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 $\sim$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** $\leftrightarrows$ **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 $\sim$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** $\leftrightarrows$ **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** $\leftrightarrows$ **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 $J_{\text{H-6,H-7}}$ = 9.6 cps and a methyl resonance at δ 3.56. In addition, one exchangeable NH proton was in evidence at δ $\sim$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	$\lambda_{\max}$,[a] mμ	Solvent, pH
6d	163–166 foaming	263	Water, 2
		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 $\rightleftarrows$ **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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(1) S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 972 (1965).

(2) S. Oba and W. Sakai, *Bull. Chem. Soc. Japan*, **40**, 681 (1967).

(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).

Table I. Some Major Oxidation Products (mm) of *trans*-2-Butene and *cis*-2-Butene[a]

	trans-2-Butene						*cis*-2-Butene					
	Reaction coordinate,[b] min											
	−1.5	+0.1	+1	+5	+6	+10	−1.5	+0.1	+1	+5	+6	+10
trans-2-Butene	82.5	41.1	31.0	29.8	28.9	22.5	...	3.6	4.9	12.6	11.3	7.6
cis-2-Butene	...	0.6	0.6	2.0	1.5	1.5	83.0	37.4	26.7	29.8	27.2	18.8
Methane	...	4.7	6.3	8.4	9.0	9.9	...	4.6	6.4	8.5	9.1	10.1
Methanol	0.6	11.6	14.0	14.0	14.2	14.0	0.7	11.8	14.0	13.8	14.3	14.2
Acetaldehyde	8.0	20.8	21.9	22.3	22.1	18.5	7.9	21.0	21.7	21.7	22.0	18.2
trans-2,3-Epoxybutane	1.0	5.5	7.8	10.4	11.1	7.2	0.6	6.4	7.0	7.8	9.8	6.2
cis-2,3-Epoxybutane	0.4	3.1	3.3	4.3	4.4	3.3	0.4	2.7	3.9	4.0	4.7	3.6
Methyl ethyl ketone	0.1	1.8	1.9	2.2	2.2	1.8	0.1	1.8	1.9	2.1	2.2	1.8

[a] Initial pressures: hydrocarbon, 100 mm; oxygen, 100 mm (277°). [b] Reaction coordinate is measured in minutes relative to the appearance time of the cool-flame.

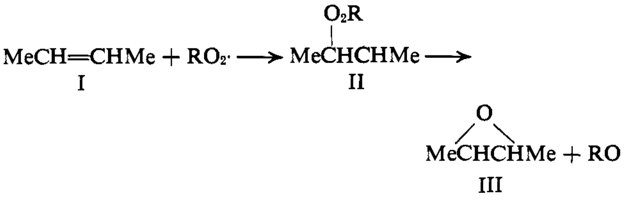
feel that the formation of epoxides in such systems should lead to useful information as to the fate of important radicals formed, in the present study we have paid particular attention to their formation.

A static vacuum system connected to a gas chromatograph has been used. The products were analyzed by both gsc (Porapak Q (100–120 mesh)) and silica gel (80–100 mesh)) and by glc (Celite (A.W. 100–120 mesh) with polyethylene glycol 1500). To confirm identification of the peaks, the chromatograph was linked to an A.E.I. MS 12 mass spectrometer.

In one series of runs, analyses were performed before and after the passage of a single cool-flame. Under our conditions, we find that a total of up to 15% 2,3-epoxybutanes are formed from 2-butene (Table I). On the chromatographic columns used, the adjusted retention times of the *trans*- and *cis*-2,3-epoxybutanes are similar to those of propionaldehyde and 2-methylpropionaldehyde, respectively. These aldehydes have previously been suggested as oxidation products,[5c] but the mass spectra confirm that the peaks must be ascribed to the epoxides.

Benson's studies[1] predict that epoxides are formed from peralkoxy radicals, ($RO_2\cdot$), either by attack on an olefin or by collapse of a hydroperoxyalkyl radical ($\cdot R'OOH$) resulting from intramolecular hydrogen abstraction, and under suitable conditions both these mechanisms could compete to produce the same product.[6] Oba and Sakai[2] suggested that 1,2-epoxypropane is formed by the attack of hydroperoxy radicals ($HO_2\cdot$) on the double bond of propene.

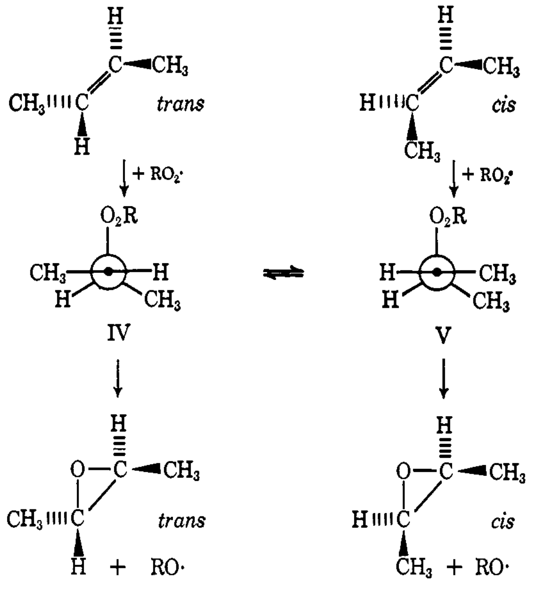
At the temperature of our experiments it is unlikely that the concentration of hydroperoxy radicals is high enough to account for anything like the amount of epoxides formed. Also we have not yet observed any hydrogen peroxide, whose presence would be an indication of significant concentrations of hydroperoxy radicals. Thus we feel that the most likely mechanism for the formation of 2,3-epoxybutanes is



$$\underset{\text{I}}{MeCH{=}CHMe} + RO_2\cdot \longrightarrow \underset{\text{II}}{Me\overset{O_2R}{\overset{|}{C}}HCHMe} \longrightarrow \underset{\text{III}}{\overset{\;\;O}{MeCHCHMe}} + RO$$

A similar reaction is suggested for the liquid-phase oxidation of 2-butene.[7]

If this is so, and there is free rotation about the central carbon–carbon bond of adduct II before ring closure to give the epoxide, one would expect to obtain similar products from both *cis*- and *trans*-2-butene. Further, studies in conformational analysis[8] predict that conformer IV is more stable than V and that the *trans*-epoxide should predominate. This is indeed shown (Table I). The formation of epoxides is found to be partially stereospecific to the *trans*-epoxide, whether the configuration of the parent olefin is *cis* or *trans*. Moreover, the formation of major oxygenated products is shown to be very similar.



It may not, however, be valid to suggest that this mechanism will hold for the formation of epoxides from alkenes at higher temperatures or from alkanes at temperatures where olefins are important primary products. In such cases the concentrations of $HO_2\cdot$ will be higher and those of $RO_2\cdot$ will be lower than in the present work.

Also of interest is the fact that a small quantity of 3,4-epoxy-1-butene has been observed among the reaction products. This indicates that the resonance-stabilized radical formed by proton abstraction from the parent olefin can add on oxygen at the 1 position to a

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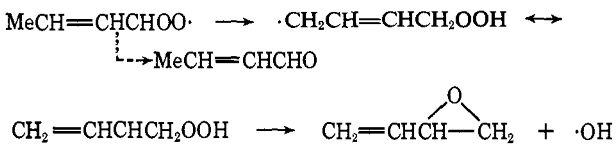
[6] A. Fish, *Angew. Chem. Intern. Ed. Engl.*, 7, 45 (1968).

[7] (a) E. M. Amir, Abstracts, American Chemical Society Meeting, Division of Petroleum Chemistry, Los Angeles, Calif., 1963, p 33; (b) W. F. Brill and B. J. Barone, *J. Org. Chem.*, 29, 140 (1964).

[8] G. Hallas, "Organic Stereochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

small extent, as well as at the major 2 position. This is further supported by the presence of small quantities of crotonaldehyde among the reaction products. The suggested mechanism is



$$\mathrm{MeCH{=}CHCHOO\cdot} \longrightarrow \mathrm{\cdot CH_2CH{=}CHCH_2OOH} \longleftrightarrow$$
$$\dashrightarrow \mathrm{MeCH{=}CHCHO}$$
$$\mathrm{CH_2{=}CHCHCH_2OOH} \longrightarrow \mathrm{CH_2{=}CH\overset{O}{CH{-}CH_2}} + \mathrm{\cdot OH}$$

Thus under our conditions $RO_2\cdot$ attack on a double bond and intramolecular proton abstraction by $RO_2\cdot$ result in different epoxides, the former mechanism occurring to a much greater extent. However, under conditions which give it greater scope, *e.g.*, the presence of weaker C–H bonds or an increase in temperature, the latter mechanism could become more important.

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Hydrocarbon Degenerate Thermal Rearrangements. II.[1] Stereochemistry of the Methylenecyclopropane Self-Interconversion

Sir:

Because of the continuing interest[2] in the theoretically significant trimethylenemethane diradical we wish to report our recent observations concerning the nature of the species involved in the degenerate thermal rearrangement of methylenecyclopropane.[2a,b]

trans- and *cis*-2,3-dimethylmethylenecyclopropanes, **1** and **2**, respectively, were synthesized from Feist's ester[3a] and the corresponding *cis* anhydride[3b] in high yield and purity. Vapor phase pyrolysis of **1** or **2** at 225° or higher for 1 hr or longer gave a mixture of **1**, **2**, *anti*-1-ethylidene-2-methylcyclopropane (**3**), and *syn*-1-ethylidene-2-methylcyclopropane (**4**) in the ratio of 2:1:14:14, respectively. The latter two compounds were synthesized individually from *anti*- and *syn*-1-carbethoxy-2-ethylidenecyclopropanes.[4a] At 170° the initial product distributions from **1** and **2** were substantially different from the equilibrium distribution (Table I). Thus, **3** and **4** did not undergo significant equilibration under the conditions of initial production at 170°.

Table I. Product Distribution from Pyrolyses of **1** and **2**

	1	**2**	**3**	**4**
1 or **2** at 225°	6.5	3.5	45	45
1 at 170° [a]		34	57 ± 2	9 ± 2
2 at 170° [a]	46 ± 4		45 ± 6	9 ± 2

[a] Distribution of products at *ca.* 10% conversion of starting material.

When optically active **1** ($[\alpha]^{21}\mathrm{D}$ −59.4° (CCl_4)) was heated at 170° to 16, 37, and 58.5% reaction, recovered **1** was 1.3, 7.4, and 23.6% racemized, respectively, and the rotation of **3** and **4** combined[4b] (CCl_4) was +13.6, +12.7, and +11.5°, respectively. Integration of the first-order rate equations for the reactions

$$\mathbf{1}(\mathrm{act}) \xrightarrow{k_1} \mathbf{2}$$
$$\mathbf{1}(\mathrm{act}) \xrightarrow{k_2} \mathbf{1}(\mathrm{rac})$$
$$\mathbf{1}(\mathrm{act}) \xrightarrow{k_3} \mathbf{3} \text{ and } \mathbf{4}$$
$$\mathbf{2} \xrightarrow{k_4} \mathbf{1}(\mathrm{rac})$$
$$\mathbf{2} \xrightarrow{k_5} \mathbf{3} \text{ and } \mathbf{4}$$

which is a good approximation during the first half-life of **1** since its racemization is relatively slow, gave the following expressions for the fraction of each material

$$(\mathbf{1}(\mathrm{act})) = \exp\{-(k_1 + k_2 + k_3)t\}$$
$$(\mathbf{2}) = [k_1/(k_4 + k_5 - k_1 - k_2 - k_3)][(\mathbf{1}(\mathrm{act})) - \exp\{-(k_4 + k_5)t\}]$$
$$(\mathbf{1}(\mathrm{rac})) = [k_1k_4/(k_4 + k_5 - k_1 - k_2 - k_3)] \times [1 - (\mathbf{1}(\mathrm{act}))/(k_1 + k_2 + k_3) - (1 - \exp\{-(k_4 + k_5)t\})/(k_4 + k_5)] + [k_2/(k_1 + k_2 + k_3)][1 - (\mathbf{1}(\mathrm{act}))]$$

Three-point kinetic runs with **1**(rac) and with **2** were performed simultaneously using separate sealed ampoules with calculated internal pressures of 150 torr in the same thermostat at 170°. First-order plots gave initial rate constants of $(8.3 \pm 0.4) \times 10^{-5}$/sec and $(13.6 \pm 0.4) \times 10^{-5}$/sec for disappearance of **1** and **2**, respectively. The individual constants, k_1, k_3, k_4, and k_5, could be deduced using the initial partitioning ratios of **1** and **2** (Table I). The best fit to the experimental data (racemization of **1**(act), $(\mathbf{1}(\mathrm{rac}))/[(\mathbf{1}(\mathrm{rac})) + (\mathbf{1}(\mathrm{act}))]$, as a function of its conversion to **2** **3**, and **4**) was provided when k_2 was set equal to 0.5×10^{-5}/sec. Thus, initially, racemization of **1** occurred *via* **2** and a direct process (k_2) to about an equal extent, and the direct racemization of **1** occurred one-eighteenth as fast as it reacted. The calculated rate constant for direct racemization of **1** was not very sensitive (±15%) to variations in rate constants within the indicated experimental errors. Finally, although the maximum rotations and relative configurations of **1**, **3**, and **4** are presently unknown, because of the structural similarity of **1** and **3** and **4** and the dominating electronic effect of the double bond, the relative signs and magnitudes of the rotations strongly suggest that inversion at the remaining asymmetric center in **3** and **4** occurred to a significant extent during the thermolysis.[5]

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[1] For part I see J. J. Gajewski and C. N. Shih, *J. Am. Chem. Soc.*, **89**, 4532 (1967).

[2] This list is not exhaustive; please see references contained therein: (a) E. F. Ullman, *ibid.*, **82**, 505 (1960); (b) J. P. Chesick, *ibid.*, **85**, 2720 (1963); (c) P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967); (d) P. Dowd, A. Gold, and K. Sachder, *ibid.*, **90**, 2715 (1968).

[3] (a) F. Feist, *Chem. Ber.*, **26**, 750 (1893); (b) M. G. Ettlinger and F. Kennedy, *Chem. Ind.* (London), 891 (1957).

[4] (a) J. J. Gajewski, Abstracts, 155th National Meeting, American Chemical Society, San Francisco, Calif., April 1968, No. 28P; J. J. Gajewski and L. T. Burka, manuscript in preparation; (b) compounds **3** and **4** could be separated only by an efficient capillary column and not preparatively.

[5] For a discussion of the theory related to this conclusion see J. A. Schullman, *Accounts Chem. Res.*, **1**, 144 (1968); see also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., pp 401–412.