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FRIEDEL-CRAFTS REACTIONS—XXVII

THE MECHANISM FOR BENZOYLATION OF DICHLOROBENZENES

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Abstract—A search for mechanisms for benzoylation of dichlorobenzenes which are consistent not only with the nature and relative proportions of the eight products but also with the pattern of the non-additivity of substituent effects on the reaction rates, produced just one candidate. It involves chloronium ion migration and secondary protodechlorination in addition to the usual displacement of protons by acylium ions.

In an earlier paper,[1] Goodman and Gore reported that the Friedel–Crafts benzoylation of dichlorobenzenes yields appreciable amounts of abnormal substitution products and that the reactivities of the dichlorobenzenes are not as expected from the application of the substituent-additivity principle[2] to the reactivity of chlorobenzene. The pattern of the non-additivity of substituent effects in this reaction of dichlorobenzenes is different from that observed by Schofield *et al.*[3] in a reaction that does not lead to abnormal substitution products, namely, nitration in sulphuric acid. Here we report a search for possible mechanisms for the reaction which are consistent with all the experimental data.

The search for mechanisms. The experimental data[1] for the Friedel–Crafts benzoylations of dichlorobenzenes in nitrobenzene by the Perrier technique are reproduced in Tables 1–3. Each dichlorobenzene isomer gives rise to at least one major product which is not formed even in trace amounts from the other two isomers. This indicates that the dichlorobenzenes do not isomerise significantly under the reaction conditions. Isomerisation of dichlorobenzenes has previously been shown to take place in the presence of aluminium chloride or related catalysts, but only in the absence of basic solvents.[4]

The observation of products that arise, at least formally, from dechlorination and from chloronium ion migration, suggested to us that the formation of σ-complexes of substrate and electrophile, in which a Cl atom is bent out of the plane of the benzene ring, might play an important part in the overall reaction mechanism. Therefore we determined theoretically (for method, see Experimental) the rates of formation of these so called "*ipso*" complexes[5] relative to the rates of formation of "*normal*" σ-complexes in which an H atom is bent out of the plane of the benzene ring. The results were that *ipso* σ-complex formation should be most favoured for the

Table 1. Products of the Friedel-Crafts benzoylation of the isomeric dichlorobenzenes, in nitrobenzene solution at 100°

Product	Substrate Isomer		
	ortho %	meta %	para %
2,3-dichlorobenzophenone	7.3		
2,4-dichlorobenzophenone		89.0	
2,5-dichlorobenzophenone			65.8
2,6-dichlorobenzophenone		11.0	
3,4-dichlorobenzophenone	78.9		10.7
o-chlorobenzophenone	0.8		1.5
p-chlorobenzophenone	9.9	trace	20.0
benzophenone	3.2		2.0

Table 2. Relative rates of Friedel–Crafts benzoylation, in nitrobenzene solution at 25°

Substrate	Relative rate	
	Observed	Calculated[a]
benzene	1.00	
chlorobenzene	2.6×10^{-2}	
o-dichlorobenzene	6.71×10^{-5}	0.82×10^{-5}
m-dichlorobenzene	1.85×10^{-4}	1.66×10^{-4}
p-dichlorobenzene	$< 0.2 \times 10^{-7}$	3.50×10^{-7}

[a] Using the additivity principle

Table 3. Relative rates of Friedel–Crafts benzoylation, in nitrobenzene solution at 25°, for individual positions of the dichlorobenzenes

Substrate isomer	Position	Relative rate	
		Observed	Calculated[a]
1,2	3	1.48×10^{-5}	0.05×10^{-5}
	4	15.9×10^{-5}	2.4×10^{-5}
1,3	2	1.23×10^{-4}	0.11×10^{-4}
	4	4.95×10^{-4}	4.92×10^{-4}
	5	20.0×10^{-7}	0.26×10^{-7}
1,4	2	0.28×10^{-7}	5.3×10^{-7}

[a] Using the additivity principle

para isomer and least favoured for the *meta* isomer. They match the observation that the *para* isomer yields the greatest percentage of abnormal substitution products and the *meta* isomer yields the least. Hence we went on to consider if the observed products could be formed in the observed proportions from the *ipso* σ-complexes of substrates and acylium-containing species.

First, we considered chloronium ion migration within the *ipso* σ-complexes to give *normal* σ-complexes. Theoretically the most stable σ-complexes should be those in which the acyl group is in the *meta* position and the second Cl atom is in the *ortho* or, preferably, the *para* position. Therefore the most likely abnormal dichlorobenzophenones to be formed via *ipso* σ-complexes should be the 3,4 isomer from *p*-dichlorobenzene, and the 2,5 isomer from *o*-dichlorobenzene. Experimentally, the former but not the latter product is found. We concluded that chloronium ion migration is a significant process only in the reaction of the *para* dichlorobenzene.

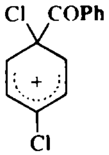
Next, we considered chloronium ion loss from the *ipso* σ-complex. This process should lead to the formation of *p*-chlorobenzophenone from *p*-dichlorobenzene, and of *o*-chlorobenzophenone from *o*-dichlorobenzene. Experimentally, both *para* and *ortho* chlorobenzenes are produced from each of the two dichlorobenzenes in the same relative proportions. The *para* : *ortho* ratio (13 : 1) in these cases is very similar to the *para* : *ortho* ratio (11·5 : 1) in the case of the production of chlorobenzophenones directly from chlorobenzene under similar conditions.[6] We considered that the chlorobenzophenones might equilibrate and tested this possibility experimentally by attempting rearrangements of pure *p*-chlorobenzophenone and of pure *o*-chlorobenzophenone under the conditions of their formation. No rearrangement was observed in the former experiment and only a very small amount of the rearranged product was observed in the latter experiment. We concluded that chlorobenzophenones are not formed via acylium-containing *ipso* σ-complexes but might well be formed via chlorobenzene.

Chlorobenzene could in principle be formed from the dichlorobenzenes via *ipso* σ-complexes, in electrophilic substitution reactions (protodechlorinations) in which the effective electrophile is the proton. The relative amounts of chlorobenzophenones formed from the three dichlorobenzenes would be explained if there was competition between the formation of the *normal* σ-complexes for proton exchange and the formation of the *ipso* σ-complexes for protodechlorination. We considered the implications of assuming that the protodechlorination does indeed occur.

The observation that even the *meta* dichlorobenzene gives rise to a trace of *p*-chlorobenzophenone whereas not even the *ortho* dichlorobenzene gives a measurable amount of abnormal dichlorobenzophenones, would indicate that the proton-containing electrophile must be less selective than the acylium-containing electrophile. The absence of isomerisation of the dichlorobenzenes, which we mentioned above, would indicate that chloronium ion must be eliminated from the proton-containing *ipso* σ-complex before it can migrate. The agent required to assist the elimination would have to be the counter-nucleophile of the electrophilic reagent since the chloronium ion is not eliminated from the acylium-containing *ipso* σ-complex. As the proton-containing electrophile has to be less selective than the acylium-containing electrophile it is reasonable to assume that it also has to be more reactive. Then, since the chlorobenzophenones are minor products of the Friedel–Crafts reaction, we would deduce that the proton-containing electrophile must contain a product of the benzoylation that is not present in the initial reaction mixture. A complex (**1**) of some of the hydrogen chloride released in the benzoylation step, and solvated aluminium chloride, is the simplest species that is likely to have the properties required for the proton-containing electrophile.

$$^{\delta+}\mathrm{H..[..Cl....AlCl_3,O_2NPh]}^{\delta-}$$

1



2

A strong argument for the reality of the secondary protodechlorination reaction is that it accounts for the observation that benzophenone is formed from the *ortho* and *para* but not the *meta* dichlorobenzenes, and for the observation that the greater proportion of benzophenone is formed from the *ortho* isomer. The explanation is as follows. Since the protonating agent is not very selective, the chlorobenzophenones may, to a significant degree, compete with the dichlorobenzenes to capture it and, thence, be dechlorinated by it.[†] Thus no benzophenone is detected in the *m*-dichlorobenzene experiment because no significant amount of chlorobenzophenone is formed. The *ortho* dichlorobenzene should intrinsically react somewhat more rapidly than the *para* isomer in the competitive dechlorination. However the concentration of chlorobenzophenone relative to that of dichlorobenzene becomes several times greater in the *o*-dichlorobenzene experiment than in the *p*-dichlorobenzene experiment, because the rate of formation of the dechlorinating agent is much greater. Thus benzophenone forms a higher proportion of the products in the former experiment.

We shall now show that the secondary protodechlorination is also consistent with the relative rate data reported in Tables 2 and 3. There is no reason why protodechlorination should significantly affect the true rate of normal benzoylation. However, the formation of acylium-containing *ipso* σ-complexes must reduce this rate. We have already seen that *ortho* and *meta* dichlorobenzenes do not form *ipso* σ-complexes to significant degrees. Theoretically, *ortho* dichlorbenzene is more likely to form an *ipso* σ-complex than is chlorobenzene, and therefore we do not expect *ipso* σ-complex formation to be significant with monochlorobenzene. We conclude that the only major reason for the pattern of non-additivity of substituent effects on the relative rates of normal benzoylation to be different from the pattern for the relative rates of nitration, mentioned above, is the formation of an *ipso* σ-complex in the *para* dichlorobenzene: this conclusion is confirmed by the experimental data.

[†] The chlorobenzophenones should not be complexed with aluminium chloride to a major degree in nitrobenzene solution.

Finally, if our mechanism is valid, chlorobenzene should yield trace amounts of benzophenone. A small amount of benzophenone is indeed produced under a wide variety of conditions.[6]

CONCLUSIONS

Our search for possible mechanisms for Friedel–Crafts benzoylations of dichlorobenzenes, which are consistent with all the data reported in Tables 1–3, produced just one candidate. The features of the mechanism are:

(i) that the dichlorobenzenes are benzoylated by the usual S_E2 mechanism;

(ii) that *p*-dichlorobenzene also forms an acylium-containing *ipso* σ-complex (**2**) which undergoes chloronium ion migration before losing a proton;

(iii) that benzoylation produces a secondary reagent which competitively protodechlorinates the dichlorobenzenes to form chlorobenzene, and also protodechlorinates the chlorobenzophenones formed by the benzoylation of that chlorobenzene.

EXPERIMENTAL

The experiments to test if chlorobenzophenones isomerised under the conditions of their formation in the Friedel–Crafts benzoylation were carried out as follows.

To a stirred soln of $AlCl_3$ (6·0 g) and benzoyl chloride (3·1 g) in nitrobenzene (20 ml) at 100°, *p*-chlorobenzophenone (0·5 g) was added, and the mixture maintained at this temp. for 9·5 hr. Isolation was achieved in the usual way, and the yield of recovered ketone was quantitative. Analysis of the product by gas chromatography (columns used were Carbowax 20M, 5%, at 180°, or silicone oil SE 30, 5%, at 162°) showed the absence of *o*-chlorobenzophenone.

An analogous reaction starting from *o*-chlorobenzophenone gave a product which consisted mainly of recovered ketone but included 2·5% of *p*-chlorobenzophenone.

The theoretical model for substituent effects. The theoretical model we used for determining substituent effects on σ-complex formation, is one that has been shown to be capable of interpreting the very marked non-additive effects in normal S_E2 reactions of polychlorobenzenes. Full details of the model and how to apply it have been given previously.[7]

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