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PROTON-INDUCED SINGLE ELECTRON TRANSFER REACTIONS: PHOTOOXYGENATION OF 1,1,2,2-TETRAARYLCYCLOPROPANES IN THE PRESENCE OF PROTIC ACIDS

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Summary: Irradiation of 1,1,2,2-tetraarylcyclopropanes with trifluoroacetic acid in the presence of oxygen produced 3,3,5,5-tetraaryl-1,2-dioxolanes. This reaction is initiated by the single electron transfer from cyclopropanes to excited carbenium ions which are formed by sequential ring opening and light absorption of protonated cyclopropanes.

Although extensive efforts have been made on the several types of single electron transfer (SET) reactions accompanied by the cation radical formation,[1] only a few examples of the proton-induced SET reactions are reported.[2] This type of reaction is quite unique since addition of an electron accepting compound is not required. We now report the first example of proton-induced SET photooxygenation of 1,1,2,2-tetraarylcyclopropanes to give 3,3,5,5-tetraaryl-1,2-dioxolanes.[3]

When an acetonitrile solution of 1,1-bis(p-methoxyphenyl)-2,2-diphenylcyclopropane (**1a**) (0.10 mmol) and trifluoroacetic acid (pk_a = 0.23, 0.10 mmol) was irradiated with a 2 kW xenon lamp (λ>390 nm) under oxygen for 1 h, 3,3-bis(p-methoxyphenyl)-5,5-diphenyl-1,2-dioxolane (**2a**) (m.p. 106°C)[4] was obtained in 92% yield. Upon similar irradiations, (**2b**) (m.p. 142°C)[4] and (**2c**) (m.p. 128°C)[4] were obtained, respectively, from (**1b**) and (**1c**). The less electron-donative cyclopropane (**1d**), however, did not afford 1,2-dioxolane (**2d**) as shown in Table 1.

Detailed mechanistic studies further provided the following observations: i) Stirring of the reaction mixtures in the dark for 48 h gave no 1,2-dioxolanes (**2**), and cyclopropanes (**1**) were quantitatively recovered; ii) Varying the amount of CF_3COOH [0.2-1.0 equiv. to (**1a**)] did not change the yield of (**2a**); iii) (**2a**) were similarly obtained by the irradiation with CF_3SO_3H (pk_a = 0, (**2a**) = 78%), CH_3SO_3H (pk_a = 0, (**2a**) = 94%), CCl_3COOH (pk_a = 0.65, (**2a**) = 93%), or $CHCl_2COOH$ (pk_a = 1.29, (**2a**) = 92%), but the

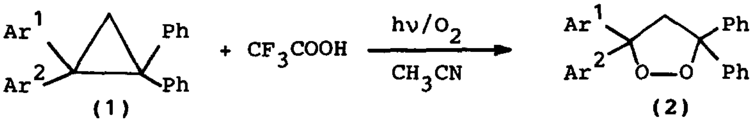


Table 1. Oxidation potentials of cyclopropanes (1) and yields of dioxolanes (2).

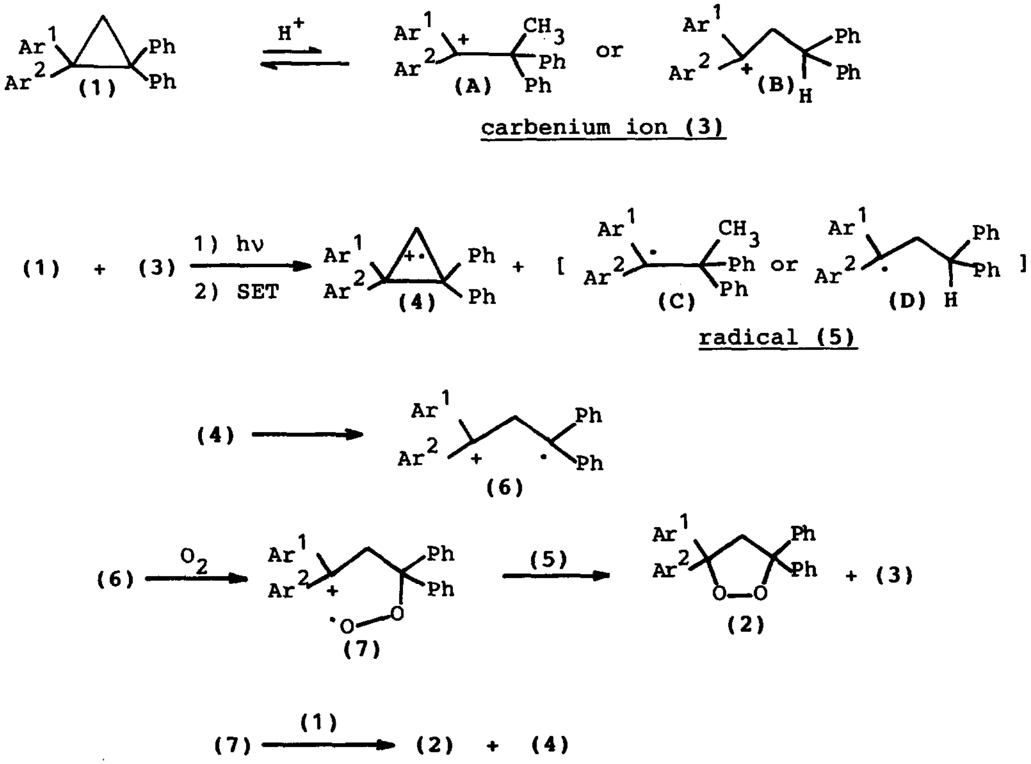
(1)[a]	$E_{1/2}^{ox}$/V[b] vs. SCE	irradiation time/h	yield of[c] (2)/%	conversion/%
1a; $Ar^1=Ar^2=p\text{-}MeOC_6H_4$	0.87	1	92	100
1b; $Ar^1=p\text{-}MeOC_6H_4$	0.94	1	trace[d]	8
$Ar^2=Ph$		7	91	100
1c; $Ar^1=Ar^2=p\text{-}MeC_6H_4$	1.11	1	0	6
		10	44	100
1d; $Ar^1=Ar^2=Ph$	1.28	1	0	0
		10	0	3

[a] (1) = 0.10 mmol, CF_3COOH = 0.10 mmol, CH_3CN = 5 ml. [b] Measured by cyclic voltammetry at a platinum electrode in CH_3CN with 0.10 M tetraethylammonium perchlorate as a supporting electrolyte, SCE = saturated calomel electrode. [c] Determined by ^1H NMR. [d] Less than 2% yield.

irradiation with $CH_2ClCOOH$ (pk_a = 2.86) or CH_3COOH (pk_a = 4.76) did not afford (2a); iv) Addition of 1,2,4,5-tetramethoxybenzene (TMB) [1.0 equiv. to (1a)],[5] which is known as an efficient quencher for SET processes,[3e,6] suppressed the oxygenation of (1a), while no quenching was observed when anisole (AN) [1.0 equiv. to (1a)][5] was added; v) Addition of pyridine[7] or 1,4-diazabicyclo[2,2,2]octane (DABCO) [1.0 equiv. to (1a)][7] completely quenched the oxygenation. The results described above would indicate that the oxygenation of cyclopropanes (1) is initiated by proton-induced SET process. A plausible mechanism taking all observations into account is proposed in Scheme 1.

The first step is the formation of carbenium ions (3; A or B) by strong acids such as CF_3COOH, CF_3SO_3H, CH_3SO_3H, CCl_3COOH, and $CHCl_2COOH$. This prediction is supported by the observations that electronic spectrum of (1a) with CF_3COOH in dichloromethane (λ_{max} = 495 nm)[8] is quite similar to that of bis(p-methoxyphenyl)methylcarbenium ion (λ_{max} = 500 nm)[2e] generated by mixing 1,1-bis(p-methoxyphenyl)ethylene with CF_3COOH in benzene, while a dichloromethane solution of (1a) with CH_3COOH did not show such absorption in the visible region (λ>390 nm). Moreover, no dioxolane forma-

Scheme 1



tion for (1d) with CF_3COOH would be explained by the fact that an appreciable absorption was not observed in the same region. Lewis bases such as pyridine and DABCO quench the formation of carbenium ions (3). Carbenium ions (3) would act as a sensitizer like triphenylcarbenium ion.[9] Thus, excited (3) abstract single electron from (1) to form cation radicals (4) and radicals (5; C or D). The electron transfer quenching of (4) by TMB suppressed the oxygenation. This explanation is supported by the observation that the more oxidizable cyclopropane ((1a)>(1b)>(1c)>(1d)) more efficiently produced the corresponding dioxolanes. The C-C bond cleavage of (4) lead to (6) followed by the O_2 addition to give rise to (7). The SET from (5) to (7) reproduces (3) accompanied by the formation of (2). The SET from (1) to (7) alternatively produces (2) along with (4).[10]

In conclusion, we have found that protic acids are useful to generate cation radical species under irradiation conditions which behave similarly to usual SET reactions. The key step of this unique reaction is the formation of carbenium ion intermediates as electron accepting sensitizers.

References and Notes

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4) Satisfactory elemental analyses and spectroscopic data were obtained for (**2a-c**).

5) $E^{ox}_{1/2}$(TMB) = 0.74 V (vs. SCE in CH_3CN), $E^{ox}_{1/2}$(AN) = 1.74 V (vs. SCE in CH_3CN).

6) E. Hasegawa and T. Mukai, Bull. Chem. Soc. Jpn., 58, 3391 (1985).

7) $E^{ox}_{1/2}$(pyridine) > 2.50 V (vs. SCE in CH_3CN), $E^{ox}_{1/2}$(DABCO) = 0.68 V (vs. SCE in CH_3CN).

8) [(**1a**)] = 5.0×10^{-3}M, [CF_3COOH] = 2.5×10^{-1}M.

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10) The proposed mechanism partly involving a radical chain process could be supported by the observations that the oxygenation of (**1a**) is catalyzed in the dark by triphenylcarbenium tetrafluoroborate[3d] or tris-(p-bromophenyl)aminium hexachloroantimonate[3e] to yield (**2a**) in 85% and 88%, respectively. Although the quantum yield measurements for the formation of (**2**) may provide direct evidence for this mechanism, it appears to be difficult to determine the quantum yields since the absorptions above 390 nm of (**1**) with CF_3COOH in CH_3CN are too weak even in high concentrations, i.e. the absorbance at 500 nm (λ_{max}) of (**1a**) (1.0×10^{-1}M) with CF_3COOH (1.0×10^{-1}M) in CH_3CN is 0.025.

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