

391. *Aromatic Alkylation. Part II.*¹ *Diarylmethylation Reactions in the Solvent Systems $\text{ZnCl}_2\text{-CH}_3\text{:CO}_2\text{H}$ and $\text{ZnCl}_2\text{-HCl-CH}_3\text{:CO}_2\text{H}$.*

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The diarylmethylation of anisole in acetic acid is catalysed by zinc chloride and by mixtures of zinc chloride and hydrogen chloride in a manner which parallels the effect of these substances on the ionisation ratios of an indicator of similar structure to the aralkylating reagent. The reagent is introduced as diarylmethyl chloride or acetate but, under the experimental conditions, it is always present predominantly in the form of the acetate. The results show that the main function of zinc chloride in the reaction is the generation of Brønsted acidity in the solution by virtue of its interaction with the co-catalysts hydrogen chloride and acetic acid, and the concomitant production of carbonium ions from the reagent. The substitution step proper is again the bimolecular reaction between diarylcarbonium ions and anisole.

With sulphuric acid as catalyst, aromatic aralkylation by diphenylmethanol XOH (or its acetate) involves a bimolecular reaction between a rapidly formed carbonium ion and the other reagent (ArH).¹ It seemed of interest to study the same reaction in the same solvent with a Friedel-Crafts catalyst of the Lewis acid metal halide type so as to afford a comparison of the mechanisms. Zinc chloride is a comparatively mild catalyst of this type and it was selected because of the known absence of complication by solvolysis,²

¹ Part I, Bethell and Gold, *J.*, 1958, 1905.

² Davidson and Chappell, *J. Amer. Chem. Soc.*, 1939, **61**, 2164.

whereas the more typical catalyst, aluminium chloride, is rapidly attacked by acetic acid.³

The plan followed that of the study of sulphuric acid catalysis¹ in that measurements of reaction rates were paralleled by indicator measurements⁴ on related diarylmethyl compounds.

In the earlier experiments the aralkylating agent was introduced in the form of the chloride, as is usual in halide-catalysed Friedel-Crafts reactions, but during the course of the investigation it became clear that a solvolytic pre-equilibrium with formation of diarylmethyl acetate is rapidly established and that the simultaneously formed hydrogen chloride functions as a co-catalyst in the reaction.

EXPERIMENTAL

Solutions of zinc chloride and hydrogen chloride were prepared as before.⁴ Whenever possible, blocks of kinetic experiments and their corresponding indicator measurements were made with a single stock solution.

Diarylmethanols and their acetates were the specimens previously prepared.¹ Diarylmethyl chlorides were prepared from the corresponding alcohols by passing hydrogen chloride through the ethereal solution and removing the water formed (CaCl₂). Diphenylmethyl chloride was twice distilled under reduced pressure (b. p. 156—158°/10 mm.; m. p. 19°); the 4-methoxy-compound was recrystallised from ether or light petroleum.

The reactions studied kinetically were also carried out on a preparative scale and the pure products isolated in yield exceeding 92%.

Kinetic runs were followed spectrophotometrically. A 5 ml. sample of the reaction mixture was quenched by ten-fold dilution with absolute or (in the case of higher catalyst concentrations) slightly aqueous ethanol. Absorption intensities of the diluted samples were related to the progress of a reaction by reference to a previously constructed calibration curve, as the spectrum at the completion of a reaction was not a simple superposition of the separate spectra of reagents and products. Synthetic mixtures of reagents, catalyst, and products in acetic acid-ethanol (10 : 90 by vol.) were therefore prepared to simulate diluted samples at the various stages of

TABLE 1. *Alkylation of anisole by diphenylmethyl chloride or diphenylmethyl acetate.*

		[XCl] _{initial} or [XOAc] _{initial} = 0.027M. No addition of hydrogen chloride.							
		10 ⁵ k ₂ (l. mole ⁻¹ sec. ⁻¹):				10 ⁵ k ₂ (l. mole ⁻¹ sec. ⁻¹):			
Series *	[ZnCl ₂]	[Anisole] _{initial}	for chloride	for acetate	Series	[ZnCl ₂]	[Anisole] _{initial}	for chloride	for acetate
A	0.046	0.463	4.13	—	A	0.461	0.463	25.8	—
B	0.070	„	6.67	—	A	0.553	„	16.8	—
A	0.092	„	8.90	—	A	„	0.926	20.3	—
B	0.176	„	18.3	—	B	0.702	0.463	13.8	4.21
A	0.184	„	22.1	—	A	0.922	„	27.8	—
A	„	„	22.9	—	B	1.053	„	31.4	17.1
B	0.351	„	26.4	0.354	A	1.199	„	54.5	—
A	0.369	„	33.0	—	B	1.404	„	72.5	49.7
A	„	0.926	34.1	—	A	1.475	„	90.7	—

* Series A and B relate to different batches of solvent.

TABLE 2. *Alkylation of anisole by 4-methoxydiphenylmethyl chloride.*

[XCl]_{initial} = 0.010M. [Anisole]_{initial} = 0.213M. No addition of hydrogen chloride. k₂ in l. mole⁻¹ sec.⁻¹.

[ZnCl ₂] (M) ...	0.011	0.022	0.054	0.108	0.162	0.216	0.323	0.398	0.431	0.597	0.796
10 ⁵ k ₂	13.6	26.1	75.3	103.0	50.7	14.0	11.1	19.0	22.0	57.5	120.7

the reaction. The observed "infinity" readings agreed satisfactorily (within 5%) with the "synthetic" values expected from the initial concentrations of reagents. In all cases the observed course of the reactions was made to be of first order by employing a large excess of

³ Funk and Schormüller, *Z. anorg. Chem.*, 1931, **199**, 93.

⁴ Bethell, Gold, and Satchell, *J.*, 1958, 1918.

the aromatic compound ArH, and rate constants were evaluated graphically by plotting $\log(100 - x)$ against t , where x is the percentage of unchanged alkylating agent remaining in solution after a time t . Second-order rate constants, k_2 , calculated as before,¹ indicated that the reaction is of first order with respect to ArH.

All rate constants relate to a temperature of 25°.

DISCUSSION

The main series of experiments relates to the aralkylation of anisole by diphenylmethyl chloride and its 4-methoxy-derivative under the influence of added zinc chloride. In each case the rate exhibits a rather characteristic dependence on the catalyst concentration (Figs. 1 and 2), unlike that found for the ionisation ratio of 4 : 4'-dimethoxydiphenylmethyl chloride under the influence of added zinc chloride, but without addition of hydrogen

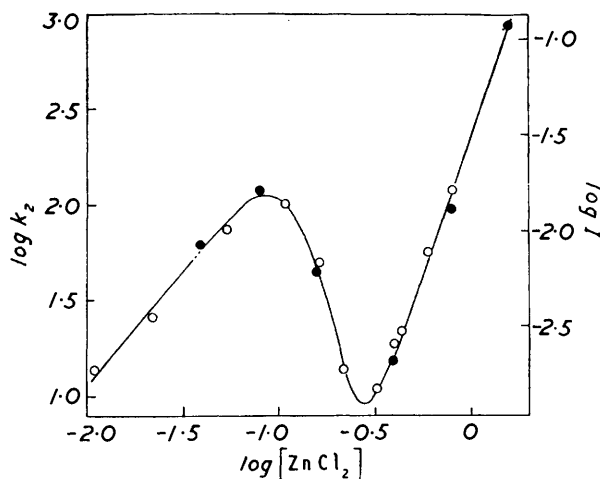


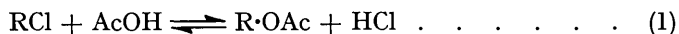
FIG. 1. *Methoxydiphenylmethylation rates and ionisation ratios.*

[HCl] or [RCl] = 0.01M.

○, Velocity constants.
●, Ionisation ratios.

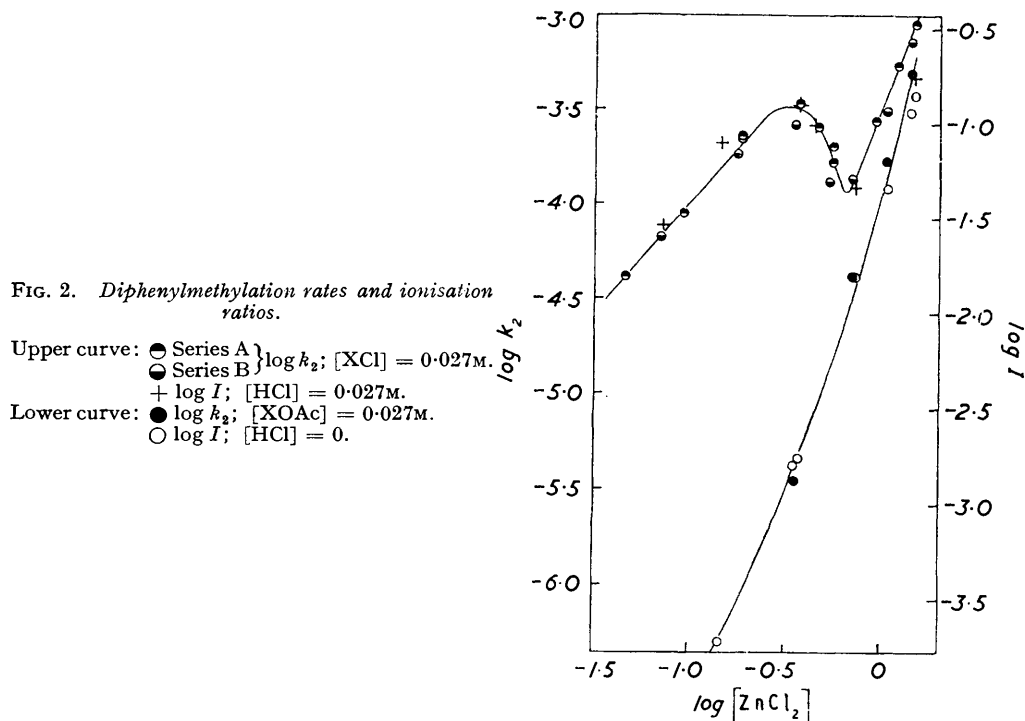
chloride.⁴ On the other hand, the curves resemble the behaviour of the indicator in the presence of both zinc chloride and hydrogen chloride.⁴ If the mechanism of aralkylation under the influence of zinc chloride is the same as for the case of catalysis by sulphuric acid,¹ then it would be expected that the rates should again parallel indicator ionisation ratios as was found in the latter case. A closer examination of the results of the present paper shows that this parallelism does indeed also obtain for the catalysis of zinc chloride.

The reason for the apparent lack of agreement lies in the setting up of the equilibrium



In absence of zinc chloride and hydrogen chloride, esterification of the organic chloride is slow, and the ultraviolet absorption spectrum of a solution of diphenylmethyl chloride in acetic acid differs significantly from that of one of diphenylmethyl acetate in the same solvent. However, upon addition of zinc chloride the absorption spectrum of the organic chloride changes rapidly and becomes identical with that of the acetate (Fig. 3). This indicates that under the conditions of these experiments diphenylmethyl chloride is quantitatively converted into the acetate. (The experiments do not disprove the possibility that some of the acetate is hydrolysed by traces of water in the solvent, but the general character of the results renders this unlikely.) Indicator measurements were carried out on very dilute solutions of the indicator, and consequently the solvolysis does not result in any appreciable concentration of hydrogen chloride in the solution. The

organic chloride concentration was considerably higher in the kinetic experiments, and consequently the media for indicator and for kinetic experiments differed in that the latter contained an appreciable concentration of hydrogen chloride, whereas the former did not. It is now apparent that the rate constants should be related to indicator measurements at a hydrogen chloride concentration equivalent to that of diarylmethyl chloride in the kinetic experiments. This is shown in Fig. 1, where the circles represent velocity constants and the dots ionisation ratios (the latter in the presence of 0.01M added hydrogen chloride); both sets of data fall on the same curve. Similarly, the half-moons in the upper curve of Fig. 2 denote velocity constants, and the crosses ionisation ratios, in the presence of the appropriate concentration of hydrogen chloride. The circles in the lower curve of Fig. 2 represent ionisation ratios for the indicator (in very low concentration), without addition of hydrogen chloride. It is evident that they are not simply related to the data in the upper curve. On the other hand, the dots in the diagram represent reaction velocities when the



reagent is introduced as acetate (so that no hydrogen chloride is set free by solvolysis). These reaction velocities are seen to fall on the lower curve. The indicator data used in both sets of comparisons (Figs. 1 and 2) relate to 4 : 4'-dimethoxydiphenylmethyl chloride (or the alcohol).⁴ The agreement obtained is very good for the results in Fig. 1; for those in Fig. 2 the rate constants increase slightly relative to the ionisation ratios. The reason for this slight discrepancy is not clear, but not entirely unexpected in the light of the more general considerations applying to this solvent system.⁴ The good agreement in the case of the results with 4-methoxydiphenylmethyl chloride indicates that ion-association phenomena must be very similar for the 4-methoxydiphenylcarbonium ion and the 4 : 4'-dimethoxydiphenylcarbonium ion formed from the indicator. This agreement also indicates that the forward reaction of equilibrium (1) must be virtually complete, even when some hydrogen chloride is present in solution, and extends the result derived from the study of absorption spectra in the presence of added zinc chloride alone. (In all cases

studied the actual concentration of hydrogen chloride in solution is considered to be very low, owing to the interaction of hydrogen chloride and zinc chloride.)

TABLE 3. *Effect of addition of hydrogen chloride on the rate of alkylation of anisole by diphenylmethyl chloride or diphenylmethyl acetate.*

[XCl]_{initial} or [XOAc]_{initial} = 0.027M. [Anisole]_{initial} = 0.463M. k_2 in l. mole⁻¹ sec.⁻¹.

Reagent	[ZnCl ₂] (M)	[HCl] _{added} +		10 ⁵ k ₂	Reagent	[ZnCl ₂] (M)	[HCl] _{added} +		10 ⁵ k ₂
		[XCl] _{initial}	[XCl] _{initial}				[XCl] _{initial}	[XCl] _{initial}	
XCl	0.070	—	0.027	6.67	XCl	0.351	0.022	0.049	76.9
XOAc	0.070	—	—	Very slow	XOAc	0.351	0.022	0.022	13.8
XOAc	0.070	0.027	0.027	6.80	XCl	1.053	—	0.027	31.4
XCl	0.351	—	0.027	26.4	XOAc	1.053	0.027	0.027	32.8

The importance of equilibrium (1) is supported by the kinetic experiments with diphenylmethyl acetate (Fig. 2). Furthermore, a mixture of diphenylmethyl acetate and

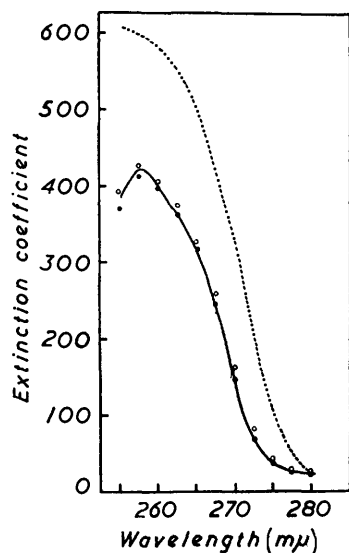
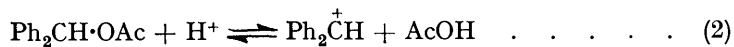


FIG. 3. *Absorption spectra of diphenylmethyl chloride and acetate.*

Full curve: Ph₂CH·OAc in AcOH.
Broken curve: Ph₂CHCl in AcOH.
Circles: " " + 0.316M-ZnCl₂.
Dots: " " + 0.702M-ZnCl₂.

hydrogen chloride is found to be alkylated at the same rate as the corresponding solution of diphenylmethyl chloride (Table 3).

By an argument analogous to that of Part I, the results indicate that the rate of reaction is proportional to the concentration of carbonium ion formed. The function of the catalyst is explained by the high proton activity of the solutions and is analogous to the catalysis by sulphuric acid. It is essentially the acid cleavage of an ester to produce the active carbonium ions



A consideration of the results along with those of Part I permits the further conclusion that no additional rôle (such as association with anisole) is to be assigned to zinc chloride in the mechanism of the reaction. In view of the esterification and solvolysis equilibria, the un-ionised form of 4:4'-dimethoxydiphenylmethanol in sulphuric acid-acetic acid (Part I) will be the same as the un-ionised form of the chloride or acetate. Consequently—leaving aside ion-association phenomena—all the indicator measurements relate to the formation of carbonium ions from the same system of un-ionised indicator. Similarly, the

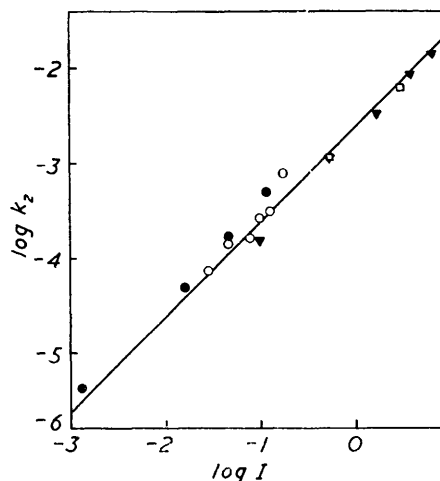
reagent diphenylmethanol will be in the same form as the reagent introduced as diphenylmethyl chloride or acetate, provided that the concentration of alcohol remains unimportant also at the higher concentration. Consequently, if we are justified in writing

$$\log \frac{[\text{XOH}]_{\text{stoich.}}}{[\text{X}^+]} = \log \frac{[\text{ROH}]_{\text{stoich.}} - [\text{R}^+]}{[\text{R}^+]} + \text{const.} \quad (3)$$

it follows that solutions which cause the same conversion of the indicator into carbonium ions will produce the same ionisation ratio for the aralkylating reagent whether it is in-

FIG. 4. Correlation of diphenylmethylation rates of anisole with indicator ionisation ratios for different catalysts and reagents.

- ▼, $\text{H}_2\text{SO}_4\text{-Ph}_2\text{CH}\cdot\text{OH}$.
- , $\text{H}_2\text{SO}_4\text{-Ph}_2\text{CH}\cdot\text{OAc}$.
- , $\text{ZnCl}_2\text{-Ph}_2\text{CHCl}$.
- , $\text{ZnCl}_2\text{-Ph}_2\text{CH}\cdot\text{OAc}$.



produced as alcohol, chloride, or acetate. If zinc chloride has no function beyond producing the acid system which induces the ionisation of the reagent, the coefficient k in the rate equation (Part I, equation 8)

$$v = k[\text{X}^+][\text{ArH}] \frac{f_{\text{X}^+} f_{\text{ArH}}}{f_{\ddagger}} \quad (4)$$

should have the same value for diphenylmethylations catalysed by zinc chloride-hydrogen chloride or by sulphuric acid. It follows from equations (3) and (4) that a graph of $\log k$ against $\log I$ should include all points on the same straight line of unit slope. On the other hand, an additional catalytic function of zinc chloride would then be revealed by the points relating to zinc chloride lying *above* the line through the points for catalysis by sulphuric acid. The correctness of the first alternative is indicated in Fig. 4, in which none of the points diverges from the best straight line of *unit slope* by more than a factor of 2. The agreement is remarkable, since the measurements apply to high concentrations of different catalysts, such as might be expected to cause a noticeable medium effect, and to different concentrations of anisole. It also points to the relative unimportance of the chemical nature of the anion associated with the reagent carbonium ion. The result also accords with our observation that zinc chloride does not affect the ultraviolet spectrum of anisole, and therefore presumably does not interact with it chemically.

It is known from other work,⁵ particularly in the field of so-called "cationic polymerisation", that at least some catalysts of the Lewis-acid type are ineffective (in the gas-phase or in non-polar media) unless a co-catalyst is present. Traces of water can fill this rôle and, for this reason, an exact study of the phenomenon in non-polar media is experimentally

⁵ Articles in Plesch (ed.), "Cationic Polymerisation and Related Complexes," Heffer, Cambridge, 1953; Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, London and New York, 1954, Chap. XI; Ipatieff, Pines, and Schmerling, *J. Org. Chem.*, 1940, **5**, 253; Toussaint and Hennion, *J. Amer. Chem. Soc.*, 1940, **62**, 1145.

difficult. The present study and the related work on deuterium exchange in acetic acid⁶ demonstrate the operation of co-catalysis in greater detail. In the terminology employed in this field, zinc chloride would be described as the catalyst, and acetic acid and hydrogen chloride as co-catalysts. Our work also shows that co-catalysis, in at least one reaction of the Friedel-Crafts type, is a manifestation of catalysis by a Brønsted acid. It does not follow that co-catalysis by Brønsted acids need be met in all reactions for which zinc chloride is a catalyst.⁷

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⁶ Satchell, preceding paper.

⁷ Bell and Skinner, *J.*, 1952, 2955.
