Free Radical Reactions in Solution. Part 9.[1] Further $\sigma^{\cdot}$ Values from Decomposition of Substituted Dibenzylmercurials

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Di-*para*-substituted dibenzylmercurials $(p\text{-}XC_6H_4CH_2)_2Hg$ (X = Br, CN, or SCH_3) have been prepared. From the rates of decomposition in octane at 140.2°, $\sigma^{\cdot}$ values for the stabilizing influence of *p*-Br, *p*-CN, and *p*-SCH_3 have been evaluated as 0.20, 0.41, and 0.49, respectively. Comparison of the rates of decomposition of dibenzylmercury, *p*-methoxydibenzylmercury, and bis-(*p*-methoxybenzyl)mercury supports a mechanistic scheme involving homolysis of one C–Hg bond in the transition state, rather than simultaneous cleavage of both C–Hg bonds.

We recently[2] reported $\sigma^{\cdot}$ radical stabilization constants for six *para*-substituents, based on the decomposition rates of substituted dibenzylmercurials. We now report $\sigma^{\cdot}$ values for three further *para* substituents, Br, CN, and SCH_3. Studies on the rate of decomposition of dibenzylmercury, *p*-methoxydibenzylmercury, and bis-(*p*-methoxybenzyl)mercury at 140.2° provide further evidence for the homolysis of one C–Hg bond in the first stage of the thermal decomposition of these mercurials.

Results and Discussion

Mechansim of Decomposition of Dibenzylmercurials.—We have previously argued in favour of the Mode 1 decomposition of dibenzylmercury [homolysis of one C–Hg bond in the rate-determining step (see Scheme 1)] rather than Mode 2 (simultaneous rupture of both C–Hg bonds) on the basis of the ' normal ' *A* factors observed, and the difference in activation energy for decomposition of dibenzylmercury and diethylmercury.[3] Further evidence for this mechanism is of interest, in view of our interpretation of substituent effects on this reaction as due to stabilization of a single benzyl radical.[2]

Comparison of the decomposition rates of unsubstituted, monosubstituted, and disubstituted dibenzylmercurials offers a method for distinction between these two modes. For Mode 1, cleavage of a particular C–Hg bond should only be significantly affected by the aryl group forming the incipient benzylic radical.† Thus the expected rates of decomposition of $(ArCH_2)_2Hg$, $ArCH_2HgCH_2Ar'$, and $(Ar'CH_2)_2Hg$ should be $2k_a$, $k_a + k_b$, and $2k_b$, respectively, with the monosubstituted compound decomposing at the arithmetic mean of the rates of the unsubstituted and disubstituted compounds. On the other hand, Mode 2 involves the simultaneous rupture of both C–Hg bonds: on the assumption that the strengths of these two types of bond are independent of the nature of the other aryl group, the activation energies for decomposition of $(ArCH_2)_2Hg$, $ArCH_2HgCH_2Ar'$, and $(Ar'CH_2)_2Hg$ should be $2x$, $x + y$, and $2y$, respectively, leading to the expectation that the monosubstituted compound should decompose at the geometric mean of the rates of the unsubstituted and disubstituted compounds.

We have carried out experiments with dibenzylmercury, *p*-methoxydibenzylmercury, and bis-(*p*-methoxybenzyl)mercury. Rates of decomposition in octane at 140.2° are shown in Table 1.

Table 1. Rates of decomposition of $p\text{-}XC_6H_4CH_2\text{–}Hg\text{–}CH_2\text{–}C_6H_4Y\text{-}p$ in octane at 140.2°

X	Y	$10^5\ k_{140.2°}/s^{-1}$	Average
H	H	8.01, 7.25	7.63
H	MeO	18.75, 17.26, 17.59	17.9
MeO	MeO	30.16, 27.08	28.6

The rate of decomposition of *p*-methoxydibenzylmercury ($17.9 \times 10^{-5}\ s^{-1}$) is extremely close to the arithmetic mean of the unsubstituted and disubstituted compounds ($18.1 \times 10^{-5}\ s^{-1}$), but substantially different from the geometric mean ($14.8 \times 10^{-5}\ s^{-1}$). On the assumption of a normal distribution of errors of the logarithms of the three rate constants with the same standard deviation, a *t*-test indicated that the geometric mean hypothesis should be rejected at the 2% level. These results thus provide further evidence for the Mode 1 decomposition of dibenzylmercurials.

Checks that no redistribution reactions were taking place were carried out. *p*-Methoxydibenzylmercury solutions in octane were partially decomposed at 140°. T.l.c. showed the absence of dibenzylmercury and bis-(*p*-methoxybenzyl)-mercury; likewise a mixture of dibenzylmercury and bis-(*p*-methoxybenzyl)mercury gave no *p*-methoxydibenzylmercury.

Experiments involving the total decomposition of *p*-methoxydibenzylmercury in octane at temperatures ranging from 126 to 159° gave total yields of bibenzyls of 82%. The excess of mono-*p*-methoxybibenzyl over that expected statistically indicated a cage effect of 29%, not varying noticeably over the temperature range covered. This is similar in magnitude to the 27—40% estimated for the decomposition of dibenzylmercury itself in *p*-chlorotoluene[4] at temperatures between 171 and 140°.

Further Substituent Constants $\sigma^{\cdot}$.—Our previous work[2] established the values of radical stabilization constants $\sigma^{\cdot}$ for six *para*-substituents, including two (Me, MeO) which are electron releasing in polar systems, but only one (NO_2) which has a substantial electron-withdrawing resonance contribution. Further substituents of this type are of particular interest, but many compounds of this type cannot be prepared by the ' normal ' synthetic route to dibenzylmercurials *via* the Grignard reagent because of competing reactions with groups such as ketones, esters, and nitriles. We solved the synthetic problem for bis-(*p*-cyanobenzyl)mercury by the reaction sequence of Scheme 2. Sodamide reacts with *p*-tolunitrile at −78° to give the sodium salt (1) without attacking the nitrile group. Evaporation of the ammonia at −78° and replacement of the solvent by diethyl ether, followed by reaction with mercury(II) chloride gave the desired bis-(*p*-cyanobenzyl)mercury.

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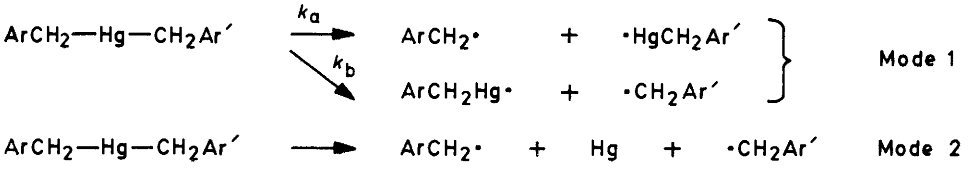
† This assumes that there is no significant effect by a substituent X on the stability of the radical $p\text{-}XC_6H_4CH_2Hg^{\cdot}$. The CH_2 group should form an effective barrier to the transmission of electronic effects from the *para*-X substituent to the mercury atom, particularly since the odd electron will be in an *sp* orbital, which is unsuitably oriented for hyperconjugative interaction.

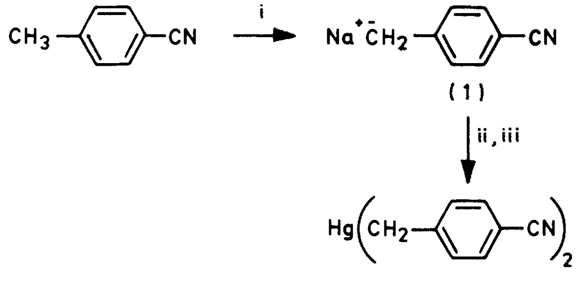


Scheme 1.

Table 2. Kinetic [a] data for the decomposition of substituted dibenzylmercury in octane

Substituent	T/°C	$10^5\ k_1/s^{-1}$	Average	$10^5\ k_{140.2°}/s^{-1}$	E/kcal mol^{-1}	log(A/s^{-1})
H	140.2	8.01	7.63	7.63		
		7.25				
p-MeO	140.2	18.75	17.9	17.9		
		17.26				
		17.59				
p,p'-(MeO)$_2$	140.2	30.16	28.6	28.6		
		27.08				
p,p'-Br$_2$	126.59	2.06				
	140.39	10.02	9.70	9.52	32.79	13.28
	140.39	9.37				
	155.49	33.37				
p,p'-(MeS)$_2$	126.69	7.86				
	140.39	23.76	25.3	24.9	30.25	12.41
	140.39	26.92				
	155.29	99.76				
p,p'-(CN)$_2$	140.19	8.08	8.02	8.03		
		7.96				

[a] Rate constants at 140.2° are either as measured at this temperature or corrected from values within ±0.2° of this temperature using the activation energy for the particular compound if available, or otherwise by using $E_{\text{dibenzylmercury}}$.



Scheme 2. *Reagents*: i, $NaNH_2$–NH_3; ii, replace NH_3 by Et_2O; iii, $HgCl_2$–THF

Bis-(p-methylthiobenzyl)mercury (of interest in that MeS has a very small inductive effect in polar reactions, but is thought to be substantially stabilizing in radical reactions) and bis-(p-bromobenzyl)mercury were prepared by the ' normal ' Grignard route.

Kinetics of the decomposition of the mercurials (*ca.* 2 × 10^{-3}M) in octane were measured by following the loss of the mercurial by h.p.l.c., using t-butylbenzene as an external standard (aromatic compounds tend to affect the rate of decomposition). The results (Table 2) were in good agreement with previous measurements on the unsubstituted and p-bis-methoxy-compounds, for which the rate of formation of the product bibenzyl had been monitored.

Following our previous practice, we plot the logarithm of the decomposition rate constant at 140.2° against σ^0 (values from ref. 5) and estimate the polar inductive contribution by drawing a regression line through the points for *meta*-substituents. $\sigma^{\cdot}$ Values were defined for *para*-substituents [by equation (1)] as the vertical distance above this regression line.

$$\log k/k_{\mathrm{H}} = \rho^0\sigma^0 + \sigma^{\cdot} \qquad (1)$$

Our choice of σ^0 rather than σ to define the polar contribution was based [2] on the interpretation of this effect as an initial state effect on the polarized $\overset{\delta-}{CH_2}$–$\overset{\delta+}{Hg}$ bond which is lost in the transition state. $J(^{13}C-^{199}Hg)$, which should be sensitive to the polarity of this bond, was found to correlate better with σ^0 than with σ. With data for 12 compounds now available, we confirm this result. For only three substituents, p-F, p-MeO, and p-MeS is there a significant difference between σ and σ^0. A regression line for $J(^{13}C-^{199}Hg)$ against $\sigma(\equiv\sigma^0)$ for the other nine substituents allows values for p-F, p-MeO, and p-MeS to be predicted. In each case, a better prediction is obtained from the σ^0 rather than the σ value. Our value for the p-cyano-compound also provides evidence against σ^- involvement: the p-cyano-point is much closer to the line if σ^0 rather than σ^- is used.

Values of $\sigma^{\cdot}$ derived from this and previous work are shown in Table 3. The p-methylthio substituent is confirmed as having a marked radical stabilizing ability, second only to the p-nitro-group, and the p-cyano-substituent is also highly stabilizing. The substantial values of $\sigma^{\cdot}$ shown by substituents which are either electron releasing (Me, MeO) or withdrawing

Table 3. $\sigma^{\cdot}$ Values for *para*-substituents

Substituent	$\sigma^{\cdot}$	Ref.
H	0.00	
F	0.12	2
Cl	0.18	2
Br	0.20	This work
Me	0.39	2
CN	0.41	This work
Ph	0.42	2
MeO	0.43	2, this work
MeS	0.49	This work
NO_2	0.76	2

(CN, NO_2) in polar situations confirms that both types of substituents can confer substantial stabilization on radicals.

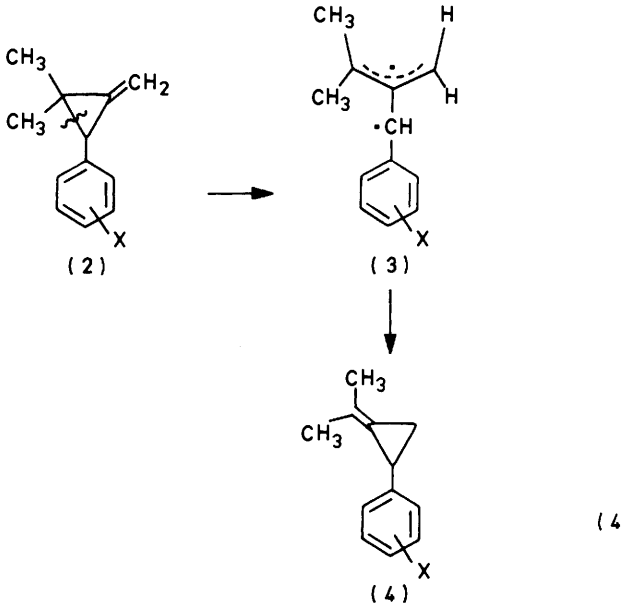
In our previous paper,[6] we pointed to a correlation of $\sigma^{\cdot}$ with $(|\sigma^{\pm} - \sigma|)/n$ where $\sigma^{\pm}$ is σ^{+} for electron-releasing and σ^{-} for electron-withdrawing substituents, and n is 1 for substituents with a multiple bond and 2 for substituents with a lone pair, and justified this in terms of orbital interaction diagrams. We suggested the use of a regression equation to predict unmeasured $\sigma^{\cdot}$ values: use of this equation gives values of 0.13, 0.54, and 0.47 for *p*-Br, *p*-SCH_3, and *p*-CN respectively, in reasonable agreement with the values presented in this paper.

Using all 10 values now available, a revised regression equation of $\sigma^{\cdot}_{\text{predicted}} = 1.557(|\sigma^{\pm} - \sigma|)/n + 0.054$ ($r = 0.979$) can be established to predict unknown $\sigma^{\cdot}$ constants. Removal of each point one at a time from this equation, and using the other nine values to predict the point removed gave a maximum deviation of 0.08 and an average deviation of 0.05 from the observed values. If the regression line is forced through the origin, the equation becomes $\sigma^{\cdot}_{\text{predicted}} = 1.753 (|\sigma^{\pm} - \sigma|)/n$, with average and maximum deviations as determined above of 0.05 and 0.10. Thus the correlation of $\sigma^{\cdot}$ with $(|\sigma^{\pm} - \sigma|)/n$ appears to have a firm experimental basis, and provides a method of estimating $\sigma^{\cdot}$ for substituents which have not been measured directly, as well as insight into the connection between radical and polar stabilization.

For reactions other than the defining reaction, the equation $\log k_{\text{rel}} = \rho^{x}\sigma^{x} + \rho^{\cdot}\sigma^{\cdot}$ should apply, where σ^{x} may be derived from whichever polar scale is appropriate. $\rho^{\cdot}$ should provide a measure of the amount of radical character produced in the transition state (*ca.* 1 for benzylic radical formation, *ca.* 0.5 for radical transfer and addition to double bonds for example). Literature data to provide values of $\rho^{\cdot}$ and test the validity of the $\sigma^{\cdot}$ approach are relatively few, and the assessment of polar effects is often made difficult by the absence of data for *meta*-substituents.

One series of reactions is of interest,[7] the thermolysis of substituted azobicumyls according to equation (3). Data for the decomposition of the unsubstituted compound, *m*-chloro, and five *para*-substituents are available. From the *m*-chloro compound, a value of ρ^{0} of +0.91 can be obtained, and application of equation (2) leads to a value of $\rho^{\cdot} = 0.83$. The positive value of ρ^{0} can be attributed to the $\overset{\delta+}{C}$–$\overset{\delta-}{N}$ bond polarization being lost in the transition state (*cf.* our value of −0.63 for dibenzylmercurials[2]) and the relatively large $\rho^{\cdot}$ value indicates substantial radical character formed in the transition state; though in the light of other work which suggests that for symmetrical azo-compounds, both C–N bonds weaken in the initial steps of the decomposition,[8] this may indicate that the two bonds are only approximately half-broken in the transition state.

$$XC_6H_4CMe_2{-}N{=}N{-}CMe_2C_6H_4X \longrightarrow 2\ XC_6H_4CMe_2^{\cdot} + N_2 \qquad (3)$$



(2) (3) (4)

(4)

Creary[9] has studied the thermal rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropanes (2) to 2-arylisopropylidenecyclopropanes (4), using a wide range of *meta*- and *para*-substituents. A plot of log k against σ shows that all *para*-substituents except fluorine lie above the line drawn through the *meta*-points [$\rho = -0.16$ (ref. 9) or -0.18 with the σ values[5] used in this paper]. The deviations from the *meta*-line for the eight substituents common to his and our systems plotted against $\sigma^{\cdot}$ give a plot with considerable scatter (r 0.69), but from the slope, a value of $\rho^{\cdot} = 0.70$ is obtained, corresponding to a high degree of development of benzylic radical stabilization in the transition state, in support of the proposed intermediacy of the benzylic stabilized radical (3).

Thus $\sigma^{\cdot}$ appears to form a useful measure of the stabilizing effect of *para*-substituents on benzylic and analogous radical systems, whilst $\rho^{\cdot}$ provides a measure of the radical character built up or destroyed in the transition state.

Experimental

Kinetic techniques were as already described,[2,3] except that analysis of the mercurial remaining was by h.p.l.c., using a stainless steel column packed with Partisil, u.v. detection, and elution by heptane [unsubstituted mercurial], 5% ether in heptane [*p*-MeO and bis-(*p*-MeS) substituted mercurials], 20% ether in heptane [bis-(*p*-MeO) and bis-(*p*-Br)], and 20% $CHCl_3$ in heptane [bis-(*p*-CN)]. t-Butylbenzene was used as an external standard except for experiments with bis-(*p*-cyanobenzyl)-mercury when biphenyl was used.

p-*Methoxydibenzylmercury*.—To benzylmagnesium chloride (0.015 mol) in ether was added *p*-methoxybenzylmercury(II) chloride (0.014 mol) in ether at room temperature with vigorous stirring, continued for 4 h after the addition. After NH_4Cl hydrolysis and two recrystallizations from ether, p-*methoxydibenzylmercury* was obtained as needles (71%), m.p. 78—79°, $\lambda_{\text{max.}}$ (octane) 263 nm ($\varepsilon_{\text{max.}}$ 14 400) (Found: C, 43.5; H, 4.0. $C_{15}H_{16}HgO$ requires C, 43.6; H, 3.9%). Prepared by the normal Grignard method were *bis*-(p-*bromobenzyl*)-*mercury*, crystallized twice from EtOAc as a powder, m.p. 160°, $\lambda_{max.}$ (octane) 266 nm ($\varepsilon_{max.}$ 27 800) (Found: C, 31.1; H, 2.2. $C_{14}H_{12}Br_2Hg$ requires C, 31.1; H, 2.2%); *bis*-(p-*methylthiobenzyl*)*mercury*, crystallized twice from EtOAc as cream microcrystals, m.p. 108—109°, $\lambda_{max.}$ (octane) 281 nm ($\varepsilon_{max.}$ 20 300) (Found: C, 40.6; H, 3.8. $C_{16}H_{18}HgS_2$ requires C, 40.45; H, 3.8%).

Bis-(p-*cyanobenzyl*)*mercury*.—To sodamide, prepared by adding Na (1.77 g, 0.077 mol) in small pieces, along with iron(III) nitrate hydrate (0.3 g) to liquid ammonia (100 ml), was added *p*-tolunitrile (9 g, 0.077 mol) in sodium-dried ether (50 ml) at −78° under nitrogen. From the resultant red-orange solution of sodio-*p*-tolunitrile, the liquid ammonia was evaporated at reduced pressure at −78°. Mercury(II) chloride (15 g, 0.055 mol) in Na-dried THF (50 ml) was added to the dark green suspension, which was then stirred vigorously for 30 min and hydrolysed with water. After separation of the organic layer, drying, and removal of the solvent, the yellowish residue was crystallized from ether, yielding *bis*-(p-*cyanobenzyl*)*mercury* (4.5 g, 30%), m.p. 148—149°, $\lambda_{max.}$ (chloroform) 290 nm ($\varepsilon_{max.}$ 16 600) (Found: C, 44.2; H, 2.9; N, 6.5. $C_{16}H_{12}HgN_2$ requires C, 44.4; H, 2.8; N, 6.5%).

N.m.r. Data for Compounds $(p\text{-}XC_6H_4CH_2)_2Hg$.—Results are given in the order: substituent, δ_{CH_2}, $J(^{199}Hg\text{-}CH_2)$, $\delta_{Ar\ mult.}$ $\delta_{H(X)}$; $\delta_{C(1)}$, $\delta_{C(2)}$, $\delta_{C(3)}$, $\delta_{C(4)}$, δ_{CH_2}, $\delta_{C(X)}$, $J(^{199}Hg\text{-}CH_2)$: Br, 2.42, 135, 7.13, —; 143.3, 129.4, 131.2, 116.5, 46.0, —, 633.8. SMe, 2.37, 132, 7.05, 2.40; 141.8,* 128.2,† 127.9,† 131.9,* 46.1, 17.0, 630.2. CN, 254, 146, 7.3, —; 150.9, 128.1, 132.0, 106.1, 46.5, 119.5, 648.5.

Check for Symmetrization of p-*Methoxydibenzylmercury*.—Three ampoules containing degassed *p*-methoxydibenzylmercury (2×10^{-3}M) in octane were heated at 140° for 20, 30, and 50 min. The octane solvent was evaporated under vacuum, benzene was added, and t.l.c. (silica gel, benzene eluant) indicated only one spot under u.v. light, confirmed by its R_F value of 0.51 as the initial *p*-methoxydibenzylmercury. Similarly, solutions of a mixture of dibenzylmercury (2×10^{-3}M) and bis-(*p*-methoxybenzyl)mercury (2×10^{-3}M) in octane heated at 140° for 20, 35, and 80 min gave spots corresponding to dibenzylmercury (R_F 0.66) and bis-(*p*-methoxybenzyl)mercury (R_F 0.28) only.

Complete Decomposition of p-*Methoxydibenzylmercury*.—Degassed solutions of *p*-methoxydibenzylmercury (1.80×10^{-3}M) in octane with nonadecane as an internal standard were heated at 126° for 96, 140° for 48, and at 159° for 24 h. The product dibenzyl mixtures had within experimental error the same composition by g.l.c.: bibenzyl (0.282×10^{-3}M), *p*-methoxybibenzyl (0.947×10^{-3}M), and *p,p'*-dimethoxybibenzyl (0.240×10^{-3}M).

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* Assignments may be reversed.
† Assignments may be reversed.