Acetylation of cyclopropane in the presence of 5-chloro-2-pentanone (I, R = CH_3). In several acetylations of cyclopropane on a 1 mole scale, 25–27 g. (31–33%) of 3-methyl-3-butene-2-one was isolated. In two experiments in which 0.3–0.4 mole of 5-chloro-2-pentanone was added to the original reaction mixture, the yield of 3-methyl-3-butene-2-one remained 24–27 g. Furthermore, the yield of 5-chloro-2-pentanone corresponded to that normally found (30–33 g.) plus that initially added.

t-Butyl chloride and cyclopropane. The procedure was similar to that which Schmerling used[39] for addition of alkyl halides to olefins. A solution of 212 g. (2 moles) of *t*-butyl chloride in 100 ml. of chloroform was cooled to −50°, 90 g. (2.2 moles) of cyclopropane was added followed by 7 g. (0.053 mole) of aluminum chloride. After 10 min. the aluminum chloride was entirely dissolved and the solution was amber. After 2 hr., during which the temperature was allowed to rise to 0°, 25 ml. of 50% methanol was added. The chloroform layer, after washing with water and drying over potassium carbonate, gave 50 g. of product boiling over the range 40–110° at 92 mm. Careful fractionation into 19 cuts gave a major flat at 70–74° with variable refractive index (n_D^{20} 1.4258–1.4301). Fractions over the entire range corresponded approximately to $C_7H_{15}Cl$, but no single pure isomer was isolated.

Anal. Calcd. for $C_7H_{15}Cl$: C, 62.47; H, 11.24; Cl, 26.4. Found: Frac. 5 (53–55° at 92 mm., n_D^{20} 1.4181): C, 61.32; H, 11.13; Cl, 27.25. Frac. 8 (67–70° at 92 mm., n_D^{20} 1.4230): C, 62.90; H, 11.29; Cl, 25.6. Frac. 14 (74° at 92 mm., n_D^{20} 1.4301): C, 63.36; H; 11.28; Cl, 25.85.

(39) L. Schmerling, *J. Am. Chem. Soc.*, **67**, 1152 (1945).

EAST LANSING, MICH.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Cyclopropane Chemistry VII. Acetylation of Nortricyclene[1,2]

HAROLD HART AND ROBERT A. MARTIN

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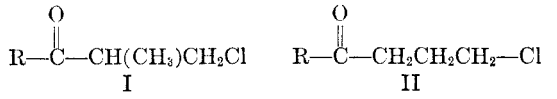
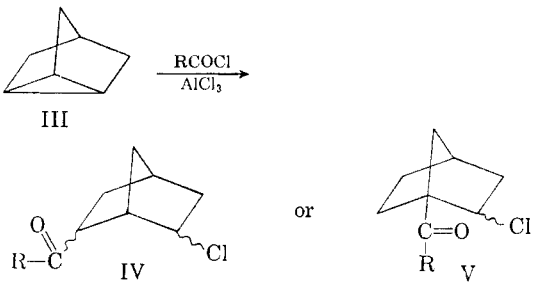
Nortricyclene reacts with acetyl chloride–aluminum chloride complex to give 2-chloro-6-acetylnorbornane (IV) which readily loses hydrogen chloride to give 1-acetylnortricyclene (VI), over-all yield 40–50%. The structure of the latter was proved by conversion to the known 1-methyl derivative. A number of 1-substituted nortricyclenes were prepared for the first time, from VI; correlations of their infrared spectra are discussed, with particular attention to bands in the 11.7μ and 12.7μ regions. A procedure is described for preparing VI from norbornene in 30–35% over-all yield.

The acylation of cyclopropane[3] and certain substituted cyclopropanes[1] was found to give predominantly β-chloroketones (I) and their related α,β-unsaturated ketones rather than the anticipated γ-chloroketones (II). I is formally produced by migration of a hydrogen from the carbon of the cyclopropane ring to which the acyl group becomes attached to one of the two remaining ring carbons, the chlorine becoming bound to the third. Because it is conceivable that both sides of the plane of the three-membered ring might be required for this shuffling of bonds, it seemed desirable to acylate a cyclopropane ring, one side of which was blocked from reaction by a cage. Nortricyclene (III) fulfilled this requirement, and was potentially of interest for several other reasons. If acylation of III were reasonably normal, one might learn something of the stereochemistry of additions to three-membered rings, a problem which has not yet been investigated. Furthermore, some of the anticipated acylation products might have intrinsic value for other mechanistic studies.



Normal addition to the three-membered ring of III would give 2-chloro-6-acylnorbornanes (IV) whereas the rearrangement observed in previous cyclopropane acylations[1,3] would be expected to give the β-chloroketones V. This paper describes the acetylation of III, a reaction which, as will be seen, has lead to a rather convenient approach to the previously inaccessible 1-substituted nortricyclenes.



Acetylation of nortricyclene (III). When pure nortricyclene[4] was acylated at 0–5° with the 1:1 acetyl chloride–aluminum chloride complex in methylene chloride, there was obtained (69%) a single chloroketone which decomposed with loss of hydrogen chloride on attempted fractionation at 14 mm. (85–95°) but could be distilled rapidly at 0.8 mm. (76–80°). Storage at Dry Ice temperature, at which the chloroketone was a solid, was possible, but dehydrohalogenation was rapid on storage at room

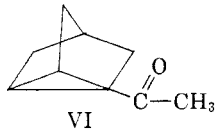
(1) For the previous paper, see H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).

(2) A portion of this work was sponsored by the Office of Ordnance Research, Contract No. DA-20-018-ORD-16492.

(3) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **79**, 931 (1957).

(4) J. D. Roberts, E. R. Trumbell, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

temperature. The dehydrohalogenation product was subsequently shown to be 1-acetylnortricyclene (VI); its precursor presumably was 2-chloro-



VI

6-acetylnorbornane (IV, R = CH_3) of undetermined stereochemistry (*vide infra*).

In subsequent experiments, when VI was the synthetic objective, the crude chloroketone was dehydrohalogenated without prior purification, either with sodium carbonate or by distillation at 14 mm. followed by refractionation. The over-all yield of VI from III was 40–50%. No other chloroketone (such as V) or unsaturated ketone was detected.

Structure proof of 1-acetylnortricyclene (VI). In view of the instability of the chloroketone (IV), the structure of its dehydrohalogenation product VI was first investigated. The absence of a carbon-carbon double bond band in the infrared, together with cyclopropyl C—H stretch bands at 3.26 μ[5,6] and 1.666, μ,[7,8] and a carbonyl absorption at 5.95 μ indicated a cyclopropane ring conjugated with a carbonyl group.[9] The 2,4-dinitrophenylhydrazone, m.p. 169.5–171°, obtained either as red plates or orange needles, had a λ_{max} at 378 mμ (log ϵ, 4.36), also characteristic of cyclopropyl conjugation.[10,11] The structure was proved chemically by conversion

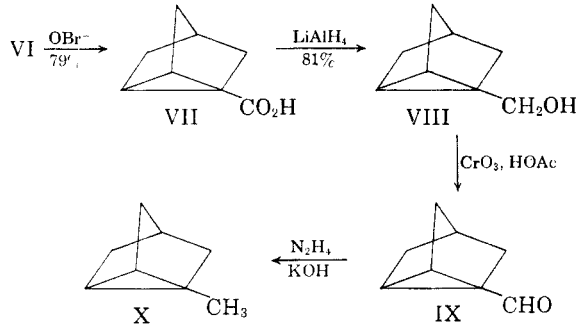
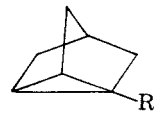


Chart I

(Chart I) to the known 1-methylnortricyclene (X).[12] Hypobromite oxidation of VI gave 1-nortricyclenecarboxylic acid (VII), m.p. 119–120°. This acid was different from the only other known nortricyclenecarboxylic acid (the 3-isomer, m.p. 49–50°, prepared according to Roberts and coworkers[4]). Lithium aluminum hydride reduction of VII gave the methanol VIII, the tosylate of which, on attempted reduction with lithium aluminum hydride gave only starting alcohol (VIII) rather than the desired 1-methylnortricyclene (X). Conversion to the latter was then accomplished by oxidation to the aldehyde IX (carbonyl band at 5.95 μ, red 2,4-DNP) which was not isolated pure but reduced directly (Wolff-Kishner) to X. The latter, purified by vapor chromatography, had an infrared spectrum identical with that of an authentic sample.[12,13]

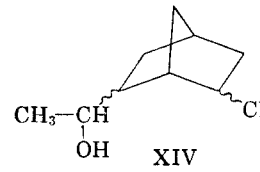
Several other new 1-substituted nortricyclenes were prepared. Lithium aluminum hydride reduction of VI gave XI, and the acid VII has been con-

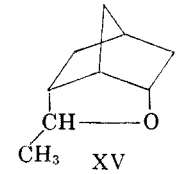


XI. R = —CH(OH)CH_3
XII. R = —$CONH_2$
XIII. R = —CH_2NH_2

verted, *via* the amide (XII), to the amine (XIII). Studies on the solvolysis of esters of VIII, XI, and related alcohols, and on the reaction of nitrous acid with XIII and related amines will be reported separately.[14]

Structure of the chloroketone (IV). IV, with a carbonyl band at 5.85 μ, was never obtained pure, but always had a carbonyl shoulder at 5.95 μ, presumably due to contamination with VI. The chlorine analysis of IV was about 8% low. That the structure of this primary acetylation product was IV and not V is apparent from its facile dehydrohalogenation to VI. It was possible to reduce IV to a chlorohydrin (XIV) using lithium aluminum hydride, with only partial dehydrohalogenation to VI. (Some methyl 1-nortricyclylcarbinol (XI) was obtained as a by-product in this reaction, presumably from VI.) Several attempts to convert XIV to the tetrahydrofuran (XV) failed, suggesting that the acetyl group in IV is predominantly *exo*. Further work is in progress on the stereochemistry of the acylation.





(5) S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

(6) See, however, C. F. H. Allen, T. J. Davis, W. J. Humphlett, and D. W. Stewart, *J. Org. Chem.*, **22**, 1291 (1957).

(7) W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958).

(8) For a more detailed analysis of the near-infrared correlations of cyclopropyl and nortricyclyl derivatives, see J. C. Sternberg and R. A. Martin, manuscript in preparation.

(9) The carbonyl band of dicyclopropyl ketone, for example, is at 5.91 μ; H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **78**, 112 (1956).

(10) M. F. Hawthorne, *J. Org. Chem.*, **21**, 1523 (1956).

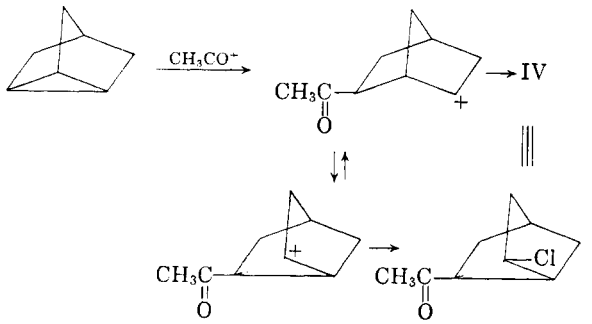
(11) See also A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, 2nd ed., Edward Arnold, Ltd., London, 1957, p. 120.

(12) We are indebted to Professor Paul von R. Schleyer, Princeton University, for an authentic sample of 1-methylnortricyclene, and for communications and discussions of the infrared spectra of nortricyclenes.

(13) A band at 12.53 μ in the spectrum of the authentic sample, and previously attributed[12] to an impurity, was absent from our spectrum; otherwise, the spectra were identical in all respects.

(14) Unpublished results with James A. Wrede and Robert A. Martin.

It should be pointed out that the acylation of nortricyclene may or may not proceed with rearrangements common in this system, since either path would lead to a product with the observed structure (IV). Examination of substituted nortri-



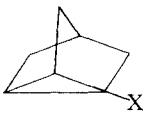
cyclenes, and further elucidation of the reactions, stereochemistry should shed light on this question.

Acetylation of the norbornene-nortricyclene equilibrium mixture. Schleyer showed recently[15] that norbornene and nortricyclene equilibrate over a silica-alumina catalyst to a mixture containing about 75% of the latter hydrocarbon. Since this might provide a much more convenient and large scale source of 1-acetylnortricyclene than the more difficultly available pure nortricyclene,[16] acetylation of the mixture was investigated. In preliminary experiments, norbornene was found to give, with acetyl chloride–aluminum chloride complex in methylene chloride, chloroketones remarkably stable to dehydrohalogenation (the structure and stereochemistry of these chloroketones will be the subject of a separate communication). It was obvious, then, in view of the ease with which IV is dehydrohalogenated, that 1-acetylnortricyclene (VI) could readily be obtained pure from the acetylation of the norbornene-nortricyclene equilibrium mixture. In the Experimental part of this paper, a procedure is described for obtaining VI from norbornene in over-all 30–35% yield, without isolation of intermediates (in addition, some chloroketone from acetylation of norbornene is also obtained).

Infrared spectra of 1-substituted nortricyclenes.[12] Having in hand a number of nortricyclenes substituted only in the 1-position, it seemed worthwhile to examine their infrared spectra for possible correlation bands. Nortricyclene itself and several 3-substituted derivatives absorb in the 12.4–12.5 μ region.[4] Another correlation at about 11.7 μ has been considered characteristic of this system[17] and a band in this region (11.83 μ) was used by Swann and Cripwell to follow the catalytic isomerization of camphene to tricyclene.[18] It was pointed out by Schleyer and O'Connor[19] that the 11.7 μ region band is associated with 1-substituted nortricyclenes, and that there is no peak of significant intensity in any nortricyclene which does not possess this structural feature. We found *both* bands to appear consistently in the spectra of every 1-substituted nortricyclene described in this paper (see Table I). Indeed, the band at 12.72 ± 0.03 is remarkably constant and independent of the nature of the 1-substituent. This band varies widely (12.1–12.7 μ) in position, however, when the 1-substituent is maintained constant (methyl) and other groups are placed elsewhere (especially in the 3-position) on the nortricyclene ring system.[19] It would seem, then, that the band at 12.72 μ is particularly characteristic of a 1-substituted nortricyclene which is otherwise unsubstituted. The somewhat more intense band in the 11.7 μ region is a bit more variable (11.60–11.95 μ) when the 1-substituent is varied, but remains more constant at about 11.75 μ when the 1-substituent remains constant (methyl)[19]; its position is relatively independent of groups elsewhere on the nortricyclene ring.

TABLE I

CHARACTERISTIC INFRARED ABSORPTION OF SOME 1-SUBSTITUTED NORTRICYCLENES,



X	11.7 μ Region	12.7 μ Region	Near-Infrared Band[a]
—$COCH_3$	11.77	12.72	1.668
—$C(=NOH)CH_3$	11.85	12.70	1.672
—$CH(OH)CH_3$	11.94	12.73	1.675
—CO_2H	11.60	12.74	1.662
—$CONH_2$	11.65	12.70	
—CH_2OH	11.78	12.74	1.674
—$CH_2OCONHC_6H_5$	11.74	12.75	
—$CH_2NH_3^+Cl^-$	11.74	12.75	
—CH_3	11.77	12.74	
—H	12.47		1.673

[a] Where no value is given, the spectrum was not investigated.

In summary, both bands seem characteristic of nortricyclenes substituted on the cyclopropane ring; the 11.7 μ band is relatively independent of other substituents, but varies somewhat in position depending upon the nature of the 1-substituent, whereas the 12.7 μ band is very constant for nortricyclenes substituted *only* on the cyclopropane ring, but is quite variable when substituents are placed elsewhere on the nortricyclene ring system. Finally, only mono-1-substituted nortricyclenes have been examined; it is quite possible that multi-

(15) P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

(16) A convenient procedure for obtaining norbornene is given by J. Meinwald and N. J. Hudak, *Org. Syntheses*, **37**, 65 (1957).

(17) J. Paasivirta, *Suomen Kemistilehti*, B31, 115 (1958).

(18) G. Swann and F. J. Cripwell, *Ind. Chemist*, **24**, 573 (1948).

(19) P. von R. Schleyer and R. E. O'Connor, private communication. See also P. von R. Schleyer, Ph.D. thesis, Harvard University, 1956 and R. E. O'Connor, A.B. thesis, Princeton University, 1957.

ple substitution on the cyclopropane ring may alter these correlations.

EXPERIMENTAL[20]

Acetylation of nortricyclene. To 40.2 g. (0.3 mole) of anhydrous aluminum chloride and 100 ml. of methylene chloride there was added (1.5 hr.) with stirring at 5° a solution of 31.4 g. (0.4 mole) of acetyl chloride in 50 ml. of methylene chloride, and the mixture allowed to stir overnight, or until a clear solution was obtained. To this was added 23.5 g. (0.25 mole) of nortricyclene[4] in 70 ml. of methylene chloride, the temperature being maintained below 5°. After addition was complete (1.5 hr.) the solution was stirred for 15 min. at 5°, then for 1.25 hr. while warming to room temperature, to complete the reaction. The ice-cold mixture was then hydrolyzed by dropwise addition of 200 ml. of 20% hydrochloric acid. The resulting water layer was extracted with two 50-ml. portions of methylene chloride. Combined organic layers were washed successively twice with 50 ml. of water, twice with 50 ml. of saturated sodium bicarbonate, once with 50 ml. of water, then dried over anhydrous sodium sulfate. Alternate procedures were then followed depending upon whether 2-chloro-6-acetylnorbornane (IV) or 1-acetylnortricyclene (VI) was the desired product.

(*a*) *2-Chloro-6-acetylnorbornane* (IV). After the methylene chloride was removed (*in vacuo*, room temperature) the residue was distilled under reduced pressure giving 30.1 g. (69.6%) of IV, b.p. 76–80° (0.8 mm.), n_D^{25} 1.4963, infrared carbonyl band at 5.85 μ with a slight shoulder at 5.95 μ.

Anal. Calcd. for $C_9H_{13}OCl$: Cl, 20.6. Found[21]: Cl, 18.9. Samples stored at room temperature evolved hydrogen chloride after a short time. In addition to IV, about 7 g. of a residue boiling above 125° (0.8 mm.) was obtained; its structure was not investigated.

(*b*) *1-Acetylnortricyclene* (VI). 1. *Dehydrohalogenation of* IV *with base.* After the methylene chloride was removed (*in vacuo*, room temperature), the residue was added dropwise (30 min.) to a refluxing solution of 60 g. of sodium carbonate monohydrate in 300 ml. of water. Reflux was continued for 15 min. after addition was complete. After cooling, layers were separated, the aqueous layer extracted with two 50-ml. portions of ether, and the combined organic layers dried over anhydrous sodium sulfate. After removal of the solvent there was obtained 13.5–17.0 g. (40–50%) of 1-acetylnortricyclene (VI), b.p. 50–52° (2 mm.) n_D^{25} 1.4926, intense carbonyl band at 5.95 μ.

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.89. Found: C, 79.26; H, 8.92.

2. *Thermal dehydrohalogenation of* IV. After distillation of the methylene chloride at atmospheric pressure, the residue was destructively distilled at 14 mm. using a water aspirator. Distillate collected at 85–95° was refractionated giving 13.5 g. (40%) of 1-acetylnortricyclene (VI).

Two derivatives, the 2,4-dinitrophenylhydrazone and oxime, of VI were prepared in conventional manners. The 2,4-DNP, obtained as red plates from 95% ethanol containing a little ethyl acetate, was converted by recrystallization from carbon disulfide or iso-octane to orange needles; both forms melted at 169.5–171° and showed λ_{max} (log ϵ) in 95% ethanol at 378 mμ (4.36), 260 mμ (4.00), 238 mμ (4.15).

Anal. Calcd. for $C_{15}H_{16}N_4O_4$: C, 56.95; H, 5.11; N, 17.71. Found: (red) C, 56.91; H, 4.96; N, 17.84. (yellow) C, 56.80; H, 5.15; N, 17.61.

The oxime, white plates from 95% ethanol, melted at 122.5–123.5°.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.48; H, 8.67; N, 9.26. Found: C, 71.47; H, 8.65; N, 9.20.

1-Acetylnortricyclene (VI) *from the nortricyclene-norbornene equilibrium mixture.* The procedure was analogous to the acetylation procedure described above for pure nortricyclene, except that an equilibrium mixture of nortricyclene-norbornene containing about 75% of the former (based on infrared analysis from 11.0 to 13.0 μ) was used.[15] Acetylation mixture prepared from 77.4 g. (0.58 mole) of aluminum chloride, 50.2 g. (0.64 mole) of acetyl chloride in 300 ml. of methylene chloride was treated as above with 54.5 g. (0.58 mole) of nortricyclene-norbornene equilibrium mixture in 150 ml. of methylene chloride. Work-up by destructive distillation at aspirator pressure followed by fractionation through a helices-packed column gave 23.6–26.6 g. (40–45%) of 1-acetylnortricyclene (VI), b.p. 50–52° (2 mm.) together with 11.0 g. (44%) of chloroketone, b.p. 83–85° (2 mm.), n_D^{25} 1.4950, derived from addition of acetyl chloride to norbornene. Since the equilibrium mixture of nortricyclene-norbornene is obtained in about 75% yield from norbornene (some polymer is produced during the isomerization),[15] the over-all yield of VI from norbornene is about 30–35%.

1-Nortricyclenecarboxylic acid (VII). To 5.0 g. (0.0368 mole) of 1-acetylnortricyclene (VI) there was added dropwise (1.5 hr.) at 0° a sodium hypobromite solution prepared by adding 17.8 g. (0.11 mole) of bromine to an ice-cold solution of 15 g. of sodium hydroxide in 100 ml. of water. The color disappeared after an additional 0.5 hr., after which the reaction mixture was stirred at room temperature for 3 hr. After acidification with hydrochloric acid and destruction of excess bromine with sodium bisulfite, the mixture was extracted with several portions of ether. Combined ether layers were extracted several times with 10% sodium hydroxide, the alkaline layers acidified (hydrochloric acid) and the crude solid acid filtered. Recrystallization from water or sublimation at 70° (1 mm.) gave 4.0 g. (79%) of 1-nortricyclenecarboxylic acid, m.p. 119–120°, neutralization equivalent 135.6 (theoretical, 138.2).

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.53; H, 7.30. Found: C, 69.65; H, 7.37. The amide (XII), obtained in 90% yield from the acid chloride (from VII and thionyl chloride) and anhydrous ammonia in ether solution, gave white lustrous crystals from benzene, m.p. 219–222° (dec.).

Anal. Calcd. for $C_8H_{11}NO$: C, 69.99; H, 8.08; N, 10.26. Found: C, 70.07; H, 8.14; N, 10.19.

1-Hydroxymethylnortricyclene (VIII). To a suspension of 8 g. (0.21 mole) of lithium aluminum hydride in 650 ml. of anhydrous ether was added (2 hr.) a solution of 12.5 g. (0.0907 mole) of VII in 100 ml. of anhydrous ether. After stirring for 2 additional hours at room temperature, the mixture was hydrolyzed with 10% sulfuric acid. Ether layers were washed successively with water, 10% sodium carbonate, water, and dried over anhydrous magnesium sulfate. After removal of solvent, there was obtained 8.81 g. (78.7%) of 1-hydroxymethylnortricyclene (VIII), b.p. 50–54° (0.8 mm.), n_D^{25} 1.4941.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.75. Found: C, 77.15; H, 9.61. The phenylurethane, recrystallized from ligroin, melted at 117.5–118°.

Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.08; H, 7.24; N, 5.78.

VIII was converted to its *p*-toluenesulfonate and reduction of the latter attempted. A solution of 2.5 g. (0.020 mole) of VIII in 100 ml. of anhydrous ether was stirred for 6 hr. with 0.48 g. (0.02 mole) of sodium hydride, during which time the white flocculent alkoxide precipitated. To the ice cold suspension was added a solution of 4.13 g. (0.02 mole) of *p*-toluenesulfonyl chloride in 75 ml. of anhydrous ether, and the whole stirred for 5 hr. After filtration, the ether was evaporated leaving an oil (presumably the tosylate) which showed no O—H bands (2.75 or 3.0 μ) in the infrared. Attempted reduction by stirring this oil with

(20) Microanalyses by Spang Microanalytical Laboratories, P. O. Box 1, Ann Arbor, Mich.

(21) This analysis was performed by R. A. M. on a freshly distilled sample, since the chloroketone is quite unstable. The method was that of R. Umhoefer, *Anal. Chem.*, **15**, 383 (1943). The results, which are about 8% low, are probably due to contamination with the dehydrohalogenation product (VI), as indicated by the infrared carbonyl shoulder at 5.95 μ.

2.0 g. (0.053 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether overnight followed by workup in the usual manner lead only to recovered VIII.

1-Formylnortricyclene (IX). The procedure was analogous to that of Lipp.[22] A solution of 5.0 g. (0.04 mole) of VIII in 100 ml. of 10% acetic acid was treated portionwise (10 min.) with 2.7 g. (0.041 mole) of chromic oxide. The mixture was heated on the steam bath for 0.5 hr., made alkaline with potassium carbonate, and steam distilled. The organic layer and ether extracts of the aqueous layer were dried (anhydrous magnesium sulfate) and solvent removed using a Vigreux column. The residue, which distilled at 83–87° (14 mm.), weighed 2.5 g. (50%) and was predominantly the desired aldehyde IX, carbonyl band at 5.95 μ, but was contaminated with some unchanged alcohol VIII. It was not further purified, but a portion was converted to the red 2,4-dinitrophenylhydrazone, m.p. 218–219.5° (recrystallized from 95% ethanol containing some ethyl acetate).

Anal. Calcd. for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67; N, 18.50. Found: C, 55.71; H, 4.77; N, 18.64.

1-Methylnortricyclene (X). The mixture of 20 ml. of diethyleneglycol, 1.9 g. of crude aldehyde (IX), 3 ml. of 85% hydrazine hydrate, and 3.5 g. of potassium hydroxide was refluxed for 1 hr., then distilled until the pot temperature reached 177°. The organic layer of the distillate was dried over anhydrous magnesium sulfate, and gave a single peak in a Perkin-Elmer vapor fractometer, preparative column with didecyl phthalate on firebrick, column temperature 76°. An authentic sample[12] showed identical retention time, and samples thus purified had identical infrared spectra.[13]

2-Chloro-6-(1-hydroxyethyl)norbornane (XIV). To a slurry of 3.7 g. (0.10 mole) of lithium aluminum hydride in 250 ml. of anhydrous ether there was added (2 hr.) a solution of 26.0 g. (0.15 mole) of crude 2-chloro-6-acetylnorbornane (IV), as obtained from the acetylation of nortricyclene, in 250 ml. of anhydrous ether. After 1 hr. of reflux, the mixture was cooled (ice) and hydrolyzed with water and dilute hydrochloric acid. Celite was added, the mixture stirred vigorously, filtered, and ether extracts of the celite-hydroxide residue combined with the organic layer and dried (anhydrous sodium sulfate). After the solvent was removed, the residue gave two main products, 6.8 g. (26%) of 1-(1-hydroxyethyl)nortricyclene (XI, *vide infra*), b.p. 55–57° (0.9 mm.), n_D^{25} 1.4858–1.4864 and 13.8 g. (53%) of 2-chloro-6-(1-hydroxyethyl)norbornane (XIV), b.p. 72–77° (0.4 mm.), n_D^{25} 1.5006–1.5040. The latter showed characteristic hydroxyl absorption (2.75 and 3.0 μ) and did not have the characteristic 1-substituted nortricyclene bands at 11.7 and 12.7 μ.

Anal. Calcd. for $C_9H_{15}CCl$: C, 61.88; H, 8.66; Cl, 20.30. Found: C, 62.00; H, 8.63; Cl, 20.35.

Several attempts to convert this chlorohydrin to a tetrahydrofuran (XV), including refluxing with powdered potassium hydroxide, led only to recovered starting material.

1-(1-hydroxyethyl)nortricyclene (XI). Reduction of 1-acetylnortricyclene (VI) with lithium aluminum hydride in the usual manner gave the corresponding alcohol (XI). From 8.0 g. (0.059 mole) of VI and 3.8 g. (0.1 mole) of lithium aluminum hydride in 150 ml. anhydrous ether there was obtained 6.6 g. (82%) of XI, b.p. 63–64° (1 mm.), n_D^{25} 1.4838.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.04; H, 10.21.

The hydrochloride of 1-aminomethylnortricyclene (XIII). To a suspension of 0.84 g. (0.0219 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was added as the solid, in several small portions, 1.0 g. (0.0073 mole) of 1-nortricyclenecarboxamide (XII), and the mixture stirred at room temperature for 3 hr., then hydrolyzed with water and 20% sodium hydroxide according to Gaylord.[23] The ether layer was dried overnight (barium oxide), then treated with anhydrous hydrogen chloride, whereupon the white crystalline hydrochloride of XIII was obtained, 1.05 g. (90%), m.p. 238–239.5° (dec.).

Anal. Calcd. for $C_8H_{14}NCl$: C, 60.19; H, 8.84; N, 8.77; Cl, 22.27. Found: C, 60.21; H, 8.76; N, 8.74; Cl, 22.39.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Addition of Halogens and Halogen Compounds to Allylic Chlorides. II. Addition of Hypochlorous Acid to Allylic Chlorides[1]

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The addition of hypochlorous acid to allylic chlorides yielded products which were not always consistent with expected results based on a comparison with the addition of hydrogen halide to the same compounds. The addition products observed were: 2,3,3-trichloropropan-1-ol (98%) and 1,1,3-trichloropropan-2-ol (2%) for 3,3-dichloropropene; 2,3,3,3-tetrachloropropan-1-ol for 3,3,3-trichloropropene; 1,1,3-trichloropropan-2-ol and a small amount of 1,1,2,3-tetrachloropropane for 1,3-dichloropropene; 1,1,1,3-tetrachloropropan-2-ol and 1,1,1,2,3-pentachloropropane for 1,1,3-trichloropropene. No detectable allylic isomerization was found to accompany the addition of hypochlorous acid to 3,3-dichloropropene and 3,3,3-trichloropropene.

Introduction. The products obtained by addition of hydrogen halides to certain allylic chlorides have been described in Part I[3] of this series on the addition of halogens and halogen compounds to allylic chlorides. This second paper of the series is concerned with the orientation of the addition of hypochlorous acid to these same allylic chlorides.

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(3) Part I, *J. Org. Chem.*, 23, 1876 (1958).