Sauers and J. A. Beisler, *J. Org. Chem.*, **29**, 210 (1964); (b) R. R. Sauers and R. J. Tucker, *ibid.*, **28**, 876 (1963); (c) R. R. Sauers, *Tetrahedron Letters*, 146 (1961); (d) R. R. Sauers, R. A. Parent, and H. M. How, *Tetrahedron*, **21**, 2907 (1965).

[2] R. R. Sauers and R. Ubersax, *J. Org. Chem.*, **31**, 495 (1966).

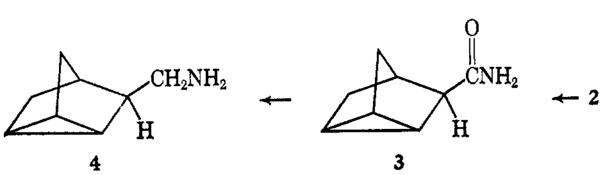
[3] Preliminary results were reported earlier; see R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964).

[4] K. B. Wiberg and G. Wenzinger [*J. Org. Chem.*, **30**, 2278 (1965)] have published some related results.

[5] For a recent review, see P. G. Gassman and F. V. Zalar, *J. Am. Chem. Soc.*, **88**, 2252 (1966). See also M. Hanack and H. M. Ensslin, *Tetrahedron Letters*, 4445 (1966).

this study, the only definitive examples of participation of this type involved relatively flexible systems or trishomocyclopropenyl systems. This account expands and details our earlier[3] communication on these questions.

Syntheses.—The systems chosen for study were 3-nortricyclylcarbinylamine (**1**, X = NH_2) and arene sulfonate esters of 3-nortricyclylcarbinol (**1**, X = OSO_2Ar). The key starting material for the preparation of these materials was the known[6] acid (**2**, 3-nortricyclene carboxylic acid). Reduction of amide **3** of this acid with lithium aluminum hydride afforded amine **4** in good yield. Reduction of the acid itself with lithium aluminum hydride produced carbinol **5**. The spectral properties of these intermediates were consistent with the assigned structures (see the Experimental Section).



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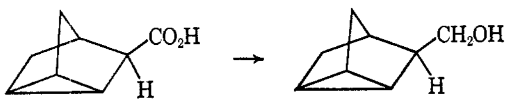
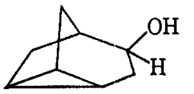


2 **5**

Results

The deamination of amine **4** in acetic acid with nitrous acid proceeded smoothly at room temperature with the formation of a complex mixture of acetate esters. Examination of the alcohols obtained by reduction of the crude acetates with lithium aluminum hydride revealed the presence of five products on gas chromatographic analysis. Unrearranged alcohol **5** accounted for only 11% of the product mixture. The major product accounted for 68% of the components and was shown to be tricyclic by the absence of absorptions in the olefinic regions in both the infrared and nmr spectra. As likely structures, the two ring-expansion products (**6** and **7**) were considered. Independent syntheses for **6** and **7** were devised which are described below. Ketone **8** had been prepared earlier by Moore and coworkers,[7] and could be converted to desired alcohol **7** with lithium aluminum hydride by inverse addition. This alcohol proved to be one of the minor products (11%) of the deamination reaction.



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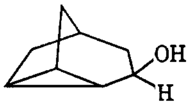

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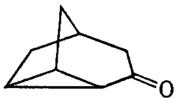

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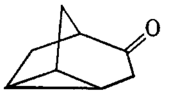

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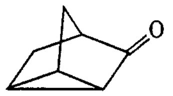

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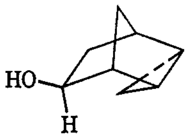
Isomeric ketone **9** was not known at the inception of this study.[8] A promising route to its preparation involved the ring expansion of nortricyclanone **10** with diazomethane.[9] In practice, this reaction led to a satisfactory yield of ketone **9** which was contaminated with about 1% of **8**. Reduction of **9** with lithium aluminum hydride gave desired alcohol **6** which was also shown to be different from the major product from the deamination reaction.

The demonstration by Winstein and Sonnenberg[10] that a cyclopropyl ring can participate in solvolysis reactions by a formal 1,3 shift, led to speculations that the unknown alcohol might be either **11** or **12**.[11] The problem was readily resolved by the synthesis of **12**[12] by methylene transfer[13] to *exo*-5-hydroxynorbornene (**13**). The product of this reaction and the unknown alcohol proved to be identical as shown by a comparison of infrared and nmr spectra.



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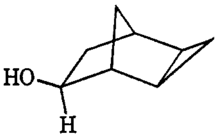

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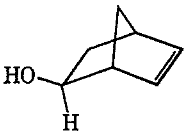

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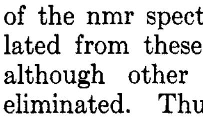
The last unidentified component of the deamination mixture was an unsaturated bicyclic alcohol as evidenced by the presence of strong absorption at 14.52 μ in the infrared spectrum and by complex absorption between τ 4.0 and 4.8 in the nmr spectrum. The close correspondence of the splitting patterns with those of the olefinic protons of bicyclo[3.2.1]oct-2-ene[1b] coupled with mechanistic speculations (see below) supported structure **14**, *exo*-bicyclo[3.2.1]oct-2-en-7-ol for this material. Confirmation of these ideas by independent synthesis of **14**, completed the product analysis of the deamination mixture. The successful synthesis of **14** originated with the observation that solutions of 3-bromobicyclo[3.2.1]oct-2-ene in formic acid exhibited only one proton in the olefinic proton region of the nmr spectrum. The bromo formate ester isolated from these solutions was assigned structure **15** although other isomers cannot be unambiguously eliminated. Thus, the proton on C_2 appears as a



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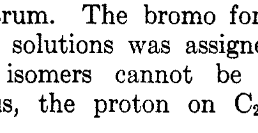

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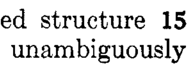

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(6) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 4116 (1950).

(7) W. R. Moore, W. R. Moser, and J. E. La Prade, *J. Org. Chem.*, **28**, 2200 (1963).

(8) Simultaneous with our studies, G. T. Lumb and G. W. Whitham [*Tetrahedron*, **21**, 500 (1965)] have reported a synthesis of **9**. We thank Professor Whitham for informing us of his result prior to publication and for his helpful comments.

(9) H. O. House, E. J. Grubbs, and W. F. Gannon [*J. Am. Chem. Soc.*, **82**, 4099 (1960)] have shown that there is a preference for migration of groups containing sp^2 carbons over saturated functions.

(10) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

(11) Precedent for this type of rearrangement was lacking at the time, however. G. E. Cartier and S. C. Bunce [*ibid.*, **85**, 932 (1963)] found no evidence for such participation in their studies on the deamination of β-cyclopropylethylamine.

(12) We thank Professors Wiberg and Wenzinger[4] for a sample of this alcohol which they prepared by hydroboration of *exo*-tricyclo[3.2.1.$0^{2,4}$]-octene. See also A. K. Colter and R. C. Musso, *J. Org. Chem.*, **30**, 2462 (1965).

(13) H. E. Simmons, E. P. Blanchard, and D. R. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964); E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

doublet at τ 3.8 in both **15** and **16**. The HCO proton appears as a doublet with splitting of 6 cps at τ 4.8,[14] in support of the *exo* stereochemistry. Reduction of this adduct with sodium in ammonia gave **14** directly.[15]

Acetolysis of the *p*-toluenesulfonate and *p*-bromobenzenesulfonate esters of 3-nortricyclylcarbinol yielded the same products as the deamination reaction with the exception of **7**. The relative amounts of the various products are summarized in Table I.

Table I

Product Distributions for Reactions of X-Substituted **1** (%)

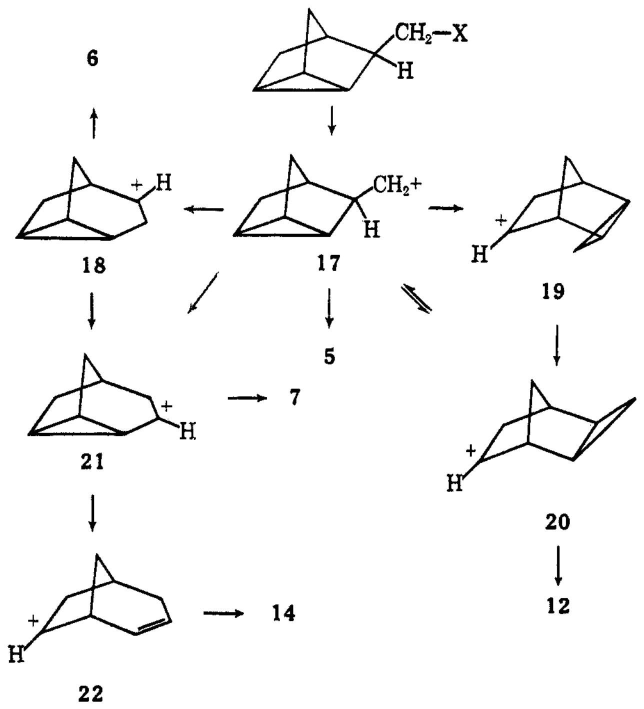
Product	Starting material, X		
	NH_2	OTs[a]	OBs[b,c]
5	11.5	35.5	22
6	2.5	3	8
7	11.5	0	0
12	68	37	47
14	6.5	24.5	23

[a] 110°. [b] 110°. [c] The yields at 85° reported in ref 4 were **5** (9.2), **12** (58.2), and **14** (32.6); **6** and **7** were not detected.

Discussion

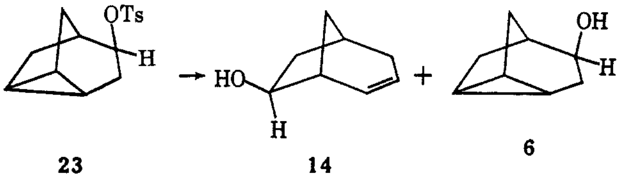
Chart I outlines what appears to be the simplest reaction scheme which accounts for the products observed in these reactions. Classical ions have been used for simplicity in the absence of compelling evidence for other possibilities.

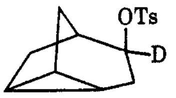
Chart I



The feasibility of the transformation of **19** to **20**, at least under solvolytic conditions has been demonstrated.[4] The interconversions among ions **18**, **21**, and **22** have been verified and are discussed below.

Solvolysis of the *p*-toluenesulfonate ester of alcohol **6** was studied in some detail. Under very mild acetolysis conditions, alcohols **6** and **14** were formed in a 1:1 ratio. In refluxing glacial acetic acid, the ratio of **6** to **14** was 1:2.6. The absence of rearranged tricyclic alcohol **7** seems best explained in terms of its instability to the reaction conditions. Furthermore, Wagner–Meerwein shifts are competitive with hydride shifts in this system as evidenced by the occurrence of deuterium scrambling in the "unrearranged" **6**-*d* formed in the solvolysis of the deuterated analog of **23**. The **14**-*d* formed was likewise not specifically labeled in the 4 position.

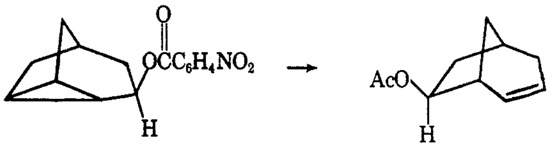




→ **14**-*d* + **6**-*d*

23-*d*

The *p*-toluenesulfonate derivative of alcohol **7** could not be readily isolated. Instead, *p*-nitrobenzoate **24** was prepared and acetolized. The only product was the acetate of unsaturated alcohol **14**.



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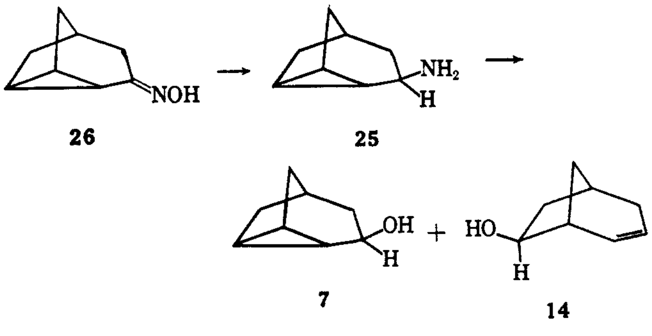
It seemed desirable to produce ion **21** under milder conditions to determine whether alcohol **7** could be a reaction product. Accordingly, amine **25** was prepared by reduction of the oxime **26** with lithium aluminum hydride. Treatment of **25** with nitrous acid at room temperature led to an equimolar mixture of alcohols **7**



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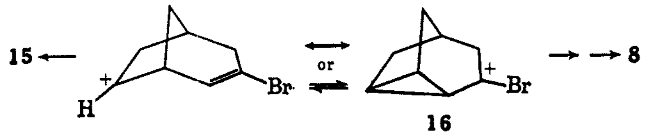
[14] *Cf.* S. J. Cristol, L. K. Gaston, and D. W. Johnson [*Tetrahedron Letters*, 185 (1963)] for analogies and references.

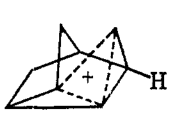
[15] Placement of the formyl group at C-7 rather than C-6 seems justified on mechanistic grounds by analogy with the hydration of **16** to give ketone **8**.[7] The following intermediates would seem to be involved in these reactions.



and **14** in qualitative agreement with the findings of the experiment with **4**.[16]

The broad features of the rearrangements of these nortricyclylcarbinyl systems are reasonably well established by the experiments outlined. Some of the subtler details remain and warrant further investigation. Of prime importance are the nature and number of intermediates involved in the transformations between nortricyclylcarbinyl and tricyclo[3.2.1.0^{2,4}]octyl systems. Although the rate data[4] for the solvolysis of 3-nortricyclylcarbinyl brosylate suggest that the transition state lies close in structure to that of the starting system, the product distribution seems abnormal. For example, whereas solvolysis of isobutyl brosylate yields 32% of isobutyl acetate, cyclopentylcarbinyl brosylate affords only 9% of unrearranged product.[17] Increasing the ring strain further as in *exo*-2-norbornylcarbinyl systems[1b,18] results in essentially complete rearrangement. In the case at hand, the potential strain relief should be of the same order of magnitude as that involved in the norbornylcarbinyl cases; yet as much as 35% of unrearranged product was found.[19]

Conceivably, primary ion **17** could be stabilized by interaction with the orbitals of the cyclopropyl ring bonds as symbolized by **27** or **28**.[20]



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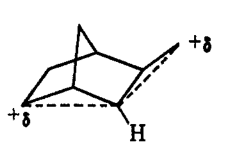

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On the other hand, product distributions could also be controlled by rapid equilibrations between ions (*e.g.*, **17** ⇆ **19** or **17** ⇆ **20**) which are conformationally unsuited for ring enlargement or hydride shifts. The decision between these various alternatives can not be made unambiguously with the available data.

Experimental Section

Analyses were by G. Robertson, Florham Park, N. J., and W. Manser, Herliberg, Switzerland. Infrared spectra were determined in carbon tetrachloride on a Perkin-Elmer Model 21 spectrophotometer unless otherwise noted. Nuclear magnetic resonance (nmr) data were obtained from a Model A-60 spectrometer by Varian Associates in carbon tetrachloride with tetramethylsilane as internal standard. Gas chromatograms were obtained from an Aerograph Model A-90-P instrument and a Barber-Colman flame ionization instrument in the cases where capillary columns were used. The packed columns were 0.25-in. (o.d.) aluminum or copper columns filled with 10–15% liquid phase on Chromosorb P. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

3-Nortricyclylcarbinylamine (**4**).—A solution of 34.5 g (0.252 mole) of 3-nortricyclenecarboxamide[6] in 600 ml of dry tetrahydrofuran was cooled in a nitrogen atmosphere and treated with 38 g (0.1 mole) of lithium aluminum hydride. After the addition was completed, the resulting mixture was stirred at reflux temperature for 18 hr. Cautious addition of water was followed by steam distillation. The distillate (1800 ml) was acidified with concentrated hydrochloric acid. Nonbasic materials were removed by extraction with ether and pentane. The free amine was liberated from the salt by addition of sodium hydroxide solution and collected by ether extraction. Removal of the solvent by evaporation left a residue which was distilled at 79–81° (19 mm) to give 22.9 g (72%) of amine **4**, $n^{22}D$ 1.4962.

Anal. Calcd for $C_9H_{13}N$: C, 77.99; H, 10.63; N, 11.37. Found: C, 78.14; H, 10.90; N, 11.40.

The **phenylthiourea** derivative had mp 136.5–137° and was crystallized from benzene–cyclohexane.

Anal. Calcd for $C_{15}H_{18}N_2S$: C, 69.67; H, 7.02; N, 10.85. Found: C, 69.53; H, 7.24; N, 10.67.

The **picrate** was purified by crystallization from dioxane–benzene and had mp 213–214° dec.

Anal. Calcd for $C_{14}H_{16}N_4O_7$: C, 47.73; H, 4.58; N, 15.91. Found: C, 47.69; H, 4.73; N, 16.32.

Deamination of 4.—A solution of 22.4 g (0.182 mole) of freshly distilled amine **4** in 225 ml of glacial acetic acid was treated with 20 g of sodium nitrite slowly with cooling. The reaction mixture was stirred for 13 hr at room temperature followed by addition of an additional 4 g of sodium nitrite. The resulting solution was diluted with 200 ml of water and treated with a cold solution of 160 g of sodium hydroxide in 300 ml of water. The products were isolated by extraction with ether. Washing of the combined extracts with sodium hydroxide solution, hydrochloric acid, and water was followed by drying of the extracts over anhydrous calcium chloride. Distillation of the solvent yielded 18.86 g (63%) of a colorless liquid, bp 110–116° (23 mm). Gas chromatography of this product on a 10-ft Carbowax 20 M column (167°) and a 12-ft Craig (butanediol succinate) column at 171° indicated only two components in a ratio of 76:24. The smaller peak was enhanced on addition of 3-acetoxymethylnortricyclene. Reduction of the acetate with lithium aluminum hydride gave 13.0 g of an oil. Gas chromatographic analysis on the same two columns revealed two main peaks in the ratio 79:21. The relative area of the minor peak was enhanced on addition of **5**. Three components could be seen on analysis of this mixture on an 8-ft NMP (γ-nitro-γ-methylpimelonitrile) column at 130°. The ratios were difficult to estimate owing to overlapping peaks, but **14** was almost completely resolved and was present to the extent of 6.5%. Analysis at 134° on a 150 × 0.01 ft column of Ucon oil (50-HB-2000) revealed a total of five components all of which could be identified by comparison with known samples. Relative area measurements indicated the presence of **12** (68%), **14** (6.5%), **7** (11.5%), **5** (11.5%), and **6** (2.5%). Resolution of **11** and **6** was incomplete and the reported analysis for **6** is subject to an error of ±1%.

The major peak on the Carbowax column was collected and submitted for elemental analysis.

Anal. Calcd for $C_9H_{12}O$: C, 77.37; H, 9.74. Found: C, 76.98; H, 9.66.

The nmr spectrum of this fraction was essentially identical with that of the sample prepared by Wiberg and Wenzinger.[4] The infrared spectrum was essentially identical with that of the sample prepared in the study (see below).

3-Nortricyclylcarbinol (**5**).—To a slurry of 3.0 g of lithium aluminum hydride in ether was added 9.0 g (0.065 mole) of 3-nortricyclenecarboxylic acid.[6] The mixture was stirred vigorously

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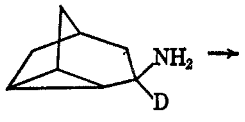
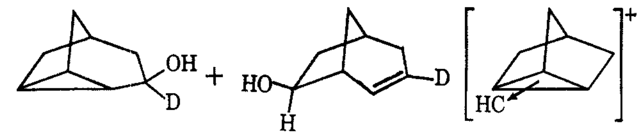
[16] Deamination of the deuterated analog, **25**-*d* led to the same two products with no scrambling of the label. This finding allows elimination of intermediates with the symmetry properties of "homonortricyclonium" ions (i) or their rapidly equilibrating counterparts. The data are consistent with less symmetrical forms of cyclopropylcarbinyl cations, *e.g.*, "bisected" forms; see P. von R. Schleyer and G. W. van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).



25-*d*



i

[17] G. Le Ny, *Compt. Rend.*, **250**, 368 (1960).

[18] J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **86**, 609 (1964).

[19] This type of argument is not without ambiguities since bicyclo[2.2.1]-heptane-7-methyl *p*-bromobenzenesulfonate yields 62% unrearranged acetate on acetolysis; see R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966).

[20] S. Winstein, P. Bruck, P. Radlick, and R. Baker [*J. Am. Chem. Soc.*, **86**, 1867 (1964)] have performed some relevant calculations. An analogy for **28** is the postulated transition state for mercurideboronation of 5-norbornene 2-boronates; see D. S. Matteson and J. O. Waldbillig, *ibid.*, **86**, 3788 (1964).

for 5 hr and kept at 25° overnight. The complex was decomposed with water and the solids were removed by filtration. The filtrate was evaporated to yield 8.4 g of crude alcohol. Distillation at 10 mm gave 7.0 g (87%) of product boiling between 89 and 92° [lit.[4] bp 92–95.5° (9.5 mm)].

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.11; H, 9.87.

The nmr spectrum showed a doublet at τ 6.67 (2 H) with 7-cps coupling and complex absorption between 9.0 and 8.0 (9 H). Strong infrared absorption (film) appeared at 9.59, 12.42, and 2.84 μ.

The **p-toluenesulfonate** ester of **5** was prepared in the usual way but could not be induced to crystallize.

The **p-bromobenzenesulfonate** was prepared in the usual way and purified by crystallization from methanol. The purified sample had mp 59.5–61.5° (lit.[4] mp 59–61°).

Anal. Calcd for $C_{14}H_{15}BrO_3S$: C, 48.99; H, 4.41. Found: C, 48.66; H, 4.45.

The **acetate** of **5** was prepared by treatment of a 1.43-g sample with 10 ml of acetic anhydride which contained 0.95 g of anhydrous sodium acetate. After heating at reflux for 1.5 hr, the reaction was quenched with water and the acetate ester was extracted into ether. The extracts were washed with sodium hydroxide solution and water. Evaporation of the dried extracts yielded 1.3 g of pure ester which was purified by molecular distillation at 0.7 mm.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.11; H, 8.33.

The nmr spectrum showed a singlet (3 H) at τ 8.07 and a doublet (2 H) at 6.14 with 7-cps coupling. Complex absorption (9 H) appeared between τ 9.15 and 8.10. Carbonyl absorption appeared at 5.74 μ in addition to strong bands at 7.32 and 9.68 μ in the infrared spectrum.

Solvolysis of 5-Tosylate.—Treatment of 12 g (*ca.* 0.043 mole) of crude tosylate with a solution of 7.8 g of sodium acetate in 2.5 ml of acetic anhydride and 50 ml of acetic acid for 66 hr at 110° served to acetolyze the tosylate. The acetates were extracted into ether after quenching the reaction mixture with 300 ml of water. The combined extracts were washed with sodium carbonate solution and water and then dried. Evaporation gave 8.0 g of crude product. Distillation at 10 mm gave 5.6 g (*ca.* 78%) of acetates bp 89–94°. The mixture of acetates was reduced with lithium aluminum hydride in ether to give a mixture of alcohols. From 1.5 g of acetates was obtained 1.1 g (98%) of alcohols. Analysis of this mixture by gas chromatography on the Ucon column indicated four main products which were identified by comparison with the known samples. Further confirmation of the identities was furnished by comparison of the nmr spectrum of the product with the spectra of the individual components. The results of the gc analysis were **5** (35.5%), **14** (24.5%), **12** (*ca.* 37%), and **6** (*ca.* 3%). The nmr analysis yielded the following percentages: **5** (36%), **14** (21%), and **12** + **6** (43%). The NMP column cleanly separated **14** from the other major products **5** and **12**; the relative percentage of **14** from area measurements was 20%.

Solvolysis of 5-Brosylate.—Acetolysis of 1.70 g of the brosylate ester of **5** was effected at 110° over a 53-hr period. The product alcohols (0.60 g 97%) were isolated as before and analyzed by gas chromatography on the Ucon column. There was found **5** (22%), **14** (23%), **12** (*ca.* 47%), and **6** (*ca.* 8%). These components could be identified by characteristic peaks in the nmr spectrum also. The NMP column revealed the presence of 23% of **14**, relative to the combined percentages of all the other alcohols.

Tricyclo[3.2.1.0^{2,7}]octanone-3 (**8**).[7]—To 250 ml of 80% sulfuric acid was added with stirring 12.5 g (67.6 mmoles) of 3-bromobicyclo[3.2.1]octadiene. The mixture was stirred at room temperature for 61 hr, then poured over 1000 g of ice. Partial neutralization was effected by addition of 100 g of sodium carbonate. The resulting solution was extracted three times with ether. The combined extracts were washed with 0.1 *N* sodium hydroxide solution and dried over magnesium sulfate. The residue after evaporation of the ether was distilled between 103 and 106° (10 mm) to give 5.36 g (65%) of ketone **8**. A small amount crystallized during the distillation and the melting point was 42–46°. A dinitrophenylhydrazone derivative had mp 211–212° (lit.[7] mp 210–211°). The infrared and nmr spectra agreed with those in the literature.[7]

Tricyclo[3.2.1.0^{2,7}]octanol-3 (**7**).—To a solution of 0.3 g (2.5 mmoles) of ketone **8** in 30 ml of anhydrous ether was added 0.15 g (3.95 mmoles) of lithium aluminum hydride over 1.25 hr. After stirring the resulting mixture for an additional 0.5 hr, the complexes were hydrolyzed with water. The precipitate was collected on a filter and washed with ether. The combined extracts were evaporated to furnish 0.3 g (98%) of a white solid, mp 130–135° (sealed capillary). Sublimation at 0.8 mm yielded the analytical sample with mp 135–137°.

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74; Found: C, 77.13; H, 9.82.

The nmr spectrum showed a multiplet at τ 5.85 (1 H) and complex absorption (11 H) between 9.2 and 7.2. The infrared spectrum showed a sharp OH band at 2.73 and a broad OH at 3.20 μ. Other strong peaks appeared at 9.30, 10.15, and 10.47 μ.

The **p-nitrobenzoate** was prepared and crystallized repeatedly from pentane at −78°. Carbon analyses were consistently low. The purest sample had mp 78.5–80°.

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.49; N, 5.13. Found: C, 65.06; H, 5.53; N, 5.03.

Two attempts were made to prepare the **acetate** of alcohol **7**. When the alcohol was treated with acetic anhydride and sodium acetate for 3.5 hr at reflux, a 70% yield of the acetate of bicyclo[3.2.1]oct-2-en-7-ol was obtained.

When the reaction was carried out at room temperature for 78 hr the product showed two resonance peaks in the expected region for acetyl groups. The larger one at τ 8.07 had a relative area about three times that of the smaller one at 8.03. The general appearance of the spectrum strongly resembled that of the acetate of bicyclo[3.2.1]oct-2-en-7-ol.

Tricyclo[3.2.1.0^{2,7}]octanone-3 Oxime (**26**).—A solution of 6.36 g (0.052 mole) of ketone **8** in 50 ml of methanol was added to 120 ml of an aqueous solution in which were dissolved 18 g of hydroxylamine hydrochloride and 35 g of potassium hydroxide. After a 2 hr reflux period, the cooled solution was poured into 200 ml of water. After neutralization with 50 g of ammonium chloride, the liberated oxime was extracted into either. The dried extracts were evaporated to give 6.75 g (95%) of white crystals, mp 111–119°. After several recrystallizations from hexane the melting point rose to 130.5–131.5°.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.12; H, 8.17; N, 10.20.

3-Aminotricyclo[3.2.1.0^{2,7}]octane (**25**).—A solution of 4.20 g (0.031 mole) of oxime **26** in 400 ml of dry ether was treated with 3.0 g (0.079 mole) of lithium aluminum hydride over a period of 2 hr. The resulting slurry was heated at reflux for 3 days. Hydrolysis of the salts by careful addition of water yielded an ether solution of the desired amine. The amine was converted to the hydrochloride salt by passage of hydrogen chloride gas through the solution. A white solid (2.46 g, 50%) was deposited which was collected and used in the deamination step.

The nmr of the hydrochloride salt could be determined in trifluoroacetic acid. The three amino protons appeared as a broad triplet (J = 50 cps) at τ 3.25. Complex absorption (11 H) appeared between 6.4 and 9.2.

A **phenylthiourea** derivative was prepared from the free amine and had mp 187–187.5°, after crystallization from ethanol.

Anal. Calcd for $C_{15}H_{18}N_2S$: C, 69.67; H, 7.02; N, 10.85. Found: C, 69.78; H, 7.14; N, 10.57.

3-*d*-3-Aminotricyclo[3.2.1.0^{2,7}]octane (**25-*d***).—Reduction of oxime **26** with lithium aluminum deuteride (96%) yielded the 3-deuterio analog **25-*d*** in 54% yield. The nmr spectrum of this amine was very similar to that of **25** with the exception that the absorption between τ 5.95 and 6.75 had disappeared.

Tricyclo[3.2.1.0^{2,7}]octanone-4 (**9**).—A solution of 27.0 g (0.25 mole) of nortricyclanone and 65 g (0.30 mole) of N-methyl-N-nitroso-*p*-toluenesulfonamide in 75 ml of 95% ethanol was treated with a solution of 3.75 g (0.63 mole) of potassium hydroxide in 25 ml of 50% ethanol. The addition was carried out at 5° over a 5-hr period. The excess diazomethane was destroyed with dilute hydrochloric acid. The ethyl *p*-toluenesulfonate was destroyed by addition of sodium iodide (150 g) followed by heating at reflux for 2 hr. About one-half of the solvents were evaporated under aspirator pressure. The remaining solution was diluted with 500 ml of water and extracted three times with 75 moles of ether. The combined extracts were washed with sodium carbonate solution and sodium thiosulfate solution and dried over magnesium sulfate. A yellow oil was obtained upon removal of the ether under reduced pressure. The oil was distilled at 83–90° (17 mm) to give 16.5 g of a mixture of ketones. Analysis of this mixture by gas chromatography on a 6-ft Carbowax 20 M column at 190° showed one component in *ca.* 90% concentration along with small amounts of nortricyclanone and higher homologs. Further purification by distillation on a spinning-band column (18 in. × 6 mm) gave 12.8 g (42%) of essentially pure ketone **9**, bp 97–98° (26 mm) [lit.[8] bp *ca.* 90° (16 mm)]. Only a trace of ketone **8** could be detected by gas chromatography. An analytical sample, mp 52–54°, was collected by preparative gas chromatography on a 15 ft × $^3/_8$ in. column of Craig succinate.

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 77.73; H, 8.06.

The material liquified on exposure to air owing to absorption of water. The low carbon analysis reflects this tendency.

The nmr spectrum of **9** showed a sharp doublet (J = 3 cps) at τ 7.6 superimposed on a multiplet (3 H total) and complex absorption between τ 9.0 and 7.8 (7 H).

The **2,4-dinitrophenylhydrazone** melted at 190–190.5° (lit.[8] mp 194.5–195°).

The *p*-**nitrophenylhydrazone** melted at 181.5–183° after crystallization from 95% ethanol.

Anal. Calcd for $C_{14}H_{15}N_3O_2$: C, 65.32; H, 5.88; N, 16.33. Found: C, 65.20; H, 5.95; N, 16.12.

Tricyclo[3.2.1.0^{2,7}]octanol-4 (6).—Ketone **8** was reduced by addition of 4.9 g (40 mmoles) to a slurry of 0.9 g (23 mmoles) lithium aluminum hydride in 20 ml of dry ether. There was obtained 4.4 g (90%) of alcohol **6**, mp 132.5–135° (lit.[8] mp 123.5–124.5°). A sample was purified for analysis by sublimation at 67° (26 mm) and had mp 136–138°.

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.30; H, 9.61.

The nmr spectrum showed a broad multiplet (1 H) centered at τ 6.4, OH resonance at 6.9, and complex absorption between 7.6 and 9.6 (9 H). The infrared spectrum showed a sharp peak at 2.75 and a broad peak at 3.0 μ. Other strong absorptions appeared at 8.63, 9.25, and 9.48 μ.

The **acetate** was prepared in 88% yield (see above) and was purified by gas chromatography on a 15 ft × $^3/_8$ in. Carbowax 20 M column.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.06; H, 8.35.

The nmr spectrum showed a sharp peak (3 H) at τ 8.05, a multiplet (1 H) at 4.55, and complex absorption (9 H) between 7.4 and 8.9.

The **3,5-dinitrobenzoate** was crystallized from 95% ethanol and had mp 103–104°.

Anal. Calcd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.43; N, 8.80. Found: C, 56.66; H, 4.46; N, 8.85.

The *p*-**toluenesulfonate** ester (**23**) was prepared in the usual way but could not be induced to crystallize. The infrared spectrum indicated complete reaction by the absence of O–H stretching bands. The sample was used directly in the solvolyses.

4-*d*-Tricyclo[3.2.1.0^{2,7}]octanol-4 (6-*d*).—Reduction of ketone **9** with lithium aluminum deuteride (96%) gave the 4-*d* isomer of alcohol **6**. The nmr spectrum was essentially that of **6** except that no carbinol proton resonance was observed at τ 6.4. The *p*-toluenesulfonate ester **23-*d*** was an oil which was used directly in the solvolyses.

***exo,exo*-Tricyclo[3.2.1.0^{2,4}]octan-6-ol (12).**—To 1.31 g of zinc-copper couple[21] was added 2.0 g (0.018 mole) of *exo*-dehydronorborneol.[22] With stirring and cooling (*ca.* 0°), 5.36 g (0.020 mole) of methylene iodide was added in one portion. It was necessary to add a crystal of iodine and to heat the solution gently to initiate the reaction. After the initial exothermic reaction ceased, the mixture was stirred and heated at reflux for 19 hr. The reaction mixture was then diluted with 75 ml of ether and treated with 50 ml of 2 N ammonium chloride solution. The layers were separated and the ethereal solution was washed with 50 ml of water and 25 ml of 10% sodium carbonate solution. The dried solution was evaporated to give 1.98 g of an oil. Gas chromatographic analysis of the oil showed that about 64% consisted of starting material. A sample of the product was collected from a 15 ft × $^3/_8$ in. preparative silicone SF 96 column. The retention time of this material was identical with that of the sample prepared by Wiberg and Wenzinger.[4,12] The infrared spectrum corresponded with that reported by Colter and Musso.[12]

***exo*-3-Bromobicyclo[3.2.1]oct-2-en-7-yl Formate (15).**—A solution of 6.5 g (0.035 mole) of 3-bromobicyclo[3.2.1]octadiene[7] in 45 ml of 98% formic acid was placed in a flask and stirred for 72 hr at 25°. The resulting dark solution was diluted with 200 ml of ice water followed by addition of 53 g (0.5) mole of sodium carbonate. Three extractions with 75 ml portions of ether served to remove the adduct. The extracts were washed with sodium bicarbonate solution and water. After drying over sodium sulfate, the extracts were evaporated to yield 8.1 g (100%) of crude adduct. Distillation in a molecular still at 17 mm and 100° pot temperature gave 6.8 g (84%) of a colorless liquid, n^{27}_{D} 1.5277.

Anal. Calcd for $C_9H_{11}BrO_2$: C, 46.75; H, 4.76; Br, 34.63. Found: C, 46.93; H, 4.81; Br, 34.75.

The nmr spectrum displayed a singlet at τ 2.1 (1 H), a broad doublet (1 H) at 3.8 with 7-cps splitting, a doublet (1 H) centered at 4.8 with 6-cps splitting, and complex absorption (8 H) from 7.0 to 8.6. The infrared spectrum showed strong absorption at 5.75, 8.55, and 11.32 μ and medium peaks at 6.06, 10.52, and 15.0 μ.

***exo*-Bicyclo[3.2.1]oct-3-en-7-ol (14).**—A solution of 2.8 g (0.12 g-atom) of sodium was dissolved in 125 ml of anhydrous ammonia. A Dry Ice condenser was used to prevent evaporation. The bromoformate (4.8 g, 0.026 mole) was added in one portion and the mixture was stirred for 10 hr. The ammonia was then allowed to evaporate and the residue was covered with 75 ml of ether. Dropwise addition of water was continued until hydrolysis was complete. The layers were separated and the aqueous phase was extracted further with ether. The combined extracts were washed with water, dried over sodium sulfate, and distilled to give 2.58 g of an oil. Sublimation of the oil at 35° (30 mm) gave 0.75 g, mp 44–45.5°, and 1.32 g, mp 39–43°. The total yield was 64%. The analytical sample was prepared by resublimation of the first fraction and had mp 45–46.5°.

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.26; H, 9.81.

The nmr spectrum of **14** showed a complex pattern (2 H) for the olefinic protons centered at τ 4.4,[23] a crude quartet (1 H) at 5.85, OH resonance at 6.7, and complex absorption (8 H) from 7.4 to 8.7. The infrared spectrum showed sharp OH absorption at 2.80 and a broad OH band at 3.12 μ. Strong peaks also appeared at 9.35 and 14.52 μ. Medium intensity peaks appeared at 6.95, 8.13, 8.58, 9.75, 10.03, and 11.0 μ.

The *p*-**nitrobenzoate** was recrystallized several times from methanol-water, mp 114.5–116°.

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.49; N, 5.13. Found: C, 65.72; H, 5.58; N, 5.20.

The **acetate** was prepared in 85% yield by treatment of alcohol **14** with acetic anhydride and sodium acetate at reflux temperatures for 3.5 hr. An analytical sample was obtained by collection of the effluent from an 8-ft NMP column operated at 125°.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.96; H, 8.35.

The nmr spectrum showed the typical olefinic pattern centered at τ 4.35 (2 H), the carbinyl proton at 5.0, and complex absorption (3 H) centered at 7.55 and 8.25 (8 H). The resonance peak of the methyl group appeared at τ 8.07. The infrared spectrum showed strong bands of 5.75, 8.12, and 14.5 μ.

Deamination of 25.—A solution of 2.25 g (0.014 mole) of the hydrochloride salt of **25** in 75 ml of glacial acetic acid was treated with 2.8 g of sodium nitrite over 1.25 hr with stirring and ice-bath cooling. The resulting mixture was stirred at room temperature overnight and quenched by pouring over 150 g of cracked ice. The acid was neutralized by addition of a solution of 56 g of sodium hydroxide in 150 ml of water. Extraction with ether was followed by washing of the combined extracts with dilute hydrochloric acid and water. Evaporation of the dried extracts gave 1.34 g of an oil. The nmr spectrum showed sharp singlets at τ 8.07 and 8.03 owing to the acetyl protons of the esters of **7** and **14**, respectively. The ratio of peak heights was 57:43, respectively. The crude acetates were reduced with lithium aluminum hydride in ether to give 1.0 g of alcohols. The nmr and infrared spectrum of this mixture proved to be identical with that of a synthetic mixture consisting of 52% **7** and 48% **14**. Retention times for these materials were identical with those of the known samples on the 150 ft × 0.01 in. Ucon column, but complete resolution was not effected.

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(21) Prepared according to R. S. Shank and H. Schechter, *J. Org. Chem.*, **24**, 1825 (1964).

(22) Available as a by-product from the addition of formic acid to norbornadiene; see H. K. Hall, *J. Am. Chem. Soc.*, **82**, 1209 (1960); S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **88**, 3087 (1966).

(23) This general pattern was almost identical with that found for numerous bicyclo[3.2.1]octenes; see ref 1b and R. R. Sauers, H. M. How, and H. Feilich, *Tetrahedron*, **21**, 983 (1964).

Deamination of 25-*d*.—The deuterated analog was treated with nitrous acid under the same conditions. From 1.23 g of amine hydrochloride was obtained 0.645 g of crude alcohols. The nmr spectrum showed an olefinic proton absorption centered at τ 5.81. Clearly, the upfield proton of the double band had disappeared. Since the relative areas of the carbinol proton and the olefinic proton were equal, one can conclude that the tricyclo-[3.2.1.0^{2,7}]octanol-4 is specifically labeled at the carbinol position.

Acetolysis of *p*-Nitrobenzoate 24.—A solution of 0.81 g of **24** in 18 ml of glacial acetic acid which also contained 0.3 g of sodium acetate was heated at reflux for 110 hr. The resulting solution was diluted with 150 ml of ice water followed by neutralization with sodium carbonate. Extraction with ether and washing of the extracts with sodium carbonate solution and water gave a solution from which 0.54 g of an oil was obtained on evaporation. The nmr spectrum revealed the presence of a small amount of unreacted *p*-nitrobenzoate (*ca.* 15%) and peaks owing to the acetate of **14**. Gas chromatography revealed only one volatile product having the same retention time as the acetate of **14** (NMP column at 120°).

Acetolyses of 23.—Acetolyses of **23** were effected at several temperatures by treatment of **23** (3.5 g, 0.012 mole) with 1.0 g of sodium acetate in 60 ml of glacial acetic acid containing 1 drop of acetic anhydride. The products were isolated as described above and analyzed as acetates on a 12-ft Carbowax 20 M column at 190°.

At Reflux (2.5 Hr).—A small amount of a hydrocarbon was isolated by collection of a peak of low retention time. The infrared spectrum was essentially that reported by Grob and Hastynek[24] for tricyclo[3.2.1.0^{2,7}]octene-3. The only esters detected were the acetates of *exo*-bicyclo[3.2.1]oct-2-en-7-ol and tricyclo[3.2.1.0^{2,7}]octanol-4 in a 2.6:1 ratio. These assignments were confirmed by comparison of infrared and nmr spectra of collected samples. At 80° (7 hr) acetates of **14** and **6** were obtained in a 2.4:1 ratio. At 25° (48 hr), a 1.1:1 ratio of the acetates of **14** and **6** was detected.

Acetolysis of 23-*d*.—The deuterated analog was solvolyzed similarly at 50° for 3 hr. The two acetate esters were formed in a ratio of one and one-half parts unsaturated ester (of **14-*d***) to one part tricyclic ester (of **6-*d***). The nmr spectrum of the ester of **14-*d*** was virtually identical with that of the protiated system, *i.e.*, no specific region appeared diminished in intensity.

The nmr spectrum of the tricyclic ester was also very similar to that of the undeuterated material. The ratio of the area of the carbinol proton at τ 5.5 to that of the upfield region was *ca.* 1:27.5 which indicates that about 0.5 proton was now present at the carbinol position.

Registry No.—**4**, 10058-22-7; phenylthiourea derivative of **4**, 10027-42-6; picrate of **4**, 10027-43-7; **5**, 10027-44-8; acetate of **5**, 10027-45-9; **7**, 10027-46-0; *p*-nitrobenzoate of **7**, 10027-47-1; **26**, 10027-48-2; **25**, 10039-10-8; phenylthiourea of **25**, 10027-49-3; **25-*d***, 10027-50-6; **9**, 10039-11-9; *p*-nitrophenylhydrazone of **9**, 10027-51-7; **6**, 10027-52-8; acetate of **6**, 10027-53-9; 3,5-dinitrobenzoate of **6**, 10027-54-0; **15**, 10027-55-1; **14**, 10027-56-2; *p*-nitrobenzoate of **14**, 10027-57-3; acetate of **14**, 10027-58-4.

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[24] C. A. Grob and J. Hastynek, *Helv. Chim. Acta*, **46**, 1676 (1963).

Mass Spectra of Certain Cycloalkylacetates and of Related Unsaturated Esters[1]

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Mass spectra are reported for five saturated esters and four unsaturated ones. The fragmentation patterns are interpreted in terms of mechanisms of fragmentation and the relationships of ion abundance to structural features. Starting material for synthesis of seven of the esters was α-campholenic acid (**1**). Hydrogenation of methyl α-campholenate yielded the saturated α-campholanic ester (**5**), which was in turn converted to the corresponding α,β-unsaturated ester (**24**). Rearrangement under suitable conditions of the α-campholenate yielded methyl β-campholenate (**4**) which was hydrogenated to yield the *cis*- and *trans*-β-campholanates, in turn converted to the α,β-unsaturated ester (**25**). Methyl 3-ethyl-3-methylcyclopentylacetate was synthesized from 3-ethyl-3-methylcyclopentanone, while methyl 2,6-dimethylcyclohexylacetate was synthesized from 2,6-dimethylcyclohexanone.

Although there have been published extensive investigations of the behavior of polycyclic compounds on fragmentation in an electron beam, the mass spectra of monocyclic compounds have received relatively little attention. Certain monocyclic terpenes have been examined,[2,3] as have some simple monocyclic hydrocarbons,[4] but examination of derivatives of monocyclic carboxylic acids appears to be limited to a previous investigation in this laboratory.[5] In connection with establishing the structure of a cyclopentylacetic acid isolated from a California petroleum,[6] basic information concerning the mass spectra of such structures was required. The present report concerns the mass spectra of the methyl esters of five saturated acids and four unsaturated acids, chosen to give information about several structural features.

Synthesis of Required Structures

Structures containing the polymethylcyclopentane ring with a quaternary carbon were approached *via* α-campholenic acid (**1**, 2,2,3-trimethyl-3-cyclopentenylacetic acid). This acid has been secured, together with several other compounds, by subjecting camphor oxime to the conditions of the Beckmann rearrangement;[7] however, Sauers[8] has reported that alkaline fusion of sodium 10-camphorsulfonate[9] is a superior method for preparation of α-campholenic acid. In our hands, the alkaline fusion gave a satisfactory yield of α-campholenic acid; however, this acid changed rapidly on distillation, or slowly on standing at room tem-

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