

Δ^3 -Norcarene.—The reaction of 1,4-cyclohexadiene, methylene iodide, and zinc-copper couple, run by a modification of the procedure of Smith and Simmons,²¹ afforded Δ^3 -norcarene, b.p. 114–116° (reported^{3b} 115–115.5°), n_D^{25} 1.4740 (reported^{3b} 1.4740), in 37% yield. Purification was effected by two preparative vapor phase chromatographic passes, collecting only peak centers, followed by distillation from calcium hydride under anhydrous conditions. Clear colorless liquid, b.p. 114.5–115.0° (749 mm.), n_D^{25} 1.4732, was obtained. This material has also been prepared by this same method by Simmons.⁹

7,7-Dibromobicyclo[4.1.0]heptane was obtained by the reaction of dibromocarbene with cyclohexene.⁶ Fractionation of the product, followed by refractionation of a center cut, gave clear colorless liquid, b.p. 87.5–88.0° (5 mm.), n_D^{25} 1.5527. We are indebted to Mr. Phillip Radlick for preparation of this compound.

Δ^3 -7,7-Dibromobicyclo[4.1.0]heptane was prepared as previously described.^{3b} Recrystallization from ethanol afforded a sample, m.p. 37–38° (reported^{3b} 37.8–38.8°).

4,4-Dibromotricyclo[5.1.0.0^{3,5}]octane.—To a stirred solution, maintained under anhydrous conditions and a nitrogen atmosphere, of 9.4 g. (0.1 mole) of Δ^3 -norcarene and 37.95 g. (0.15 mole) of bromoform, freshly distilled from mercury, in 50 ml. of *t*-butyl alcohol, distilled from calcium hydride, was added dropwise over 2 hr. 22.4 g. of potassium *t*-butoxide in 200 ml. of anhydrous *t*-butyl alcohol. The mixture was stirred for 9 hr. and then poured into 500 ml. of pentane and 100 ml. of water. The pentane was extracted with five 100-ml. portions of water, dried over anhydrous sodium sulfate, and, after filtration, the pentane was evaporated on a steam bath through a Vigreux column. The residue was pumped at 25° (30 mm.) for 6 hr. Distillation afforded a middle cut of 4.54 g. (17%), b.p. 84–85° (3 mm.), n_D^{25} 1.5631. Redistillation and collection of a middle cut gave clear colorless liquid, b.p. 73.5–74.0° (1.5 mm.), n_D^{25} 1.5651.

Anal. Calcd. for C₈H₁₂Br₂: C, 36.12; H, 3.79; Br, 60.01. Found: C, 36.20; H, 3.99; Br, 60.25.

A solution of 1.06 g. of the dibromide, n_D^{25} 1.5631, and 3.5 g. of *t*-butyl alcohol in 30 ml. of tetrahydrofuran, purified by con-

tact with potassium hydroxide pellets for 3 days and then distillation from lithium aluminum hydride, was stirred under a stream of argon while 0.66 g. of lithium wire was cut in the neck of the flask with a long point scissors. The reaction began immediately and stirring under anhydrous conditions was continued for 3 hr. The mixture was then poured into ice-water through a glass wool plug. The water was extracted with three 100-ml. portions of pentane and the pentane extracted with five 50-ml. portions of water and dried over anhydrous potassium carbonate. Vapor phase chromatography indicated that 99.3% of the hydrocarbon was the *trans* isomer, while 0.7% was the *cis* isomer.²

4,4,8,8-Tetrabromotricyclo[5.1.0.0^{3,5}]octane was prepared as previously reported.^{3b} Two recrystallizations from chloroform gave thick needles, m.p. 204.2–206.2° (reported^{3b} 205–206°).

Anal. Calcd. for C₈H₈Br₄: C, 22.46; H, 1.90; Br, 75.42. Found: C, 22.54; H, 1.82; Br, 75.21.

Tricyclo[5.1.0.0^{3,5}]octane.—Dehalogenation of 1.57 g. of the tetrabromide with lithium and *t*-butyl alcohol in tetrahydrofuran afforded after distillation 0.2 g. of a hydrocarbon which had no (<0.1%) *cis* isomer detectable by vapor phase chromatography. Purification was effected by preparative vapor phase chromatography in the same manner as above, followed by distillation from calcium hydride under anhydrous conditions. Clear colorless liquid, n_D^{25} 1.4760, b.p. (micro) 140.6° (749.6 mm.), was obtained.

Anal. Calcd. for C₈H₁₂: C, 88.82; H, 11.18. Found: C, 88.52; H, 11.05.

The infrared spectrum of this product was identical with that of the major bis-adduct obtained by Simmons⁹ and also Boikess² from the Siminons-Smith reaction on 1,4-cyclohexadiene. It was also identical with the spectrum of the predominant bis-adduct obtained by Doering¹⁰ using diazomethane-cuprous chloride.

Cyclohexene.—Eastman cyclohexene was distilled from sodium through a Todd column; the fraction boiling at 83° at 759 mm. was used.

Cyclopentene.—Aldrich cyclopentene was distilled from sodium through a Todd column; the fraction boiling at 45° at 759 mm. was used.

[CONTRIBUTION FROM THE UNION CARBIDE RESEARCH INSTITUTE, TARRYTOWN, N. Y.]

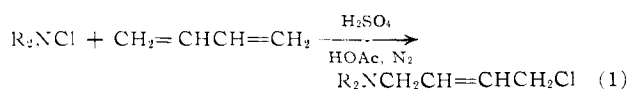
A Nuclear Magnetic Resonance Study of the Products from an Unusual Reaction of Norbornadiene. The Ionic Addition of N-Chlorodiethylamine in Sulfuric Acid-Acetic Acid

BY ROBERT S. NEALE AND EARL B. WHIPPLE

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The reaction between N-chlorodiethylamine and norbornadiene in acetic acid 4 M in sulfuric acid and 1.5 M in water, under either nitrogen or air, yielded 30% of two 1:1 adducts, *exo*-2-diethylamino-*syn*-7-chloro-5-norbornene (III) and a single isomer of 3-chloro-5-diethylaminonortricyclene (IV). Also isolated was 30% of a mixture of three isomeric derivatives of norbornadiene bearing chlorine and acetoxy substituents. An ionic pathway rather than the expected radical pathway to the basic products III and IV is indicated from the stereochemistry of III and from the insensitivity of the balance between neutral and basic products to the presence of air. It is therefore remarkable to have obtained a fair yield of *basic* products in a medium acidic enough to have completely protonated all the bases present. The carbonium ion resulting from *exo* addition of Cl⁺ to norbornadiene appears to be the precursor common to all five reaction products. It was possible to deduce completely the stereochemistry of III and two of the three nortricyclene-type products solely on the basis of their n.m.r. spectra.

In a previous paper¹ it was reported that N-chlorodialkylamines undergo free radical addition to butadiene to afford products of 1,4-chloroamination (eq. 1), but that 1,1-diphenylethylene yields only the ionically-derived product 1-chloro-2,2-diphenylethylene under identical conditions. Norbornadiene was also



employed as the olefinic substrate¹ to determine whether

the expected anchimeric participation² of one double bond might result in radical addition of the chloroamine similar to that observed for butadiene, or whether ionic chlorination might occur instead. The experiment was one of several designed to test the effect of an olefin's structure upon its ability to undergo a chloroamination reaction, a topic presently under active study. Although both neutral and basic products were formed in the reaction between norbornadiene and N-chlorodiethylamine, only ionic processes

(1) R. S. Neale and R. L. Hinman, *J. Am. Chem. Soc.*, **85**, 2666 (1963).

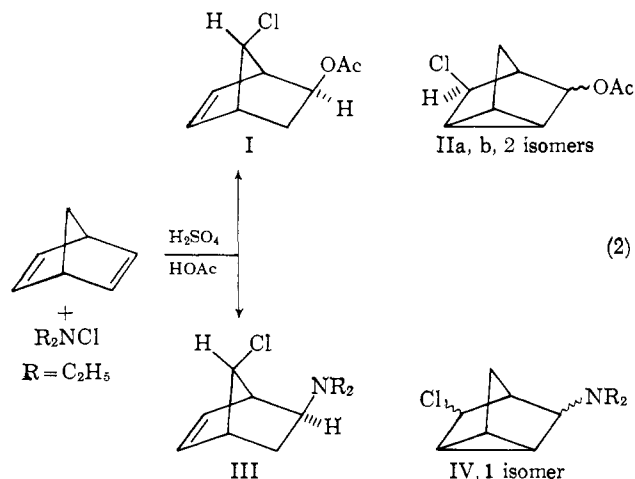
(2) S. Winstein, C. R. Lindgren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

were found to be involved.¹ Incorporation of amino groups into an adduct with norbornadiene despite the highly acidic medium was therefore surprising. We now describe this unusual reaction more fully, with particular emphasis on product determination by n.m.r. spectroscopy. The reaction is of further interest because it illustrates an ionic addition reaction of norbornadiene similar to those already described,^{3,4} but in only one instance³ rigorously studied for identification of all the rearrangement products.

Summary of Results

A spontaneous, exothermic reaction took place at 5–10° when 0.14 mole of norbornadiene was added under nitrogen in the dark to an acetic acid solution 0.65 M in N-chlorodiethylamine, 4 M in sulfuric acid, and 1.5 M in water. When the addition was complete (10 min.), the solution temperature had dropped and iodometric titration showed that no more chloroamine remained. The homogeneous reaction mixture was poured into ice-water to liberate an oil which was extracted into pentane and found to consist of about 30% of a mixture of chloroacetoxy adducts of norbornadiene; two isomers of the saturated product II, 3-acetoxy-5-chloronortricyclene, predominated (> 90%) and were accompanied by a small amount of the unsaturated isomer I, *exo*-2-acetoxy-*syn*-7-chloro-5-norbornene. Basification of the diluted reaction mixture liberated the basic products; these consisted of a single unsaturated adduct of N-chlorodiethylamine and norbornadiene, *exo*-2-diethylamino-*syn*-7-chloro-5-norbornene (III), and a single isomer of the saturated adduct 3-chloro-5-diethylaminonortricyclene (IV), in about 30% combined yield.

Reaction 2 was reproducible in all respects under nitrogen. To test whether the basic adducts III and



IV, then of undetermined stereochemical structure, were the products of a radical process,⁵ reaction 2 was carried out in the presence of air, which was known¹

(3) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956).

(4) D. Schermerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956); G. T. Youngblood, C. D. Trivette, Jr., and P. Wilder, Jr., *J. Org. Chem.*, **23**, 684 (1958).

(5) Radical additions to norbornadiene are known to yield 3,5-addition products, often accompanied by 2,3-addition products: (a) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958); S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961); N. O. Brace, *ibid.*, **27**, 3027 (1962); A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *ibid.*, **28**, 1262 (1963); C. E. Castro and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 4928 (1961), footnote 24; (b) D. J. Trecker and J. P. Henry, *ibid.*, **85**, 3204 (1963).

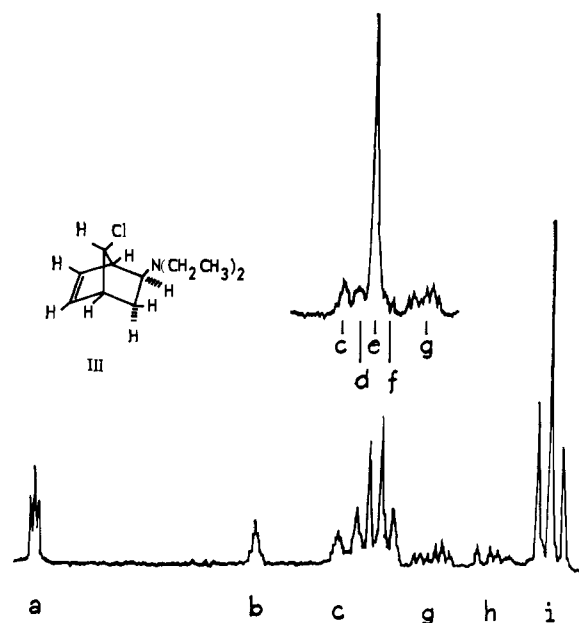


Fig. 1.—60 Mc. n.m.r. spectrum of III. Resolved regions are indicated by letters which correspond to the hydrogens identified in Table I; the insert depicts the c–g regions with the N-methylene hydrogens (e) decoupled from the methyl hydrogens (i).

to inhibit the radical addition of chloroamines to butadiene. Surprisingly, the same products I–IV were obtained in the same yield as under nitrogen. It was therefore apparent that the basic products had their principal origin in a mechanism that did not involve oxygen-sensitive radicals, especially the free $\dot{>N}H$ radical. An ionic mechanism was further indicated later by the stereochemistry of one of the basic adducts III; the Cl and NEt_2 groups would be interchanged if III resulted from a radical chain reaction involving a free aminium radical.

Characterization of Products

The structures of the basic adducts were established as follows. Acidified aqueous alcoholic solutions of the adduct mixture deposited silver chloride on heating in silver nitrate solution. Infrared and n.m.r. spectra of the norbornene-nortricyclene type. The characteristic⁶ *cis*-RCH=CHR band appeared at 14.4 μ in the infrared spectrum of the norbornene isomer III, isolated by g.l.c., and its n.m.r. spectrum indicated eighteen hydrogen atoms distributed in the ratio 2:1:7:2:6. Two vinyl⁷ hydrogens appeared at 3.92 τ (Fig. 1 and Table I), and the CHCl hydrogen⁸ appeared at 6.22 τ . The infrared spectrum of IV, however, contained the characteristic⁹ bands of a disubstituted nortricyclene at 12.13, 12.40, and 12.78 μ , but its n.m.r. spectrum (no vinyl hydrogens) again indicated eighteen hydrogens, this time in the ratio 1:5:2:4:6 (Table II). Curiously, two of the "nortricyclene" bands (12.13 and

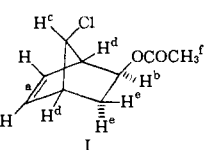
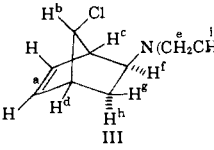
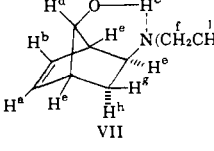
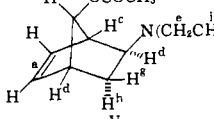
(6) (a) L. J. Bellamy, "The Infrared Spectra of Complex Organic Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 48; (b) L. Kaplan, M. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

(7) (a) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2709 (1963); (b) R. Frazer, *Can. J. Chem.*, **40**, 78 (1962).

(8) (a) Examples of this type of hydrogen in bicyclic systems are now plentiful; the range of τ -values appears to be from 5.45 in *anti*-7-chloro-2-norbornene, ref. 6b, to 6.40 in *endo*-3-chloronortricyclene, J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961); (b) other examples are provided by Miller and ref. 11.

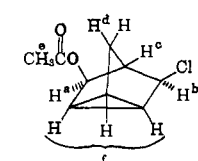
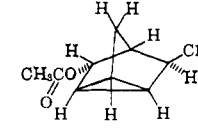
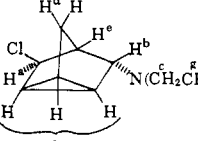
(9) G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962).

TABLE I
 N.M.R. SPECTRA OF SUBSTITUTED NORBORNENES AT 60 Mc.^a

Compound	Hydrogen assignment									
	a	b	c	d	e	f	g	h	i	
 I	3.80 m5 (1.5) 2H	5.42 m4 (7,4) 1H	6.05 m4 (3,1) 1H	7.05 um 2H	7.8-8.1 ^b —5H—	8.0 ss				
 III	3.92 m3 (2.0) 2H	6.22 m5 (1.5) 1H	7.05 m3 (2.0) 1H	7.16 ^c um —6H—	7.38 m4 (7)	7.50 ^e um 1H	7.96 m6 (12,5,4)	8.53 m8 (12,7.5,1.5)	9.05 m3 (7)	6H
 VII	3.90 ^d m8 (5.5,3.2,0.8) 1H	4.18 ^d m8 (5.5,3.7,1.2) 1H	4.68 ss 1H	6.45 bs 1H	(7.1-7.5) —7H—	7.30 m4 (7)	8.22 m6 (12,3.5,3.5)	8.53 m8 (12,7.3,0.6)	8.99 m3 (7)	6H
 V	4.00 m3 (2) 2H	5.80 bs 1H	6.78 ^e m3 (2) 1H	(7.2-7.7) —6H—	7.44 m4 (7)	8.13 ss —5H—	~8.15 m ^f	8.58 m4 (12,7.5)	9.08 m3 (7)	6H

^a Four data are listed for each hydrogen: (1) chemical shift in CCl₄ relative to tetramethylsilane (10.00 τ) with substrate concentration 10-20%; (2) description of pattern, with s = singlet, ss = sharp singlet, m = multiplet (m3 = triplet, m4 = quartet, etc.), u = unresolved, b = broad; (3) coupling constants in the pattern, in parentheses; (4) integrated relative areas. ^b Partly masked by OCOCH₃ peak. ^c Observed only on collapse of the NCH₂ quartet by simultaneous irradiation at NCH₂CH₃. ^d Probable assignment. ^e Assigned by analogy to the corresponding chloride III, wherein the low-field allylic H is adjacent to N.

 TABLE II
 N.M.R. SPECTRA OF SUBSTITUTED NORTRICYCLENES AT 60 Mc.^a

Compound	Hydrogen assignment						
	a	b	c	d	e	f	g
 IIa	5.40 m3 (~1.5) 1H	6.02 m3 (~1.5) 1H	7.75 bs 1H	7.98, 8.12 ^{b,c} m2 2H	8.02 s 3H	8.4 m2 (1) 3H	
 IIb	5.25 m3 (~1.5) 1H	5.60 m3 (~1.5) 1H	7.83 —2H—	8.0, 8.4 ^e —2H—	8.00 ss 3H	8.4 m3 (5) 4H ^d	
 II ^e	5.60 m3 (1) 1H	? —5H—	7.40 m4 (7) —5H—	—7.9-8.1— um —2H—		8.5-8.7 um 4H ^d	9.05 m3 (7) 6H

^a Four data are given for each hydrogen: (1) chemical shift in τ (see footnote a, Table I); (2) description of pattern (see footnote a, Table I); (3) hyperfine splitting, in parentheses; (4) integrated relative areas. ^b Partly masked by OCOCH₃ peak; $J_{ad} \sim 11$ c.p.s. ^c Estimated; see text. ^d Includes one d-hydrogen; see text. ^e Probable stereochemistry.

12.80 μ) also appeared in the infrared spectrum of the norbornene III. Comparison of the spectrum of III with the spectra of the acetate and alcohol derivatives of III implicated the 12.13 μ band as arising from the C-Cl group.

Elemental analyses of the chlorides III and IV were not obtained because both readily decomposed on standing. Solvolysis in boiling acetic acid-sodium acetate of the adduct mixture consisting of 57% of the

olefinic compound III afforded 75% of the corresponding acetates V and VI in the ratio 62:38. The olefinic chloride III reacted somewhat faster than its saturated isomer IV (see Experimental). Each acetate, isolated by g.l.c., analyzed correctly for C₁₃H₂₁NO₂. A sample of the olefinic acetate V was reduced with lithium aluminum hydride in ether to an alcohol VII, C₁₁H₁₉NO, which was converted with thionyl chloride in chloroform-pyridine to the original chloride III.

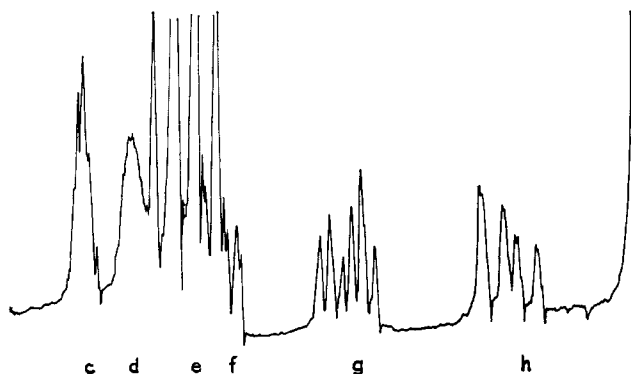
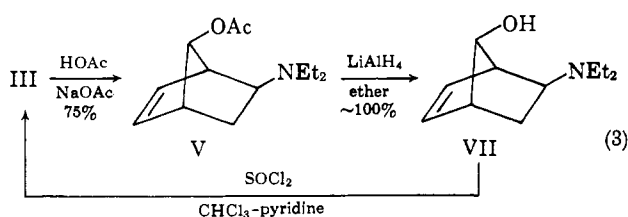
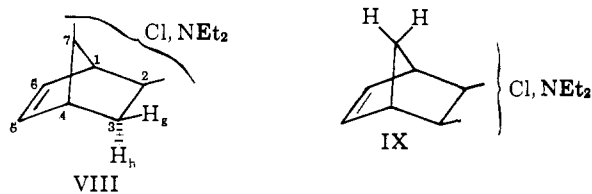


Fig. 2.—100 Mc. n.m.r. spectrum of III showing regions c-h.

This established the empirical formula of III to be $C_{11}H_{13}ClN$. These transformations are summarized by eq. 3.



Compound III was thus known to be an adduct of norbornadiene and N-chlorodiethylamine containing an unsubstituted double bond and the $CHCl$ group. The precise location and configuration of the Cl and NEt_2 substituents on the norbornene skeleton were deduced from n.m.r. spectra of III, as follows. Two allylic (bridgehead) hydrogens were located in regions c and d (Fig. 1 and 2) by observing partial collapse of the vinyl pattern on double irradiation in either region. The choice of partial structure was thereby limited to VIII or IX.



A mutual splitting of ~ 12 c.p.s. showed the patterns g and h in Fig. 1, each corresponding to a single hydrogen, to result from the CH_2 group in either VIII or IX. The very different chemical shifts of hydrogens g and h suggest structure VIII by analogy to other substituted norbornenes.^{7a,10} The presence of the CH_2 group at C-3 was confirmed and the stereochemistry of the substituents at C-2 and C-7 was derived from consideration of the secondary splittings in patterns g and h and by reference to model systems,^{7a,10,11} as follows.

The low-field pattern g contains two secondary splittings of ~ 5 and ~ 4 c.p.s. (see Fig. 2), which are of the expected magnitudes for an *exo* ring hydrogen coupled to an adjacent bridgehead hydrogen and a neighboring *endo*-hydrogen; the pattern h, containing a single secondary splitting of 7.5 c.p.s., is typical of the coupling between adjacent *endo*-hydrogens. Spin de-

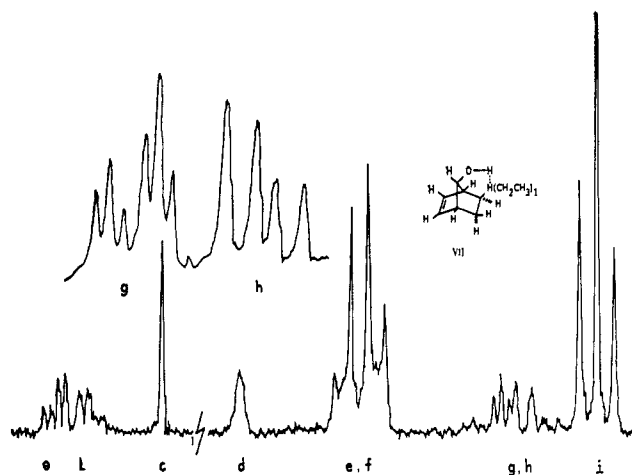


Fig. 3.—60 Mc. n.m.r. spectrum of VII with inserted 100-Mc. scan of peaks due to the ring methylene hydrogens g and h. Letters correspond to the hydrogens identified in Table I.

coupling experiments confirmed that the 7.5 c.p.s. splitting in h and one of the secondary splittings in g were due to the (*endo*) C-2 hydrogen in VIII. These data, which are clearly incompatible with structure IX, accord only with structure VIII bearing the chlorine at C-7, because none of the splittings in the patterns g and h just described are reciprocated in the $CHCl$ pattern b. The diethylamino substituent is therefore *exo* at C-2.

The 7-chloro substituent was determined to be *syn* to the *exo*-2-diethylamino group because the $CHCl$ hydrogen (quintet, $\langle J \rangle 1.5$ c.p.s.) is coupled to the two bridgehead¹² hydrogens and the *endo*-hydrogens in the 2- and 3-positions. Three of the couplings were demonstrated by double irradiation in the regions c, f, and h, which each time simplified the pattern b; furthermore, each of the quartet peaks in the *endo*-hydrogen pattern h, but not in the *exo*-hydrogen pattern g, was split by 1.5 c.p.s. (Fig. 2), clearly reciprocating the magnitude of splitting in region b. Since bridgehead hydrogens are reported not to split adjacent *endo*-hydrogens,¹¹ no source of this fine structure is likely other than coupling with a 7-hydrogen, which occurs¹³ only when the 7-hydrogen is *anti* to the interacting *endo*-hydrogens.

The olefinic adduct III was thereby proved to be *syn*-7-chloro-*exo*-2-diethylamino-5-norbornene. Proof that the hydroxyl group of the related alcohol VII was also at C-7 and *syn* to the amino group is presented next; this establishes that the stereospecificity of the sequence in eq. 3 involved retention of configuration rather than double inversion as the route $III \rightarrow V \rightarrow VII \rightarrow III$ was traversed. The same type ring methylene pattern due to hydrogens attached to C-3 was observed in the n.m.r. spectrum of VII as in III; however, it was necessary to scan the region at 100-Mc. to resolve completely the two patterns (Fig. 3). The same arguments used above for the chloride direct that the hydroxyl reside at C-7. The configuration of the C-7 hydroxyl was then determined as follows.

The infrared spectrum of VII was observed as a liquid film and in solution down to 0.0055 M in carbon tetrachloride; a strong hydroxyl band¹⁴ at 3.05μ

(12) F. S. Mortimer, *J. Mol. Spectry.*, **3**, 528 (1959).

(13) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(14) Reference 6a, p. 96.

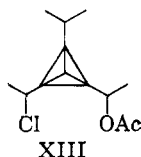
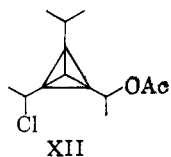
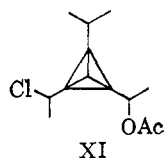
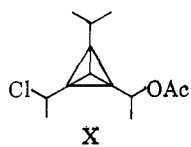
(10) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

(11) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

remained essentially unchanged in shape and intensity relative to the C-H band at 3.3μ . Even in the most dilute solution the free -OH band¹⁴ at 2.75μ was barely discernible. This behavior has been cited previously¹⁵ to be strongly indicative of intramolecular hydrogen bonding of the hydroxyl group. The 3.05μ band is of too low frequency and high intensity for an intramolecular hydrogen bonded hydroxyl-hydroxyl absorption.^{16,17} Although it is stronger than the corresponding -OH...NR₃ band in 3-dimethylamino-1-propanol, it resembles the analogous band in 2-dimethylamino-3,5-dimethylphenol.¹⁸ Accordingly, we attribute the observed hydroxyl absorption in the spectrum of VII to an association of the type -OH...NR₃; this requires the hydroxyl group on C-7 to be *syn* to the nitrogen, *i.e.*, of the same configuration as the corresponding chloride III. This, in turn, establishes that the corresponding acetate V possesses a *syn*-7-acetoxy group.

Full assignment of the structures of the neutral chloroacetates I and II also formed in reaction 1 was achieved by consideration of their infrared and n.m.r. spectra. Three components of the mixture of chloroacetates with composition C₉H₁₁ClO₂ were isolated by g.l.c. The minor, olefinic product *exo*-2-acetoxy-*syn*-7-chloro-5-norbornene (I) showed the characteristic⁹ *cis*-RCH=CHR band in the infrared at 14.1μ and a band at 12.2μ , assigned to the C-Cl group as in the basic chloride III; its n.m.r. spectrum contained peaks in the ratio 2:1:1:2:5. The skeletal positions of the lower field¹⁹ CHOAc and CHCl hydrogens were established from the magnitudes and nonreciprocity of their splitting constants (see Table I). Compound I was previously and incorrectly reported to be a 2,3-disubstituted 5-norbornene.¹

The two other components of the C₉H₁₁ClO₂ mixture were found to be isomers of 2-acetoxy-5-chloronorbornene (IIa,b) from their infrared spectra, both of which contained characteristic⁹ bands at 12.13, 12.30, and 12.95 μ , and from their distinctly different n.m.r. spectra. This limits possible structures of IIa,b to *dl* pairs of the four arrangements shown in the projection diagrams X through XIII.



The n.m.r. spectrum of one of the isolated isomers IIa shows five main regions of absorption with the intensity ratio 1:1:1:5:3 in order of increasing external

(15) P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961).

(16) H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954).

(17) P. von R. Schleyer, D. S. Trifan, and R. Baeska, *ibid.*, **80**, 6691 (1958).

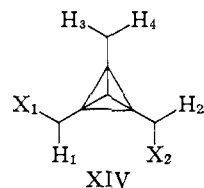
(18) A. W. Baker and A. T. Shulgin, *ibid.*, **80**, 5358 (1958).

(19) The CHOAc hydrogen always appeared at lower field than the CHCl hydrogen in comparable cases among our compounds; see also ref. 7a and 10.

field, the fourth group containing the acetate methyl peak. Since both the cyclopropyl and methylene groups consist of strongly coupled nuclei, the observed absence of strong splittings requires that the chemical shifts of the hydrogens of each structural type be approximately equal, *i.e.*, the signals may be assigned as shown for IIa in Table II. Both the low-field hydrogens have similar, poorly resolved triplet fine structure, shown by triple resonance experiments to arise almost entirely from the cyclopropyl and apex (C-4) hydrogens. One may hence expect the methylene hydrogens to give an AB pattern, each component of which has fine structure rather similar to that in the low-field peaks. Careful consideration of the detailed spectrum in the region of the acetate methyl group then enables one to estimate the chemical shifts of the two methylene hydrogens (Table II).

The n.m.r. spectrum of the other isomer IIb has similar features, except that one of the methylene hydrogens is shifted into the *high*-field region with the cyclopropyl hydrogens, while the CHCl peak occurs at 0.4 p.p.m. *lower* field. Other, smaller shifts are recorded in Table II. Since differences in the apex and cyclopropyl hydrogen shifts are minor, the changes are evidently due to nonbonded influences such as originate from magnetic anisotropy and/or electrostatic fields about neighboring groups. We assume that hydrogens similarly situated with respect to the point of attachment of neighboring acetoxy or chlorine atoms are chemically shifted in the same direction by these substituents, and that the effect is strongest at the nearest neighbors. On this basis, we assign to the first isomer Ia, whose spectrum is more or less symmetrical, one of the quasisymmetrical structures X or XIII, and to compound IIb, whose spectrum shows unequally shifted methylene hydrogens, one of the unsymmetrical arrangements XI or XII.

Consideration of the directions of the near-neighbor effects produced on interchanging X₁ and H₁ or X₂ and H₂ in the model XIV enables us to specify single structures for IIa and IIb. Interchange of X₁ and H₁ should affect H₁ and H₃ most strongly and in the



same direction, *i.e.*, to higher or lower field; interchange of X₂ and H₂ would, on the other hand, shift H₁ and H₄ most strongly, and in opposite directions. Since the principal shifts observed are in opposite directions, the indicated interchange in the unsymmetrical isomer involves X₂; this must be the acetoxy group because the CHCl hydrogen (H₁ in the model) is the one strongly shifted.¹⁹ Thus, the quasisymmetrical isomer IIa has structure X and the "unsymmetrical" isomer IIb has structure XI. Indeed, if the *lower*-field methylene hydrogen in X is *syn* to the acetoxy group, it and the CHCl hydrogen undergo equal, opposite shifts of 0.4 τ . The indicated paramagnetic "nearest neighbor" shift is in the expected direction, since the methylene hydrogens of unsubstituted

nortricyclene²⁰ appear at higher field than those of either IIa or IIb.

The structures derived for IIa,b are in fact precisely those one would have expected assuming initial *exo* attack²¹ on norbornadiene by the chlorine donor. The ratio X:XI of these compounds as immediately obtained from the reaction mixture was 2:1, as might be anticipated from the NBS bromination of norbornadiene in methanol,³ which also gave a preponderance of the type X isomer.

The n.m.r. spectrum of the chlorodiethylamino-nortricyclene IV resembles that of XI quite closely, and it is tentatively assigned a corresponding structure (see Discussion). The exact correspondence of the CHCl hydrogen shifts between the two is surely a rather remarkable coincidence, nevertheless.

Discussion

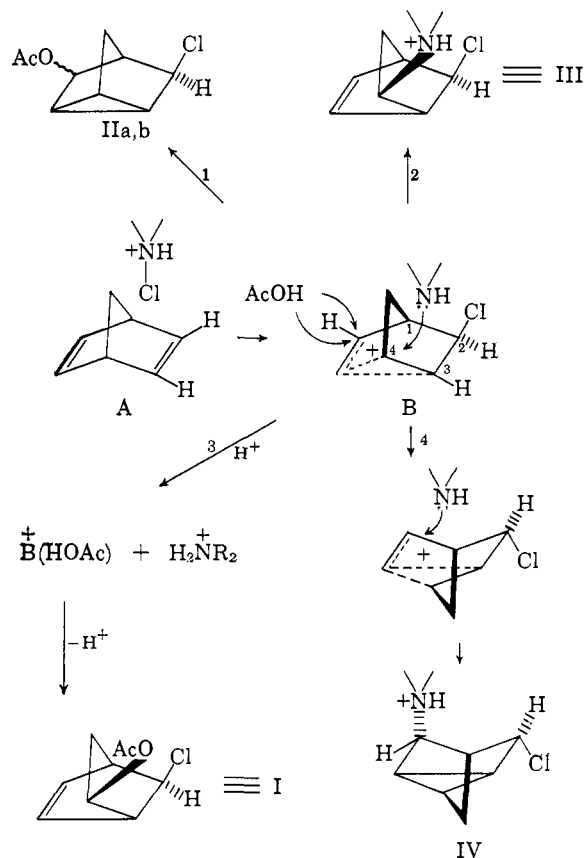
Several aspects of the reaction described above deserve brief discussion. We wish to emphasize that the deduction of detailed stereochemical structures of disubstituted nortricylenes such as IIa,b has not previously been reported without recourse to the assumption of initial *exo* attack on norbornadiene. The n.m.r. method outlined in the preceding section was suitable not only for establishing directly whether the two substituents were *cis* or *trans* to one another, as has previously been accomplished from dipole moment measurements,^{3,5b} but analysis by n.m.r. made possible for the first time the further assignment of stereochemical structure in compounds IIa,b without the requirement that their source be known. We believe the approach presented here should be generally applicable to the stereochemistry of substituted nortricyclene isomers, especially when stepwise reference to the spectrum of nortricyclene itself can be made. This could be of significant value when the order of addition of the two substituents cannot be specified with certainty.

Several points relating to the course of reaction 2 are also of note. It is evident that homoconjugation in norbornadiene is not sufficient under the conditions employed to induce a radical addition of N-chlorodiethylamine to this diene; our continuing study of other olefins should show whether radical amination of unsaturated hydrocarbons *via* N-chloramines (eq. 1) is limited only to conjugated dienes. Three observations established reaction 2 to have followed an ionic rather than a radical pathway: its insensitivity to oxygen, an inhibitor known¹ to prevent the occurrence of reaction 1; the stereochemistry of III; and the predominance of III over the isomer IV. A rearrangement product analogous to III has not yet been observed as a significant, much less major, product of a radical addition to norbornadiene.⁵ We were led, therefore, to consider how the strong bases III and IV could have formed *via* an ionic reaction in the very highly acidic medium 4 M sulfuric acid in acetic acid, which we have found will completely protonate even the weakly basic ($pK_a \sim 0$) chloramines.

(20) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963). We have also observed the predicted shift of one of the methylene hydrogens in chloronortricyclene to $\sim 0.5 \tau$ lower field than the other three.

(21) For references see E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *ibid.*, **84**, 2611 (1962).

We propose as the simplest self-consistent route to compounds I-III the scheme illustrated. All four products are presumed to arise from reactions of the carbonium ion B, generated on donation of Cl⁺ to norbornadiene (path 1)²²; the product structures require that *exo* chlorination occurs, as is usual²¹ for ionic additions to double bonds of the bicycloheptene type. The free amine, also formed in the process A \rightarrow B, certainly exists momentarily as a solvating molecule for B in such a position that its collapse with B can occur at C-4 before the amine diffuses away, forming III (path 2). If the molecule of amine does diffuse away from B, perhaps following protonation, reaction at C-4 can then be effected by a solvent molecule (path 3), forming I. The very small amount of I obtained suggests that solvolysis of B by a molecule of acetic acid occurs preferentially at C-6, which gives



the two isomers of the chloroacetate II (path 1). Because the structure of IV is not certain, it is pointless to consider its mode of formation in great detail. A possible route to the *syn-anti* isomer analogous to XI, which we feel to be the most probable configuration of IV, is that shown in path 4; this involves partial rotation of the ion-molecule pair before diffusion or protonation separates it, followed by collapse. Why the appropriate rotation should not also occur to place the amine on the other side of the one-carbon bridge, leading on collapse to the *anti-anti* isomer, is a point not accommodated by this interpretation of the formation of IV.

Three final points should be noted. First, retention of configuration during the acetolysis of III to V points

(22) It is unnecessary for this discussion to differentiate between the non-classical ion B and the alternative of several individual carbonium ions which could be written instead.

to a directive influence due to participation of the double bond in the expected manner,²³ in contrast to the possible stabilization of a carbonium ion at C-7 by the *exo*-2-nitrogen atom. Second, reaction 2 would probably occur with any dialkylchloramine. For example, *N*-chloro-di-*n*-butylamine and norbornadiene yielded 26% of the purified acetates I and II, 27% of the adducts analogous to III and IV, and 57% of di-*n*-butylamine. No evidence of a competing free radical rearrangement²⁴ of the chloramine to the 4-chloroalkylamine was found. Finally, the *N,N*-dimethyl analog of the derived alcohol VII could afford a route to the presently unknown norbornadienone by oxidation to the corresponding ketone followed by Cope elimination of the dimethylamino group,²⁵ using Cram's low-temperature modification.²⁶

Experimental

Distilled samples were obtained from a 60 cm. \times 6 mm. (i.d.) column fitted with a tantalum wire spiral within the column and an external heating jacket. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using sodium chloride optics; samples were examined as liquid films except as noted otherwise. The gas chromatograms were obtained on an Aerograph Model A90P2 instrument operated at injector and detector temperatures not exceeding 210°; except as noted, the liquid phase was 10% Carbowax 6000 on Fluropak contained in either a $\frac{3}{8}$ -in. \times 15-ft. aluminum or a 0.25 in. \times 12-ft. stainless steel coiled column.

Nuclear magnetic resonance spectra were ordinarily measured on a Varian A-60 spectrometer with a V-4012-SM electromagnet system. "Decoupling" experiments were performed under field-sweep conditions using an upper sideband frequency obtained by field modulation at 1200 c.p.s. and a perturbing sideband generated by frequency modulation of the radiofrequency transmitter; a second perturbing sideband for triple resonance experiments was obtained by additional modulation of the magnetic field. Spectra at 100 Mc. were obtained at the Application Laboratory of Varian Associates by Mr. Jerry Holcomb, to whom the authors are grateful.

Preparation of *N*-Chlorodiethylamine.—This chloramine could not be prepared as a pure liquid because it readily decomposed, even at -6°. The best distilled sample, b.p. 50.5–51° (143 mm.), n_D^{25} 1.4190, contained only 91% of the theoretical electropositive chlorine. The chloramine was prepared for use in reactions with norbornadiene as illustrated in the following typical procedure. A mixture of 20 g. (0.27 mole) of diethylamine and 20 g. (0.15 mole) of *N*-chlorosuccinimide²⁷ in 200 ml. of pentane²⁸ was stirred 3 hr. at ambient temperature and was then decanted from the insoluble succinimide. The pentane was extracted with three 25-ml. portions of 2.5 *N* aqueous sulfuric acid and dried briefly over anhydrous sodium sulfate, then extracted with 22-ml. and two 11-ml. portions of concentrated sulfuric acid. The resulting dark orange solution was freed of pentane under reduced pressure and was used immediately. The conversion to chloramine in pentane solution was ~80% according to iodometric titration.

Reactions between *N*-Chlorodiethylamine and Norbornadiene.—Each reaction was carried out as described in the following example. Two hundred milliliters of an acetic acid solution 0.65 *M* in chloramine (0.14 mole), 4 *M* in sulfuric acid, and 1.5 *M* in water was prepared by adding a solution of the chloramine in sulfuric acid to wet acetic acid at 10°. The mixture was stirred with unpurified nitrogen at ambient temperature for 20 min. in a 300-ml. flask fitted with a Teflon-bladed stirrer, thermometer, gas dispersion tube (coarse frit), side arm with rubber septum,

a 20-cm. Graham reflux condenser, and an addition funnel with a pressure equalizing tube. The exit gas was led from the condenser through a bubbler containing xylene. The yellow solution was then cooled to 10°, the nitrogen stream was slowed to maintain a slight positive pressure in the system, and 12.9 g. (0.14 mole) of freshly distilled norbornadiene²⁹ dissolved in 8 ml. of acetic acid was added to the rapidly stirred solution over 10 min. The solution temperature could be maintained at 11–13° only with the aid of an ice-acetone cooling bath. When addition of the olefin was complete, the temperature immediately fell and no electropositive chlorine remained in the solution. The homogeneous reaction mixture was then poured into 700-ml. of water containing 200 g. of ice and the resulting cloudy mixture was extracted with three 100-ml. portions of pentane. The washed and dried pentane solution on concentration in a rotary evaporator gave residue A, n_D^{25} 1.4885, which consisted of 7.5 g. (31%) of the crude chloroacetoxy adducts *exo*-2-acetoxy-*syn*-7-chloro-5-norbornene (I) and 3-acetoxy-5-chloronortricyclene (II). The aqueous acid solution was then made basic with about 350 ml. of 12 *N* sodium hydroxide solution at 15–25°. The liberated oil was extracted into four 100-ml. portions of pentane and the combined, dried pentane solutions were concentrated under vacuum to afford 7.8 g. (30%) of residue B, n_D^{25} 1.4900, which consisted of the basic adducts 2-*exo*-diethylamino-*syn*-7-chloro-5-norbornene (III) and 3-chloro-5-diethylaminonortricyclene (IV).

Work-up and Reactions of Residue A.—The predominantly saturated mixture of chloroacetoxy adducts from two reactions was distilled without good fractionation to a mixture of I and II, b.p. 92.5–93.5° (2 mm.), n_D^{25} 1.4908–1.4917, which was used for preparation of a glycol derivative, for g.l.c. isolation of the pure isomers, and for obtaining the elemental analyses. Before distillation, the ratio of the isomeric adducts was determined by g.l.c. to be: I:II = 7:93 on silicone grease at 140°; I:IIa:IIb = 6:55:39 on Carbowax at 160°.

Anal. Calcd. for C₈H₁₁ClO₂: C, 57.91; H, 5.94; Cl, 19.01. Found: C, 58.00; H, 5.82; Cl, 18.92.

The olefinic isomer I and the two saturated isomers IIa,b were obtained at 160° by preparative g.l.c. and found to be 100% pure. Their structures were deduced on the basis of their n.m.r. and infrared spectra, as already described.

The isomeric mixture was boiled with an aqueous suspension of lithium carbonate for 46 hr.; repeated sublimation of the product led only to a semisolid presumed to be a mixture of glycols C₇H₁₀O₂ (infrared: 12.2, 12.45, and 14.15 μ), of which only one saturated isomer (undefined) of m.p. 161–163° has been reported.³⁰

Anal. Calcd. for C₇H₁₀O₂: C, 66.64; H, 7.99. Found: C, 66.46; H, 7.86.

Work-up of Residue B.—The crude mixture of basic adducts, found by g.l.c. to contain nearly equal amounts of III and IV (silicone grease, 148 and 172°), could not be efficiently separated by distillation; the mixture III + IV had b.p. 86.5–88.0° (3 mm.), n_D^{25} 1.4936–1.4940. Pure samples of III and IV were obtained by g.l.c. (Carbowax, 135°), but the saturated isomer IV underwent increasingly facile decomposition to low-boiling materials with each injection. Determination of the structures of III and IV has been described above.

Formation of V + VI by Acetolysis of III + IV.—A mixture of III + IV and 30 g. of sodium acetate in 300 ml. of acetic acid was boiled 4.5 hr., then diluted to 1200 ml. with water, filtered through Celite, made basic, and extracted with pentane. The residue, examined for the presence of III, IV, V, and VI by g.l.c. (silicone grease, 158°), was twice reheated with 100 ml. of acetic acid and 5 g. of sodium acetate. The course of the acetolysis is summarized by the data in Table III; the over-all yield was

TABLE III
ACETOLYSIS OF THE AMINOCHLORIDES III + IV IN
REFLUXING ACETIC ACID-SODIUM ACETATE

Time of reflux, hr.	Mole % recovery	n_D^{25}	—Chlorides, %—		Acetates, %	
			III	IV	V	VI
0	..	1.4900	56.5	43.5
4.5	84	1.4772	3	18	61	18
10.5	95	1.4756	1	7	60	32
28.0	94	1.4753	0	0	62	38

(29) B.p. 90.5–91°, n_D^{25} 1.4679.

(30) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

(23) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(24) Reviewed by M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

(25) A. C. Cope, E. Ciganek, and N. A. LeBel, *J. Am. Chem. Soc.*, **81**, 2799 (1959).

(26) D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *ibid.*, **84**, 1734 (1962).

(27) Obtained from Matheson Coleman and Bell and recrystallized from hot benzene; m.p. 143–147°.

(28) Purified by oleum and permanganate.

75%, the total reaction time 28 hr. It is apparent that the saturated chloride IV reacted more slowly than the olefinic isomer III and that little skeletal isomerization occurred. It was later found that adjustment of the pH of the diluted acetolysis mixture to just below 7 liberated the saturated acetate VI; basification then liberated the olefinic isomer V, whose infrared spectrum was identical with that of pure V.

Distillation of a mixture of the crude acetates V + VI, b.p. 68–74° (0.25 mm.), was followed by g.l.c. isolation of pure samples of each isomer (silicone grease, 141°; use of Carbowax led to partial formation of the alcohol VII). Compound V, *exo*-2-diethylamino-*syn*-7-acetoxy-5-norbornene, had n_D^{25} 1.4726 and infrared bands 5.75 and 8.05 μ (acetate ester) and at 14.10 μ (olefinic *cis*-RCH=CHR); its n.m.r. spectrum is summarized in Table I.

Anal. Calcd. for C₁₃H₂₁NO₂: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.92; H, 9.31; N, 6.28.

Compound VI, 3-acetoxy-5-diethylaminonortricyclene, had n_D^{25} 1.4578 and in carbon tetrachloride solution rapidly reverted to a mixture of V and VI. The n.m.r. spectrum of a sample in such a solution containing 85% of VI showed 1 H at 4.90 τ (CHOAc), 10 H at 7.1–8.25 τ (including the hydrogens of NCH₂, R₂CHNR₂, and OCOCH₃ [8.05 τ]), 4 H at 8.25–8.85 τ , and 6 H at 9.03 τ (CH₃). The infrared spectrum of VI contained characteristic bands at 5.75 and 8.05 μ (acetate ester) and at 3.26, 12.06, 12.32, and 12.68 μ (substituted nortricyclene).

2-*exo*-Diethylamino-*syn*-7-hydroxy-5-norbornene (VII).—A mixture of 3.9 g. (0.0175 mole) of V and 1.33 g. (0.035 mole) of lithium aluminum hydride was refluxed under nitrogen 2.5 hr. in 200 ml. of ether. The salts and excess hydride were decomposed by the slow addition with rapid stirring of 1.4 ml. of water, 2.0 ml. of 20% sodium hydroxide, and, finally, 4.0 ml. of water. The supernatant ether solution was concentrated to 3.5 g. of a residue C, n_D^{25} 1.4846, from which a pure sample of the alcohol

VII was obtained by g.l.c., n_D^{25} 1.4853. The infrared and n.m.r. spectra of VII were discussed above.

Anal. Calcd. for C₁₁H₁₉NO: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.66; H, 10.31; N, 7.73.

One gram of residue C in 25 ml. of chloroform was converted to the original chloride III by heating it for 1 hr. with 2.3 g. of thionyl chloride and 1.5 ml. of pyridine. Dilution with ice, basification, and a rapid pot-to-pot distillation under reduced pressure afforded a liquid; collection of the material giving the only large peak present in the g.l.c. spectrum of the liquid afforded III, identified from its infrared and n.m.r. spectra. The chlorination did not proceed in the absence of pyridine.

The Reaction between Norbornadiene and N-Chloro-di-*n*-butylamine.—N-Chloro-di-*n*-butylamine was prepared from N-chlorosuccinimide in ether³¹; a solution ~ 0.5 M in the undistilled chloramine was then prepared by adding 15.8 g. (0.097 mole) to 190 ml. of 4 M sulfuric acid–1.5 M water in acetic acid. The reaction with an equivalent amount of norbornadiene was carried out under nitrogen as described above for N-chlorodiethylamine. The work-up afforded 26% of distilled I + II, 27% of the di-*n*-butyl homologs of III and IV, b.p. 82–86° (0.07 mm.), in which the saturated isomer predominated, and 57% of di-*n*-butylamine. The crude aminochloro adducts were boiled 2 hr. in acetic acid–sodium acetate to afford 48% of the corresponding acetates after distillation, b.p. 76.5–82° (0.02 mm.), n_D^{25} 1.4755–1.4712. Characteristic infrared bands were obtained of a sample containing 89% of the lower boiling, olefinic isomer (5.75, 8.05, and 14.10 μ) and one containing 67% of the saturated isomer (5.75, 8.05, 12.10, and 12.40 μ). Elemental analyses were obtained for the olefin-rich sample; the pure chlorides and acetates were not isolated.

Anal. Calcd. for C₁₇H₂₉NO₂: C, 73.07; H, 10.46; N, 5.01. Found: C, 73.16; H, 10.39; N, 5.07.

(31) E. J. Corey and W. R. Hertler, Jr., *J. Am. Chem. Soc.*, **82**, 1657 (1960)

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH., AND SAN JOSE STATE COLLEGE, SAN JOSE, CALIF.]

1H-Cyclohepta [*d,e*]-1-pyridine. A New Conjugate-Unsaturated Heterocyclic System^{1,2}

BY LANNY L. REPLOGLE³

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The syntheses of three derivatives (9a, 9b, and 10) of 1H-cyclohepta [*d,e*]-1-pyridine are described. This new heterocyclic system is iso- π -electronic with the interesting heptalene derivative 5 prepared by Hafner. The ultraviolet and visible spectra of this heterocycle are found to be quite similar to those of Hafner's hydrocarbon; these spectral properties and other data lead to the conclusion that the heterocycle does contain a delocalized π -electron system which involves the "lone pair" electrons of the nitrogen. The n.m.r. spectra of 9a, 9b, and 10 are reported and discussed.

Recently there has been considerable interest in heterocyclic analogs of nonbenzenoid aromatic hydrocarbons. The syntheses of several π -excessive⁴ heteroanalogs of azulene have been reported. Anderson, Harrison, and Anderson⁵ have described the syntheses and some properties of cyclopenta [*c*]thiapyran (1) and 2-phenyl-2-pyridine (2). The physical properties of 1 and 2 and the chemical reactivity⁶ of 2 appear to be quite similar to those of azulene. Mayer, *et al.*,⁷ have briefly described the preparation and some properties of the isomer of 1, cyclopenta [*b*]thiapyran (3). Reese⁸ has provided evidence for the

presence of the colored pseudoazulene, 1H-1-pyridine (4), in samples of 5H-1-pyridine. Both 3 and 4, which have the heteroatom in the 1-position, are less stable than 1 and 2 which have the heteroatom in the 2-position.⁹ All of the data available indicate that these π -excessive heteroanalogs of azulene have properties which correspond more or less to those of azulene.

It seemed desirable to extend studies of heterocyclic analogs of nonbenzenoid aromatic hydrocarbons. Correspondingly, we have prepared three derivatives of the new 1H-cyclohepta [*d,e*]-1-pyridine system. This heterocycle is a π -excessive heteroanalog of the interesting hydrocarbon 2,4-dimethyl[cyclopentadieno-1',5',4':1,11,10-heptalene] (5) prepared by Hafner and Schneider.¹⁰

The general synthetic method involved the intramolecular condensation of an N-methylacetamide group in the 1-position of an azulene with an 8-methyl

(8) C. B. Reese, *J. Am. Chem. Soc.*, **84**, 3979 (1962).

(9) However, it seems that 2-methyl-2-pyridine was too unstable to characterize; *cf.* ref. 5.

(10) K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1959).

(1) Supported in part by grants (G7397 and GP-250) from the National Science Foundation.

(2) Reported in part as a communication: A. G. Anderson, Jr., and L. L. Replogle, *J. Am. Chem. Soc.*, **83**, 3333 (1961).

(3) Chemistry Department, San Jose State College, San Jose, Calif.

(4) A. Albert, "Heterocyclic Chemistry. An Introduction," Essential Books, Fair Lawn, N. J., 1959.

(5) A. G. Anderson, Jr., W. F. Harrison, and R. G. Anderson, *J. Am. Chem. Soc.*, **85**, 3448 (1963).

(6) A. G. Anderson, Jr., and W. F. Harrison, *ibid.*, **86**, 708 (1964).

(7) R. Mayer, J. Franke, V. Horak, I. Hanker, and R. Zharadnik, *Tetrahedron Letters*, No. 9, 289 (1961).