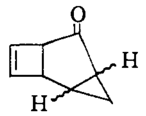
forded a semicarbazone, mp 196.5–197°.[8] The structure of this photoproduct could now be defined as VII and its dihydro derivative as VIII, and it remained to elucidate the stereochemical configuration of the cyclopropyl group. The two possible isomers of VIII were synthesized as shown in Chart II.[8] 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

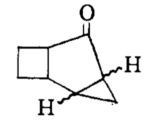
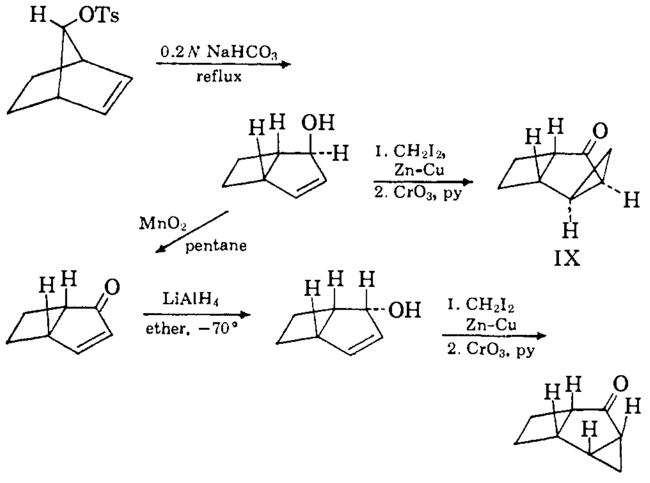
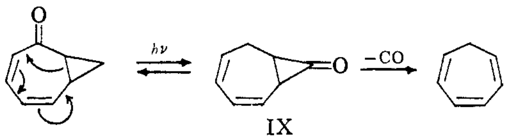

VIII

Chart II



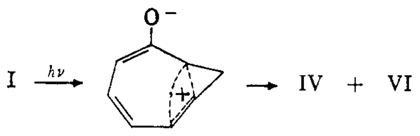
X

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



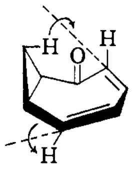
IX

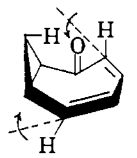
The photochemical reactions by which IV and VI result are believed to be closely related and may most conveniently be depicted in terms of the polar-state concept.[10–12] The key feature of the proposed mechanism lies in the possible intervention of the mesoionic bicyclobutonium ion XII. Experiments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



XII

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


XIII


XIV

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]

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.

---

[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 sp² hybridization is replaced by a tetrahedral carbon atom.

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

Leo A. Paquette,[16] Osvaldo Cox
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received December 5, 1966

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

---

[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).

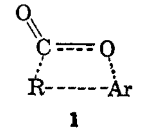
[4] H. Kobsa, *J. Org. Chem.*, 27, 2393 (1962).

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

$$RCO_2Ar + h\nu \longrightarrow RAr + CO_2 \qquad (1)$$

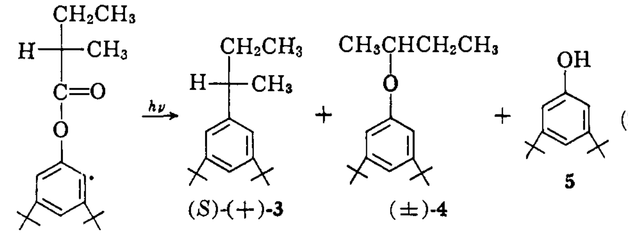
R may be alkyl or aryl

only of theoretical interest but also may prove useful for the preparation of biaryls[2,5] and alkyl aromatics[1b] which might otherwise be obtainable only with difficulty.[6] We have suggested earlier[5] that this photoexpulsion of carbon dioxide proceeds in a concerted fashion *via* a transition state schematically illustrated by **1**. Such a mechanism requires that the configuration of the α carbon in the R group be retained during the transformation. That this is indeed the case is demonstrated by experiments which we now wish to report.



1

(*S*)-(+)-2-Methylbutanoic acid, $[\alpha]_D$ +18.5° (*c* 0.140 g/ml, $CHCl_3$) (lit.[7] $[\alpha]^{25}_D$ +19.2°, neat), obtained by oxidation[8] of commercially available (−)-2-methylbutanol (98% optically pure), was converted *via* the acid chloride[8] to its 3,5-di-*t*-butylphenyl ester (**2**)[9] (mp 27°; $\nu_{\max}^{\text{film}}$ 1760 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 263 mμ (ε 215); $[\alpha]_{589}$ +14.8°, $[\alpha]_{578}$ +15.2°, $[\alpha]_{546}$ +17.4°, $[\alpha]_{436}$ +29.8°, $[\alpha]_{365}$ +47.1° (*c* 0.0425 g/ml, $CHCl_3$)) which was homogeneous by gas chromatographic criteria. Irradiation[10] of **2** (*ca.* 0.05 *M* in dioxane) for 15 hr yielded (+)-2-(3,5-di-*t*-butylphenyl)butane[9] (**3**) (15–20%; $\nu_{\max}^{\text{film}}$ 850 and 730 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 264 and 270 mμ (ε 390 and 380); $[\alpha]_{589}$ +18.8°, $[\alpha]_{578}$ +19.3°, $[\alpha]_{546}$ +22.3°, $[\alpha]_{436}$ +39.2°, $[\alpha]_{365}$ +64.8° (*c* 0.0206 g/ml, CCl_4)), an isomeric hydrocarbon[11] (6%), 3,5-di-*t*-butylphenyl *sec*-butyl ether[9] (**4**, racemic) (3%; $\nu_{\max}^{\text{film}}$ 845 and 705 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 275 and 282 mμ (ε 1400 and 1350)), and 3,5-di-*t*-butylphenol (**5**; 75%) (see eq 2). A similar irradiation of **2** in benzene solution produced the hydrocarbon **3** (13%), the racemic ether **4** (9%), and the phenol **5** (*ca.* 50%). When absolute ethanol was used as solvent, **3** and **4** were formed in barely detectable amounts with **5** being the major product. In no case were we able to isolate a Fries rearrangement product.



(*S*)-(+)-**2** (*S*)-(+)-**3** (±)-**4** **5** (2)

The positive ORD curve measured for the product **3** proves its absolute configuration to be identical with that of (+)-2-phenylbutane which is known to be (*S*).[12–15] It follows that the photochemical loss of carbon dioxide from **2** occurs with predominant retention of configuration, and thus the proposal of a concerted mechanism for this reaction is strongly supported.[16,17]

Finally, the bearing which these results have on the nature of the competing *decarbonylation* reaction[1b] (eq 3) requires comment. The proposal of Kobsa[4] that the

$$RCO_2Ar \longrightarrow ROAr + CO \qquad (3)$$

photo-Fries rearrangement involves acyl–oxygen bond homolysis with formation of a solvent–caged radical pair has enjoyed general acceptance[2,19–22] although alternative views have been advanced.[3,23–25] This intermediate radical pair[26] has also been invoked to explain the ready decarbonylation of certain esters[19,20] leading to high yields of the corresponding phenol. The phenol is thought to arise from the reaction of an aryloxy radical with a suitable hydrogen atom donor. That the ether (ROAr) is formed in sufficient quantity

---

[6] The preparative utility of this method has been enhanced by our discovery that the product distribution is apparently solvent dependent. Conversions to decarboxylation products are increased, and to Fries rearrangement products decreased, in solvents such as ether and dioxane. The converse is true when ethanol, 2-propanol, or dimethylformamide is used as solvent. The generality of this phenomenon, which is more pronounced for benzoate than for alkanoate esters, is under study and details will be published in due course.

[7] F. L. Weissenborn, J. W. Bolger, D. B. Rosen, C. T. Mann, Jr., L. Johnson, and H. L. Holmes, *J. Am. Chem. Soc.*, 76, 1792 (1954); see also J. Cassanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, 31, 3473 (1966).

[8] R. Lukeš and J. Lanthaler, *Chem. Listy*, 51, 1869 (1957).

[9] Satisfactory microanalytical data were obtained.

[10] A 450-w, medium-pressure mercury lamp (Hanovia 79A36), housed in a double-walled quartz immersion well, was employed. The progress of the reaction was monitered by gas chromatography.

[11] Infrared maxima at 890 and 820 cm^{-1} suggest that this substance is a 1,2,4-trisubstituted benzene formed by subsequent photoisomerization of the primary decarboxylation product.[1b,5] We have found, in other cases, that this isomerization can be suppressed by using a Corex filter.

[12] L. Verbit, *J. Am. Chem. Soc.*, 87, 1617 (1965).

[13] R. K. Hill and L. A. Gardella, *J. Org. Chem.*, 29, 766 (1964).

[14] V. K. Honwad and A. S. Rao, *Tetrahedron*, 20, 2921 (1964).

[15] D. J. Cram, *J. Am. Chem. Soc.*, 74, 2137, 2149 (1952).

[16] Since the optical purity of **3** is unknown, the precise degree of stereospecificity observed during its formation cannot be calculated. However, comparison of the molecular rotations of **2** and **3** with those of the unsubstituted phenyl analogs suggests that the degree is quite high.

[17] We planned initially to circumvent the problem outlined in ref 16 by studying the irradiation of (*S*)-(+)-phenyl 2-methylbutanoate ($[\alpha]_{589}$ +22.7°, $[\alpha_{578}]$ +24.1°, $[\alpha]_{546}$ +27.4°, $[\alpha]_{436}$ +47.4°, $[\alpha]_{365}$ +76.0° (*c* 0.0567 g/ml, $CHCl_3$)) since the requisite optical data for the anticipated decarboxylation product, 2-phenylbutane, are known. Surprisingly, no 2-phenylbutane was found among the reaction products which did include, however, the Fries rearrangement product: *o*-hydroxy-α-methylbutyrophenone ($\nu_{\max}^{\text{film}}$ 3500–2400 and 1640 cm^{-1}; $\lambda_{\max}^{95\%\,\text{EtOH}}$ 255 and 330 mμ (ε 18,400 and 6540); $\lambda_{\max}^{95\%\,\text{EtOH-KOH}}$ 230, 259 sh, and 372 mμ (ε 31,000, 10,800, and 8650); $[\alpha]_{589}$ +25.6°, $[\alpha]_{578}$ +27.5°, $[\alpha]_{546}$ +32.0°, $[\alpha]_{436}$ +66.7° (*c* 0.0182 g/ml, $CHCl_3$)).[18] We note that in all cases in which decarboxylation was observed,[1b,2,5] the phenol moiety of the starting ester has carried at least one alkyl substituent (*cf.* footnote 11 in ref 5).

[18] These rotations for the hydroxy ketone were measured on the product obtained by irradiation of a sample of starting phenyl ester having $[\alpha]_D$ +16.2°. The rotations given in ref 17 for the phenyl ester were measured on a specimen prepared from a portion of the same acid chloride sample used to prepare ester **2**.

[19] D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *J. Chem. Soc.*, 3571 (1965).

[20] W. M. Horspool and P. L. Pauson, *ibid.*, 5162 (1965).

[21] F. L. Bach and J. C. Barclay, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 9S.

[22] D. Belluš, P. Hrdlovič, and Z. Maˇasek, *Polymer Letters*, 4, 1 (1966).

[23] J. Saltiel in "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press, New York, N. Y., 1964, pp 312–313.

[24] E. D. A. Plank, Ph.D. Thesis, Purdue University, 1966; *Dissertation Abstr.*, B27, 415 (1966).

[25] G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, 70, 3479 (1966).

[26] As pointed out by J. J. Mattice (M.S. Thesis, The Ohio State University, 1963), the intermediate (transition state?) may, in fact, possess a considerable degree of polar character, depending on the nature of the substituents and the solvent.

for isolation implies that the separation of carbon monoxide occurs prior to the diffusion of the residual components from the cage. Furthermore, the finding that the ether **4** (eq 2) obtained in the present work was optically inactive rules out conceivable mechanisms in which the R group is not free to racemize and accords most simply with a radical recombination step.

R. A. Finnegan, D. Knutson
Department of Medicinal Chemistry, School of Pharmacy
State University of New York at Buffalo
Buffalo, New York 14214

Received January 16, 1967

Book Reviews

Carbocyclic Non-Benzenoid Aromatic Compounds. By DOUGLAS LLOYD, Senior Lecturer in Chemistry, United College of St. Salvador and St. Leonard, University of St. Andrews (Scotland). American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1966. x + 220 pp. 15.5 x 23 cm. $13.00.

I have awaited the appearance of this book with bated breath as the time has come, due to the research explosion in this field, for the publication of an up-to-date sequel to "Non-Benzenoid Aromatic Compounds" published in 1959. In the 1959 volume, a number of authorities banded together to produce a book of wide scope in which the material was critically discussed throughout. The announced size of the volume under review appeared to be just right for bringing the subject up-to-date and to introduce a discussion of systems which were unknown or just beginning to be recognized in 1959.

A monograph is of value mainly if it treats its subject critically. It may be of some, though lesser value, if the material is presented as a factual, uncritical review, provided it is at least an exhaustive treatment, enabling the reader to save time in searching the literature, even if he must do the critical evaluation himself. Unfortunately, there is very little in the present volume to commend on either count.

The first chapter on "Aromaticity and Aromatic Character" (15 pages) is superficial and not up-to-date. Although the definition of aromaticity based upon ring current, as determined experimentally from the nmr spectrum, is given and incidentally mentioned in the section on annulenes, no criticism is made, pro or con, of this method of measuring aromaticity. The second chapter on "Derivatives of Cyclopropene" (19 pages) is a short factual review of work on these compounds carried out within the past 6–7 years, including some references to the 1965 literature. This chapter as well as the next on "Derivatives of Cyclobutadiene" (20 pages) at least contain many references subsequent to 1959 though much of the information in the latter chapter may be found, critically treated by Baker and McOmie, in the 1959 volume. Relatively, this is even more evident in the chapter on "Derivatives of Cyclopentadiene" (43 pages). The next two chapters concern themselves with "Tropylium Salts" (19 pages) and "Tropone, Tropolones and Related Compounds" (45 pages). The first of these cites 68 (out of 88) references of work published since 1958; the latter cites 60 (out of 250) references of work published during the same period. The indication given by this arithmetic is amply justified by reading the text which in the main is a rehash of material previously reviewed critically by Nozoe.

The next chapter on "Medium and Large Ring Compounds" is of 19 pages' duration. Much recent information appears on annulenes, including papers after 1963 when the chemistry of annulenes, making up the bulk of this chapter, was more ably reviewed by Sondheimer (Chapter 7, ref 41). Vogel's bridged cyclodecapentaenes are recorded but though "cyclononatetraenides" form a section of 2 pages, no mention is made of the important contributions of Winstein and of others to the chemistry of cyclononatriene (*e.g.*, *J. Am. Chem. Soc.*, **86**, 4485 (1965)), which might have been of interest in the context of critical comments in this chapter were the subject treated critically.

The ultimate chapter of the book is entitled "Polycyclic Compounds" (35 pages). There is little or no justification for a rehash of synthetic methods for preparing azulenes; indeed their classification and some of the examples parrot those of Keller-Schierlien and Heilbronner in the 1959 volume, except that these authors treated the subject critically. Those of Hafner's papers which could not have been mentioned in 1959, for chronological reasons, are referred to in the present book. The last 9 pages treat cursorily the sesquifulvalenes, calicenes, pentalenes, and heptalenes, and some recent references are cited. The book is pleasant to look at, its formulas esthetically pleasing. For the reasons given above, however, it is very disappointing and is not recommended.

David Ginsburg
Department of Chemistry, Technion, Israel Institute of Technology
Haifa, Israel

BOOKS RECEIVED, *February 1967*

R. J. CREMLYN. "A Concise Organic Chemistry." Sir Isaac Pitman and Sons, Ltd., Parker St., London, WC2, England. 1966. 194 pp. 35/-net.

ESSAM E. EL-HINNAWI. "Methods in Chemical and Mineral Microscopy." American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1966. 222 pp. $16.50.

W. T. ELWELL and F. WOOD. "Analysis of the New Metals. Titanium, Zirconium, Hafnium, Niobium, Tantalum, Tungsten and their Alloys." Pergamon Press Inc., 44-01 21st St., Long Island City, N. Y. 1966. $9.50.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY. "Nomenclature of Organic Chemistry, Sections A and B." Second Edition. Butterworth Inc., 7300 Pearl St., Washington, D. C. 1966. 86 pp. $5.00.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY. "Nomenclature of Organic Chemistry, Section C." Butterworth Inc., 7300 Pearl St., Washington, D. C. 1965. 260 pp. $9.50.

TOMIHITO KAMBARA, Editor. "Modern Aspects of Polarography. A Tribute to Isamu Tachi." Plenum Publishing Corp., 227 West 17th St., New York, N. Y. 1966. 245 pp. $10.00.

IVAN IVANOVICH KORNILOV. "The Chemistry of Metallides." Plenum Publishing Corp., 227 West 17th St., New York, N. Y. 1966. 156 pp. $22.50.

GÜNTHER KRAFT. "Handbuch der Analytischen Chemie." Band IV. "Elemente der Vierten Hauptgruppe." II–IV. Springer-Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, Germany. 1966. 222 pp. DM 64.

KURT RANDERATH. Translated by D. D. LIBMAN. "Thin-Layer Chromatography." Second Revised and Enlarged Edition. Verlag Chemie, GmbH, Weinheim-Bergstr., Germany. 1966. 285 pp. $9.50.

ALLAN SHARPLES. "Introduction to Polymer Crystallization." St. Martin's Press, 175 Fifth Ave., New York, N. Y. 1966. 138 pp. $6.50.

DUNCAN J. SHAW. "Introduction to Colloid and Surface Chemistry." Butterworth Inc., 7300 Pearl St., Washington, D. C. 1966. 186 pp. $6.50.

PHILIP E. SLADE, JR., and LLOYD T. JENKINS, Editors. "Techniques and Methods of Polymer Evaluation." Volume 1. "Thermal Analysis." Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1966. 253 pp. $10.75.

E. C. SLATER, Editor. "Flavins and Flavoproteins." American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1966. 549 pp. $27.00.

FRANTIŠEK ŠORM and LADISLAV DOLEJŠ. "Guaianolides and Germacranolides." Holden-Day, Inc., 500 Sansome St., San Francisco, Calif. 1966. 153 pp. $9.75.

K. A. WILLIAMS. "Oils, Fats, and Fatty Foods. Their Practical Examination (Bolton and Revis)." Fourth Edition. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1966. 488 pp. $18.50.