CHEMISTRY LETTERS, pp. 929-930, 1985.

FORMATION OF ALLENYL CATIONS BY PHOTOLYSIS OF TRIARYLCHLOROALLENES

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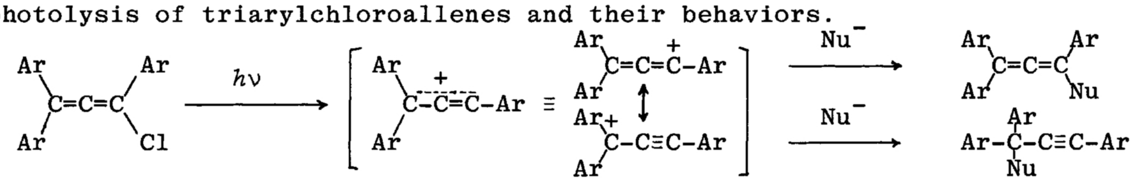
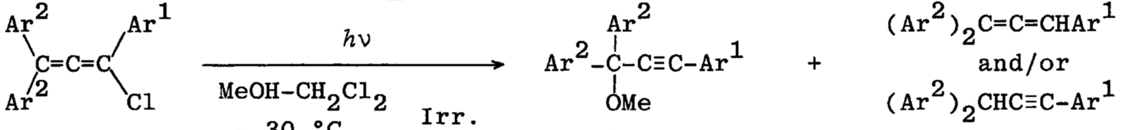
Irradiation of triarylchloroallenes in methanol afforded 1,3,3-triaryl-3-methoxypropynes, suggesting the intervention of triarylallenyl cations. Irradiation of triphenylchloroallene in ethanol and 2-propanol gave the similar results but the irradiation in _t_-butyl alcohol gave only the products from triphenylallenyl radical.

Recently much attention has been paid to the photochemical cleavage of the carbon-halogen bond in organic halides.[1,2] Many examples have been reported for the photochemical formation of carbenium ions.[2] However, practically nothing is known concerning the photochemical formation of allenyl cations.[3] Overlap of the vacant p orbital with the π bond gives rise to an ambident characteristic of allenyl cations. This paper describes the first example of triarylallenyl cations by photolysis of triarylchloroallenes and their behaviors.

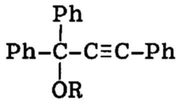


Photolysis of triarylchloroallenes in a mixed solvent of methanol and methylene chloride was carried out at - 30 °C to prevent the thermal solvolysis. Under the conditions employed above, no solvolysis products were obtained in the dark. Irradiation of triarylchloroallene _1_ (1.3 mmol) in a mixed solvent of methanol (40 ml) and methylene chloride (20 ml) containing 2,6-lutidine (0.14 ml) at - 30 °C under N_2 atmosphere by use of a Pyrex-filtered high-pressure Hg lamp (100 W). Just after the irradiation the reaction mixture was poured into water. The products were extracted with ether and chromatographed over silica gel. The identified products were 1,3,3-triaryl-3-methoxypropyne (_2-OMe_)[4] and a small amount of the reduced compounds _3_.[5]



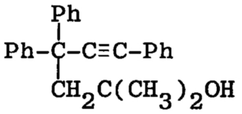
_1_	Irr. time/h	_2-OMe_	_3_
a: Ar^1=Ar^2=Ph	3	47%	7%
b: Ar^1=Ph, Ar^2=_p_-MeC_6H_4	2	51%	trace
c: Ar^1=_p_-$MeOC_6H_4$, Ar^2=Ph	1	76%	trace

Similar irradiation of triphenylchloroallene 1a was carried out in ethanol, 2-propanol, and t-butyl alcohol. Both photolyses in ethanol and in 2-propanol gave the corresponding 3-alkoxy-1,3,3-triphenylpropynes (2a-OEt and 2a-O^iPr)[4] in 33 and 37% yields, respectively, together with a small amount of the reduced compound 3. On the other hand, photolysis in t-butyl alcohol afforded an unexpected result. Irradiation of 1a in t-butyl alcohol at room temperature resulted in the absence of 3-t-butoxy-1,3,3-triphenylpropyne (2a-O^tBu) and gave isomeric alcohols 4 (16%) and 5 (11%),[4] dimer 6 (39%),[4] and the reduced compounds 3a (trace).



$\mathrm{Ph{-}\overset{Ph}{\underset{OR}{C}}{-}C{\equiv}C{-}Ph}$

2a-OR



$\mathrm{Ph{-}\overset{Ph}{\underset{CH_2C(CH_3)_2OH}{C}}{-}C{\equiv}C{-}Ph}$

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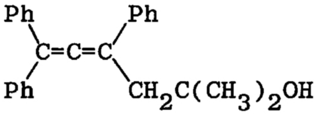

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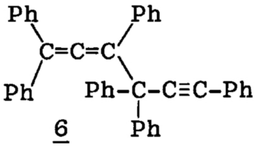

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The formation of solvent-incorporated product 2 suggested that triarylallenyl cation is formed by photolysis of the corresponding chloroallene 1. However, the product 2 obtained by photolysis was attributed to attack by nucleophiles at γ position of the allenyl cation. Although allenyl cations are ambident cations and can produce allenyl or propargyl derivatives by attack at the α or γ position, respectively,[6] only γ attack was observed in this photolysis of triarylchloroallenes. This result is parallel to that of solvolysis observed by Schiavelli et al.[7] and also supports the formation of allenyl cations in the photolysis. However, all compounds obtained from photolysis in t-butyl alcohol are derived apparently from triphenylallenyl radical. Since the resulting triphenylallenyl cation cannot react with t-butyl alcohol because of its steric hindrance, the cation reverts to the allenyl chloride 1a.

References

1) P.G.Sammes,"The Chemistry of The Carbon-Halogen Bond," ed by S.Patai, Wiley, New York (1973), Chap. 11.
2) G.Lodder,"Supplement D: The Chemistry of Halides, Pseudo-halides and Azides," ed by S.Patai and Z.Rappoport, John Wiley & Sons, New York (1983), Chap. 29.
3) Photodimerization of a bromoallene was reported; K.Ueda and F.Toda, Chem.Lett., 1975, 257.
4) 2a-OMe: Mp 127-128 °C(lit.,[8] 124 °C); NMR(CCl_4) δ=3.45(s,OMe), 7.00-7.80(m, ArH). 2b-OMe: Oil; NMR(CCl_4) δ=3.30(s,Me), 3.31(s,OMe), 6.93-7.65(m,ArH); IR 2220cm^{-1}(w). 2c-OMe: Oil; NMR(CCl_4) δ=3.40(s,OMe), 3.78(s,OMe), 6.63-7.69(m, ArH); IR 2220cm^{-1}(w). 2a-OEt: Oil; NMR(CCl_4) δ=1.30(t,J=7Hz,Me), 3.55(q,J=7Hz, CH_2), 7.10-7.80(m,ArH). 2a-O^iPr: Oil; NMR(CCl_4) δ=1.15(d,J=7Hz,Me), 4.05(sect, J=7Hz,CH), 6.80-7.80(m,ArH). 4: Mp 78-80 °C; NMR(CCl_4) δ=1.10(s,Me), 2.50(s, OH), 2.70(s,CH_2), 7.10-7.70(m,ArH); IR 3425cm^{-1}(br,OH); MS m/e(M^+) 340; ^{13}C-NMR ($CDCl_3$) δ=30.9, 47.4, 52.3, 71.6, 88.5, 93.7, 126.7, 127.2, 128.3, 128.4, 131.4, 145.7. 5: Mp 80-90 °C; NMR(CCl_4) δ=1.15(s,Me), 1.70(s,OH), 2.80(s,CH_2), 6.30-7.70(m,ArH); IR 3400(br,OH), 1920cm^{-1}(w); MS m/e(M^+) 340; ^{13}C-NMR($CDCl_3$) δ=29.6, 43.8, 71.4, 105.6, 112.0, 126.5, 127.3, 127.5, 128.3, 128.6, 136.5, 208.4. 6: Mp 169-171 °C; NMR(CCl_4) δ=6.95-7.57(m,ArH); MS m/e(M^+) 534; ^{13}C-NMR($CDCl_3$) δ=54.7, 87.1, 93.4, 114.2, 115.8, 123.4, 126.9, 127.4, 127.9, 128.1, 128.7, 131.5, 134.9, 136.2, 143.7, 209.2.
5) The reduced compounds 3 were confirmed by comparison with authentic samples.
6) P.J.Stang, Z.Rappoport, M.Hanack, and R.L.Subramanian, "Vinyl Cations," Academic Press, New York (1979), p. 246.
7) M.D.Schiavelli, S.C.Hixon, H.W.Moran, and C.J.Boswell, J.Am.Chem.Soc., 93, 6989 (1971), which shows that solvolysis of triarylchloroallenes 1 proceeds via triarylallenyl cations.
8) C.Moureau, C.Dufraisse, and H.Blatt, Bull.Soc.Chim.Fr., 35, 1412 (1924).

(Received April 6, 1985)