

PHOTOCHEMICAL CYCLOADDITION OF BENZOPHENONE TO FURANS

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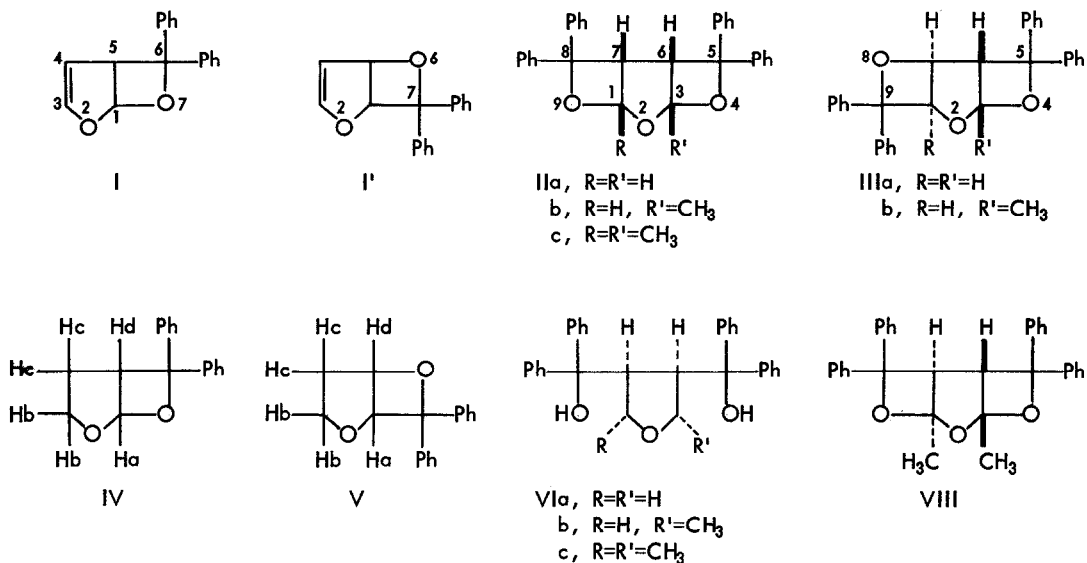
In 1963, Schenck et al. (1) reported that irradiation of benzophenone in furan gave a 1 : 1 adduct, to which they assigned the structure 6,6-diphenyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (I) in preference of the isomeric 2,6-dioxa derivative (I') in view of the acid-sensitive character of its dihydro derivative (IV). This structure assignment was confirmed by Gagnaire et al. on the basis of the n.m.r. analysis (2).

We now wish to report the formation of 2:1 adducts of benzophenone and furans under a similar irradiation.

In our experiments, a 1% benzene solution of benzophenone and furan or its derivative (mole ratio: 1 : 1) was irradiated through pyrex glass with a 450 watt high pressure mercury arc lamp (Ushio: UM-452) in an argon atmosphere at room temperature. This procedure with furan resulted in the formation of two 2 : 1 adducts (IIa), m.p. 210-217° (dec.) in 26.7% yield* and (IIIa), m.p. 191-194° in 18.2% yield.* The same products were obtained in nearly the same yield upon irradiation of benzophenone and I in benzene solution. The n.m.r. spectrum of IIa shows aliphatic proton signals at τ 4.06 (2H, doublet, $J=4$ cps) and 6.30 (2H, doublet, $J=4$ cps) while that of IIIa shows aliphatic proton signals at τ 4.08 (1H, doublet, $J=4$ cps), 4.69 (1H, doublet, $J=4$ cps), 5.02 (1H, doublet, $J=4$ cps) and 5.73 (1H, doublet, $J=4$ cps).

The spectral data obtained show that IIa has a symmetrical structure with two pairs of equivalent hydrogens and IIIa has an asymmetrical one with four different hydrogens. The n.m.r. spectrum of IV consists of aliphatic proton signals at τ 3.99 (Ha, doublet, $J=4$ cps), 5.8-6.5 (2Hb, and Hd, multiplet), 8.0-8.4 (2Hc, multiplet). The isomer of IV, 7,7-diphenyl-2,6-dioxabicyclo[3.2.0]heptane (V), m.p. 140-141.5°, was prepared by irradiation of 2,3-dihydrofuran and benzophenone in benzene solution. The n.m.r. spectrum of V was consistent

* Yield of products based on benzophenone consumed.



with the expected structure showing proton signals at τ 2.4–2.9 (10 aromatic protons, multiplet), 4.57 (Hd, triplet, $J=4$ cps), 4.92 (Ha, doublet, $J=4$ cps), 5.9–6.7 (2Hb, multiplet) and 7.7–8.7 (2Hc, multiplet).

By comparison of n.m.r. spectra between IIa, IIIa, IV and V, the structures 5,5,8,8-tetraphenyl-2,4,9-trioxatricyclo[5.2.0.0^{3,6}]nonane and 5,5,9,9-tetraphenyl-2,4,8-trioxatricyclo[5.2.0.0^{3,6}]nonane were assigned to IIa and IIIa, respectively. Further evidence for the assigned structure of IIa was obtained by the following chemical reaction. Reduction of IIa with lithium aluminium hydride in tetrahydrofuran-dioxane (1 : 4) at 95° gave the diol (VIa), m.p. 184–186°, whose n.m.r. spectrum substantiated the structure. Treatment of VIa with acetic acid-hydrochloric acid yielded known 1,1,4,4-tetraphenylbutadiene (VII) (3) in good yield. This conversion can be explained as a reversed Prins reaction (4).

The photoaddition reaction with 2-methylfuran afforded, besides a 1 : 1 adduct, m.p. 145–146° (18.5% yield) assignable as 6,6-diphenyl-1-methyl-2,7-dioxabicyclo[3.2.0]hept-3-ene, two 2 : 1 adducts: (IIb), m.p. 221–222° in 13.7% yield; (IIIb), m.p. 188–189° in 2.5% yield. Formulation of these adducts as 5-methyl derivatives of IIa and IIIa, respectively, was accomplished by their n.m.r. analyses and chemical conversion of IIb into the diol (VIb), m.p. 186–188°. This diol was also converted to VII by the same procedure as for VIa.

The photoaddition reaction of benzophenone to 2,5-dimethylfuran yielded a 2 : 1 adduct (IIc), m.p.

198–200° in 9.9% yield. IIc was readily isomerized to the compound (VIII), m.p. 275–277°, on treating it with methanolic acetic acid at room temperature. However, similar isomerization did not occur with IIa and IIb. By the same procedure described for IIa, the adduct IIc was converted to VII through the corresponding diol (VIc), m.p. 191–192°. The n.m.r. spectrum of IIc shows aliphatic proton signals at τ 6.39 (2H, singlet) 8.72 (2CH₃, singlet) and that of VIII show aliphatic proton signals at τ 6.37 (2H, singlet) and 9.15 (2CH₃, singlet). From these results, it seems quite likely that both IIc and VIII have symmetrical structures and one of them has the same orientation as IIa and IIb, the other being its stereoisomer.

In order to determine the orientations of oxetane rings with respect to the tetrahydrofuran ring, we measured the dipole moments of the compounds IIa, IIb, IIc, IIIa, IIIb, IV, V and VIII in benzene at 25° using a heterodyne beat apparatus (5). The results are shown in TABLE I, in which α and β respectively denote the changes of the dielectric constant and density of solutions with the weight fraction of the solute; other notations have their usual meanings. As the syn isomer requires a larger moment value than the anti isomer, one can unambiguously assign IIc as well as IIa and IIb to the syn structure and VIII to the anti. In the case of the asymmetric 2:1 adduct, only one counter-part IIIa or IIIb has been isolated and the assignment on the basis of relative moment size is impossible. On the assumption of a regular pentagon form for the tetrahydrofuran ring and of a square form for the oxetane ring, the angle θ between the tetrahydrofuran ring plane and the oxetane ring plane and the group moment μ_0 of oxetane ring have been calculated as 59°54' and 1.40D respectively, from the moments of IV, V and of the tetrahydrofuran in benzene (1.75D). In this calculation, the group moment of oxetane with two phenyl rings has been taken to lie in the direction of the bisector of C–O–C angle. Use of the calculated values of μ_0 and θ gives a vector sum 3.70D for IIa which is in good agreement with the observed one 3.74D to confirm the adequacy of the values of μ_0 and θ . Although the large probable error exists

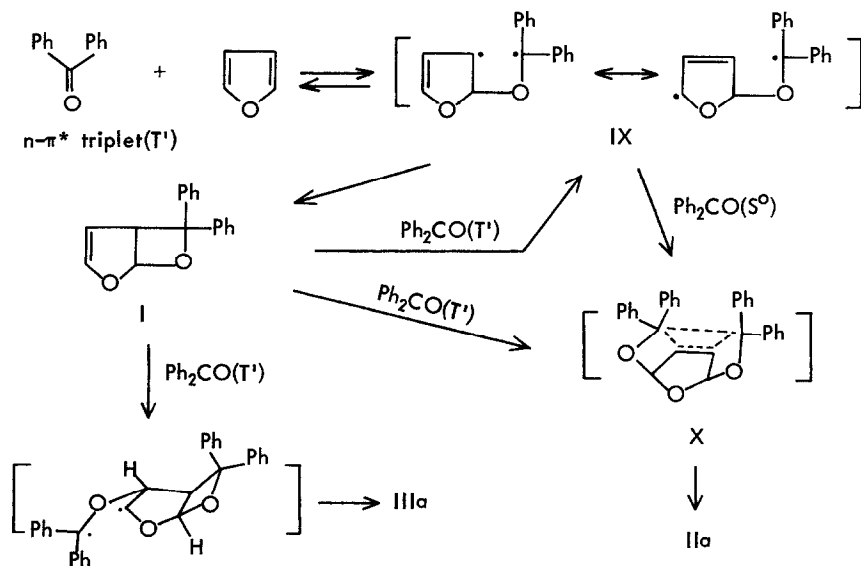
TABLE I
Dipole Moments in Benzene at 25°

Compound	α	β (g/cc)	MR _D (cc)	Dipole moment (D)
IIa	3.87	0.266	124.689	3.74
b	3.166	0.217	129.309	3.46
c	2.67	0.235	133.929	3.17
IIIa	0.979	0.316	124.689	1.45
b	0.715	0.246	129.309	1.28
IV	3.70	0.282	72.406	2.78
V	0.791	0.239	72.406	1.08
VIII	1.26	0.245	133.929	2.00

in a small moment measured in solution, the observed moment of IIIa agrees with the moment 1.56D calculated for the asymmetric anti 2:1 adduct using the above-mentioned parameters, the moment calculated for the asymmetric syn structure being 2.32D. The good agreement suggests IIIa as well as IIIb to be of anti structure.

The formation of the 2:1 adducts obtained probably proceeds through the carbonyl $n-\pi^*$ triplet state as demonstrated in the formation of oxetanes from olefins with ketones (6). The excited triplet benzophenone having electron deficient oxygen would attack the α -position of furan to give the most stable diradical (IX). Ring closure of IX gives 1:1 adduct (I), whose olefinic double bond is further attacked by the triplet benzophenone from the less hindered back side to produce IIIa. Alternatively, if the second attack of ground-state benzophenone take place on the diradical IX directly, the syn-adduct IIa could arise via an oriented allylic diradical (X)(7). The formation of IIa from I with benzophenone can be interpreted as proceed through the diradical IX arising from bond-breaking of I effected by triplet benzophenone. The bond-breaking of I with triplet benzophenone can be expected from some references (8) together with our observation that irradiation of I in acetone or a benzene solution of acetophenone also gives the 1:2 adducts, IIa and IIIa, although in low yield. Another possible route to IIa from I via X directly which compete with the route to IIIa can not be ruled out. In this case the reaction will be also controlled by the formation of the stable transition state, orientated allylic diradical X.

Full details will be appeared in a forthcoming paper.



The n.m.r. spectra were observed in deuteriochloroform containing tetramethylsilane as an internal standard, by using a Varian A-60 spectrometer. Elementary analysis of all the compounds described satisfactorily corresponded to the calculated values.

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