BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(2), 731—732 (1975)

Photoreaction of Bicyclo[5.3.0]dec-1(7)-en-2-one with Cyclopentene and Cyclohexene

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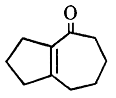
(Received July 2, 1974)

Synopsis. The photoreaction of the enone (I) with cyclopentene gave the radical coupling products, (VII) and (VIII), along with the hydrogen abstraction product (VI), but not $[2\pi+2\pi]$ photocycloadduct. On the other hand, the photoreaction of I with cyclohexene proceeded in somewhat different manner to give the $[2\pi+2\pi]$ photocycloadduct (V) other than the hydrogen abstraction product (VI) and the radical coupling product (IX).

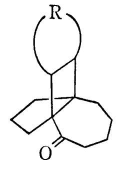
In the chemistry of α,β-unsaturated carbonyl compounds, much attention has been shown about the photochemistry of cyclic enones. Especially, the $[2\pi+2\pi]$ photocycloaddition of some cyclic enones, such as cyclopentenones and cyclohexenones, has been extensively studied[1] and utilized for preparation of a wide variety of poly fused alicyclic compounds.[1,2] On the contrary, cycloheptenone, being a next higher cyclic enone, has been of no consequence. This is because it cannot undergo the crossed photocycloaddition with olefins owing to the facile isomerization to its *trans* isomer.[3] More recently, we reported our preliminary finding concerning the crossed photocycloaddition of a certain cycloheptenone derivative, bicyclo[5.3.0]dec-1(7)-en-2-one (I), having a rigid bicyclic system, with some seven- and eight-membered ring olefins, such as cycloheptene, cyclooctene, and 1,5-cyclooctadiene.[4] In the case of I, the ethylene linkage of cycloheptenone is fixed tightly with five membered ring and, therefore, an unfavorable *cis-trans* isomerization may be entirely inhibited. This situation resulted in the predominant formation of two stereo isomers of the respective cycloadducts IIa, IIb—IVa, IVb.[4] In the present paper, emphasis has been placed on the effect of smaller ring sized olefins, such as cyclopentene or cyclohexene, on the photochemical reaction of I.

Experimental

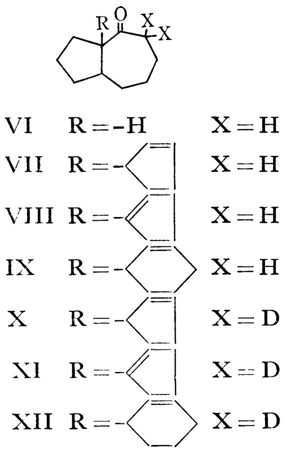
Generals. The enone (I) was prepared according to the procedure of Dev[5] and Cope and Holzman[6] and purified by fractionation using Taika Kogyo SM-NB spinning band column before use. Irradiation was carried out using a Eikosha Halos 500-W water cooled high pressure mercury lamp. Products were isolated using a Varian Aerograph 90-P gas chromatograph and analyzed by a Hitachi 063 gas chromatograph (column: PEG-20M, SE-30, or FFAP). Yields were based on the enone I reacted. The deuterium exchange reaction was carried out according to the procedure of Pfeffer[7] and Osman and the products were analyzed by mass spectra using a Hitachi RMU-6E mass spectrometer.



I



IIa, IIb $R=-(CH_2)_5-$
IIIa, IIIb $R=-(CH_2)_6-$
IVa, IVb $R=-(CH_2)_2CH=CH(CH_2)_2-$
V $R=-(CH_2)_4-$



Photoreaction of I with Cyclopentene. A mixture of I (2.97 mmol) and cyclopentene (29 mmol) placed in a sealed Pyrex tube (1 × 10 cm) was irradiated with an external mercury lamp at a distance of 2 cm at room temperature for 7 hr. After removal of remaining cyclopentene, residue was distilled *in vacuo* (10^{-3} mmHg) to afford 0.373 g of oil, which consisted of three products (glpc) mainly. Each product was isolated by preparative glpc; yields: VI 22%; VIII 12%; VIII 14%. VII: ν_{max} 1680 cm^{-1} (CO); $\delta(CCl_4)$ 1.10—2.15(m,18H), 2.20—2.40(m,2H), 5.55—5.80(m,2H); *m/e* 218(M$^+$), 152(M-C_5H_6); 2,4-dinitrophenylhydrazone, mp 171—172 °C; Found: C, 62.98; H, 6.58; N, 13.93%. Calcd for $C_{21}H_{26}O_4N_4$: C, 63.30; H, 6.58; N, 14.06%. VIII: ν_{max} 1675 cm^{-1} (CO); $\delta(CCl_4)$ 1.30—2.20(m, 19H), 2.25—2.60(m, 2H), 5.60—5.85(m, 1H); *m/e* 218(M$^+$), 152(M-C_5H_6); 2,4-dinitrophenylhydrazone, mp 172—173 °C; Found: C,63.23; H, 6.75; N, 14.26%. Calcd for $C_{21}H_{26}O_4N_4$: C, 63.30; H,6.58; N,14.06%. On treating with the solution of D_2O-dioxane-NaOD twice,[7] both VII and VIII were changed into the deuterated compounds X; *m/e* 220(M$^+$, $C_{15}H_{20}OD_2$) and XI; *m/e* 220(M$^+$, $C_{15}H_{20}OD_2$), respectively.

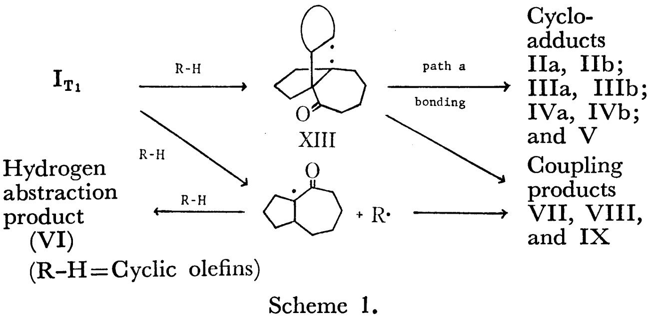
Photoreaction of I with Cyclohexene. A mixture of I (2.76 mmol) and cyclohexene (30 mmol) was irradiated for 3 hr, in a similar manner as described above. After removal of remaining cyclohexene, residue was distilled *in vacuo* (10^{-3} mmHg) to afford 0.444 g of oil, which consisted of three products (glpc) mainly. Each product was isolated by preparative glpc; yields: V 21%; VI 19%; IX 5%. V: ν_{max} 1680 cm^{-1} (CO); $\delta(CCl_4)$ 1.20—2.10 (m,22H), 2.20—2.70(m,2H); *m/e* 232(M$^+$), 151(M-C_6H_9); Found: C, 82.41; H, 10.61%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%; 2,4-dinitrophenylhydrazone, mp 147—148 °C. IX: ν_{max} 1675 cm^{-1} (CO); $\delta(CCl_4)$ 1.20—2.40(m, 20H), 2.45—2.90(m, 2H), 5.30—5.85(m, 2H); *m/e* 232(M$^+$), 152 (M-C_6H_8); 2,4-dinitrophenylhydrazone, mp 163—165 °C; Found: C,63.92; H, 6.61; N, 13.88%. Calcd for $C_{22}H_{28}O_4N_4$: C, 64.06; H, 6.84; N, 13,58%. On treating with the solution of D_2O-dioxane-NaOD twice,[7] IX was changed into the deuterated compound XII; *m/e* 234(M$^+$, $C_{16}H_{22}OD_2$).

Results and Discussion

As reported previously,[4] the photoreaction of I with some seven- and eight-membered ring olefins, such as cycloheptene, cyclooctene, and 1,5-cyclooctadiene, always afforded two stereo isomers of respective cycloadducts.

Concerning the stereochemistry of above cycloadducts, we assume, presently, that two *trans*-fused isomers of four possible ones are more probable candidates.[8] Interestingly, the photoreaction of I with cyclopentene proceeded in a quite different manner as compared to the reaction with the larger ring sized olefins described above. Namely, the formation of cycloadduct of I with cyclopentene was not observed at all. Instead, two radical coupling products, VII and VIII, and one hydrogen abstraction product VI were obtained in 12%, 14%, and 22% yields. Structural determination of VII and VIII was made on the basis of elemental analyses and spectrometric data in addition to the results of the deuterium exchange reaction. Especially, from the fact that only two hydrogens were always exchanged for deuteriums in each compound, the coupling position of the cyclopentenyl groups was determined to be α-bridgehead to the carbonyl group. On the other hand, the photoreaction of I with cyclohexene proceeded in somewhat different manner to give the cycloadduct V together with the hydrogen abstraction product VI and the radical coupling product IX.

One of the most significant results in these reactions is the finding that the variation in the ring sizes of cyclic olefins has definitive influence on the reaction paths. To account for these results, we would like to make some proposals. It appears that the photoexcited state of I would not be different in a series of the above cyclic olefins, though the excited state of I is uncertain as yet. Moreover, in the case of cyclohexene, three types of products were obtained simultaneously in moderate yields. Taking these points, into consideration it may be reasonable to assume that the photochemical reaction proceeds stepwisely in radical manner through an intermediary 1,4-biradical (XIII), formed between the triplet state of I and cyclic olefins, as shown in Scheme 1. When cyclic olefins are larger ring sized olefins, such as cycloheptene and cyclooctene, the cycloaddition from XIII, according to the path a, smoothly could occur to form the cycloadduct, possessing large strained energy. On the other hand, in the case of smaller ring sized cyclic olefin, such as cyclopentene, the formation of cycloadduct from XIII may be entirely suppressed because of instability of cycloadduct, being highly strained structure.[8] Consequently, two other types of reactions accelerate to give the radical coupling products VII and VIII, and the hydrogen abstraction product VI. Concerning the occurrence of the latter two reactions, it may be also considered that cyclopentene is the substrate having the great hydrogen-donating ability. In the case of cyclohexene, circumstance lies between and the formation of cycloadduct V has barely become feasible. As a result, three types of products are given at the same time.



Scheme 1.

Further research for the photoreaction of I in the presence of strained olefins are in progress and will be reported shortly.

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1a) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968); b) P. de Mayo, *ibid.*, **4**, 41 (1971), and references cited therein; c) P. E. Eaton and K. Nyi, *J. Amer. Chem. Soc.*, **93**, 2786 (1971); P. E. Eaton and G. H. Temme, *ibid.*, **95**, 7508 (1973); R. L. Cargill, T. E. Jackson, N. P. Peet, and D. M. Pond, *Accounts Chem. Res.*, **7**, 106(1974), and references cited therein.

2) They are utilized also in the syntheses of various natural products: see Ref. 1b); see also, E. J. Corey and S. Nozoe, *J. Amer. Chem. Soc.*, **86**, 1652 (1964); E. J. Corey, R. B. Mitra, and H. Uda, *ibid.*, **86**, 485 (1964): J. D. White and D. N. Gupta, *ibid.*, **90**, 6171 (1968).

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4) A. Kunai, T. Omori, T. Miyata, K. Kimura, and Y. Odaira, *Tetrahedron Lett.*, **1974**, 2517.

5) S. Dev, *J. Indian Chem. Soc.*, **31**, 1(1954).

6) A. C. Cope and G. Holzman, *J. Amer. Chem. Soc.*, **72**, 3062(1950).

7) P. E. Pfeffer and S. F. Osman, *J. Org. Chem.*, **37**, 2425(1972).

8) The structure of cycloadducts, IVa and IVb, is now under study by means of X-ray analysis. At the time, we suppose that, as a plausible structure, the cycloadducts have *trans*-fused structure. In the photocycloaddition of some bicyclic enones with cyclic olefins, the formation of *trans*-fused cycloadducts occasionally dominates. For example, the reaction of bicyclo[4.3.0]non-1(6)-en-7-one with cyclic olefins, such as cyclohexene and cyclooctene, afforded only *trans*-fused cycloadducts which were confirmed by means of X-ray analysis (A. Kunai, H. Omura, K. Kimura, and Y. Odaira, unpublished result, and to be published). On the other hand, the formation of *cis*-fused cycloadduct is observed only when the cycloadduct is substantially free from the repulsion of *syn* overlap. For example, cyclopentenone adds to cyclopentene to afford the corresponding *cis*-fused *anti*-adduct in good yield (P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2454 (1962)).