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THE PHOTOCYCLOADDITION OF BENZOPHENONE TO NORBORNADIENE

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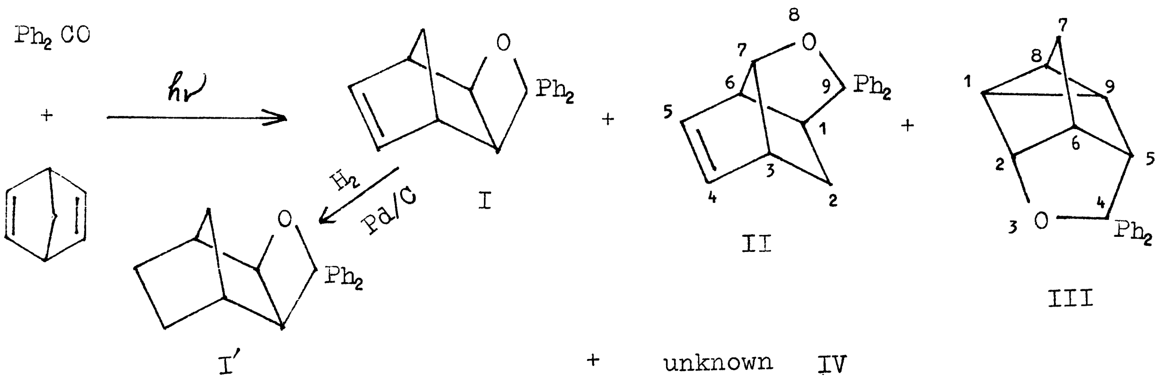
Irradiation of benzophenone and norbornadiene in benzene gave adducts I, II, III and unknown IV.

A recent report1) which established the occurrence of the oxetane formation by the photocycloaddition of benzophenone to conjugated dienes prompted us to communicate our results concerning the reaction of benzophenone with norbornadiene which is a homoconjugated diene.

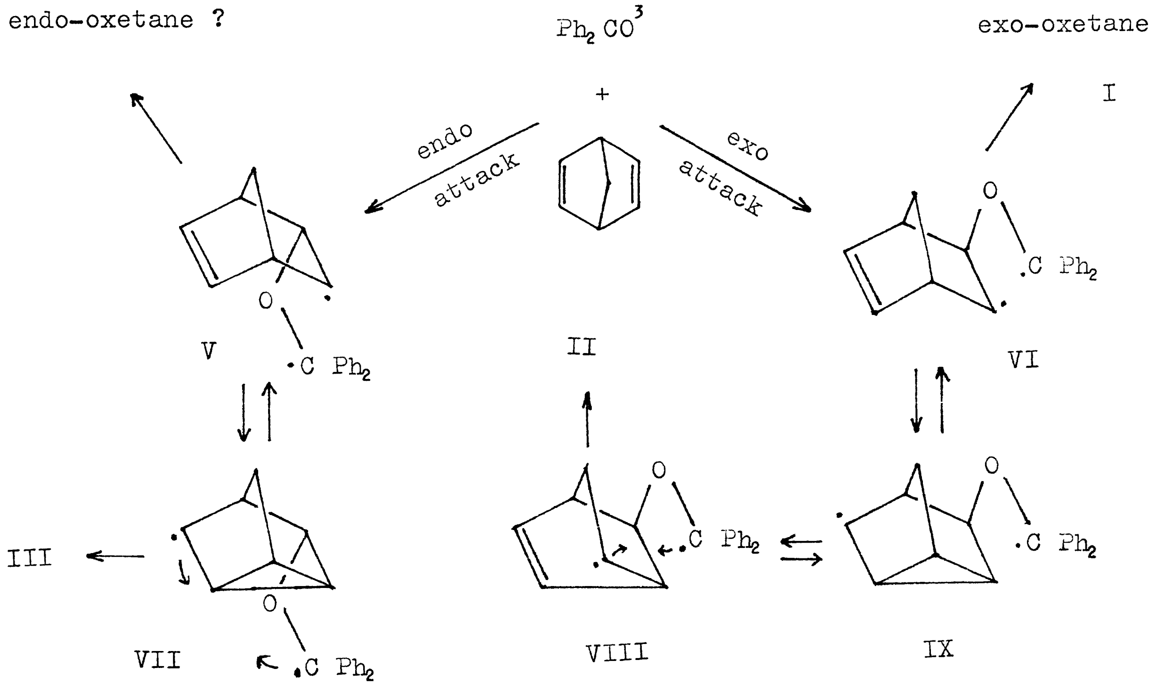
Irradiation of a solution of benzophenone and norbornadiene in benzene gave adducts I (32 %), II (15 %), III (3 %) and IV (5 %).2) Compound I was crystallized from an ether solution of the photolysate. Compounds II, III and IV were isolated by column chromatography from the filtrate. Compound I was identified as an exo-oxetane by the spectral data and by the fact that the NMR and IR spectra of I′, which is a reduction product of I, were identical with those of an authentic sample.3) Compounds II, III and IV were shown to be 1 : 1 adducts of benzophenone and norbornadiene by their mass spectra which had a molecular peak of m/e 274. The IR spectrum of II showed a strong absorption at 1027 cm^{-1}, characteristic of ethers. The NMR spectrum showed



doublets of doublets at τ 9.13 (1H, H_{2-endo} , 12.0 Hz 6.1 Hz) and 8.27 (1H, H_{2-exo}, 12.0 Hz 5.0 Hz), a·broad complex signal at 7.0-7.4 (2H, H_3 and H_6), a doublet at 7.13 (1H, H_1 , 6.1 Hz), a slightly split singlet at 5.76 (1H, H_7), and multiplets at 4.12 (2H, H_4 and H_5) and 2.8 (10H, aromatic protons). The signals at τ 9.13 and 8.27 were assigned to H_{2-endo} and H_{2-exo} , respectively. These are in accord with the chemical shifts of the H_{5-endo} and H_{5-exo} of the norbornene system and the large coupling constant is also characteristic of the geminal protons.4) The former signal is further split into a doublet due to coupling with H_1 (J = 6.1 Hz) and the latter perhaps with H_3 (J = 5.0 Hz); these were supported by decoupling experiments. These behavior is consistent with the norbornene system.4) The absence of the coupling between H_1 and H_{2-exo} , though the corresponding protons in the norbornene system are coupled to each other (J = 2.1-4.6 Hz)4), is to be expected because the Dreiding stereomodel shows that the dihedral angle H_1-C_1-C_2-H_{2-exo} is about 90°. That the signal at τ 5.76 assigned to H-C-O5) is a slightly split singlet shows the presence of a C_7-O bond.6) On the basis of the above data, II was assigned the structure of 9,9-diphenyl-8-oxatricyclo $[4.3.0.0^{3,7}]$ non-4-ene. Compound III had an infrared absorption at 1018 cm^{-1}(ethers) and at 805 cm^{-1}(doublet, nortricyclene).7) The NMR spectrum showed a multiplet at τ 9.07 (1H, H_9), a doublet at 8.78 (2H, H_1 and H_8 , 4.8 Hz), a singlet at 8.37 (2H, H_7), a multiplet at 7.91 (1H, H_6), a triplet at 6.91 (1H, H_5 , 1.6 Hz), a doublet at 5.56 (1H, H_2 , 2.2 Hz), and a multiplet for 10 aromatic protons at 2.8. The NMR spectrum shows no signals in the vinyl region, and the signals at τ 9.07 and 8.78 indicate the presence of the ring protons of cyclopropanes. Irradiation of the triplet at τ 6.91, which was assigned to H_5 , caused the multiplet at 9.07 to simplify to a triplet (J = 5.1 Hz) and the signals at τ 9.07 and 8.78 to an AB_2 pattern. This shows that the multiplet is coupled to H_5 and to the doublet at τ 8.78. Therefore, the signals at τ 9.07 and 8.78 were assigned to H_9 , and H_1 and H_8 , respectively. The proton at C_9 absorbs at higher fields than the other two cyclopropane ring protons, which seems to be due to the anisotropy of the phenyl ring. Furthermore, decoupling experiments revealed that H_6 is coupled to H_2 and H_5. Thus, the signal at τ 6.91 due to H_5 is considered to be split into a triplet by equal couplings to H_6 and H_9. From these data III was identified as 4,4-diphenyl-3-oxatetracyclo $[7.1.0.0^{2,6}.0^{5,9}]$ nonane. This is the product of formal homo-Diels-Alder addition of benzophenone and norbornadiene, and this formation is in contrast to no formation of Diels-Alder adducts in the reactions of benzophenone and conjugated dienes.[1] The NMR and IR spectra of IV show the presence of Ph_2CHO- and two olefinic protons, but it remains unidentified.

This reaction seems to occur by attack of the benzophenone triplet on the ground state norbornadiene since it was markedly quenched by 1,3-cyclohexadiene.[8] The formation of these products can be well explained by assuming biradical intermediates such as V and VI (Scheme) which are formed by endo and exo attack of the benzophenone triplet, respectively.[9] The presence of the norbornenyl (V, VI and VIII) - nortricyclyl (VII and IX) free-radical equilibrium has a precedent.[10] The formation of the products such as II and III might be evidence that the oxetane formation proceeds via the biradical intermediate. The endo-oxetane shown in Scheme was not isolated, but its formation can not necessarily be ruled out. It is reasonable to consider that it had been once formed but was decomposed on silica gel during the chromatographic separation since the exo-isomer was readily decomposed under such conditions. The mechanistic study is in progress.

Scheme



References.

1) J. A. Barltrop and H. A. J. Carless, J. Amer. Chem. Soc., 93, 4794 (1971).

2) Satisfactory elemental analyses were obtained for all new compounds.

3) D. Scharf and F. Korte, Tetrahedron Letters, 821 (1963).

4) A. P. Marchand and J. E. Rose, J. Amer. Chem. Soc., 90, 3724 (1968), and references cited therein.

5) L. M. Jackman and S. Sternhell, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry ", Pergamon Press, New York, 1969, p 230.

6) If the oxygen is bonded to C_1 , the larger coupling constant will be obserbed for this signal.4)

7) G. E. Pollard, Appl. Spectrosc., 22, 54 (1968); G. E. Pollard, Spectrochim. Acta, 18, 837 (1962).

8) 1,3-Cyclohexadiene (0.3 mol/l) caused a fourfold retardation in rate.

9) Similar behavior of norbornadiene has been reported in the photoreactions with 2-cyclohexenones, J. J. McCullough, J. M. Kelly and P. W. W. Rasmussen, J. Org. Chem., 34, 2933 (1969).

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