[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WESTERN AUSTRALIA]

The S_N Mechanism in Aromatic Compounds. Part X.

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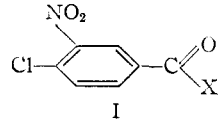
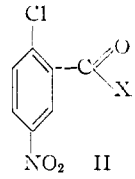
Nucleophilic substitution of Cl in a series of 2-chloro-5-nitro aromatic carbonyl compounds (II below) has been investigated. The order of activating power was found to be CONHPh > $CONH_2$ > COMe > CO_2Me > COPh > H > CO_2^- as compared with the theoretical order COPh > COMe > CO_2Me > $CONH_2$ > CO_2^- > H in the corresponding series (I below) with the carbonyl groups *para* to the Cl. The magnitude of the *ortho* effect is found to be in the order COPh > CO_2^- > CO_2Me > COMe > $CONH_2$, the effect being accelerative for the latter. No relationship is found between the size of the *ortho* group and the magnitude and direction of the *ortho* effect. The various *ortho* effects are discussed.

The activating power and electronic effects of a group of carbonyl compounds I in which the *para*-Cl is replaced by OMe, have already been discussed recently.[2] In that series the compounds X = Ph, Me, OMe, NH_2, O^- bore a simple relationship to each other and to their parent compound *o*-chloronitrobenzene. The rate constants for the corresponding aldehyde and nitrile also fitted in reasonably satisfactorily, but because of anomalous Arrhenius parameters for these two compounds they are being investigated further, in conjunction with the aldehyde and nitrile of the series considered in this paper.



I

This series II has the replaceable Cl *ortho* to the carbonyl group. The replacement of Cl by OMe, using absolute methanolic sodium methoxide, has been investigated in the compounds: (i) *p*-chloronitrobenzene,[3] (ii) sodium 2-chloro-5-nitrobenzoate,[3] (iii) and (iv) 2-chloro-5-nitrobenzamide and -anilide, (v) methyl 2-chloro 5-nitrobenzoate,[3] (vi) 2-chloro-5-nitroacetophenone, and (vii) 2-chloro 5-nitrobenzophenone.



II

The relevant results are given as Table I, which also gives the substituent rate factors (S.R.F.).[4] The data for the *ortho* and *para* series are compared in Table II, which gives also (a) values of the steric indices (*p*/*o* ratios of the S.R.F.'s)[3] and (b) the overlaps which would be present in the *ortho* series if all substituents were coplanar with the ring, and which indicate the compression and distortion in the actual compounds.

The overlaps are so large that the carbonyl group cannot be coplanar with the ring. Generally the least distorted configuration has the carbonyl oxygen toward the Cl. In the case of the ester, the lesser electronegativity of the methoxyl oxygen suggests that this oxygen atom might be toward the Cl. In benzophenone interference between the rings is the major factor, the carbonyl group and the two rings all being in different planes. The physical data used to obtain these overlaps are derived either from the measurements of Archer[5a] or from Pauling,[5b] the radius of the amino group being estimated as 1.82 Å. The C=O bond distance, 1.24 Å., is an arbitrary choice between values quoted for aldehydes and acids.

Discussion

Owing to the wide spread of activation energies, the order of activating power depends somewhat on temperature. At 50° it is CONHPh > $CONH_2$ > COMe > CO_2Me > COPh > H > CO_2^- in the *ortho* series compared with the theoretical order COPh > COMe > CO_2Me > $CONH_2$ > CO_2^- > H in the *para* series, and it is clear that separate consideration must be given to the various substituents.

The *ortho*-CO_2^- group already has been discussed[3] in a general survey of *ortho* effects. Not only is there a large steric index, but the *ortho* group is actually deactivating. It was concluded that the normal weak activation[2,4] is reversed by a repulsive field effect between carboxylate oxygen and methoxide ion. However, in forming the transition state the removal of Cl is facilitated, and the OMe and Cl rather loosely bound. Compression and repulsion forces are also released, and the result is a high value of both activation energy and frequency factor. There seems to be no reasonable side reaction which could occur, and in particular none which could occur only in the *ortho* series. The original experimental results[3] showed clearly that only one mole of OMe^- was consumed per mole of ArCl reacted, and that the product isolated direct from the reaction mixture by cold aqueous acidification was pure 2-methoxy-5-nitrobenzoic acid.

In the *para* series the amide group is the least activating of the electrically neutral groups, since it has the greatest internal compensation. In the *ortho* series it is (with the associated CONHPh) group the most activating; so much so that an *ortho* accelerative effect is found, with a steric index of 0.567. Some specific effect is seen to be required and it is here ascribed to Cl---H—N hydrogen bonding. This, together with the absence of O–O repulsive forces, more than counterbalance the effect of greater displacement of the whole group from the ring plane, when the NH_2 rather

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(2) J. Miller, THIS JOURNAL, **76**, 448 (1954).

(3) J. Miller and V. A. Williams, *J. Chem. Soc.*, 1475 (1953).

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TABLE I

Cmpd.[b]	Substituent	Rate constant ($10^5 k_2$), l. mole^{-1} sec.$^{-1}$ Exptl. (temp., °C.)	Calcd. from Arrhenius param. 0°	50°	100°	Substituent rate factor (H = 1) 0°	50°	100°	Activation energy, E, cal.[a]	Frequency factor log B[a]
i	H	8.42(71.0) 23.5(81.6) 137.5(100.8)	0.03890	0.847	128	1	1	1	24050 ±150	11.2 ±0.1
ii	CO_2^-	17.0(81.6) 34.9(87.8) 139(100.8)	0.04866	0.316	128	0.0973	0.373	1.00	28750 ±100	14.0 +0.1
iii	$CONH_2$	244(45.35) 1015(59.9) 4050(75.3) 6910(81.6)	1.06	391	29500	1190	462	230	20700 ±50	11.6 +0.05
iv	CONHPh	319 (35.0) 907(45.35) 3640(60.0)	5.11	1440	89700	5740	1700	701	19800 ±50	11.55 ±0.55
v	CO_2Me	99.8(45.35) 322(59.9) 1010(75.3) 1565(81.6)	1.14	147	5170	1280	174	40.4	17050 ±50	8.7 ±0.05
vi	COMe	130(45.35) 542(60.0) 3700(81.8)	0.570	208	15600	641	246	122	20700 ±50	11.3 ±0.05
vii	COPh	49.2(59.9) 238(75.3) 435(81.6)	0.0219	18.3	2500	24.6	21.6	19.5	23600 ±50	12.2 ±0.05

[a] The probable errors quoted are those obtained by the method of least squares and are intended to indicate the fit to a straight line of the log k_2 against $1/T$ plot. [b] Compounds (i), (ii) and (v) have been recorded previously.[3]

TABLE II

ortho Substituent	S.R.F. at 50° *para*	*ortho*	Steric index at 50°	Overlap (Å.) determng. config.	ΔE, cal. *para*	*ortho*	$\Delta \log B$ *para*	*ortho*
H	1	1	1	0.16[a]	0	0	0	0
CO_2^-	7.12	0.305	23.4	0.66[b]	−2200	+4700	−0.6	+2.8
$CONH_2$	262	462	0.567	0.66[b] 1.10[c]	−2350	−3350	+0.8	+0.4
CPNHPh	.....	1700	.....	0.66[b] 1.10[c]		−4250		+0.35
CO_2Me	1560	174	8.97	0.66[b]	−5400	−7000	−0.45	−2.5
COMe	1990	246	8.09	0.66[b]	−4900	−3350	0	+0.1
COPh	2655	21.6	123	1.32[d]	−5500	− 450	−0.3	+1.0

[a] Cl and H, [b] Cl and O, [c] Cl and N, [d] between the two rings.

than the C=O is toward the Cl atom. Models confirm the appropriate spatial relationship of N, H and Cl for H bonding. The hydrogen bonding enhances the electronegativity of the Ar–Cl bond resulting in acceleration, and also weakens the Ar–Cl bond with the same result. The *ortho* CONHPh group is similar in behavior to the amide group; the Ph group supplying alternative conjugation for the unshared electrons on the nitrogen reduces the internal compensation in the amide system, leading to a fourfold increase in rate over the simple amide.

The CO_2Me and COMe groups are less activating in the *ortho* than the *para* position, the steric indices being 8.97 and 8.09, respectively. In general terms these differences may be associated with less effective conjugation in the *ortho* compounds due to loss of coplanarity and shorter conjugation path, and with O–O repulsion. The rate constants for both compounds, and the Arrhenius parameters for the COMe compound agree well with this picture. The Arrhenius parameters for the CO_2Me compound do not fit so well, since E and log B are low. However this also applies to the *para* compound. It is possibly associated with (i) the lesser electronegativity of methoxyl as compared with carbonyl oxygen, and thus less O–O repulsion, (ii) the special ability of the ester in some unknown way to stabilize the intermediate complex. This in particular would lead to low E and log B values, and more so in the *ortho* series where the CO_2Me group is at the end of the cyclopentadienate system. The more normal parameters for the CO_2Me group in the dinitro system[3] may then be ascribed to greater relative importance of O–O repulsion in the highly hindered dinitro series. Additional stabilization of the cyclopentadienate system may also be less effective. The order of activating power COMe > CO_2Me is that expected. Possible side reactions for this compound are: (i) alkaline hydrolysis of the ester group if the solvent had picked up water after drying; (ii) reaction of the CO_2Me group with OMe^- by alkyl–oxygen fission. Both of these are irreversible reactions and would have shown up at once in the infinity readings, and as product contaminant.[3] The infinity readings were as expected from the concentrations used, and the product isolated direct from the reaction mixture as before was pure methyl 2-methoxy-5-nitrobenzoate.

The COPh group exhibits the largest *ortho* effect of all the groups considered in this paper, the steric index being 123. The relative configuration of the carbonyl group and the two rings is very restricted, and the approach of the reagent to the reactive center is much hindered. The situation is thus very similar to that for the *ortho* carboxylate and the differences in rate constants and Arrhenius parameters are parallel in the two cases. The larger value for the COPh steric index is due presumably to the accompanying reduction of an otherwise powerful -T effect, this being different from the carboxylate. However while this leads to a larger steric index, the actual hindrance is not so important as with the *ortho*-CO_2^-, the *ortho*-COPH group still being an activating group.

Experimental

Runs were carried out as in previous papers[2] in the series being duplicated at each of three temperatures for each compound.

Typical run: 2-chloro-5-nitrobenzophenone at 59.9°
Initial concn. ArCl = 0.00473, OMe^- = 0.00667 *M*

Titration reading:	11.00	11.51	11.93	12.29	12.94	13.23	13.73	14.13	14.61	14.90	15.18	16.73	19.26 (inf.)
Log term:	0.1661	1763	1833	1910	2066	2145	2295	2432	2619	2748	2886	4017	
Time (min.):	0	30	60	90	150	180	240	300	360	420	460	900	

Rate constant: $4.923 \pm 0.018 \times 10^{-4}$ l. moles^{-1} secs.$^{-1}$

Rate constants for 2-chloro-5-nitrobenzamide

45.35°	2.436	2.444	Av. 2.44×10^{-3}
59.9°	1.014	1.016	Av. 1.015×10^{-2}
75.3°	4.050		4.05×10^{-2}
81.6°	6.893	6.930	Av. 6.91×10^{-2}

Giving activation energy 20700 ± 50
$\log_{10}$ frequency factor 11.6 ± 0.05

Products.—These were isolated direct from the surplus reaction mixture by cold aqueous acidification (HCl) and found to be the pure 2-methoxy-5-nitro compounds and in all cases infinity readings agreed with those expected.

Preparation of Materials. The **2-chloro-5-nitrobenzoic acid** was prepared as in part IV.[3] The **2-chloro-5-nitrobenzamide** was obtained in 36% yield from the acid *via* the acid chloride; m.p. 179°, lit. 178°, 180°.[6,7] **2-Chloro-5-nitrobenzanilide** was prepared in 61% yield from the acid *via* the acid chloride; m.p. 158°, lit. 158°.[8] The **methyl 2-chloro-5-nitrobenzoate** was synthesized as in part IV.[3]

2-Chloro-5-nitroacetophenone (a).—A small amount was prepared in poor yield by condensing sodiomalonic ester in dry ether with the 2-chloro-5-nitrobenzoyl chloride, followed by hydrolysis and decarboxylation of the condensation product. This is analogous to the preparation by Johnson and Offenhauer[9] of 4-(*p*-hydroxyphenyl)-hexahydroacetophenone. The required product separated from the steam distillate; m.p. 58–61°, lit. 62°. The yield was 14%, and 18% of the original acid was recovered.

(b) **2-Chloroacetophenone** (b.p. 227–228° at 771 mm.) was prepared in 73% yield from 2-chlorobenzoyl chloride by the method of Walker and Hauser.[10] It was then nitrated with pure nitric acid by the method of Thorpe and Brunskill[11] in 30% yield, giving a product m.p. 62°.

2-Chloro-5-nitrobenzophenone was obtained in 61% yield from the acid chloride by a Friedel–Crafts reaction[12]; m.p. 85–86°, lit. 86°.

All m.p.'s are corrected.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

The Mechanism of Dehydrohalogenation of Benzene Tetrachloride and Related Compounds[1]

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The mechanism of the base-catalyzed dehydrochlorination of polychlorocyclohexenes, such as benzene tetrachloride, pentachlorocyclohexene and hexachlorocyclohexene, has been elucidated by kinetic and product distribution studies. Of four modes of elimination which were found to take place, at least two occur simultaneously and competitively in a given isomer. In general, the rates of these processes decrease in the following sequence: *trans*-1,2; *trans*-1,4; *cis*-1,2; *cis*-1,4. The elimination reactions exhibit second-order kinetics and are consistent with bimolecular mechanisms which may be either concerted or involve the formation of a carbanion intermediate in a multiple-stage process. The initial attack by base appears to be favored at an axial rather than an equatorial allylic hydrogen substituent. The results of this investigation clarify the mechanism of dehydrohalogenation of benzene hexachloride and related polychlorocyclohexanes.

The base-catalyzed dehydrochlorination of benzene hexachloride (BHC) has been shown by Cristol[2] to proceed by two different mechanisms, depending on whether at least one pair of vicinal chlorine and hydrogen substituents is present in a *trans* relationship. The α-, γ-, δ- and ϵ-isomers, in which *trans* elimination of hydrogen and chlorine is sterically possible, undergo a normal bimolecular (E_2) reaction in which nucleophilic attack by the base removes a β-proton, with formation of olefin and elimination of halide ion in a single synchronous process. The β-isomer, in which all vicinal pairs of hydrogen and chlorine are *cis*, reacts at a much slower rate by a multiple-stage process in which only the proton is removed in the rate-determining step and a carbanion intermediate is formed. In a subsequent step, the latter undergoes inversion and decomposes to olefin and chloride ion.

Hughes, Ingold and Pasternak,[3] on the other hand, do not consider the carbanion intermediate mechanism probable. They have suggested that the greater energy of activation (32 kcal./mole) of β-BHC, compared with that (*ca.* 20 kcal./mole) of the other isomers is employed in part to force "the relevant portion of the molecule more nearly into the desirable *anti*-configuration, and partly to force the mechanism against the still imperfect orientation of the bonds involved." We consider that the

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