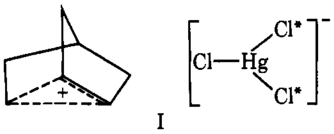
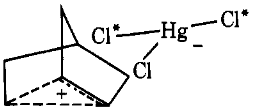
$HgCl_2$ where the slope of the least-squares line through the fixed intercept 5.15×10^{-6} sec^{-1} provides $k_{2\alpha}$ equal to $39.0 \pm 0.8 \times 10^{-5}$ M^{-1} sec^{-1}. The products of the reaction are 89.2% *exo*-norbornyl acetate and 10.8 ± 1.6% nortricyclene plus a trace of norbornene.[8]

Since k_α provides the best measure of ionization, the k_α/k_t ratio of 11.4 for *exo*-RCl in acetic acid in the absence of $HgCl_2$ demonstrates the importance of ion pair return in this system. For the unpromoted reaction, there is no evidence for return to regenerate *exo*-RCl from dissociated intermediates.[9]

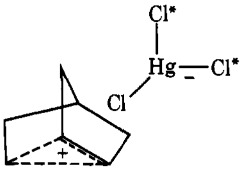
In order to interpret the results, the $HgCl_2$-promoted reaction, "the slope reaction," is assumed to proceed independently of the unpromoted reaction with little or no crossover between the two and normal salt effects are neglected since they are small even with the more ionic salt lithium acetate (*b* value = 1). In the promoted reaction, ion pair return is also important; the k_α/k_t ratio of 9.6 indicates that only 10% of the *exo*-$R^+HgCl_3^-$ ion pairs give rise to product, and 90% regenerate *exo*-RCl. As in the unpromoted reaction, return to RCl probably occurs only from intimate ion pairs. The ion pairs that regenerate *exo*-RCl racemize two times faster than they incorporate radiochlorine, as indicated by the k_{rac}/k_e ratio of 2.0. This simple ratio of 2.0 is most easily explained by regeneration of *exo*-RCl from racemic *exo*-$R^+HgCl_3^-$ pairs (II) where only two chlorine atoms of the $HgCl_3^-$ anion are associated equivalently with the bridged norbornyl cation, one labeled chlorine from the originally labeled $HgCl_2$ and one unlabeled chlorine from RCl. Regeneration of racemic RCl from II where the two chlorine atoms do not further randomize with other chlorine atoms will incorporate radiochlorine only once out of two chances. The k_{rac}/k_e ratio of 2.0 may also be the result of a blend of other intermediates such as I, where the three chlorine atoms on $HgCl_3^-$ are equivalent (k_{rac}/k_e = 1.5),[2,3] or III in which only the chlorine atom originally on RCl returns to regenerate covalent RCl (k_{rac}/k_e = ∞).[10]



I



II



III

In formic acid at 25.0° the various reactions display the same kinetic behavior as in acetic acid. The increase in k_t due to added $HgCl_2$ (up to 0.0450 *M*) is fit by a least-squares line with slope $13.9 \pm 0.2 \times 10^{-4}$ M^{-1} sec^{-1} and intercepts $15.0 \pm 0.2 \times 10^{-6}$ sec^{-1}. Similarly, the k_e values are linearly dependent on [$HgCl_2$] where the slope of the line through the origin is $2.66 \pm 0.05 \times 10^{-4}$ M^{-1} sec^{-1}. Finally, the dependence of k_α on [$HgCl_2$] provides the second-order constant equal to 27.1×10^{-4} M^{-1} sec^{-1}, where k_α in the absence of $HgCl_2$ is $60.7 \pm 1.5 \times 10^{-6}$ sec^{-1}.

On going from acetic to formic acid, the importance of ion pair return is reduced[11]—k_α/k_t decreases from 11.4 to 4.0—for the unpromoted reaction. In the promoted reaction, ion pair return is also reduced—k_α/k_t diminishes from 9.6 to 1.95—indicating that only half of the *exo*-$R^+HgCl_3^-$ ion pairs return to covalent RCl. Of the ion pairs that return, only *ca.* 20% undergo exchange. The amount of chlorine exchange that accompanies the racemization of RCl is also less in formic acid. These results are in line with racemization in acetic acid proceeding *via* two intermediates, a "solvent-separated" ion pair like I which dissociates and gives product in the more dissociation solvent formic acid, and an "intimate" ion pair like III which is less susceptible to dissociation.

In contrast to the racemization process of the benzhydryl derivatives,[2,3] the front side rearrangement in the $HgCl_2$-promoted reactions of the *exo*-norbornyl chloride does not proceed *via* ion pair intermediates where all the chlorine atoms in $HgCl_3^-$ become equivalent. Instead, the bridged cation in the ion pair intermediates can scrutinize the chlorine atoms and the one originally from *exo*-RCl remains pointed toward the cation some of the time.

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[8] In contrast, the acetolysis products of *exo*-norbornyl chloride at 100° are 72.5% *exo*-norbornyl acetate, 23.1% nortricyclene, and 4.4% norbornene: E. Vogelfanger, Doctoral Dissertation, University of California, Los Angeles, 1963.

[9] S. Winstein, P. Klinedinst, and G. C. Robinson, *J. Amer. Chem. Soc.*, **83**, 885 (1961); and references listed in ref 8 above.

[10] Similar results are reported for the ^{18}O equilibration which accompanies the solvolysis of 2-phenyl-1-propyl *p*-brosylate (D. B. Denny and B. Goldstein, *J. Amer. Chem. Soc.*, **79**, 4948 (1957)), and *threo*-3-phenyl-2-butyl *p*-tosylate and *endo*-bicyclo[3.2.1]octan-2-yl *p*-tosylate (H. L. Goering and R. W. Theis, *ibid.*, **90**, 2967 (1968)).

(11) (a) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, No. **19**, 109 (1965); (b) A. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 6546 (1968).

(12) CNR (Rome) Fellow, 1966–1967.

(13) Deceased Nov 23, 1969.

* Author to whom inquiries should be addressed: Department of Chemistry, University of California, San Diego, La Jolla, Calif. 92037.

James P. Hardy, Alberto Ceccon,[12] A. F. Diaz,* S. Winstein[13]
Department of Chemistry, University of California
Los Angeles, California 90024

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Ring Expansion Reactions of Homoadamantane Derivatives. Synthesis of Bishomoadamantane Skeletons[1]

Sir:

The carbocyclic bishomoadamantane ring system[2] has not been reported yet, though some of the aza analogs have been known.[3] We now wish to report the Demjanov–Tiffeneau ring expansion reaction of 4-hydroxy-4-aminomethylhomoadamantane (III) and solvolytic ring enlargement of 3-homoadamantylcarbinyl tosylate (XIVa) as synthetic routes to 1,1-

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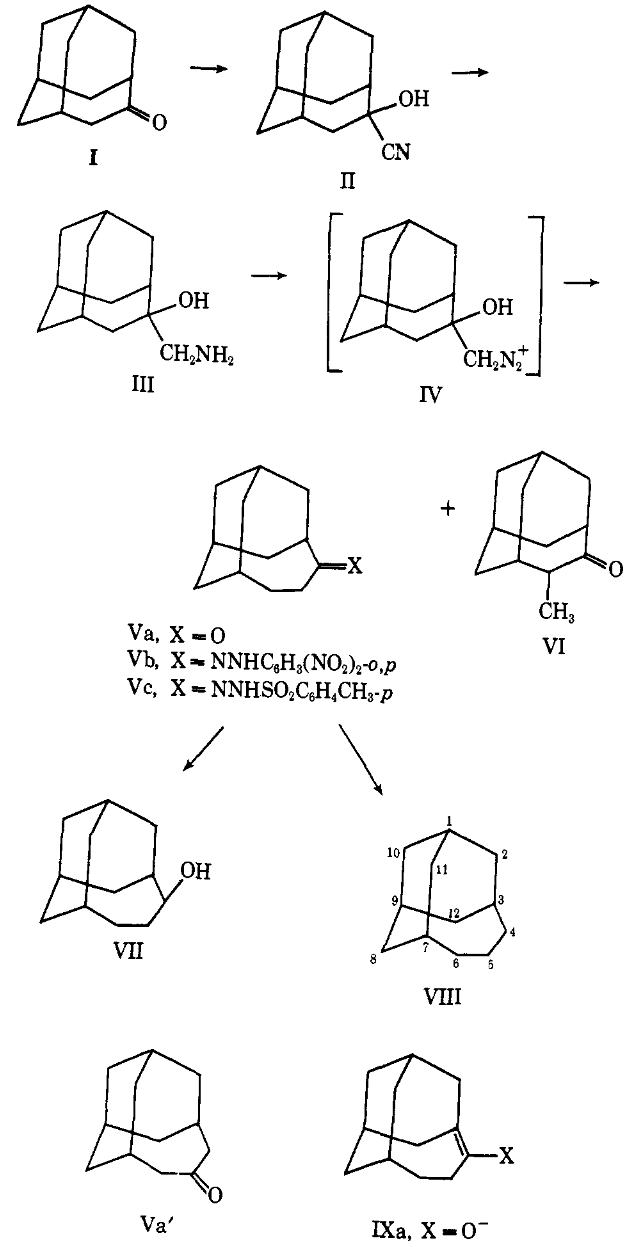
(1) Synthesis of Adamantane Derivatives. XX. Part XIX: T. Sasaki, S. Eguchi, T. Kiriyama, and H. Suzuki, *Syn. Commun.*, in press.

(2) We used this trivial name in this paper, and the three possible isomers, 1,1-, 1,3-, and 1,5-bishomoadamantanes, correspond to tricyclo[5.3.1.1^{3,9}]dodecane, tricyclo[4.4.1.1^{3,9}]dodecane, and tricyclo-[4.4.1.1^{3,8}]dodecane, respectively.

(3) (a) For 4,6-diazatricyclo[5.3.1.1^{3,9}]dodecan-5-one, see V. G. Keizer, J. G. Korsloot, F. W. v. Deursen, and M. E. v. d. Heeden, *Tetrahedron Lett.*, 2059 (1970); (b) for 4-azatricyclo[5.3.1.1^{3,9}]dodecan-5-one, see T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **36**, 2454 (1971); (c) for 1,3,6,9-tetraazatricyclo[4.4.1.1^{3,8}]dodecane, see F. G. Riddell and M. Rust, *Chem. Commun.*, 1075 (1970).

Scheme I



and 1,3-bishomoadamantane skeletons, respectively (Schemes I and II).

Homoadamantan-4-one (I)[4] was treated with a large excess of hydrogen cyanide in pyridine[5] at 20–25° for 30 hr. Removal of the excess hydrogen cyanide and pyridine gave a crude cyanohydrin II, ir (neat) 3400 and 2270 cm^{-1} in *ca.* 50% yield, which was reduced with lithium aluminum hydride in tetrahydrofuran to amino alcohol III in 24% overall yield, mp 233–234°;[6] *m/e* 195 (M$^+$). Treatment of III with sodium nitrite in aqueous acetic acid at 0–40° afforded deamination products which revealed two major peaks in a 7:1 ratio (vpc). Purification by column chromatography (silica gel–benzene) and preparative vpc (Silicone SE-30 at 180°) gave 1,1-bishomoadamantan-4-one (Va), mp 145.5–146.5°, and 5-methylhomoadamantan-4-one (VI), mp 102–104°, in 64 and 8.8% yields, respectively. Va had: ir (KBr) 1685 ($\nu_{C=O}$) cm^{-1}; *m/e* 178 (M$^+$); nmr (C$_6$H$_6$)[7] τ 7.45–7.80 (t, J = 6.0 Hz, 2, CH$_2$CO), 7.80–8.90 (s, 1, COCH), 7.90–8.90 (m, 15, other ring protons). Its 2,4-dinitrophenylhydrazone Vb had: mp 207–209°; nmr (CDCl$_3$) τ 7.0–7.5 (m, 3, CH$_2$(=N)CH), and 7.5–8.9 (m, 15, other ring protons). The nmr data support the presence of methylene and methine protons adjacent to a carbonyl group, though the methine proton appears at abnormally higher field compared with that of I.[8] The observed abnormally lower carbonyl stretching frequency (1685 cm^{-1}) of Va than I (1698[4a] and 1700[4c] cm^{-1}) and adamantanone (1715 cm^{-1}) corresponds to a larger C(C=O)C angle,[9] suggesting an extraordinarily highly strained ketone like Va as expected from its geometrical constraint.

The unsymmetrical structure of Va was further supported by deuteration experiments. Va was refluxed in 60% D$_2$O–dioxane containing NaOD for 1 and 10 days. The diluted mixture was extracted with chloroform to give deuterated Va which was analyzed with nmr and mass spectrometry after purification on preparative vpc. Va-d_2 and Va-d_3 were produced in 53 and 26% yields after 1 day, and in 16 and 77% yields after 10 days, respectively. However, no trace of Va-d_4 was produced in both cases, verifying the above-assigned structure Va, and excluding the symmetrical structure Va′.

Compound VI had: ir (KBr) 1685 cm^{-1}; *m/e* 178 (M$^+$); nmr (CDCl$_3$) τ 7.10–7.70 (m, 2, C$_3$H and C$_5$H), 7.70–8.65 (broad s, 13, other ring protons), and 8.83 (d, J = 6.0 Hz, 3, C$_5$CH$_3$, s on irradiation at C$_5$H).

The selective ring expansion of III to Va[10] could be explained by the conformational effect in the intermediate IV, because the migration aptitude favors in the C$_3$–C$_4$ bond rather than in the C$_5$–C$_4$ bond.[11] VI might be produced by apparent 1,3-hydride shift,[12] followed by 1,2-methyl migration.[13]

The fact that deuteration of C$_3$H in Va was achieved under milder conditions suggests 1,1-bishomoadamant-3-ene (IXb) or more precisely the corresponding enol (IXa), while I has been shown not to be deuterated at its bridgehead methine even under more drastic conditions (*tert*-BuOK–*tert*-BuOD).[4b,14]

Although Va afforded alcohol VII, mp 147.5–149°, on reduction with lithium aluminum hydride in 90% yield,

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[4] (a) J. E. Nordlander, F. Y-H. Wu, S. P. Jindal, and J. B. Hamilton, *J. Amer. Chem. Soc.*, **91**, 3964 (1969); (b) P. v. R. Schleyer, E. Funke, and S. H. Liggero, *ibid.*, **91**, 3965 (1969); (c) J. L. M. A. Schlatmann, J. G. Korsloot, and J. Schut, *Tetrahedron*, **26**, 949 (1969); (d) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Amer. Chem. Soc.*, **92**, 6670 (1970).

[5] Cyanohydrin II was not produced at all with potassium cyanide in ethanol–acetic acid.

[6] All melting points were measured in a sealed tube and are corrected; all new compounds reported had satisfactory analyses.

[7] Nmr (CCl$_4$) τ 7.25–7.60 (unsymmetrical t, J = 6.0 Hz, 2) and 7.60–8.68 (m, 16).

[8] I had the methine proton signal at τ 7.28 and the methylene protons at τ 7.42 in CCl$_4$.

[9] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, pp 189–199, and references cited therein.

[10] The deamination products revealed a third peak (in less than 3% yield) on vpc, which might be due to Va′, though its isolation was unsuccessful.

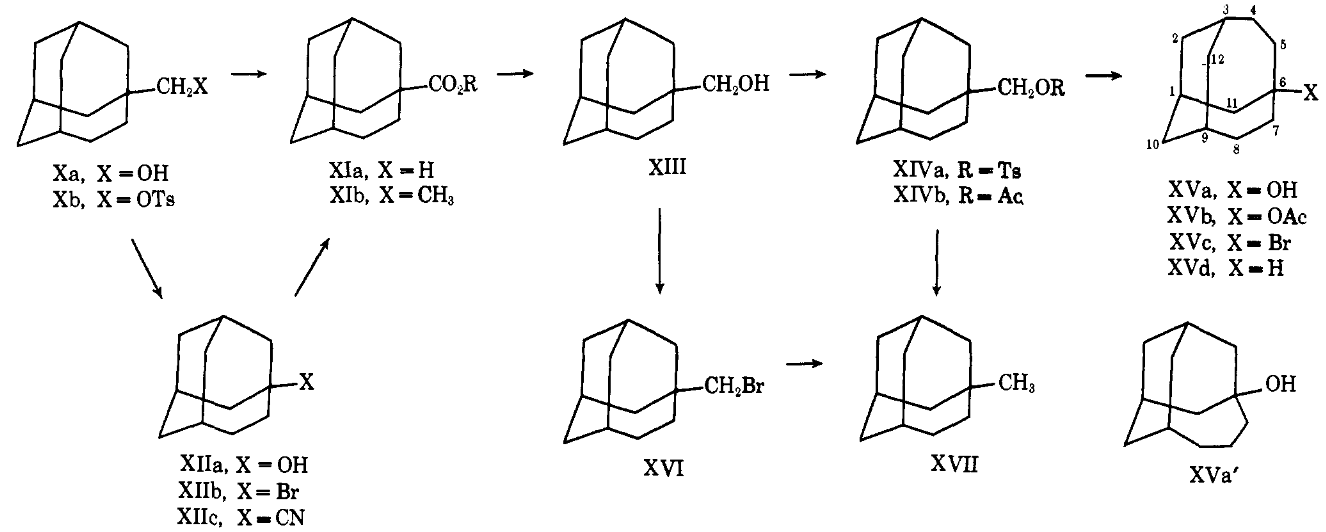
[11] For a review, see C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, pp 61–80; *cf.* T. Sasaki, S. Eguchi, and T. Ishii, *J. Org. Chem.*, **35**, 2257 (1970).

[12] For an example of 1,3-hydride shift in deamination reactions, see S. H. Graham and D. A. Jonas, *J. Chem. Soc. C*, 188 (1969).

[13] The referee suggested a protonated cyclopropane which affords a cyclopropanol on loss of proton as the possible intermediate, though the detailed mechanism of this deamination remains unclear.

[14] For bisdecarboxylation of homoadamantane-2,7-dione-3,6-dicarboxylic acid, see B. R. Vogt, *Tetrahedron Lett.*, 1579 (1968).

Scheme II



its mesylation and tosylation were unsuccessful under several conditions. However, Va gave tosylhydrazone Vc, mp 167–169°, which was reduced with sodium borohydride in refluxing methanol to afford 1,1-bishomoadamantane (VIII) in 65% yield: mp 221–223°; nmr ($CDCl_3$) τ 7.6–9.3 (broad m); *m/e* 164 (M^+), 149 (M − CH_3), 136 (M − C_2H_4), 135 (M − C_2H_5), and 121 (M − C_3H_7).

At the same time, solvolytic ring expansion of 3-homoadamantylcarbinyl tosylate (XIVa) may provide another route to 1,1- or 1,3-bishomoadamantane depending on the C_3–C_4 bond or C_3–C_2 (C_3–C_{11}) bond migration. Furthermore, solvolytic behavior of XIVa would be of interest in comparison with 1-adamantylcarbinyl tosylate (Xb),[15] where considerable strain increase is expected.[16]

While the Koch–Haaf carboxylation of Xa under normal conditions[17] affords a mixture of 3- (XIa) and 1-homoadamantanecarboxylic acid,[18] the same carboxylation under high dilution conditions,[19] as suggested by Schleyer, *et al.*,[18a] yielded exclusively XIa in 82% yield: mp 158–159°; nmr ($CDCl_3$) τ 0.4 (s, 1), and 7.7–8.8 (m, 17); *m/e* (rel intensity) 194 ($M,^+$ 80), 150 (M − CO_2, 75), and 149 (M − CO_2H, 100). The structure of XIa was confirmed by an alternative synthesis from 3-homoadamantanol (XIIa)[20] *via* bromide XIIb[15a,20] and cyanide XIIc, mp 176–178°, followed by hydrolysis.[21] XIa was esterified with diazomethane to give XIb which was reduced with lithium aluminum hydride to 3-homoadamantylcarbinol (XIII): mp 85–87°; nmr ($CDCl_3$) τ 6.84 (d, J = 1.2 Hz, 2, CH_2O), 7.89 (s, 1, OH), and 7.9–8.9 (m, 17, ring protons); *m/e* 180 (M^+). The tosylate XIVa, mp 86–88°, was obtained by the usual procedure.

Solvolysis results of XIVa under several conditions are summarized in Tables I and II. The alkaline hydrolysis in 70% aqueous diglyme afforded a new alcohol after purification by chromatography (silica gel-chloroform): mp 256–258°; ir (KBr) 3380 cm⁻¹; nmr ($CDCl_3$) τ 7.6–8.8 (m, 19, ring protons) and 8.45 (s, *ca.* 1, OH); *m/e* 180 (M^+, 50), 163 (M − 17, 32), and 41 (100). Absence of the signals due to CH_2O in the

Table I. Solvolysis Products of 3-Homoadamantylcarbinyl Tosylate (XIVa)

Solvent	Products, %	Recovered XIVa, %
70% aqueous diglyme[a]	XVa (60)	6
AcOH	XIVb (69)[b]	
AcOH (ACO^-)[c]	XIVb (42) + XVb (40)	

[a] A mixture of XIVa (1 g), Na_2CO_3 (1 g), water (25 ml), and diglyme (50 ml) was refluxed for 1 week. [b] Analysis was based on vpc at 10 half-lives at 120°. Unidentified minor products amounted to 31%. [c] A mixture of XIVa (0.2 g), AcONa (0.2 g), AcOH (15 ml), and Ac_2O (0.15 ml) was heated at 120° for 48 hr. Unidentified minor products were *ca.* 18%.

Table II. Acetolysis Rate of XIVa[a]

Compound	T, °C	k, sec⁻¹	k_{rel}, 100°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
XIVa	120	4.08×11^{-5}			
	100	5.13×10^{-6}	2.9	29.5	4.1
Xb[b]	100	2.18×10^{-6}	1.2	27.3	12
Me_3CH_2OTs[b]	100	1.74×10^{-6}	1.0	30.7	3.1
Et_3CH_2OTs[c]	100	9.75×10^{-6}	5.6		

[a] The rate was calculated by the first-order kinetics using an ampoule technique and titration with AcOH–NaOAc. [b] See ref 15a. [c] See ref 16b.

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(15) (a) J. E. Nordlandor, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, **88**, 4475 (1966); (b) S. H. Liggero, R. Sustmann, and P. v. R. Schleyer, *ibid.*, **91**, 4571 (1969).

(16) For solvolysis of other related neopentyl systems, see: (a) A. P. Krapcho and M. Benson, *ibid.*, **84**, 1036 (1962); (b) R. L. Heidke and W. H. Saunders, Jr., *ibid.*, **88**, 5816 (1966); (c) P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969); (d) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *ibid.*, **90**, 1014 (1968); (e) W. G. Dauben and J. L. Chitwood, *ibid.*, **92**, 1624 (1970).

(17) H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, **92**, 1929 (1959).

(18) (a) P. v. R. Schleyer, L. K. M. Lam, D. J. Raber, J. L. Fry, M. A. Mckervey, J. R. Alford, B. D. Cuddy, V. G. Keizer, M. W. Gluk, and J. L. M. A. Schlatmann, *J. Amer. Chem. Soc.*, **92**, 5246 (1970); (b) F. N. Stepanov and S. S. Goots, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2, 430 (1970); *Chem. Abstr.*, **73**, 3518t (1970); A. G. Yurchenko, F. N. Stepanov, and S. S. Isaeva, *Org. Mass Spectrom.*, **3**, 1401 (1970).

(19) The reaction was carried out using a solution of 1.2 mmol of Xa in 5 ml of CCl_4, 300 ml of 95% H_2SO_4, and 50 ml of formic acid at 15–25° for 4 hr. It should be noted that standing of the reaction mixture overnight resulted in the formation of a mixture of XIa and its 1 isomer.

(20) H. Stetter and P. Goebel, *Chem. Ber.*, **96**, 550 (1963).

(21) The similar synthesis of XIa has been reported recently: F. N. Stepanov and S. S. Isaeva, *Zh. Org. Khim.*, 7, 850 (1971); *Chem. Abstr.*, **75**, 48515x (1971).

nmr spectrum supports a ring-expanded structure of XVa and/or XVa′. Treatment of this alcohol with phosphorus tribromide in *n*-hexane–benzene at 5–30° for 20 hr afforded an oily bromide mixture (6.5:1) in 25% yield after purification on preparative tlc (silica gel–*n*-hexane) and sublimation: nmr ($CDCl_3$) τ 6.78 (s, CH_2Br) and 7.5–9.0 (m, ring protons) (the integral ratio was 1:10.5); *m/e* 244 (M + 2) and 242 (M^+) (*ca.* 1:1 ratio). The major product was assignable as 3-bromomethylhomoadamantane (XVI) by spectral and vpc comparisons with a specimen prepared from XIII, and hence, the minor product as a bridgehead bromide. The reduction products of the bromide mixture with tri-*n*-butyltin hydride[22] in cyclohexane at 80–85° for 20 hr, and with Raney Ni catalyst at 40–50° for 2 days, revealed two major peaks in *ca.* 7.5:1 ratio (vpc). The major product was 3-methylhomoadamantane (XVII) by comparison with an authentic sample prepared from XIVa and/or from XVI: mp 114–116°; *m/e* 164 (M^+); nmr (CCl_4) τ 7.75–8.95 (m, 17) and 9.11 (s, 3). However, the minor product was not 1,1-bishomoadamantane (VIII) obtained above, and consequently, it appears to be 1,3-bishomoadamantane (XVd), though its isolation was not successful yet. Therefore, the hydrolysis product was tentatively concluded to be 1,3-bishomoadamantan-6-ol (XVa).[23]

Although the unbuffered acetolysis of XIVa gave no trace of the ring expanded acetate but only the ring retained acetate XIVb, the buffered acetolysis (AcOH–AcONa) afforded both XIVb and a rearranged acetate XVb in 1:1 ratio; the latter acetate was identical with a specimen prepared from XVa.

The acetolysis rate (Table II) of XIVa was 2.4 times faster than Xb,[15a] and 2.9 faster than neopentyl tosylate, but slower than Et_3CH_2OTs.[16b] The observed slight rate enhancement compared with Xb might suggest a similar anchimeric assistance[15b] operative in the present system.[24,25]

The above two ring expansion reactions may provide a facile entry into 1,1- and 1,3-bishomoadamantane chemistry.

Acknowledgment. We wish to thank Professor P. v. R. Schleyer for his interest and kind suggestions on this work.

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(22) 1-Adamantyl and 3-homoadamantyl bromides were also reduced to the corresponding hydrocarbons in good yields with this reagent: *cf.* E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 764 (1964).

(23) The X-ray crystallography on this alcohol is in progress: Dr. K. Mani, private communication.

(24) The solvolysis study on the homoadamantylcarbinyl system derived from normal Koch–Haaf carboxylation of Xa was carried out in 1964 at Princeton: P. v. R. Schleyer, private communication.

(25) Professor P. v. R. Schleyer has kindly informed us of a preliminary result of the strain energy calculation on bishomoadamantane: 16.1 (1,1 isomer), 19.6 (1,3 isomer), and 15.8 (1,5 isomer) kcal/mol at 25°. The value predicts a very slight rate enhancement for XIVa compared to Xb.

T. Sasaki,* S. Eguchi, T. Toru, K. Itoh
Institute of Applied Organic Chemistry
Faculty of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya, 464, Japan

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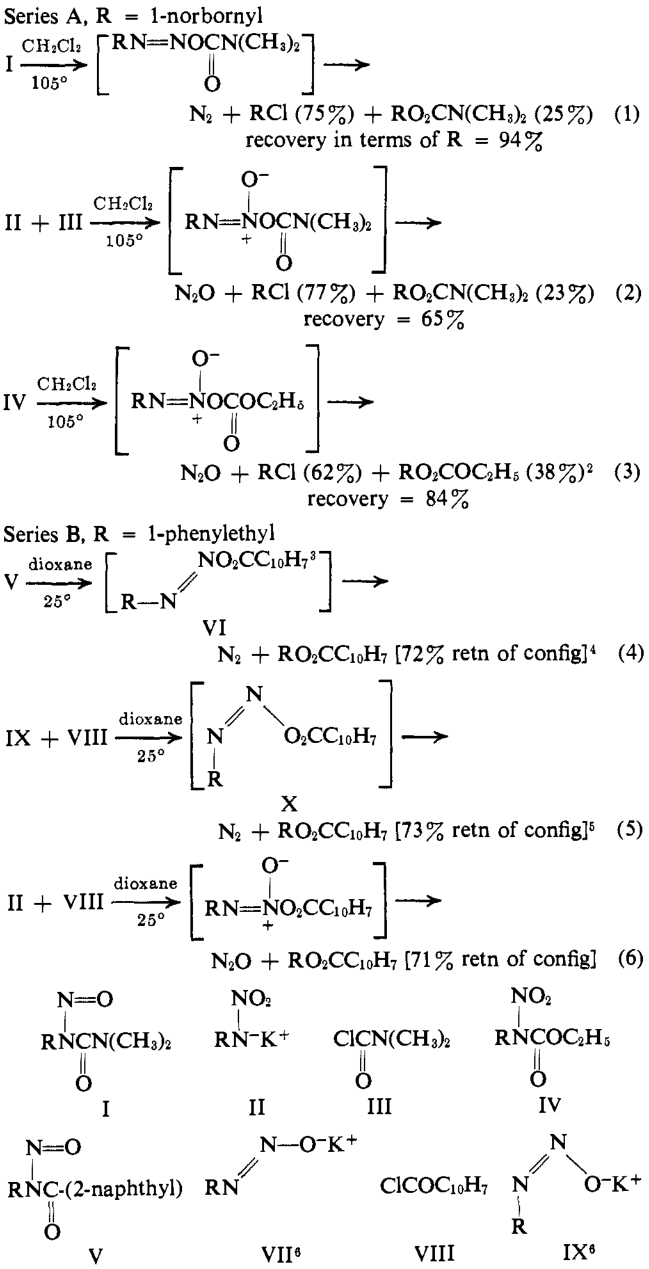
The Deamination of Aliphatic Amines

Sir:

We wish to report that the deamination of 1-norbornylamine leads to the same product distribution whether nitrogen is the gas molecule ejected or nitrous oxide. Further, the same stereochemical outcome is observed in the deamination of 1-phenylethyl derivatives whether *syn-* or *anti-*diazo structures are involved.

Variations of the nitrosoamide approach to deamination were used (reactions 1–6) rather than one involving nitrous acid because of the versatility of the former approach and the ease of distinguishing intramolecularly derived products from those derived intermolecularly.[1]

Chart I



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(1) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968.

(2) E. H. White, H. P. Tiwari, and M. J. Todd., *J. Amer. Chem. Soc.*, **90**, 4734 (1968).

(3) Models indicate that the first formed intermediate VI must be anti [R. Huisgen and H. Nakaten, *Justus Liebigs Ann. Chem.*, **586**, 84 (1954)].

(4) Per cent overall retention is listed. A value of 73% was reported by E. H. White and C. A. Aufdermarsh, Jr. [*J. Amer. Chem. Soc.*, **83**, 1179 (1961)] for the reaction in the presence of formic acid. All optically active esters were analytically pure.

(5) No detectable amounts of the product of N-acylation (compound V) were formed either at 25 or −25° ($T_{1/2}$ for V at −25° is ~ 5 days; salt reaction times were hours).