

Reactions of Trichloromethyl Anions with Diformylbenzenes. Estimation of Hammett Substituent Constants of the Formyl, Trichloroacetyl, and 2,2,2-Trichloro-1-hydroxyethyl Groups

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o- and *p*-diformylbenzenes react at room temperature with trichloroacetic acid in dimethyl sulphoxide to yield insoluble products corresponding to the addition of trichloromethyl anion to carbonyl groups. The addition of one $^-CCl_3$ ion to the *o*-isomer leads to the formation of a cyclised phthalan product. The Hammett σ_p constants of the groups CHO, CH(OH)CCl₃, and COCCl₃ have been estimated as 0.40, 0.32, and 0.70 respectively.

It has recently been reported^{1,2} that the use of dimethyl sulphoxide (DMSO) allows a facile route for the isolation of products, derived from trichloromethyl anion, of the type ArCH(OH)CCl₃ [reaction (1)]. Such compounds and the corresponding trichloromethyl ketones are of interest not only as potentially useful products³ with high biological activity, but also as precursors in other synthetic applications.⁴



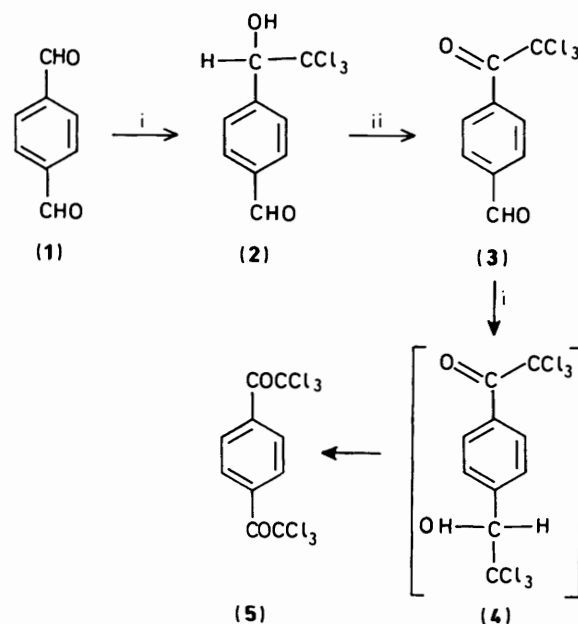
As part of our studies on the preparation of pesticides and herbicides of the DDT family, we have now investigated the preparation of bis(trichloroacetyl)benzenes. Our interest in this reaction is justified not only by the growing concern with pesticides and their degradation products but also by the fact that some obscure points regarding this reaction remain to be clarified.

Khcheyan *et al.*⁵ have shown that the chlorination of a mixture of *m*- and *p*-(MeCO)₂C₆H₄ at 200 °C for 15 h gave (Cl₃CCO)₂C₆H₄. They stated that it was difficult to chlorinate pure *p*-(MeCO)₂C₆H₄ by itself, but chlorination of a mixture of isomers gave an isomeric mixture of products.⁶ It seemed of interest to examine the preparation of the pure *para*-isomer by a less drastic and less expensive method and to investigate further the reaction with the *ortho*-isomer.

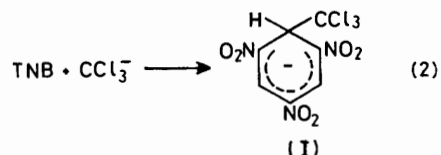
Results and Discussion

Reaction of Trichloromethyl Anion with *p*-Diformylbenzene.—Treatment of *p*-diformylbenzene (1) in DMSO with an equimolar amount of trichloroacetic acid (TCAA) for 1 h at 20 °C led to the formation of (2) in 75% yield showed by the expected spectral and analytical properties. Addition of acetic anhydride to the reaction mixture containing (2) led to the formation of 4'-formyl- α,α,α -trichloroacetophenone (3) after it was left at 60 °C overnight. Compound (3) reacts easily with TCAA in DMSO at 20 °C to give 1,4-bis(trichloroacetyl)benzene (5) (80%), presumably through the intermediate (4) (Scheme 1).

Despite the ease of reaction with (1) and (3), trapping of trichloromethyl anion does not appear to be general for all electron-poor aldehydes. Thus compound (2) does not undergo further nucleophilic addition of trichloromethyl anion, either when additional TCAA was added to the reaction mixture containing (2) or when (2) was isolated and redissolved in DMSO with TCAA at 20 °C. When a 1:2.2 mixture of (1)–



Scheme 1. Reagents: i, CCl₃COOH–DMSO, 20 °C; ii, Ac₂O–DMSO, 60 °C

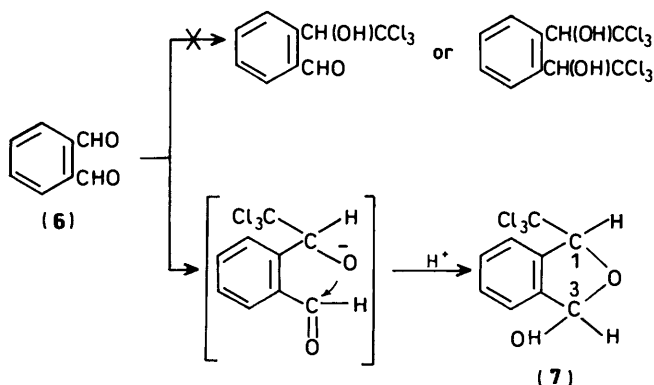


TCAA in DMSO was allowed to react at 20 °C, (2) was obtained in 50% yield along with unchanged (1). Apparently the observed decrease in the yield of (2) on increasing the TCAA molar ratio is due to the competition of solvated proton with the aldehydes for trichloromethyl anion. We have detected the formation of trichloromethane in the n.m.r. spectra of the reaction of (1) with TCAA in 1:2 ratio.

Competition Experiments.—In order to compare the relative reactivity of the aldehydes (1)–(3) towards CCl₃⁻, we calculated the Hammett σ values for the *p*-CHO, *p*-CH(OH)CCl₃, and *p*-COCCl₃ substituents by measuring the final absorption A_0 at 431 nm of the coloured Meisenheimer

Table. ^1H N.m.r. data for compound (7)^a

Proton	δ		Relative integration	$J_{1,3}$ Hz <i>trans</i>
	<i>cis</i>	<i>trans</i>		
1-H	5.61(br s)	5.82(d)	2	2.4
3-H	6.43(br s)	6.66(d)		
ArH	7.83—7.3(m)		5 (including OH)	

^a Spectrum taken in CDCl_3 - CD_3CN .

Scheme 2.

adduct anion (I) formed by the reaction of trinitrobenzene and TCAA in DMSO¹ [reaction (2)]. In the presence of added aldehyde (which competes with TNB for trichloromethyl anion [reaction (1)] the absorbance is reduced to A which depends on the concentration of the added aldehyde $[C]$. The predicted linear dependence of the ratio $(A_0 - A)/A$ upon the ratio $[C]/[\text{TNB}]$ is obeyed. The proportionality constant r of equation (3) is effectively a measure of the reactivity of the added aldehyde.¹

$$(A_0 - A)/A = r[C]/[\text{TNB}] \quad (3)$$

σ Values were calculated from a $(\sigma, -\log r)$ correlation for a series of aromatic aldehydes with known Hammett substituent constants,¹ by extrapolation. The σ values obtained for *p*-CHO, *p*-CH(OH)CCl₃, and *p*-COCl₃ substituents are 0.40 (lit.,⁷ 0.42), 0.32, and 0.70, respectively. The agreement of the σ value for *p*-CHO with that in the literature makes it reasonable to place limits of ± 0.05 on the σ values estimated by this method. Exner⁸ gives values of σ_p for CHO of 0.43 and 0.45, with uncertainties of 0.03 and 0.02, respectively, so a value between 0.40 and 0.47 seems reasonable. There appear to be no value in the literature with which those for the other two groups may be compared directly. However, σ_p for COCF₃ is given by Exner as 0.80, so the slightly less positive value of 0.70 for COCCl₃ is reasonable, since the CCl₃ moiety will be less electron-attracting than CF₃. In CH(OH)CCl₃ it appears that the CH(OH) moiety contributes little; the σ_p value for CH₂OH is given by Exner as 0.01. This means that the observed value of 0.32 for CH(OH)CCl₃ is due mainly to the CCl₃ moiety. If this makes roughly the same contribution in COCCl₃, then we may calculate the σ_p value of the latter by adding together the values for CHO and CH(OH)CCl₃. Taking the present value for CHO, this gives 0.72; Exner's extremes for CHO would give 0.72. At all events the observed value of 0.70 is reasonable, both in relation to the literature and to the measurements for CHO and CH(OH)CCl₃.

Reaction of Trichloromethyl Anion with o-Diformylbenzene.—The reaction of *o*-diformylbenzene (6) and TCAA in DMSO

solution, at room temperature for 1 h, afforded a solid, m.p. 129—133 °C, in 90% yield. This product proved to be a *cis-trans* mixture of (7). This conclusion follows from the observations (i) that elemental analysis suggests a 1:1 addition product and (ii) that the i.r. spectrum of (7) indicates the absence of $\nu_{\text{C=O}}$ and the presence of monomeric OH; it also shows $\nu_{\text{C-O-C}}$ at 1 320 cm^{-1} , which suggests a phthalan structure.⁹ (iii) The n.m.r. spectrum (see Table) shows the presence of (7) in a *cis-trans* ratio of ca. 1:2. The attribution of the ^1H chemical shifts (Scheme 2) was based on comparison with spectra of similar protons in ArCH(OH)CCl₃¹ and the spectrum of (2). The low-field absorption of 1- and 3-H was assigned to the *trans* isomer for reasons put forward previously by Petracek *et al.*,⁹ who studied corresponding 1,3-phthalan systems obtained from the reaction of *o*-benzoylbenzaldehyde and cyanide ion. They gave a higher coupling constant for the *trans* isomer. A downfield assignment and larger $J_{1,3}$ values were also attributed to *trans* isomers in other phthalan systems studied by Fraser *et al.*¹⁰ In our case the presence of the more sterically stable *trans* isomer in a higher proportion (2:1 from n.m.r.) confirms the *trans* assignment.

Experimental

I.r. spectra were recorded on a Perkin-Elmer model 398 spectrophotometer as KBr discs, u.v. spectra on a Perkin-Elmer 555 u.v. spectrophotometer, and n.m.r. spectra on a JEOL PMK 60 spectrometer with SiMe₄ as internal standard.

2,2,2-Trichloro-1-(4-formylphenyl)ethanol (2).—Trichloroacetic acid (2.4 g, 0.015 mol) was added with stirring to a solution of 1,4-diformylbenzene (1) (2.0 g, 0.015 mol) in DMSO (30 cm^3). After ca. 1 h at room temperature, the solution was poured into ice-cold water (400 cm^3). The solid product was washed with water and gently crystallised from light petroleum (b.p. 60—80 °C) to give (2) (2.8 g, 75%), m.p. 87—88 °C. Prolonged heating during crystallisation lead to partial oxidation of (2) to (3). *Aldehyde* (2) (Found: C, 42.8; H, 2.8; Cl, 42.1. C₉H₇Cl₃O₂ requires C, 42.6; H, 2.8; Cl, 42.0%) had ν_{max} 3 200—3 500br, 1 670s, and 810s cm^{-1} ; δ_{H} (CDCl₃) 10.11 (1H, s, CHO), 7.9—7.7 (4H, br s, ArH), 5.35 (1H, s, CH), and 3.95 (1H, br s, OH).

Compounds (5) and (7) were prepared by corresponding procedures, except that (7) was crystallised from chloroform. *1-Hydroxy-3-trichloromethylphthalan* (7) had m.p. 129—133 °C (Found: C, 42.4; H, 2.9; Cl, 41.85. C₉H₇Cl₃O₂ requires C, 42.6; H, 2.8; Cl, 42.0%); ν_{max} 3 420sh and 1 032 (C—O—C) cm^{-1} (for ^1H n.m.r. data see Table).

1,4-Bis(trichloroacetyl)benzene had m.p. 160—161 °C (lit.,⁵ 151—153 °C) (Found: C, 32.4; H, 1.0; Cl, 57.5. C₁₀H₄Cl₆O₂ requires C, 32.5; H, 1.1; Cl, 57.7%); ν_{max} 1 705 cm^{-1} ; δ_{H} (DMSO) 8.4—8.2 (m, ArH).

4-Formyl- α,α,α -trichloroacetophenone (3).—Acetic anhydride (5 ml) was added to a hot solution of (2) (2 g, 0.008 mol) in DMSO and left overnight at 60 °C. The solution was then poured into ice-water. An oil separated which solidified on standing. Crystallisation of the solid product from *n*-heptane gave *compound* (3) (70%), m.p. 105—106 °C (Found: C, 42.35; H, 2.05; Cl, 42.5. C₉H₅Cl₃O₂ requires C, 42.9; H, 2.0; Cl, 42.35%); ν_{max} 1 690s and 810 cm^{-1} ; δ_{H} ([²H₆]DMSO) 10.25 (1 H, s, CHO) and 8.2—8.1 (4 H, br s, ArH).

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