carbonate according to Streitwieser, Verbit, and Stang.[43] Isotopic analyses were performed by J. Nemeth of Urbana, Ill.

Triphenylsilane-*d* was prepared by reduction of chlorotriphenylsilane by lithium aluminum deuteride as described by Gilman and Dunn.[5a]

Tribenzylsilane-*d*. According to the foregoing procedure for the preparation of the triphenyl compound, lithium aluminum deuteride (0.087 g, 2.07 mmol) and tribenzylchlorosilane (1.33 g, 3.94 mmol) were caused to react, resulting in 1.175 g (3.89 mmol) of crude product and 0.813 g (2.68 mmol, 68%) of pure tribenzylsilane-*d*, mp 87.5-88.5°, ir (CHCl$_3$) 1550 cm^{-1} (s), near absence of absorption at 2135 cm^{-1}.

Tri-*n***-butylsilane-***d*. According to the same procedure the reaction of 0.228 g (11.1 mmol) of lithium aluminum deuteride and 2.593 g (11.0 mmol) of tri-*n*-butylchlorosilane afforded several milliliters of a clear, colorless liquid product. Distillation through a short-path microassembly gave 1.643 g (8.16 mmol, 74%) of pure tri-*n*-butylsilane-*d*, bp 210-215°, ir (CHCl$_3$) 1520 cm^{-1} (s), no absorption at 2045 cm^{-1}.

Titrimetric Kinetic Method. A sampling technique was developed for this investigation which has two major advantages over the usual manometric method: (a) reactions can be studied over a wider temperature range with better temperature control; and (b) much slower reactions can be studied, which greatly increases the number of silanes open to investigation. The main disadvantages are (a) the requirement of a large volume (50-100 ml) of reaction solution; (b) the limited number of samples in single kinetic runs; and (c) only moderately good precision (1-2%) of first-order rate constants. Although these are not generally serious problems, they are undesirable in isotopic work.

Our analytical method for the quantitative determination of silane is an adaptation of an iodimetric technique reported by Westermark.[18] Triorganosilanes react with iodine to form iodosilanes. Thus, by treating the silane with a known excess amount of iodine, the silane concentration can be deduced by titration of the remaining iodine with standard sodium thiosulfate.

(43) A. Streitwieser, Jr., L. Verbit, and P. Stang, *ibid.*, 29, 3706 (1964).

A 10-ml sample was removed from the reaction flask by pipet and allowed to drain into a 125-ml erlenmeyer flask containing about 3 ml of glacial acetic acid to quench the reaction. In long kinetic runs, an ampoule was removed from a thermostated collection and broken, and the contents were washed with methanol into 3 ml of acetic acid for analysis. About 4 ml of saturated aqueous sodium acetate solution was added as a buffer, and methanol was added to effect solution of any silane precipitate. It was necessary to maintain a delicate balance of methanol and water throughout the analysis to keep both organic and inorganic materials in solution. Iodine was generated *in situ* as triiodide ion by adding first 1 ml of 0.03361 *M* aqueous potassium iodate solution with a tuberculin syringe and then roughly 0.25 g of solid potassium iodide. The flask was heated on a hot plate just to boiling to effect solution and to create an atmosphere of methanol and water above the liquid, stoppered with a cork stopper, and allowed to sit out of direct light to complete the reaction. The reactions of triphenyl-, tribenzyl-, and tri-*n*-butylsilane with iodine required 45, 30, and 15 min, respectively. After the allotted time the stopper was carefully removed to avoid splashing, and the excess iodine was titrated with 0.02681 *M* sodium thiosulfate to the colorless end point. Starch indicator cannot be used in alcoholic solutions because of the decomposition of the starch-iodine complex.

Rate constants were calculated by subjecting the data to a linear least-squares computer program.

Manometric Kinetic Method.[19] A Datametrics Corporation Type 1023 electronic manometer with Barocel pressure sensor, Model 523-11, equipped with solvent shields, was connected to a Heath Model AUW-2 servo-recorder. A flask of methanol was attached to the reference side of the electronic manometer; a two-neck flask with a pressure equalizing pipet in one neck was attached through the other neck to the sample side of the manometer. The sample flask was stirred magnetically and both flasks were immersed in a constant-temperature bath. Substrate stock solution was thermally equilibrated in the sample flask, with catalyst solution in the pipet. Runs were initiated by draining the pipet contents into the sample flask. The apparatus has been fully described elsewhere.[19] Rate constants were treated as above.

Communications to the Editor

Excited State Interactions between Nonconjugated Chromophores. Unusual Polar Photochemical Methanol Additions and Reductions in the 1,3-Diarylpropene System

Sir:

Until recently, reported examples of the photochemical addition of methanol to olefins in a polar fashion had been restricted to those cases where the double bond was either contained within a six-eight-membered ring or was conjugated to an electron-withdrawing group or where the addition required the presence of added acid.[1a-d] We have recently reported an unusual exception to these generalities in that 3-(*p*-cyanophenyl)-1-phenylpropene (1) photochemically adds

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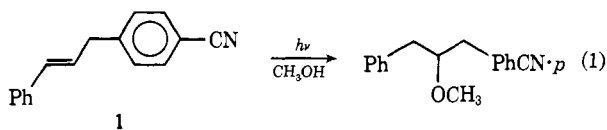
(1) (a) J. A. Marshall, *Accounts Chem. Res.*, 2, 33 (1969); (b) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, 91, 6190 (1969), and references therein; (c) H. Kato and M. Kawanisi, *Tetrahedron Lett.*, 865 (1970); (d) N. Miyamoto, M. Kawanisi, and H. Nozaki, *ibid.*, 2565 (1971).

methanol in an anti-Markovnikov fashion in the absence of added acid (eq 1).[2] We now report (1) further studies on the photochemical addition of methanol to 1,3-diarylpropenes which provide strong evidence that an interaction between the nonconjugated chromophores comprising these molecules is involved in the addition, and (2) a novel polar photoreduction occurring simultaneously with the addition.

The irradiation[3] of a 0.01 *M* methanol solution of *trans*-3-(*p*-methoxyphenyl)-1-phenylpropene (2)[4] was monitored closely by gc and nmr, which revealed a gradual buildup of at least two products along with the transient appearance and disappearance of *cis*-2 and of small amounts of *cis*- and *trans*-cyclopropanes 3.[5] Silica gel chromatography of the reaction mixture after all 2 had disappeared provided 21% of a compound whose nmr and ir spectra and gc retention times were identical with those of reduction product 4,[6] indepen-

(2) S. S. Hixson, *ibid.*, 4211 (1971).
(3) Irradiations were carried out under nitrogen with Vycor-filtered light from a Hanovia 450-W medium-pressure mercury arc.
(4) C. S. Rondestvedt, *J. Amer. Chem. Soc.*, 73, 4509 (1951).
(5) S. S. Hixson, *ibid.*, 93, 5293 (1971).
(6) R. Royer, P. Demerseman, J-P. Lechartier, and A. Cheutin, *J. Org. Chem.*, 27, 3808 (1962).

dently prepared *via* catalytic reduction of **2**, and 61% of a mixture of two ethers, predominantly **5**[5] containing 10–20% **6**.[5,7]

Since it has been shown that **3** on irradiation gives a 60:40 mixture of **6:5**,[5] at least some of these ethers in the present case must arise *via* **3**. On the other hand, deuterium labeling studies (*vide infra*) and the results of low conversion runs (where **5** but not **6** is found) indicate that olefin **2** yields only ether **5** directly. Similarly, observations of the relative rates of formation of **3** and **4** and deuterium labeling studies (*vide infra*) show that **4** likewise arises from **2** directly.

In a similar manner, a 1.6 × 10⁻³ *M* methanol solution of *trans*-1-(*p*-methoxyphenyl)-3-phenylpropene (**7**)[4]
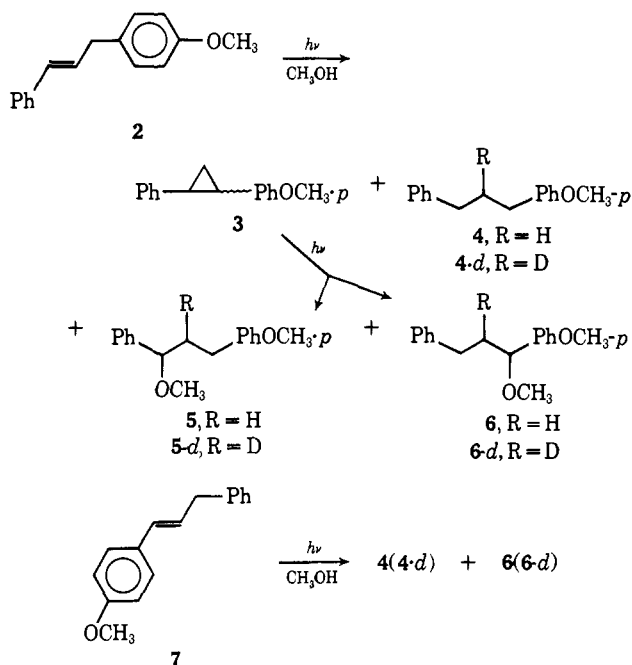
was converted to **4** (6%) and **6** (42%). In this case no traces of the cyclopropanes **3** were seen (gc). Gc analysis of the photolysis of **2** and of **7** in cyclohexane revealed in both cases a small amount of product with the same retention time as **4** was formed in this solvent.

Dark controls with and without added acid showed the reactions are truly photochemical. Moreover, the reactions are not changed when carried out in the presence of 0.05 *M* sodium methoxide. Xanthone sensitization of **2** and **7** gave no detectable amounts of **4–6**. Thus, these additions are similar to that observed for **1**[2] but differ from previous ones[1a–d] in that (a) they do not require added acid, (b) they appear to proceed *via* the singlet state, and (c) the olefins are acyclic and not conjugated to a highly electron-withdrawing group. They differ from the addition to **1** in that they proceed in a Markovnikov fashion. Moreover, no reduction was noted in the case of **1**.

Perhaps more intriguing are the results of photolyses in CH₃OD. As expected, **2** and **7** gave **5-d** and **6-d**, respectively, with nmr spectra showing the deuterium was incorporated at C-2 in both cases. Surprisingly, however, the **4-d** obtained from **2** showed only 1.05 hydrogens in the δ 1.69–2.15 region assigned to the C-2 hydrogens and 3.8 hydrogens in the δ 2.51–2.68

(7) Separate irradiation of **5** and **6** under the same conditions gave only traces (≪1%) of **4** (gc).

region assigned to the C-1 and C-3 protons. Likewise, the **4-d** obtained from **7** showed only 1.2 hydrogens at C-2 and 3.9 hydrogens at C-1 and C-3. In other words, most if not all of the **4-d** isolated in both cases is of the structure indicated with deuterium at C-2.

Since we have found (a) 1,3-diphenylpropene (**8**) neither adds methanol[2] nor is reduced by it but merely rearranges to 1,2-diphenylcyclopropane (**9**),[8] and (b) **2** rearranges to **3** faster than **8** forms **9** (in cyclohexane),[9,10] it is evident that the *p*-methoxy group in **2** (like the *p*-cyano in **1**) brings about an electron drift not found or unimportant in **8**. Some sort of interaction between the nonconjugated chromophores comprising **2** must be occurring. **10** is one way of formalizing this interaction; a similar sort of bonding (with charges reversed) was suggested as a possibility in **1**. It is now seen that this picture involving 1,4 bonding nicely rationalizes the mode of addition in both cases; it is thus a mechanistically useful way of picturing the reactive excited states. That a similar interaction is occurring in **7** seems possible since *o*-anethetol photochemically adds methanol only in the presence of acid.[1d]

The reduction deserves special comment, for the deuterium distribution in **4-d** is the opposite of what one would expect from a normal radical hydrogen abstraction mechanism. Rather, an interesting ionic pathway seems to be involved. Marshall[11] has found this to be the case also in the photosensitized reduction of 10-methyl-Δ¹(⁹)-octalin by 2-propanol-2-*d*, and it is most likely true for other cyclic olefins where reduction is commonly observed concomitant with photochemical ionic-type addition of alcohols.[12,13] Thus, the behavior of **2** is best rationalized by a mechanism involving initial protonation at C-2 of the polarized singlet state to form cation **11**. Methoxide addition to
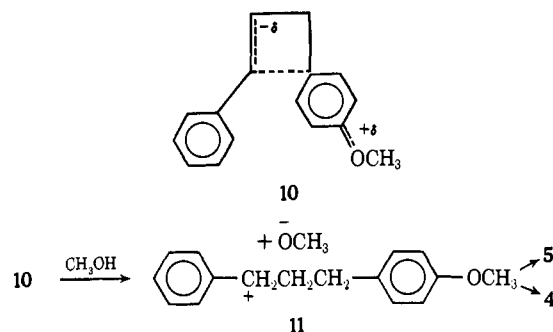
11 would lead to **5**; hydride abstraction,[14] to **4**. A similar pathway would explain the behavior of **7**.

(8) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965).

(9) S. S. Hixson, *ibid.*, **94**, 2507 (1972).

(10) Thus, the failure of **8** to add methanol does not seem to arise from a very fast rate of rearrangement.

(11) J. A. Marshall and A. R. Hochstetler, *Chem. Commun.*, **296** (1968).

(12) P. J. Kropp, *Pure Appl. Chem.*, **24**, 585 (1970).

(13) Professor Paul Kropp has studied the photochemical reduction of norbornene and bornene derivatives by methanol in which ionic mechanisms quite certainly are involved; P. J. Kropp, private communication.

(14) P. D. Bartlett and J. D. McCollum, *J. Amer. Chem. Soc.*, **78**, 1441 (1958).

and Professor Paul Kropp for making available and discussing his unpublished work.

Stephen S. Hixson

Department of Chemistry, University of Massachusetts
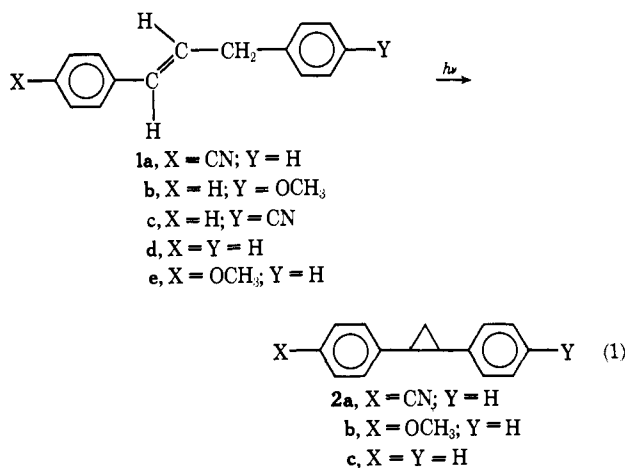*Amherst, Massachusetts 01002*
Received October 8, 1971

Substituent Effects on the Di-π-methane Rearrangement

Sir:

The photochemical rearrangement of 1,3-diphenyl-propene to 1,2-diphenylcyclopropane[1] and the analogous rearrangements of other polyarylpropenes[2] provide some of the earliest examples of the di-π-methane rearrangement,[3,4] a reaction which has been extensively studied by Zimmerman and coworkers.[3,6] Mechanistic studies have provided much insight into the nature of the rearrangement; yet many details of the reaction remain unknown. In the past studies of substituent effects on the photochemical reactions of ketones have provided much information concerning the electronic nature of species undergoing rearrangements.[7] We have likewise found such an approach to be useful in interpreting arylcyclopropane photochemistry.[8] In the hope that such studies would prove to be similarly informative in excited state olefin rearrangements, we have examined the effects of para substituents on the rate of cyclopropane formation of 1,3-diarylpropenes to probe further the di-π-methane rearrangement.

Olefins **1b, d,** and **e** were synthesized according to literature procedures;[9] **1a** and **c** were prepared from the corresponding chloro compounds[9] with cuprous cyanide in *N*-methylpyrrolidone. As previously found for **1d**,[1] irradiations of the *trans*-propenes **1a–e** gave rise to the corresponding cyclopropanes **2a–c**[8] as determined by a comparison of the nmr spectra and gc retention times of the product mixtures with those of independently synthesized cyclopropanes (eq 1). Mixtures of *cis-* and *trans*-cyclopropanes were produced in all cases. The only other products observed at low conversions were the corresponding *cis*-olefins. Olefin **1e** cyclized very inefficiently; only after very long irradiation periods could traces of the corresponding cyclopropanes **2b** be detected with the gas chromatograph. Triplet sensitization (xanthone) of **1a–e** gave no sign of **2a–c**.[10] Thus, like other acyclic di-π-methane

systems,[3,6] these olefins appear to rearrange *via* the singlet state.

1a, X = CN; Y = H
b, X = H; Y = OCH₃
c, X = H; Y = CN
d, X = Y = H
e, X = OCH₃; Y = H

2a, X = CN; Y = H
b, X = OCH₃; Y = H
c, X = Y = H

Relative efficiencies of rearrangement at 254 nm were determined on a "merry-go-round" apparatus and are listed in Table I. Conversions to cyclopropanes were

Table I. Relative Rate, Quantum Yield, and Fluorescence Data for Olefins 1a–e

Compd	$\Phi_{r(rel)}{}^a$	$k_f \times 10^{-8\,b}$	$\Phi_{f(rel)}{}^c$	$k_{r(rel)}$
1a	3.60 ± 0.72^d	5.8	0.115^g	41
1b	1.03 ± 0.15	4.7	0.086^h	13
1c	0.26 ± 0.05	6.6	0.102^h	3.8
1d	1.00^e	4.4	1.00^h	1.0
1e	$<0.05^f$	4.3	1.32^i	<0.04

^{a} Approximately 5×10^{-3} M in cyclohexane. ^{b} Calculated from the absorption spectrum, *cf.* N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 48. ^{c} Computed from the relative intensities at the maximum in the fluorescence spectrum (values computed from integrated areas under the emission curves correspond closely); λ(excitation) = 268 nm; concentrations ~4 × 10⁻⁶ M in cyclohexane. ^{d} Assuming equal amounts of *cis-* and *trans*-cyclopropanes were formed; see text. ^{e} $\Phi_{254} = 0.005$.[11] ^{f} No cyclopropane detected except at very long irradiation times with more intense light. ^{g} λmax 319 nm. ^{h} λmax 313 nm. ^{i} λmax 333 nm.

(1) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965).

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

(3) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(4) We[5a] have shown that phenyl migration is overwhelmingly (95 ± 5%) preferred relative to hydrogen migration in the rearrangement of 1,3-diphenylpropene to diphenylcyclopropane. Others[2,5b] have also found only aryl migration to occur in photocyclizations of arylpropenes to cyclopropanes in cases where both aryl and hydrogen migration were *a priori* possibilities.

(5) (a) S. S. Hixson, *Tetrahedron Lett.*, in press; (b) D. Kumari and S. K. Mukerjee, *Tetrahedron Lett.*, 4169 (1967).

(6) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971); H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **93**, 3655 (1971), and references cited in both of these papers.

(7) See, for example, H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967).

(8) S. S. Hixson, *ibid.*, **93**, 5293 (1971).

(9) C. S. Rondestvedt, Jr., *ibid.*, **73**, 4509 (1951).

(10) That energy transfer occurred was indicated by the observation of trans–cis isomerization in all cases.

kept to less than 10% to minimize competing light absorption by the products. In the cases of **1c** and **1d** conversion to the corresponding cis isomers of the olefins was significant. However, this does not affect the relative quantum yield data since Sigal[11] has shown that both *cis-* and *trans-***1d** give the same proportion of *cis-* and *trans-***2c** with the same efficiency (Φ = 0.005).[11] We found this to be true also of both isomers of **1c**. Since we were not able to separate *trans-***2a** from *trans-***1a**, the amount of *trans-***2a** formed was assumed to be equal to the amount of *cis-***2a** produced. Thus, the relative quantum yield and rate data for **1a** are minimum values, since in the other cases a predominance of *trans*-cyclopropane was found.

It is well known, however, that relative efficiencies are not always a good indication of relative rates. Moreover, we had evidence that a type of interaction between the styryl and 3-aryl groups not leading to migration did occur in the singlet state of some of the propenes, at least in methanol solvent,[12] so that a discrepancy be-

(11) E. W. Valyocsik and P. Sigal, *J. Org. Chem.*, **36**, 66 (1971).

(12) S. S. Hixson, *Tetrahedron Lett.*, 4211 (1971); S. S. Hixson, *J. Amer. Chem. Soc.*, **94**, 2505 (1972).