Bromide Catalysis in the Preparation of Benzylidyne Trichlorides *via* Photochlorination

By R. GARTH PEWS* and RALPH A. DAVIS†

(*Central Research Laboratory, and †Halogens Research Laboratory, Dow Chemical Company, Midland, Michigan* 48640)

Summary Bromine catalyses the photochlorination of substituted toluenes to benzylidyne trichlorides.

AROMATIC trichloromethyl derivatives are conveniently prepared *via* the free radical chlorination of the corresponding methyl derivative. For example, an 87% yield of 1,4-bis(trichloromethyl)benzene is obtained from the photochlorination of *p*-xylene.[1] We report our results that demonstrate bromine catalysis of the photochlorination. This is a surprising observation in view of the literature that shows chlorine to be a better hydrogen abstractor than bromine.[2]

The results of the photochlorination of 4-chlorotoluene and toluene-4-sulphonyl chloride are summarized in the Table. Without bromine 4-chlorotoluene requires over 8 h

TABLE. Bromine-catalysed photochlorinations

				Analyses/%				
Substrate	Br_2 (g)	Temp./°C	Time/h	$-CH_3$	$-CH_2Cl$	$-CHCl_2$	$-CCl_3$	Unknown
4-Chlorotoluene[a]	None	80	2·25	7	59	33	1	
			5·2	—	14	40	46	
			8·5	—	1	2	97	
,,[a]	15[b]	80	2	—	—	—	97	
Toluene-4-sulphonyl chloride[c]	None	80	6·0	—	6	66	28	—
,,[c]	10	80	1·5	—	3	51	45	2
			3·0	—	2	38	58	2
			4·0	—	1	16	82	1
			5·5	—	<1	<1	97	2
4-Bromotoluene[d]	None	—	2·5[e]	—	—	2	95	3

[a] Reaction was carried out with 2 mol of substrate and 300 g of CCl_4 as solvent. Solution was irradiated with General Electric 275 W sunlamp. Chlorine utilization was *ca.* 90%. [b] Bromine was added after 1 h. [c] Reaction was carried out with 1 mol of substrate and 300 g of CCl_4 as solvent. [d] Reaction was carried out with 0·55 mol of substrate and 300 g of CCl_4. [e] Reaction was carried out for 1 h at 60 °C, then for an additional 1·5 h at 80 °C.

for complete conversion into 4-chlorobenzylidyne trichloride. With the addition of 5 mol % of elemental bromine, the photochlorination is complete in 2 h. Similar results were obtained for toluene-4-sulphonyl chloride, with and without bromine. Displacement of an aromatic chlorosulphonyl group by chlorine under photochlorination conditions as described by Walling,[3,4] occurs in both instances. Elemental bromine need not be the source of bromine. For example, 4-bromotoluene is rapidly converted into 4-chlorobenzylidyne trichloride; the aromatic bromine, being photo-labile to chlorination,[3] is the source of elemental bromine. Other bromine containing compounds, *e.g.*, bromoform, anhydrous hydrogen bromide, *etc.*, have been found to function as catalysts. No organic bromide derivatives of the benzylidyne trichloride were detected in the reaction mixture. Since chlorine atoms are better hydrogen abstractors than bromine atoms, the origin of the catalytic effect may be due to a very high concentration of bromine atoms relative to chlorine atoms. Such a concentration is not unreasonable since bromine is a much better absorber of light than chlorine.

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[1] G. Sosnovsky in 'Free Radical Reactions in Preparative Organic Chemistry,' MacMillan, New York, 1964, p. 323.
[2] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 370.
[3] B. Miller and C. Walling, *J. Amer. Chem. Soc.*, 1957, **79**, 4187.
[4] B. Miller, *J. Org. Chem.*, 1973, **38**, 1243.