Free Radical Reactions in Solution. Part 6.[1] Thermal Decomposition of Substituted Dibenzyl Mercurials in Solution. An Improved σ· Scale [2]

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The kinetics of the decomposition of ten substituted dibenzylmercury compounds in solution have been determined in the temperature range 126—156°. From the relative rates at 140.2°, a new scale of substituent constants σ· applicable to free radical reactions is derived. E.s.r. spectra for seven substituted benzyl radicals show a reasonable correlation of $a_{\alpha\text{-CH}_2}$ with σ·.

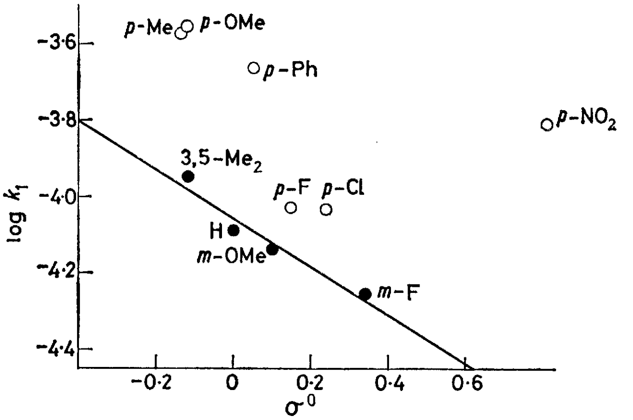
SUBSTITUENT effects on free radical reactions are influenced by polar, resonance, and steric factors. Numerous efforts have been made to disentangle these factors and several scales of Hammett-type substituent constants have been proposed for radical systems.† Difficulties in establishing a suitable model reaction system include the separation of polar and resonance effects, side reactions especially those involving radical attack at substituent groups rather than at the desired reaction centre, and the magnitude of the kinetic effect involved. Our model reaction, the thermal decomposition of substituted dibenzylmercury compounds in solution offers a number of advantages over previously studied systems.

RESULTS AND DISCUSSION

Dibenzylmercury decomposes on heating in solution into mercury and two benzyl radicals; the rate-determining step appears to be the homolysis of one of the carbon–mercury bonds.[4] We reasoned that the decomposition of substituted dibenzylmercury compounds would form a suitable model system for measuring substituent effects on a radical reaction for several reasons. Polar effects would be anticipated to be small, since in the transition state one of the C–Hg bonds will be almost completely broken, corresponding closely to the formation of a free benzyl radical. As a free benzyl radical is produced in the rate-determining step, the full stabilizing effect of a *para*-substituent should be felt, giving rise to larger kinetic effects than would be given for example in transfer or addition reactions. Since the reaction studied is the first step in a radical decomposition, and the products are the relatively unreactive substituted benzyl radicals, we hoped that by working in dilute solution, problems of radical attack on the original substrate mercurial would be minimized.

Ten symmetrically disubstituted dibenzylmercury compounds were used: the unsubstituted compound, three compounds with *meta*-substituents, and six with *para*-substituents. All but one were made by the reaction of the corresponding benzyl Grignard reagent with mercury(II) chloride. Substituents such as nitro or acetyl are of considerable interest with regard to radical stabilization but are incompatible with Grignard reagents. We attempted to protect the carbonyl group in the benzoyl or acetyl derivatives by conversion into the 1,3-dioxolanyl group, but were unable to convert the protected benzyl halides into the dibenzylmercury derivatives by the Grignard route. We were however able to prepare bis(*p*-nitrobenzyl)mercury by photolysis of *p*-nitrobenzyl bromide in acetone solution in the presence of mercury to give *p*-nitrobenzylmercury(II) bromide,[5] which was then symmetrized by potassium iodide to bis(*p*-nitrobenzyl)mercury.

Decompositions were carried out on *ca.* 1—5 × 10^{-3}M solutions in octane (except as noted) in individual degassed ampoules, and the reactions were followed by g.l.c. of the bibenzyl formed, or h.p.l.c. or u.v. analysis of the remaining mercurial. No deviations from first order were noted, and the results are summarized in Table 1.



Plot of log k_1 at 140.2° for substituted dibenzylmercury compounds against σ°: ●, *meta*-substituted compounds; ○, *para*-substituted compounds

In view of the relatively small spread of activation energies and the uncertainty involved, we base our discussion of substituent effects on the logarithms of rate constants obtained at 140.2°, *i.e.* on free energy differences, and in so doing follow the normal pattern used by workers on both homolytic and heterolytic systems. In view of the small spread in activation energies, there would have been little difference in relative rates if a different temperature had been chosen.

The first order rate constants obtained at 140.2° gave, as expected, no good overall correlation with any of the

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† See ref. 3 for a recent investigation, and papers cited therein.

polar substituent constants σ, σ^+, or σ^-. Plots of log k_1 against σ or σ° (Figure) show however that the *meta*-substituents lie close to a line of slope −0.6, indicating that there is in fact a significant polar influence on the reaction. We interpret this as being due to the destruction of the partial negative charge on the benzylic carbon atom on going from the ground state of the molecule to the transition state in reaction (1).

TABLE 1

Kinetics[a] of decomposition of $(XC_6H_4CH_2)_2Hg$ in octane [reaction (1)]

X	$\log_{10}(A/s^{-1})$	E/kcal mol^{-1}	$10^5k_{140.2^\circ}$	$\sigma^\bullet$
H	14.38 ± 0.20	34.91 ± 0.38	8.1	0
m-F	14.38 ± 0.16	35.24 ± 0.31	5.6	
m-OMe	14.39 ± 0.62	35.07 ± 1.19	7.3	
3,5-Me_2 [b]			11.3	
p-F	13.86 ± 0.11	33.83 ± 0.20	9.4	0.12
p-Cl			9.3	0.18
p-Me	15.78 ± 0.16	36.63 ± 0.31	26.6	0.39
p-OMe	14.90 ± 0.68	34.94 ± 1.28	27.8	0.42
p-Ph	15.53 ± 0.34	36.31 ± 0.64	21.7	0.42
p-NO_2 [c]	15.37 ± 0.31	36.28 ± 0.59	15.6	0.76

[a] Rate constants at 14.02° are the means of at least two determinations, and are either as measured at this temperature or corrected from values obtained at temperatures within ±0.2° of this value, using the activation energy for the particular compound if available, otherwise using $E_{\text{dibenzylmercury}}$. [b] Iso-octane solution. [c] Dibenzyl ether solution (compound insufficiently soluble in octane). A single check run of dibenzylmercury itself in dibenzyl ether gave k_1 8.5 × 10^{-5} s^{-1} indicating that this solvent change had little effect, although a value of 4.8 × 10^{-5} s^{-1} can be calculated from the data in ref. 4 for the decomposition of dibenzylmercury in toluene at 140.2°.

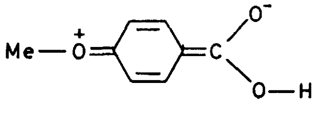
$$X_6H_4\overset{\delta-}{C}H_2\text{-}\overset{\delta+}{Hg}\text{-}CH_2C_6H_4X \longrightarrow XC_6H_4CH_2^{\bullet} + {}^{\bullet}Hg\text{-}CH_2C_6H_4X \quad (1)$$

$$^{\bullet}Hg\text{-}CH_2C_6H_4X \longrightarrow Hg + {}^{\bullet}CH_2C_6H_4X \quad (2)$$

$$2\ XC_6H_4CH_2^{\bullet} \longrightarrow XC_6H_4CH_2\text{-}CH_2C_6H_4X \quad (3)$$

The points for all the *para*-substituents lie above the *meta*-line. Since both electron-withdrawing and electron-releasing substituents are involved, this cannot be explained by operation of a polar factor and we ascribe the enhancement in rate to the stabilization of the benzyl radical produced in the reaction by conjugating groups, whether electron withdrawing or releasing.

Before we can ascribe any quantitative values to these deviations, we must consider what set of σ values is appropriate to take account of the polar influence, which we postulate arises from stabilization of a partial negative charge on the benzylic carbon of the original mercurial. For substituents such as *p*-halogen or *p*-methoxy the σ scale based on the ionization of substituted benzoic acids includes stabilizing contributions of type (1) which



(1)

have no counterpart in our system, so the σ° scale which is defined on the basis of reactions (such as the ionization of phenylacetic acids) where these conjugating effects cannot take place thus appears to be the appropriate scale to determine the polar effects in our system. (For the substituents we use, σ° differs significantly from σ only for *para*-fluoro and -methoxy.) The decision to use σ° rather than σ receives some support from the ^{13}C n.m.r. spectra of the mercurials. $J(^{13}C_\alpha-^{199}Hg)$ should reflect electronic influences from substituents on the benzene ring, with electron-withdrawing groups increasing the coupling constant (*cf.* ref 6). Plots of $J(^{13}C_\alpha-^{199}Hg)$ against σ or σ° showed much scatter, but the correlation with σ° (r 0.82) is somewhat better than that with σ (r 0.73), suggesting that the substituent effects on the ground state of the mercurial are better correlated by σ°.

We therefore construct a plot of log k_1 against σ° and draw the regression line through the points for the *meta*-substituted compounds and dibenzylmercury itself to establish the polar influence on the reaction: a slope corresponding to ρ° −0.63 is obtained.* The points for all the *para*-substituted compounds lie above the line: we attribute the faster rate of decomposition of these compounds to the stabilizing effect of substituents at the *para*-position of the benzyl radical produced. (Substituent effects on the $HgCH_2C_6H_4X$ radical are likely to be insignificant because of the insulating effect of the CH_2 group.) Radical stabilization constants $\sigma^\bullet$ are defined for the different *para*-substituents as the difference between log k_1 at 140.2° and the appropriate point on the regression line obtained for the *meta*-compounds [equation (4)].

$$\log(k_{\text{subst}}/k_{\text{H}}) = \rho^\circ\sigma^\circ + \sigma^\bullet \quad (4)$$

These $\sigma^\bullet$ values, listed in Table 1, are all positive, in line with the accepted view that conjugating substituents, whether electron withdrawing or releasing, can all stabilize free radicals. The magnitudes are however not in line with polar influences: thus methoxy and halogen substituents are less effective in stabilizing a radical than a cation, by comparison with the methyl group. Delocalization of the free electron onto a fluorine substituent for example would involve charge separation, ex-

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* σ° Values were taken from ref. 7.

pansion of the octet, or use of an antibonding orbital, which would be unfavourable. Delocalization of a positive charge, which involves one less electron in the system, is therefore energetically more favourable, which explains the lesser effectiveness of halogen and alkoxy-groups in stabilizing a radical. The nitro-group is by far the most effective stabilizing substituent of those we have studied: delocalization of the electron onto either oxygen atom of the group can take place.

We suggest that our scale of $\sigma^{\cdot}$ values can be used to assess the contribution of radical stabilization in other reactions, by using an extended Hammett equation of the form (5) where the $\rho\sigma$ term measures the polar

$$\log k_{\mathrm{rel}} = \rho\sigma + \rho^{\cdot}\sigma^{\cdot} \qquad (5)$$

influence (using whatever σ scale is appropriate). Since $\rho^{\cdot}$ is unity for our model reaction in which the stabilization energy of one benzyl radical is fully developed in the transition state, the value of $\rho^{\cdot}$ obtained in other reactions should provide a quantitative measure of the radical character developed or destroyed in the reaction concerned. This question is considered in more detail in the following paper.

E.s.r. Spectra of Substituted Benzyl Radicals.—Substituents which stabilize benzyl radicals would be expected to reduce the spin density at the α-carbon atom, and thus the α-CH_2 coupling constants in the e.s.r. spectra. There has been one previous study in this area (see below), but a number of groups have investigated the effects of *para*-substituents on aryl nitroxide radicals:[8] variations in a_{N} have been interpreted as due to polar effects of the substituents. Benzyl radicals should be less susceptible to these polar influences, and variations in $a_{\alpha-\mathrm{CH}_2}$ should reflect the radical stabilizing influence of the *para*-substituent.

Neta and Schuler[9] obtained the e.s.r. spectra of a number of substituted benzyl radicals in aqueous solution by electron irradiation of the toluene at high pH. The substituent effect on the coupling constants was small, and no significant correlation could be derived with available substituent constant scales, nor with theoretical calculations. The highly alkaline aqueous conditions used in this study may have had a perturbing influence on the radicals: e.s.r. parameters obtained in non-polar organic solvents might be expected to correlate better with reactivity studies of benzylic radicals.

Table 2 presents the e.s.r. parameters obtained by u.v. irradiation of mixtures of t-butyl peroxide with either the substituted toluene or the substituted benzyl chloride and triethylsilane. The results are broadly in agreement with those of Neta and Schuler:[9] the $a_{\alpha-\mathrm{CH}_2}$ coupling constants have a range of only 1.2 G from benzyl (maximum) to *p*-benzoylbenzyl (minimum). The maximum divergence in absolute values of $a_{\alpha-\mathrm{CH}_2}$ between the two sets of data was 0.15 G. The main qualitative difference is that our results show that all *para*-substituents lower the α-CH_2 coupling constants, whereas Neta and Schuler found a higher value for *p*-fluorobenzyl than for benzyl itself. Since all conjugating substituents would be expected to withdraw spin density from the α-CH_2 position our results accord with this: the anomalous result for *p*-fluorobenzyl in aqueous solution may reflect perturbation by the strongly alkaline aqueous solvent used by Neta and Schuler.

We were unable to obtain spectra of the potentially interesting *p*-nitrobenzyl or *p*-phenylbenzyl radicals. Weak signals were obtained for *p*-nitrotoluene or *p*-nitrobenzyl chloride which could not be interpreted as due to the *p*-nitrobenzyl radical; it seems likely that attack on the nitro-group takes place. U.v. irradiation of *p*-methylbiphenyl with t-butyl peroxide gave an intense spectrum of an unidentified persistent radical which swamped any *p*-phenylbenzyl radical which may have been present.

TABLE 2

Hyperfine splitting constants and spin-withdrawing parameters (Gauss) of *para*-substituted benzyl radicals.

X	a_o	a_m	a_p	a_α	$(\alpha\alpha)_{\mathrm{H}} - (a\alpha)_{\mathrm{X}}$
p-OMe	5.09	1.54	0.77[c]	15.99	0.48
p-Me	5.04	1.66	6.61[c]	16.04	0.43
H	5.19	1.77	6.24	16.47	0.00
p-F[a]	5.23	1.71	14.33	16.29	0.18
p-Cl[b]	5.19	1.83	0.53	16.07	0.40
p-COC_6H_5	5.00	1.74		15.29	1.18
p-CN	5.05		0.90[d]	15.49	0.98

[a] The hyperfine splitting constants were reported previously as 5.47, 1.74, 14.53, and 16.89 by Hudson and Lewis.[10] [b] The hyperfine splitting constants were reported previously as 5.2, 1.7, 0.6, and 16.2 by Hudson and Hussain.[11] [c] Methyl quartet. [d] Nitrogen triplet.

The trend in coupling constants parallels the $\sigma^{\cdot}$ values obtained from the rates of decomposition of *para*-substituted dibenzylmercurials, with fluorine and chlorine having a small effect and methyl and methoxy having a larger and almost equal effect. The spin-withdrawing effect is more pronounced for PhCO and CN: unfortunately $\sigma^{\cdot}$ values are not available for these substituents, but the radical stabilizing effect of CN is well documented (see *e.g.* ref. 12), and the PhCO group should allow substantial delocalization of the spin onto the carbonyl oxygen atom. For the five substituents in common, the α-CH_2 coupling constants correlate with $\sigma^{\cdot}$ with a coefficient of -0.91 (significant at the 2% level). Perhaps this is as good as can be expected. In addition to experimental error the effects of which are magnified by the small spread in values, a further possible source of disagreement is that the extent of spin-withdrawal may not exactly correspond to increase in stabilization energy of different radicals. For example, Hückel calculations on a number of substituted benzyl radicals gave ratios of $(\pi_{\mathrm{X\text{-}C_6H_4CH_2^{\cdot}}} - \pi_{\mathrm{C_6H_5CH_2^{\cdot}}})/(\alpha\text{-spin density}_{\mathrm{C_6H_5CH_2^{\cdot}}} - \alpha\text{-spin density}_{\mathrm{XC_6H_4CH_2^{\cdot}}})$ ranging from 0.63 to 0.76 β units per electron.

The small range of values of $a_{\alpha-\mathrm{CH}_2}$ in substituted benzyl radicals together with the uncertainty of the exact dependence of stabilization energy on spin delocalization makes measurements of this type unsuitable as the basis of a primary scale of substituent constants,* but the good correlation of the e.s.r. parameters with $\sigma^{\bullet}$ values increases confidence in the use of the $\sigma^{\bullet}$ scale as a measure of radical stabilization.

EXPERIMENTAL

Dibenzylmercury was made from benzylmagnesium chloride and mercury(II) chloride.[14] Prepared analogously (from the substituted benzyl chloride unless indicated) were the following: bis(*p*-methylbenzyl)mercury (from the bromide) 62%, m.p. 113—115° (Found: C, 46.6; H, 4.4. Calc. for $C_{16}H_{18}Hg$: C, 46.8; H, 4.4%); bis(*p*-fluorobenzyl)-mercury, 80%, m.p. 79—80° (Found: C, 39.9, H, 2.9. Calc. for $C_{14}H_{12}F_2Hg$: C, 40.15, H 2.9%); bis(*m*-fluorobenzyl)mercury (from the bromide), 59%, m.p. 99—101°C (Found: C, 39.9, H 2.9%); *bis*(m-*methoxybenzyl*)*mercury*, 82%, m.p. 94—95° (Found: C, 43.4; H, 4.1. $C_{16}H_{18}HgO_2$ requires C, 43.4; H, 4.1%); *bis*(p-*methoxybenzyl*)*mercury* (Grignard reaction and coupling carried out at −10 to 0°, to minimize production of *p,p'*-dimethoxybibenzyl), 74%, decomp. 115°, $\lambda_{max.}$ (octane) 239 nm ($\varepsilon_{max.}$ 30 400) (Found: C, 43.4; H, 4.1%); bis(*p*-chlorobenzyl)mercury, 51%, m.p. 169° (lit.,[15] 169—170°) (Found: C, 36.8; H, 2.8. Calc. for $C_{14}H_{12}Cl_2Hg$: C, 37.2; H, 2.7%). Bis(3,5-dimethylbenzyl)mercury, 45%, m.p. 68 ° (lit.,[16] 66°) (Found C, 49.3; H, 5.1. Calc. for $C_{18}H_{22}Hg$; C, 49.2; H, 5.05%), was made from 3,5-dimethylbenzylmercury(II) chloride, m.p. 93.5—94° (lit.,[16] 89°), itself made by reaction of the Grignard of 3,5-dimethylbenzyl bromide with mercury(II) chloride. *p*-Phenylbenzylmercury(II) chloride and bis(*p*-phenylbenzyl)mercury were obtained along with *p*-methylbiphenyl when the Grignard from *p*-phenylbenzyl chloride was allowed to react with mercury(II) chloride and the product was extracted with ether. Evaporation of the ether and extraction with a chloroform–carbon tetrachloride mixture at room temperature left a residue from which p-*phenylbenzylmercury*(II) *chloride* was crystallized from chloroform to give a cream-white solid, decomp. 170° (Found: C, 40.0; H, 3.1. $C_{13}H_{11}ClHg$ requires C, 38.7; H, 2.75%). The chloroform–carbon tetrachloride extract was evaporated, and extraction of the residue with heptane at room temperature left behind as residue *bis*(p-*phenylbenzyl*)*mercury*, crystallized from acetone to give a powdery solid, decomp. 150°, $\lambda_{max.}$ (octane) 297 nm ($\varepsilon_{max.}$ 53 700) (Found: C, 58.0; H, 4.5. $C_{26}H_{22}Hg$ requires C, 58.4; H, 4.1%). *p*-Phenylbenzylmercury(II) chloride could be symmetrized to bis(*p*-phenylbenzyl)mercury by treatment of an alcoholic solution with aqueous alkaline tin(II) chloride.[17]

p-*Nitrobenzylmercury*(II) *Bromide*.—Recrystallized *p*-nitrobenzyl bromide (21.6 g, 0.1 mol) was dissolved in dried acetone (200 ml) in a cylindrical quartz tube (70 × 400 mm) containing mercury (60.2 g, 0.3 g atom), and nitrogen was bubbled through the solution to expel dissolved air. The mixture was vigorously stirred mechanically to break the mercury into fine droplets, and irradiated by a 500 W medium pressure u.v. lamp *ca.* 10 cm from the reaction vessel. Acetone was added at intervals to make up for evaporation losses. The reaction was monitored by n.m.r. to check the consumption of *p*-nitrobenzyl bromide; after 40% consumption, a further 100 ml of acetone was added to reduce precipitation of *p*-nitrobenzylmercury(II) bromide on the surface of the reaction vessel, and reaction was continued until 80—85% of the *p*-nitrobenzyl bromide had been consumed. Extraction of the reaction product with hot acetone in the presence of zinc (15—20 g) to amalgamate the mercury gave, after filtration and evaporation of the acetone, a red-brown solid, which was recrystallized from dioxan to give *p*-nitrobenzylmercury(II) bromide (30.8 g, 0.074 mol, 74%), m.p. 183° (lit.,[5] 181—182°) (Found: C, 20.2; H, 1.8; N, 3.3. Calc. for $C_7H_6BrHgNO_2$: C, 20.2; H, 1.45; N, 3.4%).

TABLE 3

N.m.r. data[a,b] for compounds $(XC_6H_4CH_2)_2Hg$

	^{1}H N.m.r. (δ)				^{13}C Data (δ units)								
X	CH_2	$J(^{199}Hg–CH_2)$	Ar	X	C-1	C-2	C-3	C-4	C-5	C-6	C_X	CH_2	$J(^{13}C–^{199}Hg)$
H	2.37	135	7.09		144.4	127.7	128.3	123.1				46.6	633.5
m-F	2.43	137	6.88		147.0	114.3	162.9	110.0	129.6	123.3		46.3	638.4
m-OMe	2.45	135	6.85	3.8	146.1	113.3	159.6	108.5	129.2	120.3	55.0	46.5	633.5
3,5-Me_2	2.27	133	6.62	2.21	144.3	125.6	137.7	124.8			21.3	46.4	626.2
p-F	2.45	132	6.96		139.8	128.8	115.0	159.8				45.9	637.2
p-Cl	2.4	132	7.0		142.8	129.0	128.4	130.1				46.1	633.6
p-Me	2.36	131	6.95	2.30	141.1	127.7	128.9	132.3			20.7	46.2	625.0
p-OMe	2.40	127	6.90	3.82	136.3	128.5	113.8	156.0			55.3	46.0	627.4
p-Ph	2.5	136	7.4		143.6	128.1	127.0	136.2			*c*	46.4	625.0
p-NO_2[d]	2.5	164	7.45									44.1	732

[a] In $CDCl_3$ except as indicated. [b] ^{13}C Chemical shifts in $CDCl_3$ for ring carbon atoms can be calculated to within an average error of 0.3 by using additive increments for $ArCH_2HgCH_2$: C-1 + 15.9, C-2 −0.8, C-3 −0.2, C-4 −5.4 p.p.m. and values for other substituents from ref. 18. [c] Peaks at δ 126.7, 128.6, and 141.1 p.p.m. assigned to carbon atoms on the phenyl substituent. [d] In [$^2H_5$]-pyridine.

Bis(p-*nitrobenzyl*)*mercury*.—A solution of potassium iodide (16.5 g, 0.1 mol) in water (10 ml)–acetone (100 ml) was added rapidly to a suspension of *p*-nitrobenzylmercury-(II) bromide (4.16 g, 0.01 mol) in water (10 ml) and acetone (50 ml) with vigorous stirring under nitrogen. After 1 h, the mixture was filtered through a glass sinter, and the residue was washed with water, dried at room temperature under vacuum, and extracted with cold pyridine to remove *p*-nitrotoluene and *p,p'*-dinitrobibenzyl. Crystallization of the residue from acetone gave *bis*(p-*nitrobenzyl*)*mercury* (1.58 g, 0.0033 mol, 67%) as an orange powder, m.p. 209°, $\lambda_{max.}$ ($CHCl_3$) 350 nm ($\varepsilon_{max.}$ 9 900) (Found: C, 35.9; H, 2.7; N, 5.8. $C_{14}H_{12}HgN_2O_4$ requires C, 35.6; H, 2.6; N, 5.9%).

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* Larger substituent effects are found on e.s.r. parameters for substituted methyl radicals[13] but effects of substituents on a methyl radical are not expected to be exactly the same as those at the *para*-position of a benzyl radical, partly for steric reasons. Thus for example a phenyl substituent would have a greater relative effect at a methyl centre than at the *para*-position of a benzyl radical.

Attempted Preparation of Bis(p-*acetylbenzyl*)*mercury and Bis*(p-*benzoylbenzyl*)*mercury*.—2-Phenyl-2-*p*-tolyl-1,3-dioxolan was made by dehydrating a mixture of *p*-methylbenzophenone (49 g) and ethylene glycol (150 ml) in benzene (300 ml) in the presence of toluene-*p*-sulphonic acid (200 mg), using a Dean and Stark apparatus. After cooling, neutralization and addition of water, the benzene layer was vacuum-distilled to yield 2-*phenyl*-2-p-*tolyl*-1,3-*dioxolan*, which was further purified by crystallization from heptane, to give a solid (49 g, 82%), m.p. 58° (Found: C, 79.7; H, 6.9. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%). Bromination of this compound with *N*-bromosuccinimide in carbon tetrachloride gave after crystallization from heptane 2-*phenyl*-2-(4-*bromomethylphenyl*)-1,3-*dioxolan* as a solid (47%), m.p. 58—60°. 2-*Phenyl*-2-(4-*chloromethylphenyl*)-1,3-*dioxolan* was prepared as a powder, m.p. 62°, by protection of the carbonyl group of *p*-benzoylbenzyl chloride as described above (Found: C, 70.0; H, 5.45. $C_{16}H_{15}ClO_2$ requires C, 69.9; H, 5.5%).

2-Methyl-2-*p*-tolyl-1,3-dioxolan was made from *p*-methylacetophenone as described above as a liquid, b.p. 62° at 0.6 mmHg (lit.,[19] 131° at 34 mmHg). Chlorination by sulphuryl chloride in the presence of benzoyl peroxide gave exclusive chlorination in the ω-methyl group (n.m.r.) to yield 2-*chloromethyl*-2-p-*tolyl*-1,3-*dioxolan* (77%) as a liquid, b.p. 92° at 0.4 mmHg (Found: C, 62.05; H, 6.1. $C_{11}H_{13}ClO_2$ requires C, 62.1; H 6.2%). Bromination of the parent dioxolan with *N*-bromosuccinimide took place on both methyl groups to yield after crystallization from heptane 2-*bromomethyl*-2-(4-*bromomethylphenyl*)-1,3-*dioxolan* (40%), m.p. 72° (Found: C, 39.3; H, 3.6. $C_{11}H_{12}Br_2O_2$ requires C, 39.3; H, 3.6%). Protection of the carbonyl group of methyl *p*-acetylbenzoate gave 2-*methyl*-2-(4-*methoxycarbonylphenyl*)-1,3-*dioxolan* (62%), b.p. 96—98° at 0.1 mmHg (Found: C, 65.1; H 6.7. $C_{12}H_{14}O_4$ requires C, 64.85; H, 6.35%). Reduction of this compound ($LiAlH_4$) followed by vacuum distillation furnished 2-*methyl*-2-(4-*hydroxymethylphenyl*)-1,3-*dioxolan* (55%), b.p. 108 ° at 0.1 mmHg (Found: C, 67.9; H, 7.2. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.3%). Treatment of this alcohol with thionyl chloride in pyridine gave a small quantity of an oily residue, identified as 2-methyl-2-(4-chloromethylphenyl)-1,3-dioxolan by n.m.r., δ 7.4 (AB), 4.5 (CH_2Cl), 3.85 (A_2B_2), and 1.7 (CH_3).

A number of attempts were made to convert 2-phenyl-2-*p*-chloromethylphenyl-1,3-dioxolan into the corresponding Grignard, but success was only achieved by using activated magnesium, made from magnesium chloride and potassium.[20] This Grignard solution gave no mercurial with mercury(II) chloride, but from the product, crystallization from ethanol yielded the *bisdioxolanyl derivative of* p,p′-*dibenzoylbibenzyl* (probably formed mainly during the production of the Grignard) as a pale yellow powder, m.p. 125° (Found: C, 76.9; H, 6.4. $C_{32}H_{30}O_4$ requires C, 80.3; H, 6.3%).

p,p′-Disubstituted bibenzyls needed for calibration purposes were all known compounds prepared by standard methods. Kinetic runs were carried out using individual degassed ampoules as described previously.[4] n-Octane, used as solvent, was dried over CaH_2, fractionated, and its purity checked by g.l.c. Analysis was by three methods. (1) For the unsubstituted, *p*-Me, *m*-F, *p*-F, 3,5-Me_2, and *m*-OMe substituted mercurials, analysis was by g.l.c. estimation of the bibenzyl produced, using pentadecane, heptadecane, or docosane as internal standards. Final yields of bibenzyl (from dibenzylmercury solutions under the decomposition conditions at 140°) were 79, 80, and 82% with evidence for the formation of a little toluene. (2) For *p*-OMe, *p*-C_6H_5, and *p*-Cl substituted mercurials, h.p.l.c. analysis on a 25 cm, 5 mm OD, stainless steel column packed with Partisil PXS was used, employing biphenyl, terphenyl, and t-butylbenzene respectively as internal standards, and a mixture of 90% n-heptane with 10% ether, chloroform, and ether respectively as eluants, with u.v. detection of the residual mercurial. The tiny amounts of biphenyl and terphenyl used as internal standards should have an insignificant effect on the octane solvent, but t-butylbenzene with its lower extinction coefficient is required in much larger quantities and appears to show a marked effect on the reaction rate: the bis(*p*-chlorobenzyl)mercury runs were therefore repeated using t-butylbenzene added as an external standard after the ampoules were opened. (3) Bis(*p*-nitrobenzyl)mercury solutions were analysed by the change in u.v. absorption at 355 nm. Individual kinetic results were as follows, in octane solution unless otherwise stated [results given in the order: substituent, temperature (°C), $10^5k_1/s^{-1}$]: unsubstituted, 126.4°, 2.01, 1.90; 140.2°, 8.04, 8.25; 154.8°, 33.6, 35.8; unsubstituted (dibenzyl ether) 140.2°, 8.48; *m*-F, 126.4°, 1.26, 1.32; 140.2°, 5.57, 5.62; 154.8°, 23.9, 25.0; *p*-F, 126.4°, 2.22, 2.31; 140.2°, 9.40, 9.41; 154.8°, 37.7, 38.6; *p*-Me, 126.4°, 5.56, 5.58; 140.2°, 25.9, 27.3; 154.8°, 116.5, 120.6; 3,5-Me_2 (in isooctane) 140.2°, 10.3, 12.3; *m*-OMe, 128.5°, 1.79, 2.06; 140.35°, 7.17, 7.64; 142.2°, 8.75, 10.3; 156.3°, 32.6, 33.7; *p*-OMe, 126.5° 6.04, 6.72; 140.35°, 26.5, 28.5, 29.7; 154.4°, 108, 117; *p*-Ph, 126.5°, 4.45, 5.19; 140.35°, 21.6, 21.7, 22.9; 154.4°, 94.4, 95.5; *p*-Cl (internal standard), 126.5°, 2.00, 2.13; 140.35°, 6.97, 7.74; 154.4°, 34.1, 35.0; *p*-Cl (external standard) 140.3°, 8.92, 9.62, 9.64; *p*-NO_2 (in dibenzyl ether), 126.5°, 3.17, 3.52; 140.25°, 15.0, 15.5, 16.1, 16.2; 154.4°, 63.4, 68.3.

E.s.r. Experiments.—The substituted benzyl radicals were generated in a static system in the cavity of a Varian E104A spectrometer, using a GEC ME/D 250 W mercury lamp, or a Hanovia 1 kW high pressure Hg–Xe lamp either from a mixture of the substituted toluene and t-butyl peroxide,[21] or from a mixture of t-butyl peroxide, triethylsilane, and the substituted benzyl chloride[22] (*ca.* 2 : 1 : 1 by volume), at a temperature of *ca.* −60 °C. Spectra were calibrated by recording a spectrum of Fremy's salt (a_N 13.091 G)[23] before and after the spectrum of the substituted benzyl radical, and interpretation was either carried out manually or by computer simulation.

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