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PHOTOCYCLOADDITION OF CARVENONE TO OLEFINS

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The photodimerisation of 2-cyclohexenones and their photoaddition to carbon-carbon multiple bonds to give cyclobutane derivatives have been the subjects of recent investigations.[1] Dauben and co-workers[2] investigated the effect of alkyl substituents on the photochemistry of 2-cyclohexenone, and reported that whereas the 3-alkylcyclohexen-1-ones underwent dimerisation easily the 3-isopropyl-6-methyl-cyclohexen-1-one (carvenone), I, was stable to light under normal conditions.[3] They concluded that in the latter case the excessive steric hinderance either slows the reaction to the point where demotion from the triplet to the ground state is the only efficient process open to the molecule, or, less likely, decreases the efficiency of S_1-T_1 intersystem crossing. As it is generally agreed, on the basis of experiments involving sensitisers and quenchers, and on the study of emission spectra, that the reactive excited states in dimerisations and crossed cycloadditions of 2-cyclohexenones are n-π^* triplets,[4] we thought it of interest to see if carvenone could be added photochemically to alkenes.

Irradiation of carvenone and cyclohexene in benzene using a 250 W Hanovia lamp through a pyrex filter for 20 hours gave the photoadduct in excellent yield (90%). Although t.l.c. on silica showed one spot in various solvent systems, g.l.c. showed the presence of two compounds (ca. 2:1 ratio) which were separated by preparative g.l.c. The major fraction, a crystalline solid, m.p. 52-54° (2,4-DNP, m.p.156-157°), was assigned structure II on the basis of elemental analysis and spectral data.[5] The minor fraction, a viscous liquid (2,4-DNP, m.p. 172-173°), was assigned structure III. Both II and III could be recovered unchanged after refluxing for 24 hours with sodium methoxide in methanol, indicating that in both the isomers the cyclohexanone-cyclobutane ring junction was cis and the C-4 methyl group was probably equatorial. The n.m.r. spectrum of II showed the C-2 methine proton as a doublet at δ 2.39 (J=9 Hz) while the same proton in III appeared as a broad singlet

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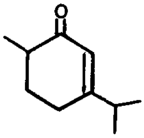
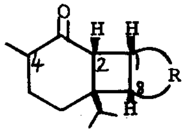
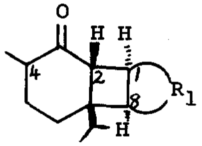


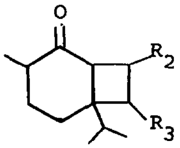
I



II, $R=-(CH_2)_4-$



III, $R_1=-(CH_2)_4-$



VI, $R_2=H$; $R_3=OEt$

IV, $R=-(CH_2)_2CH=CH(CH_2)_2-$ V, $R_1=-(CH_2)_2CH=CH(CH_2)_2-$ VII, $R_2=R_3=COOMe$

at δ 2.6. The large coupling constant obtained for the cyclobutane protons in II requires that they have the syn relationship as shown, and the value is in agreement with those reported in the literature.[6] The compound III with the small coupling constant has, therefore, the C-1 and C-2 methine protons trans to each other. Although the stereochemistry at C-8 in both II and III could not be determined conclusively from the available data, it is very probably cis.

The generality of the above reaction was demonstrated by irradiating carvenone with cycloocta-1,5-diene when the I:I adducts IV and V were obtained in good yield (60%). Carvenone was also found to give the normal I:I photoadducts, VI, VII (stereochemistry unspecified), with both the electron rich and electron poor olefins ethoxyethylene and dimethyl maleate.[7] These results, therefore, indicate that compared to photodimerisation the photocycloaddition of 2-cyclohexenones is less prone to steric requirements.

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References:

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2. W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyre, J. Org. Chem., 33, 4060, (1968)

3. We found that irradiation of carvenone, with or without a solvent, for more than a week gave no photodimer, and the whole of carvenone was recovered unchanged.

4. J. L. Ruhlen and P. A. Leermakers, J. Amer. Chem. Soc., 88, 5671, (1966); P. E. Eaton and W. S. Hurt, ibid., 88, 5038, (1966); E. Y. Lam, D. Valentine, and G. S. Hammond, ibid., 89, 3482, (1967); O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, ibid., 90, 1657, (1968); P. deMayo, A. A. Nicholson, and M. F. Tchir, Canad. J. Chem., 48, 225, (1970).

5. All the new compounds gave satisfactory elemental analyses and their structures were supported by i.r., n.m.r., and m.s. data.

6. I. Fleming and D. H. Williams, Tetrahedron, 2747, (1967); J. W. Hanifin and E. Cohen, J. Amer. Chem. Soc., 91, 4494, (1969).

7. 3-t-Butylcyclohexen-1-one was also found to give 1:1 photoadduct with cyclohexene