[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Amine Oxides. VI. The Formation of 2,5-Norbornadiene and 2-Norbornene from 5-Dimethylamino-2-norbornene and 2-Dimethylaminonorbornane[1,2]

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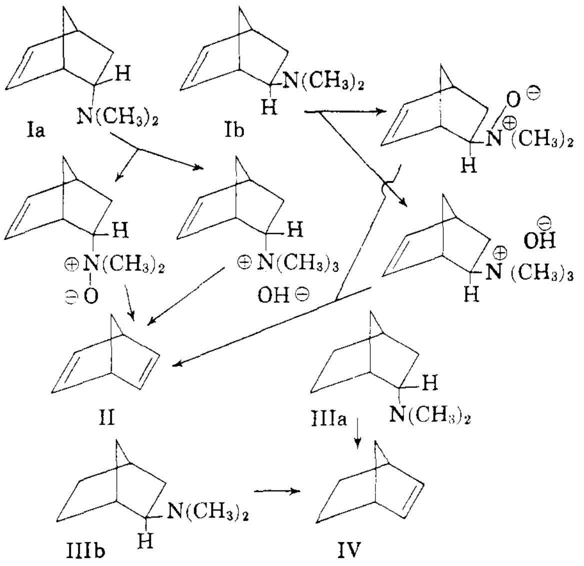
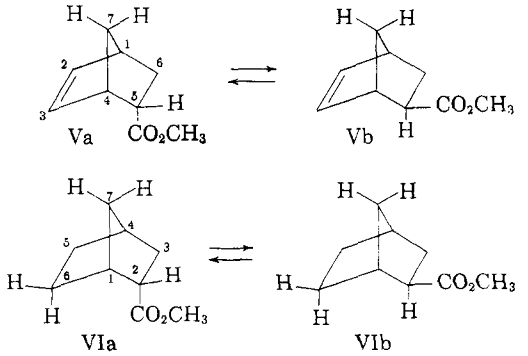
Pyrolysis of *exo*-5-dimethylamino-2-norbornene N-oxide gave a 32% yield of 2,5-norbornadiene (II), whereas only 1.4% of II was formed from the *endo* isomer. 2-Norbornene (IV) was obtained in yields of 65 and 2.9% from *exo*- and *endo*-2-dimethylaminonorbornane N-oxides, respectively. Thermal decompositions of the corresponding quaternary ammonium hydroxides also produced higher yields of olefins from the *exo* isomers; the ratio of the yields (*exo*/*endo*) of II was 18.7 and that of IV was 22.0. In each case the amount of olefin formed by the Hofmann elimination reaction was greater than that from the corresponding amine oxide. A steric explanation for the observed results is presented. The isomeric 5-carbomethoxy-2-norbornenes and 2-carbomethoxynorbornanes have been equilibrated in the presence of sodium methoxide. Within experimental error, there is no change in the composition of the equilibrium mixtures at three temperatures between 73.6 and 108.3°, the mean values of the equilibrium constants being 0.939 and 2.36, respectively. The significance of these values is discussed.

A comparative study of the amine oxide and Hofmann exhaustive methylation routes from tertiary amines to olefins has been extended to include the 5-dimethylamino-2-norbornenes and 2-dimethylaminonorbornanes. 1,2-*cis*-Substituents in these rigid bicyclic systems are held coplanar, a situation that is favorable for an intramolecular *cis* elimination of the amine oxide type,[4] while 1,2-*trans* substituents cannot become coplanar without excessive strain (resulting in a higher activation energy for bimolecular *trans* eliminations).[5] Parham has reported that thermal decomposition of the methohydroxide of *endo*-5-dimethylamino-2-norbornene (Ia) produced no 2,5-norbornadiene (II) and inferred that this bicyclic diene is not easily formed.[6] It was later shown that II could be obtained in good yield by the dechlorination of *endo-cis*- or *trans*-5,6-dichloro-2-norbornene with magnesium iodide[7,8] and in 25% yield by dehydrochlorination of 5-chloro-2-norbornene.[8] Neither *endo*-5-norborn-2-enyl acetate nor the corresponding xanthate formed appreciable amounts of II on pyrolysis.[6]

We have now subjected *endo*-5-dimethylamino-2-norbornene (Ia) and *exo*-5-dimethylamino-2-norbornene (Ib) to the conditions of the amine oxide pyrolysis and Hofmann elimination reaction. In order to compare the influence of an ethano bridge relative to an ethylenic bridge on the amount of olefin formed in each of these elimination reactions, *endo*- and *exo*-2-dimethylaminonorbornane (IIIa and IIIb, respectively) were included in the study. A reported example of a Hofmann reaction in the norbornane series is that of "2-phenyl-3-dimethylaminonorbornane," (configuration not specified), however, the yield of the products was not given.[9]



Compounds Ia and Ib, each free from the other isomer, were prepared from *endo*- and *exo*-5-carbomethoxy-2-norbornene (Va and Vb) by application of the Curtius degradation followed by methylation. The product from the Diels–Alder addition of methyl acrylate to cyclopentadiene[10] was shown by gas chromatography to contain 76% of the *endo* ester Va and 24% of the *exo* isomer Vb. Preparations of Va previously described accordingly probably contained Vb as an impurity. The pure *endo* compound was obtained by fractional



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[1] Paper V in this series THIS JOURNAL, **80**, 355 (1958).

[2] Supported by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-4542.

[3] National Institutes of Health Fellow, 1955–1957.

[4] See A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, THIS JOURNAL, **79**, 4720 (1957).

[5] S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952).

[6] W. E. Parham, W. T. Hunter, R. Hanson and T. Lahr, *ibid.*, **74**, 5646 (1952).

[7] L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **78**, 2819 (1956).

[8] J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, *ibid.*, **77**, 594 (1955).

[9] W. E. Parham, W. T. Hunter and R. Hanson, *ibid.*, **73**, 5068 (1951).

[10] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

distillation of this mixture. Sodium methoxide-catalyzed isomerization of the adduct afforded a mixture enriched in the *exo* isomer from which the lower boiling Vb was distilled. Repeated fractionation of the distillate gave pure Vb.

The equilibria Va ⇄ Vb and VIa ⇄ VIb (the latter produced by hydrogenation of the unsaturated compounds) have been studied with the aim of obtaining information concerning the relative steric effects of an ethano and an ethylenic bridge and the interaction between the π-orbital of the double bond and C_5-*endo* substituents as in Va. For these investigations, mixtures of the following composition were employed: *exo/endo* = 6; and *endo/exo* = 12.5. The equilibrations were carried out in methanol solution with sodium methoxide as the catalyst, and the compositions of the equilibrium mixtures were determined by gas chromatography. Analysis of standard mixtures of the *endo* and *exo* isomers indicated that the percentage of each at equilibrium is accurate to ±1% or less. The same mixture of isomers was obtained starting from either side of the point of equilibrium. The results, summarized in Table I, show that for both series of esters the point of equilibrium is constant within experimental error, over the temperature range of 73.6–108.3°. In order to preclude the possibility that a rapid equilibration was occurring during the isolation, a sample of Va, containing 7.4% of Vb, was heated under the same conditions for 1.5 minutes at 110°. After recovery and analysis by gas chromatography, 12.2% of Vb was found to be present. Accordingly the rate of isomerization is sufficiently slow so that little or no change in composition occurred during the isolation. At equilibrium, 48.5 ± 1% of Vb and 51.5 ± 1% of Va were present, indicating little, if any, interaction between the carbonyl group of the ester and the carbon–carbon double bond in the *endo* isomer Va. The difference in position of equilibrium in the saturated and unsaturated systems is not very large. The somewhat larger amount of *exo* isomer at equilibrium in the norbornyl series (70.2 ± 1% of VIb and 29.8 ± 1% of VIa) must be due to the 1,3-boat–axial interaction between the *endo*-2-carbomethoxy group and the C_6-*endo* hydrogen atom. Steric interference between the *exo* substituent in VIb and the C_7-*syn*-hydrogen is presumably not as great. These observations are consistent with the accepted explanations for the greater stability of *exo*-norborneol[11] and for *exo* additions to norbornene and its derivatives.[12]

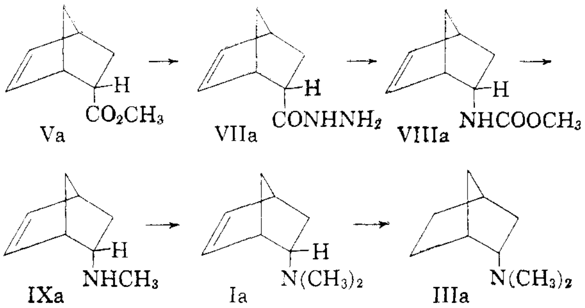
TABLE I

EQUILIBRIA BETWEEN ESTERS VA AND VB AND BETWEEN VIA AND VIB

Ester	Temp., °C.[a]	Time, hours	% *exo*	% *endo*	$K^{b,c}$ *exo/endo*
Va ⇄ Vb	73.6	60	49.0	51.0	0.961
	90.0	35	48.1	51.9	0.927
	108.3	19	48.2	51.8	0.930
VIa ⇄ VIb[d]	73.6	60	70.8	29.2	2.425
	90.0	35	69.7	30.3	2.300
	108.3	19	70.2	29.8	2.356

[a] Values ±0.1°. [b] Mean values of the equilibrium constants are $K_{Va \rightleftarrows Vb} = 0.939$, $K_{VIa \rightleftarrows VIb} = 2.360$. [c] Calculated values for the thermodynamic functions are as follows: for Va ⇄ Vb, $\Delta H = 0$, $\Delta F_{90}° = 45$ cal./mole, $\Delta S = R \ln K = -0.12$ cal./mole°; for VIa ⇄ VIb, $\Delta H = 0$, $\Delta F_{90}° = -619$ cal./mole, $\Delta S = +1.71$ cal./mole°. [d] The equilibrium mixture VIa ⇄ VIb has previously been estimated to contain 70–80% of the *exo* isomer.[11a]

endo-5-Carboxy-2-norbornene hydrazide (VIIa), prepared from Va, was converted by a Curtius reaction into methyl *endo*-2-norbornen-5-yl carbamate (VIIIa), which was reduced with lithium aluminum hydride[13] to *endo*-5-methylamino-2-norbornene (IXa). Methylation of this amine by the Clarke–Eschweiler method afforded *endo*-5-dimethylamino-2-norbornene (Ia). The corresponding *exo* isomer Ib was prepared by the same sequence of reactions from Vb. The tertiary amines Ia and Ib prepared in this manner were shown by gas chromatography to be free of the other isomer. However, Ib was found to contain approximately 5% of an impurity, the major part of which appears to be *exo*-2-dimethylaminonorbornane (IIIb). This conclusion is based upon identical retention times in gas chromatography and on the fact that a small amount of 2-norbornene (IV) was found in the products of the amine oxide pyrolysis and the Hofmann elimination reaction of Ib. Furthermore, Ib absorbed only 95% of the theoretical amount of hydrogen on catalytic hydrogenation. Contamination of Ib probably occurred during the lithium aluminum hydride reduction of the carbamate VIIb, since traces of impurities were found to be present in the secondary amine VIIIb as well.



endo- and *exo*-2-Dimethylaminonorbornane (IIIa and IIIb) were prepared by hydrogenation of the corresponding unsaturated amines.

The tertiary amines Ia, Ib, IIIa and IIIb were converted to the amine oxides with hydrogen peroxide. The amine oxides (or their hydrates) obtained by concentration of these solutions were pyrolyzed and the yields of olefins were determined by gas chromatography because of losses occurring during attempted distillation of these highly volatile products. The yields calculated from the chromatograms were corrected using conversion factors that were obtained by analysis of solutions of the olefins of known concentration under the same conditions. The olefins produced in these

[11] (a) K. Alder and G. Stein, *Ann.*, **514**, 211 (1934); (b) **525**, 183 (1936).

[12] S. J. Cristol, R. P. Arganbright, G. D. Brindell and R. M. Heitz, THIS JOURNAL, **79**, 6035 (1957), and references cited therein; S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957).

[13] R. L. Dannley, M. Lukin and J. Shapiro, *J. Org. Chem.*, **20**, 92 (1955).

pyrolyses were identified by retention times in gas chromatography and by their infrared spectra.[14]

The methohydroxides of the tertiary amines were prepared from the methiodides by reaction with silver oxide. The thermal decompositions and analysis and identification of the products were conducted as described for the amine oxides. The results are summarized in Table II.

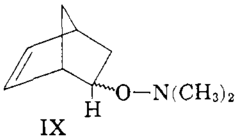
TABLE II

THERMAL DECOMPOSITION OF THE AMINE OXIDES AND QUATERNARY AMMONIUM HYDROXIDES OF *endo* AND *exo*-5-DIMETHYLAMINO-2-NORBORNENE AND *endo*- AND *exo*-2-DIMETHYLAMINONORBORNANE

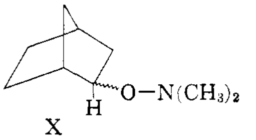
Amine	Elimination reaction	Temp., °C.	Olefin formed	Yield, %[a]	*exo*/*endo*[b]	Amine recovd. %[c]
Ia	Amine oxide	170–190	II	1.4	22.9	28
Ib	Amine oxide	187–200	II	32		13
Ia	Hofmann	110–120	II	3.1	18.7	51
Ib	Hofmann	110–125	II	58		12
IIIa	Amine oxide	170–200	IV	2.9	22.4	25
IIIb	Amine oxide	110–133	IV	65		4
IIIa	Hofmann	110–125	IV	3.5	22.0	53
IIIb	Hofmann	90–110	IV	77		1

[a] The yields are based on the amines in the case of the amine oxide pyrolysis, and on the methiodides in the case of the Hofmann reactions. [b] Ratio of the yields of olefin from the *exo* isomer and the *endo* isomer. [c] The balance of material could be accounted for by the presence of tarry residues in the decomposition reactions.

A small amount of high-boiling material was isolated among the products of the pyrolysis of the amine oxide of Ib. Analysis of the picrate of this compound indicated that it had the formula $C_9H_{15}NO$. This product is tentatively assigned the structure O-(5-norborn-2-enyl)-N,N-dimethyl-hydroxylamine (IX), which can be visualized as arising by rearrangement of the amine oxide.[15] A material, presumably O-(2-norbornyl)-N,N-dimethylhydroxylamine (X), having properties similar to IX, was obtained by pyrolysis of the amine oxide of IIIb. That these compounds differ only by the presence of two extra hydrogen atoms in X was demonstrated by the catalytic hydrogenation of IX to X. Since pure Ib (recovered from the amine oxide pyrolysis) once again formed IX when subjected to the conditions of the amine oxide decomposition, this by-product could not have originated from an impurity present in the tertiary amine Ib. Compounds IX and X were not characterized further.



IX



X

The results in Table II show that the yields of olefins in the two elimination reactions are much higher in the *exo* than in the *endo* series, differing by a factor of about 22. This preference for elimination in the *exo* compounds is undoubtedly due mainly to steric factors.[16] The *endo* quaternary nitrogen substituents are subject to large repulsive forces due to the 1,2-ethylene or 5,6-ethano bridges. These non-bonded interactions make it more difficult for the ammonium group to become coplanar with either a *cis*- or a *trans*-β-hydrogen atom. Interactions between *exo*-groups and the C_7-*syn* hydrogen atom in the transition states for elimination from Ib and IIIb are not as great (*cf.* the discussion concerning the *exo*$\rightleftarrows$*endo* equilibria for the corresponding carbomethoxy compounds). Thus, the low yield of olefins obtained from the *endo*-amines *via* both elimination routes can be attributed to the fact that the preferred coplanar orientation in the transition states cannot be attained readily. It would be expected that the steric strain would be greater in the case of the saturated compounds (from IIIa) because of the C_6-*endo* hydrogen atom. However, as shown by the earlier described equilibrium studies, the difference is not large. The close similarity of results for elimination from the two series probably is a result of the steric requirements of the quaternary nitrogen functions. Yields of 40 and 70%, respectively, of bicyclo[2.2.2]octa-2,5-diene have been obtained by application of the Hofmann elimination reaction and the amine oxide pyrolysis to *endo*-5-dimethylamino bicyclo[2.2.2]oct-2-ene,[17] which models indicate to have quite different steric effects from 5-dimethylamino-2-norbornene.

The fact that lower yields of olefins are obtained by the amine oxide route compared to the Hofmann elimination reactions described in this paper may be ascribed to greater double bond character in the transition state of the amine oxides, which would involve some steric strain. Other workers have also suggested that the double bond is more highly developed in pyrolytic *cis* eliminations than in E_2 reactions. For example, Depuy and co-workers have reported that the double bond development in the pyrolysis of acetates determines the rate of elimination, whereas it is too small to be significant in the E_2 reaction of sulfonium salts.[18]

The similar product ratios obtained from the Hofmann and amine oxide elimination reactions

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[14] An authentic sample of 2,5-norbornadiene (II) was supplied by the Shell Development Co., and 2-norbornene (IV) by Professors J. D. Roberts and R. C. Lord.

[15] Similar rearrangements of amine oxides have been observed: A. C. Cope and P. H. Towle, THIS JOURNAL, **71**, 3423 (1949); D. W. Henry and E. Leete, *ibid.*, **79**, 5254 (1957).

[16] An additional possible contributing factor is a type of anchimeric assistance by the double bond (in the case of Ib) or the proximal C_6-saturated carbon atom (in IIIb) enhancing $C-N^{\oplus}$ bond breaking and which can only operate in the *exo* compounds where the geometry is favorable. This effect implies partial E_1 character for both elimination reactions and would be expected to be more likely for the Hofmann elimination in which a medium of high polarity is involved. After this paper had been submitted for publication, J. McKenna and J. B. Slinger, *J. Chem. Soc.*, 275 (1958), reported evidence for E_1 kinetics and a Wagner–Meerwein rearrangement in the Hofmann elimination of neobornyltrimethylammonium iodide in boiling aqueous alkaline ethylene glycol, the products being camphene containing traces of bornylene and tricyclene. No camphene was found in the products of the pyrolysis of the dry quaternary hydroxide. It cannot be decided whether the Hofmann elimination of IIIb involves a Wagner–Meerwein rearrangement or not because the products obtained by either of the two reaction mechanisms would be norbornene. However, no nortricyclene was detected in the decomposition products from IIIb. It is estimated that 0.02% of this hydrocarbon could have been detected in the vapor phase chromatograms of norbornene formed from IIIb (we are indebted to Dr. P. Schleyer for an authentic sample of nortricyclene).

[17] C. A. Grob, H. Kny and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

[18] C. H. Depuy and R. E. Leary, THIS JOURNAL, **79**, 3705 (1957); C. H. Depuy and D. H. Froemsdorf, *ibid.*, **79**, 3710 (1957). The results were obtained, however, in 2-phenylethyl systems.

of norbornane and norbornene derivatives was quite surprising, and suggests the possibility that the quaternary ammonium hydroxides are decomposing by a *cis* elimination, perhaps *via* an ylid intermediate.[19] A preference for *cis*-dehydrochlorination over *trans* has been observed for the 2,3-dichloronorbornanes.[20]

The higher yields of olefins obtained from IIIa and IIIb relative to those from the unsaturated compounds (Ia and Ib) in both thermal elimination reactions must be due in part to the strain associated with 2,5-norbornadiene (II).

Experimental[21]

endo-**5-Carbomethoxy-2-norbornene** (Va).—The Diels–Alder addition of methyl acrylate to freshly distilled cyclopentadiene[10] yielded 84% of *endo*-5-carbomethoxy-2-norbornene, b.p. 80–83° (12 mm.), n^{25}D 1.4730 (lit.[10] b.p. 63.5° at 5.2 mm., n^{25}D 1.4718). Gas chromatography showed this material to be composed of 76% *endo* and 24% *exo* ester. Pure Va was obtained by repeated fractional distillation through a spinning band column (90 × 0.5-cm.; 1550 r.p.m.; reflux ratio 20–30:1); the receiving flask was cooled in Dry Ice–acetone. The foreruns were used in the preparation of the *exo* isomer (see below). The *endo* isomer as obtained by fractional distillation boiled at 88–88.5° (18 mm.), n^{25}D 1.4717. Gas chromatography showed it to contain less than 0.5% of the *exo* ester.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.91; H, 7.93.

exo-**5-Carbomethoxy-2-norbornene** (Vb).—The foreruns from the distillation described above were treated with 5 mole per cent. of sodium methoxide and stirred at an oil-bath temperature of 105° for 12 hours. The reaction mixture was distilled without removing the sodium methoxide; the column employed and the conditions were the same as described for the distillation of the *endo* isomer. The distillate contained about 90% of the *exo* and 10% of the *endo* ester. It was redistilled twice (reflux ratio 35–40:1) to afford a product containing 0.6% of the *endo* isomer as determined by gas chromatography. *exo*-5-Carbomethoxy-2-norbornene boiled at 86.5° (17 mm.), n^{25}D 1.4710.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.98; H, 8.13.

endo-**2-Carbomethoxynorbornane** (VIa).—Hydrogenation of *endo*-5-carbomethoxy-2-norbornene with prereduced platinum oxide as catalyst in methanol yielded VIa, b.p. 70° (10 mm.), n^{25}D 1.4625 (lit.[22] b.p. 82° at 15 mm., n^{20}D 1.4649).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.08; H, 9.30.

exo-**2-Carbomethoxynorbornane** (VIb).—The *exo* isomer VIb, obtained in the same manner as the *endo* ester, boiled at 72° (10 mm.), n^{25}D 1.4622 (lit.[22] b.p. 84° at 15 mm., n^{20}D 1.4643).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.02; H, 9.30.

Equilibrium Studies.—*exo*-5-Carbomethoxy-2-norbornene (Vb) containing 14.3% (by weight) of the *endo* isomer Va, and *endo*-5-carbomethoxy-2-norbornene (Va) containing 7.4% of Vb were used in the determination of the equilibrium mixture. The corresponding mixtures, obtained by hydrogenation in methanol with platinum oxide, were employed for the determination of the point of equilibrium of the saturated compounds (VIa $\rightleftarrows$ VIb).

Samples of 250 to 350 mg. of ester were treated with an equal amount (by weight) of anhydrous methanol and 20 mole per cent. of sodium methoxide and heated in sealed tubes in a constant temperature bath for the time specified in Table I. The tubes were removed and immediately immersed in an ice-bath. Ether and water were added to the reaction mixture, and the layers were separated. The ether layer was washed with water until neutral and dried over magnesium sulfate.

The dried ether solutions were analyzed by gas chromatography. For the 5-carbomethoxy-2-norbornenes the determination was carried out at 115° on a column packed with 25% by weight of tetrahydroxyethylethylene diamine. The 2-carbomethoxynorbornanes were analyzed at 105° on a column packed with 30% by weight of 3-methyl-3-nitropimelonitrile. Mixtures having identical compositions (within 0.5%) were obtained starting from both the *endo* and the *exo* isomers, indicating that equilibrium had been reached in all cases. Results are compiled in Table I.

endo-**5-Carboxy-2-norbornene Hydrazide** (VIIa).—A solution of 120 g. (0.79 mole) of *endo*-5-carbomethoxy-2-norbornene (Va) and 150 g. (2.51 moles) of 85% hydrazine hydrate in 200 ml. of ethanol was heated under reflux for 15 hours. The mixture was evaporated to dryness under reduced pressure on a steam-bath, and the residue was washed with cold *n*-hexane and cold water, and dried. The yield of the hydrazide was 96.5 g. (80.5%), m.p. 97–99°. An analytical sample was obtained by three crystallizations from a mixture of benzene and cyclohexane and melted at 98–99° (lit.[9] m.p. 82–87°).

Anal. Calcd. for $C_8H_{12}N_2O$: C, 63.13; H, 7.95; N, 18.41. Found: C, 63.12; H, 7.86; N, 18.50.

Methyl *endo*-**N-5-Norborn-2-enyl Carbamate** (VIIIa).—*endo*-5-Carboxy-2-norbornene hydrazide (80 g.) was dissolved in a solution of 51.5 g. of concentrated hydrochloric acid in 500 ml. of water. Ether (500 ml.) was added and the mixture was cooled to 0°. A solution of 36 g. of sodium nitrite in 80 ml. of water was added dropwise with stirring to this mixture over a period of 40 minutes. The temperature was kept at 0° by addition of small pieces of Dry Ice. The mixture was stirred for an additional 30 minutes, the ether layer was separated, and the aqueous layer was extracted with two 100-ml. portions of ether. The combined extracts were washed with dilute sodium bicarbonate solution and dried over calcium chloride. Absolute methanol (250 ml.) was added to the filtered ether solution, and the ether was distilled through a 30-cm. Vigreux column. Decomposition of the azide, which set in during the fractional distillation, was completed by heating the methanol solution under reflux for 12 hours. Evaporation of the solvents gave 53.5 g. (61%) of the crude carbamate, m.p. 58–63°. An analytical sample was prepared by three crystallizations from *n*-hexane, m.p. 69–70° (lit.[9] m.p. 90–92°).

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. *Found:* C, 64.77; H, 8.03; N, 8.50.

endo-**5-Methylamino-2-norbornene** (IXa).—To a suspension of 30 g. of lithium aluminum hydride in 600 ml. of anhydrous ether was added, with stirring, a solution of 50 g. of crude methyl *endo*-N-5-norborn-2-enyl carbamate (VIIIa) in 250 ml. of anhydrous ether at such a rate as to maintain gentle reflux. The addition required 40 minutes. After being stirred for 30 minutes, the mixture was refluxed for 18 hours. The excess lithium aluminum hydride was decomposed by the successive addition of 30 ml. of water, 30 ml. of 15% aqueous sodium hydroxide solution and 90 ml. of water. The suspension was stirred at room temperature for 1 hour and the white precipitate was removed by filtration and washed with ether. The combined ethereal solutions were extracted with two 100-ml. and two 50-ml. portions of 10% sulfuric acid. Sodium hydroxide pellets were added to the acid extracts with cooling and swirling; the amine was taken up in ether, and the aqueous layer was ex-

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[19] The elimination reaction of quaternary salts with phenyllithium as the base has been reported by G. Wittig and R. Polster, *Ann.*, **599**, 13 (1956). The proposed mechanism (*cf.* also ref. 16) involves prior formation of an ylid intermediate followed by intramolecular proton transfer and collapse to products. We have confirmed this mechanism using deuterium tracer studies; N. A. LeBel, unpublished results. After this paper had been submitted for publication, F. Weygand, H. Daniel and H. Simon, *Chem. Ber.*, **91**, 1691 (1958), reported evidence that such a reaction also occurs to some extent in the thermal decomposition of ethyltrimethylammonium hydroxide.

[20] S. J. Cristol and E. F. Hoegger, THIS JOURNAL, **79**, 3438 (1957).

[21] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses and to Mrs. Marianne Taylor for infrared spectra. The spectra were obtained with a Perkin–Elmer recording spectrophotometer, model 21, using a sodium chloride cell. The gas chromatographic analyses were obtained with 190 × 0.8-cm. Pyrex columns containing the liquid phase absorbents (as specified) on a 48–80 mesh firebrick support. The fractions from the chromatograms were eluted with helium (at 15 p.s.i.) and detected with a thermal conductivity cell.

[22] H. Bode, *Ber.*, **70**, 1167 (1937).

tracted with three 100-ml. portions of ether. The combined ether extracts were dried over potassium hydroxide pellets, concentrated, and the residue was distilled. The yield of *endo*-5-methylamino-2-norbornene (IXa), b.p. 60–61° (17 mm.), n^{25}D 1.4810, was 21.8 g. (59%). Analysis indicated that the amine IXa may have been slightly impure.

Anal. Calcd. for $C_8H_{13}N$: C, 77.99; H, 10.64; N, 11.37. Found: C, 77.54; H, 10.76; N, 11.35.

The phenylthiourea of this amine was prepared and melted at 110°; the melting point of an analytical sample, obtained by three crystallizations from aqueous methanol, was unchanged.

Anal. Calcd. for $C_{15}H_{18}N_2S$: C, 69.72; H, 7.02; N, 10.84. Found: C, 70.03; H, 7.29; N, 10.67.

***endo*-5-Dimethylamino-2-norbornene (Ia).**—Twenty grams of *endo*-5-methylamino-2-norbornene (VIIIa) was dissolved, with external cooling, in 43 g. of formic acid (88%) and 32 g. of 37% aqueous formaldehyde solution was added. The mixture was heated to 100° and the reaction was allowed to proceed spontaneously. After the initial vigorous reaction, the mixture was heated under reflux for 6 hours. The cooled solution was treated with 35 ml. of concentrated hydrochloric acid and concentrated under reduced pressure. The sirupy residue was diluted with water and made basic with solid sodium hydroxide. The liberated amine was taken up in ether and the aqueous solution was extracted twice with ether. The combined extracts were dried over potassium hydroxide pellets and the ether was distilled. The residue, after distillation through a semi-micro column, yielded 16.1 g. (72%) of *endo*-5-dimethylamino-2-norbornene (Ia), b.p. 65–67° (17 mm.), n^{25}D 1.4744 (lit.[6] b.p. 167–175°, 47° at 5 mm.).

Anal. Calcd. for $C_9H_{15}N$: C, 78.77; H, 11.02; N, 10.21. Found: C, 79.00; H, 11.20; N, 10.32.

The amine Ia was shown to be free of the *exo* isomer by gas chromatography through a column containing 25% by weight of tetrahydroxyethylethylenediamine at 140°. The infrared spectrum of Ia has strong bands at 759 and 1277 cm.$^{-1}$ and medium bands at 836 and 1304 cm.$^{-1}$ which are absent in the spectrum of the *exo* isomer. The picrate of this amine melted at 191–193° dec.; an analytical sample, prepared by three crystallizations from ethanol, melted at 192–193° dec. (lit.[6] m.p. 190–195° dec.).

Anal. Calcd. for $C_{15}H_{18}N_4O_7$: C, 49.18; H, 4.95; N, 15.30. Found: C, 49.43; H, 4.88; N, 15.33.

***endo*-5-Dimethylamino-2-norbornene Methiodide.**—*endo*-5-Dimethylamino-2-norbornene (Ia) (3.5 g.) was treated with 7.8 g. of methyl iodide in 50 ml. of anhydrous ether and the solution was allowed to stand at room temperature for 24 hours. The yield of crude methiodide was 6.66 g. (93.5%), m.p. 265–266° dec. An analytical sample prepared by three crystallizations from a mixture of ethanol and ether melted at 266–267° dec. (lit.[6] m.p. 160° dec.).

Anal. Calcd. for $C_{10}H_{18}NI$: C, 43.02; H, 6.50; I, 45.46. Found: C, 42.82; H, 6.41; I, 45.45.

***endo*-2-Dimethylaminonorbornane (IIIa).**—Eight grams of *endo*-5-dimethylamino-2-norbornene (Ia), in 60 ml. of absolute methanol, was hydrogenated at 28° with 400 mg. of prereduced platinum oxide. The theoretical amount of hydrogen was taken up within 90 minutes. The platinum was removed by filtration, and the filtrate was distilled through a semi-micro column. The yield of *endo*-2-dimethylaminonorbornane (IIIa) was 7.42 g. (91.5%), b.p. 68–69° (19 mm.), n^{25}D 1.4669. The infrared spectrum of IIIa has a strong band at 795 cm.$^{-1}$ which is absent in the spectrum of the *exo* isomer.

Anal. Calcd. for $C_9H_{17}N$: C, 77.63; H, 12.31; N, 10.06. Found: C, 77.77; H, 12.38; N, 10.08.

The picrate of this amine melted at 221–224° dec. (lit.[6] m.p. 213–216° dec.). The melting point was not changed by three crystallizations from ethanol.

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.91; H, 5.47; N, 15.21. Found: C, 49.16; H, 5.57; N, 15.50.

***endo*-2-Dimethylaminonorbornane Methiodide.**—A solution of 3.40 g. of *endo*-2-dimethylaminonorbornane (IIIa) and 14 g. of methyl iodide in 20 ml. of anhydrous ether was allowed to stand at room temperature for 3 days. The precipitated methiodide (5.93 g., 86%) melted at 290° dec. An analytical sample, after three crystallizations from a mixture of ethanol and ether, melted at 290° dec. (lit.[6] m.p. 291–293°).

Anal. Calcd. for $C_{10}H_{20}NI$: C, 42.71; H, 7.17; I, 45.14. Found: C, 42.46; H, 7.25; I, 45.37.

***exo*-5-Carboxy-2-norbornene hydrazide (VIIb)** was prepared from Vb in 88% yield, m.p. 110–114°. An analytical sample, after three crystallizations from benzene, melted at 114°.

Anal. Calcd. for $C_8H_{12}N_2O$: C, 63.13; H, 7.95; N, 18.41. Found: C, 63.46; H, 7.94; N, 18.37.

Methyl *exo*-N-5-Norborn-2-enyl Carbamate (VIIIb).—The yield of crude VIIIb, m.p. 83–90°, was 67%. An analytical sample, prepared by three crystallizations from *n*-hexane, melted at 95–96°.

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.97; H, 8.05; N, 8.67.

***exo*-5-Methylamino-2-norbornene (IXb).**—The secondary amine was prepared in 50.5% yield by lithium aluminum hydride reduction of VIIIb and had the following properties: b.p. 63–64° (19 mm.), n^{25}D 1.4827. Analysis indicated that IXb may have been slightly impure.

Anal. Calcd. for $C_8H_{13}N$: C, 77.99; H, 10.64; N, 11.37. Found: C, 77.34; H, 10.81; N, 11.35.

A small higher boiling fraction (b.p. 64–75° at 19 mm.) was obtained which absorbed 91.5% of the theoretical amount of hydrogen upon hydrogenation, indicating contamination by the saturated derivative.

The phenylthiourea of IXb melted at 114°; the melting point was unchanged by three recrystallizations from aqueous methanol.

Anal. Calcd. for $C_{15}H_{18}N_2S$: C, 69.72; H, 7.02; N, 10.84. Found: C, 69.82; H, 7.18; N, 10.77.

***exo*-5-Dimethylamino-2-norbornene (Ib).**—The Clarke–Eschweiler methylation of IXb afforded Ib in a yield of 73.5%, b.p. 66–68° (20 mm.), n^{25}D 1.4737. Gas chromatography of this material showed it to be free of the *endo* isomer. However, it contained about 5% of an impurity, the probable identity of which was mentioned earlier.

Anal. Calcd. for $C_9H_{15}N$: C, 78.77; H, 11.02; N, 10.21. Found: C, 78.86; H, 11.33; N, 10.18.

The infrared spectrum of Ib has medium bands at 865, 990 and 1240 cm.$^{-1}$ which are absent in the spectrum of the *endo* isomer.

The picrate of Ib melted at 190–191°; an analytical sample, prepared by three crystallizations from ethanol, melted at 193° dec.

Anal. Calcd. for $C_{15}H_{18}N_4O_7$: C, 49.18; H, 4.95; N, 15.30. Found: C, 49.31; H, 4.98; N, 15.18.

***exo*-5-Dimethylamino-2-norbornene Methiodide.**—The methiodide was prepared in 92% yield from Ib; when heated, it turned violet to black at 270°, but did not melt below 350°. An analytical sample was prepared by three crystallizations from a mixture of ethanol and ether.

Anal. Calcd. for $C_{10}H_{18}NI$: C, 43.02; H, 6.50; I, 45.46. Found: C, 43.30; H, 6.70; I, 45.42.

***exo*-2-Dimethylaminonorbornane (IIIb).**—Hydrogenation of Ib resulted in the uptake of 95% of the calculated amount of hydrogen within 75 minutes. The product was distilled through a spinning-band column (30 × 0.5-cm., 1500 r.p.m.) to yield 88% of IIIb, b.p. 71° (20 mm.), n^{25}D 1.4682. The infrared spectrum of IIIb has a strong band at 1022 cm.$^{-1}$ and a medium band at 820 cm.$^{-1}$, which are absent in the spectrum of IIIa.

Anal. Calcd. for $C_9H_{17}N$: C, 77.63; H, 12.31; N, 10.06. Found: C, 77.74; H, 12.47; N, 10.14.

The picrate of IIIb melted at 214–216° dec.; an analytical sample, prepared by three crystallizations from ethanol, melted at 218–220° dec.

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.91; H, 5.47; N, 15.21. Found: C, 49.07; H, 5.62; N, 15.36.

***exo*-2-Dimethylaminonorbornane Methiodide.**—The methiodide, prepared in 97% yield from IIIb, melted at 295° dec. An analytical sample was prepared by three crystallizations from a mixture of ethanol and ether and melted at 295° dec.

Anal. Calcd. for $C_{10}H_{20}NI$: C, 42.71; H, 7.17; I, 45.14. Found: C, 42.59; H, 7.06; I, 45.11.

Thermal Decomposition of the Amine Oxides and Quaternary Ammonium Hydroxides of *endo*- and *exo*-5-Dimethyl-

amino-2-norbornene and *endo*- and *exo*-2-Dimethylaminonorbornane.—Amine oxides were prepared by slow addition of a threefold excess of hydrogen peroxide (30% in water) to a cooled and stirred solution of the tertiary amine in twice its volume of methanol. The mixture was allowed to stand at room temperature for 18 hours and the excess hydrogen peroxide was decomposed with a suspension of platinum black. After filtration, an aliquot of the amine oxide solution was removed and added to a hot (60°) saturated solution of picric acid (a small excess over the calculated amount) in 30% aqueous ethanol. The remainder of the filtrate, containing the amine oxide, was concentrated under reduced pressure to a white solid residue, and this material was used directly for the pyrolysis as described below.

Quaternary ammonium hydroxides were obtained by stirring a mixture of the methiodides with two equivalents of commercial silver oxide (previously washed with methanol) in 50% aqueous methanol at room temperature for 18 hours. The silver salts were removed by filtration, and the filtrate was evaporated to a sirup under reduced pressure and slightly elevated temperature (40° and 0.1 mm.). The residue was used directly for the thermal decomposition.

The pyrolysis of the amine oxides and the quaternary ammonium hydroxides was carried out in the following way: the compound to be pyrolyzed (0.02–0.035 mole) was placed in a 50-ml. flask fitted with a capillary nitrogen inlet and the flask was connected through a short distilling head to two traps in series; the first cooled in Dry Ice–acetone, and the second immersed in liquid nitrogen. In a number of runs, the liquid nitrogen was replaced by Dry Ice–acetone. Nitrogen was admitted through a capillary inlet and the pressure was reduced to 60 mm. The compound was heated by means of a stirred oil-bath at a rate of about two degrees per minute. Throughout the decomposition the distilling head was heated. The pressure was further lowered to 30 to 40 mm. toward the end of the pyrolysis.

When the decomposition was complete, the contents of the two traps were taken up in pentane, the aqueous layer was removed, and the pentane solution was washed twice with water. The basic materials were extracted with three portions of cold 10% sulfuric acid. The pentane solution was washed with water until neutral, and dried over anhydrous magnesium sulfate. The filtered pentane solution was either analyzed directly by gas chromatography, or concentrated by distillation through a semi-micro column to a small volume and subsequently analyzed, depending on the concentration of the olefin in the pentane solution. The yields of olefin were determined by gas chromatography through a column containing 30% by weight of Dow-Corning 550 Silicone oil at 80–90°. Solutions of known concentration of the olefins (II and IV) in pentane were employed as standards. After analysis by gas chromatography, the pure olefins were isolated either by distillation or by gas chromatography and identified by their infrared spectra.

The sulfuric acid extracts were made strongly alkaline by the addition of solid sodium hydroxide. The liberated amines were taken up in ether and the aqueous layer was extracted twice with ether. The combined ether extracts were dried and concentrated, and the residue was distilled through a semi-micro column. The results are summarized in Table II.

Pyrolysis of *endo*-5-Dimethylamino-2-norbornene N-Oxide.—The amine oxide picrate was obtained in 95% yield, m.p. 193–194° dec. An analytical sample, prepared by three crystallizations from ethanol, melted at 196–198° dec.

Anal. Calcd. for $C_{15}H_{18}N_4O_8$: C, 47.12; H, 4.75; N, 14.66. Found: C, 47.27; H, 4.82; N, 14.40.

The amine oxide of Ia decomposed at 170–190° to give 1.4% of 2,5-norbornadiene (II) and 28% of the recovered amine Ia, $n^{25}\text{D}$ 1.4743.

Pyrolysis of *endo*-5-Dimethylamino-2-norbornene Methohydroxide.—This compound decomposed at 110–120° to give 3.1% of II and 51% of Ia, $n^{25}\text{D}$ 1.4744.

Pyrolysis of *endo*-2-Dimethylaminonorbornane N-Oxide.—The amine oxide picrate of IIIa was obtained in 89% yield and melted at 233–234° dec.; an analytical sample, prepared by three crystallizations from ethanol, melted at 236° dec.

Anal. Calcd. for $C_{15}H_{20}N_4O_8$: C, 46.87; H, 5.25; N, 14.58. Found: C, 47.07; H, 5.29; N, 14.43.

The amine oxide of IIIa decomposed at 170–200° to yield 2.9% of 2-norbornene (IV) and 25% of IIIa, $n^{25}\text{D}$ 1.4670.

Pyrolysis of *endo*-2-Dimethylaminonorbornane Methohydroxide.—Decomposition of this compound occurred at 110–125° to give 3.5% of 2-norbornene (IV); 53% of *endo*-2-dimethylaminonorbornane (IIIa), $n^{25}\text{D}$ 1.4669, was recovered.

Pyrolysis of *exo*-5-Dimethylamino-2-norbornene N-Oxide.—The amine oxide picrate of Ib, obtained in 95% yield, melted at 193–194° dec. An analytical sample, prepared by three crystallizations from ethanol, melted at 194–195° dec.

Anal. Calcd. for $C_{15}H_{18}N_4O_8$: C, 47.12; H, 4.75; N, 14.66. Found: C, 47.21; H, 4.81; N, 14.73.

The amine oxide of Ib decomposed at 187–200° to yield 32% of II and 2% of 2-norbornene (IV), identified by its retention time on two different columns, packed with 30% by weight of 3-methyl-3-nitropimelonitrile and 30% by weight of Dow-Corning 550 Silicone oil, respectively. *exo*-5-Dimethylamino-2-norbornene (Ib), 0.6 g., 13%, $n^{25}\text{D}$ 1.4750, was also recovered. Gas chromatography of this amine showed that it did not contain the trace impurity (presumably IIIb) present in synthetic Ib. In addition to Ib, another weakly basic compound (270 mg. from 4.80 g. of Ib) was recovered from the acid extracts, b.p. 97–99° (20 mm.). Final purification by gas chromatography through a Silicone oil column at 150° gave a faintly colored liquid. The infrared spectrum of this product was different from that of *exo*-5-dimethylamino-2-norbornene N-oxide. It is formulated as O-(5-norborn-2-enyl)-N,N-dimethylhydroxylamine (IX), which was converted to the picrate for analysis; m.p. 156–162° dec. A sample that was recrystallized once from ethanol melted at 157–164° dec.

Anal. Calcd. for $C_{15}H_{18}N_4O_8$: C, 47.12; H, 4.75; N, 14.66. Found: C, 47.25; H, 4.60; N, 14.46.

Pyrolysis of *exo*-5-Dimethylamino-2-norbornene Methohydroxide.—This quaternary hydroxide decomposed at 110–125° to yield 58% of II and 12% of Ib, $n^{25}\text{D}$ 1.4738. In addition to II, 2% of 2-norbornene (IV) was found to be present in the neutral (pentane) fraction. It was identified by its retention time in gas chromatography.

Pyrolysis of *exo*-2-Dimethylaminonorbornane N-Oxide.—The amine oxide picrate of IIIb was obtained in 98% yield and melted at 209° dec. An analytical sample, prepared by three crystallizations from ethanol, melted at 210° dec.

Anal. Calcd. for $C_{15}H_{20}N_4O_8$: C, 46.87; H, 5.25; N, 14.58. Found: C, 46.96; H, 5.48; N, 14.59.

The amine oxide of IIIb decomposed at 110–133° to yield 65% of 2-norbornene (IV), m.p. 46° (sealed tube) (lit.[23] m.p. 44–46°). There was obtained from the acid extracts 4% of the amine IIIb, $n^{25}\text{D}$ 1.4681, and 50 mg. (from 3.75 g. of IIIb) of a compound boiling at 101° (17 mm.). The retention time on gas chromatography of this product was different from that of IX. This material is formulated as O-(2-norbornyl)-N,N-dimethylhydroxylamine (X).

Hydrogenation of IX.—The compound IX (29.2 mg.) was hydrogenated in 5 ml. of 5% hydrochloric acid with 26 mg. of prereduced platinum oxide as catalyst at room temperature; 91% of the calculated amount of hydrogen was taken up. The platinum was removed by filtration, the filtrate extracted with ether, and the aqueous layer concentrated to a small volume. The ether extracts contained no volatile products as shown by gas chromatography. The aqueous solution was made strongly alkaline, extracted with ether, and the ether extracts, after drying, were analyzed by gas chromatography. The only volatile compound detected in the ether solution had a retention time identical with that of X.

Pyrolysis of *exo*-2-Dimethylaminonorbornene Methohydroxide.—This compound decomposed smoothly at 90–100° to yield 77% of IV, m.p. 46° (sealed tube) (lit.[23] m.p. 44–46°). About 1% of *exo*-2-dimethylaminonorbornane (IIIb) was recovered.

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