More recently, structural evidence derived from endor experiments on **1** in crystalline 1,1-diphenylethylene has come forth which shows that, while **1** is bent, the rings are not very nearly coplanar.[10] The angle between the plane of each ring and the plane determined by the methylene and immediately adjacent carbons is 54°, and thus the structure is quite twisted.

We report here experiments which demonstrate that the mode of reaction of **1** with olefins is most sensitive to olefin structure. Either cycloaddition to give cyclopropanes or abstraction to give olefins can dominate the reaction. We feel that these results are well reconciled with a structure of **1** in solution similar either to that originally postulated by Skell[2] or to that shown to obtain in crystalline diphenylethylene,[10] but not with a structure similar to that of fluorenylidene.[9]

Almost any combination of cycloaddition and abstraction–recombination can be achieved simply by varying the structure of the olefin. As found by Closs and Closs,[3,4] reaction with the 2-butenes is primarily by abstraction. When the more substituted olefins are used abstraction becomes the sole path followed.[11] However, when the olefin contains a terminal methylene the pattern changes and cyclopropane formation becomes dominant. Two factors must influence this change in mechanism. One is of steric origin and simply reflects the reduced ease of entry of triplet **1** to the π electrons of the more highly substituted olefins. The other factor is electronic and involves the increased stability of the radicals formed from the di-, tri-, and tetramethylethylenes. We feel that the first factor is of more importance as methylenecyclohexane reacts primarily by cycloaddition. This parallels the behavior of isobutylene which has no alkyl groups which stabilize the allyl radical produced by abstraction. Were the electronic effect the more important, we would have expected methylenecylcohexane to react primarily by abstraction.

**Table I.** Mode of Reaction of Diphenylcarbene with Olefins[a]

| Olefin | Cyclopropane | Abstraction–recombination |
|---|---|---|
| 2,3-Dimethyl-2-butene | 0 | 100 |
| 2-Methyl-2-butene | ⩽8 | ⩾92 |
| *trans*-2-Butene | 22 | 78 |
| 3-Methyl-1-butene | 52 | 48 |
| Methylenecyclohexane | 87 | 13 |
| Isobutylene | 100 | 0 |
| Propylene | 100 | 0 |

[a] Products were identified by nmr spectroscopy and elemental or mass spectral analysis. In the cases where we note 0 or 100% of one kind of product we were unable to detect any peaks which might correspond to the missing products, either in crude or purified material. Traces would have escaped us, but a few per cent could have been seen.

If the notion is accepted that steric factors determine the mode of reaction of **1**, then it becomes difficult to accept similar structures in solution for **1** and **2**. Compound **2** is not so influenced, but reacts in each instance to give cyclopropane.[6,9] A structure in solution approximating that originally proposed by Skell[2] or recently found to obtain in crystalline medium[10] seems appropriate to us.

**Acknowledgment.** We thank Ronald H. Levin for pithy comments.

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(10) C. A. Hutchison, Jr., and B. E. Kohler, *J. Chem. Phys.*, **51**, 3327 (1969).

(11) Analysis of the cyclopropanes produced from **1** and the 2-butenes showed that the stereochemical relationship of the methyl groups in the olefin was largely maintained in the cyclopropane, although the exact result was temperature dependent.[4] This was attributed to reaction of singlet **1** in equilibrium with the more stable triplet which was thought to produce the compounds formed by abstraction–recombination.[4] Our work indicates that with the less substituted olefins either both spin states are giving cyclopropane or the rate of reaction of the singlet is enhanced in some way. We prefer the former explanation, but resolution of this point must await the results of work currently in progress.

(12) Alfred P. Sloan Research Fellow, 1967–1969.

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## Hydrogen Abstraction by Electronically Excited 1,1-Diphenylethylene

*Sir:*

The photoreduction of ketones in hydrogen-donating solvents has been thoroughly investigated.[1] The reactivity of the carbonyl group with respect to hydrogen abstraction depends dramatically on the configuration of the lowest lying triplet state.[2] The reactivity of $n,\pi^*$ triplets approximates that of alkoxy radicals,[3] whereas hydrogen abstraction by $\pi,\pi^*$ triplets is not observed or occurs at significantly lower rates.[4] The higher unpaired electron density on oxygen appears responsible for the greater reactivity in the former state.

In contrast to ketones, examples of hydrogen abstraction in the direct and sensitized photolysis of olefins are rare and are confined almost exclusively to cyclopentanes.[5] The intermediacy of the triplet state seems likely in these cases. Competitive decay processes are thought to be responsible for the general inability of triplet olefins to abstract hydrogen.[2]

In an earlier paper[6] we reported the formation of 2-(1,1-diphenylethyl)-2H,5,6-dihydropyran and 4-(1,1-diphenylethyl)-2H,5,6-dihydropyran during the photolysis of 1,1-diphenylethylene (DPE) in 2,3-dihydropyran. We postulated that these products occurred *via* allylic hydrogen abstraction by the $\pi,\pi^*$ DPE triplet followed by free-radical coupling reactions. Subsequently, it has been reported that 9,9′-bifluoroenylidene abstracts hydrogen during direct and sensitized photolysis.[7] We were therefore motivated to conduct a more detailed investigation of the photolysis of DPE.

Irradiation of DPE in 2-propanol at 2537 Å produced 2-methyl-3,3-diphenyl-2-butyl alcohol, 2,2,3,3,-tetraphenylbutane, and 2,3-dimethyl-2,3-butanediol in molar ratio 1:2.1:2.7, in addition to small quantities of

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(1) For a review, see D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold, New York, N. Y., 1967, Chapter VII.

(2) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 99 (1968).

(3) A. Padua, *Tetrahedron Lett.*, 3465 (1964); S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **87**, 2996 (1965); C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

(4) G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962).

(5) P. J. Kropp, *ibid.*, **89**, 3650 (1967); R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 4763 (1967).

(6) P. Servé, H. M. Rosenberg, and R. Rondeau, *Can. J. Chem.*, **47**, 4295 (1969).

(7) J. Nasielski, M. Jauquet, E. Vander Donckt, and A. Van Sinov. *Tetrahedron Lett.*, 4859 (1969).

unidentified products. Product identification was established by comparing ir and nmr spectra with those of authentic samples. The quantum yield for disappearance of DPE in neat 2-propanol at 2800 Å was 0.16.

Xanthone ($E_T$ = 74 kcal/mol) sensitized the photolysis at 3500 Å. DPE is transparent at this wavelength. The photolysis of DPE (0.01 *M*) at 2800 Å was completely quenched by piperylene (0.10 *M*). The reaction must therefore proceed *via* the excited triplet.[8] We propose the following mechanism.

$$\mathrm{DPE} \xrightarrow{h\nu} {}^1\mathrm{DPE}$$

$${}^1\mathrm{DPE} \xrightarrow{k_d} \mathrm{DPE}$$

$${}^1\mathrm{DPE} \xrightarrow{k_{isc}} {}^3\mathrm{DPE}$$

$${}^3\mathrm{DPE} \xrightarrow{k_1} \mathrm{DPE}$$

$${}^3\mathrm{DPE} + \mathrm{RH} \xrightarrow{k_2} \mathrm{C_6H_5\dot{C}CH_3} + \mathrm{R\cdot}$$

$$2(\mathrm{C_6H_5})_2\mathrm{\dot{C}CH_3} \xrightarrow{k_3} (\mathrm{C_6H_5})_2(\mathrm{CCH_3})_2(\mathrm{C_6H_5})_2$$

$$(\mathrm{C_6H_5})_2\mathrm{\dot{C}CH_3} + \mathrm{R\cdot} \xrightarrow{k_4} (\mathrm{C_6H_5})_2\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{-CH_3}$$

$$2\mathrm{R\cdot} \xrightarrow{k_5} \mathrm{R-R}$$

$$\mathrm{R} = \mathrm{CH_3\dot{C}OHCH_3}$$

Stern–Volmer quenching studies of DPE were performed in degassed acetonitrile solutions containing varying concentrations of 2-propanol ($1-5 \times 10^{-2}$ *M*) and piperylene at 2900 Å and 25°. Relative quantum yields for DPE disappearance were determined by uv and glpc. Stern–Volmer plots (eq 1) were linear.

$$\Phi_0/\Phi = 1 + k_q\Upsilon[\mathrm{Q}] \qquad (1)$$

$k_q$ and $\Upsilon$ represent quenching rate constant and triplet lifetime, respectively. Values for $k_q\Upsilon$ and $\Upsilon$ are given in Table I in which $k_q$ is assumed to be $1.1 \times 10^{10}$ $M^{-1}$ sec$^{-1}$.[9] Rate constants for unimolecular triplet decay ($k_1$) and triplet hydrogen abstraction ($k_2$) were obtained from the plot of $1/\Upsilon$ *vs.* [2-propanol] according to eq 2 and were found to be $0.74 \times 10^7$

$$1/\Upsilon = k_1 + k_2\,[\text{propanol}] \qquad (2)$$

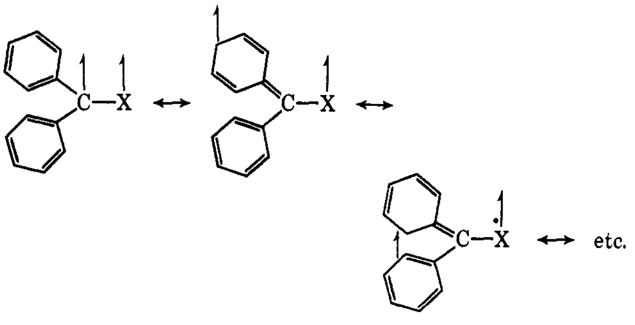
sec$^{-1}$ and $1.4 \times 10^9$ $M^{-1}$ sec$^{-1}$, respectively. The triplet decay rate constant is in agreement with the work of Ullman and Henderson,[10] who determined this value to be greater than $0.45 \times 10^7$ sec$^{-1}$.

**Table I.** Quenching of the Reaction of 1,1-Diphenylethylene with 2-Propanol by Piperylene in Acetonitrile

| [2-Propanol], $10^{-2}M$ | $k_q\Upsilon$, $M^{-1}$ | $\Upsilon$,[a] $10^{-8}$sec |
|---|---|---|
| 1.1 | 472 | 4.29 |
| 2.9 | 224 | 2.03 |
| 3.4 | 196 | 1.78 |
| 4.6 | 151 | 1.38 |

[a] Assuming $k_q = 1.1 \times 10^{10}$ $M^{-1}$ sec$^{-1}$.

It is noteworthy that the bimolecular rate constant for triplet DPE hydrogen abstraction is considerably greater than the corresponding value reported for benzophenone triplet, $10^6$ $M^{-1}$ sec$^{-1}$.[11] We suggest that the electron repulsion between the unpaired electrons in triplet DPE and benzophenone strongly induces delocalization of one electron so that the reaction sites in these biradical species resemble free radicals. The relative reactivities of triplet DPE and benzophenone may therefore parallel those of alkyl and alkoxy radicals.[12]



X = O, CH$_2$

The ability of triplet olefins to abstract hydrogen is probably related to the rate of other processes such as triplet decay and competitive reactions.

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[8] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

[9] P. J. Wagner and I. Kochvar, *ibid.*, **90**, 2232 (1968).

[10] E. F. Ullman and W. A. Henderson, *ibid.*, **89**, 4390 (1967).

[11] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); S. G. Cohen and W. V. Sherman, *J. Amer. Chem. Soc.*, **85**, 1642 (1963); J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

[12] We have been unable to find comparative data for rates of hydrogen abstraction by alkyl and alkoxy radicals in solution.

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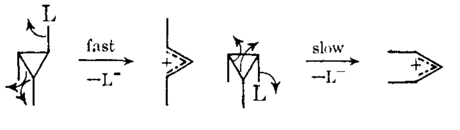
## Transannular Phenyl Participation and Electrocyclic Ring Opening in the Solvolysis of the Epimeric *exo*-3,3-Diphenyltricyclo[3.2.1.0$^{2,4}$]oct-8-yl Tosylates

*Sir:*

Stereospecific disrotatory opening of the ring has been used to rationalize the disparate solvolytic reactivities of cyclopropyl substrates.[1] We have sought



to combine this effect with possible transannular phenyl participation in solvolysis. We here report an instance of such a combination, *viz.*, an unusual 1,4-phenyl migration in the solvolysis of a cyclopropyl compound which appears to involve transannular

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[1] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); P. v. R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966); C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966); U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. Van Dine, *Tetrahedron Lett.*, 3639 (1967).