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The Photo-induced Diels-Alder Reaction of 2-Cycloocten-1-one and 2-Cyclohepten-1-one

Hiraku SHINOZAKI, Susumu ARAI, and Masaru TADA
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku, Tokyo 160

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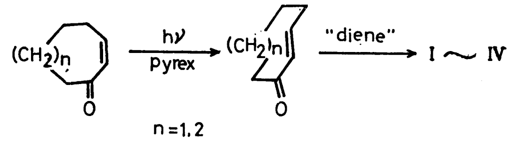
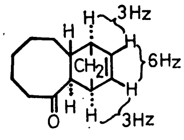
Synopsis. *trans*-2-Cycloocten-1-one and *trans*-2-cyclohepten-1-one, which are supposed to be formed by the ultra-violet irradiation of *cis*-2-cycloocten-1-one and *cis*-2-cyclohepten-1-one, give Diels-Alder addition products with cyclopentadiene and isoprene.

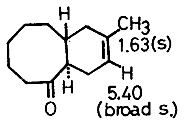
It is well established that the irradiation of a medium ring cycloalkenone, such as 2-cycloocten-1-one and 2-cyclohepten-1-one, induces a *cis-trans* isomerization.[1–3] The *trans* isomer of these enones is highly strained and has been reported to enter into a Diels-Alder addition with some dienes. This facile cycloaddition provides a promising method of constracting a carbocyclic system with a medium ring. Previously *trans*-2-cyclohepten-1-one was found to undergo a photochemically-induced cycloaddition with cyclopentadiene.[1] In this paper we wish to extend the scope of the photo-induced Diels-Alder addition of *trans*-2-cycloocten-1-one and *trans*-2-cyclohepten-1-one with dienes.

The irradiation of a mixture of *cis*-2-cycloocten-1-one and an excess amount of cyclopentadiene or isoprene gave two adducts, I and II, in yields of 66 and 58% respectively. In these runs a large excess of dienes was used to suppress the dimerization of the enone. In the same manner, *cis*-2-cyclohepten-1-one gave the Diels-Alder adducts, III with cyclopentadiene[1,4] and IV with isoprene, in yields of 95%. The 2-cyclohepten-1-one disappeared within 1 hr, while 2-cycloocten-1-one required a longer reaction period—2 hr with cyclopentadiene and 4.5 hr with isoprene. This difference in the reactivity must be a reflection of the strain energy in *trans*-2-cyclohepten-1-one and *trans*-2-cycloocten-1-one.





I



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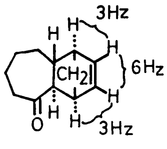

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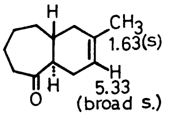

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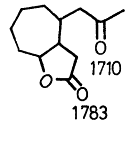

V

The adducts with 2-cycloocten-1-one were difficult to purify so as to give satisfactory results on elemental analysis due to the *retro*-Diels-Alder reaction which occurred on distillation or gas chromatography. High resolution mass spectrometry, however, defined the molecular formula of the adducts. The mass spectra of these adducts showed base peaks at $m/e=110$ and 124 due to 2-cyclohepten-1-one and 2-cycloocten-1-one cations formed by the fragmentation of the *retro*-Diels-Alder type. The structure of the I adduct, including its stereochemistry, was deduced from a comparison of the spectral data with those of the III adduct between *trans*-2-cyclohepten-1-one with cyclopentadiene. The proton magnetic resonance of the olefinic hydrogens of the I adduct and that of the III adduct show the same signal pattern with the same coupling constants, as is shown in the figures, and the structure of the latter was unambiguously established by chemical degradation.[1] The structures of II and IV adducts were deduced from their spectroscopic data and from their chemical degradation. These two adducts show almost identical NMR signals; the position of the methyl group was assigned by the transformation of the IV adduct into the ketolactone, V. The transformation was achieved by the hydride reduction of the IV adduct, the hydroxylation of the resulting alcohol at the double bond by osmium tetraoxide in pyridine, and successive oxidations by lead tetraacetate and chromic anhydride in acetic acid. The ketolactone, V, had infrared absorptions at 1783 and 1710 cm^{-1} due to γ-lactone and methyl ketone. The *trans*-fusion of the ring system in the II and IV adducts was deduced from its innertness to acid or base treatment and from mechanistic considerations.[5]

Experimental

General Precedure of the Photo-Diels-Alder Reaction. *cis*-2-Cycloocten-1-one or *cis*-2-cyclohepten-1-one (500 mg) and a 20-fold amount of a diene dissolved in 100 ml of hexane were placed in a reaction vessel, after which the mixture was internally irradiated by a 100-W medium-pressure mercury lamp in a Pyrex immersion jacket under an atomosphere of nitrogen. In the case of cyclopentadiene, the mixture was cooled in an ice-salt bath during irradiation. The reaction was monitored by the disappearance of the infrared absorptions due to the conjugate carbonyl groups. After the complete disappearance of the starting ketone–after 2 hr for I adduct, 4.5 hr for the II adduct, and 1 hr for the IV adduct–the solvent and the excess of diene were removed by distillation. The residues were distilled under reduced pressure by using a short-path distillation apparatus, Kugelrohr, to give the adducts in yields of 66% (I), 58% (II), and 95% (IV).

The photo-dimer of 2-cycloocten-1-one contaminated in the fraction with a higher boiling point was removed by chromatography on silica gel eluted with hexane–ether (1: 1); the products were found to be essentially pure by gas-chromatographic analysis (5% SE-30 on Chromosorb W and 5% Carbowax 20M on Chromosorb W).

Adduct I. Bp 75—80 °C/0.7 mmHg. Mass: M^+= 190.138. Calcd for $C_{13}H_{18}O$ m/e=190.135. IR (neat): 1685 and 720 cm^{-1}. NMR (CCl_4): δ=6.34—5.93 (2H, octet, J=3 and 6 Hz), 2.93 (1H, diffused singlet), and 2.7—1.4 ppm (15 H).

Adduct II. Bp 77—82 °C/0.5 mmHg. Mass: M^+= 192.150. Calcd for $C_{13}H_{20}O$ m/e=192.151. IR(neat): 1685, 795, and 780 cm^{-1}. NMR (CCl_4): δ=5.40 (1H, diffused singlet), 1.63 (3H, singlet), and 2.6—1.3 ppm (16 H).

Adduct IV. Bp 90—95 °C/0.2 mmHg. Found: C, 80.80; H, 10.18%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%. IR (neat): 1701 and 785 cm^{-1}. NMR (CCl_4): δ=5.33 (1H, diffused singlet), 1.63 (3H, singlet), and 2.6—1.3 ppm (14H).

Ketolactone V. A solution of the IV adduct (1.10 g) in 20 ml of ethanol was treated with 500 mg of sodium borohydride, after which the mixture was allowed to stand for 14 hr at room temperature (*ca.* 27 °C). After the evaporation of the solvent *in vacuo*, the residue was treated with 10 ml of the saturated solution of tartaric acid to destroy the excess of the hydride. The subsequent ethereal extraction of the mixture gave 1.18 g of crude alcohol. IR (neat): 3470, 1637, 1033, and 785 cm^{-1}. NMR (CCl_4): δ=5.25 (1H, diffused singlet) and 3.87 ppm (1H, diffused doublet, J=5 Hz). The alcohol (450 mg) obtained above in 2 ml of pyridine was treated with 600 mg of osmium tetraoxide in 1 ml of pyridine under cooling in an ice-bath, and the reaction mixture was stirred at room temperature for 12 hr under nitrogen. After the destruction of the osmium complex by adding 20 g of sodium hydrogensulfite in 40 ml of water, the product was extracted with ether to give 171 mg of the triol. IR(neat): 3500, 1117, and 1042 cm^{-1}. The triol (171 mg) in 10 ml of benzene was treated with lead tetraacetate (480 mg) in acetic acid, and the mixture was stirred for 5 hr in a nitrogen atmosphere. The reaction mixture was condensed *in vacuo*, and the condensate was extracted with ether after the addition of a saturated solution of sodium hydrogencarbonate to give a crude oil. The oil in 4 ml of acetic acid was treated with 100 mg of chromic trioxide in 1 ml of water over a 10-min period with cooling, after which the reaction mixture was stirred for 12 hr at room temperature. The product was extracted with ether after the destruction of the excess chromic trioxide by sodium hydrogensulfite to give 71 mg of crude ketolactone. The recrystallization of the product from carbon tetrachloride gave pure V. Mp 68—69 °C. Mass: M^+=210.129. Calcd for $C_{12}H_{18}O_3$ m/e=210.126. IR (neat): 1783, 1710, 1178, and 1010 cm^{-1}.

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References

1) E. J. Corey, M. Tada, R. LeMahieu, and L. Libit, *J. Amer. Chem. Soc.*, **87**, 2051 (1965).

2) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).

3) P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).

4) This reaction was previously reported in Reference 1, but the NMR data is now reported for the first time.

5) 2-Cyclohepten-1-one gave the photo-induced adducts with butadiene (79%) and 2,3-dimethylbutadiene (37%), though a detailed description is omitted in the present report.