600. *Aromatic Alkylation. Part IV.* The Velocity of Diphenylmethylation, and Indicator Measurements in Boron Trifluoride–Acetic Acid.*

By V. Gold and T. Riley.

Boron trifluoride is shown to have a powerful catalytic effect on the diphenylmethylation of anisole in acetic acid. Comparison of this catalysis with indicator measurements on methoxydiphenylmethanols (present in solution as acetates) shows that the catalytic function of boron trifluoride is solely concerned with inducing more extensive ionisation of the alkylating agent to form diphenylcarbonium ions in a rapidly established pre-equilibrium. The slow step of the alkylation is the reaction between anisole and diphenylcarbonium ions.

In earlier parts of the series it was shown that the reaction between diphenylmethanol and anisole in acetic acid, under the catalytic influence of either sulphuric acid [1] or zinc chloride–hydrogen chloride,[2] involves the rapid, reversible generation of diphenylcarbonium ions which subsequently attack anisole in the slow step. The similarity of reaction velocities [2] in media of the same concentration of carbonium ion, as shown by indicator measurements on methoxydiphenylmethanols, indicated that the common rôle of the catalyst in the two systems was the generation of acidity and hence the displacement of the equilibrium

$$Ph_2CH{\cdot}OAc + H^+ \rightleftharpoons Ph_2CH^+ + AcOH$$

to the right, and that zinc chloride therefore had no additional catalytic function.

In the present investigation the same reaction has been examined with boron trifluoride, in order to discover whether the same kind of mechanism applies when a more typical and powerful Friedel–Crafts catalyst is employed.

Experimental

Boron Trifluoride.—A commercial sample of the complex BF_3–$2CH_3{\cdot}CO_2H$ (technical grade) was purified by repeated distillation at atmospheric pressure with exclusion of moisture. The final product was a viscous colourless liquid, b. p. 144°. Solutions of boron trifluoride in acetic acid were prepared by dissolving measured quantities of the complex in acetic acid ("AnalaR," dried by azeotropic distillation with benzene; m. p. $>16{\cdot}7°$; water concentration, by Karl Fischer method, $<0{\cdot}03$M). The composition of the purified complex was determined gravimetrically by an adaptation of the method of Walters and Miller [3] by reaction of a measured quantity of complex (*ca.* 5 g.) with a known weight of dried sodium fluoride (*ca.* 3 g.) under reflux in the presence of purified acetic acid (2 hr.) followed by volatilisation of acetic acid and heating to constant weight at 250°. The solid residue consists of sodium borofluoride (which is stable up to 300°) and excess of sodium fluoride. The analyses were reproducible but indicated that different batches of complex contained varying amounts of boron trifluoride, and always *ca.* 10—20% less than corresponded to the composition BF_3–$2CH_3{\cdot}CO_2H$. Concentrations of boron trifluoride in catalyst solutions are based on the gravimetric analyses.

The preparation of other materials and general procedures were the same as in Part I.[1]

Discussion

The kinetic measurements on the reaction between diphenylmethanol and anisole in acetic acid under the influence of boron trifluoride fall into the pattern established in previous work with sulphuric acid [1] or zinc chloride [2] as catalysts. Diarylmethanols are again found to be rapidly esterified to the acetates and to be partly converted into diarylcarbonium ions, the concentration of which is conveniently measurable in the case of

---

* Part III, *J.*, 1959, 3134.

[1] Bethell and Gold, *J.*, 1958, 1905.

[2] Bethell and Gold, *J.*, 1958, 1930.

[3] Walters and Miller, *Ind. Eng. Chem. Anal. Ed.*, 1946, **18**, 658.

TABLE 1. *Ionisation of 4-methoxydiphenylmethanol* (ROH) *in acetic acid–boron trifluoride.*

Wavelength used for measurements = 4600 Å. ε_{R^+} = 59,800.

(*a*) No additional water.

BF_3 (M)	ε	log *I* *	BF_3 (M)	ε	log *I* *
1·003	87·98	−2·83	3·505	7263	−0·86
1·150	122·9	−2·69	4·025	12,950	−0·56
2·006	765·4	−1·89	4·307	17,080	−0·40
2·153	1044	−1·75	4·677	22,940	−0·21
2·305	1257	−1·67	5·309	36,590	+0·20
2·502	1708	−1·53	5·802	47,840	+0·60
2·875	2863	−1·30	6·015	50,420	+0·78
3·338	4364	−1·10	6·647	53,250	+0·98

(*b*) In presence of additional water.

BF_3 (M)	H_2O (M)	log *I* *	BF_3 (M)	H_2O (M)	log *I* *
ca. 3·5	0	−0·90	*ca.* 4·5	2·22	−0·51
,,	1·11	−0·80	*ca.* 6	0	+0·60
,,	2·22	−0·90	,,	0·28	+0·66
,,	3·33	−1·12	,,	1·11	+0·71
ca. 4·5	0	−0·51	,,	2·22	+0·60
ca. 4·5	1·11	−0·39			

* $I = [R^+]/([ROH]_{stoich} - [R^+])$.

TABLE 2. *Ionisation of 4,4′-dimethoxydiphenylmethanol* (R′OH) *in acetic acid–boron trifluoride.*

No additional water. Wavelength used for measurements: 5040 Å. ε_{R^+} = 121,200.

BF_3 (M)	0·090	0·225	0·316	0·452	0·456	0·563	0·789	0·911	1·150
ε	1175	6040	11,815	23,810	23,960	35,590	58,430	70,210	86,920
log *I* *	−5·17	−4·44	−4·13	−3·77	−3·78	−3·54	−3·19	−3·02	−2·76

* $\log I = \log \frac{[R'^+]}{[R'OH]_{stoich} - [R'^+]} - 3{\cdot}16$. (The constant 3·16 was found to give satisfactory coincidence between the data of Tables 1 and 2. In the system AcOH–H_2SO_4 [with 1·0M-water] the corresponding constant was 3·23.)

TABLE 3. *Velocity constants for diphenylmethylation of anisole at 25°.*

(*a*) [Anisole] = 4·13 × 10^{-2}M. $[Ph_2CH{\cdot}OH]_0$ = 4·17 × 10^{-3}M.

BF_3 (M)	10^4k_2 (l. mole^{-1} sec.$^{-1}$)	8 + log k_2	log *I* (interpolated)	log k_2 − log *I*
0·23	1·23	4·09	−4·43	0·52
0·46	5·67	4·75	−3·75	0·50
$0{\cdot}57_5$	9·19	4·96	−3·52	0·48
$0{\cdot}80_5$	22·7	5·36	−3·13	0·49
$0{\cdot}80_5$ *	$22{\cdot}7_5$	5·36	−3·13	0·49
$1{\cdot}03_5$	45·0	5·65	−2·82	0·47
1·16	69·1	5·84	−2·66	0·50
1·39	115·0	6·06	−2·40	0·46

* Diphenylmethyl acetate being used in place of diphenylmethanol.

(*b*) $[BF_3]$ = 1·16M. $[Ph_2CH{\cdot}OH]_0$ = 4·17 × 10^{-3}M.

10^2[Anisole] (M)	4·13	6·19	8·26
10^4k_2 (l. mole^{-1} sec.$^{-1}$)	69·1	65·4	63·1

TABLE 4. *Diphenylmethylation velocities of dimethoxybenzenes at 25°* (single experiments).

ArH	10^3[ArH] (M)	$10^4[Ph_2CH{\cdot}OH]_0$ (M)	$[BF_3]$ (M)	log *I* (interpolated)	10^3k_2
ortho	6·21	5·83	0·805	−3·14	14·9
meta	14·9	14·2	0·173	−4·69	37·2
para	13·1	12·6	0·805	−3·14	1·70

methoxydiphenylmethanols. The diphenylmethylation velocities are related to the ionisation of a methoxydiphenylmethanol according to the equation log k_2 = constant + log *I*, derived[1] on the assumption that diphenylcarbonium ions are formed in a rapid pre-equilibrium and consumed in a rate-determining reaction with anisole. The correlation is established by the good constancy of the values in the last column of Table 3(*a*).

Comparison with previous studies[1,2] shows that a medium which has a certain tendency to convert ionisable diarylmethyl compounds into diarylcarbonium ions (as determined by indicator measurements) will produce virtually the same velocity for the diphenylmethylation reaction irrespective of whether sulphuric acid, zinc chloride, or boron trifluoride is employed. This comparison is shown in the first row of Table 5, at the acidity corresponding to log $I = -3$. The agreement demonstrates the analogous function of all three catalysts in promoting reaction by increasing the equilibrium concentration of carbonium ions, and eliminates the need for ascribing any other rôle to these catalysts in acetic acid. Presumably this simple result implies that the associative forces between catalyst and acetic acid are stronger than those between catalyst and the reagents, which assume prominence in more inert solvents. It follows that a comparison of aralkylation velocities or indicator ionisation for the three catalysts affords a generally valid measure of their intrinsic ability to promote an ionisation of the form

$$\mathrm{ROAc} + \text{acid} \rightleftharpoons \mathrm{R}^{+} + \mathrm{AcOH} + \text{base} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Reaction (1) is to be considered in a thermodynamic sense, in that it is intended to show that the catalyst in acetic acid is, or generates, a strongly acidic species, and that an equilibrium is set up in this reaction between this acid and the aralkyl acetate. However, there is no proof that the formation of carbonium ions actually proceeds *via* this acid in every case. The acid–base system (which appears in this equation) is determined by the nature of the catalyst in a particular solution. The carbonium ion is likely to be present in ion pairs [4] (formed with the base) but, as the first row of Table 5 indicates, the nature of the gegenion appears to have no major effect on the reactivity of the diphenylcarbonium ion. The second row of Table 5 shows that different concentrations of catalyst are required to achieve the same extent of ionisation to diarylcarbonium ions. The efficacy of the three catalysts follows the order $BF_3 > H_2SO_4$ (in presence of 1M-water) $> ZnCl_2$. This sequence is not confined to the point log $I = -3$ but holds at all concentrations studied.

TABLE 5. *Diphenylmethylation velocities and catalyst concentrations for different catalysts at log* I $= -3$.

	H_2SO_4 (1M-water)	$ZnCl_2$	BF_3
$8 + \log k_2$	5·60 (ref. 5)	5·6 (ref. 2)	5·49 (this work)
Catalyst concn. (M)	1·17 (ref. 5)	2—3 (ref. 4)	0·93 (this work)

In anhydrous solution, sulphuric acid would have a catalytic effect more similar to that of boron trifluoride (on an equimolar basis). Whereas addition of water lowers the effectiveness of sulphuric acid [1] or of zinc chloride,[2] the ionising power of solutions of boron trifluoride in acetic acid is slightly increased by small amounts of water (up to 1M,) a solution containing two moles of water per litre being about as effective as an anhydrous system (Table 1*b*). For preparative purposes, the rigorous exclusion of moisture from boron trifluoride solutions in acetic acid therefore appears to be superfluous and in fact slightly disadvantageous. It is probable that this behaviour of water may also be connected with the preferred use of this catalyst for the preparative alkylation of alcohols.

An approximate comparison of the reactivities of the isomeric dimethoxybenzenes and anisole agrees satisfactorily with the more detailed study with sulphuric acid as catalyst [5] (Table 4).

It has previously been pointed out [4] that the ionisation of diarylmethyl acetates is largely but not entirely controlled by the Brønsted acidity of the medium. The most obvious difference between the ionisation of a diphenylmethyl acetate indicator and that of a Brønsted base is the presence of acetic acid among the products of ionisation of the former compound [see equation (1)]. The above sequence of catalyst efficiency is therefore not necessarily also a sequence of Brønsted acidities of solutions of equal catalyst concentration. Conversely, the observed Brønsted acidity of solutions of stannic chloride in acetic acid,[6] for example, does not necessarily establish the relative position of stannic

---

[4] Bethell, Gold, and Satchell, *J.*, 1958, 1918.
[5] Bethell, Gold, and Riley, *J.*, 1959, 3134.
[6] Satchell, *J.*, 1958, 3910.

chloride as a catalyst. This conclusion is confirmed by a comparison of the ionising powers of anhydrous solutions of sulphuric acid and of zinc chloride in acetic acid, the results being taken from published indicator measurements.[1,4,7] It can be shown from these that solutions of the two catalysts, of such concentrations that they are equally effective regarding the ionisation of 4,4'-dimethoxydiphenylmethyl acetate, will differ markedly in their acidity towards 4-chloro-2-nitroaniline, sulphuric acid being much more effective in this respect. (log $[BH^+]/[B]$ is greater by about 1·35 compared with the zinc chloride solution.) It therefore follows that zinc chloride owes its relatively high activity as an aralkylation catalyst (or its ionising power towards diarylmethyl acetate indicators) in acetic acid to some additional factor besides the Brønsted acidity of its solution. It seems probable that this effect consists of a lowering of the activity of acetic acid by zinc chloride by virtue of a high affinity of the two compounds for each other. A similar effect is likely to contribute towards the high catalytic activity of boron trifluoride. The strong interaction of acetic acid and boron trifluoride is well established and manifests itself, for example, in the existence of the compound $BF_3,2CH_3{\cdot}CO_2H$.

We thank Dr. D. Bethell for interesting discussions.

KING'S COLLEGE, STRAND, LONDON, W.C.2.

[*Received, February 1st*, 1960.]

[7] Gold and Hawes, *J.*, 1951, 2102.