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Bicyclic Heterocycles and Hetero-ylides. Addition Reactions of Cyclopentadienylidenemethylene to Pyridines and Thiophens†

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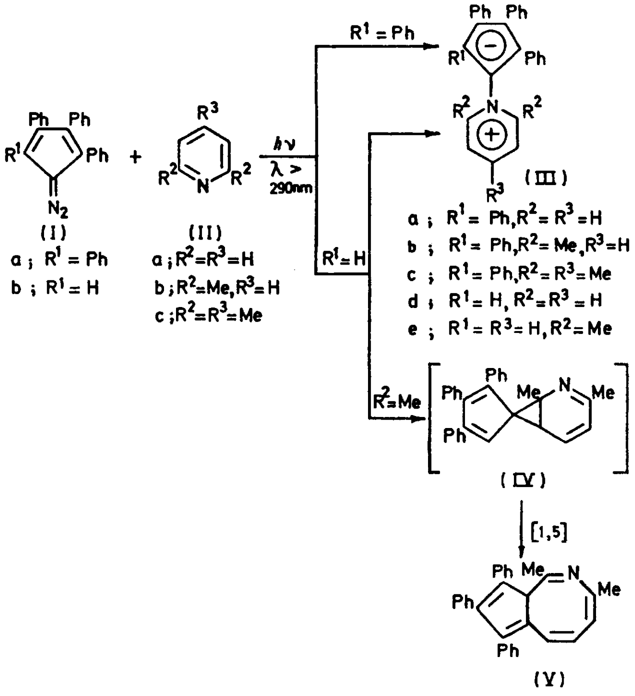
Summary Irradiation of substituted diazo-cyclopentadienes in pyridines or thiophens gives bicyclic hetero-compounds formed by thermal or photochemical rearrangements, in addition to the main hetero-ylide products.

Cycloadditions of cycloalkene-carbenes, generated photochemically from corresponding diazo-cyclopentadienes (I), to benzene and its derivatives lead to benzo-cycloheptatrienes[1] or homoazulenes,[2] and, with care, the intermediates [*e.g.*, the spiro-norcaradienes (IV)], can be isolated.[3] We report now on the addition of substituted cyclopentadienylidenes (I) to pyridine, thiophen, and their derivatives.

The investigations are of interest because: (i) The reactions with pyridines predominantly yield the pyridinium cyclopentadienides (III), some of which can be prepared only photochemically by this reaction path. (ii) A second route leads to bicyclic heterocycles (V) and (VIII) and provides a potentially general synthesis of the latter.



The tetraphenyl- (Ia) and triphenyl-diazocyclopentadiene (Ib) were irradiated under nitrogen in the pyridines (IIa—c) with a high-pressure mercury lamp through a Pyrex filter. Recrystallization afforded the pyridinium-cyclopentadienides (IIIa—e) [a, 80% yield; b, 81% (+6% unidentified 1:1 adduct); c, 39%; d, 17%; e, 48%].§ (IIId) has not been obtained thermally from (Ib) and

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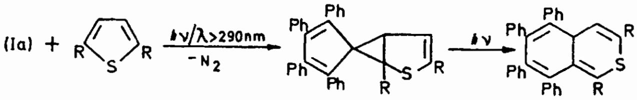
† For previous paper in series Cyclo-alkene-carbenes see: H. Dürr and H. Koher, *Allg. prakt. Chem.*, **1972**, **23**, 73.

‡ Chemische Werke Hüls. Marl.

§ Satisfactory analytical data were obtained for all new compounds.

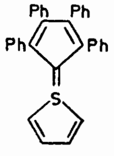
pyridine,[4] whereas (IIIa) and (IIIb) have been obtained thermally from the same precursors as in our work. Spectroscopic data for (IIIa—e) agree well with literature data.[4–6] These ylides are formed by electrophilic attack of a carbene on the nucleophilic pyridine nitrogen.



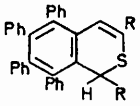
(VI)
a; R = Me
b; R = H

(VII)

(VIII)



(IX)



(X)

Irradiation of (Ib) in (IIb) afforded, after chromatography on silica gel, the bicyclic aza-pentaene (V) (26%) in addition to (IIIe). Structure (V) was assigned mainly on the basis of its n.m.r. spectrum, which is in good agreement with that of the carbocyclic system.[2] (V) is formed by [1 + 2]-cycloaddition of carbene resulting from (Ib) to (IIb) giving (IV), which then rearranges by a thermal sigmatropic [1,5]-shift to (V).[3]

Irradiation of (Ia) (same conditions as above) in 2,5-dimethylthiophen (VIa) gave, after recrystallisation, the bicyclic thiatetraene (VIIIa) (30%). The cycloaddition product (VII) was also isolated (1·5%). (VIIIa) was identified mainly by its n.m.r. spectrum, and also its i.r., u.v. and mass spectrum. Structure (VIIa) was clearly established by ^{13}C n.m.r. spectroscopy.

Catalytic hydrogenation of (VIII) as well as bromination were unsuccessful. However thermolysis gave the aromatised product (X) which gave satisfactory analytical data.[7]

(VIIIa) is formed by a photochemical (di-π-methane) rearrangement of the primary [1 + 2]-cycloaddition product (VIIa) analogous to the formation and rearrangement of (IV) to (V). Reaction of (Ia) with thiophen (VIb) affords in addition to (VIIb), the ylide, (IX).

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[5] D. Lloyd, J. S. Sneezum, and I. B. M. Band, *Tetrahedron*, 1958, 334.

[6] D. Lloyd, M. I. C. Singer, and F. J. Wasson, *Chem. Comm.*, 1966, 544.

[7] A. Ohno, T. Koizumi, and Y. Onishi, *Bull. Chem. Soc. Japan*, 1971, **44**, 2511, have prepared similar compounds.