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[3+2] CYCLOADDITION OF CYCLOPROPANE WITH VINYL ETHER VIA PHOTOINDUCED ELECTRON TRANSFER

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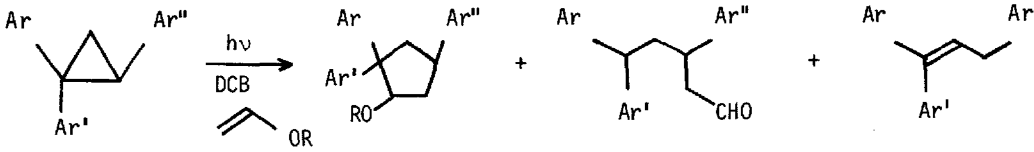
Abstract: Irradiation of 1,1,2-triarylcyclopropanes and vinyl ether in acetonitrile in the presence of cyano aromatic sensitizers resulted in the formation of cyclopentanes as a result of [3+2] cycloaddition of cyclopropyl cation radical with the nucleophilic alkene.

The scope of alkene photochemistry has been greatly broadened by electron-transfer-sensitized reactions.[1] For example, alkene radical cations generated as a result of electron-transfer-sensitized reaction undergo isomerization, dimerization, mixed addition, nucleophilic addition, oxygenation and reaction with the counterpart radical anions. Most of these reactions reflect the characteristics of a cation and therefore undergo with high selectivity and efficiency, which can not be attained by direct and/or traditional triplet sensitized excitation of alkene generating neutral radical. On the other hand, the photochemistry of cyclopropanes has been considerably stimulated by these findings in the electron-transfer-sensitized reactions of alkenes and many useful reactions involving cyclopropane cation radicals have been reported in recent years.[1-5] However, the reactions of cyclopropane cation radicals have not been thoroughly exploited. For example, no attempts seem to have been made to trap the cation radical with nucleophilic alkenes e.g., vinyl ethers, which have been frequently employed to trap the alkene cation radical resulting in an efficient formation of [2+2] cycloadducts [1,6] although the cation radical should have potential ability to react with nucleophilic alkenes in a [3+2] fashion leading to the construction of synthetically important cyclopentane skeleton. We wish to report here that such reaction was realized using 1,1,2-triarylcyclopropane and vinyl ether via photoinduced electron transfer.

When an acetonitrile solution containing 1,1-di(p-anisyl)-2-phenylcyclopropane (**1a**, 8mM) and methyl vinyl ether (**2a**, 250mM) was irradiated with a 300 W high-pressure mercury arc through quartz for 4 h, more than 95% of the starting materials was recovered unchanged. Only product isolated was 1,1-di(p-anisyl)-3-phenylpropene (**5a**) and no reaction products between **1a** and **2a** were detected. In marked contrast, similar irradiation of **1a** and **2a** in the presence of an equimolar amount of p-dicyanobenzene (DCB), where roughly 2/3 of the incident light (253nm) was absorbed by DCB, led to rapid disappearance of the starting materials and concurrent formation of adduct **3a**



1 2 3 4 5

as a major product along with **4a** as well as **5a**. About 80 % of DCB was also recovered from the photolysis mixture. The structure of 3 and **4** were mainly assigned from their 400 MHz ^{1}H NMR spectra. The analysis of the spectra revealed the partial structures -CH(OH$_3$)-CH$_2$-CH-CH$_2$- for **3** and HC(=O)-CH$_2$-CH-CH$_2$-CH- for **4**. The spectrum[7] of **3** showed the presence of two diastereoisomers in a 2:1 ratio.

Similar irradiation of other 1,1,2-triarylcyclopropanes also afforded the product (**3**-**5**), although the product distributions were sensitively changed with the substituents on aryl rings (Table 1). Thus, 1-(p-anisyl)-1,2-diphenylcyclopropane (**1b**) also afforded the products (**3b**-**5b**) in roughly similar ratio upon irradiation, while similar irradiation of 1,1,2-triphenyl derivative (**1c**) resulted in an increase in the aldehyde (**4c**) formation at the expense of the cyclopentanes (**3c**). Irradiation of **1** (**d**,**e**) bearing such electron-withdrawing groups as CN either on 1-phenyl or on 2-phenyl ring afforded no trace of the expected adducts (**3** and/or **4**).

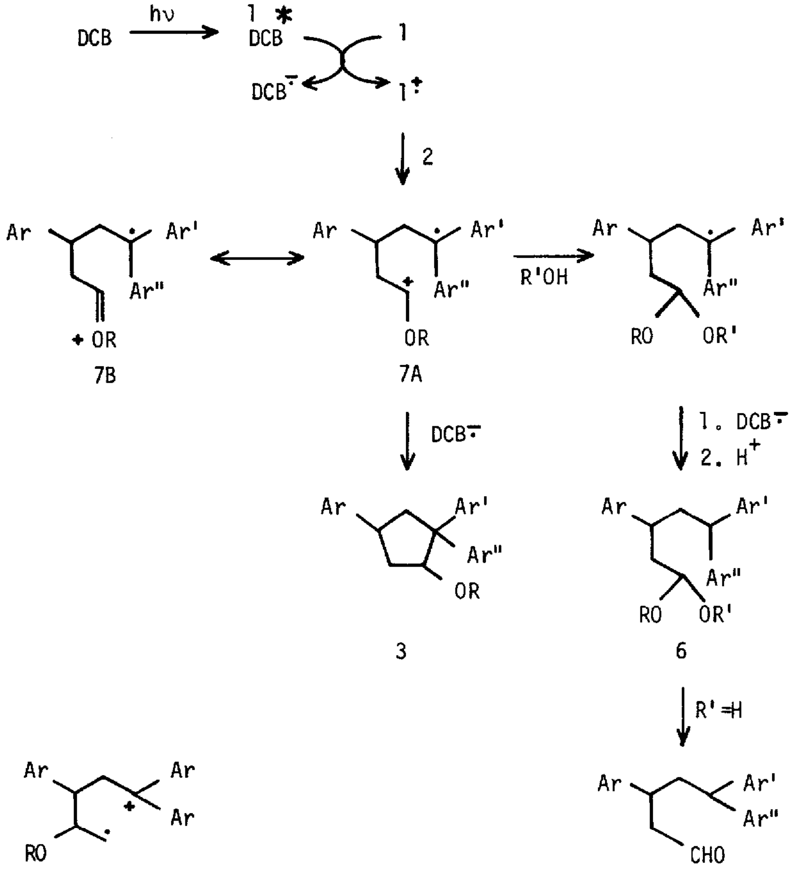
Table 1. Effect of aryl substituents in photochemical reactions of triarylcyclopropanes (**1**) and vinyl ethers (**2**)[a)]

	1			**2**		Yield(%)[b)]		
	Ar	Ar'	Ar"	R	Conv(%)[b)]	**3**	**4**	**5**
a	4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	Ph	Me	68.5	40.6	23.1	32.3
				Et	77.6	60.0	12.3	20.9
b	4-MeOC$_6$H$_4$	Ph	Ph	Me	57.8	43.7	24.1	6.1
				Et	61.9	61.8	13.5	6.7
c	Ph	Ph	Ph	Me	33.6	9.8	55.1	15.9
				Et	28.4	8.3	47.2	20.7
d	4-NCC$_6$H$_4$	Ph	Ph	Et	2	0	0	0
e	Ph	Ph	4-NCC$_6$H$_4$	Et	2	0	0	0

[a)] Irradiations were carried out on 8mM degassed solution of **1** and DCB in MeCN in the presence of a 30 molar excess of **2** for 4h through a quartz with a 300 W high-pressure Hg lamp. [b)] Determined by GC.

In order to obtain insight into the mechanism of the present novel photocycloaddition, we carried out some additional experiments. First, the sensitizers play a critical role in the present photoaddition. Thus, dimethyl terephthalate acted as an equally effective sensitizer, whereas use of benzonitrile in place of DCB resulted in a considerable decrease in the rate of the reaction although the adducts were also formed albeit in a poor yield. More importantly, irradiation with 1,4-dicyanonaphthalene (DCN) with long wavelength light (>300 nm) which is not absorbed by **1** also produced the adducts, although the efficiency of reaction was somewhat reduced. The results clearly indicate that the present photoaddition must be cyano-aromatics-sensitized reaction, most probably via single electron transfer. Further supporting evidence was obtained in the effect of solvent. Thus, the reaction was found to be quite sensitive to the nature of the solvent employed. The reaction proceeded quite smoothly in acetonitrile, while **1** was essentially unreactive in most of other less polar solvents (e.g., ethers, benzene, cyclohexane, and chloroform). Prolonged irradiation in those less polar solvents afforded only the propene (**5**) and no trace of the adducts were detected even in the presence of DCB. Such a critical effect of solvent is now well-known[1] as characteristic feature of the electron transfer reactions.

The foregoing observations are strongly reminiscent of the related photosensitized electron transfer reactions[1-5] of cyclopropanes and can be better explained in terms of a mechanism involving initial single electron transfer rather than a simple free-radical mechanism. The next problem to be solved is then whether cycloaddition takes place through the reactionof vinyl ether cation radical with cyclopropane or that of cyclopropane cation radical with vinyl ether. From the Rehm-Weller equation[8], the free energy changes(Δ G) for the photoinduced electron transfer process are estimated to be -120.7 kJ/mol[4] for **1b** and - 120.9 kJ/mol[6] for **2b**, when DCB was used as the electron acceptor. This implies that the electron transfer process should be spontaneous for both **1**



Scheme 1

and 2. However, quenching constants ($k_q\tau$) for fluorescence of DCB with **1** and **2** are 99.3 and 33.8 M^{-1}, respectively, suggesting that the excited singlet state DCB accepts electron mainly from **1**.

The origin of adduct **4** seemed to give us a clue to the nature of intermediate. Irradiation of **3** under similar conditions did not lead to the formation of **4**, suggesting that **4** is a primary photoproduct, not derived from 3 by the secondary photochemical reaction. The irradiation in the presence of water resulted in a marked increase in the yield of **4** at the expense of **3**, strongly suggesting that 3 is formed via attack of water on the intermediate leading to **4**. More intriguingly, the irradiation carried out in the presence of ethanol afforded diethyl acetal (**6**) of **4** at the expense of not only **4** but also 3. These findings suggest that the intermediate leading to **3**,**4** and **6** must be **7**, which should be formed by nucleophilic attack of vinyl ether on the cyclopropane cation radical rather than the electrophilic attack of cyclopropane on the vinyl ether cation radical (Scheme 1); the latter mode of attack should result in the generation of cation radical intermediate **8** where the cation is located on cyclopropyl carbon whereas radical on alkene carbon. The direction of addition, i.e., complete regioselective formation of 3 is in agreement with the results [4] in the DCB-sensitized addition of alcohol on **1** where nucleophilic attack of alcohol on the cyclopropyl cation radical occurred regioselectively on the monophenyl-substitited carbon. Apparently, the intermediate **7**, where cationic center is stabilized by the unshared electron on adjacent oxygen whereas radical center is delocalized through two phenyl rings, is the most stabilized one among the other possible intermediates including **8** and explained the observed highly regioselective cycloaddition.

Further work in the area is warranted, not only on more simple cyclopropanes, but also on other classes of nucleophilic alkenes.

References and Notes

1 See for recent review, a) S. L. Mattes and S. Farid, "Organic Photochemistry", Vol. VI, A. Padwa, Ed. Marcel Dekker, Inc., New York, 1983, p 233; b) K. Mizuno, J. Syn. Org. Chem., Jpn., **44**, 1010 (1986); c) T. Miyashi and M. Kamata, Ibid., **44**, 986 (1986); d) G. J. Kavarnos and N. J. Turro, Chem. Rev., **86**, 401 (1986); e) J. J. McCullough, Ibid., **87**, 811 (1987); f) J. Mattay, Angew. Chem. Int. Ed. Engl., **26**, 825 (1987).
2 See for example, Y. Otsuji and K. Mizuno, Rep. Asahi Glass Found. Ind. Technol., **49**, 215 (1986), and references cited therein.
3 V. R. Rao and S. S. Hixson, J. Am. Chem. Soc., **101** 6458 (1979).
4 H. Tomioka, and O. Inoue, Bull. Chem. Soc. Jpn., **61**, 1404 (1988).
5 See also a) H. Tomioka and O. Inoue, Bull. Chem. Soc. Jpn., **61**, 3725 (1988). b) H. Tomioka and H. Miyagawa, J. Chem. Soc., Chem. Commun., 1183 (1988).
6 K. Mizuno, H. Ueda and Y. Otsuji, Chem. Lett., 1237 (1981).
7 ^{1}HNMR ($CDCl_3$, δ) 2.15-2.32 (3H,m), 2.98 (1H, dd, J=13.4, 8.5Hz), 3.44(3H, s), 3.45-3.57 (1H, m), 3.81 (6H, s), 4.42 (1H, dd, J=7.9, 7.9Hz), 6.79-6.88 (4H, m), 7.14-7.38 (9H, m) for the major isomer; 2.02 (1H, dd, J=14.7, 6.0Hz), 2.47 (1H, ddd, J=14.7, 10.6, 4.6Hz), 2.72 (1H, dd, J=12.0, 11.8Hz), 2.87 (1H, dd, J=12.0, 7.0Hz), 3.05-3.15 (1H, m), 3.31 (3H, s), 3.76 (3H, s), 3.81 (3H, s), 4.47 (1H, d, J=4.6Hz), 6.79-6.88 (4H, m), 7.14-7.38 (9H, m) for the minor isomer.
8 D. Rehm and A. Weller, Isr. J. Chem., **8**, 259 (1970).

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