Reaction of Aryl Substituted Cyclopentadiene Carbenes with Norbornadiene†

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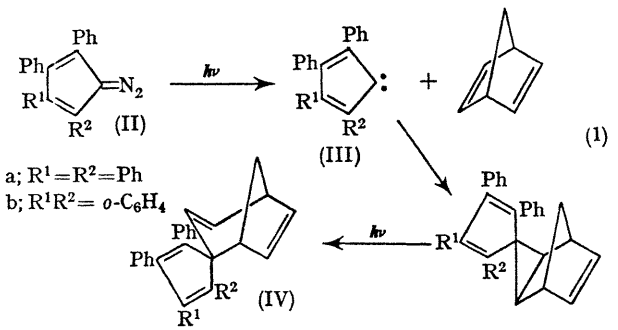
PHOTOLYSIS of diazofluorene (I) in the presence of norbornadiene has been reported to give a pyrazoline; photolysis of this then gave a cyclopropane addition compound. These results differ from our observations on photolysis of the pentadienes (IIa)[2] and (IIb) in norbornadiene (high-pressure Philips 125 w, HPK mercury lamp, pyrex filter, 45—90 min.) where the spiro-compounds (IVa) and (IVb) were formed directly. The intermediate carbene (III) adds to norbornadiene [Equation (I)]:



After work up (fractional recrystallisation or chromatography on silica gel) (IVa) [16%; m.p. 178—180°; i.r.: 1625 (C=C), 3040 (Ar C–H), 1600, 1480, and 1440 cm.$^{-1}$ (ArC=C); n.m.r.: τ 2·70 and 2·96 (20H), 3·63 (3-H, J 10 c./sec.), 4·06 (m, 2-H), 4·44 (m, 6-H, 7-H), 7·69 (q, 1-H, 5-H), and 8·18 (q, 8-H_2)] or (IVb) [12%, m.p. 129—131°; i.r.: 1620 (C=C), 3040 (Ar C–H), and 1600, 1480, and 1440 cm.$^{-1}$ (Ar C=C) n.m.r.: τ 1·97 (1H); 2·60 and 2·68 (13H), 3·95 (m, 2-H) 4·19 (d, 13-H, J 8 c./sec.) 4·37 (m, 6-H, 7-H), 7·33 (m, 1-H, 5-H), and 8·09 (q, 8-H_2)] was obtained. The photolysis of 5-diazo-1,2,3-triphenylcyclopentadiene did not give compound (IV): hydrogenation of (IVa) led to a complex mixture of products. The direct formation of (IV) is due to the low tendency of (IIa) or (IIb) compared with (I)‡ to form pyrazolines by 1,3-dipolar addition. We therefore believe that the photolysis of (IIa or b) proceeds *via* the carbene (III).

Such a compound could be obtained from (I) only by a thermal reaction.[1]

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† Part of the series, "Photochemistry of small rings". For previous part see: H. Dürr und L. Schrader, *Chem. Ber.*, in the press.
‡ No 1,3-dipolar addition product is formed on leaving (IIa) and norbornadiene at room temporature for several days.

[1] N. Filipescu and J. R. DeMember, *Tetrahedron*, 1968, **24**, 5181.
[2] G. Scheppers, Thesis, Universität Saarbrücoken, 1968.