Photolysis of 2-Diazo[1-^{13}C]naphthalen-1(2*H*)-one

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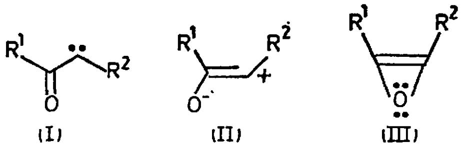
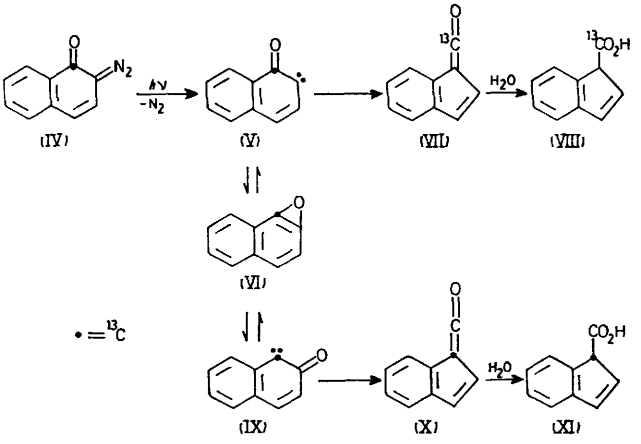
Summary Oxiren participation in the Wolff rearrangement of 2-diazo[1-^{13}C]naphthalen-1(2*H*)-one (IV) is investigated; photolysis of (IV) yields indene-1-carboxylic acid containing all the label in the carboxy-group, excluding intermediate formation of an oxiren.

In addition to α-oxocarbenes (I) and 1,3-dipoles (II) the potentially antiaromatic oxirens (III) have been discussed as intermediates in the Wolff rearrangement of α-diazoketones.[1] The isomerisation of α-oxocarbenes (I) to oxirens (III) has been demonstrated in the photolysis of aliphatic[2,3] and aromatic[2,4] substituted, open-chain α-diazoketones.[5] Here the possible participation of oxirens in the photolysis of cyclic *o*-quinone diazides is investigated.



(I) (II) (III)

2-Diazo[1-^{13}C]naphthalen-1(2*H*)-one (IV; 59% ^{13}C-enrichment) was synthesized as follows. $Ph(CH_2)_3MgBr$ and $^{13}CO_2$ (from $Ba^{13}CO_3$) gave $Ph(CH_2)_3{}^{13}CO_2H$, cyclization of which with $AlCl_3$ gave [1-^{13}C]dihydronaphthalen-1(2*H*)-one. Dehydrogenation (Pd; 200 °C), nitration (diacetyl-*o*-nitric acid),[6] reduction ($S_2O_4{}^{2-}$, OH^-; then HCl), followed by diazotisation of the amine hydrochloride formed gave (IV) in 8% overall yield.



The photolysis of 5 mm solutions of (IV) in dioxan–water (10:1) with Pyrex-filtered light from a 450 W medium-pressure mercury lamp or the 254 nm emission from a lowpressure mercury lamp yielded indene-1-carboxylic acid containing all the label in the carboxy-group, as shown by ^{13}C n.m.r. spectroscopy and thermal decarboxylation followed by mass spectrometric analysis of the ^{13}C-content of the indene and CO_2 formed.

This result shows that isomerisation of the α-oxocarbene (V) formed by N_2 elimination to the α-oxocarbene (IX) does not take place. Either (V) resists ring closure to the oxirene (VI) or (VI) is formed but reopens exclusively to (V) without formation of the isomeric (IX). The latter is only understandable if the two α-oxocarbenes were substantially different in energy. Alternatively, (VII) may be formed directly *via* Wolff rearrangement of the quinone diazide (IV) by concerted N_2 expulsion and ring contraction.

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[1] Review: H. Meier and K.-P. Zeller, *Angew. Chem.*, 1975, **87**, 52.

[2] J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1973, **95**, 124.

[3] S. A. Matlin and P. G. Sammes, *J.C.S. Perkin I*, 1972, 2623.

[4] K.-P. Zeller, H. Meier, H. Kolshorn, and E. Müller, *Chem. Ber.*, 1972, **105**, 1875.

[5] Oxiren participation was not found in the photolysis of α-diazo-homoadamantanone: Z. Majerski and C. S. Redvanly, *J.C.S. Chem. Comm.*, 1972, 694.

[6] A. V. Topchiev, 'Nitration of Hydrocarbons and other Organic Compounds,' Pergamon, London, 1959, p. 298.