masked by the sharp singlet at τ 8.48 (three protons) assigned to the remaining methyl. The remaining methyl signal in the spectrum of VIIIa appears at τ 9.18, and the cyclopropyl hydrogen at τ 8.98.

The infrared spectrum of VIIIa (neat) has significant absorption bands at 3.28 (m), 3.30 (m), 3.36 (s), 3.39 (s), 3.42 (s), 3.50 (m), 4.47 (vs) 6.71 (s), 6.90 (s), 8.69 (m), 8.88 (m), 8.98 (m), 9.07 (s), 9.30 (m), 9.77 (s), 9.98 (w), 10.60 (w), 12.70 (s), 13.40 (s), 14.30 (vs), 14.80 (w), 16.53 (w), 17.54 (m), 19.40 (m) μ; $\lambda_{\max}^{\mathrm{CCl_4}}$ for VIIIb: 3.25 (w), 3.27 (m), 3.30 (m), 3.33 (s), 3.38 (s), 3.42 (s), 3.49 (m), 4.48 (vs), 6.71 (m), 6.87 (s), 6.94 (s), 7.30 (m), 8.95 (m), 9.05 (m), 9.30 (m), 9.71 (m), 9.90 (m), 9.98 (w), 10.18 (m), 10.35 (w), 10.47 (m), 10.89 (w), 12.75 (s), 13.10 (s), 14.28 (vs), 14.81 (w), 17.54 (m) μ.

A priori it would appear that the nonbonded interactions in the transition state leading to VIIIa should be less significant than those involved in the formation of the alternate isomer VIIIb. Indeed VIIIa is formed in higher yield, but it must be emphasized that cyclopropanes are known to fragment and/or isomerize photochemically,[1c] and the stability of VIIIa and VIIIb under the reaction conditions must be confirmed before any mechanistic significance can be attached to the stereochemical results.[9a]

Concomitant fragmentation of Ia in the alternate manner (path B) to give phenylcarbene and benzoyl cyanide and of Ib to diphenylcarbene and benzoyl cyanide was expected on the basis of our previous work.[1b,c] However, only traces of benzyl methyl ether and benzhydryl methyl ether (<5%) were produced upon irradiation of these oxiranes in methanol, and no benzoyl cyanide was detected. Furthermore, when Ib was irradiated in 2,3-dimethyl-2-butene and 2-methyl-2-butene, only the corresponding benzophenone oxetanes, mp 105–109° (lit.[10] 106–109°) and 120–122° (lit.[10] 123–125°), were detected among the by-products. It must be concluded that in the case of Ia and Ib the preferred mode of fragmentation is almost entirely by path A to give cyanophenylcarbene.

Esr and luminescence studies conducted in collaboration with Trozzolo and Yager[1f] confirm that carbene intermediates are generated upon photolysis of tri- and tetraphenyloxiranes. These results, in addition to those described herein, provide convincing evidence that phenylcyanocarbene is implicated in the photoreactions of Ia, Ib, and IV. The spin states of the carbene(s) generated from these precursors are under study.

Acknowledgments. We wish to thank the Army Research Office (Durham) for financial support of this research and Professor R. C. Petterson of Loyola University (New Orleans) for helpful discussions during the course of the study.

[9a] NOTE ADDED IN PROOF. We have recently confirmed that VIIIa and VIIIb are stable under the reaction conditions. Thus it appears that the thermodynamically more stable isomer VIIIa is favored in the addition of II to 2-methyl-2-butene.

[10] D. R. Arnold, R. L. Hinman, and A. Glick, *Tetrahedron Letters*, 1425 (1964).

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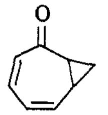
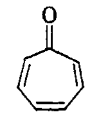
Photochemical Transformations of 2,3-Homotropone

Sir:

We wish to report the results of our examination of the photochemical behavior of 2,3-homotropone (I), a cyclic ketone which, because of its unique structural features, would be expected to undergo several competitive reactions from its photoexcited state. In common with other homoconjugated systems, the effects of the cyclopropyl group in I are not insignificant,[1] but such conjugation is not favorably disposed to permit the existence of a ring current such as is present in tropone (II).[2]



I

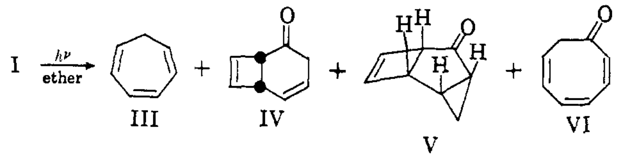


II

Exposure of a dilute solution of I[3] in anhydrous ether to a Hanovia 200-w mercury arc lamp for 2 hr, using internally cooled quartz or Pyrex vessels, resulted in the complete disappearance of I and clean conversion to a mixture of four substances as determined by vapor phase chromatography (vpc) (see Chart I). Preparative vpc of the reaction mixture permitted the isolation and purification of the four components. The products were identified (in their order of elution) as cycloheptatriene (III, 6%), bicyclo[4.2.0]octa-4,7-dien-2-one (IV, 15%), 1α,2α,4α,6α-tricyclo[4.2.0.0^{2,4}]oct-7-en-5-one (V, 68%), and 1,3,5-cyclooctatrien-7-one (VI, 11%). Spectral comparisons with authentic samples served to confirm the structures of III, IV,[4] and VI.[5]

The elemental analysis of the major component (V) (*Anal.* Calcd for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.95; H, 6.78) indicated it to be a photoisomer.

Chart I



III IV V VI

The colorless liquid exhibited pertinent infrared absorption (in CCl_4) at 3030 and 1720 cm^{-1}, a near-infrared band at 1.6339 μ (molar absorptivity = 0.385),[6] and the following ultraviolet spectrum: $\lambda_{\max}^{\text{isooctane}}$ 271 mμ (ϵ 76), 278 (86), 296 (114), 306 (118), 318 (107), and 334 (56). These data were strongly indicative of a nonplanar β,γ-unsaturated ketone, as indicated by the high intensity n → π^* transition,[7] in which the cyclopropyl group had been retained and a strained double bond had been introduced. These conclusions were reinforced by the nmr spectrum which suggested, *inter alia*, the presence of only two vinyl protons. Furthermore, catalytic hydrogenation of this ketone led to the uptake of 1 molar equiv of hydrogen; the resulting dihydro derivative af-

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[1] J. D. Holmes and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2531 (1963).

[2] C. E. Keller and R. Pettit, *ibid.*, **88**, 606 (1966).

[3] 2,3-Homotropone was prepared by a modification of the procedure of Holmes and Pettit.[1] We wish to thank Professor Pettit for his synthetic procedure in advance of publication.

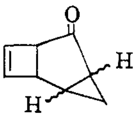
[4] The authors are indebted to Professor G. Büchi for making available to them the infrared spectrum of IV: G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962).

[5] A. C. Cope and B. D. Tiffany, *ibid.*, **73**, 4158 (1951); C. Ganter, S. M. Pokras, and J. D. Roberts, *ibid.*, **88**, 4235 (1966).

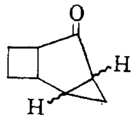
[6] P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, **31**, 166 (1966).

[7] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

forded a semicarbazone, mp 196.5–197°.[8] The structure of this photoproduct could now be defined as VII and its dihydro derivative as VIII, and it remained to elucidate the stereochemical configuration of the cyclopropyl group. The two possible isomers of VIII were synthesized as shown in Chart II.[8] Ketone X and its semicarbazone (mp 196–197°) were identical with the hydrogenated photoproduct and its derivative.[9] Thus, structure V for the photoproduct was secured.

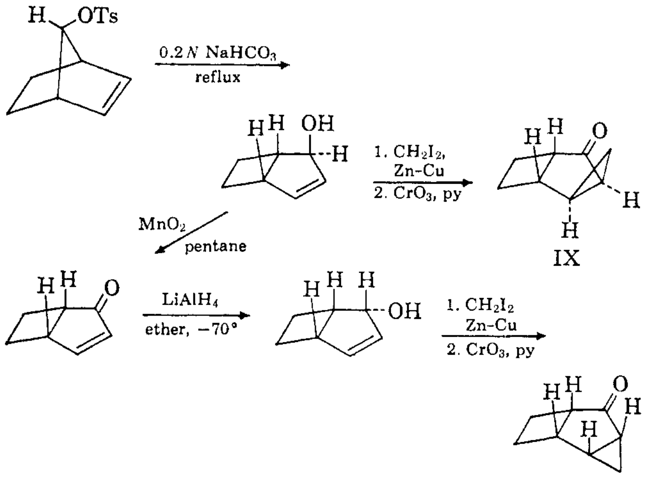


VII



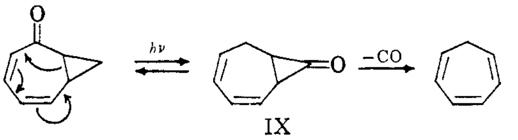
VIII

Chart II



X

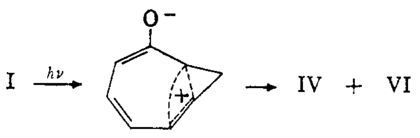
A reasonable mechanism for the formation of cycloheptatriene involves valence-bond rearrangement to the cyclopropanone derivative XI and loss of carbon monoxide.[10]



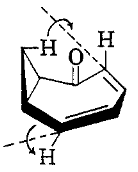
IX

The photochemical reactions by which IV and VI result are believed to be closely related and may most conveniently be depicted in terms of the polar-state concept.[10–12] The key feature of the proposed mechanism lies in the possible intervention of the mesoionic bicyclobutonium ion XII. Experiments designed to establish further, or possibly to rule out, the intervention of XII are in progress.

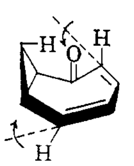
The formation of a lone tricyclic valence-bond isomer (V) is likewise theoretically interesting. This particular photochemically induced electrocyclic reaction very likely follows a concerted, disrotatory pathway.[13] However, as depicted in XIII and XIV, two disrotatory modes of cyclization are possible. Yet the process illustrated by structure XIII is followed exclusively. We attribute this high degree of stereospecificity to secondary steric forces operative during the bond reorganization. Thus, as bond rotation in XIV commences, the two vinyl protons at the terminus of the diene system and the *endo*-cyclopropyl hydrogen are effectively brought into close proximity.[14] Such repulsive forces, which are absent when the same process is effected with XIII, are apparently sufficient to raise the energy of activation which would lead to the *exo*-cyclopropyl photoproduct to an extent which permits exclusive formation of V *via* XIII.[15]



XII



XIII



XIV

Acknowledgment. The authors wish to acknowledge a grant from the Graduate School of The Ohio State University which was used in partial support of this research. We are also grateful to Badische Anilin- & Soda-Fabrik AG for their generous gift of cyclooctatetraene which was employed in the synthesis of I.

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[8] Satisfactory elemental analyses were obtained for all new compounds.

[9] The semicarbazone of IX displayed a melting point of 148.5–149°.

[10] A similar mechanistic pathway has been invoked for the low-yield conversion of tropone into benzene: O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

[11] H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88**, 5352 (1966), and references cited therein.

[12] The possibility that V may be a precursor of III, IV, or VI was eliminated by the finding that V can be recovered when subjected to the same photolytic conditions that were used for I. Furthermore, although IV is the valence tautomer of VI, Büchi and Burgess[4] have indicated that the rate of photorearrangement of VI to IV is very slow and would not be expected to assume importance during the short reaction times employed in our study. Ketones IV and VI are also not converted photochemically into III. Finally, it has been our experience that IV is not unusually sensitive to heat as suggested earlier.[4]

[13] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

[14] For the purposes of simplicity of illustration, XIII and XIV are depicted only in the *cis* conformation [for definition of the conformational nomenclature in such systems, see W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963)]. The same interpretation applies to the *trans* conformer.

[15] Indeed, the lone tricyclic photoisomer of homotropilidene (50% yield) bears a direct stereochemical relationship to V [W. R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965)] and thus the same forces seem to be operative when the carbonyl group with its sp^2 hybridization is replaced by a tetrahedral carbon atom.

[16] Fellow of the Alfred P. Sloan Foundation.

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Stereochemistry of Photodecarboxylation and Photodecarbonylation Reactions of Aryl Esters. The Photolysis of (*S*)-(+)-3,5-Di-*t*-butylphenyl 2-Methylbutanoate[1]

Sir:

The photo-Fries rearrangement[2–4] of aryl esters is accompanied in several cases by the decarboxylation process[1b,2,5] represented in eq 1. This reaction is not

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[1] (a) Photochemical Studies. V. (b) For part IV, see R. A. Finnegan and D. Knutson, *Chem. Commun*, 172 (1966). (c) This work was supported by Grant GP-5785 from the National Science Foundation.

[2] R. A. Finnegan and J. J. Mattice, *Tetrahedron*, **21**, 1015 (1965).

[3] J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963).

[4] H. Kobsa, *J. Org. Chem.*, **27**, 2393 (1962).

[5] R. A. Finnegan and D. Knutson, *Chem. Ind.* (London), 1837 (1965).