Tetrahedron Letters,Vol.24,No.1,pp 41-44,1983 0040-4039/83/010041-04$03.00/0
Printed in Great Britain

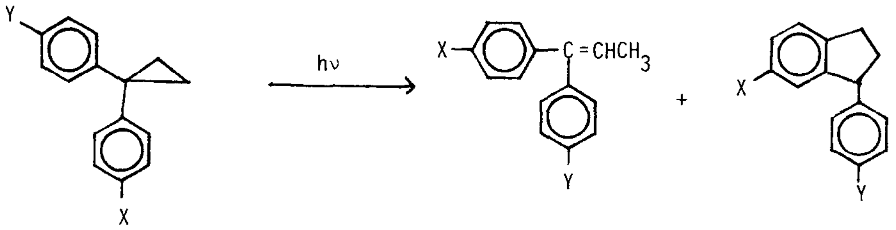
ARYLCYCLOPROPANE PHOTOCHEMISTRY. SUBSTITUENT EFFECTS ON THE PHOTOCHEMICAL CONVERSION OF 1,1-DIARYLCYCLOPROPANES TO 1,1-DIARYLPROPENES AND 1-ARYLINDANES.

Stephen S. Hixson* and Lothar A. Franke
Chemistry Department, University of Massachusetts, Amherst, Massachusetts 01003

Abstract: The rate of photochemical rearrangement of 1,1-diarylcyclopropanes to 1,1-diarylpropenes and 1-arylindanes is enhanced by electron-withdrawing groups on the aromatic rings and diminished by electron-donating groups.

Two general photochemical reactions of arylcyclopropanes are alkene and indane formation (equation 1)[1]. The former reaction is particularly common and has abundant analogy in ground state chemistry. The structural and electronic details of neither photochemical process have been studied to any extent. We report here a study of the effect of aromatic substituents on the conversion of 1,1-diarylcyclopropanes to 1,1-diarylpropenes and 1-arylindanes.

Irradiation[2] of cyclohexane solutions of cyclopropanes **1a** - **g** resulted in every case in formation of the corresponding 1,1-diarylpropenes **2a** - **g**. In most cases a 1-arylindane (**3**) was also produced[3]. Product yields obtained at 50% conversion of reactant are listed in Table 1. Time course experiments revealed that both **2** and **3** are primary photoproducts of **1**. When the photolyses of **1b** and **1c** were carried out for much longer than the time required for 50% conversion of starting material, products believed to be 3,3-diarylpropenes were detected by NMR analysis (no other cyclopropanes were irradiated for extended periods). It is assumed that these are secondary photoproducts arising by photolysis of the 1,1-diarylpropenes[4].



(1)

1 **2** **3**

a, X = Y = CF_3
b, X = Y = CN
c, X = Y = H
d, X = H, Y = CF_3
e, X = OCH_3, Y = CF_3
f, X = Y = CH_3
g, X = Y = OCH_3

Table 1. Chemical Yields of Products of Photolysis of 1,1-Diarylcyclopropanes (1) [a].

Cyclopropane	mmol	time, h [b]	Propene (2), %	Indane (3), %
1a	1.51	1.5	60 ± 3	36 ± 2
1b	0.28	1.75	52 ± 3	46 ± 2
1c	2.57	10	32 ± 2	36 ± 2
1d	1.90	7.5	26 ± 1	40 ± 2
1e	1.71	12	34 ± 2	4 ± 0.5 [c]
1f	2.25	13	46 ± 2	20 ± 1
1g	1.97	16	14 ± 1	d

[a] yields were determined at 50% conversion of cyclopropane and are based on the total amount of cyclopropane consumed; [b] time required for 50% conversion of cyclopropane; [c] identity uncertain, see Footnote 3; [d] none detected.

Table 2. Singlet Lifetimes, Reaction Quantum Yields, and Reaction Rate Constants for Cyclopropanes 1.

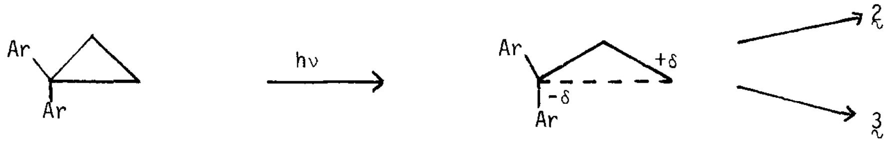
Cyclopropane	τ_s, ns	ϕ_2	ϕ_3	k_{r_2} $\times 10^{-6} s^{-1}$	k_{r_3} $\times 10^{-6} s^{-1}$
1a	0.6 ± 0.1	0.13 ± 0.01	0.020 ± 0.002	220 ± 40	33 ± 6
1b	< 0.6 [a]	0.078 ± 0.008	0.018 ± 0.002	> 130 [b]	> 30 [b]
1c	2.5 ± 0.4	0.048 ± 0.005	0.018 ± 0.002	19 ± 4	7.2 ± 1.4
1d	3.1 ± 0.4	0.038 ± 0.004	0.012 ± 0.001	12 ± 2	3.9 ± 0.6
1e	3.2 ± 0.5	0.025 ± 0.002	0.0047 ± 0.0005 [c]	7.8 ± 1.4	1.5 ± 0.3
1f	3.2 ± 0.3	0.013 ± 0.001	0.0058 ± 0.0006	4.1 ± 0.5	1.8 ± 0.2
1g	2.9 ± 0.4	0.0046 ± 0.0005	< 0.00039 [d]	1.6 ± 0.3	< 0.1

[a] lower limit; [b] upper limit; [c] identity uncertain, see footnote 3; [d] none detected.

Prolonged triplet sensitization of cyclopropanes 1a - g with acetone afforded no detectable product. Since (a) commonly the only reaction of arylcyclopropane triplets is cis-trans isomerization [1], a non-detectable process with 1a - g and (b) energy transfer from triplet acetone to 1a - g should be efficient [5], we assume that in the present work triplet energy transfer from acetone to 1a - g occurs, and conclude that the triplet states of the latter do not form 2 and 3. Products 2 and 3 are therefore singlet-derived.

Quantum yields for product formation were determined using 254 nm light [7]. Measurements of the singlet lifetimes of 1a - g were made using the single-photon-counting technique [8]; the lifetime of 1b was too short to measure with the apparatus available. Excited state reaction rate constants were then derived using the relationship $k_r = \Phi_r/\tau_s$. See Table 2 [9].

We assume a two-stage mechanism for product formation. The first step is cyclopropane bond stretching to form a diradical state [10,11] in which the excitation energy, initially largely confined to the aromatic rings, has become concentrated in the stretched cyclopropane bond [6]. This diradical state then undergoes hydrogen or carbon migration to give product.



A polar effect is evident in the pathways for formation of both 2 and 3, and, within the framework of the assumed mechanism, it seems probable that this is the result of a combination of factors. The enhanced rates of reaction of 1a and 1b are likely due in part to a relatively strong donor-acceptor interaction between the cyclopropane and aromatic rings in both cases [12]. This interaction would promote C-1, C-2 bond weakening on excitation to give the diradical state. Furthermore, the polarization of this diradical state should facilitate hydrogen migration to form the alkenes and carbon migration to give the indanes. In 1g much less demand is made by the aromatic rings on the electron-donating ability of the cyclopropane ring, and the initial excitation energy should be relatively more localized within the former. As a result, three-ring bond opening would be relatively slow. Also, any electron drift in the ring-opened diradical state should result in a polarization opposed to the favorable polarization obtained with 1a and 1b.

We thank the National Science Foundation for support of this research, and Dr. Charles Dorian for measuring the lifetime of 1b.

NOTES AND REFERENCES

1. Hixson, S. S. In "Organic Photochemistry," Vol. 4, Padwa, A. (ed.), Dekker, New York, 1979, p. 191.
2. Preparative photolyses were carried out under nitrogen using Corex-filtered light

from a Hanovia 450 W medium pressure mercury arc.

3. Products **2a** - **g**, **3c** and **3d** were identified by comparison with independently-prepared samples. Products **3a**, **3b** and **3f** were characterized spectroscopically. In the photolysis of **1e** a small amount of material with a G.C. retention time appropriate for an indane was observed; however, insufficient material was produced to allow for isolation and identification.
4. Griffin, G. W., Marcantonio, A. F., Kristinsson, H., Petterson, R. C., Irving, C. S., *Tetrahedron Lett*. **1965**, 2951.
5. Acetone has been used to sensitize the cis-trans isomerization of mono-arylcyclopropanes; see, for example, ref. 6.
6. Hixson, S. S., Gere, J. A., Franke, L. A. *J. Amer. Chem. Soc*. **1979**, *101*, 3677.
7. Potassium ferrioxalate was used as the actinometer.
8. We thank Professors N. Turro and A. Halpern for the use of their facilities.
9. The lack of correlation between the chemical yields (Table 1) and the quantum yields (Table 2) is due at least in part ot photochemical conversion of the propenes **2** back to the cyclopropanes **1**; see Hixson, S. S. *J. Chem. Soc., Chem. Commun*. **1975**, 607.
10. Becker, R. S., Edwards, L., Bost, R., Elam, M., Griffin, G. *J. Amer. Chem. Soc*. **1972**, *94*, 6584.
11. The ring-opened state need not be in a potential energy minimum for the purposes of this discussion.
12. See reference 6 and work cited therein.

(Received in USA 6 August 1983)