

## Photoaddition of Ketones to Imidazoles: Synthesis of Oxetanes

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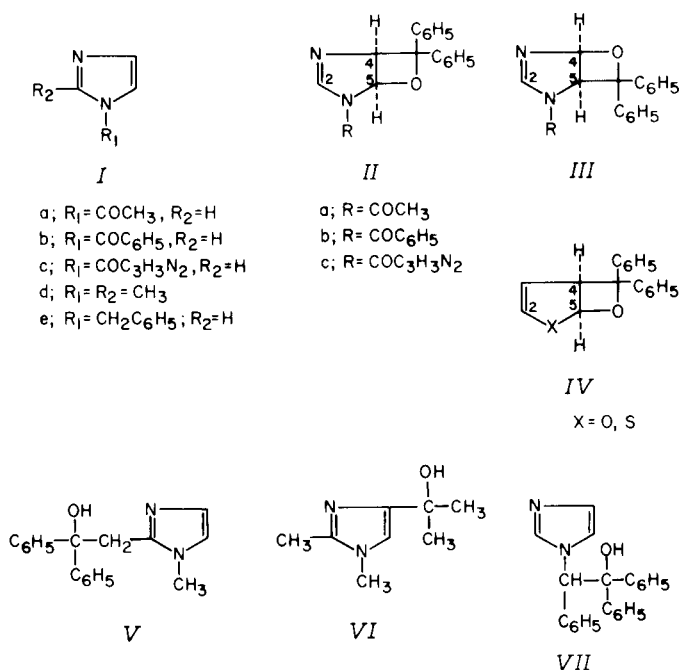
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Received September 15, 1975

Sir:

In spite of increasing interest (1) in the photocycloaddition reactions of ketones to heteroaromatic systems, the synthesis of the oxetanes of imidazoles (2) has not hitherto been achieved. One of us (3) has previously reported the photoaddition of benzophenone to 1-benzoylpyrrole yielding an oxetane, in which it was demonstrated that an electron-withdrawing protecting group on nitrogen is essential (4). We now report the first example of the synthesis of the oxetanes with the imidazole nucleus.

Irradiations (5) of 1-acetyl (Ia), 1-benzoylimidazole (Ib), and 1,1'-carbonyldiimidazole (Ic) in the presence of benzophenone in benzene yielded the oxetanes IIa, m.p. 75-80° (yield, 50%; pmr (acetone-d<sub>6</sub>): δ 2.31 (s, 3, 1-CH<sub>3</sub>CO), 5.68 (q, 1, J<sub>4,5</sub> = 4.5 Hz, J<sub>4,2</sub> = 1.5 Hz, 4-H), 6.63 (d, 1, J<sub>5,4</sub> = 4.5 Hz, 5-H), 7.18-7.90 ppm (m, 10, benzenoid protons), and 7.98 (d, 1, J<sub>2,4</sub> = 1.5 Hz, 2-H); mass spectrum (70 eV): m/e 292 (M<sup>+</sup>) (6); IIb, m.p. 138-140° (yield, 34%); pmr (chloroform-d<sub>1</sub>): δ 5.83 (q, 1, J<sub>4,5</sub> = 4.5 Hz, J<sub>4,2</sub> = 1.0 Hz, 4-H), 6.46 (d, 1, J<sub>5,4</sub> = 4.5 Hz, 5-H), 7.40-8.25 (m, 15, benzenoid protons), and 8.30 ppm (d, 1, J<sub>2,4</sub> = 1.0 Hz, 2-H); mass spectrum: (70 eV) m/e 354 (M<sup>+</sup>); and IIc, m.p. 265-268° (yield, 51%); pmr (chloroform-d<sub>1</sub>) δ 5.78 (q, 1, J<sub>4,5</sub> = 4.5 Hz, J<sub>4,2</sub> = 1.5 Hz, 4-H), 6.71 (d, 1, J<sub>5,4</sub> = 4.5 Hz, 5-H), 7.32-7.99 (m, 13, benzenoid protons and 2', 4', and 5'-H), and 8.05 ppm (d, 1, J<sub>2,4</sub> = 1.5 Hz, 2-H); mass spectrum (70 eV): m/e 344 (M<sup>+</sup>), respectively. The alternative structures III for the oxetanes were excluded from the following pmr evidence. We have previously noted (7) that in the case of the oxetanes IV from furans and thiophenes, the proton at C-2 couples with the proton at C-4 with J ~ 1.2 Hz (allylic coupling), but does not couple to an appreciable degree with the proton at C-5 ('W' path coupling). In the pmr spectra of the oxetanes IIa, IIb, and IIc from the imidazoles, the proton at C-4 appears as a quartet, due to the coupling with both protons at C-5 and C-2 (8). On the other hand, the proton at C-5, which resonates at lower field than the proton at C-4 due to the proximity to both the nitrogen and oxygen atoms, couples only with the proton at C-4, thus occurring as a doublet. If the oxetanes were postulated to have structures III, then the proton at C-4, which would resonate at lower field, would appear as a quartet.



In the case of 1,2-dimethylimidazole and 1-benzylimidazole, no oxetane formation was observed but a hydroxyalkyl or hydroxyphenyl derivative was obtained. Irradiation of 1,2-dimethylimidazole (Ic) with benzophenone and with acetone gave the alcohols V, m.p. 187-188° (yield, 4%); pmr (chloroform-d<sub>1</sub>): δ 3.33 (s, 3, 1-CH<sub>3</sub>), 3.53 (s, 2, 2-CH<sub>2</sub>), 6.66 (d, 1, J<sub>4,5</sub> = 1.2 Hz, 4(5)-H), 6.88 (d, 1, J<sub>5,4</sub> = 1.2 Hz, 5(4)-H), and 7.30 ppm (m, 10, benzenoid protons); mass spectrum (70 eV): m/e 278 (M<sup>+</sup>); and VI, m.p. 95-96° (yield, 30%) (9); pmr (chloroform-d<sub>1</sub>): δ 1.53 (s, 6, 3-C(CH<sub>3</sub>)<sub>2</sub>), 2.33 (s, 3, 2-CH<sub>3</sub>), 3.50 (s, 3, 1-CH<sub>3</sub>), and 6.63 ppm (s, 1, 5-H); mass spectrum (70 eV): m/e 154 (M<sup>+</sup>), respectively. 1-Benzylimidazole (Ie), on irradiation with benzophenone in *t*-butyl alcohol, yielded the alcohol VII, m.p. 220-221° (yield, 20%); pmr (chloroform-d<sub>1</sub>): δ 6.31 (s, 1, 1-CHC<sub>6</sub>H<sub>5</sub>), 6.98 (t, 1, 4(5)-H), 7.20 (t, 1, 5(4)-H), 7.45 (m, 15, benzenoid protons), and 7.73 ppm (t, 1, 2-H); mass spectrum (70 eV): m/e 340 (M<sup>+</sup>) (10). A full account of this paper and its related work will be published in the future.

## Acknowledgement.

We would like to thank Mrs. M. Cerhalmi de Hazos for the pmr and mass spectra.

## REFERENCES AND NOTES

- (1) G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963); D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968); C. Rivas, M. Velez, and O. Crescente, *Chem. Commun.*, 1474 (1970); C. Rivas and E. Payo, *J. Org. Chem.*, **32**, 2918 (1967); M. Ogata, H. Watanabe, and H. Kano, *Tetrahedron Letters*, 533 (1967); G. R. Evanega and E. B. Whipple, *ibid.*, 2163 (1967); E. B. Whipple and G. R. Evanega, *Tetrahedron*, **24**, 1299 (1968); D. R. Julian and G. D. Tringham, *J. Chem. Soc., Chem. Commun.*, 13 (1973).
- (2) Attempts to synthesize the oxetanes of the imidazoles have been made but without success. See T. Matuura, A. Banba, and K. Ogura, *Tetrahedron*, **27**, 1211 (1971).
- (3) C. Rivas, M. Velez, M. Cucarella, R. A. Bolivar, and S. E. Flores, *Acta Cient. Venez.*, **22**, 145 (1971).
- (4) The failure of preparing an oxetane of pyrrole itself may be due to greater electron density in the heterocyclic  $\pi$ -system or a quenching effect on the excited ketone by the non-bonded electrons on the nitrogen atom [S. G. Cohen and A. D. Litt, *Tetrahedron Letters*, 837 (1970)]. This situation may be overcome by protecting the NH group in its molecule with an electron-withdrawing group, such as acetyl, benzoyl, etc.
- (5) All irradiations were carried out using a 450 W medium pressure mercury vapor lamp with a Pyrex filter.
- (6) The mass spectrometric fragmentation patterns of all these products will be reported in a full paper.
- (7) T. Nakano, C. Rivas, C. Perez, and K. Tori, *J. Chem. Soc., Perkin Trans. 1*, 2322 (1973).
- (8) That the proton at C-4 was in coupling with the proton at C-2 was confirmed by decoupling experiments.
- (9) The alcohol VI may be formed by a mechanism either involving an oxetane intermediate, such as II, followed by the subsequent opening of the oxetane ring, or involving the attack of a ketyl radical, which may be formed by hydrogen abstraction from the  $n, \pi^*$  triplet of acetone. This will be discussed in a full paper after the unambiguous assignment (C-4 or C-5) of the position of a hydroxyisopropyl group in the alcohol VI has been made on the basis of the cmr spectrum. In this irradiation, there was also obtained another alcohol, presumably derived from the coupling of two molecules of 1,2-dimethylimidazole. The structure of this alcohol is now being studied and will be published in a full paper.
- (10) Satisfactory analytical data (CHN) were obtained for all compounds reported.