Arylcyclopropane Photochemistry. The Photochemical Addition of Hydroxylic Compounds to 1,2-Diarylcyclopropanes

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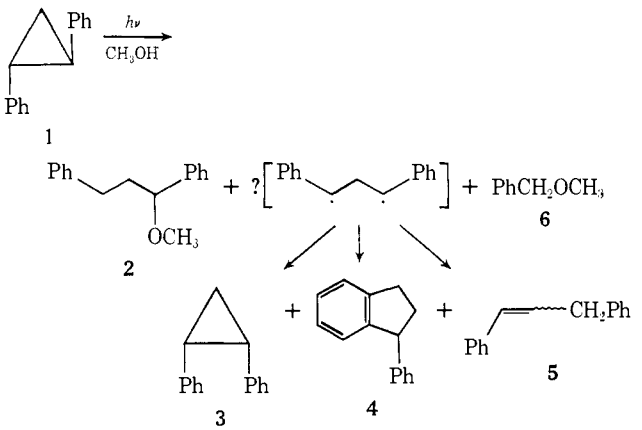
Abstract: The orienting effect of aromatic ring substituents on the photochemical addition of methanol to 1,2-diphenylcyclopropane has been investigated. The *p*-methoxy group of 1-(*p*-methoxyphenyl)-2-phenylcyclopropane (**7**) and the *m*-methoxy group of 1-(*m*-methoxyphenyl)-2-phenylcyclopropane (**8**) have negligible orienting effects, whereas the *p*-cyano group of 1-(*p*-cyanophenyl)-2-phenylcyclopropane (**9**) has a very strong one. The photoadditions of acetic acid, methanol, and *tert*-butyl alcohol to dibenzotricyclo[3.3.0.0^{2,8}]octadiene (dibenzosemibullvalene, **20**) produce a mixture of *syn*- and *anti*-4-substituted dibenzobicyclo[3.3.0]octadienes in which the syn isomer always predominates. Studies with CH_3OD and CH_3COOD reveal predominant syn addition of deuterium. The photochemical addition of methanol to *trans*-1-(β-naphthyl)-2-phenylcyclopropane (**27**) produces equal amounts of ethers resulting from attack α to the phenyl and to the naphthyl groups. Essentially no isotope effect is found in the photoaddition of CH_3COOH (CH_3COOD) to 1,2-diphenylcyclopropane: $\Phi_H/\Phi_D = 0.95 \pm 0.04$. A reaction pathway proceeding *via* initial complex formation between the hydroxylic compound and excited diarylcyclopropane is discussed.

The photochemical addition of alcohols and carboxylic acids to 1,2-diphenylcyclopropane (**1**) and other polyphenylcyclopropanes was discovered by Griffin and coworkers several years ago.[1] At that time the reaction presented an intriguing mechanistic problem, for it appeared that the excited state of **1** was simultaneously exhibiting both polar and radical-like behavior (Scheme I). Probably the best analogy for this reaction

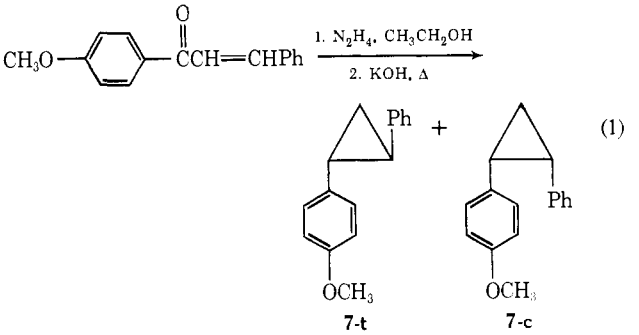
Scheme I. Photolysis of *trans*-1,2-Diphenylcyclopropane in Methanol



then was the photochemical addition of protic solvents to cyclic olefin studies by Kropp[2] and Marshall,[3] a process which apparently occurs by initial protonation of either a twisted triplet or more likely a highly strained trans ground-state olefin to give the most stable carbonium ion followed by anion addition, proton loss, or rearrangement. More recently it has been found that photochemical addition of alcohols and acids to the singlet states of cyclic and acyclic olefins of the styryl type occurs,[4-6] but this process is relatively poorly understood at present. On the basis of the frequently noted analogy in structure and chemical reactivity between cyclopropanes and olefins one might expect that these photochemical polar additions to the two chromophores would be mechanistically similar phenomena. However, while there may be some similarity between the olefin and the cyclopropane additions, the differences between the two are important and meaningful. In this paper we report our studies on the photochemical additions to various 1,2-diarylcyclopropanes. Part of this work has appeared in preliminary form.[7]

Results

Synthesis of Cyclopropanes. Cyclopropanes **7** and **8** were readily prepared by the method of Beach, *et al.*,[8] illustrated for **7** in eq 1. The *p*-cyano derivative **9** was



(1)

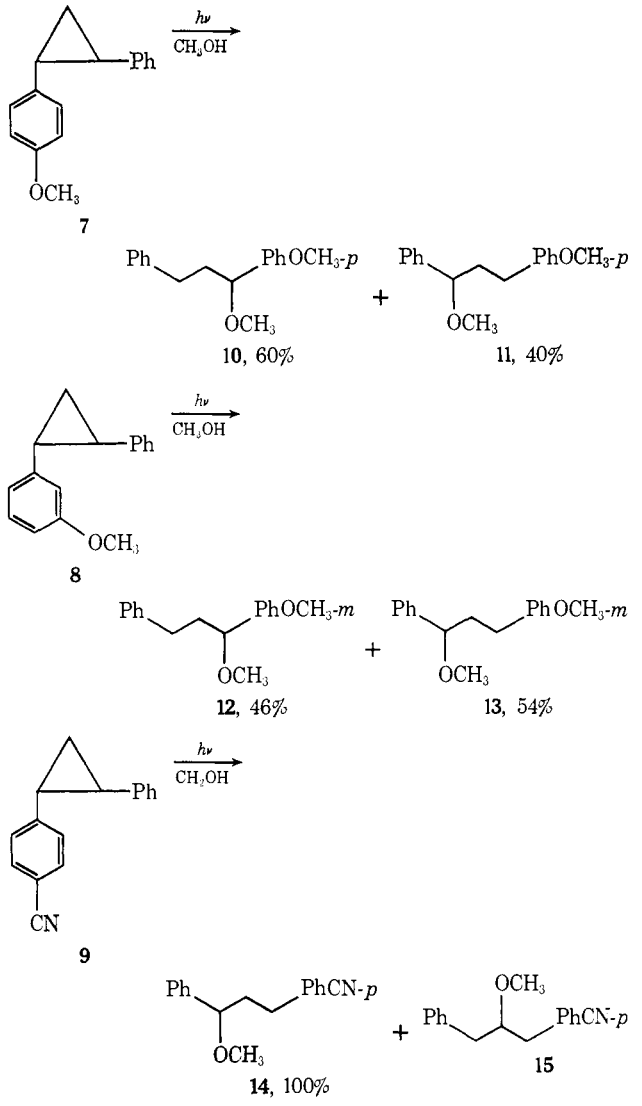
prepared from the *p*-chloro compound[9] using cuprous cyanide in *N*-methyl-2-pyrrolidone. Cyclopropane stereochemistry was assigned using nmr data.[10] In every

(1) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinnson, C. S. Aaron, G. W. Griffin, and G. J. Boudreau, *J. Amer. Chem. Soc.*, 88, 5675 (1966).
(2) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, 89, 5199 (1967); P. J. Kropp, *ibid.*, 91, 5783 (1969).
(3) J. A. Marshall, *Accounts Chem. Res.*, 2, 33 (1969); J. A. Marshall, *Science*, 170, 137 (1970).
(4) (a) S. S. Hixson, *Tetrahedron Lett.*, 4211 (1971); (b) *J. Amer. Chem. Soc.*, 94, 2505 (1972); (c) *Tetrahedron Lett.*, 277 (1973).
(5) N. Miyamoto, M. Kawanisi, and H. Nozaki, *Tetrahedron Lett.*, 2565 (1972).
(6) P. J. Kropp, *J. Amer. Chem. Soc.*, **95**, 4611 (1973), and references therein.
(7) (a) S. S. Hixson, *J. Amer. Chem. Soc.*, **93**, 5293 (1971); (b) S. S. Hixson and D. W. Garrett, *ibid.*, **93**, 5294 (1971).
(8) S. G. Beach, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).
(9) L. B. Rodewald and C. H. Depuy, *Tetrahedron Lett.*, 2951 (1964).
(10) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Amer. Chem. Soc.*, 83, 4838 (1961); C. G. Overberger and J. P. Anselme, *ibid.*, 86, 658 (1964); D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind. (London)*, 1205 (1958).

case the trans isomer was the predominant one produced as expected.

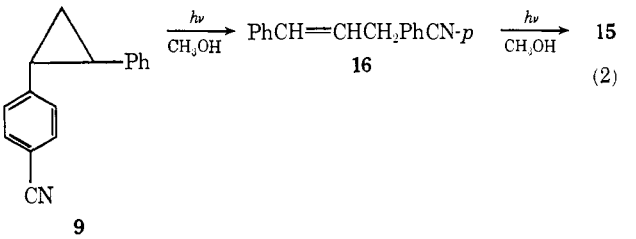
Substituent Effects on Methanol Addition. Cyclopropanes **7**, **8**, and **9** were irradiated in methanol to ascertain the effect of aromatic substituents on the directionality of methanol addition to 1,2-diphenylcyclopropane. The results, showing only the solvent incorporated products, are depicted in Chart I.

Chart I. Methanol Addition to Cyclopropanes **7**, **8**, and **9** (yields shown are percentages of each product of the total yield of cyclopropane solvent addition products)



Products **10** and **11** obtained from **7** could not be separated. However, their structures were readily derived *via* nmr and mass spectral data and an elemental analysis of the ether mixture. Most definitively **10** and **11** were separately prepared by methylation of the corresponding alcohols and a mixture of these independently prepared ethers was shown to be identical with that isolated from the photolysis. The **10**:**11** ratio was determined by integration of the partially separated methoxy signals in the nmr spectrum and is accurate to about 5%. Products **12**–**15** were identified from their nmr, ir, and mass spectral data. The mass spectral data were particularly helpful in distinguishing isomers, for the fragment $[ArCHOCH_3]^{\cdot+}$ derived by cleavage next to the carbon bearing the methoxy group was in **12**–**14** the base peak. In **15** the major fragments were $[PhCH_2CHOCH_3]^{\cdot+}$ and $[pCNPhCH_2CHOCH_3]^{\cdot+}$.

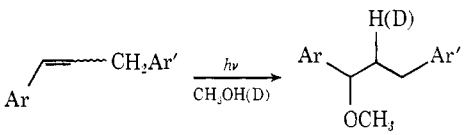
The **10**:**11** and **12**:**13** ratios given in Chart I remained essentially constant upon separate irradiation of these two mixtures for an extended period. These experiments also revealed that **10**–**13** are relatively stable when irradiated. We also determined that the **10**:**11** ratio was the same at different extents of conversion of cyclopropane **7** to product. Ether **15** had previously been shown[4a] not to arise from cyanocyclopropane **9** directly but rather from an intriguing anti-Markovnikov photochemical addition of methanol to olefin **16**, itself produced from **9** (eq 2).[4a]



(2)

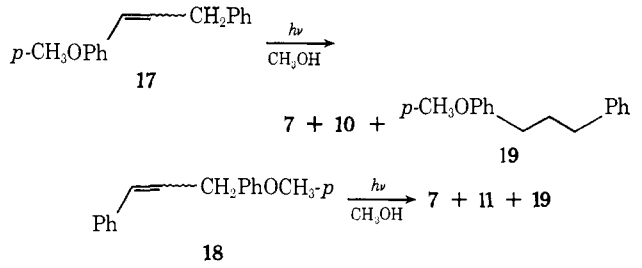
The results in Chart I indicate that the *p*-methoxy group of **7** and the *m*-methoxy group of **8** exert a very small orienting effect on the addition of methanol. On the other hand the *p*-cyano group of **9** has a substantial influence, the incoming methoxide moiety going only to the benzylic as opposed to the *p*-cyanobenzylic position.

In related work we discovered[4a,b] that photochemical addition of methanol to certain 1,3-diarylpropenes does occur to give ethers similar to those obtained *via* addition of methanol to 1,2-diarylcyclopropanes (eq 3).



(3)

Moreover, in the photolysis of **7** very small amounts of materials with the same gc retention times as 1-(*p*-methoxyphenyl)-3-phenylpropene (**17**) and 3-(*p*-methoxyphenyl)-1-phenylpropene (**18**) were observed to be formed. Olefins were likewise obtained from **8** and **9** (nmr). However, that the predominant mode of solvent addition to the cyclopropanes here was not *via* prior isomerization to olefins and that such a secondary reaction did not affect the product ratios was shown by carrying out the photolyses of **7**, **8**, and **9** in CH_3OD. Analyses of the nmr spectra of the resulting products **10-d**–**14-d** (see Experimental Section) indicated that deuterium was incorporated predominantly, if not exclusively, at C-3. (A similar result had been found earlier by Griffin, *et al.*)[1] Addition to olefins formed from the cyclopropanes would have resulted in deuterium at C-2 (eq 3) (as was indeed found).[4,6] The independence of the **10**:**11** ratio with extent of conversion of **7** also indicates that olefin addition was not affecting the results. However, when the photolysis of **7** was carried out until **7** was completely consumed, a small amount of 1-(*p*-methoxyphenyl)-3-phenylpropane (**19**) was isolated in addition to **10** and **11**. Photoreduction of propenes **17** and **18** to form **19** has been noted by us elsewhere.[4b] Since we did observe small amounts of **17** and **18** in the photolysis of **7**, it is likely that the **19** isolated from the complete pho-



tolysis of **7** arises *via* the propenes **17** and **18**. Thus a small amount of the ethers **10** and **11** produced at very high conversions of **7** likewise arises *via* the olefin route.

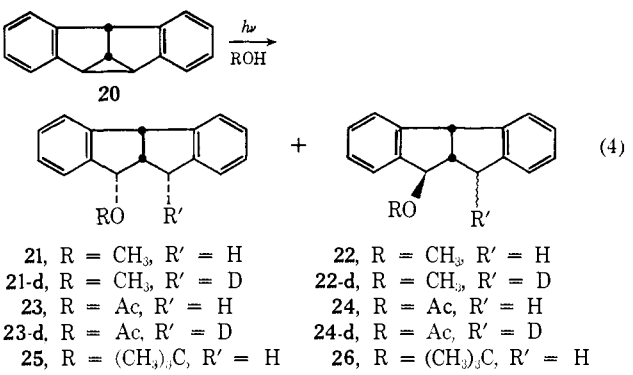
It has been found by others that some photochemical reactions in methanol may be explained by a photochemical oxidation of methanol (or of an impurity in the methanol) to produce traces of acid which then bring about dark, acid-catalyzed reactions.[11] Such was not the case here, for the additions proceeded equally well in the presence of 0.1 *M* sodium methoxide. This was also noted by Griffin[1] in the additions to 1,2-diphenylcyclopropane (**1**).

Irradiation of methanol solutions of **7** or **9** containing either acetophenone or xanthone under conditions where the latter absorbed over 95% of the light resulted only in cis–trans isomerization, indicating the additions do not proceed *via* the triplet states of the cyclopropanes.[12] The triplet-sensitized isomerization of **1** has been previously reported.[13]

The methanol addition to **7** was studied using solvents of different polarity as cosolvents. In 10% methanol–ether (v/v) the same 60:40 mixture of **10** and **11** was produced. However, the ratio in 10% methanol–benzene increased slightly but reproducibly to *ca.* 70:30, indicating a slightly greater selectivity in the less polar medium.

Stereochemistry of Addition of Hydroxylic Solvents. Addition to Dibenzosemibullvalene 20. To ascertain the stereochemistry of the addition process the photochemical addition of methanol to dibenzosemibullvalene (dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**20**))[14] was studied. The addition proceeded as expected to give known[15] ethers **21** and **22** in a 2.5:1 ratio (eq 4). Products **21** and **22** were shown not to interconvert upon photolysis and are relatively stable to the reaction conditions.[16]

Irradiation of **20** in methanol-*O*-*d* gave products **21**-*d* and **22**-*d*. Inspection of the nmr spectra of these two products (see Experimental Section) revealed that the deuterium in **21**-*d* was located entirely in the syn



position while that in **22**-*d* was located 60% in the syn position and 40% in the anti.

Upon irradiation of **20** in acetic acid and in *tert*-butyl alcohol products **23**–**24** and **25**–**26** were formed, respectively (eq 4). Once again a preference for the formation of the syn isomers (**23** and **25**) was found: 1.3:1 with acetic acid and 5.0 ± 0.5:1 with *tert*-butyl alcohol. Acetates **23** and **24** could not be separated chromatographically. However, it was possible to obtain **23** in pure form by fractional crystallization. The structures of **23** and **24** were proven definitively by conversion (lithium aluminum hydride reduction; methyl iodide methylation) to **21** and **22**, respectively. The structures and stereochemistry of **25** and **26** derive from their nmr spectra (see Experimental Section).[17] As with the acetates it was possible to obtain only the syn isomer **25** in analytically pure form.

Photolysis of **20** in acetic acid-*O*-*d* gave acetates **23**-*d* and **24**-*d* which were converted to ethers **21** and **22** for nmr analysis. Once again we found that in the syn isomer **23**-*d* all the deuterium was located in the syn position whereas in **24**-*d* it was distributed between the syn (60%) and anti (40%) positions.

Photochemical Addition of Methanol to 1-(β-Naphthyl)-2-phenylcyclopropane. The photochemistry of *trans*-1-(β-naphthyl)-2-phenylcyclopropane (**27**) in methanol was studied to determine the effect of excitation energy localization on the methanol addition. Furthermore, the photochemistry of **27** was deemed particularly interesting because of its relation to the naphthalene-sensitized isomerization of **1**, a poorly understood process.[13b,19] When a solution of **27** in methanol was irradiated there was obtained, in addition to the usual isomerization to the cis isomer and to olefins, a 50:50 mixture of ethers **28** and **29** (eq 5). These ethers could not be separated. However, their structures were readily determined by nmr and mass spectral data and an elemental analysis of the product mixture. Triplet sensitization of **27** with xanthone resulted only in trans–cis isomerization.

Isotope Effect on the Photochemical Addition of Acetic Acid to 1,2-Diphenylcyclopropane (1). The relative efficiencies of addition of acetic acid and acetic

(11) P. J. Kropp, E. J. Reardon, Jr., Z. L. F. Gaibel, K. R. Williard, and J. H. Hattawag, Jr., *J. Amer. Chem. Soc.*, **95**, 7058 (1973), footnote 11.

(12) (a) This does not rule out the intermediacy of a higher triplet state; see ref 12b, footnote 9; (b) S. S. Hixson, *J. Amer. Chem. Soc.*, **96**, 4866 (1974).

(13) (a) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964); (b) C. D. DeBoer, Ph.D. Thesis, California Institute of Technology, 1966; (c) C. Ouannès, R. Beugelmans, and G. Roussi, *J. Amer. Chem. Soc.*, **95**, 8472 (1973).

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

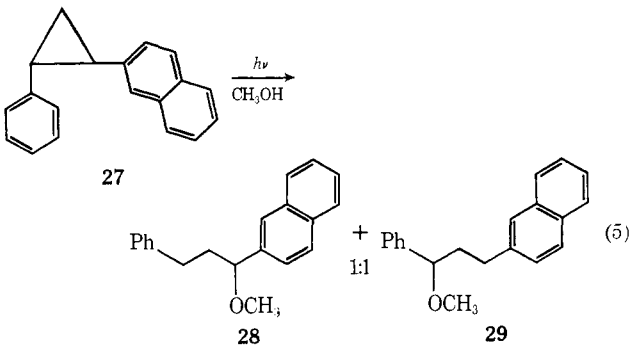
(15) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, 92, 4013 (1970).

(16) (a) Professor S. Cristol has informed us that he likewise has carried out the photomethanolysis of **20** and observed predominant formation of **21**. 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 **20**. The stereochemistry of the addition was not determined, however.

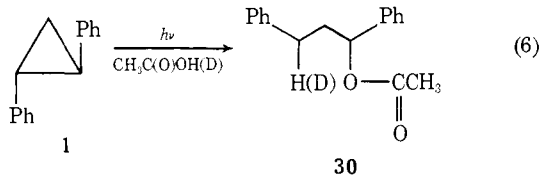
(17) The cis coupling constants ($J_{4,5(anti)}$) for various *syn*-4-substituted dibenzobicyclo[3.3.0]octadienes have been found to be in the range of 7.0–10.0 Hz, and are invariably greater than the trans coupling constants ($J_{4,5(syn)}$) in the isomeric anti compounds which range from 2.3 to 7.0 Hz.[7b,12b,15,18]

(18) S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, 89, 5885 (1967).

(19) G. S. Hammond, and R. S. Cole, *J. Amer. Chem. Soc.*, 87, 3256 (1965); S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968); R. S. Cole, Ph.D. Thesis, California Institute of Technology, 1968.



acid-*O*-*d* to 1,2-diphenylcyclopropane (**1**) were measured by irradiating solutions of **1** in neat CH_3COOH or CH_3COOD (99% d_1) in a merry-go-round apparatus with 254-nm light. Analyses for acetate **30** were carried out at very low conversions of **1** to product acetate and to cis isomer **2**. These analyses for acetate revealed essentially no difference in the quantum yields of addition of the deuterated and nondeuterated acids to **1**: $\Phi_H/\Phi_D = 0.94 \pm 0.05$ (eq 6).



Discussion

We have discussed in a separate paper our studies on the photochemical addition of primary and secondary amines to 1,2-diphenylcyclopropane (**1**).[12b,20] It was suggested that the amine additions occurred *via* initial complex formation between the amine and excited-state cyclopropane. However, conclusions as to the identity of the reactive excited state of **1**—whether the very short-lived spectroscopic singlet or another state, possibly the "radical-like" singlet discussed by Becker and Griffin[21]—could not be made, though the latter seemed a strong possibility.[21-23]

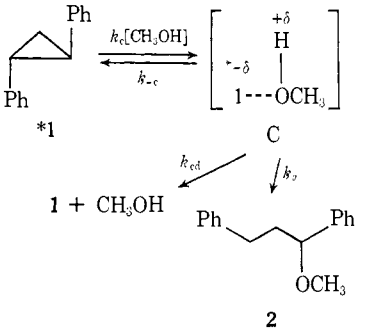
The photochemical addition reactions of hydroxylic compounds to 1,2-diarylcyclopropanes reported here appear to be entirely analogous to the amine additions (although we have observed qualitatively that the former are much less efficient): both reactions occur in a polar fashion, the O–H (N–H) bond adding across the C–C bond of the cyclopropane; both proceed with a preference for formation of the more hindered (syn) product in the additions to dibenzosemibullvalene **20**; neither process shows an observable isotope effect when the rates of addition of deuterated and nondeuterated species are compared; neither addition occurs when the cyclopropane triplet state is generated with a triplet sensitizer.[12] Thus all the evidence points to the same excited state being involved in both processes.

We note at this point that there are important differences between the polar photoadditions to cyclopropanes reported here and the photoadditions of protic solvents to cyclic olefins studied by Kropp and Marshall.[2,3] The negligibly small substituent effect exerted by a *p*-methoxy group in the cyclopropane addition is not what one would expect from a mechanism involving initial protonation to form the more stable carbonium ion as in the olefin case. Indeed, other cleavage reactions of arylcyclopropanes which almost certainly produce carbonium ion intermediates are greatly accelerated by a *p*-methoxy substituent.[24] Likewise, the lack of an observable isotope effect in the addition of acetic acid to 1,2-diphenylcyclopropane stands in contrast to the substantial isotope effect ($\Phi_H/\Phi_D \sim 7$) found in the photoaddition of water to 2,10-dimethyl-*trans*-2-octalin.[25]

That the additions proceed equally well in the presence of high concentrations of base and even take place with the nonacidic compound *tert*-butyl alcohol further differentiates the present reactions from the common olefin additions which are notably dependent on the presence of acid (although the additions to styryl singlets likewise proceed in strongly basic solution).[4] Moreover, our observation that additions to dibenzosemibullvalene **20** produce in every case a predominance of the more hindered syn product rules out the intermediacy of a planar, free carbonium ion intermediate.

A mechanism which accommodates these differences is one similar to that postulated for the amine additions.[12b] This is outlined in Scheme II, which shows the addition of methanol to 1,2-diphenylcyclopropane (**1**).

Scheme II. Photochemical Addition of Methanol to 1,2-Diphenylcyclopropane



We point out that our data do not demand the general mechanism shown in Scheme II, and other pathways may be visualized, *e.g.*, a direct nucleophilic attack on a "radical-like" state. However, the present scheme seems to provide the best framework for rationalizing and discussing our results. In this scheme we once again suggest that the addition occurs *via* prior formation of a complex (exciplex) with charge-transfer character between the hydroxylic compound and the excited-state cyclopropane—very possibly a "radical-like" singlet. In our studies on the addition of *n*-butylamine to diphenylcyclopropane (**1**)[12b] we observed no deuterium isotope effect when the quantum yields of addition of *n*-butylamine and *n*-butylamine-*N*,*N*-d_2 were compared. This was a strong indication that hydrogen transfer was not occurring in the rate-determining step, but that either complex formation was rate-limiting or the rate-

(20) S. S. Hixson, *J. Chem. Soc., Chem. Commun.*, 1170 (1972).
(21) R. S. Becker, L. Edwards, R. Bost, M. Elam, and G. W. Griffin, *J. Amer. Chem. Soc.*, **94**, 6584 (1972).
(22) R. J. Buenker and S. D. Peyerimhoff, *J. Phys. Chem.*, **73**, 1299 (1969); R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); A. K. Q. Siu, W. M. St. John, III, and E. F. Hayes, *ibid.*, **92**, 7249 (1970).
(23) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, 11, 92 (1972).
(24) R. J. Oulette, R. D. Robbins, and A. South, Jr., *J. Amer. Chem. Soc.*, **90**, 1619 (1968); A. South, Jr., and R. J. Oullette, *ibid.*, **90**, 7064 (1968).
(25) J. A. Marshall and M. J. Wurth, *J. Amer. Chem. Soc.*, 89, 6788 (1967).

determining step leading from complex to product did not involve hydrogen transfer. The fact that in the present work we find essentially no isotope effect when we compare the quantum yields for the addition of acetic acid and acetic acid-*O*-*d* to **1** has similar implications. This non-involvement of hydrogen transfer is also consistent with our qualitative observation that the additions of hydroxylic solvents to arylcyclopropanes proceed much less efficiently than do the amine additions, in view of the lower ionization potentials and lower acidities of the amines,[26] and with the fact that the reaction with methanol qualitatively appears to be insensitive to the acidity of the reaction medium.

The results of our studies on the substituent effects on the methanol additions to cyclopropanes **7**, **8**, and **9** likewise become understandable when considered in light of this mechanism, especially when they are compared with uv studies of arylcyclopropanes. Moreover, such a comparison provides further insight into the electronic nature of the reactive excited state. The results of several workers indicate that in the excited states of arylcyclopropanes the cyclopropane ring acts as an electron donor to the aromatic ring but that this interaction is strong only when the aromatic ring is substituted by a highly electron-withdrawing group.[27] For example, no conjugative interaction is noted for the three-ring case when the uv spectra of *p*-methyl- and *p*-cyclopropylanisole are compared, whereas a very large effect is seen with the corresponding nitro derivatives.[27a] Likewise, Hahn[27c] has found that the interaction between a cyclopropane and an attached aromatic ring is a spectroscopically detectable function of geometry only when the electron demand of the aromatic ring is substantial.

It would appear that we are observing chemical manifestations of the same phenomena. In the *p*-methoxy (**7**), *m*-methoxy (**8**), and unsubstituted (**1**) diphenylcyclopropanes the excited state is apparently polarizable but not polar. The methoxy groups have but a small effect on complex orientation for little electron drift occurs prior to solvent addition. On the other hand, the *p*-cyano moiety substantially polarizes the excited state such that an oriented complex is obtained and proton addition occurs only at the benzylic position.

Conversion of exciplex to product *via* either (a) proton transfer from alcohol to cyclopropane to form an ion pair, in the case where exciplex formation is rate limiting, or (b) initial C–O bond formation between alcohol and cyclopropane seems equally attractive. In either case it is interesting to note that whereas the additions of electrophiles to the ground state of dibenzosemibullvalene **20** proceed with complete retention (syn addition),[15] the present excited-state additions to **20** exhibit merely preferential but not complete retention at the site of protonation. However, since it is clear that there is a substantial difference in the details of the excited-state and ground-state reactions of **20**, the differences in stereochemistries of excited-state *vs.* ground-state electrophilic additions do not simply reflect differences in selectivity for electrophilic addition *per se*.

Finally, our results with the naphthylphenylcyclopropane **27** indicate that excitation energy localization is not an important factor in determining the course of the addition. In **27** the singlet energy should be heavily localized in the naphthyl moiety; however, addition of methoxide occurs α to the phenyl and naphthyl group with equal facility. In a sense, though, it is interesting that methanol addition to **27** occurs at all. Cole and Hammond[19] have examined the naphthalene-sensitized isomerization of 1,2-diphenylcyclopropane (**1**). Although the observed interaction was between the singlet state of naphthalene and ground-state cyclopropane, only cis–trans isomerization of the cyclopropane was observed both in benzene and in methanol. None of the other reactions obtained upon direct irradiation of **1**[1,28] were noted, indicating that the singlet state of **1** had not been formed and that the energy available in ^{1}S naphthalene had been dissipated in another manner. One might wonder, then, how a system in which the naphthalene was directly attached to a phenylcyclopropane would decay upon excitation to its singlet. Our results indicate that the singlet of **27** behaves essentially like that of **1** and that the presence of the naphthalene group imparts no special behavior to the cyclopropane.[29]

Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are corrected. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer; nmr spectra were obtained with either a Varian A-60 or a Perkin-Elmer R12 A instrument using tetramethylsilane as an internal standard; mass spectra were run on an Hitachi-Perkin-Elmer Model RMU-6L mass spectrometer. Gas chromatography was carried out with either a Perkin-Elmer Model 990 or a Varian Model 1200 gas chromatograph both equipped with a flame ionization detector. Peak areas were determined by the cut and weigh method; averages of at least three injections of each sample were used. Microanalyses were performed by the University of Massachusetts Microanalytical Laboratory.

Methanol was Fisher Spectral grade; it was used as obtained. Glacial acetic acid was dried by treating it with chromium trioxide (2 g/100 ml) and the theoretical amount of acetic anhydride for 1 hr at just below the boiling point of the acetic acid followed by distillation. *tert*-Butyl alcohol was refluxed with and distilled from calcium hydride and then stored over molecular sieves. Acetic acid-*O*-*d* (99% *d*) and methanol-*O*-*d* (99% *d*) were obtained from Stohler Isotope Chemicals, Waltham, Mass.

1-(*m*-Methoxyphenyl)-2-phenylcyclopropane (8). The general procedure of Beach, *et al.*,[8] was used. Thus 16.9 g (0.071 mol) of 3′-methoxychalcone[30] and 11.5 ml of hydrazine hydrate in 32 ml of absolute ethanol were refluxed for 1.5 hr and then cooled in ice. The solid pyrazoline was filtered off, combined with 0.6 g of powdered KOH, and heated under nitrogen for 1.5 hr at 200–210°. The mixture was cooled and taken up in benzene. The benzene solution was washed, dried, concentrated, and distilled at 115° (0.7 mm) to afford 8.3 g (52%) of a mixture of *cis*- and *trans*-1-(*m*-methoxyphenyl)-2-phenylcyclopropanes. The nmr spectrum of the mixture showed 2 H multiplets at δ 1.20–1.48 and 2.00–2.52

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(29) (a) After our work on 27 had been completed we learned that Professor Howard Zimmerman had also observed a photochemical polar addition (of water) to a naphthylphenylcyclopropane (benzo-2,3-naphthosemibullvalene). We thank Professor Zimmerman for informing us of his results prior to publication; see H. E. Zimmerman and M.-L. Viriot-Villaume, *J. Amer. Chem. Soc.*, **95**, 1274 (1973). (b) We have found that *trans*-1-(α-naphthyl)-2-phenylcyclopropane likewise undergoes a photochemical addition of methanol: S. S. Hixson, unpublished results.

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(cyclopropane hydrogens), two methoxy singlets at δ 3.50 and 3.68, and a 9 H multiplet at δ 6.42–7.31 (arom).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.63; H, 7.20.

1-(*p*-Methoxyphenyl)-2-phenylcyclopropane (7). *trans*-1-(*p*-Methoxyphenyl)-2-phenylcyclopropane was prepared from 4-methoxychalcone[31] according to the procedure used above for **8** except that the crude product was a solid which upon crystallization from methanol afforded pure *trans*-1-(*p*-methoxyphenyl)-2-phenylcyclopropane: mp 82.5–83.5°; nmr ($CDCl_3$) δ 1.20–1.47 (m, 2, cyclopropyl $-CH_2-$), 1.97–2.21 (m, 2, benzylic H's), 3.75 (s, 3, OCH_3), 6.80–7.27 (m, 9, arom).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.60; H, 7.17.

Preparative gas chromatography (a 12 ft × 0.25 in. 20% SE-30 column operated at 160° was used) of the concentrated mother liquors of the methanol crystallizations afforded a small amount of the cis isomer: nmr ($CDCl_3$) δ 1.24–1.64 (m, 2, cyclopropyl $-CH_2-$), 2.18–2.43 (m, 2, benzylic H's), 3.44 (s, 3, OCH_3), 6.42–6.92 (m, 9, arom).

1-(*p*-Cyanophenyl)-2-phenylcyclopropane (9). A solution of 25 g (0.11 mol) of 1-(*p*-chlorophenyl)-2-phenylcyclopropane[9] (prepared as for **8** from 4-chlorochalcone)[32] and 14.72 g (0.164 mol) of cuprous cyanide in 62 ml of *N*-methyl-2-pyrrolidone was refluxed under nitrogen 40 hr. The mixture was cooled, taken up in 1 l. of ether, washed with ammonium hydroxide until the washes were no longer blue and with water, dried, and concentrated. The crude oil was chromatographed on a 5 × 50 cm silica gel column packed in hexane and eluted with 1 l. 2%, 1 l. 3%, and then 4% ether–hexane. The 4% ether fractions yielded 18 g of impure product which was distilled to give 10 g of distillate, bp 143–148° (0.2 mm), consisting of a mixture of cis and trans cyclopropanes. The residue, 6.0 g, contained only the trans isomer. This residue was purified by passing it through a short alumina column (10% ether–hexane) and then crystallizing it from methanol to give the pure *trans*-1-(*p*-cyanophenyl)-2-phenylcyclopropane: mp 45–47°; nmr ($CDCl_3$) δ 1.33–1.61 (m, 2, cyclopropyl $-CH_2-$), 2.05–2.30 (m, 2, benzylic H's), 7.03–7.60 (m, 9, arom).

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.48; H, 6.20; N, 5.99.

A small portion of the cis isomer was obtained by preparative gas chromatography (12 ft × 0.25 in. 20% SE-30 column at 200°): nmr ($CDCl_3$) δ 1.35–1.74 (m, 2, cyclopropyl $-CH_2-$), 2.40–2.70 (m, 2, benzylic H's), 6.95–7.39 (m, 9, arom).

Photolysis of *trans*-1-(*p*-Methoxyphenyl)-2-phenylcyclopropane (7) in Methanol. A solution of 0.499 g (2.13 mmol) of *trans*-1-(*p*-methoxyphenyl)-2-phenycyclopropane in 200 ml of anhydrous methanol was irradiated under nitrogen in an immersion apparatus with Vycor-filtered light from a Hanovia 450-W medium-pressure mercury arc. Nitrogen was bubbled through the solution 0.5 hr prior to irradiation as well as throughout the course of the reaction. The progress of the reaction was followed by gas chromatography on a 6 ft × 1/8 in. 10% SE-30 column at 200°. After 2 hr of irradiation the solvent was removed and the residue chromatographed on a 1.5 × 100 cm silica gel column packed and eluted with 10% ether–hexane. This provided 0.038 g (8%) of 1-(*p*-methoxyphenyl)-3-phenylpropane and 0.378 g (69%) of a 60:40 mixture of 1-methoxy-1-(*p*-methoxyphenyl)-3-phenylpropane (**10**) and 1-methoxy-3-(*p*-methoxyphenyl)-1-phenylpropane (**11**). The nmr spectrum of the ether mixture was seen to be a superposition of the spectra of the independently synthesized ethers. The ratio of ethers was determined by quantitative integration of both pairs of methoxyl signals.

Anal. Calcd for $C_{17}H_{20}O_2$ (ether mixture): C, 79.65; H, 7.86. Found: C, 79.55; H, 7.82.

Photolysis of *trans*-1-(*p*-Cyanophenyl)-2-phenylcyclopropane (9) in Methanol. In a manner similar to that described above for **7** a solution of 0.299 g (1.32 mmol) of *trans*-1-(*p*-cyanophenyl)-2-phenylcyclopropane in 200 ml of methanol was irradiated (5 hr) and chromatographed to give, in addition to 0.128 g (43%) of a mixture of cis and trans cyclopropanes and olefins, 0.099 g (29%) of 1-methoxy-3-(*p*-cyanophenyl)-1-phenylpropane (**14**) and 0.042 g (12%) of 2-methoxy-1-(*p*-cyanophenyl)-3-phenylpropane (**15**). For **14** the spectral data were: nmr ($CDCl_3$) δ 1.78–2.21 (m, 2, C-2 H's), 2.64–2.92 (m, 2, Ar–CH_2-), 3.22 (s, 3, OCH_3), 4.10 (t, 1, C*H*-OCH_3), 7.20–7.63 (m, 9, arom); ir (neat) 2935, 2230, 1607, 1452, 1090 (br), 825, 756, and 695 cm^{-1}; mass spectrum *m/e* (rel intensity) 251 (2), 219 (13), 149 (12), 122 (25), 121 (100), 116 (18), 91 (25), 77 (31).

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.14; H, 6.77; N, 5.56.

For **15** the spectral data were: nmr ($CDCl_3$) δ 2.68–2.87 (m, 4, benzylic), 3.24 (s, 3, OCH_3), 3.36–3.64 (m, 1-C*H*OCH_3), 7.14–7.66 (m, 9, arom); ir (neat) 2930, 2230, 1607, 1093 (br), and 694 cm^{-1}; mass spectrum *m/e* (rel intensity) 251 (2), 160 (85), 149 (16), 135 (100), 116 (18), 91 (24).

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.00; H, 6.80; N, 5.45.

Photolysis of 1-(*m*-Methoxyphenyl)-2-phenylcyclopropane (8) in Methanol. In a manner similar to that described above for **7** a solution of 0.499 g (2.24 mmol) of 1-(*m*-methoxyphenyl)-2-phenylcyclopropane (a mixture of cis and trans isomers) in 200 ml of anhydrous methanol was irradiated (130 min) and then chromatographed to give, along with 0.096 g (19%) of recovered cyclopropanes and olefins, 0.109 g (19%) of 1-methoxy-1-(*m*-methoxyphenyl)-3-phenylpropane (**12**) and 0.129 g (22%) of 1-methoxy-3-(*m*-methoxyphenyl)-1-phenylpropane (**13**). The spectral data for **12** were: nmr ($CDCl_3$) δ 1.78–2.22 (m, 2, C-2 H's), 2.53–2.85 (m, 2, CH_2Ph), 3.22 (s, 3, OCH_3), 3.79 (s, 3, OCH_3), 4.06 (t, 1, C*H*-OCH_3), 6.72–7.42 (m, 9, arom); ir (neat) 2915, 1595, 1482, 1448, 1429, 1244, 1142, 1092, 772, 742, and 690 cm^{-1}; mass spectrum *m/e* (rel intensity) 256 (10), 224 (13), 152 (100), 91 (20).

For **13** the spectral data were: nmr ($CDCl_3$) δ 1.79–2.24 (m, 2, C-2 H's), 2.57–2.82 (m, 2, CH_2Ar), 3.24 (s, 3, OCH_3), 3.78 (s, 3, OCH_3), 4.12 (t, 1, C*H*OCH_3), 6.75–7.35 (m, 9, arom); ir (neat) 2930, 1592, 1484, 1452, 1254, 1143, 1094, 1034, 748, and 690 cm^{-1}; mass spectrum *m/e* (rel intensity) 256 (35), 224 (65), 151 (81), 135 (17), 121 (100).

Photolysis of *trans*-1-(*p*-Methoxyphenyl)-2-phenylcyclopropane (7), *trans*-1-(*p*-Cyanophenyl)-2-phenylcyclopropane (9), and 1-(*m*-Methoxyphenyl)-2-phenylcyclopropane (8) in Methanol-*O*-*d*. The photolyses of the cyclopropanes in methanol-*O*-*d* (99% *d*) were carried out and the products isolated in a manner similar to that used for the photolyses in nondeuterated methanol. 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 **10**-*d* and **11**-*d*, 80% of that in **12**-*d* and **13**-*d*, and 95% of that in **14**-*d* were located at C-3. The presence of a triplet for the C-1 hydrogens of **12**-*d* and **13**-*d* and a doublet of approximately equally intense triplets for C-1 hydrogens of the **10**-*d*–**11**-*d* mixture likewise shows the lack of a substantial incorporation of deuterium at C-2.

Photolysis of *trans*-1-(*p*-Methoxyphenyl)-2-phenylcyclopropane (7) in Methanol–Ether and in Methanol–Benzene. The photolyses of *trans*-1-(*p*-methoxyphenyl)-2-phenylcyclopropane in 10% (v/v) methanol–ether and 10% (v/v) methanol–benzene were carried out as in pure methanol. Once again the ratios of the two methanol-addition products **10** and **11** were determined by nmr integration of the methoxy signals of the purified product ether mixture.

Acetophenone-Sensitized Photolysis of *trans*-1-(*p*-Methoxyphenyl)-2-phenylcyclopropane (7) in Methanol. A methanol solution (10 ml), 1.00 *M* in acetophenone and 2.22 × 10^{-2} *M* in *trans*-1-(*p*-methoxyphenyl)-2-phenylcyclopropane, was placed in a quartz test tube, stoppered with a serum cap, purged with nitrogen, and then irradiated 370 min in a Rayonet photochemical reactor using the 350-nm lamps. No methanol addition products (**10** or **11**) could be detected (gc) after this period. Net isomerization of the pure *trans*-cyclopropane to an approximately 2:1 cis:trans mixture was observed. A very small amount of another unidentified product was observed.

Xanthone-Sensitized Photolysis of *trans*-1-(*p*-Cyanophenyl)-2-phenylcyclopropane (9) in Methanol. A solution of 49.8 mg (0.227 mmol) of *trans*-1-(*p*-cyanophenyl)-2-phenylcyclopropane and 139.4 mg (0.710 mmol) of xanthone in 25 ml of methanol was placed in a Pyrex test tube, stoppered with a serum cap, and purged with nitrogen. The tube was then strapped to a cylindrical Pyrex flask surrounding a quartz immersion well containing a Hanovia 450-W medium-pressure mercury lamp. The Pyrex flask contained a stannous chloride filter solution (67.3 g of $SnCl_2 \cdot 2H_2O$ in 500 ml of 10% HCl) which eliminated all light below 334 nm (6.7-cm path length). Irradiation for 255 min provided an approximately 2:1 cis:trans mixture of cyclopropanes as the only detectable products.

1-Methoxy-1-(*p*-methoxyphenyl)-3-phenylpropane (11) and 1-Methoxy-3-(*p*-methoxyphenyl)-1-phenylpropane (10). A mixture of 1.58 g (0.0375 mol) of 57% sodium hydride dispersion in 10 ml of dimethyl sulfoxide was heated at 70–75° under nitrogen until hydrogen evolution ceased and then cooled on an ice bath. To this

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was added dropwise 2.0 g (0.0083 mol) of 1-(*p*-methoxyphenyl)-3-phenylpropan-1-ol[33] in 15 ml of dimethyl sulfoxide and then 5 ml of methyl iodide. After 1 min the reaction was taken up in benzene, washed with water, dried, and concentrated to an oil which was chromatographed on a 2.0 × 150 cm silica gel column packed and eluted with 10% ether–hexane. This provided 0.734 g (35%) of 1-methoxy-1-(*p*-methoxyphenyl)-3-phenylpropane (**10**): nmr ($CDCl_3$) δ 1.78–2.23 (m, 2, C-2 H's), 2.56–2.75 (m, 2, CH_2Ph), 3.15 (s, 3, OCH_3), 3.64 (s, 3, OCH_3), 4.00 (t, 1, $CHOCH_3$), 6.71–7.27 (m, 9, arom).

An identical procedure was used to prepare 1-methoxy-3-(*p*-methoxyphenyl)-1-phenylpropane (**11**) from 3-(*p*-methoxyphenyl)-1-phenylpropan-1-ol:[33] nmr ($CDCl_3$) δ 1.75–2.18 (m, 2, C-2 H's), 2.52–2.78 (m, 2, CH_2PhOCH_3-*p*), 3.17 (s, 3, OCH_3), 3.57 (s, 3, OCH_3), 4.16 (t, 1, $CHOCH_3$), 6.70–7.27 (m, 9, arom).

Photolysis of Dibenzotricyclo[3.3.0.0^{2,8}]octadiene (Dibenzosemibullvalene, 20) in Methanol and Methanol-*O*-*d*. A solution of 0.589 g (2.88 mmol) of dibenzosemibullvalene[14] in 200 ml of methanol was irradiated in the usual manner with unfiltered (quartz immersion well) light for 75 min. Chromatography of the crude product on a 1.5 × 45 cm alumina column (activity grade 2) with benzene as eluent provided 0.328 g (43%) of *syn*-4-methoxydibenzobicyclo[3.3.0]octadiene (**21**)[15] and 0.131 g (17%) of *anti*-4-methoxydibenzobicyclo[3.3.0]octadiene (**22**).[15] The nmr spectra of the products were in accord with those reported by Cristol.[15]

The photolysis of dibenzosemibullvalene in methanol-*O*-*d* was carried out and worked up similarly. The nmr spectrum of the syn isomer (**21**-*d*) showed a slightly broadened doublet ($J_{5,6(anti)}$ = 10 Hz) at δ 2.92 arising from the C-6 anti proton. The doublet centered at δ 3.00 ($J_{5,6(syn)}$ = 7 Hz) due to the C-6 syn proton had disappeared. The nmr spectrum of the anti isomer (**22**-*d*) indicated that the upfield quartet at δ 2.72 arising from the C-6 anti hydrogen in the anti isomer (**22**) had collapsed to a broad signal integrating for 0.6 proton in **22**-*d*; 0.4 proton was present at the C-6 syn position (which overlaps the signals of the C-5 and the methoxy protons).

Photolysis of Dibenzotricyclo[3.3.0.0^{2,8}]octadiene (20) in *tert*-Butyl Alcohol. A solution of 0.488 g (2.39 mmol) of dibenzotricyclo[3.3.0.0^{2,8}]octadiene in 375 ml of *tert*-butyl alcohol was irradiated in the usual manner for 14.5 hr. The solvent was removed *in vacuo*. Inspection of the nmr spectrum of the crude product revealed the presence of *syn*- and *anti*-4-*tert*-butoxydibenzobicyclo[3.3.0]octadienes (**25** and **26**) in a ratio of 5.0 ± 0.5:1.0. Chromatography on a 2 × 38 cm alumina column with benzene as eluent provided 0.315 g (47%) of the syn isomer (**25**) and 0.052 g (8%) of the anti (**26**). Crystallization of the syn isomer from ethanol followed by vacuum sublimation afforded the pure compound: mp 97–98°; nmr ($CDCl_3$) δ 1.34 (s, 9, *tert*-butyl), 2.92–3.68 (m, 3, C-5 and C-6 H's), 4.44 (d, 1, C-1 H, $J_{1,5}$ = 7.0 Hz), 5.21 (d, 1, C-4, $J_{4,5}$ = 7.0 Hz), 6.82–7.68 (m, 8, arom).

Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 86.18; H, 7.88.

The nmr spectrum of the anti isomer showed δ 1.34 (s, 9, *tert*-butyl), 2.92–3.68 (m, 3, C-5 and C-6 H's), 4.37–4.95 (m, 2, C-1 and C-4 H's), 6.84–7.58 (m, 8, arom). The multiplet at δ 4.73–4.95 is seen to consist of a doublet ($J_{4,5}$ = 2.5 Hz), which we assign to the C-4 syn hydrogen, superimposed on the signal for the C-1 hydrogen. We were unable to obtain this isomer in analytically pure form.

Photolysis of Dibenzotricyclo[3.3.0.0^{2,8}]octadiene (20) in Acetic Acid. A solution of 0.500 g (2.45 mol) of dibenzotricyclo[3.3.0.0^{2,8}]-octadiene in glacial acetic acid was irradiated in the usual manner (Corex filter) for 370 min. The solvent was removed *in vacuo* and the residue chromatographed on a 2.5 × 50 cm silica gel column with 5% ether–hexane as eluent. This provided 0.113 (23%) of starting material contaminated by a small amount of an unknown product and 0.234 g (36%) of a 1.3:1 mixture of *syn*- and *anti*-4-acetoxydibenzobicyclo[3.3.0]octadienes (**23** and **24**). The two acetates could not be separated chromatographically. However, it was possible to obtain by fractional crystallization from methanol the pure syn isomer (**23**): nmr ($CDCl_3$) δ 2.08 (s, 3, CH_3), 2.92 (d, 2, C-6 H's), 3.74 (distorted quintet, 1, C-5 H), 4.60 (d, 1, C-1 H), 6.30 (d, 1, C-4 H), 7.10–7.27 (m, 8, arom); $J_{1,4}$ = 7.2 Hz, $J_{1,5}$ = 7.2 Hz, $J_{1,6(syn)} = J_{1,6(anti)}$ = 8.0 Hz.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.94; H, 6.10.

Concentration of the mother liquors obtained above yielded a syn–anti mixture containing approximately 75% anti isomer (**24**): nmr ($CDCl_3$) δ 2.04 (s, 3, CH_3), 2.74–3.40 (m, 3, C-5 and C-6 H's), 4.80 (d, 1, C-1 H), 6.04 (d, 1, C-4 H), 7.07–7.41 (m, 8, arom); $J_{1,5}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz.

Photolysis of Dibenzotricyclo[3.3.0.0^{2,8}]octadiene (20) in Acetic Acid-*O*-*d*. A solution of 0.763 g (3.74 mmol) of dibenzotricyclo[3.3.0.0^{2,8}]octadiene in 100 g of acetic acid-*O*-*d* (99% d_1) was irradiated as in the acetic acid photolysis. The residue was chromatographed on a 2.5 × 150 cm silica gel column. Elution with 2% ether–hexane provided 0.295 g (39%) of starting material. Elution with 5% ether–hexane provided 0.039 g of an unknown compound and 0.224 g (23%) of a 1.2:1 (syn:anti) mixture of acetates **23**-*d* and **24**-*d*. The acetate mixture (0.848 mmol) was refluxed with 0.068 g (1.7 mmol) of lithium aluminum hydride in 25 ml of ether for 1.5 hr under nitrogen. The usual work-up provided a mixture of alcohols which was directly converted to the methyl ethers. Thus, 0.2 g (4.25 mmol) of 53% sodium hydride dispersion in mineral oil was stirred under nitrogen in 5 ml of dimethyl sulfoxide at 70–75° until hydrogen evolution has essentially ceased. The mixture was cooled and the alcohol mixture in 5 ml of dimethyl sulfoxide added dropwise followed by 2 ml of methyl iodide. The reaction mixture was taken up in ether, washed with water, dried, and concentrated to give a residue which was chromatographed on a 2.5 × 50 cm silica gel column packed and eluted with 2% ether–hexane. This provided 0.074 g of *syn*- and 0.079 g of *anti*-4-methoxybicyclo[3.3.0]octadienes.

The nmr spectrum of the deuterated syn isomer (**21**-*d*) showed a slightly broadened doublet ($J_{5,6(anti)}$ = 10 Hz) at δ 2.92 arising from the C-6 anti proton.[15] The doublet centered at δ 3.00 ($J_{5,6(syn)}$ = 7 Hz) due to the C-6 syn proton had disappeared. The nmr spectrum of the deuterated anti isomer (**22**-*d*) indicated that the upfield quartet at δ 2.72 arising from the C-6 anti hydrogen in the nondeuterated anti isomer **22** had collapsed to a broad signal integrating for 0.6 hydrogen; 0.4 hydrogen was present at the C-6 syn position.[15]

***trans*-1-(β-Naphthyl)-2-phenylcyclopropane (27).** In a manner similar to that used for the preparation of **8** (*vide supra*), 3-phenylacrylonaphthone[34] was converted to 1-(β-naphthyl)-2-phenylcyclopropane. In this case the crude product was a solid which upon crystallization from 95% ethanol afforded the pure trans isomer: mp 79.5–80°; nmr ($CDCl_3$) δ 1.13–1.57 (m, 2, cyclopropyl $-CH_2-$), 2.10–2.35 (m, 2, C-1 and C-2 H's), 7.10–7.79 (m, 12, arom).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.07; H, 6.64.

The mother liquors from the trans cyclopropane crystallizations were concentrated to give a solid which upon repeated recrystallization from methanol afforded the cis isomer (contaminated by some trans): mp 40–44°; nmr ($CDCl_3$) δ 1.24–1.52 (m, 2, cyclopropyl $-CH_2-$), 2.22–2.59 (m, 2, C-1 and C-2 H's), 6.97–7.69 (m, 12, arom).

Photolysis of *trans*-1-(β-Naphthyl)-2-phenylcyclopropane (27) in Methanol. A solution of 0.500 g (2.04 mmol) of *trans*-1-(β-naphthyl)-2-phenylcyclopropane in 185 ml of methanol was irradiated in the usual manner (Pyrex filter) for 11 hr 40 min. The solvent was removed and the residue chromatographed on a 2.5 × 50 cm silica gel column packed and eluted with hexane followed by 2% ether–hexane. This provided 0.147 g (29%) of a mixture of cis and trans cyclopropanes and olefins and 0.269 g (28%) of an inseparable mixture of 1-methoxy-1-(β-naphthyl)-3-phenylpropane (**28**) and 1-methoxy-3-(β-naphthyl)-1-phenylpropane (**29**): nmr ($CDCl_3$) δ 1.87–2.31 (m, 2, C-2 H's), 2.52–2.98 (m, 2, C-3 H's), 3.20 and 3.22 (2s, 3, OCH_3), 3.96–4.31 (2 overlapping triplets appearing as a quartet, 1, C-1 H's), 7.20–7.85 (m, 12, arom); mass spectrum *m/e* (rel intensity) 276 (53), 244 (81), 243 (21), 224 (39), 171 (100), 153 (20), 142 (41), 141 (23), 121 (58), 115 (24).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.81; H, 7.27.

Isotope Effect Study on the Photochemical Addition of Acetic Acid and Acetic Acid-*O*-*d* to *trans*-1,2-Diphenylcyclopropane (1). Identical solutions of 0.151 g (0.780 mmol) of *trans*-1,2-diphenylcyclopropane in 25 ml of glacial acetic acid or acetic acid-*O*-*d* (99% d_1) were prepared and 6.5-ml aliquots of each were irradiated in triplicate (30 min) in quartz tubes on a merry-go-round apparatus using 254-nm light from a low-pressure mercury arc. Prior to irradiation samples were stoppered with serum caps and flushed with nitrogen. Following irradiation solvent was removed and internal standard (docosane) added in cyclohexane solution for gas chromatographic analysis for acetate **30** (6 ft × 1/8 in. 10% SE-30 column at

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180°). In each case *ca.* 2% isomerization to the cis isomer of the cyclopropane had occurred. Optical density changes of each solution as a result of irradiation were negligible.

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Photosensitized Cycloadditions to 1,3-Dimethyl-6-azauracil and 1,3-Dimethyl-6-azathymine. An Imine Linkage Unusually Reactive toward Photocycloaddition

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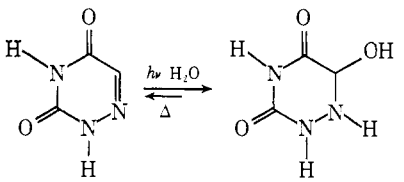
Abstract: The acetone-sensitized cycloaddition of 1,3-dimethyl-6-azathymine (**1b**) and 1,3-dimethyl-6-azauracil (**2b**) to olefins has been studied. For **2b** high yield cycloadducts were formed with ethylene, tetramethylethylene, isobutylene, ethyl vinyl ether, vinyl acetate, and isopropenyl acetate. In the case of the oxygen-substituted olefins, epimeric 8-substituted 1,2,4-triazabicyclo[4.2.0]octane-3,5-diones were formed with greater than 95% regioselectivity. Photosensitized cycloaddition studies of **1b** with tetramethylethylene and vinyl acetate indicate that the photochemical reactivity of **1b** and **2b** is qualitatively similar. These results are discussed with reference to the general low photochemical reactivity of imines in cycloaddition reactions.

The photochemical reactivity of excited pyrimidine bases[2] and their aza analogs[3] has attracted much attention in recent years. In particular 6-azathymine (**1a**) and 6-azauracil (**2a**) derivatives, which theoretically[4] should show photochemical behavior similar to thymine and uracil, have shown photochemical reactivity much to the contrary. Thus, Prusoff[3a,b] has reported that 6-azathymine and its ribonucleoside were essentially resistant to the effects of uv irradiation. In addition, the presence of **1a** in bacterial DNA and the incorporation of **1a** in *Enterococcus stei* increased the resistance of these materials toward uv irradiation. While facile photodimerization of neither **1a** nor **2a** has been observed, photohydration of **2a** has been recently reported to afford 5-hydroxy-5,6-dihydro-6-azauracil (**3**).[3f,g] This hydration product results from the opposite mode of water addition than that observed in uracil derivatives.

The low reactivity of these 6-aza analogs toward photodimerization may be viewed in a much larger context, namely the reluctance of >C=N– systems to undergo bimolecular 2 + 2 additions. Thus, while



2 **3**

photocycloadditions of olefins to other olefins,[5] to ketones,[6] and to thioketones[7] to yield the expected four-membered ring compounds are well characterized, until recently we knew of only two formal examples of >C=N– additions to carbon–carbon double bonds.[8] These processes involved the photoaddition of 2,5-diphenyl-2,3,4-oxadiazole to indene and furan.[8] Our preliminary report of the photoaddition of ethyl vinyl ether to 6-azauracil[1c] and that of Koch's work with 3-ethoxyisoindolone[9a] and 2-phenyl-2-oxazolin-4-one[9b] serve as the only simple examples of these cycloaddition processes.

Our interest in 6-azauracil and 6-azathymine photochemistry initially evolved from our studies of uracil photoaddition reactions.[2] However, in view of the rare occurrence of cycloadditions to the >C=N– linkage we have investigated the generality of this process. We wish to report here the high yield acetone photosensitized cycloadditions of 1,3-dimethyl-6-aza-

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