Tetrahedron Letters Vol. 21, pp 3131 - 3134 0040-4039/80/0808-3131$02.00/0

THE GENERATION AND REACTIONS OF SOME DIARYL-DIHALOMETHYLCARBONIUM IONS[1a]

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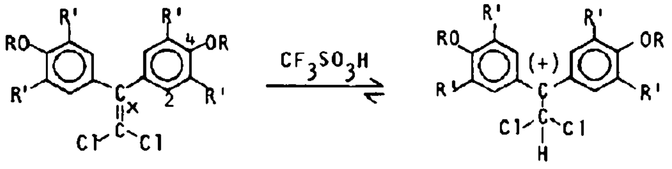
Summary: Previously unknown diaryl-dihalomethylcarbonium ions, formed in high yield from the respective alkenes in trifluoromethanesulfonic acid (triflic acid) undergo facile rapid equilibration of aryl groups in triflic acid with a second added aryl component.

Although the diphenylmethylcarbonium ion,[1b] styryl,[2,3] and substituted styryl[2,3] cations have been extensively studied, neither the generation nor any reactions of diaryl-dichloromethylcarbonium ion analogs have been reported. A high yield formation of these diaryl-dichloromethyl cations has now been found to occur upon treatment of the respective olefin with triflic acid at ambient temperature, e.g.



1-3

4-6

Solutions of diarylalkenes 1-3[4] in triflic acid display changes in their ^{13}C and electronic spectra summarized in Table 1 which are consistent[3] with the formation of the respective carbonium ions. Moreover, the ^{1}H spectra of the triflic acid

Table 1. ^{13}C and Electronic Spectra of Compounds 1-3 in Triflic Acid at 25°

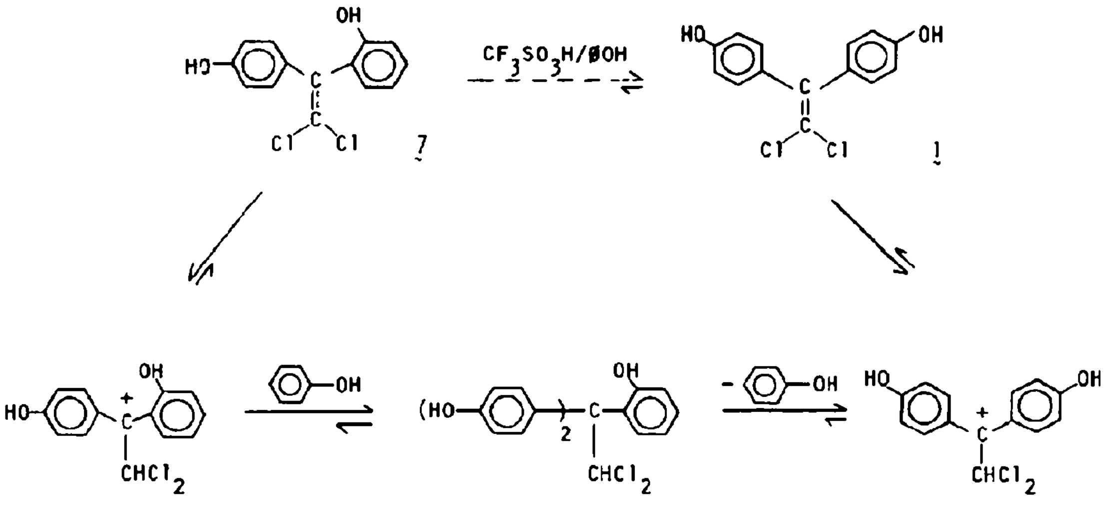
	Electronic Spectra		^{13}C Shifts	
Compound	λ max.	ε	Nucleus	ΔPPM*
1 (R=R'=H)	343	3800	C_x	45.1
	520	21500	C_2	14.5
			C_4	15.5
2 (R=H, R'=CH_3,	362	3600	C_x	42.7
	555	22800		
3 (R=CH_3, R'=H)	351	3130	C_x	45.9
	545	13700		

*Chemical shift in triflic acid minus that in DMSO-d_6.

solutions of alkenes 1-3 indicate virtually complete formation of the carboniu ions as evidenced by the presence of an additional peak in the form of a sligh broadened singlet (1.0 H), at 6.7 - 7.0 PPM.

Carbonium Ion Rearrangements

The solutions of these carbonium ions are sufficiently stable at room temperature (less than 5% decomposition being observed over a two-hour period) th some reactions of the ions can be observed. In particular, o,p-isomer 7 undergoes a facile isomerization[5] in triflic acid containing phenol to greater than 99% of the more stable p,p-isomer (Scheme 1). For example, at a 8.5 phenol to 1 mole ratio,[5] 7 is ca. 50% isomerized in 2.5 hours.

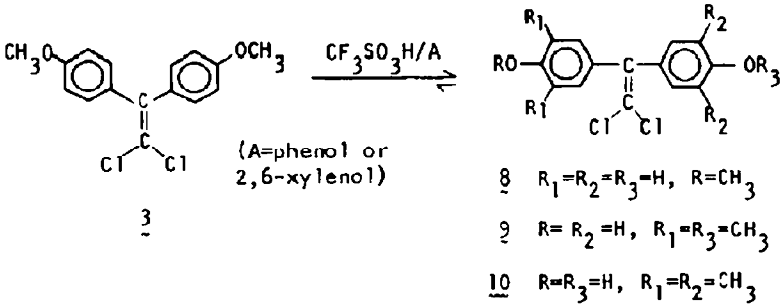


SCHEME I

At a given phenol concentration the isomerization follows first order kinetics to greater than 98% of 1 with the rate constants determined at various phenol concentrations displaying a first order dependence on phenol concentration. T isomerization, thus, may be rationalized in terms of the alkylation-dealkylati mechanism depicted in Scheme 1. This mechanism involves essentially the equilibration of ions 8 and 4 since the olefinic species are virtually complet protonated in triflic acid. Moreover, Scheme 1 indicates that the o-alkylated phenol group of 7 is replaced by a different phenol group. Consequently, in t presence of a different phenol or aryl component the mechanism of Scheme 1 predicts the incorporation of the second aryl component. In fact, in some cas e.g. the reaction of 3 with phenol,[5] the exchange is remarkably facile and giv virtually the statistical distribution of exchanged alkenes.

However, when the same exchange is attempted in the presence of 2,6-xylenol, a build-up of the partially exchanged isomer, 9, is noted.

In summary, a high yield formation of the moderately stable, previously unknown diaryldihalomethylcarbonium ions 4-6, occurs in triflic acid. These ions are sufficiently stable in this medium that alkylation-dealkylation reactions with different aryl components can be achieved.



8 $R_1=R_2=R_3=H$, $R=CH_3$

9 $R=R_2=H$, $R_1=R_3=CH_3$

10 $R=R_3=H$, $R_1=R_2=CH_3$

Table 2. Reaction of 3 With Phenol and 2,6-Xylenol in Triflic Acid

		% Composition**				
Time (min)	A	3	8	9	1	10
150	Phenol	1.2	14.0	--	84.8	--
280	Phenol	0.6	14.1	--	85.3	--
Statistical* Distribution	Phenol	0.3	10.7	--	89.0	--
79	2,6-xylenol	51	--	43	--	4
900	2,6-xylenol	1	--	73	--	23
Statistical* Distribution	2,6-xylenol	7	--	19	--	74

*Distribution of aryl groups calculated if complete equilibration occurs.

**Analysis performed as per Reference 5(a).

Acknowledgment

Grateful acknowledgment is made to Dr. C. M. Orlando for many stimulating discussions.

References and Footnotes

1a. Presented in part, John R. Campbell, American Chemical Society Conference, September, 1978.

1b. G. A. Olah, J. Amer. Chem. Soc., 86, 932 (1964).

2. G. A. Olah, R. D. Porter, and D. P. Kelley, J. Amer. Chem. Soc., 93, 464 (1971).

3. G. A. Olah, C. U. Pittman, Jr., R. Waack, and M. Doran, J. Amer. Chem. Soc., **88**, 1488 (1966).
4. The known dichloroalkenes were prepared by condensing the appropriate phenol derivative with 2,2,2-trichloroacetaldehyde and subsequently dehydrochlorinating the trichloroethyl intermediates (c.f. M. R. MacLaury and A. Saracino, *J. Org. Chem.*, *44* 3344 (1979); D. J. McLennan and R. J. Wong, *J. Chem. Soc. Perkin Trans.*, *2*, 379 (1972); C. M. Orlando and R. A. Gardner, unpublished results.
5. A typical experiment consisted of adding the substrate (e.g. o,p-isomer **7**, 0.1068 g) and phenol (0.3034 g) under a nitrogen atmosphere to triflic acid (1.9034 g) at 25°C to give a deep red solution. Product analysis was performed by adding weighed aliquots of reaction mixture to excess bis(trimethylsilyl)acetamide. The quenched samples were then analyzed by vpc after adding an internal standard and, in some cases, tetramethylurea to prevent phase separation.
6. Products were isolated by adding the triflic acid solution to excess 10% aqueous sodium hydroxide at 5°C. After acidification the precipitated solid was collected and recrystallized (55% yield of **1** from **7**). Materials isolated gave spectral data identical to those of authentic samples.

(Received in USA 15th February 1980)