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Effects of Aryl Substituents on Electron-Transfer-Mediated Photochemical Addition of Alcohol to 1,1,2-Triarylcyclopropanes

Hideo Tomioka* and Osamu Inoue
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514

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Synopsis. Direct irradiation of 1,1,2-triarylcyclopropanes in alcohol resulted in the formation of all possible products arising from trimethylene biradicals, while DCB-sensitized irradiation gave a novel "anti-Markownikoff" addition product of alcohol almost exclusively. In order to get insight into the nature and fate of intermediates in the reactions, the effects of nucelophiles and aryl substituents are examined.

Since the early 1980s the scope of cyclopropane photochemistry[1)] was greatly broadened through electron transfer sensitized reaction. Among the important features of electron-transfer sensitization are higher reactivity and anomalous but simpler product distributions.[2)] Thus, Hixson et al.[3)] found that 1,4-dicyanobenzene (DCB)-sensitized photolysis of several phenylcyclopropanes in methanol-acetonitrile resulted in a novel "anti-Markownikoff" addition of methanol to the cyclopropane ring. The reactions are rationalized as proceeding via initial electron transfer from the cyclopropane to the excited DCB to give the cyclopropane cation radicals.

As a part of our program of work on the photochemical generation of ionic intermediates,[4)] we became interested in the nature of intermediates that are involved in the electron-transfer-sensitized reaction of cyclopropanes. Thus, we have irradiated several 1,1,2-triarylcyclopropanes in the presence of sensitizers (electron acceptors) in alcohols and examined the effects of nucleophiles and aryl substituents on the product distributions.

Results and Discussion

Irradiation of 1,1,2-triphenylcyclopropane (**1c**) in ethanol-acetonitrile with a light of 300W Hg lamp through quartz was monitored by GC which revealed the gradual disappearance of the starting cyclopropane along with the formation of at least five products. Separation followed by characterization of each components demonstrated that these products are diphenylethoxymethane (**2c**, R=Et), 1,1,3-triphenylpropene (**3c**), 1,1,3-triphenylpropane (**4c**), 1,1,3-triphenyl-1-ethoxypropane (**5c**, R=Et), and 1,1,3-triphenyl-3-ethoxypropane (**6c**, R=Et), all of which are the most commonly observed photoproducts of arylcyclopropanes in alcohols as a result of ring opening.[5)] In a marked contrast, similar irradiation of **1** in the presence of *p*-dicyanobenzene (DCB) resulted in a rapid disappearance of **1c** and concurrent appearance of single major product which was assigned as polar addition product **6c** (R=Et) of the OH bond across the ring in "anti-Markownikoff" fashion.

Similar marked enhancement of photoreactivity of the triphenylcyclopropane caused by DCB was also observed when other alcohols are employed as a trapping reagent although yield of anti-Markownikoff addition product decreased in *t*-butyl alcohol (Table 1). In 2,2,2-trifluoroethanol (TFE), **1c** was equally rapidly photolyzed in the presence of DCB, but the addition product was formed in only 12% yield. This

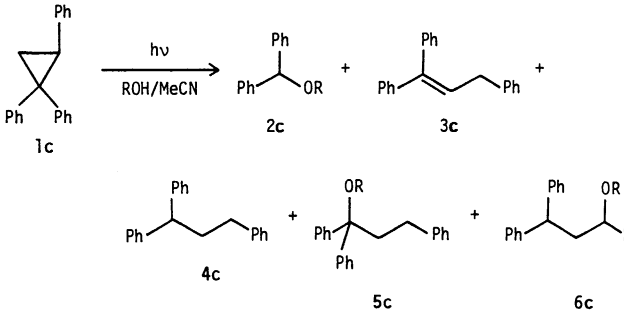


Table 1. Irradiation of **1c** in Various Alcohols[a)]

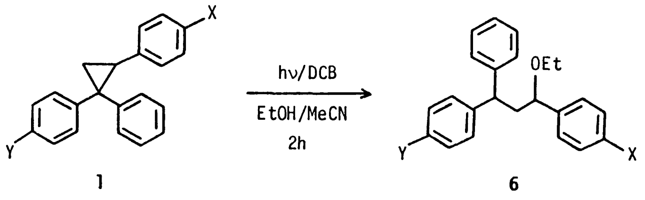
ROH	Condition[b)]	Irradiation time/h	Conversion	Yield/%[c)]				
			%	**2c**	**3c**	**4c**	**5c**	**6c**
MeOH	D	16	68.7	15.8	28.2	<1	<1	<1
	S	2	98.1	5.3	0	0	0	75.0
EtOH	D	16	75.9	15.9	4.6	<1	5.6	3.1
	S	2	95.2	4.3	0	0	0	85.3
^{i}PrOH	D	16	65.0	18.4	26.1	<1	0	0
	S	2	96.8	3.2	0	0	0	87.2
^{t}BuOH	D	16	70.4	9.4	12.9	<1	0	0
	S	2	95.0	1.5	0	0	0	51.8
CF_3CH_2OH	D	16	70.4	19.5	18.7	<1	0	0
	S	2	93.9	0	0	0	0	12.1

a) Direct irradiations were conducted on 10 mM solution of **1c** in ROH/MeCN (1 : 4) at 10 °C in quartz tubes. For sensitized run, *p*-DCB (10 mM) was added to the solution. b) D refers to direct irradiation while S refers to sensitized run. c) Determined by GC.

Table 2. Effect of Aryl Substituents on DCB-Sensitized Photoreaction of 1,1,2-Triarylcyclopropane in EtOH/MeCN[a)]

1	X	Y	OX $E_{1/2}$/V[b)]	ΔG/kJ · mol^{-1}[c)]	Conversion %	**6**/%
a	MeO	H	0.98	−138.2	96.8	72.3
b	Me	H	1.25	−112.7	98.1	57.5
c	H	H	1.25	−112.7	95.2	85.3
d	CN	H	1.40	−97.8	30.2	23.6
e	NO_2	H	1.47	−91.3	4.8	0
f[d)]	H	MeO	1.17	−120.7	96.1	63.4
g[d)]	H	CN	1.39	−99.0	90.7	44.6
h[d)]	H	NO_2	1.41	−97.1	2.4	0

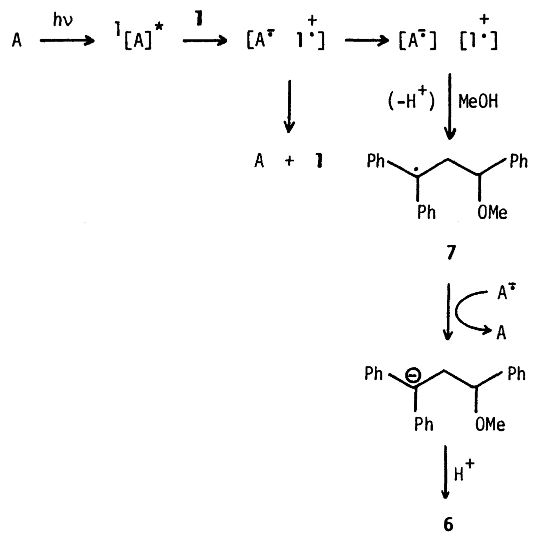
a) All irradiations were conducted on 10 mM solution of **1** in the presence of 10 mM of *p*-DCB in EtOH/MeCN (1 : 4) for 2 h in quartz tubes. Yields were determined by GC. b) Oxidation potentials were obtained by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 mol dm^{-3}) in acetonitrile solution, vs. Ag/Ag$^+$. c) Calculated using Eq. 1. d) Roughly 1 : 1 cis-trans mixtures were used.



suggests that an intermediate generated by the interaction of excited DCB with **1c** is not efficiently trapped by TFE presumably due to its decreased nucleophilicity. Complete absence of addition products in the direct run, however, indicates that the intermediate formed in the DCB-sensitized run should be considerably electrophilic.

A series of *p*-monosubstituted triphenylcyclopropanes (**1a**,**b**,**d**—**h**) were prepared by conventional method and the effect of these substituents on the electron-transfer-mediated photoreaction was investigated. The results summarized in Table 2 suggest that the introduction of strongly electron-withdrawing group (i.e., nitro) suppressed the reaction almost completely. It is also noted that the reaction is somewhat more sensitive to the substituent (X) on 2-phenyl ring than that (Y) on 1-phenyl ring. Thus, the reaction was essentially unaffected by *p*-cyano group on 1-phenyl ring while the same group on 2-phenyl ring considerably suppressed the reaction.

The foregoing observations are explained in terms of the mechanism involving electron transfer originally proposed by Hixson.[3)] Thus, excitation of the sensitizer is followed by electron transfer from the cyclopropane to the sensitizer[6)] to give the geminate sensitizer anion radical-cyclopropane cation radical pair. The initially formed radical cation has the three-membered ring intact since it has been suggested that the electron has been taken from a phenyl ring.[7)] This radical ion pair can either deactivate by back electron transfer, or dissociate to separated radical ions, where the radical cation is attacked by alcohol followed by proton loss to afford diphenylmethyl radical (**7**).



Reduction of **7** with the sensitizer anion radical ($A^{\bar{\cdot}}$) leads to the adduct **6**.

What is the origin of the effect of ring substituents, then? A possible explanation would be that electron transfer becomes less feasible as more electron withdrawing groups are introduced on phenyl ring. The free energy change (ΔG) associated with the electron-transfer process can be estimated using Wellers' equation[8)] originally proposed to account for fluorescence quenching by electron-transfer mechanism,

$$\Delta G(\text{kJ mol}^{-1}) = 96.8[E(\text{D/D}^+)_\text{v} - E(\text{A/A}^-)_\text{v} - e^2/(\varepsilon a)] - E\text{s} \qquad (1)$$

where $E(\text{D/D}^+)$ and $E(\text{A/A}^-)$ are the oxidation potentials of the donor (in this case the cyclopropanes) and the reduction potential of the acceptor (in this case the sensitizer), respectively. Thus, the oxidation potential of **1** were measured by cyclic voltammetry and the free energy of electron transfer to DCB ($E\text{s}$=408.4 kJ mol^{-1}, $E^{\text{red}}_{1/2}$=2.00 eV)[9)] from various cyclopropanes **1a**—**h** in MeCN was estimated (Table 3). In all cases ΔG is significantly negative. This means that the electron transfer process should be spontaneous for all cyclopropanes employed.

Complete lack of reactivity of the cation radical from *p*-nitro derivatives, then, can be interpreted as indicating that the lifetime of the cation radical is too short, due to the strongly destabilizing effect of *p*-nitro group, to be trapped by alcohol and hence it undergoes the back electron transfer in the geminate pair before it dissociates and/or is intercepted by alcohol.[10)]

Experimental

Instrumentation. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO A-100 spectrometer and ^{1}H NMR spectra were determined with JEOL JNM-MH-100 NMR spectrometer in CCl_4 with Me_4Si as an internal reference. Mass spectra were recorded on Shimadzu QP-1000 mass spectrometer (70 eV). Oxidation potentials were measured on Yanaco polarographic analyzer P-1100.

Materials. All 1,1,2-triarylcyclopropanes (**1a**—**h**) were prepared by the reaction of the corresponding diaryldiazomethanes with styrenes in refluxing benzene, followed by column chromatography. The data are shown below.

1a: Yield 24.7%; mp 109—112 °C (lit,[11a] 111—112 °C).

1b: Yield 78.1%; Liquid; ^{1}H NMR δ=7.10—6.96 (10H, m), 6.79—6.56 (4H, m), 2.74 (1H, dd), 2.19 (3H, s), 1.93—1.63 (2H, m); MS *m/z* 284.

1c: Yield 73.5%; mp 47—48.5 °C (lit,[11b] 49.5—50.0 °C).

1d: Yield 55.5%; mp 111.0—112.0 °C; ^{1}H NMR δ=7.20—6.45 (14H, m), 2.92—2.70 (1H, m), 2.02—1.68 (2H, m); MS *m/z* 295.

1e: Yield 76.4%; mp 97.2—99.8 °C; ^{1}H NMR δ=7.79 (2H, d), 7.40—6.80 (12H, m), 2.85 (1H, dd), 2.10—1.80 (2H, m); MS *m/z* 315.

1f: Yield 79.0%; mp 57.0—59.5 °C; ^{1}H NMR δ=7.10—6.40 (14H, m), 3.60 and 3.56 (each s, 3H), 2.76—2.60 (1H, m), 1.87—1.54 (2H, m); MS *m/z* 300.

1g: Yield 53.5%; mp 55.0—57.0 °C; ^{1}H NMR δ=7.40—6.60 (14H, m), 2.90—2.60 (1H, m), 2.10—1.60 (2H, m); MS *m/z* 295.

1h: Yield 85.3%; mp 120.0—121.0 °C; ^{1}H NMR δ=8.10—7.80 (2H, m), 7.40—6.80 (12H, m), 3.10—2.80 (1H, m), 2.20—1.70 (2H, m); MS *m/z* 315.

Authentic samples of **3c**—**5c** were prepared according to the literature procedures.[5,12] The ethers **6** were isolated from the DCB-sensitized photolytic mixtures by preparative TLC and characterized spectroscopically. ^{1}H NMR data are shown below.

6a (R=Et): ^{1}H NMR δ=7.2—6.6 (14H, m), 4.12 (1H, dd), 3.94 (1H, dd), 3.58 (3H, s), 3.35—2.87 (2H, m), 2.56—2.02 (2H, m), 1.06 (3H, t).

6b (R=Et): ^{1}H NMR δ=7.1—6.5 (14H, m), 4.10 (1H, dd), 3.80 (1H, dd), 3.38—2.90 (2H, m), 2.54—2.00 (2H, m), 2.18 (3H, s), 1.05 (3H, t).

6c (R=Me): ^{1}H NMR δ=7.6 (15H, bs), 4.10 (1H, dd), 3.82 (1H, dd), 3.03 (3H, s), 2.60—2.05 (2H, m).

6c (R=Et): ^{1}H NMR δ=7.5—6.8 (15H, m), 4.17 (1H, dd), 3.87 (1H, dd), 3.30—2.95 (2H, m), 2.46—2.00 (2H, m), 1.08 (3H, t).

6c (R=^{i}Pr): ^{1}H NMR δ=7.4—6.9 (15H, m), 4.12 (1H, dd), 3.95—3.40 (2H, m), 2.52—2.00 (2H, m), 1.20 (3H, d).

6c (R=^{t}Bu): ^{1}H NMR δ=7.6 (15H, bs), 4.12 (1H, dd), 3.90 (1H, dd), 2.75—2.00 (2H, m), 1.20 (9H, s).

6c (R=CH$_2$CF$_3$): ^{1}H NMR δ=7.4—6.8 (15H, m), 4.15 (1H, dd), 3.98 (2H, q), 3.90 (1H, dd), 2.50—2.09 (2H, m).

6d (R=Et): ^{1}H NMR δ=7.4—6.6 (14H, m), 4.12 (1H, dd), 3.85 (1H, dd), 3.32—2.87 (2H, m), 2.55—2.00 (2H, m), 1.08 (3H, t).

6f (R=Et): ^{1}H NMR δ=7.3—6.5 (14H, m), 4.2—4.0 (1H, m), 4.0—3.8 (1H, m), 3.66, 3.63, (3H, s), 3.5—2.8 (2H, m), 2.6—2.1 (2H, m), 1.10 (3H, t).

6g (R=Et): ^{1}H NMR δ=7.5—7.0 (14H, m), 4.14 (1H, dd), 3.85 (1H, dd), 3.4—2.9 (2H, m), 2.5—2.1 (2H, m), 1.09 (3H, t).

Irradiation for Product Identification. In a typical run, a solution of **1** (1 mmol) and *p*-DCB (1 mmol) in ROH (10 dm^3)-MeCN (40 dm^3) was placed in a quartz tube and irradiated using a high pressure, 300W, Hg lamp with a water-cooled quartz jacket. The progress of the reaction was monitored by TLC. After irradiation of 5 h, the irradiation mixtures were concentrated on a rotary evaporator and chromatographed on preparative TLC (silica gel) eluted with chloroform-hexane.

Irradiation for Analysis Purposes. All irradiations outlined in Tables were carried out on 10 mM solutions of **1** in a quartz tube of 5 dm^3 capacity at 15 °C. The yields were conveniently determined by standard GC techniques, and the identity of the products was confirmed by GC-MS comparison with authentic samples prepared as above.

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