and Professor Paul Kropp for making available and discussing his unpublished work.

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

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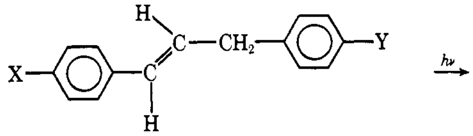
Substituent Effects on the Di-π-methane Rearrangement

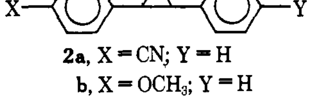
Sir:

The photochemical rearrangement of 1,3-diphenylpropene 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 = OCH$_3$
c, X = H; Y = CN
d, X = Y = H
e, X = OCH$_3$; Y = H



(1)

2a, X = CN; Y = H
b, X = OCH$_3$; 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 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-

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] Φ_{254} = 0.005.[11] [f] No cyclopropane detected except at very long irradiation times with more intense light. [g] λ_{max} 319 nm. [h] λ_{max} 313 nm. [i] λ_{max} 333 nm.

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(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.

(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).

tween efficiencies and rates might be expected. Therefore we determined the relative *rates* of migration using absorption and fluorescence data according to eq 2,

$$\frac{k_r}{k_{r_0}} = \frac{\Phi_r}{\Phi_{r_0}} \frac{\Phi_{f_0}}{\Phi_f} \frac{k_f}{k_{f_0}} \qquad (2)$$

where $k_r \equiv$ rate constant for cyclopropane formation, $\Phi_r \equiv$ quantum yield for cyclopropane formation, $k_f \equiv$ rate constant for fluorescence, and $\Phi_f \equiv$ quantum yield for fluorescence. The results of these determinations are listed in Table I.

It is immediately clear that the polar substituents exert dramatic effects on the rate of cyclopropane formation. Such effects are most pronounced at the styryl migration terminus as may be seen by comparing **1a**, **d**, and **e**. Decreasing the electron density at the migration terminus (**1a**) greatly enhances the rate of migration. Conversely, increasing the electron density at C-2 (**1e**) drastically lowers the rate. On the other hand, substituent effects on the migrating group are not nearly so large but are still quite evident. It is seen that both a *p*-methoxy (**1b**) and a *p*-cyano (**1c**) increase the rate of rearrangement of a phenyl group relative to the unsubstituted compound **1d**.

The pattern of substituent effects observed for **1a**, **d**, and **e** is seen to be strikingly analogous to that predicted for ground-state phenyl migration from one carbon atom to an adjacent carbon center, where the migration is predicted to become less favorable as the migration terminus goes from cationic to radical-like to anionic.[13] The excited state migration appears to be sensitive to the same effects of charge density. In the cases **1b**, **c**, and **d**, one would expect the migration terminus to show predominantly odd-electron character. (The excitation is initially largely localized in the nonpolar styryl portion of the molecule.) The relative migratory aptitudes observed are indeed consistent with and support this view.[14] Indeed the pattern observed is quite similar to that seen in other photochemical reactions where odd-electron reaction centers seem to be involved.[7] The faster rate of migration of a *p*-methoxyphenyl (**1b**) as compared to a *p*-cyanophenyl (**1c**) may be an indication that polar effects play a role here also.

While this is the only study of which we are aware of ring substituent effects on the di-π-methane rearrangement, it is perhaps relevant to point out that polar solvent effects have been noted previously by Zimmerman and Samuelson.[15] Thus, the efficiency of rearrangement of 4,4-diphenyl-1-methylenecyclohexene to cyclopropane was twice as great in methanol as in cyclohexane. These separate observations may be related.

It is interesting and gratifying that the observed substituent effects appear to be easily and logically interpreted as has been found to be the case for excited state transformations of ketones[7] and recently for cyclopropanes.[8] With this encouragement we are expanding our investigation of structure–reactivity relationships in olefin photochemistry.

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

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[13] H. E. Zimmerman and A. Zweig, *J. Amer. Chem. Soc.*, **83**, 1196 (1961).

[14] For a discussion of the assumptions involved see ref 7. The situation regarding energy localization and correlation of excited-state and ground-state reactivities is quite analogous in the two cases.

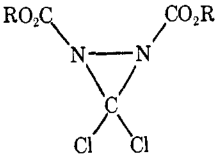
[15] H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **91**, 5307 (1969).

New Reactions of Phenyl(trihalomethyl)mercury Compounds. Dihalocarbene Addition to Azodicarboxylate Esters

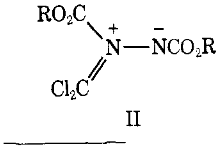
Sir:

We describe here the novel course of the first reported reaction of dihalocarbenes with compounds containing an N=N bond, the azodicarboxylate esters. Recent studies in these laboratories have shown that the phenyl(trihalomethyl)mercury reagents react not only with compounds containing C=C and C≡C bonds,[1] but also with compounds containing C=N,[2,3] C=S,[3,4] and C=O[5] bonds. We have extended these studies to compounds containing N=N bonds.

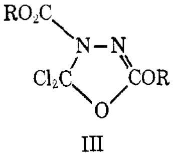
When a mixture of 20 mmol of $PhHgCCl_2Br$ and 26 mmol of $EtO_2CN{=}NCO_2Et$ in benzene solution was stirred and heated under nitrogen for 3 hr, the orange color of the reaction mixture gradually was discharged and phenylmercuric bromide (98% yield) precipitated. The filtered benzene solution was shown by glc to contain a single product (87% yield), which was isolated by distillation (bp 88° (0.24 mm), $n^{25}\text{D}$ 1.4730). Its analysis (C, H, N, Cl) indicated the composition $C_7H_{10}O_4N_2Cl_2$. In its mass spectrum (at 70 eV) the largest fragment corresponded to $C_7H_{10}O_4N_2Cl^+$, most probably the $(M - Cl)^+$ species. Addition of CCl_2 to the azodicarboxylate ester thus had been achieved, and a similar reaction was observed with $MeO_2CN{=}NCO_2Me$ to give a product of composition $C_5H_6O_4N_2Cl_2$ in good yield. These products, however, were *not* the expected diaziridines I. The ir spectrum of the $EtO_2CN{=}NCO_2Et$-derived product showed, in addition to the ester carbonyl bands at 1805 and 1770 cm^{-1}, a band at 1590 cm^{-1} assignable to a C=N stretching vibration. This product also showed absorption in the ultraviolet region, $\lambda_{\max}^{\text{cyclohexane}}$ 238 nm (ε 1655). Three structures isomeric with I were given further consideration: II, III, and IV. Structures II and



I



II



III

$(RO_2C)_2NN{=}CCl_2$

IV

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[1] D. Seyferth, *Accounts Chem. Res.*, **5**, 65 (1972).

[2] D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **21**, P3 (1970).

[3] D. Seyferth, R. Damrauer, H. Shih, W. Tronich, W. E. Smith, and J. Y.-P. Mui, *J. Org. Chem.*, **36**, 1786 (1971).

[4] D. Seyferth and W. Tronich, *J. Amer. Chem. Soc.*, **91**, 2138 (1969).

[5] D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **18**, P8 (1969).