Photochemical Reaction of Chloroform with the Electron-rich Aromatic Compounds Phenol and Diethylaniline

By KEN-ICHI HIRAO* and OSAMU YONEMITSU

(*Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo, Japan*)

Summary Chloroform reacts with phenol or diethylaniline under u.v. irradiation to give benzaldehydes in fairly good yields; the reaction may be an example of photochemical cleavage of the C–Cl bond of chloroform.

IRRADIATION of *N*-chloroacetyl derivatives of phenethylamines gives novel N-heterocycles;[1] the proposed mechanism[2] involves ejection of an electron from an excited aromatic nucleus *via* an exciplex which cleaves the chloroacetyl group into an acetamide radical and a chloride anion. The same type of cleavage (1) of the C–Cl bond of chloroform has been observed in the reaction with hydrated electron[3] or iron(II) ion,[4] whereas in photochemical[5] or normal radical reactions[6] the C–H bond of chloroform is cleaved to form the trichloromethyl radical (2).

$$CHCl_3 \longrightarrow \cdot CHCl_2 + Cl^- \qquad (1)$$

$$CHCl_3 \longrightarrow \cdot CCl_3 + \cdot H \qquad (2)$$

We now report that the photochemical reaction of chloroform with phenol or diethylaniline which on u.v. irradiation generates hydrated electron.[7] A solution of phenol (I) (5 mM) and $CHCl_3$ (55 mM) in 50% aqueous MeOH or CH_3CN was irradiated with a 10 W low-pressure mercury lamp under nitrogen for 2—3 h. The reaction was silylated with excess of chlorotrimethylsilane and hexamethyldisilazane in pyridine at room temperature and analysed by g.l.c. (see Table). In case (a), the yields of salicylaldehyde (II) and *p*-hydroxybenzaldehyde (III) are similar to those in the Reimer–Tiemann reaction.[8] When Et_2NH (b,c) was added to remove HCl, the yield of (III) increased, whereas KOH (e) and NEt_4OH (f) reduced the yield of both products. In hydrochloric acid (g), neither (II) nor (III) were formed.

The formation of the benzaldehydes indicates that the chloroform does not decompose as in reaction (2), but that detachment of chloride anion effected by an electron released from the excited phenol occurred [reaction (1)], followed by radical coupling of the dichloromethyl radical with a phenoxy-radical.

TABLE

		Yield (%)		
	Conditions	(I)	(II)	(III)
(a)	50% MeOH; 3h	6·2	18·6	11·9
(b)	Et_2NH (125 mM); 50% MeOH; 2 h	13·9	22·2	30·9
(c)	Et_2NH (125 mM); 50% MeCN; 2 h	4·8	19·1	46·0
(d)	K_2CO_3 (155 mM); 50% MeOH; 2 h	8·0	15·5	16·5
(e)	KOH (150 mM); 50% MeOH; 2 h	16·8	8·9	6·5
(f)	$Et_4N^+OH^-$ (100 mM); 50% MeOH, 3 h	4·8	6·7	4·6
(g)	17% HCl; 50% MeOH; 2 h	1·3	—	—
(h)	Et_2NH (125 mM); 50% MeOH; 2 h[a]	4·5	4·8	7·0
(i)	Et_2NH (225 mM); 50% MeCN; 8 h[b]	21·4	12·3	39·2

[a] $CHBr_3$ was used instead of $CHCl_3$. [b] Preparative scale; a solution of (I) (7·5 mM) and $CHCl_3$ (75 mM) was irradiated with a 100 W high-pressure mercury lamp.

The photo-reaction of diethylaniline (50 mM) with chloroform (400 mM) in the presence of diethylamine (800 mM) in 80% aqueous acetonitrile gave *o*-diethylaminobenzaldehyde (35·6%) and *p*-diethylaminobenzaldehyde (50·4%). In this case, the reactive species must be the radical cation from diethylaniline.

Since the photochemical reaction of chloroform with electron-rich aromatic compounds gives the corresponding benzaldehydes in fairly good yield under mild conditions, this simple method may be applicable to compounds sensitive to alkali. Further, the photoreaction may be the first example of the synthetically useful photochemical formation of the dichloromethyl radical from chloroform.

Finally, irradiation (100 W lamp; N_2) of CCl_4 (100 mM) and phenol (20 mM) in 90% aqueous MeOH for 1·5 h gave methyl salicylate (16·5%), methyl *p*-hydroxybenzoate (26·1%), methyl 4-hydroxyisophthalate (7·3%), and unchanged phenol (19·5%).

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