

# Selective Photosubstitution Reactions of Tertiary 1-Alkyl-1,1-diarylmethyl Chloride: Simultaneous Formation of Radicals and Carbocations from the Excited State of 1-Alkyl-1,1-diarylmethyl Chloride

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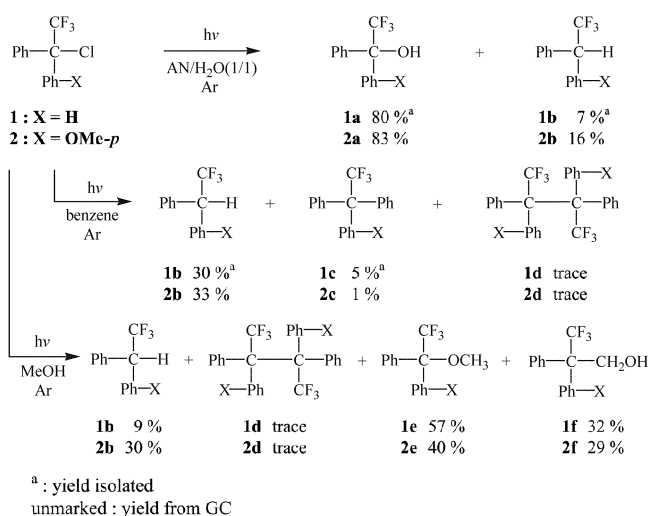
Received May 6, 2003

**Key Words :** Excited state partition, Heterolysis, Homolysis, Selective photosubstitution, 2,2,2-Trifluoro-1,1-diarylethyl chloride

Photochemical reactions of arylmethyl halides are interesting and invaluable in synthetic methods because of a possible complement for thermal reactions and in their own rights. In 1963, Zimmerman and Sandel<sup>1</sup> reported that *m*-methoxybenzyl chloride underwent photochemical solvolysis in aqueous dioxane. Since then, it has been reported that photochemical reactions of a variety of substituted benzyl halides gave solvolysis products and homolysis products.<sup>2-5</sup> For benzhydryl chloride, steady state and laser flash photolyses have been studied;<sup>6</sup> photochemical reaction of benzhydryl chloride in acetonitrile (AN) containing *n*-octane gave six products; transient species such as benzhydryl radicals and cations, and excited benzhydryl radical have been identified. Several mechanisms for these reactions have been proposed.<sup>2-5,7</sup> Generally, benzyl type carbocations and radicals generated from the reactions proceed solvolysis and radical/radical coupling, respectively. We wish to report that upon change of medium conditions the selective photoreactions of tertiary arylmethyl chloride are accomplished: in polar solvent solvolysis reactions principally undergo, whereas in nonpolar solvent reduction reactions occur. In addition the intermediates, radical and carbocation are simultaneously generated from the excited states in the reactions.

When a 1.9 mmolar solution of 1,1-diphenyl-2,2,2-trifluoroethyl chloride (**1**) in aqueous AN (1/1 v, 400 mL) was irradiated in a quartz immersion well photolysis apparatus with circulating oxygen, the substrate was consumed within 1 h. After evaporation of the solvent, column chromatography (silica gel) using *n*-hexane as eluent gave two fractions. The first small fraction was reduction product **1b** (7%) and the latter principal one was hydrolysis product **1a** (80% in isolated yield, Scheme 1).

When a 1.9 mmolar solution of **1** in benzene under argon was irradiated and treated as above, reduced product (**1b**) was mainly obtained in yield 30% with trace dimer **1d** and small amount of phenyl-substituted product, 1,1,1-trifluoro-2,2,2-triphenylethane (**1c**, 5%, Scheme 1). Since deuterated **1b** was detected in GC/MS [ $M^+(D)$  237;  $M^+(H)$  236] when **1** was subjected to the photochemical reaction in deuterated benzene, benzene molecules act as hydrogen donor and solvent; hydrogen donor is probably, Dewar benzene and benzvalene which were generated from the photochemical reaction of benzene. The results of other preparative



Scheme 1

reactions are shown in Scheme 1. Dark reactions in all of these cases were negligible.

Relative kinetic experiments were performed to understand the photoreactivities of the tertiary arylmethyl chloride: relative product yields from the photoreactions of 1,1-diaryl-2,2,2-trifluoroethyl chlorides were measured by analyzing GC spectra. In aqueous AN solution, hydrolysis product **1a** (34.6%) was mainly obtained with small amounts (3%) of reduced and trace amount of dimerized products (**1b**, **1d**, entry 1 in Table). The carbocations formed in the reaction are probably stabilized in the polar solvent to afford ion-derived product.<sup>8</sup> In aqueous acetonitrile in the presence of oxygen, alcohol **1a** (39%) was mainly obtained as observed in preparative reaction (entry 2). In addition to the formation of ion-derived alcohol, alcohol **1a** can be formed *via* 1,1-diphenyl-2,2,2-trifluoroethyl hydroperoxide which might be generated by reacting 1,1-diphenyl-2,2,2-trifluoroethyl radical<sup>8</sup> with oxygen. In benzene, reduced product, **1b** was mainly acquired with small amounts of **1c** and **1d** as described in preparative reaction (entry 3). In methanol, methanolysis product **1e** (57%) was formed with three radical-derived products (**1b**, **1d**, **1f**, 43% altogether, entry 4). Surprisingly, in the presence of oxygen, alcohol **1a** was mainly produced (59%) in spite of anhydrous condition. The relative ratio of ion-derived product yield (**1e**, 41%)

**Table 1.** Relative Product Formation of Photosubstitution of 1,1-Diaryl-2,2,2-trifluoroethyl Chlorides<sup>a</sup>

Entry	Substrate	Solvent	atm	Reacted <sup>b</sup> reactant	Relative product formation (%)						ion/radical (%)
					1a	1b	1c	1d	1e	1f	
1	1	AN:H <sub>2</sub> O (9:1)	Ar	37.6	34.6	2.9	–	<0.5	–	–	91/9 <sup>c</sup>
2	1	AN:H <sub>2</sub> O (9:1)	O <sub>2</sub>	51.1	39.0	2.1	–	0	–	–	84/16 <sup>d</sup>
3	1	Benzene	Ar	32.7 <sup>d</sup>	0	25.9	4.0	2.8	–	–	0/100 <sup>e</sup>
4	1	AN:MeOH (9:1)	Ar	34.7 (68.6)	0 (0)	3.1 (6.2)	–	0.8 (1.6)	19.7 (39.4)	11.1 (22.2)	57/43 <sup>e</sup>
5	1	AN:MeOH (9:1)	O <sub>2</sub>	68.6	39.5	0	–	0	28.1	1.0	41/59 <sup>e</sup>
					2a	2b	2c	2d	2e	2f	
6	2	AN:MeOH (9:1)	Ar	56.6 (71.2)	0 (0)	17.3 (21.8)	–	<0.5 (0.6)	22.7 (28.6)	16.3 (20.5)	40/60 <sup>f</sup>
7	2	AN:MeOH (9:1)	O <sub>2</sub>	71.2	31.3	8.3	–	0	24.1	7.4	34/66 <sup>f</sup>

<sup>a</sup>Light source: broad light of 450W Xe-lamp. Irradiation time: 30 min. AN: acetonitrile. <sup>b</sup>Calculated values from recovered reactant percentages. <sup>c</sup>a+e/b+c+d+f. <sup>d</sup>a-4.4/b+d+4.4. <sup>e</sup>e/a+b+d+f. <sup>f</sup>Irradiation time: 35 min. ( ): Normalized to the values under O<sub>2</sub> for comparison.

decreased by 16 percent as compared with that under argon. Alcohol **1a** obviously came from quenching triplet state of **1** by oxygen and from snatching of radicals formed in the medium by oxygen. It has been known that oxygen in a medium is an effective quencher for the free radical<sup>9a,9b</sup> and triplet state.

Substrate **2** with methoxy group on the one of phenyl rings was more reactive than substrate **1**, comparing reacted percentages of the substrate for 30 min (entry 4 and 6). Substrate **2** in MeOH/AN solvent under argon gave ion-derived product in 40% yield (**2e**) and radical-derived products (**2b**, **2d**, **2f**) in 60% yield. In the presence of oxygen, alcohol **2a** was newly produced by simultaneous expenditure of most of radical-derived products. Methanolysis product (**2e**) was formed with small effect by oxygen compared with that of **2** under argon (normalized values in entry 6 and those in entry 7); the ion-derived product yield ratio decreased by 6 percent in the presence of oxygen. If the oxygen is assumed to retard methanolysis due to completely quenching of triplet state of **2** (6%) and then to convert the quenched triplet into alcohol, the rest of substrate (94%) suffer homolysis and heterolysis via the excited singlet state. The excited state must be partitioned between 60% radical-derived product and 34% ion-derived products to totally afford the resulting 34/66 (ion/radical) percentages. These partitions can interpret the experimental results in the absence of oxygen (40/60 percentage in entry 6 and Scheme 2); of excited singlet state of **2**, 6% the singlet states experience intersystem crossing to give the triplet states and eventually undergo heterolysis to afford ion-derived products, and 94% of the singlet states undergo 60% homolysis and 34% heterolysis as in the case of oxygen. These results imply that the carbocation and radical are rather simultaneously than

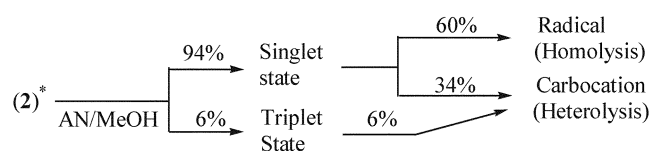
consecutively in this case. If consecutive reactions of which the carbocations are formed from the radicals operated in the medium, the partition of 34/60 ratio would not appear. This dichotomy is possible for **1** (entry 4 and 5).

In summary, our work has shown for the first time that a preparative and selective photosubstitution of tertiary 1-alkyl-1,1-diarylmethyl chloride is possible upon change of medium. We propose that the tertiary radicals and carbocations are simultaneously generated from the excited singlet state in steady state photoreaction and carbocation additionally are produced from the excited triplet state.

**Acknowledgment.** This work was supported by Korea Research Foundation Grant (KRF-2002-005-C00009).

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**Scheme 2**