Branch, Division of Research Resources, National Institutes of Health, under Grant No. PR-330.

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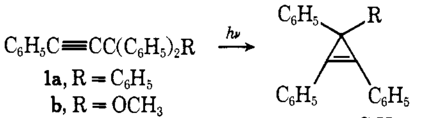
Received February 16, 1971

Photocyclization of Aryl-Substituted Acetylenes; Application of Di-π-methane-like Rearrangements to Arylcyclopropene Syntheses[1]

Sir:

In a continuation of previous studies on the photocyclization of aryl-substituted propenes[2] and related functionalized propenyl systems, such as 3-alkoxy-substituted propenes,[3] we have investigated the photochemistry of several aryl-substituted acetylenes with the intent of developing a convenient route to cyclopropenes including functionalized systems which in turn might serve as precursors for cyclopropenium derivatives.[4] Our continuing interest in the photochemistry of cyclopropenes[5a-d] provided an additional incentive for this study.

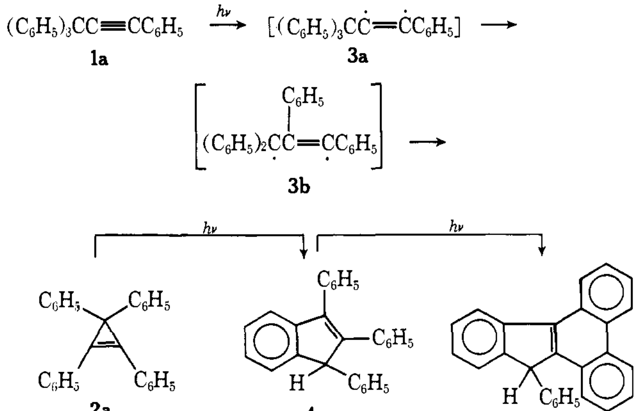


1a, R = C_6H_5
b, R = OCH_3

2a, R = C_6H_5
b, R = OCH_3
c, R = OC_2H_5
d, R = H

Tetraphenylpropyne (**1a**) was synthesized by a procedure[6a] which is a modification of the Wieland and Closs method.[6b] Irradiation of **1a** (500 mg) in 500 ml of cyclohexane (0.003 *M*) at 253.7 nm for relatively short periods (3.4 hr) in a preparative photochemical reactor[7a] while simultaneously sparging with a slow stream of argon provided 230 mg (46%) of **2a**, mp 177.5–9° (lit.[5b] mp 176–178°) which may be isolated by elution chromatography on alumina.

For convenience the mechanism for the rearrangement of **1a** is formulated as a diradical process as outlined below.[4]



2a 4 5

The formation of **2a** indicates that the intermediate, perhaps **3b**, formed by rearrangement of a diradical-like intermediate such as **3a** cyclizes at least in part in a process analogous to the photochemical rearrangement of propenes to cyclopropanes.[2,3] Alternatively, and perhaps more likely, the reaction proceeds in a concerted manner.[8]

Additional photoproducts begin to form when the irradiation time is extended as evidenced by the appearance of nmr signals at τ 4.94 and 4.67 ($CDCl_3$), characteristic of the benzyl protons of **4** and **5**, respectively.[5a,b] An nmr study[9a] of the variation in product composition as a function of time under standard irradiation conditions in benzene[7b] proved instructive. The quantitative data summarized in Table I were determined utilizing the four-proton aromatic multiplet for **2a** centered at τ 2.30 ($CDCl_3$) in addition to the singlets for the benzyl protons of **4** and **5**. Although these data confirm that the photolysis of **1a** in cyclohexane[7b] proceeds in high conversion (~80%) upon

Table I

Time, hr	%		
	2a	**4**	**5**
24	25	42	19
4	46	35	9
1	70	Trace	Trace

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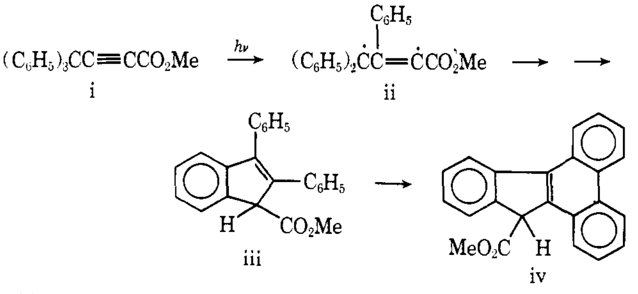
(1) A preliminary report of this work was presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(2) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(3) J. J. Brophy and G. W. Griffin, *ibid.*, 493 (1970).

(4) Recently, J. W. Wilson and K. L. Huhtanen (*Chem. Commun.*, 454 (1968)) described the photochemical rearrangement of methyl 3,3,3-triphenylpropyne carboxylate (i) to the indenophenanthrene (iv). The diradical species ii was proposed as a possible intermediate leading to the indene iii which in turn undergoes subsequent dehydrocyclization to iv. A similar diradical species has been postulated by us as an intermediate in the thermal[5a] and photochemical[5b] rearrangement of tetraphenylcyclopropene (**2a**) to triphenylindene **4**.



(5) (a M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 907 (1967); (b) R. H. Grubbs, M.S. Thesis, University of Florida, 1965; (c) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 1579 (1966); (d) H. Kristinsson, *Tetrahedron Lett.*, 2343 (1966); (e) A. S. Monahan, J. D. Freilich, and J. J. Fong, *ibid.*, 1865 (1970); (f) H. Dürr, *Justus Liebigs Ann. Chem.*, **723**, 102 (1969).

(6) (a) A. W. Herriot, Ph.D. Thesis, University of Florida, 1967; (b) H. Wieland and H. Closs, *Justus Liebigs Ann. Chem.*, **470**, 201 (1929).

(7) (a) The preparative irradiations were conducted in a Rayonet RPR 208 Reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) with 8 RUL 253.7-nm lamps; (b) an RPR-100 unit equipped with 16 8-W 253.7-nm lamps; (c) an RPR-100 unit fitted with 16 8-W 310.0- or 350.0-nm lamps.

(8) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

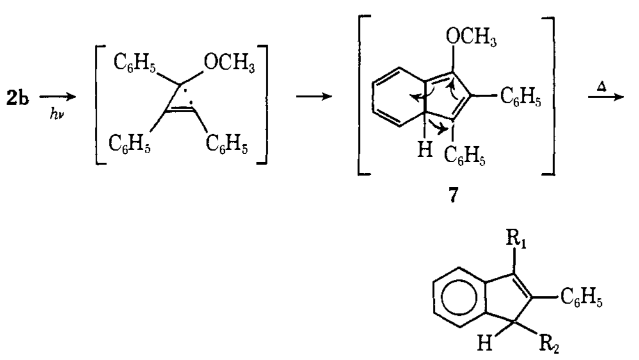
(9) (a) All nmr spectra were recorded on a Varian A-60 instrument in the solvent indicated with tetramethylsilane as an internal standard; (b) all new compounds gave satisfactory combustion and/or mass spectral analyses; (c) mass spectral data were obtained on a Perkin-Elmer Hitachi RMU-6 spectrometer.

prolonged irradiation (24 hr) the separation of the products by column chromatography proved difficult. In general, the fractions contained at least two components; however with care, **2a**, **4**, and **5** were separated in a state of purity sufficient for definitive characterization albeit in low yields (8, 7, and 4%, respectively).

The presence of tetraphenylcyclopropene (**2a**) in aliquots of irradiated cyclohexane solutions[7b] of **1a** is also evident from the ultraviolet absorption maximum apparent at 334 mμ (lit.[5b] λ_{max} 334 mμ (ϵ 23,700)). The photorearrangement of **1a** was monitored at 15-min intervals by ultraviolet spectroscopy and in agreement with the nmr data **2a** is the major product and only traces of **4** and **5** are formed during the first hour of irradiation. These results indicate that the indene **4** and indenophenanthrene **5** obtained upon photolysis of **1a** are secondary products arising from rearrangement of cyclopropene **2a**, a result clearly consistent with the known photolability of this and other cyclopropenes (*vide infra*).[4,5]

No cyclopropenyl or indenyl products are observed when **1a** is irradiated[7c] in a Pyrex vessel for up to 20 hr in acetone solution or in the presence of such sensitizers as benzophenone or acetophenone. This result is indicative that the rearrangement of tetraphenylpropyne (**1a**) to tetraphenylcyclopropene (**2a**) proceeds by a singlet mechanism.

The functionalized acetylene **1b** also cyclizes upon irradiation to give a cyclopropene **2b**, which is a convenient precursor for cyclopropenium salts.[10] 1,3,3-Triphenylprop-1-yn-3-ol,[11] mp 79–80° (lit.[11] mp 82°), prepared by addition of phenylethynylmagnesium bromide to benzophenone and subsequent hydrolysis, was converted to the methyl ether (mp 122–123°) in high yield by treatment with methyl iodide in dimethyl sulfoxide under basic conditions according to the method of Gillis.[12] Irradiation[7b] of degassed solutions of **1b** (0.011 *M* in benzene) gives methoxycyclopropene (**2b**) in an amount which also is dependent on the duration of irradiation. The nmr signal at τ 6.66 arising from the methoxy protons of **2b** as well as the benzyl proton signal at τ 5.30 may be differentiated from the aliphatic signal of the precursor **1b** at τ 6.59 after 10-hr irradiation provided the spectra are determined in benzene, the irradiation solvent. The yield of **2b** does not exceed 5% and at this time the appearance of an additional photoproduct (17%) was evident because of the emergence of a second methoxy signal at τ 6.37. This product was shown to be the indenyl ether **8a** by hydrolysis to 2,3-diphenyl-1-indanone identical in all respects with an authentic sample of this material.[13] The ratio of **8a** to **1b** as determined by nmr reaches 1:1.7 after photolysis (53 hr).[7b,14] That **8a** may arise from **2b** in a secondary photoprocess was confirmed by irradiation of **2b** in benzene for 16 hr[7b] whereupon the conversion to **8a** reaches 43% The indenyl ether **8c** was prepared independently from 2,3-diphenyl-1-indenone[15] by reduction with sodium borohydride in methanol followed by methylation with diazomethane and boron trifluoride etherate[16] and the characteristic nmr signals at τ 4.40 and 7.03 (benzyl and methoxy protons, respectively) were conspicuously absent from the benzene solution obtained upon photolysis of **2b** or for that matter **1b**.[7b] This is not unexpected since opening and recyclization of **2b** would give the isoindene intermediate **7** which can undergo a thermally allowed 1,5-sigmatropic shift[8] with aromatization leading to **8a**.[17] In contrast, formation of **8c** from **8a**, in the absence of base, requires two additional successive 1,5 shifts involving formation of an *o*-xylylene intermediate[18] and concomitant loss of aromaticity, an overall process which is energetically unfavorable at room temperature, but does occur to some extent at elevated temperatures.[14] It has been demonstrated previously[10] that **2b** is readily converted to triphenylcyclopropenium bromide by treatment with anhydrous hydrogen bromide and thus a new route to these ionic species becomes available if convenient separation techniques can be devised.



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8a, $R_1 = OCH_3$; $R_2 = C_6H_5$
b, $R_1 = OC_2H_5$; $R_2 = C_6H_5$
c, $R_1 = C_6H_5$; $R_2 = OCH_3$
d, $R_1 = C_6H_5$; $R_2 = H$

Irradiation of **1b** in cyclohexane[7b] leads to a complex mixture of products including **8d** and perhaps **2d** although further studies are necessary to characterize the reaction products obtained in this solvent fully.

An examination of the photochemical behavior of the arylpropynes $R_1R_2R_3CC{\equiv}CC_6H_6$ where $R_1 = R_2 = R_3 = H$ (**9**), $R_1 = R_2 = H$, $R_3 = C_6H_5$ (**10**), and $R_1 = R_2 = C_6H_6$, $R_3 = H$ (**11**) also has been performed; however no products analogous to those obtained with **1a** and **1b** were detected. In fact **9** is relatively photostable[7b] while **10** and **11** gave products whose structures remain to be determined.[19]

Acknowledgment. We wish to thank Dr. N. Portnoy, Dr. R. Bost, Dr. D. J. Keyton, and Mrs. J. Thompson for invaluable technical assistance provided during the course of this work. Support for this research by the National Science Foundation (Grants GP 9434 and GP 9412), the Petroleum Research Fund (PRF 2813-

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(10) R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958).

(11) K. Hess and W. Weltzien, *Chem. Ber.*, **54**, 2511 (1921).

(12) R. G. Gillis, *Tetrahedron Lett.*, 1413 (1968).

(13) C. F. Koelsch, *J. Amer. Chem. Soc.*, **56**, 1337 (1934).

(14) We found that tractable quantities of **8a** were conveniently prepared in high yield (86.5%) by thermolysis of **2b** at 250° (10 min). Additional products included 1-methoxy-2,3-diphenylindene (**8c**) (~3%) and an oxidation product, 2,3-diphenyl-1-indanone (9.5%). The thermal reactions of **2a**, **2b**, and a variety of other cyclopropenes including the cyano analog of **2b** will be the subject of a subsequent communication.

(15) K & K Laboratories, Inc., Plainview, N. Y.

(16) M. C. Caserio, J. D. Roberts, M. Neeman, and W. S. Johnson, *J. Amer. Chem. Soc.*, **80**, 2584 (1958); E. Müller and W. Rundel, *Angew. Chem.*, **70**, 105 (1958).

(17) Monahan and coworkers have shown in independent studies that **2c**, the ethoxy analog of **2b**, is converted to the ethoxy indene **8b** in 70% yield upon irradiation in benzene under nitrogen with 350-nm lamps.[5e]

(18) W. Roth, *Tetrahedron Lett.*, 1009 (1964).

(19) J. J. Brophy and G. W. Griffin, unpublished results.

Al), and the Alfred P. Sloan Foundation is also gratefully acknowledged.

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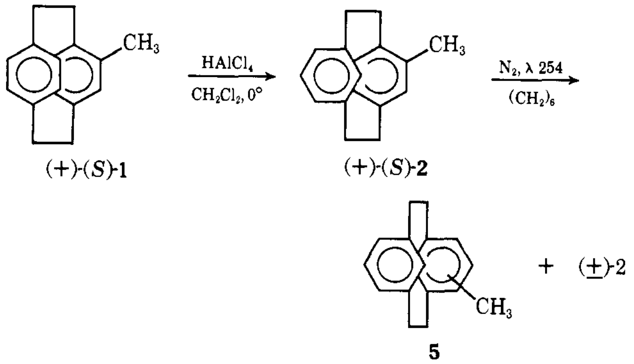
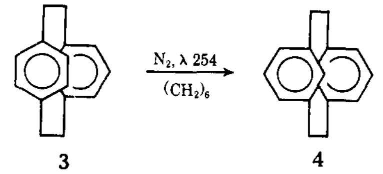
Received January 21, 1971

Stereochemistry of [2.2]Cyclophane Rearrangements[1]

Sir:

We report the acid-catalyzed rearrangement of optically pure (+)-(*S*)-4-methyl[2.2]paracyclophane ((+)-**1**) to optically pure (+)-(*S*)-12-methyl[2.2]metaparacyclophane ((+)-**2**), the photolytic conversion of [2.2]metaparacyclophane (**3**) to [2.2]metacyclophane (**4**), and the photolytic racemization and rearrangement of (−)-**2** to a mixture of methyl[2.2]metacyclophanes (**5**).

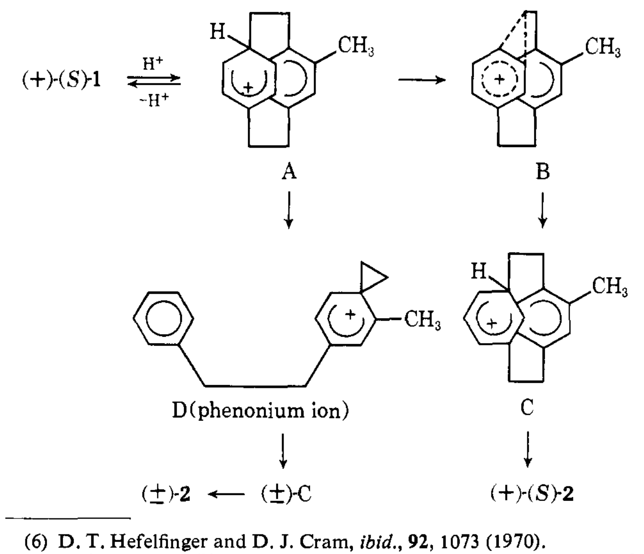




Optically pure (+)-(*S*)-**1**[2] [mp 150–152°, $[\alpha]^{25}_{546}$ +114° (*c* 1.0 $CHCl_3$)] (the configuration of (−)-(*R*)-**1** is established)[3a] was prepared[3b] and submitted to the acid conditions used to rearrange [2.2]paracyclophane to [2.2]metaparacyclophane.[4] The product, (+)-**2**, was isolated (52%) by chromatographic and sublimation procedures free of optical fractionation, mp 61–64.5°, $[\alpha]^{25}_{546}$ +27.0°, $[\alpha]^{25}_{436}$ +28.0° (*c* 1.02 $CHCl_3$). Recrystallization gave material, mp 66–67°, rotation unchanged. The enantiomer, (−)-**2**, was prepared from (+)-12-carboxy[2.2]metaparacyclophane ((+)-**6**),[5a] mp 164–168°, $[\alpha]^{25}_{546}$ +33.7°, $[\alpha]^{25}_{436}$ +115° (*c* 1.0 $CHCl_3$). Reduction of this acid with lithium aluminum hydride (in THF) gave (64%) (−)-12-hydroxymethylene[2.2]metaparacyclophane[2] ((−)-**7**), mp 99–100°, $[\alpha]^{25}_{546}$ −7.3°, $[\alpha]^{25}_{436}$ +0.2°, $[\alpha]^{25}_{365}$ +38.2° (*c* 1.0 $CHCl_3$), which with phosphorus tribromide in methylene dichloride gave (67%) (+)-12-bromomethylene[2.2]metaparacyclophane[2] ((+)-**8**), mp 92–93°, $[\alpha]^{25}_{546}$ ±85.7°, $[\alpha]^{25}_{436}$ +193° (*c* 1.0 $CHCl_3$). Reduction of this bromide with lithium aluminum hydride (THF) gave (60%) (−)-**2**,[2] mp 65–66°, $[\alpha]^{25}_{546}$ −26.3°, $[\alpha]^{25}_{436}$ −27.4° (*c* 1.0 $CHCl_3$). At each stage, the above compounds were recrystallized to maximum melting points and rotations. Admixture of equal amounts of the above samples of (−)- and (+)-**2** gave mp 43–45°, undepressed by admixture with authentic (±)-**2**.[5b] The fact that the rotations of **2** prepared by rearrangement of (+)-**1** and from (+)-**6** are of equal magnitude indicates that (+)-**1**, (+)-**2**, and (−)-**2** were essentially optically pure, and that (+)-**1** → (+)-**2** proceeded stereospecifically.

Of the two most likely general mechanisms formulated, these results eliminate the phenonium ion route ((+)-**1** → A → D → (±)-C → (±)-**2**), since D possesses a mirror plane, and only (±)-**2** would be produced. The route (+)-(*S*)-**1** → A → B → C → (+)-**2** provides the required fully chiral reaction coordinate if rotation of the methyl-substituted benzene ring with respect to the other benzene ring is sterically inhibited in A, B, and C. Molecular models point to such steric inhibition of rotation, and such rotation in (+)-12-carbomethoxy[2.2]metaparacyclophane does not occur up to 200°.[5a] Structure B might be an intermediate or a transition state in this mechanism.

The absence of alternate mechanisms with fully chiral reaction coordinates allows assignment of configuration to (+)-**2**. The fact that the meta ring of **2** rotates with respect to the para ring at 25° to provide a conformational equilibrium mixture[5a,6] complicates the structure and name given to compound (+)-**2**. However, the facts that the equilibrium mixture is dominated by the form with the methyl anti to the meta ring and crystallizes only in that form[5a,6] suggest that the structure written for (+)-**2** is the more appropriate and this structure possesses the *S* configuration.[7] This assignment fixes the configurations of (+)-**6**, (−)-**7**, and (+)-**8** as *R*.



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[1] The authors warmly thank the National Science Foundation for a grant that supported part of this research. M. H. Delton thanks the Regents of the University of California for a First Year Fellowship, and R. E. Gilman thanks the National Science Foundation for a Science Faculty Fellowship, 1970–1971.

[2] All new compounds gave carbon and hydrogen analyses within 0.3% of theory and nmr spectra expected for the assigned structures.

[3] (a) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **91**, 4557 (1969); (b) M. H. Delton and D. J. Cram, *ibid.*, **92**, 7623 (1970).

[4] D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *ibid.*, **88**, 1324 (1966).

[5] (a) D. T. Hefelfinger and D. J. Cram, *ibid.*, in press; (b) *ibid.*, in press.

[6] D. T. Hefelfinger and D. J. Cram, *ibid.*, **92**, 1073 (1970).

[7] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 400 (1966).