alcohol XXXV. The entire material was oxidized in acetic acid solution with 0.4 g. of chromium trioxide and then processed in the standard manner. Distillation of the crude product gave a colorless oil, whose infrared spectrum (run as a film as well as in chloroform solution) was completely superimposable upon that of synthetic *trans*-5,10-dimethyl-3α-isopropyldecalone-2 (XXIX). The substance exhibited a positive Cotton effect, similar to that of the synthetic ketone XXIX, the only difference being that the amplitude was somewhat reduced (peak in methanol solution at $[\alpha]_{312}$ +436°). A portion of the ketone was transformed into its semicarbazone, m.p. 178–181°, which proved to be identical by mixture melting point determination with the semicarbazone of the synthetic specimen.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

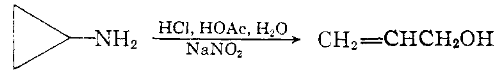
Cyclopropane Chemistry. IX. Nitrous Acid Deamination of 1-Amino- and 1-Aminomethylnortricyclene[1,2]

BY HAROLD HART AND ROBERT A. MARTIN

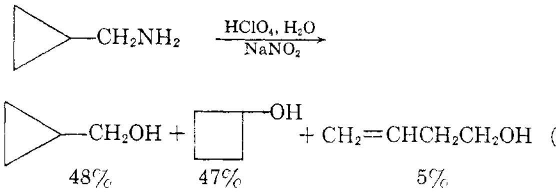
RECEIVED JUNE 16, 1960

The bridgehead cyclopropylamine 1-aminonortricyclene (XI), when treated with nitrous acid in glacial acetic acid, gave a single acetate, 1-acetoxynortricyclene (XII) in 55% yield, confirming earlier work of Lipp and Padberg[6] on apotricyclylamine. 1-Aminomethylnortricyclene (XV), a cyclopropylcarbinylamine, gave under similar conditions a comparable yield of esters, *91–92% of which was unrearranged acetate XVI*. The balance was 5% of 6-acetoxynorcamphor (XVII) and 3–4% of nitrate ester. Thermal rearrangement of the acetates (XVI → XVII) was observed on vapor chromatography (silicone, 132°). Possible reasons for the relatively small amount of rearrangement on deamination of XV are discussed.

As with most primary aliphatic amines, the nitrous acid deamination of both cyclopropylamine and cyclopropylcarbinylamine is known to give large percentages of rearranged products. Thus allyl alcohol is reportedly[3] the only neutral product from the action of aqueous nitrous acid on cyclopropylamine. In aqueous perchloric acid, the three alcohols shown in 2 were obtained from cyclopropylcarbinylamine in 60% yield[4]; the methylene carbons were extensively scrambled.[5]



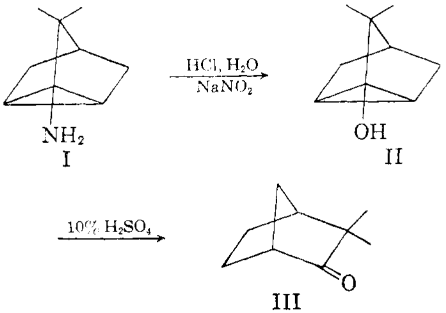
(1)



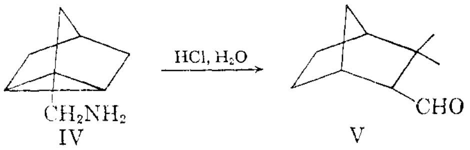
(2)

The number of cyclopropyl compounds of this type that has been studied, however, is relatively small and the only precise work by modern standards is that of Roberts.[4,5]

A few examples appear in the older terpene literature, of deaminations of primary amines in which the amino group is either directly attached to, or one carbon removed from, a three-membered ring. Lipp and Padberg[6] reported that apotricyclylamine (I) hydrochloride gave apotricyclol (II) in 50–55% yield. The structure was inferred from the ready conversion of II to camphenilone (III) with acid.[7] The tricyclic structure of I precludes rearrangement of the cyclopropyl cation to an allylic structure[3]; hydride or methyl shifts are conceivable but were not observed.



Lipp also investigated the corresponding carbinylamine (ω-aminotricyclylamine, IV).[8] The amine itself was relatively unstable in acid. An aqueous solution of its hydrochloride, when saturated with hydrogen chloride and heated for 10 minutes, gave camphenilaldehyde (V) on steam distillation.[9] With aqueous nitrous acid, IV-hydrochloride gave an aldehyde-smelling oil which reduced ammoniacal silver.[8,10]



Two cyclopropylcarbinyl amines are reportedly deaminated without rearrangement. The reduc-

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[1] This work was supported in part by a grant from the Office of Ordnance Research, Contract No. DA-20-018-ORD-16492, and in part by a fellowship from the Upjohn Co., Kalamazoo, Mich. We are deeply indebted to both for financial assistance.

[2] For the previous paper in this series, see H. Hart and J. A. Wrede, *J. Org. Chem.*, **25**, 1811 (1960).

[3] P. Lipp, J. Buchkremer and H. Seeles, *Ann.*, **499**, 1 (1932).

[4] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

[5] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[6] P. Lipp and C. Padberg, *Ber.*, **54B**, 1316 (1921).

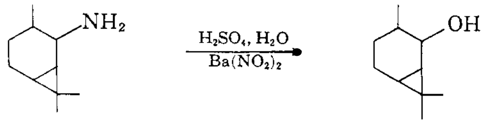
[7] II was obtained analytically pure only as the phenylurethane; the alcohol itself was an unstable solid, m.p. 75–80°, which became an oil on standing for a few hours in air.

[8] P. Lipp, *Ber.*, **53B**, 769 (1920).

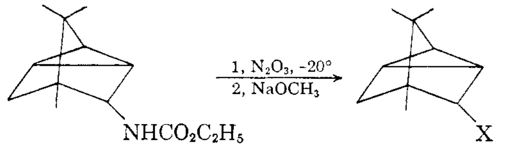
[9] An analogous rearrangement of 2-aminotricyclene to camphor (and polymer) was reported by H. L. Hoyer, *ibid.*, **87**, 1849 (1954).

[10] The product was obviously a mixture (it contained nitrogen) and was not further investigated by Lipp. The statement in J. L. Simonsen, "The Terpenes," 2nd Ed., Vol. 2, Cambridge University Press, 1949, pp. 335–336, is somewhat misleading, in that V is reported to be the product of the reaction of IV with nitrous acid. Lipp[8] did not make this claim in the original paper.

tion product of carone oxime (5-carylamine, VI) gave optically active alcohol (VII) in 30% yield.[11] In an attempt to prepare a quadricyclene[12] derivative, Lipp[13] treated the urethane VIII in dry ether at $-20°$ with N_2O_3, followed by 2% $NaOCH_3$. The products were the corresponding alcohol IX and methyl ether X.[14]



VI VII



VIII

IX, X = OH
X, X = OCH_3

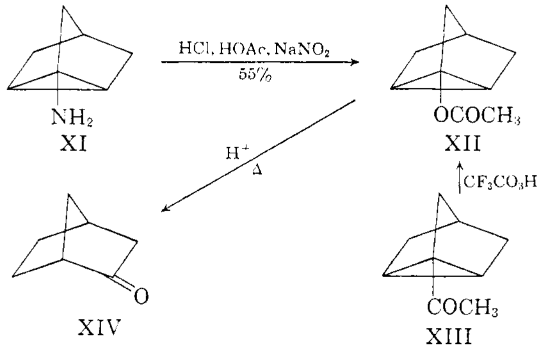
Since the early investigations summarized here were frought with the experimental difficulties of working with small quantities of oils without adequate techniques, it seemed desirable to re-examine the situation with the benefit of infrared and vapor phase chromatography (v.p.c.). 1-Aminonortricyclene (XI) and 1-aminomethylnortricyclene (XV), the nor-compounds analogous to those studied by Lipp[6,8] were selected for critical study.

Results and Discussion

A good preparative method for 1-substituted nortricyclenes was recently described.[15] Of three procedures tried for the preparation of 1-aminonortricyclene (XI), the best was a modification[16] of the Hofmann rearrangement of 1-nortricyclenecarboxamide.[15] The preparation of XV, by lithium aluminum hydride reduction of the same amide, was described previously.[15]

The deaminations were run in glacial acetic acid, rather than in dilute aqueous mineral acid, because the three-membered ring is susceptible to attack by strong acids[8,9]; rearrangement by this path might lead to ambiguous results. Furthermore, the anticipated acetates were likely to be more stable than their corresponding alcohols.

1-Aminonortricyclene (XI).—When XI-*HCl* was treated in glacial acetic acid with sodium nitrite, one acetate, as shown by a single symmetrical peak on the vapor chromatograph, was obtained in 55% yield. Bands at 3.23μ (C–H stretch on the three-membered ring) and at 11.82 and 12.8μ (1-substituted nortricyclene)[15] indicated that the ring skeleton was retained. The acetate was not 3-acetoxynortricyclene,[17] a possible product of 1,2-hydride shift, as shown by comparison of their infrared spectra. The deamination product was identical (infrared) with an acetate synthesized from 1-acetylnortricyclene (XIII)[15] and peroxytrifluoroacetic acid.[18] Finally, the acetate, when refluxed with 10% hydrochloric acid, gave a solid ketone (presumably norcamphor, 5.65μ) which was converted directly to its 2,4-DNP. The latter was identical (m.p., m.m.p.) with an authentic sample[19] of norcamphor-2,4-DNP. The structure of the acetate from the deamination of XI is therefore unequivocally established as 1-acetoxynortricyclene (XII) as shown in the scheme.



XI XII XIV XIII

This reaction provides another example of the rather facile replacement of bridgehead-NH_2[20] *via* diazotization, and confirms the earlier results[6] with apotricyclylamine. These results should be contrasted with the difficulty with which a cyclopropylcarbonium ion is formed, and with the rearrangement common to such ions,[21] and suggest that the intermediate is in fact a diazonium acetate ion pair which collapses to acetate and nitrogen.[22,23]

1-Aminomethylnortricyclene (XV).—The infrared spectrum of the mixture of acetates obtained (52% yield) from 1-aminomethylnortricyclene (XV) indicated that the predominant product was a 1-substituted nortricyclene (bands at 11.73 and 12.73μ),[15] presumably 1-nortricyclylcarbinyl acetate (XVI). Extraneous bands at 5.97, 6.02, 6.10, 8.90 and 11.30μ indicated the presence of unsatu-

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[11] K. N. Menon and J. L. Simonsen, *J. Indian Inst. Sci.*, **10A**, 1 (1927). The structure was established by oxidation to the original ketone.

[12] S. J. Cristol and R. L. Snell, This Journal, **80**, 1951 (1958).

[13] M. Lipp, *Ber.*, **74B**, 1 (1941).

[14] The deamination of homocyclopropylcarbinyl amines, of some interest because of the remarkable nature of such carbonium ions (S. Winstein, J. Sonnenberg and L. de Vries, This Journal, **81**, 6523 (1959)), has scarcely been investigated. A. G. Short and J. Read, *J. Chem. Soc.*, 2016 (1938), deaminated two thujylamines but did not characterize the products, except to conclude that they were not thujyl alcohols.

[15] H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959).

[16] E. Magnien and R. Baltzly, *ibid.*, **23**, 2029 (1958).

[17] N. V. de Bataafsche Petroleum Maatschappij, British Patent 717,010, Oct. 20, 1954.

[18] W. D. Emmons and G. B. Lucas, This Journal, **77**, 2289 (1955).

[19] K. Alder, H. K. Schafer, H. Esser, H. Krieger and R. Reubke, *Ann.*, **593**, 23 (1955).

[20] For reviews describing replacements of $-NH_2$ by $-OH$, $-Cl$, $-OC_2H_5$ and $-OSO_2R$, see D. E. Applequist and J. D. Roberts, *Chem. Revs.*, **54**, 1065 (1954), and U. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960).

[21] J. D. Roberts and V. C. Chambers, This Journal, **73**, 5034 (1951).

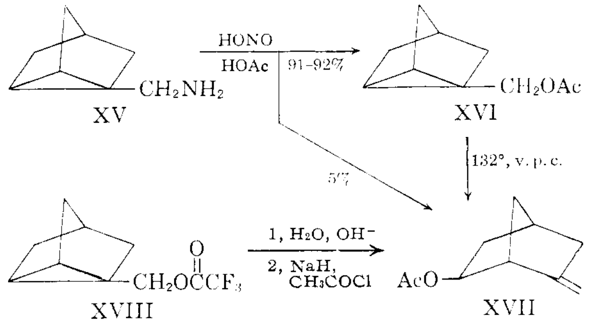
[22] For other examples, see R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1, 21 (1956); A. Streitwieser, Jr., and C. E. Coverdale, This Journal, **81**, 4275 (1959), and leading references cited there.

[23] During the preparation of this manuscript, the deamination of 3′-amino-1,2-cyclopropanoacenaphthene to the corresponding chloride was described by R. Pettit, *ibid.*, **82**, 1972 (1960). In this case the free carbonium ion, had it formed, would presumably have rearranged to the more stable perinaphthenylium cation; instead, a diazonium chloride ion pair is the probable intermediate. It is of further interest that the diazotization, carried out in concentrated hydrochloric acid-glacial acetic acid, did not cleave the cyclopropane ring.

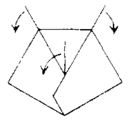
rated material, terminal methylene and possibly some nitrate ester.

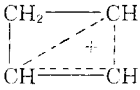
Attempts to resolve the mixture by v.p.c. were not successful; complete band separation could not be achieved but, more disconcerting, the band areas varied with the column temperature, pressure of carrier gas and, in short, with residence time on the column. To test the premise that isomerization was occurring on the column authentic XVI, synthesized from the carbinol,[15] was passed slowly through the column (silicone on firebrick) at 132°; the 1-nortricyclyl bands (11.73 and 12.73 μ) in XVI were virtually absent from the collected effluent, and new bands appeared at 5.97, 6.02 and 11.30μ (intense). The rearrangement product was presumably 6-acetoxynorcamphene (XVII); the same acetate (identical infrared) was also obtained by acetylation of the alcohol obtained from hydrolysis of 1-nortricyclylcarbinyl trifluoroacetate (XVIII).[24,25]

Following the failure of v.p.c., the deamination products were analyzed by a combination of permanganate oxidation, bromine titration and differential infrared analysis, all described in detail in the Experimental part of the paper. The products, as shown in the scheme, were *91-92% unrearranged acetate XVI*, 5% homoallylic acetate XVII and 3-4% of an unidentified product with distinctive absorption bands at 6.10 and 8.90μ.[26]



In view of the known propensity of the cyclopropylcarbinyl system to rearrange, the nearly complete lack of such rearrangement in the deamination of XV is striking. Two structural features of the nortricyclylcarbonium ion (from XV) may explain the difference between it and the cyclopropylcarbinyl case. (1) From models, it seems that the cage structure of nortricyclene derivatives would result in distorted angles for the three remaining bonds on the cyclopropane ring; these bonds would be bent outward, away from the center and toward the plane of the three-membered ring, as shown. Lippincott,[27] for example, assumed an angle of 100° for C_1, C_2, C_3 in nortricyclene, in order to interpret its Raman and infrared spectrum. The corresponding angle in simple cyclopropanes is about 16-24° larger than this.[28] The chemical consequence of this distortion[29] should be appreciably less overlap of the three-membered ring with a developing 1-nortricyclylcarbinyl cation than is possible in the cyclopropylcarbinyl system. (2) Nortricyclylcarbinyl cationic structures analogous to the bicyclobutonium ion XIX, which is the currently preferred[5] intermediate used to explain the rapid rates and extensive rearrangements in cyclopropylcarbinyl solvolyses, would require partial double bonds to bridgehead carbon atoms.[30] One can rationalize the results by having the deamination proceed *via* a diazonium acetate ion pair which collapses predominantly without rearrangement, because the cation which would be obtained from the diazonium ion if it lost nitrogen would not be remarkably stabilized.





XIX

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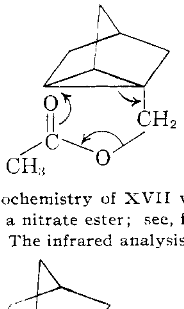
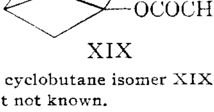
[24] Prepared by James A. Wrede, Ph.D. Thesis, Michigan State University, 1959.

[25] The mechanism of this thermal rearrangement (XVI → XVII) has not been investigated; a cyclic transition state or an ion-pair may be involved. The stereochemistry of XVII was not determined.



[26] This is probably a nitrate ester; see, for example, Streitwieser and Coverdale, ref. 22. The infrared analysis is subject to the limitation that XVI and its cyclobutane isomer XIX have different infrared spectra; XIX is as yet not known.



XIX

[27] E. R. Lippincott, THIS JOURNAL, **73**, 2001 (1951).

[28] O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947); L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937); O. Bastiensen and O. Hassel, *Tidsskr. Kjemi, Bergvesen Met.*, **6**, 71 (1946); *C. A.*, **40**, 6059 (1946); J. M. O'Gorman and V. Schomaker, THIS JOURNAL, **68**, 1138 (1946).

[29] The distortion is only hypothesized; the precise geometry of the nortricyclene structure has not yet been determined. An electron diffraction study of nortricyclene vapor (E. Heilbronner and V. Schomaker, *Helv. Chim. Acta*, **35**, 1385 (1952)) leads to a value of 70.5° for the acute angle between the C_1-C_3 bond and the plane of the cyclopropane ring. The corresponding angle in 1,1,2,2-tetramethylcyclopropane is only 57 ± 3° (H. P. Lemaire and R. L. Livingston, *Acta Cryst.*, **5**, 817 (1952)).

[30] On these grounds, one would predict that solvolysis of 1-nortricyclylcarbinyl derivatives by an S_N1 mechanism should proceed more slowly than the corresponding simple cyclopropylcarbinyl compounds, but more rapidly than 3-nortricyclyl derivatives (for examples of the latter, see J. D. Roberts and W. Bennett, THIS JOURNAL, **76**, 4223 (1954), and S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950)). Preliminary results on XVIII indicate that the situation is complicated. Whereas at room temperature for 24 hours in 10% sodium hydroxide XVIII was converted (80%) to 6-hydroxynorcamphene (see Experimental), solvolysis in 70% aqueous dioxane gives acyl-oxygen rather than alkyl-oxygen fission (unpublished results of James A. Wrede).

Experimental[31]

1-Aminonortricyclene Hydrochloride (XI-HCl).—A mixture of 6.0 g. (0.044 mole) of 1-nortricyclenecarboxamide,[15] 72 ml. of sodium hypochlorite solution[16] and 24 ml. of purified dioxane was gradually heated (0.5 hour) with magnetic stirring until the temperature of the mixture reached 50°, at which time no solid remained. After stirring for 1 hour without heating, the mixture was again brought to 50°, stirred for an additional 1.25 hours, then steam distilled into dilute hydrochloric acid, the distillate being collected until it was no longer basic (600 ml.). The hydrochloric acid solution was evaporated to dryness at 40° in a rotary evaporator, the residue taken up in methanol and filtered. Treatment of the filtrate with anhydrous ether deposited white needles, 4.0 g., of XI-HCl, m.p. above 250° dec.

Anal. Calcd. for $C_7H_{12}NCl$: C, 57.73; H, 8.31; N, 9.62. Found: C, 57.76; H, 8.32; N, 9.61.

The residue from steam distillation deposited 1.05 g. of unreacted amide; the yield of amine hydrochloride based on unrecovered amide was 75%. It was readily converted to a benzamide, white needles, m.p. 223.5–224° (from ethanol–water).

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.73; H, 7.14; N, 6.50.

Two alternative methods for preparing XI gave some difficulty at the final hydrolytic stage, but are instructive and will be described. (1) A sodium methylate solution (from 0.24 g. of sodium and 7 ml. of methanol) was added during 15 minutes to an ice-cooled suspension of 1.0 g. (0.0073 mole) of 1-nortricyclenecarboxamide[15] in 3 ml. of anhydrous methanol. To this mixture was added 0.77 g. (0.0048 mole) of bromine, and the whole refluxed for 1 hour. The urethan which remained after the methanol was evaporated was taken up in hot pentane (a residue of 230 mg. of unreacted amide was recovered). Evaporation of the pentane gave 580 mg. (75%) of methylurethan, m.p. 86.5–87.5°.

Anal. Calcd. for $C_9H_{13}O_2N$: C, 64.64; H, 7.83; N, 8.37. Found: C, 64.61; H, 7.77; N, 8.44.

The urethan was heated with 1.2 g. of powdered potassium hydroxide for 8 minutes in an oil-bath at 160°, then steam distilled into dilute hydrochloric acid. Recovery as above gave 100 mg. (19%) of XI-HCl. (2) A mixture of 1.35 g. (0.009 mole) of 1-nortricyclyl methyl ketoxime,[15] 2.3 g. of sodium carbonate, 8 ml. of water and 4 ml. of dioxane was heated to gentle reflux and 1.8 g. of benzenesulfonyl chloride was added over 20–25 minutes. After 10 more minutes of reflux, the mixture was cooled, whereupon 1.10 g. (81%) of mixed amides, m.p. 104–125°, was obtained. Attempted saponification with potassium hydroxide in aqueous ethylene glycol gave only an oily, neutral solid with intense carbonyl at 5.65μ (presumably norcamphor).

Deamination of 1-Aminonortricyclene (XI).—To a magnetically stirred solution of 2.0 g. (0.014 mole) of XI-hydrochloride, 30 ml. of glacial acetic acid and 2 ml. of acetic anhydride was added, over 1 hour, 2.0 g. of sodium nitrite. The mixture was stirred for 1 hour, treated similarly with another 2.0 g. of sodium nitrite, and stirred for another hour at which time gas evolution had stopped. After neutralization with saturated sodium bicarbonate, the mixture was extracted with several small portions of pentane. The pentane extracts were washed successively with water, sodium bicarbonate, water, dilute hydrochloric acid, water, and dried over anhydrous magnesium sulfate. The residue, after the pentane was removed, was distilled to give 1.14 g. (55%) of acetate, b.p. 41–42° at 2 mm. The residue (175 mg.) with an infrared band at 6.08 μ, was probably nitrate ester.

The distillate showed one symmetrical band in the v.p.c., either with a didecyl phthalate or a silicone column. A sample purified this way had significant bands at 3.23 (C–H on cyclopropane ring), 5.68 (carbonyl), 11.82 and 12.81μ (1-substituted nortricyclene).

Anal. Calcd. for $C_9H_{12}O$: C, 71.02; H, 7.94. Found: C, 70.81; H, 7.81.

1-Acetoxynortricyclene (XII).—Trifluoroacetic anhydride,[32] (2.3 g., 0.018 mole) was added dropwise to an ice-cold suspension of 0.4 ml. of 90% hydrogen peroxide in 5 ml. of methylene chloride. This solution was added (15 minutes) to an ice-cold mixture containing 1.0 g. (0.0074 mole) of 1-acetylnortricyclene (XIII), 5.26 g. of dry disodium hydrogen phosphate and 10 ml. of methylene chloride. The mixture was stirred for 0.5 hour in the ice-bath, 1.5 hours while warming to room temperature and finally refluxed for 1.5 hours. It was then cooled, decanted, and the mixed salts washed with several small portions of methylene chloride. The combined methylene chloride extracts were washed with water and 10% sodium carbonate and dried over anhydrous magnesium sulfate. After the methylene chloride was stripped, the residue was distilled yielding 300 mg. of nearly pure acetate (XII); the remaining 250 mg. was a mixture of acetate and starting ketone. The distillate, further purified by v.p.c., had an infrared spectrum identical with the acetate obtained from deamination of XI.

Norcamphor (XIV) from 1-Acetoxynortricyclene (XII).—A mixture of 200 mg. of XII (from the deamination of XI), 2 ml. of carbon tetrachloride and 10 ml. of 10% hydrochloric acid was refluxed with stirring for 12 hours, the layers separated, and the aqueous layer extracted with several small portions of carbon tetrachloride. After drying and removal of the solvent, a solid residue with an intense 5.65μ band was obtained. It was converted to its 2,4-dinitrophenylhydrazone which melted at 129–130° and showed no depression when mixed with an authentic sample of norcamphor-2,4-DNP[19] prepared from 2-acetoxy-5-norbornene[33] by hydrogenation, hydrogenolysis with lithium aluminum hydride and oxidation with chromic acid.

Deamination of 1-Aminomethylnortricyclene (XV).[34]—The procedure was the same as that described for XI, except that 3.0 g. (0.019 mole) of XV and two 3.0-g. portions of sodium nitrite were used. The acetate distillate (58–61°, 2.2 mm.) amounted to 1.6 g. (52%), and appeared from the infrared to be mainly 1-nortricyclylcarbinyl acetate (XVI, see below), with extraneous significant bands at 5.97, 6.02, 11.30 and 6.10μ. Vapor chromatographic analysis of this mixture over didecyl phthalate on firebrick gave inconclusive results, the shapes of the curves varying considerably with the temperature and carrier gas pressure.

A higher boiling (110–130° at 0.7 mm.) product, about 0.6 g., was not investigated, except that it had infrared bands at 5.97 and 6.02, but not 11.30μ.

1-Nortricyclylcarbinyl Acetate (XVI).—A solution of 8.0 g. (0.065 mole) of 1-nortricyclylcarbinol[15] in 50 ml. of anhydrous ether was added, during 30 minutes, to a stirred suspension of 1.54 g. (0.065 mole) of sodium hydride in 100 ml. of ether, and the mixture stirred for 24 hours. A solution of 5.06 g. (0.065 mole) of acetyl chloride in 50 ml. of ether was added, and the mixture stirred for another 24 hours. After filtration, the salts were washed thoroughly with ether and the combined ether layers were washed successively with water, sodium bicarbonate (3X), water, then dried over magnesium sulfate. The residue, after the solvent was removed, gave 8.3 g. (77%) of XVI, b.p. 58–60° at 2 mm.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.25; H, 8.49. Found: C, 72.27; H, 8.50.

When 0.25 ml. of XVI was passed through a preparative scale silicone-on-firebrick gas chromatographic column at 132° with N_2 carrier gas, the product obtained (band from 43 to 60 minutes after sample was injected) showed virtually complete absence of the characteristic 1-nortricyclyl bands present in XVI (at 11.73 and 12.73 μ), and showed new bands at 5.97 and 6.02 and 11.30 μ (very intense). This acetate is presumably 6-acetoxynorcamphene (XVII).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.25; H, 8.49. Found: C, 72.09; H, 8.44.

Hydrolysis of 1-Nortricyclylcarbinyl Trifluoroacetate (XVIII).—The trifluoroacetate[24] (2.6 g., 0.012 mole) was stirred at room temperature for 24 hours with 10 ml. of 10% sodium hydroxide, then extracted with ether, the extracts dried with magnesium sulfate and distilled to give 1.2 g. (80%) of alcohol, b.p. 53–55° at 0.8 mm. The spectrum

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[31] Analyses by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Mich. Melting points are uncorrected.

[32] E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2977 (1949).

[33] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

[34] This amine (hydrochloride) was described previously[15] but without a derivative. The phenylthiourea was prepared in the usual way; recrystallized from 95% ethanol, m.p. 159.5–160.0°. *Anal.* Calcd. for $C_{15}H_{18}N_2S$: C, 69.72; H, 7.02; N, 10.85. Found: C, 69.66; H, 7.04; N, 11.02.

was grossly different from that of 1-nortricyclylcarbinol,[15] with no bands at 11.78 and 12.74μ, but an intense terminal methylene band at 11.30μ.

This alcohol was converted to its acetate by the same general procedure as outlined for XVI. The acetate thus obtained, b.p. 51–52.5 at 1.8 mm., had an infrared spectrum identical with that obtained from the thermal gas chromatographic rearrangement of XVI (except for a trace band at 12.7 μ in the latter, presumably due to a slight amount of unrearranged XVI).

Analysis of the Acetates from Deamination of XV. (1) **Permanganate Oxidation.**—In order to determine the structure of the non-oxidizable acetate(s), the ester mixture was subjected to limited permanganate oxidation. A solution of 500 mg. of acetate in 5 ml. of ether was stirred at 0° with 10 ml. of 2% aqueous potassium permanganate containing a pinch of detergent. During the 8 hours, three 5-ml. portions of permanganate solution were added. Recovery of the ester from the ether layer (after filtration, water wash and drying) gave material with an infrared spectrum virtually identical with that of authentic 1-nortricyclylcarbinyl acetate. Trace bands at 5.97, 6.02, 6.10 and 8.90 μ were all attributable to slight contamination with material from the original mixture, but were greatly diminished in intensity when compared with the starting acetate mixture.

(2) **Titration for Unsaturates.**—The method of Reid and Beddard,[35] which is designed for determining small amounts of unsaturates in large quantities of saturates, was used. Accurately weighed 0.1-g. samples of ester were dissolved in 25 ml. of methanol, in 500-ml. iodine flasks and chilled to 0° (30 minutes). Standard bromine solution (10 ml. of 0.01155 N bromine in glacial acetic acid, standardized with thiosulfate to a starch end-point) was added, mixed thoroughly, kept at 0° for 3 minutes, diluted with 100 ml. of water, 10 ml. of 10% potassium iodide added and the solution titrated with standard 0.01 N sodium thiosulfate to a starch end-point. After correction for a small "blank" using pure 1-nortricyclylcarbinyl acetate, the mixture was shown to contain 8.2–8.4% unsaturation.

(3) **Infrared Analysis.**—Infrared spectra of mixtures of known concentrations of 1-nortricyclylcarbinyl acetate (XVI) and 6-acetoxynor-camphene (XVII) were compared with the deamination product. A carbon disulfide solution of deamination product in the "reference" beam and a mixture of 95% XVI and 5% XVII of identical concentration in the "sample" beam showed only two small deflections, at 6.10 and 8.90μ, both apparently due to the nitrate ester. All other bands were compensated.

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[Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass.]

Proximity Effects. XXI. Establishment of 1,3- and 1,5-Hydride Shifts in the Solvolysis of *cis*-Cycloöctene Oxide

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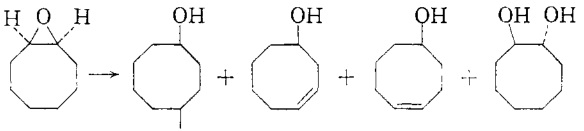
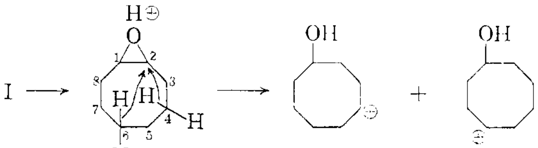
The solvolysis of *cis*-cycloöctene oxide with 90% formic acid has been studied with deuterium labeling on C_5 and C_6 of the epoxide. It has been established that *cis*-1,4-cycloöctanediol is formed to the extent of 61% by a 1,5-hydride shift and 39% by a 1,3-hydride shift, whereas 3-cycloöcten-1-ol is formed to the extent of 94% by a 1,5-hydride shift and 6% by a 1,3-hydride shift.

The solvolysis of *cis*-cycloöctene oxide (I) with formic acid has been shown to form *cis*-1,4-cyclooctanediol (II), 3-cycloöcten-1-ol (III), 4-cycloocten-1-ol (IV) and other minor products in addition to the expected *trans*-1,2-cycloöctanediol (V).[2–5]



I II III IV V

Formation of the transannular products (II, III and IV) must involve rearrangement of VI to VII by a 1,3-hydride shift or to VIII by a 1,5-hydride shift. Attack of a solvent molecule at C_4 of VII or at C_6 of VIII would then form II as its monoformate ester, whereas elimination of a proton from C_3 of VII or C_7 of VIII would give rise to III and elimination of a proton from C_5 of VII or VIII would form IV.



VI VII VIII

Deuterium tracer studies were undertaken to determine the relative amounts of 1,3- and 1,5-hydride shifts in this solvolysis. The compound chosen for study was *cis*-cycloöctene-5,6-d_2 oxide (IX). Figure 1 shows the reaction sequence employed. 4-Cycloöcten-1-ol and *trans*-1,2-cyclooctanediol are not shown since no degradation studies were made on these products. Formolysis of IX would yield the glycol X if a 1,3-hydride shift were involved and the glycol XII or XIII by a 1,5-hydride or deuteride shift. Similarly, the 3-cycloöcten-1-ol would be labeled as indicated by XI in the case of the 1,3-hydride shift and as indicated by XIV or XV in the case of the 1,5-hydride or deuteride shift.

Oxidation of the labeled 1,4-cycloöctanediol to adipic acid and esterification with diazomethane would form XVI or a mixture of XVII and XVIII, depending on whether the dimethyl adipate arises from X or a mixture of XII and XIII. Similarly, the labeled 3-cycloöcten-1-ol would be converted to either XVI or a mixture of XVII and XVIII by the same procedure. Finally, equilibration of

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(1) (a) Postdoctoral Fellow, 1959–1960; (b) National Institutes of Health Postdoctoral Fellow, 1956–1958; (c) Postdoctoral Fellow, 1958–1959.

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