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.

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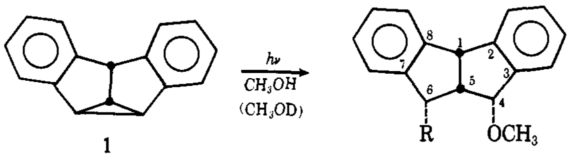
The Photochemical Methanolysis of Arylcyclopropanes. Stereochemistry

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 ($J_{5,6(\mathrm{syn})}$ = 7 Hz) due to the syn C-6 proton in **2** had disappeared; only the (slightly broadened) doublet ($J_{5,6(\mathrm{anti})}$ = 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.



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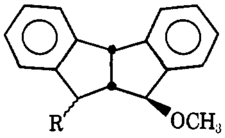
2, R = H
2-*d*, R = D



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 $J_{5,6(\mathrm{anti})}$ is invariably greater than the trans coupling constant $J_{5,6(\mathrm{syn})}$ (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 ($J_{5,6(\mathrm{syn})}$) 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 ($J_{5,6(\mathrm{anti})}$) 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.

was present at the C-6 syn position (which overlaps the signals of the C-5 and the methoxy protons). That is, the addition of deuterium proceeded with 60% retention and 40% inversion in the formation of **3**-*d*.

These results are quite different from most ground-state electrophilic and nucleophilic ring openings of cyclopropanes where predominant or exclusive inversion at the site of nucleophilic attack is the rule,[3a,b] in contrast to the predominant retention in the present case. In this respect our observations are somewhat similar to those on the addition of HBr to **1** which proceeds with retention of configuration at both sites of attack.[3b] However, the preferential formation of the more hindered syn product here and the pattern of the substituent effects observed in the diphenylcyclopropane case which indicate ionic intermediates are probably not involved[1] suggest a pathway for the photochemical addition different from the carbonium ion mechanism postulated in the HBr and other electrophilic additions.

We prefer a mechanism involving attack of methanol on an excited polarizable arylcyclopropane, the addition of proton and nucleophile being concerted and not involving any highly charged intermediates.[11] The reason for the intriguing predominance of retention of configuration in the attack is unknown. We are currently investigating the photochemical addition of other hydroxylic solvents of varying size, acidity, and polarity to **1** in order to probe this matter further.

Acknowledgment. We are very grateful to Professor S. Cristol for helpful discussions about this work. We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Council of the University of Massachusetts for financial support.

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[11] The bonds to proton and nucleophile need not be formed to the same extent throughout the course of the addition. Moreover, the proton and nucleophile need not come from the same molecule. Such would be the case where inversion is observed.

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Cobalt(II)–Tetraphenylporphyrin Complex with Carbon Monoxide

Sir:

Planar low-spin cobalt(II) complexes have recently served as models for reversible O_2 carrying systems[1-4] and in understanding aspects of vitamin B_{12} chemistry.[4-6] The cobalt(II) analog of hemoglobin (coboglobin) has recently been synthesized and reported to form O_2 complexes reversibly, but attempts to observe an interaction of carbon monoxide with coboglobin and with the separated metalloporphyrin, cobalt(II) protoporphyrin IX dimethyl ester, were unsuccessful.[3] Reactions of CO with vitamin B_{12} derivatives and cobaloximes have been extensively studied. The reduction of cobaloxime(III) by CO is catalyzed by cobaloxime(II).[5] This reaction is thought to involve an interaction of CO with cobaloxime(II), but no direct evidence for an adduct has been reported. Complexes of CO with methylcobaloxime(III)[7] and cobaloxime(I)[8] have been identified, but to our knowledge no carbon monoxide adduct of a cobalt(II) corrin, oxime, or porphyrin complex has been reported.

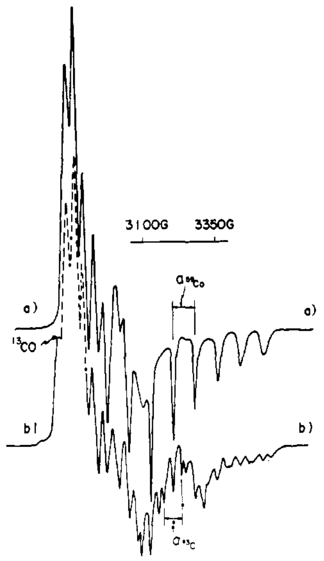

Figure 1. Epr spectra for the 1:1 carbon monoxide adduct of cobalt(II) tetraphenylporphyrin: (a) ^{12}CO; (b) 55% ^{13}CO, 45% ^{12}CO.

We wish to report that cobalt(II) tetraphenylporphyrin [Co(TPP)] forms a 1:1 adduct with CO which can be conveniently studied by epr in frozen solutions. In addition to the possible biological interest in the interaction of CO with cobalt(II) porphyrins, paramagnetic low-spin d^7 complexes of this type have a single unpaired electron in the d_{z^2} used in σ bonding with CO and provide an unusual opportunity to examine the σ spin delocalization to carbon monoxide.

Samples for epr studies were prepared in a vacuum line by subjecting degassed toluene solutions of cobalt(II) tetraphenylporphyrin to CO gas (155 mm, 296°K) and cooling to N_2 temperature. Representative epr spectra for both ^{12}CO and enriched ^{13}CO adducts of Co(TPP) appear in Figure 1. Measurements of the epr line intensities in the 55% ^{13}CO sample show that each peak in the ^{12}CO adduct splits into two equal intensity components in the ^{13}CO adduct which demonstrates the presence of a 1:1 complex with carbon monoxide (theoretical intensity ratio $^{13}C/^{12}C = 0.61$; observed ratio $= 0.64 \pm 0.05$). The epr parameters for Co(TPP) and 1:1 adducts with CO and CH_3CN in frozen toluene solution (90°K) appear in Table I. Epr data for the CO adduct are consistent with an axially symmetric complex with a $(d_{xz,yz}, d_{xy})^6(d_{z^2})^1$ ground configuration. Solving the relationships for

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