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SYNTHESIS AND PROPERTIES OF THE NOVEL 2-AZIDOOXIRANES

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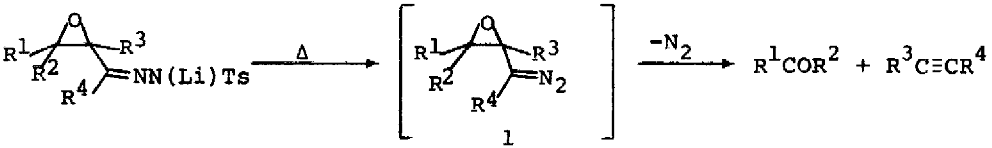
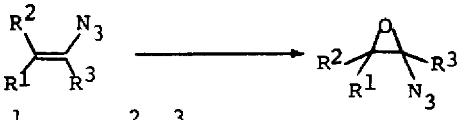
We wish to report the synthesis of the previously unknown 2-azidooxiranes (3). These species are isoelectronic with the 2-diazooxiranes (1), which are presumably intermediates in the Eschenmoser[1] cleavage of the tosylhydrazones of α,β-epoxyketones. The 2-azidooxiranes have been postulated[2] as intermediates in the formation of carbonyl compounds and nitriles in the epoxidation of vinyl azides, using m-chloroperbenzoic acid (MCPBA).



1

Treatment of vinyl azides 2[3] with MCPBA even in the presence of sodium bicarbonate[4] leads either to fragmentation (e.g., 2b gave pinacalone and hydrogen cyanide) or ring-opened materials (e.g., 2a gave 4a). On the other hand, treatment of 2a-c with N-benzoylperoxycarbamic acid (5)[5] led to essentially quantitative conversion to 3a-c.[6] Azide 2d, however, upon treatment with 5 even at -10°



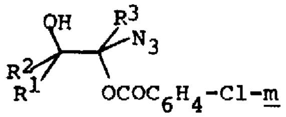
2a; R^1=t-Bu,R^2,R^3=H

b; R^1=t-Bu,R^2=Me,R^3=H

c; R^1,R^2=Ph,R^3=H

d; R^1=H,R^2,R^3=Ph

3



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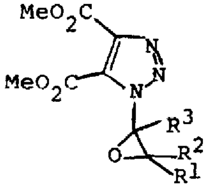
$PhCONHCO_3H$

5



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gave quantitative yields of benzaldehyde, benzonitrile and nitrogen, apparently as rapidly as epoxidation to **3d** occurred.

Although azidooxiranes **3a**-**c** are acid sensitive, they are relatively stable thermally, having half-lives on the order of two days in refluxing benzene. These thermal stabilities, however, are much lower than those of normal alkyl azides[7] and are quite similar to those of the known cyclopropyl azides.[8] The products of thermolysis of **3a**-**c** are the corresponding ketones (R^1R^2CO), nitriles (R^3CN), and nitrogen in high yields. However, the azido group in **3** undergoes normal 1,3-dipolar cycloadditions with dimethylacetylenedicarboxylate to give the oxiranotriazoles **6** in moderate yields.[5]

We are continuing to investigate the thermal and photochemical properties of this novel class of heterocycles.

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References

1. For a recent brief review see: E. J. Corey and H. S. Sachdev, *J. Org. Chem.*, **40**, 579 (1975).
2. E. Zbiral, *Synthesis*, 285 (1972).
3. The vinyl azides were available via procedures described by Hassner, or minor variations thereof; A. Hassner, *Acc. Chem. Res.*, **4**, 9 (1971), and references contained therein.
4. Use of sodium or potassium carbonate led to a neutralization of the peracid, and to the cessation of the epoxidation.
5. (a) V. E. Höft and S. Ganschow, *J. Prakt. Chem.*, **314**, 145 (1972); (b) J. Rebek S. F. Wolf, and A. B. Mossman, *J. Chem. Soc. Chem. Commun.*, 711 (1974).
6. The spectroscopic and analytical properties of these species were completely in accord with the structures indicated.
7. R. A. Abramovitch and E. P. Kyba in "The Chemistry of the Azido Group," S. Patai, Ed., Interscience Publishers, 1971, Chapter 6.
8. For representative examples see (a) A. B. Levy and A. Hassner, *J. Am. Chem. Soc.*, **93**, 2051 (1971); (b) G. Szeimies, U. Siefken and R. Rinck, *Angew. Chem. Int. Ed. Engl.*, **12**, 161 (1973).