920. *The Activation of Carbon–Carbon Double Bonds by Cationic Catalysts. Part VI.* Effect of Substituents on the Dimerisation of 1 : 1-Diarylethylenes catalysed by Trichoroacetic Acid.*

By ALWYN G. EVANS, PETER M. S. JONES, and J. H. THOMAS.

The kinetics and equilibria for the dimerisation of 1-*p*-bromophenyl-1-phenylethylene catalysed by trichloroacetic acid in benzene have been studied dilatometrically, thus extending our previous work.[1a, 1b] The olefins 1 : 1-di-*o*-tolylethylene and 1 : 1-di-*o*-methoxyphenylethylene do not dimerise in trichloroacetic acid–benzene solutions, and we suggest this to be due to steric blocking by the bulky *ortho*-groups. The effect of *para*-substituents on the thermodynamic constants for the dimerisation of 1 : 1-diarylethylenes by trichloroacetic acid in benzene is discussed.

EXPERIMENTAL

Materials.—Trichloroacetic acid and benzene were purified as before.[1a]

1-p-*Bromophenyl-1-phenylethylene.* 1-*p*-Bromophenyl-1-phenylethanol was prepared by the action of *p*-bromoacetophenone on phenylmagnesium bromide in dry ether. It was extracted and steam-distilled to remove volatile impurities, and the residual alcohol distilled twice under reduced pressure to dehydrate it. The middle fraction of olefin (b. p. 145—150°/1—2 mm.; lit.[2] b. p. 200°/19 mm.) [Found: M (cryoscopic in benzene), 247·2. Calc. for $C_{14}H_{11}Br$: M, 259. Purity at least 95%] was redistilled under high vacuum in a one-piece glass apparatus,[1a, 1b] the colourless oil being kept under vacuum until required.

1 : 3-Di-*p*-bromophenyl-1 : 3-diphenylbut-1-ene was prepared from 1-*p*-bromophenyl-1-phenylethylene by the action of either concentrated sulphuric acid in acetic acid or trichloro-acetic acid in benzene, as for the dimer of 1 : 1-diphenylethylene.[1a] The product was a viscous oil which, unlike the monomer, was insoluble in acetic acid, with which it was washed. It was distilled under high vacuum in a one-piece glass apparatus, the product setting to a glass [Found, M 510 (for both methods of preparation). Calc. for $C_{28}H_{22}Br_2$: M, 518]. By analogy with the olefins studied previously [1a, 1b] we assume this to be the but-1-ene dimer, and not the

* Part V, A. G. Evans and J. Lewis, *J.*, 1957, 2975.

[1] (a) Part I, A. G. Evans, N. Jones, and J. H. Thomas, *J.*, 1955, 1824; (b) A. G. Evans, P. M. S. Jones, and J. H. Thomas, *J.*, 1956, 2757.

[2] Stenner and Simon, *Ber.*, 1904, **37**, 4168.

indane (see below). This dimer can possess both optical and geometrical isomerism, and may be a mixture of 4 isomers, which could account for its remaining as an oil.

1 : 1-*Di-o-tolylethylene*. 1 : 1-Di-*o*-tolylethanol, from ethyl acetate and *o*-tolylmagnesium bromide, was dehydrated and the 1 : 1-di-*o*-tolylethylene purified as for 1 : 1-di-*p*-tolylethylene [1b] (m. p. 40—41°; lit.,[3] m. p. 42·6°).
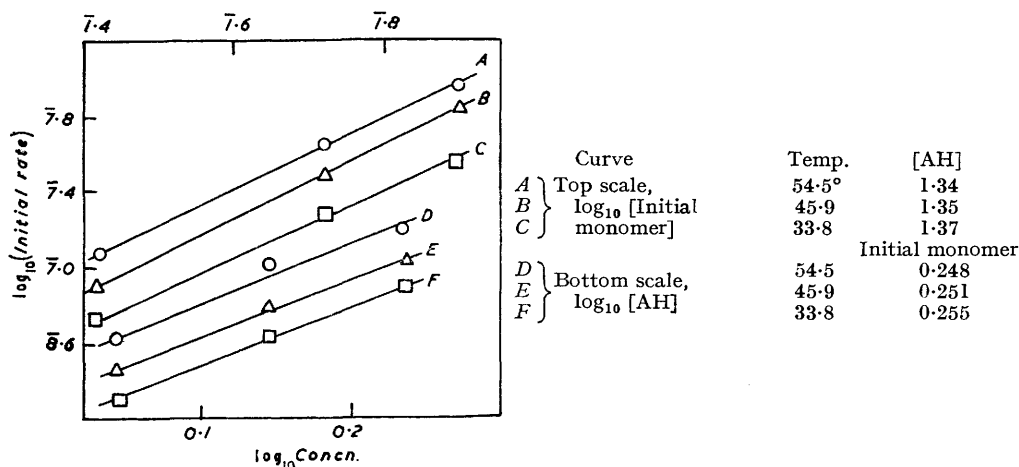
1 : 1-*Di-o-methoxyphenylethylene*. 1 : 1-Di-*o*-methoxyphenylethanol, from ethyl acetate and *o*-methoxyphenylmagnesium bromide, was recrystallised several times from light petroleum (b. p. 60—80°). The pure alcohol, m. p. 124—125° (lit.,[4] m. p. 125°), did not lose water on vacuum distillation, so we used Bergman and Bondi's method [4] (sulphuric–acetic acid). The crude olefin was recrystallised seven times from absolute ethanol–benzene, the final product having m. p. 90—91° (lit.,[4] m. p. 90°) [Found: M (cryoscopic in benzene), 238. Calc. for $C_{16}H_{16}O_2$: M, 240].

Technique.—The procedure for preparing the olefin–acid–benzene solutions, and following their volume change dilatometrically, was identical with that used in Part I.[1a]

RESULTS

1. *The* 1-p-*Bromophenyl-*1-*phenylethylene–Trichloroacetic acid–Benzene System.*—(a) *Products.* Solutions of the olefin in benzene do not change in volume, but in the presence of trichloroacetic acid the solutions become pale green and their volumes decrease with time to a

FIG. 1. *Orders in reagents for initial rate of dimerisation of* 1-p-*bromophenyl-*1-*phenylethylene* The initial rate is expressed in terms of moles of dimer formed or lost per l. per sec. Concns. in moles l.$^{-1}$ at 19°.

Curve		Temp.	[AH]
A	Top scale,	54·5°	1·34
B	$\log_{10}$ [Initial	45·9	1·35
C	monomer]	33·8	1·37
			Initial monomer
D	Bottom scale,	54·5	0·248
E	$\log_{10}$ [AH]	45·9	0·251
F		33·8	0·255

steady value. Density measurements on separate solutions of the monomer and the high vacuum-distilled dimer oil in benzene (see Part I [1a]) gave the following volume changes for the complete conversion of 1 mole of monomer into 0·5 mole of dimer in 1 l. of solution: 11·87 ml. at 33·8°, 11·85 ml. at 45·9°, and 12·60 ml. at 54·6°. These values agree closely with those for the dimerisation of 1 : 1-diphenylethylene,[1a] 1 : 1-di-*p*-tolylethylene,[1b] and 1-*p*-methoxyphenyl-1-phenylethylene,[1b] all in benzene, and this helps to confirm the identity of the dimer oil as 1 : 3-di-*p*-bromophenyl-1 : 3-diphenylethylene.

The quantity of trichloroacetic acid titratable with sodium hydroxide after reaction is equal within experimental error ($\pm 2\%$) to the original.

The benzene solutions, after removal of the acid and evaporation in a high vacuum, deposited a viscous oil which was washed several times with acetic acid to remove traces of monomer, and dried under vacuum. Its weight agreed to within 5% with that of the dimer expected to be present from the volume change.

[3] Coops, Hoijtink, Kramer, and Faber, *Rec. Trav. chim.*, 1953, **72**, 765.
[4] Bergman and Bondi, *Ber.*, 1931, **64**, 1455.

(*b*) *Rate constants.* The initial rates of dimerisation were measured from volume–time plots as described in Part I. The acid orders were found from the slopes of plots of $\log_{10}$ (Initial rate) against $\log_{10}$ [Acid] at constant initial olefin concentrations {see Fig. 1, curves *D*, *E*, and *F* (where [AH] is the concentration of trichloroacetic acid *dimer*}: and the monomer orders similarly from plots of $\log_{10}$ (Initial rate) against $\log_{10}$ [Initial monomer] at constant [AH] (see Fig. 1, curves *A*, *B*, and *C*). The acid and olefin orders thus found are given in Table 1; the

TABLE 1. *Reagent orders, initial rate constants, and energy and entropy of activation*
for the dimerisation of 1-*p*-*bromophenyl*-1-*phenylethylene.*

Temp.	Acid order	Olefin order	$10^7 k_f$ (mole^{-4} l.^{4} sec.$^{-1}$)	E_f (kcal. mole^{-1})	A_f (mole^{-4} l.^{4} sec.$^{-1}$)	K (mole^{-1} l.)
33·8°	3·1	1·95	2·6		24·9	33·8 ± 2
45·9	3·2	2·0	5·4	11·2 ± 0·5	25·8	17·1 ± 2
54·5	3·1	2·0	7·4		22·1	8·1 ± 2

mean values are 3·1 ± 0·2 and 2·0 ± 0·2 respectively. Thus the initial rate of dimerisation is $k_f[M]^2[AH]^3$, where k_f is the (forward) rate constant and [M] the initial monomer concentration. The mean values of k_f thus found are given in Table 1.
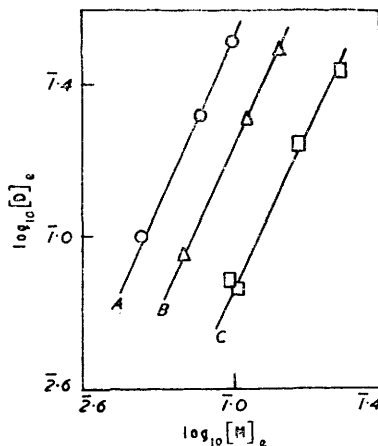

FIG. 2. *Relationship between* [D]$_e$ *and* [M]$_e$ *for* 1-*p*-*bromophenyl*-1-*phenylethylene.*

Curves *A*, *B*, and *C* are for solutions at 33·8°, 45·9°, and 54·6° respectively.

The mean activation energy for the dimerisation, E_f, found from the dependence of log k_f on $1/T$, is given in Table 1, together with values of the temperature-independent factor, A_f. In Table 2 these results are expressed as the free energy of activation, $\Delta G_f{}^\ddagger$, the enthalpy of activation $\Delta H_f{}^\ddagger$ (= $E_f - RT$), and the entropy of activation $\Delta S_f{}^\ddagger$.

TABLE 2. *Thermodynamic constants for the dimerisation of* R·C$_6$H$_4$·C(C$_6$H$_4$R′):CH$_2$.

Rate-determining step	R	R′	$+\Delta G^\circ$ (kcal. mole^{-1})	$+\Delta H^\circ$ (kcal. mole^{-1})	$+\Delta S^\circ$ (cal. deg.$^{-1}$ mole^{-1})	$+\Delta G_f{}^\ddagger$ ($\Delta G_{1a}{}^\circ + \Delta G_{2a}{}^\ddagger$) (kcal. mole^{-1})	$+\Delta H_f{}^\ddagger$ ($\Delta H_{1a}{}^\circ + \Delta H_{2a}{}^\ddagger$) (kcal. mole^{-1})	$+\Delta S_f{}^\ddagger$ ($\Delta S_{1a}{}^\circ + \Delta S_{2a}{}^\ddagger$) (cal. deg.$^{-1}$ mole^{-1})
Reaction 2a	*p*-Br	H	−2·16	−14·0	−38·6	27·2	10·6	−54
	H	H	−1·69	−10·1	−27·4	26·0	8·5	−57
	p-Me	*p*-Me	−1·41	−8·4	−22·8	22·6	6·0	−54
	p-MeO	H	−1·32	−6·0	−15·3	22·1	4·6	−57
						$\Delta G_f{}^\ddagger$ ($\Delta G_{1a}{}^\ddagger$)	$\Delta H_f{}^\ddagger$ ($\Delta H_{1a}{}^\ddagger$)	$\Delta S_f{}^\ddagger$ ($\Delta S_{1a}{}^\ddagger$)
Reaction 1a	*p*-MeO	*p*-MeO	−0·93	−3·3	−7·8	18·4	8·8	−31·3

Values of ΔG°, $\Delta G_f{}^\ddagger$, ΔS°, and $\Delta S_f{}^\ddagger$ are quoted for the standard state 1 mole l.$^{-1}$ at 33·8° c.

(*c*) *Equilibrium constants.* The equilibrium concentrations of monomer, [M]$_e$, and dimer, [D]$_e$, were found (as in Part I [1a]) from the equilibrium volume changes. The latter were independent of the acid concentration, showing that the orders in acid for the forward and the reverse reaction were the same. Plots of $\log_{10}$ [D]$_e$ against $\log_{10}$ [M]$_e$ (Fig. 2) are all of slope 2 ± 0·02, showing that the ratio of monomer order to dimer order is 2 over this temperature
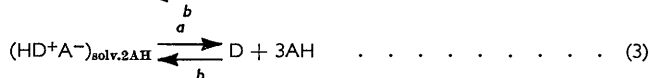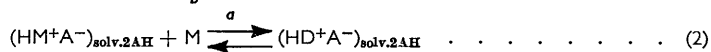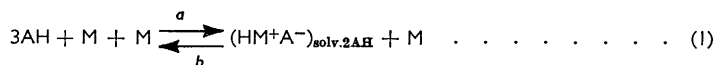
range. The mean equilibrium constants $K = [D]_e/[M]_e^2$ are given in Table 1. The exothermicity of the dimerisation $(-\Delta H°)$ was found from the slope of a plot of $\log_{10}$ (mean K) against $1/T$ to be $14·0 \pm 0·7$ kcal. mole^{-1}. Table 2 also gives the free-energy change, $\Delta G°$ $(= -RT \ln K)$, and the entropy change, $\Delta S°$, accompanying the dimerisation at $33·8°$.

2. *Attempted Dimerisation of* 1 : 1-*Di-o-tolylethylene.*—The volume of a solution (33·2 ml.) of 1 : 1-di-*o*-tolylethylene (0·115 mole l.$^{-1}$) and trichloroacetic acid (0·346 mole l.$^{-1}$) in benzene did not change at 45·9° during several months, after which all ($\pm 2\%$) of the acid was recovered. All the olefin was recovered as described previously and, after one crystallisation, had the m. p. of the monomer. The solution became intensely blue during the time of observation ($\lambda_{max.} = 598$ mμ).

3. *Attempted Dimerisation of* 1 : 1-*Di-o-methoxyphenylethylene.*—The volume (32·7 ml.) of a solution of 1 : 1-di-*o*-methoxyphenylethylene (0·229 mole l.$^{-1}$) and trichloroacetic acid (0·101 mole l.$^{-1}$) in benzene did not change during 3 months at 45·9°, after which monomer and acid were completely recovered.

DISCUSSION

1. *Dimerisation of* 1-p-*Bromophenyl-1-phenylethylene.*—The order in acid, 3, and in olefin, 2, for the rate of dimerisation, and the dependence of the position of equilibrium on total olefin concentration, show that this olefin reacts by the same mechanism as does 1 : 1-diphenylethylene: [1a, 1b]

$$3AH + M + M \underset{b}{\overset{a}{\rightleftharpoons}} (HM^+A^-)_{solv.2AH} + M \quad \ldots \ldots \ldots \quad (1)$$

$$(HM^+A^-)_{solv.2AH} + M \underset{b}{\overset{a}{\rightleftharpoons}} (HD^+A^-)_{solv.2AH} \quad \ldots \ldots \ldots \quad (2)$$

$$(HD^+A^-)_{solv.2AH} \underset{b}{\overset{a}{\rightleftharpoons}} D + 3AH \quad \ldots \ldots \ldots \quad (3)$$

The rate-controlling step of the dimerisation is reaction 2a, *i.e.*, $k_f = K_1 k_{2a}$, $\Delta G_f^{\ddagger} = \Delta G_{1a}° + \Delta G_{2a}^{\ddagger}$, $\Delta H_f^{\ddagger} = \Delta H_{1a}° + \Delta H_{2a}^{\ddagger}$, and $\Delta S_f^{\ddagger} = \Delta S_{1a}° + \Delta S_{2a}^{\ddagger}$. In Table 2 we give our results for the dimerisation of 1-*p*-bromophenyl-1-phenylethylene together with our previous results for various *para*-substituted 1 : 1-diphenylethylenes.[1a, 1b] These results may be discussed as follows.

2. *Effect of* para-*Substituents on the Dimerisation Equilibrium.*—(a) *Energy considerations.* Table 2 shows that an increase in the electron-releasing power of the *para*-substituents down the series 1-*p*-Br, unsubstituted, 1 : 1-di-*p*-CH$_3$, 1-*p*-MeO, 1 : 1-di-*p*-MeO decreases the exothermicity $(-\Delta H°)$ of the dimerisation. That is, an electron-releasing *para*-group stabilises the final state of reaction 3, D + 3AH, less than it stabilises the initial state of reaction 1, M + M + 3AH. Since the change from M + M + 3AH to D + 3AH, involves the loss of a double bond, it appears that the olefin double bond (which is conjugated with two benzene rings) is stabilised by the presence of an electron-releasing *para*-substituent. The more the olefin double bond is stabilised, the more energetically favourable is M + M + 3AH which involves two olefins than D + 3AH which involves only one (see Fig. 3).

(b) *Entropy considerations.* An increase in the electron-releasing power of the *para*-substituent causes $\Delta S°$, the entropy change from M + M + 3AH to D + 3AH, to become more positive, partly offsetting the decrease in exothermicity, and thus making the decrease in K, and the positive increase in $\Delta G°$, small.

3. *Effect of* para-*Substituents on those Dimerisation Reactions for which Reaction 2a is Rate-determining.*—(a) *Energy considerations.* Table 2 shows that here an increase in the electron-releasing power of the *para*-substituents decreases the activation enthalpy for the forward reaction, $\Delta H_f^{\ddagger}(= E_f - RT)$. That is, an electron-releasing *para*-substituent stabilises the transition state of reaction 2a more than it stabilises M + M + 3AH (see Fig. 3). This may be because, for the reaction between two olefins containing conjugated

double bonds there is resonance energy in the transition state; [5] the π-electrons are more mobile in the transition state because there are more carbon centres available for them. A similar increase in electron mobility is possible in the transition state of reaction $2a$ where a monomer molecule and a monomer ion are pushed close together (I) and the 26 electrons can move in the field of 27 nuclei (II).

(b) *Entropy considerations.* A change in the electron-releasing power of the *para*-substituent has no effect on the entropy of activation, $\Delta S_f^{\ddagger}$, that is, on the entropy change from $M + M + 3AH$ to the transition state of reaction $2a$. This is different from the

FIG. 3. *Diagram of the reaction paths for dimerisation of* (●) 1 : 1-*diphenylethylene and* ■ 1-p-*methoxyphenyl*-1-*phenylethylene.*
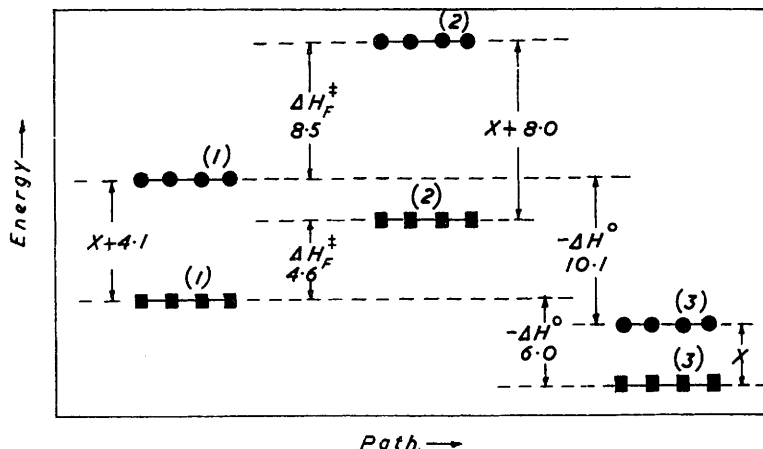
(1) Initial state of reaction $1a$, $M + M + 3AH$.
(2) Transition state of reaction 2.
(3) Final state of reaction 3, $D + 3AH$.

X is an arbitrary value for the stabilisation of the dimer double bond due to the introduction of a p-MeO substituent.

effect of these groups on the total entropy change ΔS° from $M + M + 3AH$ to $D + 3AH$ (section 2b). Our results show, therefore, that the effect of electron-releasing groups on
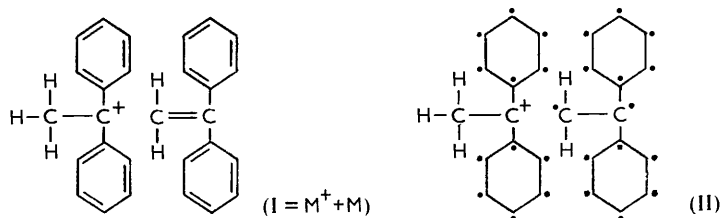
the entropy of the transition state of reaction $2a$ is different from their effect on the entropy of $D + 3AH$. We cannot yet interpret this difference.

4. *Dimerisation when Reaction 1a is Rate-determining.*—As more powerful electron-releasing *para*-groups are introduced into the olefin, at one point the mechanism of dimerisation changes. The order in monomer changes from 2 to 1, that is, the rate-determining step changes from reaction $2a$ to reaction $1a$. This occurs between 1-*p*-methoxyphenyl-1-phenylethylene and 1 : 1-di-*p*-methoxyphenylethylene [1b] (Table 2). This means that the stabilisation by electron-releasing *para*-groups is greater for the

[5] M. G. Evans and Warhurst, *Trans. Faraday Soc.*, 1938, **34**, 614; M. G. Evans, *Trans. Faraday Soc.*, 1939, **35**, 832.

transition state of reaction 2a, in which a monomer molecule and a monomer ion are pushed close together, than for that of reaction 1a in which the two olefins are, as yet, independent. Introduction of more powerful electron-releasing *para*-groups not only reduces the energy of the transition state of reaction 2a faster than that of the initial state of reaction 1a, but also faster than that of the transition state of reaction 1a. Thus, eventually, the transition state of reaction 1a lies higher in energy than that of reaction 2a, and the rate-determining step becomes reaction 1a instead of reaction 2a. This change does not occur just when the energy of the transition state of reaction 2a falls below that of reaction 1a, but when the free energy of the former falls below that of the latter. The entropy of the transition state of reaction 1a is more positive than that of the transition state of reaction 2a, since in the latter case two molecules of monomer are specially oriented with respect to each other, whereas in the former the two molecules of monomer have not yet been pushed into each other. Thus, at the point where the change occurs (Table 2) the activation enthalpy, $\Delta H_f^{\ddagger}$, increases appreciably, although the free energy of activation falls.
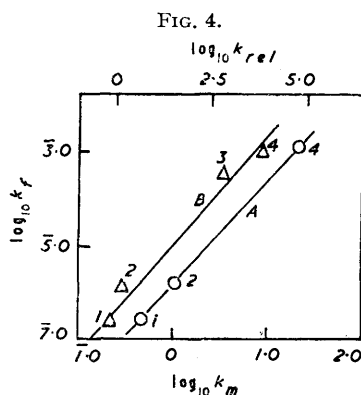

FIG. 4.

FIG. 5.

FIG. 4. *Relationships involving k_f. Plots of its logarithm at 33·8° against (A)* $\log_{10}$ *(k_m = relative monomer reactivity, that of styrene being taken as unity [5]) and (B)* $\log_{10}$ *(k_{rel} = relative rate constant of ethanolysis of substituted diphenylmethyl chloride at 25°, that of diphenylmethyl chloride being taken as unity [6]).*

Number	1	2	3	4
Substituent	*p*-Br	Unsubstituted	Di-*p*-Me	*p*-MeO

FIG. 5. *Relationships between the thermodynamic constants.*

A, $-\Delta G°$ (kcal. mole⁻¹) against $-\Delta H°$ (kcal. mole⁻¹); *B,* $\Delta H_f^{\ddagger}$ (kcal. mole⁻¹) against $-\Delta H°$ (kcal. mole⁻¹) (when reaction 2a is rate-determining); *C,* $-pK_{R^+}$ against $-\Delta G°$ (kcal. mole⁻¹).

| Number	1	2	3	4	5
Substituent	*p*-Br	Unsubstituted	Di-*p*-Me	*p*-MeO	Di-*p*-MeO

5. *Relation to Other Reactions.*—The sequence which we obtain for the effect of *para*-substituents on the rate of dimerisation is the same as that obtained (a) for the relative reactivities of substituted styrenes,[6] and (b) for the relative rates of solvolysis of substituted diphenylmethyl chlorides [7] (see Fig. 4). As regards the equilibrium 2M ⇌ D, the plots of $-\Delta G°$ against $-\Delta H°$, and of $-\Delta H°$ against $\Delta H_f^{\ddagger}$, are straight lines (Fig. 5). $\Delta G°$ also varies linearly with pK_{R^+} for substituted diphenylmethyl alcohols in sulphuric acid [8] (Fig. 5).

[6] Pepper, *Quart. Rev.*, 1954, **8**, 89.
[7] Altscher, Baltzly, and Blackman, *J. Amer. Chem. Soc.*, 1952, **74**, 3649.
[8] Deno, Janizelski, and Schreiskeine, *J. Org. Chem.*, 1954, **19**, 155; *J. Amer. Chem. Soc.*, 1955, **77**, 3044.
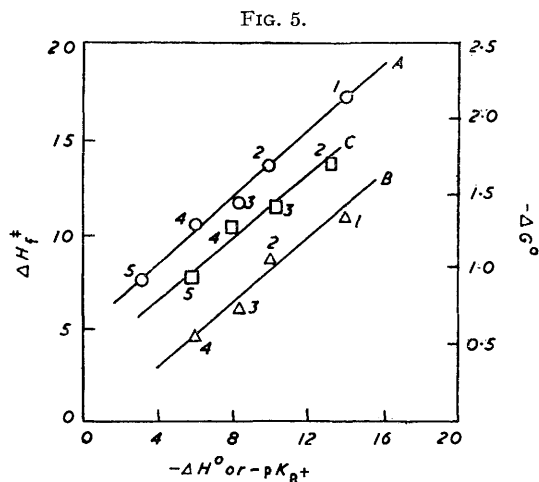
6. *Effect of* ortho-*Substituents.*—The fact that neither 1 : 1-di-*o*-tolylethylene nor 1 : 1-di-*o*-methoxyphenylethylene dimerises in benzene–trichloroacetic acid, whereas all the *para*-substituted 1 : 1-diphenylethylenes [1b, 8] and the *meta–para*-disubstituted olefins [9, 10] dimerise readily, is, we believe, due to steric hindrance. The dimer of 1 : 1-diphenylethylene, 1 : 1 : 3 : 3-tetraphenylbut-1-ene is so highly strained that further addition of monomer is not possible. *para*-Substituents will not affect the steric strain in the dimer since they point away from the cramped parts of the molecule, but *ortho*-substituents will increase the steric strain in the dimer, and we believe that in the 1 : 1-di-*o*-methyl- and 1 : 1-di-*o*-methoxy-compounds this strain prevents the formation of the dimer.

UNIVERSITY COLLEGE,
    CATHAYS PARK, CARDIFF.   [*Received, May 14th,* 1958.]

[9] Schmitz-Dumont, Thömke, and Diebold, *Ber.,* 1937, **70**, 175.
[10] Wolf, *J. Amer. Chem. Soc.,* 1953, **75**. 2673.