Mechanism of the Wolff Rearrangement of α-Diazohomoadamantanone: Evidence Against Oxiren Participation

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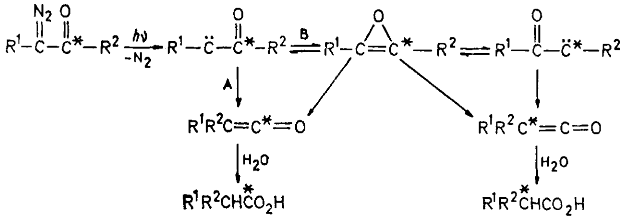
Summary Photolysis of 5-diazo[5-^{14}C]homoadamantan-4-one in aqueous tetrahydrofuran leads to adamantane 2-carboxylic acid with only 0·9% of the label in the carboxylic group indicating that oxiren participation is insignificant in the Wolff rearrangement of this polycyclic system.

THE mechanism of the photochemical Wolff rearrangement of α-diazo-ketones is still ambiguous.[1-7] Franzen[2] and Huggett *et al.*[3] suggested formation of a carbene intermediate by loss of nitrogen followed by migration of the group next to the carbonyl to give the corresponding keten and the carboxylic acid. Consequently, the same carbon atom should be attached to the oxygen in both the carboxylic acid and the starting diazo-ketone (Scheme 1, path A).



SCHEME 1

This was demonstrated for $PhCOCN_2Ph$.[2] Kaplan and Meloy[4] suggested that the formation of the keten occurs by synchronous loss of nitrogen and migration of the R^2 group.[‡] However, Strausz *et al.* have shown the importance of the oxiren pathway (Scheme 1, path B) in the Wolff rearrangement of 3-diazobutan-2-one, 3-diazopropan-2-one, and alkyl diazoacetates in the gas phase[6] as well as of 3-diazobutan-2-one in solution.[7] Moreover, they repeated Franzen's experiments and found, contrary to the earlier results,[2] 46% oxiren participation in the Wolff rearrangement of [^{13}C]$PhCOCN_2Ph$ in dioxan–water.[7]

These results prompted us to call attention to the photochemical Wolff rearrangement of 5-diazo[5-^{14}C]homoadamantan-4-one (**1**)[8][§] in 75% aqueous tetrahydrofuran.[8] Two possible reaction pathways are shown in Scheme 2. Adamantane 2-carboxylic acid (**3**)[‡][¶], formed from (**1**), was diluted with unlabelled material to a specific activity of 0·775(5) nCi/mg C[**] and degraded using the Schmidt reaction.[10] We were unable to isolate the amine, but the CO_2 obtained was almost inactive [0·0748(54) nCi/mg C].[**]

The symmetric oxiren intermediate (**2**) (path B) should give adamantane 2-carboxylic acid (**3b**) with 50% of the label at the position 2 and 50% in the carboxylic group. Since all the activity in (**1**) arose from one carbon atom the specific activity of this carbon was: 0·775 × 11 = 8·525 nCi/mg C. Therefore, the activity found in the CO_2 (and

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[‡] Mechanisms have been suggested which involve nucleophilic attack prior to rearrangement.[5]

[§] Satisfactory analysis and spectral data were obtained for all new compounds.

[¶] The product was identical with an authentic sample and after recrystallization from $MeOH-H_2O$ was $\geqslant$ 98% pure by g.l.c. m.p. 142—143°.[9]

[**] The activities were determined by a gas counting [(**3**) was combusted to CO_2]; the uncertainties are standard errors of at least 4 determinations.

the carboxylic group) corresponds to less than 1·8% of oxiren participation and 0·9% of the label in (**1**), respectively.

Although oxiren participation may be important in the Wolff rearrangement of open chain α-diazo-ketones such participation appears to be insignificant in a strained, polycyclic system like (**1**). The oxiren intermediate (**2**) in the last case would be too strained and the direct rearrangement into the adamantane derivative should be the preferred reaction pathway (path A).

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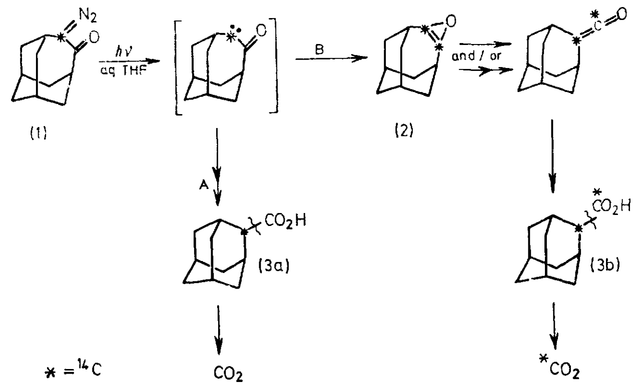

Scheme 2

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[1] W. Kirmse, 'Carbene Chemistry,' Academic Press, New York, 1964, pp. 123—127; R. Huisgen, G. Binsch, and L. Ghosez, *Chem. Ber.*, 1964, **97**, 2628; A. Melzer and E. F. Jenny, *Tetrahedron Letters*, 1968, 4503; W. Jugelt and D. Schmidt, *Tetrahedron*, 1969, **25**, 969; D. C. Richardson, M. E. Hendrick, and M. Jones, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 3790, refs. therein.

[2] V. Franzen, *Annalen*, 1958, **614**, 31.

[3] C. Huggett, R. T. Arnold, and T. I. Taylor, *J. Amer. Chem. Soc.*, 1942, **64**, 3043.

[4] F. Kaplan and G. K. Meloy, *J. Amer. Chem. Soc.*, 1966, **88**, 950.

[5] B. Eistert, *Ber.*, 1935, **68**, 208, A. L. Wilds, N. F. Woolsey, J. Van Den Berghe, and C. H. Winestock, *Tetrahedron Letters*, 1965, 4841.

[6] I. G. Csizmadia, J. Font, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1968, **90**, 7360; D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *ibid.*, 1970, **92**, 1768.

[7] G. Frater and O. P. Strausz, *J. Amer. Chem. Soc.*, 1970, **92**, 6654.

[8] Z. Majerski, A. P. Wolf, and P. v. R. Schleyer, *J. Labelled Compounds*, 1970, **6**, 179.

[9] H. Stetter, H. Held, and J. Mayer, *Annalen*, 1962, **658**, 151.

[10] A. P. Wolf, C. S. Redvanly, and R. C. Anderson, *J. Amer. Chem. Soc.*, 1957, **79**, 3717.