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PHOTOCHEMICAL REACTIONS OF 2,6-CYCLOHEPTADIENONE

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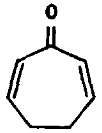
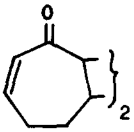
The photochemistry of cross-conjugated cyclohexadienones has been well documented (1). In view of a variety of possible transformations, we have investigated the photochemical reactions of the next higher homologue, 2,6-cycloheptadienone (I) (2), and observed that the behaviour is markedly influenced by the nature of the medium employed.

First, irradiation of cyclohexane solution of I (3) for 24 hr gave a mixture of stereoisomeric cyclodimers (II, head-to-head and/or head-to-tail) in 40-50% yield (4), from which a crystalline dimer, m.p. 134-135°, was isolated in a pure state. Spectral evidences supported the given structure (5), though the stereochemistry remained unspecified. The infrared spectrum (KBr) presented an α,β-unsaturated carbonyl band at 1670 cm^{-1}, while the nmr (6) consisted of peaks at δ 6.25 (m, 2, $=C\underline{H}CH_2$), 5.80 (dd, 2, $\underline{J}$ = 12 and 2 Hz, =CHCO), 3.70 (d, 2, $\underline{J}$ = 9 Hz, >CHCO), and 2.6-1.2 ppm (m, 10, >CH and $>CH_2$). To our knowledge, photochemical dimerization of simple cross-conjugated dienone seems to be without precedent (7).

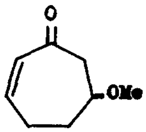
In contrast, irradiation of I in protic media was found to induce polar addition of the solvent at the expense of the dimerization. Irradiation of methanolic solution of I for 8 hr yielded 6-methoxy-2-cycloheptenone (III) as the major product. This novel polar addition to the dienone was reminiscent of the similar reactivity of 2-cycloheptenone previously observed (8). Glpc separation of the reaction mixture gave the pure sample, which exhibited infrared bands (9) at 1670 (C=O) and 1090 cm^{-1} (COC), and nmr signals at δ 6.55 (m, 1, $=C\underline{H}CH_2$), 5.95 (dd, 1, $\underline{J}$ = 12 and 6 Hz, =CHCO), 3.65 (m, 1, $C\underline{H}OMe$), 3.30 (s, 3, OMe), 2.75 (d, 2, $\underline{J}$ = 6 Hz, CH_2CO), 2.50 (m, 2, $=CHC\underline{H}_2$), and 1.95 ppm (m, 2, CH_2). As might be expected, prolonged exposure (24 hr) gave <u>cis</u>- and <u>trans</u>-



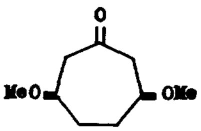
I



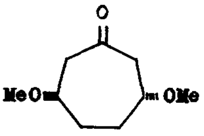
II



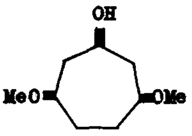
III



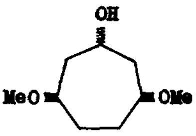
IV



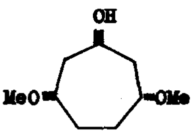
V



VIa



VIb

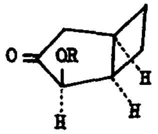


VIc

2,6-dimethoxycycloheptanone (IV and V in a 35:65 ratio) in an 80% yield, b.p. 100-110° (10 mm), each isomer being isolated by glpc. The infrared spectra (1700 and 1090 cm^{-1}) as well as the nmr showed a remarkable resemblance and were in accord with the assigned structures. Differentiation between the two stereoisomers was made on the basis of the chemical transformation. Sodium borohydride reduction of the *cis* isomer IV in ethanol gave an isomeric mixture of the corresponding alcohols VIa and VIb, whereas the *trans* isomer V a single reduction product VIc (10).

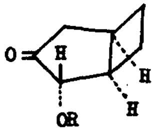
Another mode of polar addition was observed in certain acidic media. Irradiation of acetic acid solution of I for 20 hr afforded a mixture of *endo*- and *exo*-2-acetoxy-*cis*-bicyclo[3.2.0]heptan-3-one (VII and VIII, *ca.* 1:1), b.p. 100-110° (5 mm), in a 60% yield. These ketones as separated on glpc presented characteristic bands at 1760-1740 (cyclopentanone and ester) and 1230 cm^{-1} (acetate). The *endo* structure was assigned to VII on the basis that the nmr signal due to the methine proton at C-2 occurred at δ 5.25 ppm as a doublet (J = 9 Hz). The corresponding signal of the *exo* isomer VIII appeared at δ 4.65 ppm with J = 3 Hz. In a five-membered ring vicinal protons would be more strongly coupled in the *cis* configuration than the *trans* one. Furthermore, occurrence of the latter at the higher field should be ascribed to the diamagnetic anisotropy of the adjacent C-1—C-7 bond. Treatment of these acetoxy ketones with zinc dust in acetic acid yielded *cis*-bicyclo[3.2.0]heptan-3-one (IX), which was identified by comparison with the authentic specimen (ir, nmr, and glpc) (11).

Finally, similar photochemical conversion of I was observed also in *t*-butyl alcohol



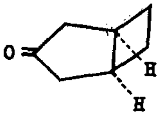
VII R = Ac

X R = Bu-*t*



VIII R = Ac

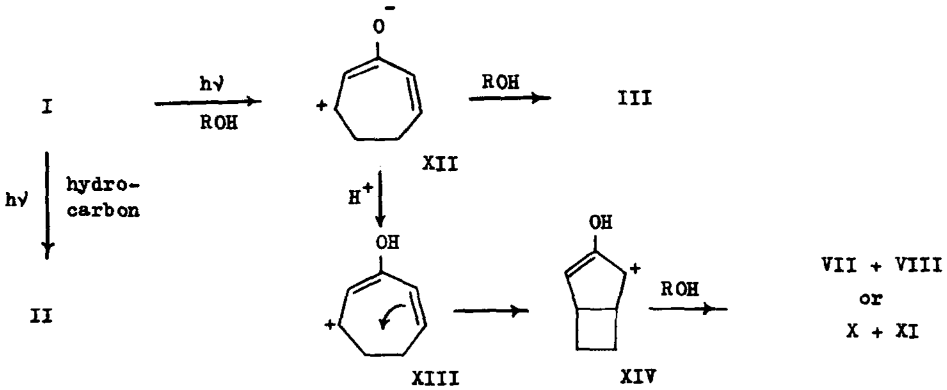
XI R = Bu-*t*



IX

in the presence of a trace amount of sulphuric acid. Thus, irradiation for 6 hr resulted in formation of an isomeric mixture of *endo*- and *exo*-2-*t*-butoxy-*cis*-bicyclo[3.2.0]heptan-3-one (X and XI, *ca.* 1:1) in a 60% yield, b.p. 110-120° (10 mm). Glpc separation gave the pure isomers. The typical carbonyl absorption at 1750-1740 cm^{-1} established the cyclopentanone structures. The stereochemistry was verified by means of nmr signal arising from the C-2 methine proton: the *endo* isomer X gave a doublet at δ 4.00 ppm (*J* = 8 Hz) while the *exo* one XI a singlet at δ 3.40 with a peak-width at the half-height of 3 Hz. Notably, in the absence of sulphuric acid such adducts could not be obtained (12). This would imply that protonation at some stage of the reaction plays an important role in this case.

Full account for the strongly solvent dependent reactions is open to studies in the future. A working hypothesis may be as follows:



Photochemical excitation of the dienone I in protic solvents would give rise to a *polar state* (13) or its chemical equivalent (XII) which is most probably hydrogen-bonded with the solvent. Polar addition of methanol, a solvent with high nucleophilicity, affords a monocyclic product III. This was the case even in the presence of sulphuric acid. In less nucleophilic media, on the other hand, protonation occurs preferentially to produce carbonium ion XIII, which is followed by ring closure and solvent attack yielding ultimately the corresponding bicyclic ketones VII and VIII (or X and XI).

REFERENCES

1. For a detailed review see P. J. Kropp, Organic Photochemistry (O. L. Chapman Ed.) Vol. 1, p. 1, Marcel Dekker, Inc., New York, N. Y. (1967).
2. E. W. Garbisch, Jr., J. Org. Chem. **30**, 2109 (1965).
3. All photolyses were effected in 0.1 *M* solution by means of a 200W high-pressure Hg arc (no filter) under nitrogen atmosphere at room temperature. The use of Pyrex filter gave practically the same results.
4. Glpc indicated that it consisted of at least three components.
5. Satisfactory elemental analyses were obtained for all new compounds.
6. All nmr spectra were obtained in 5-10% CCl_4 solution at 60 Mc using tetramethylsilane as an internal standard.
7. A number of photochemical dimerizations of *p*-quinones and γ-pyrones have been recorded. For example, (a) E. Zavarin, J. Org. Chem. **23**, 47 (1958); (b) R. C. Cookson and J. Hudec, Proc. Chem. Soc. 11 (1959).
8. H. Nozaki, M. Kurita and R. Noyori, Tetrahedron Letters 2025 (1968). Unlike well-known photoinduced polar addition of simple olefins or enones, such a type of addition to cross-conjugated dienone has not been recorded.
9. Unless otherwise stated, all ir spectra were obtained in neat liquid film.
10. Although alcoholic products VIa-VIc provided quite similar spectral data, they were differentiated on glpc each other.
11. J. Meinwald, P. Anderson and J. J. Tufariello, J. Am. Chem. Soc. **88**, 1301 (1966). The sample was generously supplied by Prof. J. Meinwald and Dr. J. Hammer, Cornell University.
12. Complex mixture was obtained. Formation of dimers II was indicated by glpc. An attempt of characterizing the other products, however, has not been made yet.
13. O. L. Chapman, Advances in Photochemistry (W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr. Ed.) Vol. 1, p. 323, Interscience Publishers, New York, N. Y. (1963). See also ref 1.