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.

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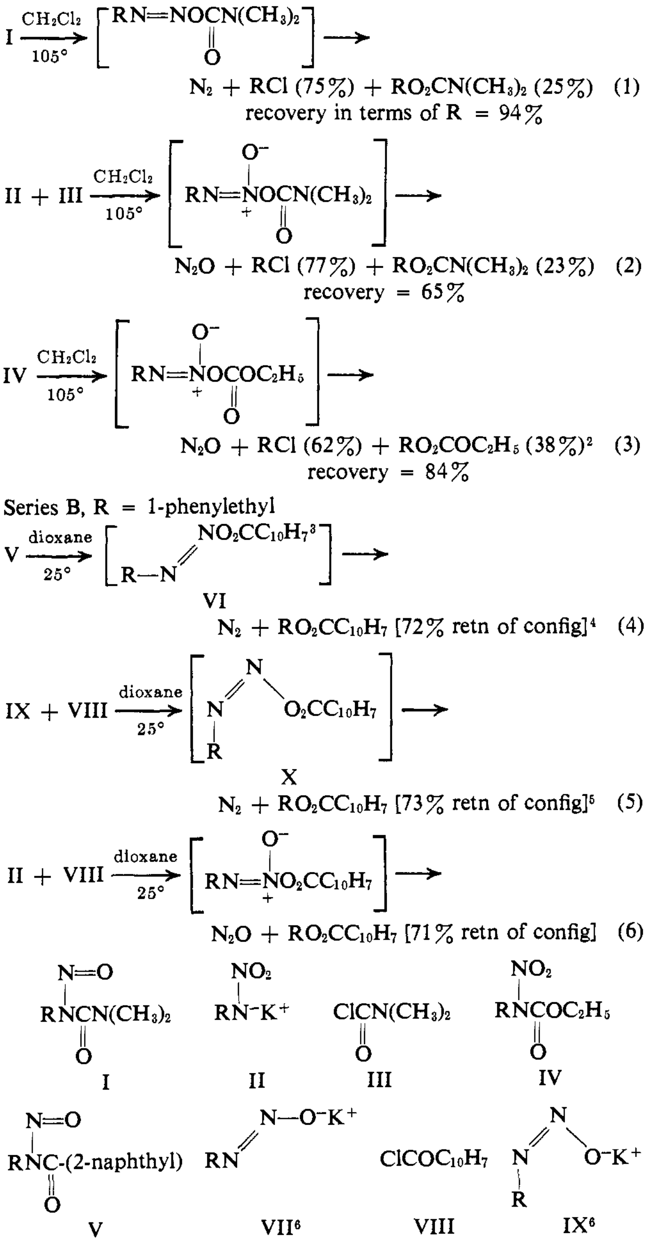
The Deamination of Aliphatic Amines

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).

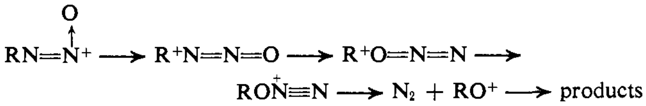
[3] Models indicate that the first formed intermediate VI must be anti [R. Huisgen and H. Nakaten, *Justus Liebigs Ann. Chem.*, **586**, 84 (1954)].

[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).

Ureas (I) and carbamates (IV) were used (in addition to the nitrosoamides (V)) because of the stabilities of these derivatives. The reactions shown in Chart I were compared.

A comparison of reactions 1,2 (and 4,6) shows that the formation of nitrous oxide rather than nitrogen has no pronounced effect on the reaction. If the gas molecules were effectively solvating the carbonium ions, nitrous oxide should be superior to nitrogen as indicated by the relative solubilities in water (N_2O, 58 m*M*; N_2, 1 m*M* at 0°)[7] and the boiling points (N_2O, −89°; N_2, −196°),[7] etc. No evidence was found for the following process ("A" reaction series)



$$RN{=}\overset{\overset{\displaystyle O}{\uparrow}}{N}{}^{+} \longrightarrow R^{+}N{=}N{=}O \longrightarrow R^{+}O{=}N{=}N \longrightarrow RO\overset{+}{N}{\equiv}N \longrightarrow N_2 + RO^{+} \longrightarrow \text{products}$$

and the addition of a large excess of nitrous oxide to reaction 3 had no effect on the product distribution.[8] Thus, neither the size nor solvating ability of the gas molecule are important variables, and externally added nitrous oxide does not appear to enter into the reaction.

Reactions 4 and 5 show that the stereochemistry of the diazo species (VI *vs.* X) is not an important variable.[9] The yields for runs 4–6 were essentially the same (20–25%), and a similar yield was obtained for the acylation of the anti salt VII. These results suggest that VI and X react *via* a common intermediate, candidates being the anti form VI, the diazonium ion pair XI, and the carbonium ion pair XII.[10] In any event, the syn form is clearly not responsible for characteristic features of deamination such as overall retention of configuration and intramolecular ester (or alcohol) formation.[1,11]

The above results show that the gas molecule (N_2 or N_2O) is not involved detectably in the product forming steps, and they suggest strongly that the products are determined at the carbonium ion stage of the reaction.

$$\text{VI} \longrightarrow \underset{\text{XI}}{RN_2{}^{+}X^{-}} \longrightarrow \underset{\text{XII}}{R^{+}N_2X^{-}} \longrightarrow R^{+}N_2X^{-} \longrightarrow \text{products} \quad (7)$$

The transient separation of carbonium ion and counterion by an inert molecule, XII, can, in principle, account for the counterion effect (runs 2 and 3) and for certain of the characteristic features of deamination, such as extensive hydride shifts and skeletal rearrangements (relative to solvolysis). However, an additional factor is required to account for: (1) the virtual identity of the product distribution, whether nitrogen or nitrous oxide is ejected, (2) the observation that in deaminations 1–3 the cation is captured preferentially by a relatively inert solvent molecule rather than by the negatively charged counterion, and (3) the fairly general observation in deamination of product RX formed with inversion of configuration by an *intramolecular* pathway.[1,12] The additional factor is probably the existence of disorder in the product-forming steps,[1] undoubtedly a result of the energetic formation of the nitrogen (or N_2O) molecule (recoil).[13,14]

Acknowledgment. We thank the National Science Foundation for its support of this work (GP-8993).

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(6) The anti salt *dl*-VII was prepared by the method of J. Thiele [*Justus Liebigs Ann. Chem.*, **376**, 239 (1910)]: mp 208° (dec); ir (Nujol mull) 1600, 1490, 1410, 1300, 1166, 1079, 1015, 760, 695, and 611 cm^{-1}; nmr (CD_3SOCD_3) δ 1.36 (d, 3.0, J = 6.8 Hz, $CHCH_3$), 3.59 (s, 0.7, H_2O), 4.79 (q, 1.0, J = 6.8 Hz, $CHCH_3$), 7.09–7.44 (broadened s, 4.9,C_6H_5). *Anal.* Calcd for $C_8H_9N_2OK \cdot 0.5H_2O$: C, 48.71; H, 5.11; N, 14.20. Found: C, 48.87; H, 4.70; N, 14.28. The syn salt IX was prepared by methods similar to those of A. Hantzsch and M. Lehmann [*Chem. Ber.*, **35**, 897 (1902)] and R. A. Moss [*J. Org. Chem.*, **31**, 1082 (1966)]: mp 153–154°; ir (Nujol mull) 1600, 1490, 1375, 1160, 1150, 1087, 758, and 697 cm^{-1}; nmr (CD_3SOCD_3) δ 1.19 (d, 3.0, J = 6.8 Hz, $CHCH_3$), 5.58 (q, 1.0, J = 6.8 Hz, $CHCH_3$), 7.05–7.43 (m, 5.2, C_6H_5). The corresponding methyl diazotates have been distinguished on the basis of their nmr spectra [H. Suhr, *Chem. Ber.*, **96**, 1720 (1963)], and the structure of the syn form has been determined by X-ray diffraction [E. Müller, W. Hoppe, H. Hagenmaier, H. Haiss, R. Huber, W. Rundel, and H. Suhr, *ibid.*, **96**, 1712 (1963)].

(7) "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, p B-199.

(8) Dr. M. J. Todd, unpublished results.

(9) The stereochemical results in the decomposition of nitrosoamides of 1-phenylethylamine are relatively independent of the solvent [ref 4 and E. H. White, *J. Amer. Chem. Soc.*, 77, 6014 (1955)].

(10) Formed either in a one- (M. C. Whiting, *Chem. Brit.*, 2, 482 (1966)), or two-step process.

(11) It appears unlikely that the anti derivatives isomerize to the syn forms (*e.g.*, VI → X) before decomposition in view of the low activation energy estimated for the decomposition of alkyldiazonium ions [(3–5 kcal): A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 2888 (1957)]. The results of M. Wilhelm and D. Y. Curtin [*Helv. Chim. Acta*, **40**, 2129 (1957)] also suggest a low value. These authors have estimated that the activation energy for the decomposition of a bridgehead diazonium ion in ether is 21 kcal lower than the value for the solvolysis of the corresponding bromide in ethanol. The activation energy for the conversion of a series of *cis*-diazocyanides into the trans forms is about 23 kcal [R. J. W. LeFevre and J. Northcott, *J. Chem. Soc.*, 944 (1949)]. Similarly, both cis and trans forms of azobenzenes, oxime derivatives, hydrazenes, etc., can be isolated ($E_{act} > \sim 15$ kcal). The thermal equilibrium favors the trans forms by a large margin ($K \geq \sim 100$) and thus $\Delta G_{s \rightarrow t} \geq \sim 3$ kcal. Thus, it seems reasonable that the conversion of VI to X, *e.g.*, would require more than 3–5 kcal.

(12) R. A. Moss, D. W. Reger, and E. M. Emery, *J. Amer. Chem. Soc.*, **92**, 1366 (1970).

(13) This description is essentially the same as that presented previously.[1,2]

(14) Because there are striking similarities between the nitrous acid, nitrosoamide, nitroamide, and triazene methods of deaminations,[1,15] the views expressed above, we believe, can be generally applied to deamination type reactions leading to carbonium ions and a gas such as nitrogen ($RNH_2 \rightarrow RX + N_2(N_2O)$, etc.).

(15) E. H. White and D. W. Grisley, Jr., *J. Amer. Chem. Soc.*, **83**, 1191 (1961); H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965).

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Stereochemical Consequences of Adjacent Electron Pairs. A Theoretical Study of Rotation–Inversion in Ethylene Dicarbanion

Sir:

The notion that there is stereochemistry, *i.e.*, nonspherical symmetry, associated with lone electron pairs is very widely held. It is seen, for example, in the valence shell electron pair repulsion theory,[1] in the rabbit-ear effect,[2] in discussions of the anomeric effect,[3] and in the continuing controversy over the size of the lone pair.[4] It also forms the conceptual basis of the recently postulated[5] "gauche effect," a term which describes in an

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(1) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); 47, 18 (1970); R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970).

(2) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, *J. Amer. Chem. Soc.*, **90**, 7174 (1968); E. L. Eliel, *Sv. Kem. Tidskr.*, **81**, 22 (1969).

(3) J. T. Edward, *Chem. Ind.*, 1102 (1955); C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1969).

(4) R. A. Y. Jones, A. R. Katritzky, A. C. Richards, R. J. Wyatt, R. J. Bishop, and L. E. Sutton, *J. Chem. Soc. B*, 127 (1970); N. L. Allinger, J. A. Hirsch, and M. A. Miller, *Tetrahedron Lett.*, 3729 (1967).

(5) (a) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972); (b) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971). (c) In ref 5b this statement is presented as Rule 2 of the gauche effect.