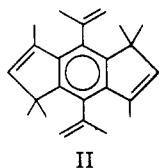


Treatment of I in purified isooctane with ozone from a Welsbach T-23 ozonizer resulted in "breakthrough" of ozone into a 2% potassium iodide trap after approximately the same interval (4 min.) as was required for a solvent blank. Normal olefins are completely ozonized before breakthrough occurs. Further treatment for 1.5 hr. gave about the same 3.2-fold excess of ozone used by Haaijman and Wibaut⁷ for ozonolysis of *o*-xylene. This was apparently sufficient to produce extensive attack since nearly twice the amount needed to ozonize the six double bonds was absorbed.

Although relatively impervious to addition of large external reagents to its system of double bonds, I is sensitive to photolysis and attack by strong acid. The photolysis product is currently under examination. Sulfuric acid (96%) apparently converts I to an orange carbonium ion whose color is half quenched between 65 and 70% H₂SO₄⁸ and which, upon complete quenching with aqueous base, yields an isomer for which we tentatively advance structure II on the basis of n.m.r., infrared, and mass spectra.^{8a}



(7) P. W. Haaijman and J. P. Wibaut, *Rec. trav. chem.*, **60**, 842 (1941).

(8) N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2998 (1963).

(8a) NOTE ADDED IN PROOF. The above interpretation of the low reactivity of hexaisopropenylbenzene is supported by the fact that we have just prepared hexavinylbenzene and find it to exhibit normal reactivity to double bond reagents.

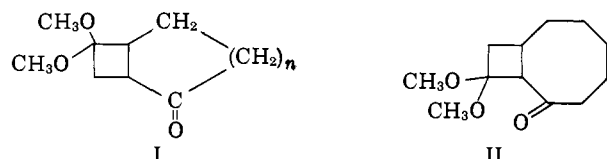
(9) National Institute of Health Predoctoral Fellow.

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 Received March 11, 1965

trans-2-Cycloheptenone

Sir:

In a previous study of the photochemical addition of conjugated enones to other unsaturated substances it was found that 1,1-dimethoxyethylene is especially effective in capturing the reactive species which arise from the $n-\pi^*$ electronic transition of 2-cyclopentenone and 2-cyclohexenone.¹ The products resulting from these ketones and 1,1-dimethoxyethylene are I, $n = 1$, and I, $n = 2$ (as a mixture of *trans*- and *cis*-fused isomers in a ratio of 2.3:1), respectively. The reaction of *cis*-2-cyclooctenone was found to involve prior photo-



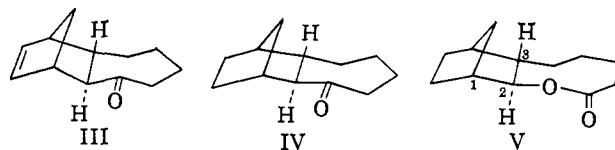
isomerization² to *trans*-2-cyclooctenone followed by a nonphotochemical cycloaddition to form the adduct II.

(1) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

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

Under the same conditions the irradiation of a mixture of 1,1-dimethoxyethylene (15-fold excess) and 2-cycloheptenone gave no 1:1 adduct, but only self-condensation products (mainly dimers) of the ketone. The rate of self-condensation of 2-cycloheptenone was close to the rate of *cis* → *trans* isomerization of 2-cyclooctenone under the same photochemical conditions. This and other considerations, including the recent detection of *trans*-cycloheptene in these laboratories,³ suggested that the rapid photodimerization of *cis*-2-cycloheptenone might be the result of the intervention of the highly strained *trans* isomer, and an investigation of this possibility was undertaken. Starting with the assumption that *trans*-2-cycloheptenone preferentially reacts with itself rather than with 1,1-dimethoxyethylene or *cis*-2-cycloheptenone, the most promising approach to its interception appeared to be the use of a reactive 1,3-diene which could make available a low-energy Diels-Alder pathway.

Irradiation ($\lambda > 300 \text{ m}\mu$) of a mixture of *cis*-2-cycloheptenone and cyclopentadiene (excess) at *ca.* -50° afforded a single 1:1 adduct (C₁₂H₁₆O) in 95% yield, which is formulated as III on the basis of chemical and physical data.^{4,5} The adduct was homogeneous as judged by vapor phase chromatographic (v.p.c.) and thin layer chromatographic (t.l.c.) analysis. The presence of a ketonic carbonyl group was indicated by infrared absorption at 5.86μ ; n.m.r. analysis revealed two olefinic protons as quartets centered at 5.93 and 6.20 p.p.m.⁶ (the peaks of the latter somewhat broadened) with the splittings for each proton ~ 5.3 and ~ 2.6 c.p.s.; peaks due to 14 other protons appeared upfield. Mass spectrometry indicated a parent peak of m/e 176. Catalytic hydrogenation over palladium afforded a saturated ketone (IV) by addition of two hydrogens to the olefinic bond. Treatment of the dihydro derivative IV with peracetic acid produced the crystalline saturated lactone V,⁴ which shows lactonic carbonyl absorption at 5.78μ . Significantly, the lactone exhibits a single n.m.r. peak due to the proton of $>\text{CH}-\text{O}-\text{C}(=\text{O})-$ at 3.92 p.p.m. with a band width at half-height of 4.5 c.p.s. The width of this peak indicates that the proton at C-2 must be *trans* to that at C-3, and further that the proton at C-2 must be *endo*.⁷



Saponification of V afforded a crystalline hydroxy acid, m.p. $109-111^\circ$, which was oxidized by chromic

(3) E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, **87**, 934 (1965).

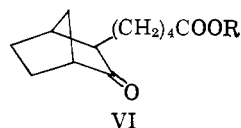
(4) Satisfactory elemental analyses were obtained.

(5) *cis*-2-Cycloheptenone was prepared by chromic acid oxidation of 2-cycloheptenol [A. C. Cope, T. A. Liss, and G. W. Wood, *ibid.*, **79**, 6287 (1957)].

(6) All chemical shifts are expressed as p.p.m. downfield from internal tetramethylsilane.

(7) The following are the expected values of vicinal coupling constants for the norbornane system $J_{2,3}(\text{exo,exo}) \sim 10$ c.p.s., $J_{2,3}(\text{endo,endo}) \sim 7$ c.p.s., $J_{2,3}(\text{exo,endo}) \sim 4$ c.p.s., $J_{1,2}(\text{bridgehead endo}) \sim 0$ c.p.s., $J_{1,2}(\text{bridgehead exo}) \sim 3.5$ c.p.s. See, for example, P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964); also E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964). From these values it is apparent that only stereof ormula V satisfies the n.m.r. data for the lactone.

acid to the corresponding keto acid VI (R = H), infrared absorption (CCl₄) at 3.6–4.3 and 5.84 μ due to carboxyl and 5.73 μ due to the bridged ring



carbonyl.⁸ Esterification of the keto acid with diazomethane produced the ester VI, R = CH₃,⁴ infrared absorption (liquid film) at 5.73 μ due to ester and ketone carbonyls.⁸ The keto acid and keto ester obtained by these reactions were identical with authentic samples of VI obtained by an unambiguous route: alkylation of bicyclo[2.2.1]heptanone-2 with 5-bromopentene-1, hydroboration, and chromic acid oxidation.

The tricyclic ketone III was also obtained when 2-cycloheptenone in glassy methylcyclohexane at -195° was irradiated with ultraviolet light for 6 hr. (>300 mμ), maintained in the dark at -195° for 5 min., and then treated with a cold (-78°) solution of excess cyclopentadiene in pentane. The resulting solid mixture was allowed to warm slowly with vigorous agitation during the process of melting. The formation of the adduct III under the conditions of this experiment shows that this product results not from an electronically excited state of 2-cycloheptenone but from a transformation product of 2-cycloheptenone which is in the ground electronic state; the stereochemistry of III indicates that the reactive intermediate is *trans*-2-cycloheptenone.⁹

The irradiation of 2-cycloheptenone and excess furan in pentane leads to the formation of two stereoisomeric Diels–Alder adducts. As might be expected, however, the reactive *trans*-enone is not trapped as efficiently by furan as by cyclopentadiene.

The photochemical isomerization of *cis*-2-cycloheptenone is of interest not only as a route to the highly strained *trans*-cycloheptene series, but also as a method for effecting Diels–Alder additions which cannot be carried out thermally from the stable *cis* isomer.

We have also obtained direct spectroscopic evidence for the photochemical generation of *trans*-2-cycloheptenone.¹⁰

A 0.4% solution of *cis*-2-cycloheptenone in methylcyclohexane–isopentane (95:5) was cooled in an infrared cell with sodium chloride windows to -190° to produce a clear rigid glass. The sample cell was itself enclosed in a Pyrex vessel which could be evacuated and which had sodium chloride windows on opposite sides to allow the passage of infrared light through the sample. The infrared absorption due to the carbonyl group of *cis*-2-cycloheptenone in the solid hydrocarbon matrix was found to be a maximum at 6.01 μ.¹¹ Irradiation of the frozen mixture with ultraviolet light through Pyrex filters (to remove light of wave length below 300 mμ) resulted in a steady de-

(8) The position of the ketonic carbonyl band is inconsistent with that expected for the cyclobutanone derivative (5.60–5.63 μ) which would be derived from the photoproduct with fused five-, four-, and seven-membered rings.

(9) The photoadduct was obtained in 9.8 and 12.6% yield (based on 2-cycloheptenone) in two runs. Unchanged 2-cycloheptenone and its dimers and some polymer account for the remaining material.

(10) These results, first received on March 29, 1965, were added to the earlier results received on March 16, 1965.

(11) The same mixture exhibited absorption in the liquid state at 25° at 5.94 μ with a shoulder at 5.98 μ.

crease in the absorption at 5.94–6.07 μ with a concomitant increase in a new absorption band at 5.84 μ. After about 45 min. a steady-state condition was reached in which the new absorption band was much more intense than the original; the latter though attenuated by *ca.* 90% at this time did not disappear completely. The new absorption band persisted for 1 hr. at 190° after cessation of irradiation without loss of intensity. When the frozen, irradiated mixture was allowed to warm slowly the original carbonyl band of *cis*-2-cycloheptenone reappeared and the absorption at 5.84 μ had greatly diminished. After thawing, the absorption at 5.84 μ still remained but was less than that characteristic of *cis*-2-cycloheptenone. Vapor phase chromatographic analysis revealed that 45% of the original *cis*-2-cycloheptenone remained at the end of the experiment. The balance of the material was mainly a mixture of dimers of 2-cycloheptenone, clearly formed during the thawing of the irradiated material.

The new carbonyl absorption band produced by irradiation of *cis*-2-cycloheptenone in the solid hydrocarbon matrix at -190° can be reasonably assigned only to the *trans* isomer of this ketone which is expected to exhibit a carbonyl band in the region 5.84–5.86 μ since the carbonyl and α,β-carbon π-systems are essentially orthogonal in the *trans*-2-cycloheptenone structure. Other isomeric structures which do not have a carbonyl group such as I can be ruled out. The circumstance that the reactive inter-



mediate (VII) reverts to *cis*-2-cycloheptenone, dimerizes, and forms Diels–Alder adducts of *trans*-2-cycloheptenone allows no other ketonic structure than that of *trans*-2-cycloheptenone.

Similar experiments performed with *cis*-2-cyclooctenone showed clearly that it is converted to the *trans* isomer by ultraviolet irradiation in rigid hydrocarbon matrix at -190°.² In contrast, however, the irradiation of *cis*-2-cyclohexenone under the same conditions for 45 min. causes neither disappearance nor shift of the carbonyl absorption band.¹²

Acknowledgment. We thank the National Science Foundation for generous support of this work.

(12) After submission of this work for publication we learned that Professor P. E. Eaton and co-workers had also carried out studies on 2-cycloheptenone. The results of the two investigations are being published simultaneously by mutual agreement.

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Received March 16, 1965

trans-2-Cycloheptenone¹

Sir:

In a previous communication we described the preparation and properties of *trans*-2-cyclooctenone.² We

(1) By mutual agreement, this work and that of E. J. Corey, M. Tada, R. A. LeMahieu, and L. Libit on the same subject have been submitted for simultaneous publication.