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## Photolytic Decomposition of Dihydrooxadiazinones

*Sir:*

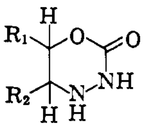
The oxadiazinones I–V form a group of closely related heterocycles which until 1956 were unknown. At that time we described the preparation of IVa ($R_1 = R_2 = C_6H_5$; $R_3 = H$) from benzoin and carbethoxyhydrazine and reportedi ts thermal decomposition to *cis*- and *trans*-stilbenes.[1] Subsequently the diphenyl derivatives Ia ($R_1 = R_2 = C_6H_5$, *trans*) and Va ($R_1 = R_2 = C_6H_5$) were synthesized and transformed by oxidation with lead tetraacetate through the thermally unstable intermediates IIIa and IIa ($R_1 = R_2 = C_6H_5$) to *trans*-stilbene and tolane, respectively.[2] At the same time a number of other dihydrooxadiazinones (IV), derived from cyclic and acyclic $\alpha$-ketols as well as from $\alpha$-diketones, were also prepared and characterized.[2]

We wish now to report that dihydrooxadiazinones (IV) undergo smooth photolytic decomposition affording products which largely parallel those obtained pyrolytically.[3] These data are summarized in Table I.

Table I

| Dihydrooxadiazinone | Decomposition products[a] | Yield, % Thermal | Photochemical | Tosylhydrazones[b] |
|---|---|---|---|---|
| IVa, $R_1 = R_2 = C_6H_5$; $R_3 = H$ | *cis*-Stilbene | 38[c] | 33 | |
| | *trans*-Stilbene | 32[c] | 9 | |
| IVb, $R_1 = R_2 = \text{-(CH}_2)_8\text{-}$; $R_3 = H$ | *cis*-Cyclodecene | 10 | 18 | 14 |
| | *trans*-Cyclodecene | <1 | | 6 |
| | *cis*-Bicyclo[5.3.0]decane | 55 | 44 | 62 |
| | *cis*-Decalin | <1 | | 18 |
| | *trans*-Decalin | 4 | <1 | |
| IVc, $R_1 = R_2 = \text{-(CH}_2)_7\text{-}$; $R_3 = H$ | *cis*-Cyclononene | 32 | 51 | 22 |
| | *trans*-Cyclononene | | 5 | |
| | *cis*-Hydrindan | 24 | 2 | 66 |
| | *cis*-Bicyclo[6.1.0]nonane | | | 10 |
| IVd, $R_1 = R_2 = \text{-(CH}_2)_6\text{-}$; $R_3 = H$ | *cis*-Cyclooctene | 75 | 65 | 45 |
| | *cis*-Bicyclo[3.3.0]octane | 7 | | 46 |
| | *cis*-Bicyclo[5.1.0]octane | | | 9 |
| IVe, $R_1 = CH_3$; $R_2 = R_3 = \text{-(CH}_2)_5\text{-}$ | Ethylidenecyclohexane | <1 | 75 | |
| IVf, $R_1 = R_2 = R_3 = CH_3$ | 3-Methyl-2-butene | <1 | 52 | |

[a] The identification of products was accomplished by glpc, ir, and nmr analyses. Comparison was made in all cases with authentic materials. The bicyclic compounds were prepared through Bamford–Stevens reactions on the corresponding ketones.[6] The medium-ring olefins were supplied by Dr. W. R. Moore, whose assistance is gratefully acknowledged. [b] L. Friedman and H. Shechter *J. Am. Chem. Soc.*, **83,** 3159 (1961); A. C. Cope, M. Brown, and G. L. Woo, *ibid.*, **87,** 3107 (1967). [c] M. Rosenblum, A. Longroy, M. Neveu, and C. Steel, *ibid.*, **87,** 5716 (1965).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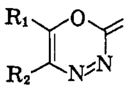
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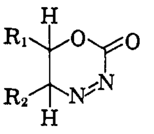
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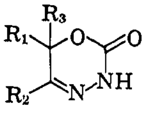
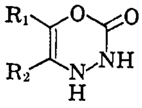

IV


V

The close similarity of products is particularly evident for those dihydrooxadiazinones derived from medium-ring $\alpha$-ketols which, in addition to olefinic products, yield bicyclic compounds through apparent transannular reactions. These results are in striking contrast to the behavior of dihydrooxadiazinones derived from 1-acetylcyclohexanol and 3-methyl-3-hydroxybutanone (IVe,f). Photolytic decomposition of these substances affords moderate yields of the expected olefins, but their thermal decomposition results principally in the formation of unidentified high-boiling materials and virtually no olefinic product.

The photolytic reactions of the dihydrooxadiazinones are more closely paralleled by their behavior under electron impact.[4] Decomposition of the molecular ion by the successive loss of $CO_2$ and $N_2$ is a common initial fragmentation path for all of the dihydrooxadiazinones examined and is a predominant process for IVe, IVf, and IVa in which structural factors may be expected to facilitate O–alkyl bond cleavage within the urethan function. By contrast, the loss of CO competes with the loss of $CO_2$ for those dihydrooxadiazinones (IVb–d) which are derived from secondary $\alpha$-ketols.

We had previously adduced evidence for a very similar

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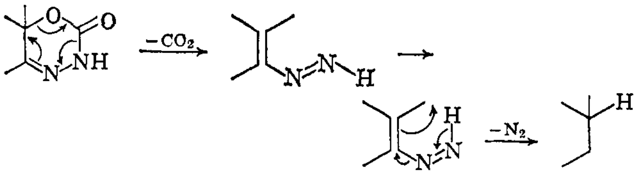
(1) M. Rosenblum and H. Moltzan, *Chem. Ind.* (London), 1480 (1956).

(2) M. Rosenblum, V. Nayak, S. K. DasGupta, and A. Longroy, *J. Am. Chem. Soc.*, **85,** 3874 (1963).

(3) Irradiation of ether solutions of IVa–f ($\lambda_{max}$ ~240 m$\mu$) were carried out in quartz vessels using Sylvania G8T5 gemicidal lamps. Solutions of IVa ($\lambda_{max}$ 282 m$\mu$) were irradiated with Rayonet R.P.R. 3000 Å lamps. Pyrolyses were conducted by subliming the compounds under high vacuum through a 8 mm × 30 cm tube packed with sand and heated to 400°. The pyrolysate was collected in a liquid nitrogen trap.

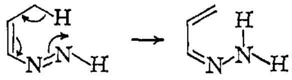
(4) Similar correspondence between photolytic reactions and the primary processes which occur in the mass spectrometer have been noted. For a discussion with leading references, see H. Budzikiewicz, C. Djerassi, and D. H. Williams Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 26.

successive loss of $CO_2$ and $N_2$ in the thermal decomposition of IVg, but the mode by which the intermediate vinyldiimide is transformed to olefin could not then be defined.[5] The present results suggest that in general this latter process proceeds largely if not exclusively through a carbene intermediate the formation of which may conveniently be pictured as taking place intramolecularly. This is evident from a comparison of the bicyclic products formed in either the photolysis or



the thermal decomposition of dihydrooxadiazinones derived from cyclic acyloins with those reported from decomposition of the related cycloalkanone tosylhydrazones[6] for which a carbene mechanism is well established.[7,8]

The failure of those dihydrooxadiazinones (IVe,f) derived from tertiary $\alpha$-ketols to follow this course of events may be due to isomerization of the intermediate vinyldiimide to an unsaturated hydrazone. Such a process, which is not available to vinyldiimides derived from the medium-ring derivatives, evidently is able



to compete successfully with *trans–cis* isomerization of the vinyldiimide which must precede its transformation to a carbene by intramolecular rearrangement. Thus the ratio $CO_2$:$N_2$ formed in the thermal decomposition of IVd is 1.5, while that from IVe is 6. By contrast, the vinyldiimide formed in the photochemical process must be capable of more rapid *trans–cis* isomerization, and in conformity with this conclusion we observed that the ratio $CO_2$:$N_2$ formed in the photochemical decomposition of IVd and IVe was 1.4 and 0.9, respectively.

The scope and mechanism of this photochemical process is currently being investigated.

**Acknowledgment.** This work was supported by Grant GP-5438 from the National Science Foundation.

[5] See Table I, footnote *c*.

[6] See Table I, footnote *b*.

[7] J. W. Powell and M. C. Whiting, *Tetrahedron*, 7, 305 (1959); L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

[8] It has recently been shown that, in the presence of bases stronger than alkoxide, aliphatic tosylhydrazones containing an $\alpha$ hydrogen are decomposed to olefins through the intermediacy of the vinyldiimide anion rather than through a carbene: W. Kirmse, B. von Bülow, and H. Schepp, *Ann.*, **691**, 41 (1966); M. Fischer, Z. Pelah, D. H. Williams, and C. Djerassi, *Ber.*, **98**, 3236 (1965); R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

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## Dialkyl Polyoxides

*Sir:*

Several recent reports have described the synthesis and decomposition of di-*t*-butyl trioxide,[1] di-*t*-butyl tetroxide,[2,3] and bis(perfluoroalkyl) trioxides.[4–6] We wish to report the results of a study of the interaction of alkylperoxy radicals at −95 to −140°. Our results indicate that although di-*t*-alkyl tetroxides and trioxides are stable at these temperatures, in agreement with the work on di-*t*-butyl polyoxides,[2,3] diisopropyl tetroxide decomposes too rapidly to be detected. Detailed product studies on di-*t*-butyl polyoxide decompositions are reported.

Alkylperoxy radicals were generated by photolysis of the corresponding azoalkanes in 1:2 $CFCl_3$–$CF_2Cl_2$ saturated with oxygen. Three tertiary alkylperoxy radicals and one secondary alkylperoxy radical were prepared in this way: *t*-butylperoxy, 2-cyano-2-methylpropylperoxy, 1-cyanocyclohexylperoxy, and 2-propylperoxy. At −95 to −120° all three *t*-alkylperoxy radicals formed stable polyoxides, as was confirmed by evolution of oxygen from the (dark) degassed solutions on warming to ∼−70° and then to 25°. Additional slow oxygen evolution was looked for and observed around −20° from solutions containing *t*-butyl polyoxides, indicating that initial oxygen evolution in these systems at −70° arises from decomposition of the corresponding tetroxides[2,7] and that the additional small amounts detected at 25° are from the corresponding trioxides.

$$2RO_2\cdot \rightleftarrows RO_4R \longrightarrow 2RO\cdot + O_2 \qquad (1)$$

$$RO\cdot + RO_2\cdot \rightleftarrows RO_3R \qquad (2)$$

No oxygen evolution was detected in any experiments in which 2,2′-azoisopropane was photolyzed, even at −140°. That isopropylperoxy radicals were indeed generated was demonstrated by the formation of about equal amounts of acetone and 2-propanol, products expected from the terminating interaction of these

$$2(CH_3)_2CHO_2\cdot \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH + O_2$$

radicals.[8] These experiments are summarized in Table I.

**Table I.** Detection of Dialkyl Tetroxides by Oxygen Evolution at −70° in $CFCl_3$

| Photolysis[a] temp, °C | Time, min | $R_2N_2$, R | $R_2N_2$,[b] μmole | $N_2$, μmole | $O_2$ evolved, μmole |
|---|---|---|---|---|---|
| −140 | 60 | *i*-Pr | 500 | 10 | 0 |
| −95 | 60 | $(Me)_2CCN$ | 420 | 28 | 6.2 |
| −95 | 90 | $C_6H_{10}CN$ | 300 | 18 | 8 |
| −120 | 1280 | *t*-Bu | 460 | 400 | 30 |

[a] Photolyses were carried out in Pyrex apparatus using unfiltered light from a PEK-201 200-W mercury lamp. [b] All concentrations are close to 0.1 *M*.

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[1] P. D. Bartlett and P. Gunther, *J. Amer. Chem. Soc.*, **88**, 3288 (1966).

[2] P. D. Bartlett and G. Guaraldi, *ibid.*, **89**, 4799 (1967).

[3] N. A. Milas, and B. Plesničar, Abstracts, Symposium on Chemistry of Organic Peroxides, Berlin-Aldershof, Sept 1967, p 68.

[4] L. R. Anderson and W. B. Fox, *J. Amer. Chem. Soc.*, **89**, 4313 (1967).

[5] P. G. Thompson, *ibid.*, **89**, 4316 (1967).

[6] V. A. Ginsburg, *et al.*, *Dokl. Akad. Nauk SSSR*, **149**, 97 (1963)

[7] We assume that the nature of the substituent R in the polyoxides does not significantly affect their stabilities; see S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 3922 (1964); S. W. Benson and R. Shaw, Preprints, International Oxidation Symposium, San Francisco, Calif., Aug 1967, p I-565.

[8] We assume that isopropylperoxy radical interactions give diisopropyl tetroxide rather than isopropyl hydroperoxide and isopropyl-