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R. L. Markezich,[6] H. W. Whitlock, Jr.,*
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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The Photochemical Methanolysis of Arylcyclopropanes. Substituent Effects

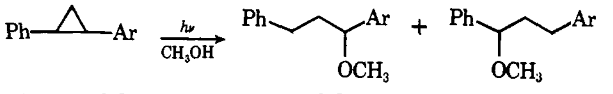
Sir:

In 1966 Griffin and coworkers[1] reported the photochemical addition of methanol to 1,2-diphenylcyclopropane and to other polyphenylcyclopropanes. As suggested by these investigators, the products can best be rationalized as arising from a polar addition to the excited three-ring compound. Thus the reaction is a very intriguing one, for the other photochemical reactions undergone by these cyclopropanes seem to be very adequately rationalized as proceeding *via* diradical intermediates.[1] Since the polar addition could occur *via* a variety of interesting pathways, we have studied the photochemical methanolysis of various aryl-substituted diphenylcyclopropanes in order to obtain more insight into the mechanism of this reaction.

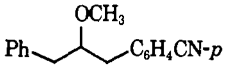
Irradiation[2] of a methanol solution of *trans*-1-(*p*-methoxyphenyl)-2-phenylcyclopropane (**1a**)[3] afforded, after initial rapid cis–trans isomerization, a 76% yield of a 60:40 (nmr) mixture of **2a** and **3a**.[4,5] Although **2a** and **3a** could not be separated on the several chromatographic systems tried, the mixture isolated had nmr and mass spectra consistent with the structures shown. Moreover, its behavior on thin-layer and gas chromatographic systems was identical with that of samples of **2a** and **3a** prepared *via* an independent route.[6] Likewise, the nmr spectrum of the mixture was seen to be a superposition of the spectra of the independently synthesized **2a** and **3a**.

Similarly, when a methanol solution of **1b** was irradiated a 47% yield of a 40:60 mixture of **2b** and **3b** was obtained.[4,5] In this case the ethers could be obtained essentially free of one another and identified.[8]

In marked contrast to the very slight effect of a methoxy group in orienting the addition, a para cyano moiety exerts complete control. When a methanol solution of **1c** was irradiated, two ethers, **3c** (33%)[8] and **4** (14%),[8] were isolated. However, **4** was shown to be a secondary photoproduct arising from the photoaddition of methanol to 3-(*p*-cyanophenyl)-1-phenylpropene, a photoproduct of **1c**.[9] Significantly, no **2c** was found.



1a, Ar = *p*-OCH_3-Ph **2a**, Ar = *p*-OCH_3-Ph **3a**, Ar = *p*-OCH_3-Ph
1b, Ar = *m*-OCH_3-Ph **2b**, Ar = *m*-OCH_3-Ph **3b**, Ar = *m*-OCH_3-Ph
1c, Ar = *p*-CN-Ph **2c**, Ar = *p*-CN-Ph **3c**, Ar = *p*-CN-Ph



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Appropriate controls showed the observed transformations are truly photochemical and not thermal or acid-catalyzed dark reactions. Furthermore, similar to the diphenylcyclopropane case,[1] the transformation of **1a** proceeded equally well in the presence of 0.05 *M* sodium methoxide to give the same product distribution. Nmr analysis of reaction mixtures obtained upon irradiation in CH_3OD showed that most if not all of the addition was to the cyclopropanes directly and not to olefins formed from the cyclopropanes.[10a,b] In addition, triplet sensitization of **1a–c** gave only cis–trans isomerization.[11]

These results provide a good indication of the nature of the species undergoing the addition. The very small effect of the para methoxy group in orienting the addition is quite surprising and is in contrast to what might be expected from a mechanism involving ionic intermediates, as in the photoaddition of alcohols to olefins,[12] or indeed any mechanism in which a very substantial charge is developed at the carbons undergoing the addition.[13,15] Likewise, the present reaction bears only a surface resemblance to the photochemical solvolysis of methoxy-substituted benzyl acetates,[16] where a meta methoxy group has a greater activating effect than a para methoxy.

On the other hand, the strong orienting effect of the para cyano group indicates that the ability of an aromatic ring to accept electron density from the cyclopropane ring is very important in orienting the addition. This is nicely in accord with recent uv studies of cyclopropyl-substituted aromatic compounds which show that cyclopropane rings behave as electron donors to aromatic rings and that excited state interaction be-

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[1] C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *J. Amer. Chem. Soc.*, **88**, 5675 (1966), and references therein.

[2] Irradiations were carried out under nitrogen with a Hanovia 450-W medium-pressure mercury arc fitted with a Vycor filter. Progress of the reactions was monitored by gas chromatography.

[3] Details of all synthetic and experimental procedures will be presented in a full paper.

[4] Other products, probably analogous to those found in the diphenylcyclopropane case,[1] were found.

[5] This ratio did not change on further irradiation.

[6] From the corresponding hydrochalcols[7] *via* a Williamson synthesis.[3]

[7] G. S. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, 73, 4509 (1951).

[8] Nmr and mass spectral data define the structures as shown.

[9] S. S. Hixson, manuscript in preparation.

[10] (a) Integration of the incompletely separated nmr signals of the C-2 and C-3 hydrogens of the products indicated at least 90% of the deuterium in **2a** and **3a**, 80% of that in **2b** and **3b**, and 95% of that in **3c** was located at C-3. The presence of a triplet for the C-1 hydrogens of **2b** and **3b** and a doublet of approximately equally intense triplets for the C-1 hydrogens of the **2a–3a** mixture likewise shows the lack of a substantial amount of deuterium at C-2. (b) Photochemical addition of methanol to 1,3-diarylpropenes does occur.[9]

[11] Triplet-sensitized cis–trans isomerization of 1,2-diphenylcyclopropane has been reported: G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964); C. D. DeBoer, Ph.D. Thesis, California Institute of Technology, 1966.

[12] J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).

[13] A para methoxy group exerts a large enhancement on the rate of cleavage of arylcyclopropanes by thallium triacetate and mercuric acetate.[14]

[14] R. J. Oullette, R. D. Robbins, and A. South, Jr., *J. Amer. Chem. Soc.*, 90, 1619 (1968); A. South, Jr., and R. J. Ouellette, *ibid.*, **90**, 7064 (1968).

[15] (a) Thus a zwitterionic intermediate such as that discussed by Salem (Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971)) appears not to be involved. (b) Cram has invoked a zwitterionic intermediate to explain the photochemical methanolysis and racemization of [2.2]metaparacyclophanes. The analogy in photochemical reactivity between Cram's and the diarylcyclopropane systems in interesting. (c) M. H. Delton, R. E. Gilman, and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 2324 (1971).

[16] H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963).

tween the two rings is strong only when the electron demand of the aromatic system is strong.[17a–c] Thus, we picture the reactions as proceeding *via* very polarizable excited states. In the methoxy- and unsubstituted cases electron drift is brought about by the attacking polar solvent molecules with addition of proton and nucleophile occurring nearly simultaneously by-passing intermediates with appreciable charge. In the para cyano case the electron drift is greatly enhanced by the very polar cyano group, and incoming nucleophile goes only to the benzylic position.[18]

Acknowledgment. Acknowledgment is made to the Petroleum Research Fund administered by the American Chemical Society for support of this research.

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(17) (a) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Amer. Chem. Soc.*, **86**, 4628 (1964); (b) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *ibid.*, **91**, 3558 (1969); (c) R. M. Kellog and J. Butler, *J. Org. Chem.*, **36**, 2236 (1971).

(18) The possibility that an intermediate protonated on the nitrile group is involved here, as suggested by a referee, cannot be excluded. However, in light of the work cited above[17a–c] and the fact that such substituent protonation is not necessary for the photoaddition of methanol to other diarylcyclopropanes, invoking a cationic intermediate appears unnecessary.

Stephen S. Hixson
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

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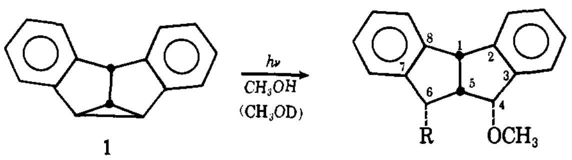
The Photochemical Methanolysis of Arylcyclopropanes. Stereochemistry

Sir:

A study of substituent effects[1] on the photochemical methanolysis of diarylcyclopropanes[2] has provided some information about the nature of the reactive excited states of these molecules. Since the stereochemistry of the ground-state ring opening reactions of cyclopropanes has been probed in some detail[3a,b] we wished to examine the stereochemistry of the photochemical process in order to learn more about the nature of the addition and to elucidate any difference in stereochemistry between the excited state and ground-state processes. One difficulty in doing this with optically active cyclopropanes lies in the fact that the most efficient photochemical reaction of diarylcyclopropanes is, in general, cis–trans isomerization.[4] To avoid this problem we have investigated the photochemical methanolysis of dibenzotricyclo[3.3.0.0^{2,8}]octadiene[5] (dibenzosemibullvalene (**1**)), a *cis*-diphenylcyclopropane which cannot cis–trans isomerize.

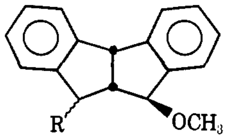
Irradiation[6] of a 0.014 *M* methanol solution of **1** afforded a mixture of methanol addition products. The major product, isolated in 48% yield, was identified as the syn methoxy compound **2** by comparison of its melting point and nmr spectrum with those reported.[3b] The minor product (19%) proved to be the anti isomer **3**.[3b,7] Compounds **2** and **3** are both primary photoproducts; they do not interconvert and are relatively stable under the reaction conditions. Furthermore, the reaction is entirely a photochemical one since no addition was observed on refluxing **1** in the dark in methanol or in methanol containing 24% concentrated sulfuric acid. Thus, the addition occurred with a 2.5:1 preference for retention of configuration at the site of nucleophilic attack.[8]

To ascertain the reaction stereochemistry at the site undergoing electrophilic attack the irradiation was carried out in CH_3OD with very interesting results. In the nmr spectrum[9a,b] of the major product **2-*d***, the doublet centered at δ 3.00 ($J_{5,6(\text{syn})}$ = 7 Hz) due to the syn C-6 proton in **2** had disappeared; only the (slightly broadened) doublet ($J_{5,6(\text{anti})}$ = 10 Hz) at δ 2.92 arising from the anti proton remained. In addition, integration showed that 1.0 deuterium atom had been incorporated at the C-6 position. Therefore, the major product is formed with retention of configuration at both ring positions undergoing attack.



1

2, R = H
2-*d*, R = D



3, R = H
3-*d*, R = D

The situation with the minor isomer **3-*d*** is more complex. The upfield quartet at δ 2.72 arising from the C-6 anti hydrogen[10] in **3** had collapsed to a broad signal integrating for 0.6 proton in **3-*d***; 0.4 proton

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(1) S. S. Hixson, *J. Amer. Chem. Soc.*, **93**, 5293 (1971).

(2) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *ibid.*, **88**, 5675 (1966).

(3) (a) E. W. Yankee and D. J. Cram, *ibid.*, **92**, 6329 (1970); (b) S. Cristol, W. Y. Lim, and A. R. Dahl, *ibid.*, 4014 (1970), and references therein.

(4) S. S. Hixson, unpublished results.

(5) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2883 (1966).

(6) Irradiations were carried out under nitrogen with Vycor-filtered light from a Hanovia 450-W medium-pressure mercury arc. Progress of the reactions was followed by gas chromatography.

(7) Unreacted **1** (20%), at least two very minor unidentified photoproducts (3% total), and higher molecular weight materials make up the balance of the material.

(8) (a) Professor S. Cristol has informed us that he likewise has carried out the photomethanolysis of **1** and observed predominant formation of **2**. Moreover, he has found that the reaction is not affected by the presence of sodium carbonate or pyridine, thus providing further evidence that the reaction is photochemical. (b) Likewise, Professor Gary Griffin has informed us that he and Mr. Ben Bowen have found that both methanol and benzyl alcohol photochemically add to **1**. The stereochemistry of the addition was not determined, however.

(9) (a) The nmr spectra of **2** and **3** are analyzed in ref 3b. Chemical shifts and splitting patterns of the C-1 and C-5 protons are similar to those of other compounds in this series.[3b,9c] (The splitting pattern of the C-5 hydrogen of **3** could not be determined due to peak overlap.) Assignments of signals to the C-6 syn and anti hydrogens are made on the basis of chemical shift and, in particular, coupling constants, for it has been found that the cis coupling constant $J_{5,6(\text{anti})}$ is invariably greater than the trans coupling constant $J_{5,6(\text{syn})}$ (as predicted on the basis of molecular models).[3b,9c] (b) In all cases syn and anti refer to the orientation of the substituent (methoxy or hydrogen) and not to the relative orientations of the C-5 and C-6 hydrogens. (c) S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, **89**, 5885 (1967).

(10) The magnitude (J = 9.5 Hz) of the coupling constant of this hydrogen with that at C-5 indicates this hydrogen is very probably in the anti configuration instead of the syn as was reported in ref 3b. Trans coupling constants ($J_{5,6(\text{syn})}$) for various substituted dibenzobicyclo-[3.3.0]octa-2,5-dienes have been found to be in the range of 2.3–7.0 Hz, while cis couplings ($J_{5,6(\text{anti})}$) have ranged from 7.0 to 10.0 Hz.[3b,9c] We have discussed this assignment with Professor Cristol and he agrees that this is most likely the case.