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PHOTOCHEMICAL CYCLOADDITION OF BENZOPHENONE WITH 1,5-DIMETHYL-6-METHYLENETRICYCLO[3.2.1.$0^{2,7}$]OCT-3-EN-8-ONE AND A RELATED ALCOHOL: A STRIKING SUBSTITUENT EFFECT ON THE PRODUCT COMPOSITION

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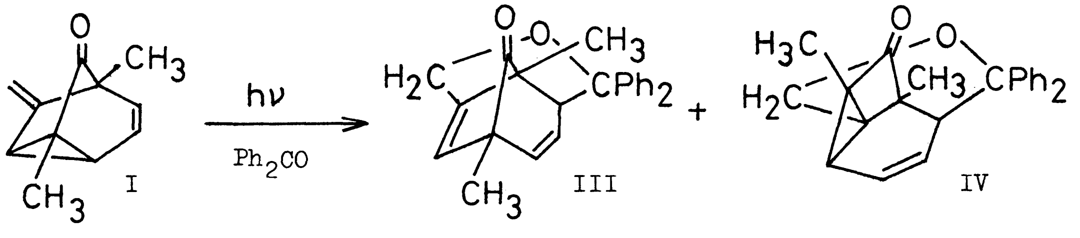
Irradiation of 1,5-dimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]-oct-3-en-8-one (I) in the presence of benzophenone afforded two adducts (III) and (IV) : the alcohol derivative (II), however, the only one (V).

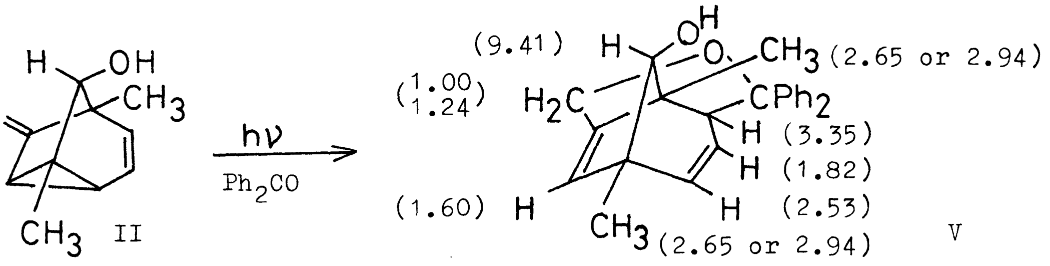
Photoreaction of benzophenone with olefins afforded oxetanes,[1] while with cyclopropyl ethylenes, oxetanes and tetrahydrooxepines originated from cleavage of the cyclopropane ring.[2] Since this kind of reaction with constrained divinylcyclopropane system has not been clarified, we investigated the photoreaction of 1,5-dimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one (I)[3] and a corresponding alcohol (II)[4] in the presence of benzophenone, and found that the cycloaddition to the six-electron system (formally 6+2 cycloaddition) is the only mode. In addition, a striking substituent effect on the product composition was observed. These results are described in this paper.

When a solution of I (0.1 M) in anhydrous benzene was irradiated using a Rayonet photoreactor (MGR-100, 350 nm) for 7 hr in the presence of benzophenone (1.0 M), adducts (III),[5] mp 270-272° in 15 % yield and (IV), mp 166-167° in 47 % yield were obtained. III and IV exhibited the following spectral data ; III, ν (KBr), 1750,

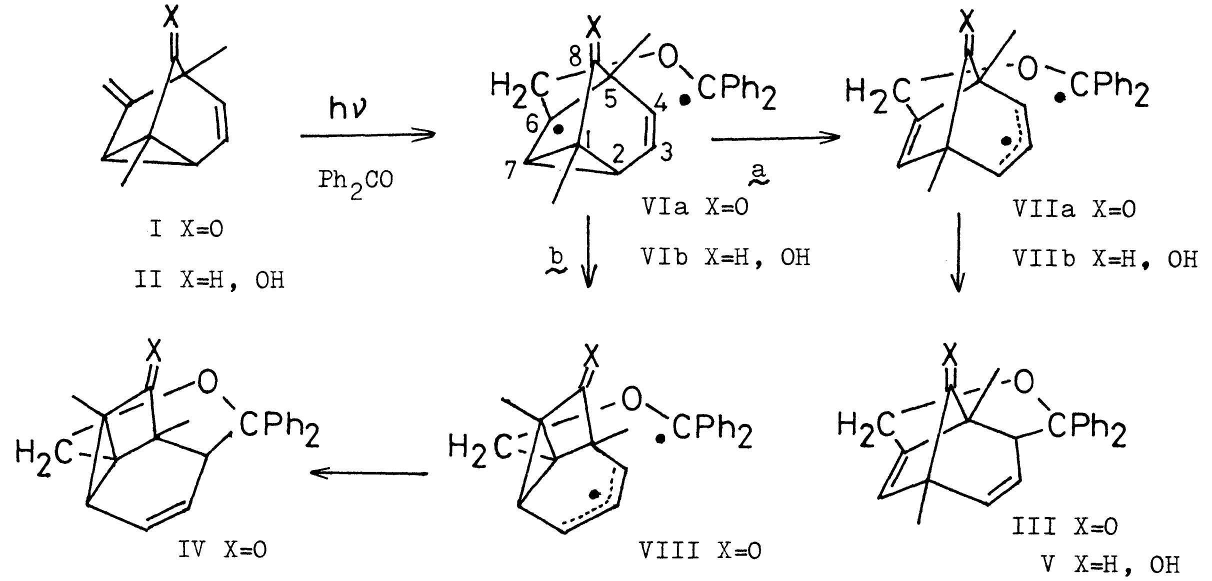


1180 cm^{-1}; δ ($CDCl_3$), 0.68 (3H, s), 1.57 (3H, s), 3.87 (1H, m), 4.05 (1H, d, J=13.0 Hz), 4.53 (1H, d, J=13.0 Hz), 4.90 (1H, s), 5.50 (1H, dd, J=10.0, 4.0 Hz), 5.68 (1H, dd, J=10.0, 2.0 Hz), 7.2-7.8 (10H, m); IV, ν (KBr), 1777, 1180 cm^{-1}; δ ($CDCl_3$), 0.92 3H, s), 1.56 (3H, s), 2.10 (1H, d, J=4.0 Hz), 3.50 (1H, d, J=7.8 Hz), 4.34 (1H, d, J=10.0 Hz), 4.90 (1H, d, J=10.0 Hz), 5.60 (1H, dd, J=7.8, 8.2 Hz), 6.20 (1H, dd, J=4.0, 8.2 Hz), 7.2-8.2 (10H, m). These spectral characteristics of III and IV are consistent with the proposed structures as shown above.[6] Since the di-π-methane rearrangement of III was suspected to afford IV which is a highly constrained compound, III and IV were submitted to irradiation in the presence or absence of benzophenone under the same conditions. However III and IV were recovered quantitatively, and hence III and IV would be the primary photocycloadducts originated from I and triplet benzophenone.[1]

On the other hand, the irradiation of alcohol II (0.2 M) in the presence of benzophenone (0.1 M)[7] was carried out under the same condition, and after 4hr-irradiation an only adduct (V), mp 74-76° in 76 % yield was obtained in addition to 20 % of the starting material. The structure of V was characterized from the following spectral data: ν (KBr), 3400, 1600, 1155, 1125 cm^{-1}; δ ($CDCl_3$), 0.97 (3H, s), 1.09 (3H, s), 1.72 (1H, s), 3.17 (1H, m), 3.49 (1H, broad s), 4.09 (1H, d, J=11.2 Hz), 4.38 (1H, d, J=11.2 Hz), 5.15 (1H, dd, J=3.8, 9.5 Hz), 5.34 (1H, broad d, J= 9.5 Hz), 6.15 (1H, s), 7.1-7.8 (10H, m). The configuration of hydroxy group of V was assigned as depicted above, according to the relative down field shifts (ppm/mol) of δ in the presence of $Eu(fod)_3$, which are given in parentheses on V.[8]



These results seem likely that the carbonyl function of I plays an important role in this photocycloaddition reaction. It is well documented that the bond strength of cyclopropane ring is affected by various substituents according to the ability of cyclopropane to enter into π-type conjugation with neighboring π-electron system.[9] Therefore, the plausible mechanistic schemes (path a and path b) are presented below to rationalize the results. In the case of II (X=H, OH), the constrained vinylcyclopropylcarbinyl radical species VI rearranges into a strain free radical VII, then it collapses to product V. The vinyl function in VI probably contributes to weaken the C_2-C_7 bond as well as the C_1-C_2 bond, because of the



interaction of an unoccupied molecular orbital of vinyl group with the antisymmetric component of the occupied degenerate Walsh orbital pair in cyclopropane.[9] Then the rearrangement of VI into VII (path a) can be facilitated as compared to the cyclopropylcarbinyl radical itself.[2] In addition, the concominant loss of the strain energy also would assist the rearrangement of VI into VII. However, in the case of I (X=O), possible intermediate VI rearranges to VII (path a) and VIII (path b), and then leads to III and IV, respectively. Although VIII is considered to be less stable than VII due to the strain energy of cyclopropane ring, IV is the main product and III is the minor one.[10] This fact would be explained by the reason that the π-electron accepting carbonyl group contributes to weaken the C_1-C_2 bond and strengthen the C_2-C_7 bond in addition to the effect of vinyl group mentioned above. Thus the energy barrier for path b is expected to be reduced and that of path a is expected to be raised, and hence path b would become preferable to path a kinetically.

To our best knowledge, the only example concerning photochemical cycloaddition of benzophenone to a constrained divinylcyclopropane moiety is of barbaralone.[11] The results described in this paper are another examples of this kind exhibiting a remarkable substituent effect. Futher studies clarifying the scope and limitation of this kind of reactions, as well as mechanistic aspect are in progress.

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References and Notes

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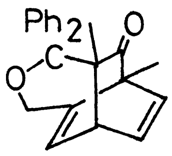
3. J. Zsindely, H. Schmid, Helv., 51, 1510 (1968). They have reported that photolysis of I affords 3,7-dimethylindan-2-one via a ketene intermediate. See also, J. P-Katalinic, J. Zsindely, H. Schmid, Helv., 56, 2796 (1973).

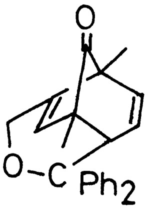
4. J. P-Katalinic, J. Zsindely, H. Schmid, Helv., 57, 223 (1974).

5. Elemental analyses were satisfactory for all new compounds.

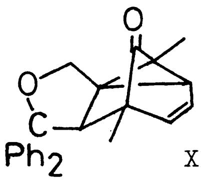
6. The alternative structures IX for III, XI and XII for IV, were ruled out on the basis of the coupling patterns of nmr spectra and the ir spectra. The structure X may explain the spectral data of III, but it contains a trans-double bond in a bridged tetrahydrooxepine (analogue of a bridged cycloheptene). Therefore X is expected to be very unstable and hence it would be ruled out. See, J. R. Wiseman, H-K . Foon, C. J. Ahola, J. Amer. Chem. Soc., 91, 2812 (1969). J. R. Wiseman, J. A. Chong, J. Amer. Chem. Soc., 91, 7775 (1969).



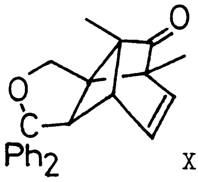
IX



X



XI



XII

The nmr spectra of III and IV were similar to those of the trimethyl analogue which were obtained in the similar ratio, by the photoreaction of benzophenone and 1,3,5-trimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one.

7. When excess of benzophenone was used, futher addition of benzophenone to V took place.

8. Although the orientation of hydroxy group of II is not mentioned,[4] it seems to be syn to the endocyclic double bond, based on the result shown here.

9. R. Hoffman, Tetrahedron Letters, 2907 (1970). R. Hoffman, W. Stohrer, J. Amer. Chem. Soc., 93, 6941 (1971).

10. The ratio of III to IV was almost same at the temperature range between 15° C and 60° C.

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