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EXPERIMENTAL TEST OF AN ALTERNATIVE HYPOTHESIS FOR ISOTOPE-POSITION SCRAMBLING IN THE PHOTOCHEMICAL WOLFF REARRANGEMENT OF AZIBENZIL

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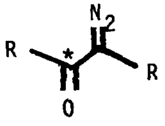
Photolysis of azibenzil-^{13}CO in methanol gives partially scrambled methyl diphenylacetate and unscrambled recovered azibenzil.

The photochemical (and occasionally, the thermal) Wolff rearrangement of an appropriately labeled α-diazoketone (1) gives a ketene (2) (or a product derived from a ketene) in which part of the label is at C-1 and part at C-2. This scrambling has been attributed to reversible formation of an oxirene intermediate (3), either from the α-ketocarbene (4) or directly during deazetation of 1[1,2]. A further position-marking experiment that implicates an oxirene intermediate is the observation[3] that gas-phase photolysis of ^{14}CH$_2$=C=O gives some ^{14}CO. Moreover, an *ab initio* SCF MO calculation using a double zeta basis set shows that oxirene (3, R=H) is protected by a barrier of 7.3 kcal/mole from rearrangement to formylcarbene (4, R=H)[4], which suggests that oxirene should suffer thermal decomposition only slowly ($t_{1/2}$ ∿ 20 min.), even at temperatures as high as 100K. It is therefore remarkable that the literature does not contain any direct spectroscopic observations of oxirenes, despite efforts in several laboratories to create such species at cryogenic temperatures in matrix isolation.



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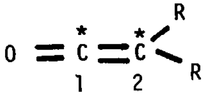

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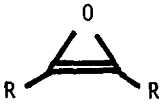

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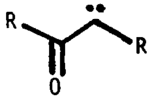

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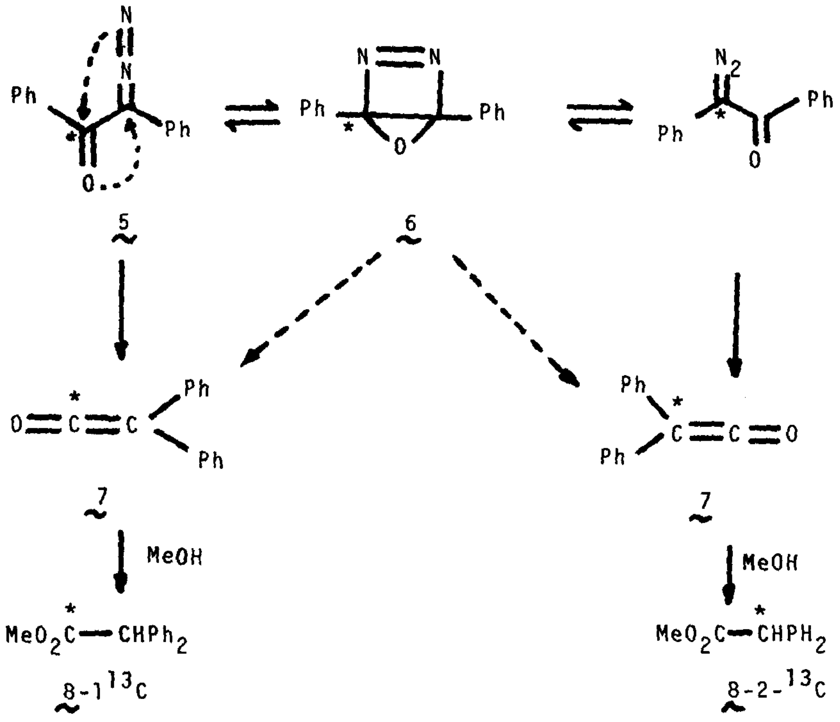
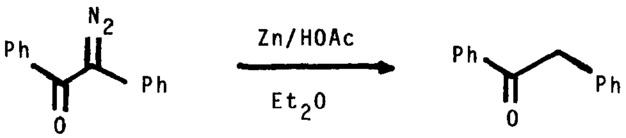
The present paper reports a test of an alternative hypothesis for position-scrambling in the product of photolysis of an α-diazoketone, azibenzil (5)[5]. Structural equivalence of the carbonyl and diazo carbons might be achieved by formation of the bicyclic intermediate (6), which could be imagined to result from an intramolecular 1,3-dipolar addition of the diazoalkane function to the carbonyl group (Scheme I). This species might produce diphenylketene without passing through oxirene. If irreversible formation of 6 were competitive with direct deazetation of 5, the labeling experiment would not distinguish this mechanism from one involving diphenyloxirene, However, if the reaction **5** $\rightleftharpoons$ **6** were *reversible*, partially scrambled *starting material* would be formed.

Scheme I



Azibenzil-^{13}CO[6], 15% isotopically enriched, was thermally decomposed in boiling methanol to give specifically labeled methyl diphenylacetate-1-^{13}C(**8**). The location of the label was determined with the Hewlett-Packard Model 5985 system by chemical ionization mass spectrometric observation of the intensities of the $(C_6H_5)_2CH^+$(167) and $(C_6H_5)_2{}^{13}CH^+$(168) fragment ions compared to those of unlabeled compound **8**. This result agrees with the previous report[6] that little or no scrambling occurs in the thermal Wolff rearrangement of azibenzil at 65°.

Photolysis of azibenzil-^{13}C, 90% enriched, in methanol solution was effected by irradiation at 2537Å. The course of the reaction was monitored by UV spectrophotometry of the azibenzil (ε_{3150}=6200). Aliquots of the reaction mixture consisting of methyl diphenylacetate and recovered azibenzil were concentrated and treated in ether solution with zinc and acetic acid to convert the azibenzil to desoxybenzoin (**9**). The resulting mixture of **8** and **9** was analyzed by gas chromatography-CI-MS using a 2% Carbowax 20M column. The overall ^{13}C content of product 8, as measured by the relative intensities of the MS peaks of m/e 227 and 228, was 90%, corresponding to that of the starting material. The location of the label, determined as before, showed extensive scrambling in the Wolff rearrangement product, 8. It was easy to obtain misleading values for the amount of scrambling unless the temperature was carefully controlled during photolysis, because any thermal decomposition would lead to unscrambled 8. This artifact manifested itself as a steady growth in the observed percent of scrambling with larger % conversions in runs at 35° or even at 15-20°C. Apparently, at low conversions, the product was made up of a larger fraction of thermally derived, unscrambled material. When the photolysis was carried out at 5-10°, however, the % scrambling was invariant with % conversion: conversions of 6.6, 22, 31, 47, and 60% gave, respectively, scramblings [2(%8-2-^{13}C)] of 36.2, 41.9, 39.1, 41.0, and 43.2%. The experimental error in the % scramblings was estimated to be ±4% absolute.



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The distribution of the label in the desoxybenzoin (9), corresponding to that in recovered starting material (5), was determined from the intensities of the m/e $C_6H_5CH^+$(90) and $C_6H_5{}^{13}CH^+$(91) fragment ion peaks. Control experiments showed that desoxybenzoin-90%-^{13}CO gave a mass spectrum indicative of 8% scrambling of the label. That this scrambling probably occurred in the mass spectrometer was suggested by the observation that the scrambling of desoxybenzoin-90%-^{13}CO-70%-α-$\underline{d}_2$ was only 4%. The isotope effect $k_H/k_D \cong 2.8$ for the scrambling.

Analysis of the desoxybenzoin samples derived from azibenzil-^{13}C recovered from photolysis showed only 8% scrambling of the label, essentially all of which was accounted for by the mass spectral scrambling just described. Thus, no additional chemical scrambling of azibenzil occurred during photolysis.

We conclude that any actual or time-averaged symmetrical species (including but not limited to 6) that is formed in the photolysis of 5 (Scheme I) does not revert to 5 at a rate competitive with its rearrangement to diphenyl ketene 7. An oxirene (3, R=Ph) therefore remains the most economical explanation for the observed scrambling of the label in the photolysis of 5[7].

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References and Notes

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(5) For a previous discussion, see J. A. Berson in "Rearrangements in Ground and Excited States," P. de Mayo, ed., Academic Press, New York, 1980, Vol. I, p. 311.

(6) J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Am. Chem. Soc*., **95**, 124 (1973).

(7) H. Tomioka, H. Okuno, S. Kondo, and Y. Izawa, *J. Am. Chem. Soc*., **102**, 7123 (1980) recently have obtained experimental results which they state "clearly eliminate...the precursor diazoketone as a possible intermediate for oxygen migration." It should be pointed out that the scrambling mechanism in Scheme I of the present paper is not excluded by their evidence.

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