undeuterated compounds IV and VIII by decoupling the methyl or methylene group at C-2.)

Since the large upfield shift of H-2 in N,N,2-trimethyl-1,3-diazane (III) and N,N-dimethyl-2-ethyl-1,3-diazane (VII) upon introduction of geminal methyl groups at C-5 is not a direct effect (*vide supra*), it can only be explained as an indirect effect on the N-methyl groups. The only reasonable interpretation we can think of is to assume that, in the N,N-dimethyl-5,5-di-H compounds, one methyl group on nitrogen is axial, but that, in the 5,5-dimethyl compounds, both methyl groups must be equatorial in order to avoid a serious *syn*-axial methyl–methyl interaction. It is known[9] that the signal of an axial hydrogen on carbon next to amino nitrogen undergoes an appreciable upfield shift when the nitrogen bears an axial electron pair and equatorial methyl group as compared to the case where the electron pair is equatorial and the methyl group axial or absent. It is still controversial whether that shift is caused by the axial pair[9a,10] or by the equatorial N-methyl group,[9b,11] or both. For the present purpose, however, the origin of the shift is immaterial; it suffices to record that it occurs in going from III to IV or from VII to VIII and that therefore IV and VIII are likely to have axial pairs and equatorial N-methyl groups where III and VII have one equatorial pair and axial N-methyl. (The second N-methyl group is assumed to be equatorial.)

The conclusion that N,N-dimethyldiazane[12] contains an axial N-methyl group is in agreement with recent findings that N,N′,N″,N‴-tetramethyl-1,2,4,5-tetrazane contains two axial N-methyl groups[5] and that certain N-methyl-, N-ethyl-, and N-*n*-propyl-1,3-oxazanes (but not the corresponding N-isopropyl or N-*t*-butyl compounds) bear axial alkyl groups.[6] Since the conformational strain in an axial N-methyl-1,3-diazane (one *syn*-axial methyl–H plus one *syn*-axial methyl–pair interaction) is probably close to 1 kcal/mol[13] and, since some of the oxazanes previously investigated[6] appear to have *syn*-axial methyl and nitro groups, the magnitude of the rabbit ear effect appears to be substantial.

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(9) *E.g.*, (a) J. B. Lambert, F. G. Keske, R. E. Carhart, and A. P. Jovanovitch, *J. Amer. Chem. Soc.*, **89**, 3761 (1967); (b) M. J. T. Robinson, *Tetrahedron Letters*, 1153 (1968).

(10) F. Bohlmann, D. Schumann, and C. Arndt, *ibid.*, 2705 (1965).

(11) H. Booth and J. Little, *Tetrahedron*, **23**, 291 (1967).

(12) The nmr spectra of the N-unsubstituted diazanes show H-2 at lower field than those of the N-methyl homologs, presumably because the former contain no equatorial N-methyl group whereas the latter have at least one such group. The insensitivity of the H-2 shift toward introduction of geminal methyl groups at C-5 (*cf.* I *vs.* II, V *vs.* VI) means either that the H-2 shift is insensitive toward the axial or equatorial nature of the unshared pairs on nitrogen or (much more likely) that both series (5,5-di-H and 5,5-di-Me) have one of the N–H hydrogens axial in order to avoid a rabbit-ear effect.

(13) Adding one *syn*-axial Me–H interaction (0.85 kcal/mol[1]) and one *syn*-axial Me–pair interaction [0.4 kcal/mol: E. L. Eliel and M. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968)] and offsetting the entropy of mixing of the *dl*-ea form would give 0.85 kcal/mol at 25°. See, however, R. J. Bishop, L. E. Sutton, D. Dineen, R. A. Jones, A. R. Katritzky, and R. J. Wyatt, *J. Chem. Soc.*, *B*, 493 (1967), who report a *syn* axial Me–H interaction in N-methylpiperidine (axial Me) of only 0.2 kcal/mol.

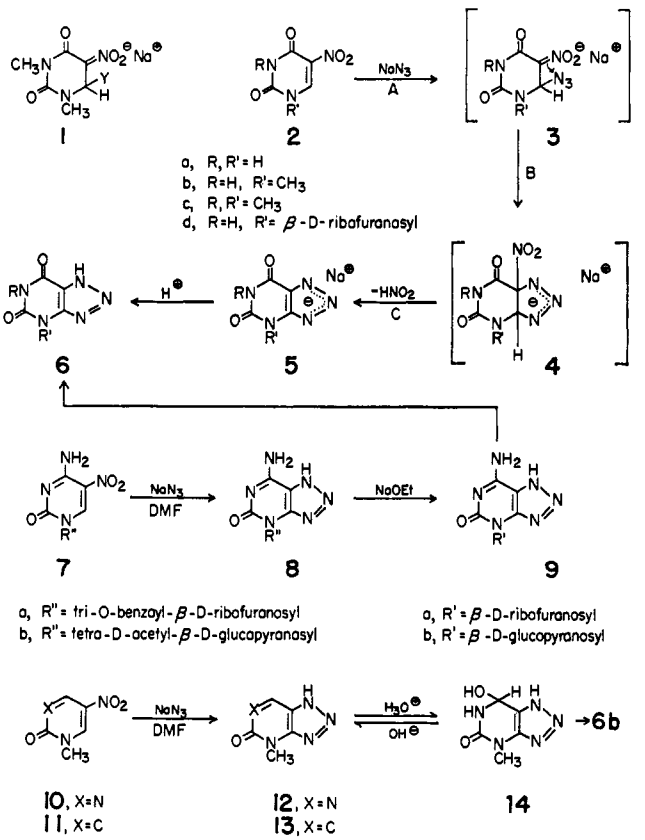
Pyrimidines. VII. A Simple Conversion of 2-Oxo-5-nitro Heterocycles to *v*-Triazolo Derivatives by Sodium Azide[1]

Sir:

In the course of our attempts to synthesize the sodium salt of 6-azido-1,3-dimethyl-5,6-dihydro-5-nitrouracil (**1**, Y = N_3) we found that treatment of certain 5-nitropyrimidines with sodium azide in various solvents leads to a novel, one-step synthesis of 2-oxo-8-azapurines. For example, reaction of the readily available 5-nitrouracil (**2a**) or its mono- and dimethylated derivatives (**2b**, **2c**) with sodium azide in DMF or refluxing alcohol followed by acidification afforded the known[2] 8-azaxanthines (**6**)[3] in 70–90% yields.[4]

To our best knowledge, this type of reaction has not been previously described. We propose the following plausible mechanism for this unexpected cyclization (see Scheme I). The first step is the nucleophilic attack

Scheme I



(1) This investigation was supported in part by funds from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA 08748).

(2) G. Nübel and W. Pfleiderer, *Chem. Ber.*, **98**, 1060 (1965), and leading references therein.

(3) The trivial nomenclature (*e.g.*, "8-azaxanthines") is used throughout this paper in order to emphasize analogy with the biologically important purines. Such heterocycles should be listed as derivatives of *v*-triazolo[4,5-*d*]pyrimidines.

(4) In the case of **2a** it was necessary to add ammonium chloride to the reaction in order to prevent ionization at N-1.

by azide ion on C-6 of **2** to form **3** (step A). It should be noted that Pfleiderer and Mosthaf[5] had treated 1,3-dimethyl-5-nitrouracil with sodium alkoxide and obtained **1** (Y = OEt) which is analogous to **3**.[6] Compound **3** would then undergo an intramolecular nucleophilic attack by C-5 of the *aci*-nitro group on the terminal azide nitrogen to form the 4,5-dihydro-8-azaxanthine derivative (**4**) (step B) which by elimination of nitrous acid yields the sodium salt of the 8-azaxanthines (**5**) (step C). Acidification of **5** affords **6**. During the course of this reaction, the liberation of nitrous acid can be detected.

This new route to 2-oxo-8-azapurines is easily adaptable to the synthesis of 3-β-D-glycosyl-2-oxo-8-azapurines, a hitherto unknown class of nucleosides of potential biochemical interest. For example, treatment of 5-nitrouridine[7] (**2d**) with sodium azide in DMF for 2 days at room temperature gave an 85% yield of the monohydrate of 3-β-D-ribofuranosyl-8-azaxanthine (**6d**). Reaction of tri-*O*-benzoyl-5-nitrocytidine[8] (**7a**) with sodium azide afforded the blocked 3-β-D-ribofuranosyl-8-azaisoguanine (**8a**) which, after saponification, yielded 3-β-D-ribofuranosyl-8-azaisoguanine (**9a**) in ~50% yield. Similarly, from 1-(tetra-*O*-acetyl-β-D-glucopyranosyl)-5-nitrocytosine[8] (**7b**), 3-β-D-glucopyranosyl-8-azaisoguanine (**9b**) was obtained. The structures of nucleosides **6d**, **8**, and **9** were confirmed by nmr and ultraviolet spectroscopy, by elemental analyses,[9] and by conversion of the ribosyl derivative **9a** to **6d** with nitrous acid.

5-Nitro-2-oxopyrimidines without substituents in position 4 will also undergo this reaction. Thus, treatment of 1-methyl-5-nitro-2-oxopyrimidine[10] (**10**) with sodium azide gave good yields of 3-methyl-2-oxo-8-azapurine (**12** ⇌ **14**). The nmr spectrum of the anion of **12** in DMSO-d_6 with added NaOD showed a singlet for one proton at C-6 at δ 9.00 and a methyl signal at δ 3.62. The product isolated from the reaction of **10** from an aqueous solution at pH ~2 gave an nmr spectrum in DMSO-d_6 which showed the absence of the C-6 vinylic proton singlet and the presence of two doublets[11] at δ 8.81 and 7.19 consistent with the splittings expected for the water adduct **14**. The ultraviolet absorption spectrum of **12** ⇌ **14** was similar to that for 2-oxo-8-azapurine[8] but differed markedly from that of 1-substituted-2-oxo-8-azapurine.[8] Albert[12] had demonstrated that 2-oxo-8-azapurine also undergoes covalent 1,6 hydration in aqueous acid. Oxidation of **12** ⇌ **14** with iodine at pH 8 gave 3-methyl-8-azaxanthine, identical with **6b** obtained by treatment of 1-methyl-5-nitrouracil (**2b**) with sodium azide.

This cyclization reaction is also applicable to 5-nitro-2-oxopyridines. Treatment of **11** with sodium azide afforded 4-methyl-5-oxo-*v*-triazolo[4,5-*b*]pyridine (**13**)[9] in good yield. The nmr spectrum of **13** showed two coupled vinylic protons at δ 6.57 (probably H-6) and 8.02 (probably H-7), with $J_{H\text{-}6,H\text{-}7}$ = 9.6 cps and a methyl resonance at δ 3.56. In addition, one exchangeable NH proton was in evidence at δ ~11.6. These data, as well as the elemental analysis, are consistent with structure **13**.

The reactions described herein may be the first examples of a more general reaction of azide ion with nitro olefins which could give rise to 4,5-disubstituted *v*-triazoles. Table I lists some physical properties of new compounds discussed herein.

Table I. Some Physical Properties Of New Compounds

Compound	Mp, °C	λ_{max},[a] mμ	Solvent, pH
6d	163–166	263	Water, 2
	foaming	262	Water, 8
		243, 269	Water, 13
8a	219–221 dec	225 (254), 275 (281)	Ethanol
8b	230 dec	253 (273)	Ethanol
9a	>210 dec	279	Water, 1
		249, 281	Water, 11
9c	>220 dec	279	Water, 1
		249, 280	Water, 11
12 ⇌ **14**[b]	>280 dec	245	Water, 2
		(277), 311	Water, 9
13	276–278	244, 306	Water, 2
		(268), 314	Water, 10

[a] Wavelengths in parentheses denote an inflection. [b] Material isolated from water at pH 2–3.[9]

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(5) W. Pfleiderer and H. Mosthaf, *Chem. Ber.*, 90, 728 (1957).
(6) (a) Further support for **3** as the most plausible first intermediate is indicated from a recent report[6b] which showed that certain trinitrobenzene derivatives react with azide ion to form stable addition complexes analogous to Meisenheimer-type compounds. (b) P. Caveng and H. Zollinger, *Helv. Chim. Acta*, 50, 861 (1967).
(7) I. Wempen, I. L. Doerr, L. Kaplan, and J. J. Fox, *J. Am. Chem. Soc.*, 82, 1624 (1960). A simpler synthesis of this compound from 5-nitrouracil and halogenose by the mercuric cyanide–nitromethane procedure has since been achieved in our laboratory [N. Yamaoka and J. J. Fox, manuscript in preparation].
(8) J. J. Fox and D. van Praag, *J. Org. Chem.*, 26, 526 (1961).
(9) Satisfactory elemental analyses were obtained for all new compounds reported herein, except compound **14**. The structure of **14** was established by its conversion to the known **6b** (see text).
(10) Obtained by methylation of 2-oxo-5-nitropyrimidine [L. M. Stempel, G. B. Brown, and J. J. Fox, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 14-O].
(11) Compound **14** was poorly soluble in DMSO-d_6. Addition of NaOD produced the nmr spectrum of anion **12** as described above.
(12) A. Albert, *J. Chem. Soc.*, *B*, 427 (1966).

Low-Temperature Oxidation of 2-Butene in the Gas Phase

Sir:

One would expect, on thermochemical grounds, to find epoxides as important products in the oxidation of hydrocarbons in the gas phase.[1] Although such epoxides have been observed, 1,2-epoxypropane from propene,[2] 1,2-epoxy-3-methylpropane from 2-methylpropene,[3] and 2,3-epoxy-2-methylbutane from 2-methylbutane,[4] the mechanism for their formation has not been fully elucidated. Epoxybutanes have not been reported from the combustion of 2-butene,[5] and, as we

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(3) (a) W. E. Falconer and J. H. Knox, *Proc. Roy. Soc.*, A250, 493 (1959); (b) A. P. Zeelenberg and A. F. Bickel, *J. Chem. Soc.*, 4014 (1961); (c) J. Hay, J. H. Knox, and J. M. C. Turner, Tenth International Symposium on Combustion, Cambridge, England, 1965, p 331.
(4) C. F. Cullis and E. Fersht, *Combust. Flame*, 7, 353 (1963).
(5) (a) A. Blundell and G. Skirrow, *Proc. Roy. Soc.*, A244, 331 (1958); (b) R. G. W. Norrish and K. Porter, *ibid.*, A272, 164 (1963); (c) R. S.-M. Tse, *Dissertation Abstr.*, *B*, 4356 (1967); (d) K. C. Salooja, *Combust. Flame*, 11, 320 (1967).