**635.** *Aromatic Alkylation. Part III.* Comparison of the Reactivities of Some Aromatic Compounds towards Diphenylcarbonium Ions.*

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The rate of reaction of diphenylmethanol with benzene, anisole, and the three dimethoxybenzenes in acetic acid–sulphuric acid solutions show a similar dependence on solvent acidity and, even for the most reactive compound (*m*-dimethoxybenzene), the reaction remains of first order with respect to both diphenylmethanol and the aromatic compound. The relative reactivities of the aromatic compounds fall into a sequence similar to those of these compounds towards bromination in acetic acid, but the effect of substitution on the reactivity is more marked in the latter case. It is shown that the measurements cannot be analysed satisfactorily on the assumption of independent substituent effects to yield information about the activating or deactivating influence of the methoxyl group.

THE formation of 4-methoxytriphenylmethane by acid-catalysed interaction of diphenyl-methanol (or its acetate) and anisole is a bimolecular reaction (sometimes also denoted[1] by the symbol S_N2C^+) between rapidly formed carbonium ions and anisole,[2] *i.e.*:

$$Ph_2CH^+ + ArH \longrightarrow Ph_2CHAr + H^+$$
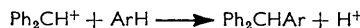
It seemed possible that an increase in the reactivity of the aromatic compound might lead to the observation of a different mechanism of aralkylation. There are the possibilities of either an S_N1 reaction in which the ionisation of the aralkylating agent, $Ph_2CHX \longrightarrow Ph_2CH^+ + X^-$, controls the rate or of a bimolecular reaction between the un-ionised aralkylating agent (or its conjugate acid) and the aromatic compound. These two cases would correspond respectively to the unimolecular zero-order nitrations in which the generation of NO_2^+ ions is rate-controlling[3] and to nitration by the species HNO_3 (or $H_2NO_3^+$).[4]

The experiments now reported were carried out with the dual objective of (*a*) investigating the substituent effects on the aromatic compound, taking as main example the effect of introducing one or two methoxyl groups into the aromatic nucleus, and (*b*) examining whether the expected enhancement of reactivity thus produced is sufficient to change the mechanism of the reaction in the above-mentioned manner. In view of the reported very much faster bromination of *m*-dimethoxybenzene[5] than of anisole, it was considered that *m*-dimethoxybenzene was perhaps one of the compounds most likely to exhibit a different mechanism of aralkylation if it can be realised with diphenylmethanol in acetic acid solution, *i.e.*, under conditions which appear favourable to the rapid generation of carbonium ions.

The alternative mechanisms would differ from the S_N2C^+ mechanism observed so far, not only in the order with respect to ArH, but also in their dependence on the solvent acidity. The S_N1 and S_N2 reactions involving $Ph_2C\cdot OH_2^+$ in the rate-controlling step are expected to depend on Hammett's acidity function H_0 much less steeply than the S_N2C^+ reaction. The rate should follow the relation, $\log k = \text{Constant} - H_0$, if we neglect the explicit consideration of effects of ion association, as seems justified in this context.[2,6,7]

* Part II, *J.*, 1958, 1930.

[1] Gelles, Hughes, and Ingold, *J.*, 1954, 2928.
[2] Bethell and Gold, *Chem. and Ind.*, 1956, 741; *J.*, 1958, 1905.
[3] Benford and Ingold, *J.*, 1938, 929; Hughes, Ingold, and Reed, *J.*, 1950, 240.
[4] Halberstadt, Hughes, and Ingold, *J.*, 1950, 2441.
[5] de la Mare and Robertson, *J.*, 1943, 279; de la Mare and Vernon, *J.*, 1951, 1764.
[6] Bethell and Gold, *J.*, 1958, 1930.
[7] Cf. Satchell, *J.*, 1958, 1915, 1927; Bethell, Gold, and Satchell, *J.*, 1958, 1918.

EXPERIMENTAL

The method of purification of acetic acid and diphenylmethanol, and the preparation of indicators and of solvent mixtures, were as described earlier.[2,6] All rate comparisons reported in this paper relate to uniform batches of solvent, and to a constant concentration of water (0·55M).

o- and p-Dimethoxybenzene were purified by steam-distillation and crystallisation from benzene (at 0°) and ethanol, respectively (to m. p. 22° and 56°). m-Dimethoxybenzene and

TABLE 1. *Results of kinetic measurements. Velocity constants for diphenyl-methylation at 25°.*

H_2SO_4 (M)	k_2	$-\log I$	H_2SO_4	k_2	$-\log I$

Anisole.* $[ArH]_0 = 2 \cdot 57 \times 10^{-2}$M; $[Ph_2CH \cdot OH]_0 = 2 \cdot 21 \times 10^{-3}$M; $[H_2O]_{added} = 0 \cdot 55$M.

0·633	$5 \cdot 52 \times 10^{-4}$	3·88	1·588	$1 \cdot 11 \times 10^{-2}$	2·56
1·149	$4 \cdot 16 \times 10^{-3}$	3·00	1·774	$1 \cdot 56 \times 10^{-1}$	2·40
1·381	$6 \cdot 78 \times 10^{-3}$	2·74			

* The values now reported differ slightly from those reported earlier.[2] The cause of the discrepancy is uncertain. The new values were obtained under the same conditions as the other results in this paper, and should therefore be comparable with them.

p-*Dimethoxybenzene.*

(A) $[ArH]_0 = 1 \cdot 62 \times 10^{-2}$M; $[Ph_2CH \cdot OH]_0 = 1 \cdot 63 \times 10^{-3}$M; $[H_2O]_{added} = 0 \cdot 55$M.

(B) $[ArH]_0 = 1 \cdot 47 \times 10^{-2}$M; $[Ph_2CH \cdot OH]_0 = 1 \cdot 29 \times 10^{-3}$M; $[H_2O]_{added} = 0 \cdot 55$M.

(A)			(B)		
1·241	$2 \cdot 90 \times 10^{-3}$	2·89	1·176	$2 \cdot 77 \times 10^{-3}$	2·97
1·390	$4 \cdot 92 \times 10^{-3}$	2·74	1·306	$4 \cdot 70 \times 10^{-3}$	2·82
1·490	$7 \cdot 02 \times 10^{-3}$	2·65	1·428	$6 \cdot 21 \times 10^{-3}$	2·70
1·639	$8 \cdot 35 \times 10^{-3}$	2·52	1·734	$7 \cdot 51 \times 10^{-3}$	2·43
1·738	$1 \cdot 05 \times 10^{-2}$	2·43	1·897	$1 \cdot 28 \times 10^{-2}$	2·30
1·986	$1 \cdot 15 \times 10^{-2}$	2·23	2·070	$1 \cdot 58 \times 10^{-2}$	2·16
2·235	$1 \cdot 94 \times 10^{-2}$	2·02	2·475	$2 \cdot 86 \times 10^{-2}$	1·82

o-*Dimethoxybenzene.*

(A) $[ArH]_0 = 9 \cdot 34 \times 10^{-3}$M; $[Ph_2CH \cdot OH]_0 = 7 \cdot 94 \times 10^{-4}$M; $[H_2O]_{added} = 0 \cdot 55$M.

(B) $[ArH]_0 = 9 \cdot 31 \times 10^{-3}$M; $[Ph_2CH \cdot OH]_0 = 9 \cdot 48 \times 10^{-4}$M; $[H_2O]_{added} = 0 \cdot 55$M.

(A)			(B)		
0·993	$1 \cdot 02 \times 10^{-2}$	3·20	0·476	$1 \cdot 55_5 \times 10^{-3}$	4·25
1·092	$1 \cdot 46 \times 10^{-2}$	3·06	0·641	$3 \cdot 29 \times 10^{-3}$	3·85
1·390	$2 \cdot 22 \times 10^{-2}$	2·74	0·864	$8 \cdot 10 \times 10^{-3}$	3·42
1·492	$2 \cdot 88 \times 10^{-2}$	2·65	1·097	$1 \cdot 38 \times 10^{-2}$	3·06
1·589	$4 \cdot 08 \times 10^{-2}$	2·56	1·103	$1 \cdot 41 \times 10^{-2}$	3·04
			1·180	$1 \cdot 65 \times 10^{-2}$	2·96
			1·289	$1 \cdot 99 \times 10^{-2}$	2·83
			1·659	$4 \cdot 04 \times 10^{-2}$	2·50

m-*Dimethoxybenzene.*

(A) $[ArH_0] = 1 \cdot 53 \times 10^{-2}$M; $[Ph_2CH \cdot OH]_0 = 1 \cdot 51 \times 10^{-3}$M; $[H_2O]_{added} = 0 \cdot 55$M.

(B) $[Ph_2CH \cdot OH]_0 = 1 \cdot 99 \times 10^{-3}$M; $[H_2SO_4] = 0 \cdot 107$M; $[H_2O]_{added} = 0$.

(A)			(B)		
0·102	$2 \cdot 81 \times 10^{-3}$	5·81	$10^2[ArH]_0$	2·08	4·15
0·122	$4 \cdot 29 \times 10^{-3}$	5·64	10^3k_2	3·62	3·59
0·153	$5 \cdot 09 \times 10^{-3}$	5·45			
0·153	$5 \cdot 96 \times 10^{-3}$	5·45			
0·204	$9 \cdot 83 \times 10^{-3}$	5·18			
0·224	$1 \cdot 29_5 \times 10^{-2}$	5·08			
0·407	$4 \cdot 51 \times 10^{-2}$	4·43			

Benzene. $[ArH]_0 = 2 \cdot 88 \times 10^{-1}$M; $[Ph_2CH \cdot OH] = 1 \cdot 456 \times 10^{-2}$M; $[H_2O]_{added} = 0 \cdot 55$M.

H_2SO_4 (M)	k_2	$-\log I$
3·75	$3 \cdot 59 \times 10^{-6}$	0·96
3·89	$4 \cdot 68 \times 10^{-6}$	0·86
4·89	$2 \cdot 63 \times 10^{-5}$	0·19

anisole were purified by successive extractions with aqueous sodium hydroxide and water. The liquids were dried, finally by sodium, from which they were fractionally distilled.

2,4- and 3,4-Dimethoxytriphenylmethane were made on a preparative scale by the method based on that used by Kundiger and Ovist[8] and described in Part I, starting from

[8] Kundiger and Ovist, *J. Amer. Chem. Soc.*, 1954, **76**, 2501.

5 K

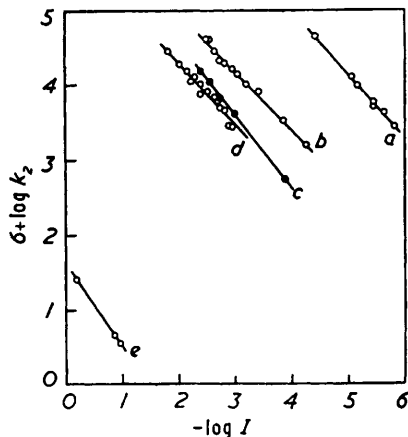diphenylmethanol and *m*- and *o*-dimethoxybenzene respectively (m. p.s of products 124° and 111—112°).

The interaction of diphenylmethanol and *p*-dimethoxybenzene is complicated by the formation of a disubstituted product under certain conditions, and was examined under two slightly differing sets of conditions. The reaction between diphenylmethanol (2·0 g.) and *p*-dimethoxybenzene (15 g.) in acetic acid (70—100 ml.) under the influence of sulphuric acid (10 ml., added dropwise, with vigorous shaking) gave, after 2½ hr., by usual methods of product separation, crude 2,5-dimethoxytriphenylmethane (3·0 g.; m. p. 97—99°, raised on recrystallisation from ethanol to 104—105°). The same reaction, when carried out with rapid addition of sulphuric acid or by the use of a higher ratio of *p*-dimethoxybenzene to diphenylmethanol, gave also a small amount of a white product, m. p. 207—208°, insoluble in ethanol. This material was the only product in the reaction of *p*-dimethoxybenzene with diphenylmethanol in the molar ratio 1 : 2 or on treatment of 2 : 5-dimethoxytriphenylmethane with diphenylmethanol in acetic acid–sulphuric acid. It was therefore considered to be a di-aralkylated dimethoxybenzene and, from the theory of aromatic substitution, therefore 1,4-*bisdiphenylmethyl-2,5-dimethoxybenzene* [Found: C, 86·6; H, 6·6; OMe, 14·5%; *M* (Rast), 452. $C_{34}H_{30}O_2$ requires C, 86·8; H, 6·4; OMe, 13·2%; *M*, 470]. This compound was also formed as a by-product, in addition to 2 : 5-dimethoxytriphenylmethane, when the reaction between

FIG. 1. *Indicator ionisation in acetic acid-sulphuric acid containing water* (0·55 mole $l.^{-1}$).
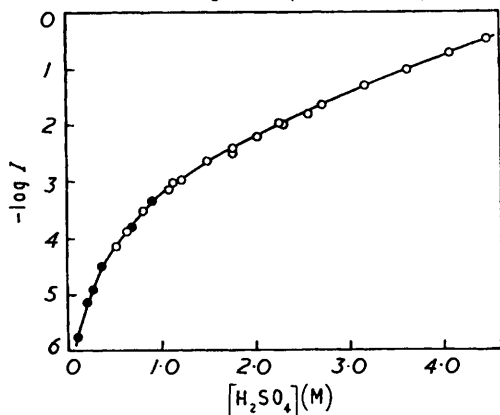
◯, 4 - Methoxydiphenylmethanol; ●, 4,4′ - dimethoxydiphenylmethanol [adjusted by equation (1)].

FIG. 2. *Relation between diphenylmethylation rates and indicator ionisation.*

(*a*) *m*-Dimethoxybenzene, (*b*) *o*-dimethoxybenzene, (*c*) anisole, (*d*) *p*-dimethoxybenzene, (*e*) benzene.

p-dimethoxybenzene (12 g.) and diphenylmethanol (2 g.) was carried out in benzene solution (50 ml.) in the presence of toluene-*p*-sulphonic acid.

Reaction velocities at 25° were measured spectrophotometrically, as previously described.[2] In every case the extrapolated values of the optical density for reaction mixtures at zero time and at the completion of the reaction agreed satisfactorily with values calculated on the basis of Beer's law from the previously determined spectra of the reactants and products in acetic acid.

In the experiments with benzene the solutions became turbid towards the end of the reaction owing to the precipitation of triphenylmethane. Timed samples were removed only during the earlier stages. To obtain " infinity " values in these experiments the whole of the suspension at the completion of the reaction was diluted with acetic acid so as to dissolve all the precipitate before the removal of portions for spectrophotometric examination.

The nature of the product (triphenylmethane) was in this case also established by the infrared spectrum of a sample of isolated product.

In all runs the concentration of benzene or methoxybenzene was greatly in excess (10- to 20-fold) of the concentration of diphenylmethanol, so that individual reactions followed a first-order course. The bimolecular nature of the reaction had been established earlier for anisole [2] and

has now been found again for the most reactive compound studied (*m*-dimethoxybenzene) by variation of that excess of concentration. Second-order rate constants, evaluated as before,[2] are in Table 1, the units being 1. mole^{-1} sec.$^{-1}$ throughout.

Ionisation ratios of diarylmethanol indicators (4-methoxydiphenylmethanol, ROH, and 4,4′-dimethoxydiphenylmethanol, R′OH) were determined in this solvent system. In the short range of acidities in which measurements on both indicators were practicable, the two sets of ionisation ratios were related by the expression

$$\log \frac{[R^+]}{[ROH]_{\text{stoich.}} - [R^+]} = \log \frac{[R'^+]}{[R'OH]_{\text{stoich.}} - [R'^+]} - 3\cdot23 \quad . \quad . \quad . \quad (1)$$

the last term denoting the difference between the logarithms of the ionisation constants of the two indicators. The combined indicator results are summarised graphically in Fig. 1.

The kinetic and indicator results were again found to be related (Fig. 2) by the equation [2]

$$\log k_2 = \lambda \log I + \text{Constant}$$

where $I = \log \dfrac{[R^+]}{[ROH]_{\text{stoich.}} - [R^+]}$. Values of the slopes λ and of $\log k_2$ at selected values of I were also computed by the method of least squares and are given in Table 2.

TABLE 2. *Summary of results.*

Compound	λ	$\log I = 0$	$8 + \log k_2$ $\log I = -3$	$\log I = -6$
Benzene	$1\cdot12_1$	$\overline{3}\cdot632$	$0\cdot269$	$\overline{4}\cdot906$
Anisole	$0\cdot97_9$	$8\cdot541$	$5\cdot604$	$2\cdot667$
o-Dimethoxybenzene	$0\cdot79_7$	$8\cdot585$	$6\cdot194$	$3\cdot803$
m-Dimethoxybenzene	$0\cdot87_4$	$10\cdot526$	$7\cdot904$	$5\cdot282$
p-Dimethoxybenzene	$0\cdot84_8$	$8\cdot017$	$5\cdot473$	$2\cdot929$
Mesitylene *	$0\cdot98_1$	$8\cdot005$	$5\cdot062$	$2\cdot119$

* Kinetic results from ref. 2.

TABLE 3. *Relative reactivities in bromination and diphenylmethylation.*

Compound	Bromination [5]	Diphenylmethylation $I = 1$	$I = 10^{-3}$	$I = 10^{-6}$
Benzene	$8\cdot3 \times 10^{-10}$	$1\cdot2 \times 10^{-5}$	$4\cdot6 \times 10^{-6}$	$1\cdot7 \times 10^{-6}$
Anisole	(1)	(1)	(1)	(1)
o-Dimethoxybenzene	$3\cdot30$	$1\cdot1$	$3\cdot9$	14
m-Dimethoxybenzene	$>10^4$	97	200	410
p-Dimethoxybenzene	$0\cdot075$	$0\cdot3$	$0\cdot74$	$1\cdot8$
Mesitylene	$0\cdot150$	$0\cdot29$	$0\cdot29$	$0\cdot28$

DISCUSSION

The experimental results show that the dependence of the alkylation velocity on acidity is not significantly altered when the reactivity of the aromatic compound is increased. The slopes obtained for the linear graphs of $\log k_2$ against H_0 are almost identical for the three dimethoxybenzenes, which span an approximately 100-fold range of reactivity. On the other hand, the slopes for anisole and mesitylene [2] are appreciably different, although the reactivities of these compounds are close to that of *p*-dimethoxybenzene. The difference is therefore not thought to arise from a difference in reaction mechanism but from a salting-out or " medium " effect of sulphuric acid, which is more or less constant for the isomeric dimethoxybenzenes but is different for anisole and mesitylene. The results obtained with benzene are not sufficiently detailed to warrant any conclusions in this respect.

The reaction velocity remains proportional to the concentration of aromatic compound ArH even for the most reactive compound investigated. This observation, taken in conjunction with the acidity dependence of the reaction velocity and earlier results,[2] indicates that the rate-controlling step of all the reactions studied is the bimolecular attack of the diphenylcarbonium ion upon ArH.

The measurements allow an estimate of the relative reactivities of benzene, anisole, mesitylene,[2] and the three dimethoxybenzenes towards diphenylcarbonium ions. This problem is also of some interest in view of seemingly conflicting evidence as to whether a methoxyl group activates or deactivates a *meta*-position.[5,9,10] Since the different lines in Fig. 2 are not exactly parallel, it is evident that the present study cannot provide a precise comparison of reactivities: the numerical values will depend on the solvent acidity chosen for making the comparison. In particular, there is an actual crossing over of the curves for anisole and *p*-dimethoxybenzene.

The lower values of the slopes for the dimethoxybenzenes cannot be attributed to basic behaviour of these compounds in the media investigated (in the sense of partial protonation of the compounds). Such behaviour would lead to a distinct curvature of the plots in Fig. 2. This point has also been directly examined in some detail for *m*-dimethoxybenzene. It was found that the ultraviolet absorption spectrum of *m*-dimethoxybenzene in acetic acid is identical with the spectrum immediately observed for this substance in the acidic media used in the kinetic experiments, and absence of any significant amount of protonation is therefore indicated. (A slow and irreversible reaction of unknown nature takes place in the acid solutions of *m*-dimethoxybenzene, but it makes no noticeable progress within the duration of the alkylation runs.)

Table 3 shows a comparison of the reactivities towards diphenylcarbonium ions of the different aromatic substrates studied at two different solvent acidities. The most direct comparison of our data is that with results on bromination in acetic acid [5] which have been included in the same Table. The different sets of results show the same general features, but the bromination velocities span a wider range of reactivities, *i.e.*, the effective brominating agent appears to be more discriminating than the diphenylcarbonium ion in its attack upon aromatic molecules.

It should be pointed out that the relative bromination reactivities quoted are also subject to some uncertainty. Since the different compounds studied [5] exhibit slightly different reaction orders with respect to bromine (at any rate those whose reaction orders have actually been established), the exact values of the relative reactivities depend upon the bromine concentration chosen for the comparison.

de la Mare and Vernon [5] used the bromination rates for benzene, anisole, and two dimethoxybenzenes to assess the effect of a methoxyl group at a position *meta* relative to it. This estimate was effectively based on the assumption that the effect of two methoxy-groups on another position in a dimethoxybenzene would be governed by independent additive contributions by each of the two groups towards the free energy of activation for substitution at that position. The conclusion reached on this basis was that a methoxyl group had a weakly activating effect at the *meta*-position. This conclusion is in contrast to the more recent direct experimental result that, for electrophilic hydrogen isotope exchange, a methoxyl group deactivates *meta*-positions.[9]

One can attempt to analyse the diphenylmethylation rates in the same manner as the bromination data. For example, by making use of diphenylmethylation velocities at (or extrapolated to) $\log I = -3.0$ for benzene, anisole, and *o*- and *m*-dimethoxybenzene, one arrives at the conclusion that a methoxy-group activates *all* positions in an aromatic ring and that it causes the rate to increase *ca.* 100-fold at an *ortho*-position, *ca.* 2-fold at a *meta*-position, and *ca.* 10^6-fold at the *para*-position, in qualitative agreement with de la Mare and Vernon's conclusions. (At other acidities rather different partial rate factors would be obtained, and at very low values of $\log I$ the *meta*-position would apparently be deactivated.) However, if these figures are now used to calculate the reactivity of *p*-dimethoxybenzene, one obtains an answer which is about 10^3 times too small. Thus, the most significant conclusion to be drawn from the results is that the method of analysis is not self-consistent. A similar discrepancy cannot be detected in the bromination

[9] Satchell, *J.*, 1956, 3911.
[10] Okamoto and Brown, *J. Amer. Chem. Soc.*, 1957, **79**, 1909.

results, since the four rate constants available for the calculation provide just the requisite number of simultaneous equations to permit solution for the partial rate factors, but no more. However, the diphenylmethylation results indicate that any conclusions about substituent effects derived from the additivity principle must be treated with reserve.

The analysis can, of course, be made mathematically self-consistent by introducing one or more additional variables, *e.g.*, by assuming different values for the substituent effects exerted by vicinal methoxy-groups such as could be rationalised in terms of some kind of steric or electronic interaction between the neighbouring substituents. In view of the dependence of the relative reactivities on solvent acidity such further calculations do not seem justified. (A steric interpretation has, for instance, been put forward to explain the relative velocities of hydrolysis of 4- and 3 : 4-dimethoxybenzyl chloride.[11] These results suggest that, whereas a single 3-methoxy-group is expected to deactivate the side chain towards S_N1 substitution,[10] a 3-methoxy-group introduced into 4-methoxy-benzyl chloride activates it. Here again, therefore, additivity of substituent effects is not observed.)

In connection with the failure of the additivity principle in diphenylmethylation, it should be recalled that many years ago Holleman drew attention [12] to its lack of success (*i.e.*, breakdown of the " product rule ") when applied to the further substitution of disubstituted benzenes in those cases where " the substituents already present endeavour to bring the new group to different places."   The cases of *o*- and *p*-dimethoxybenzene fall into this category, and the failure of a treatment based on what is in effect the product rule would therefore perhaps not have been unexpected by Holleman.

KING'S COLLEGE, STRAND, LONDON, W.C.2.   [*Received, August 20th*, 1958.]

[11] N. H. P. Smith, Discussion remarks in " Steric Effects in Conjugated Systems," Butterworths, London, 1958.
[12] Holleman, " Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910, pp. 480—488; *Chem. Rev.*, 1924, **1**, 187.