Stabilization of benzylic radicals by substituents: an EPR study of *para*-substituted benzyl radicals

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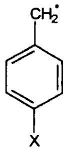
Accurate determinations have been made for the EPR coupling constants of 15 *para*-substituted benzyl radicals. These data, along with literature data for other systems have been used to reassess the stabilizing effect of *para*-substituents on benzylic radicals, and to throw light on the possible destabilizing effects of *para* F and CF_3 substituents.

Several Hammett-type $\sigma^{\bullet}$ scales have been proposed to correlate the effects of substituents on radical reactions; the advantages and disadvantages of a number of these scales have been reviewed recently.[1] In 1983, Dust and Arnold[2] suggested a $\sigma^{\bullet}_{\alpha}$ scale, based on the $\alpha(CH_2)$ coupling constants of *para*-substituted benzyl radicals. This scale is convenient, but the relatively small range of $\alpha(CH_2)$ couplings (1.4 G) and the uncertainties of individual values (estimated[2] to be about 0.03 G) makes it worthwhile to improve the precision of measurement in order to facilitate comparisons with other scales of radical stabilization. In the time since the $\sigma^{\bullet}_{\alpha}$ scale was proposed we have developed computer assisted methods[3] of determining coupling constants with greater precision. This paper presents the results for 15 *para*-substituted benzyl radicals, throwing light on the connection between $\alpha(CH_2)$ coupling constants and radical stabilization, and in particular the question of whether or not *para* F and CF_3 substituents destabilize benzylic radicals.

Experimental

para-Substituted toluenes $XC_6H_4CH_3$, [XAr, X = F, CF_3, Me, Bu^t, MeO, MeS, Cl (A); H (Fi); MeO_2C (Fl); MeCO (K)] and benzyl bromides $YC_6H_4CH_2Br$, [YAr′, Y = NC (A); Me (K)] were commercial samples from Aldrich (A), Fisons (Fi), Fluka (Fl), or Koch-Light (K) unless otherwise indicated, and were purified by distillation or recrystallization from ethanol if < 98% pure by GC, otherwise they were used as supplied. FAr (A) was distilled, washed with H_2SO_4, then with H_2O and dried over Na_2SO_4, bp 117 °C. Me_3SiAr (kindly supplied by C. Eaborn and P. M. Jackson) and PhCOAr′ were available in the laboratory. MeO_3SAr was prepared[2,4] by reaction of toluene-*p*-sulfonyl chloride with excess MeOH, mp 27–28 °C. $MeCO_2Ar$ was prepared[2] from *p*-cresol and AcCl, bp 212–214 °C. SrO (which contains Mn^{2+} as an impurity) was prepared[5] by heating $SrCO_3$ with charcoal.

Radicals were generated photolytically from mixtures of *tert*-butyl peroxide with either the substituted toluene or the benzyl bromide (chloride) and triethylsilane at −40 °C in the cavity of a Varian E104A EPR spectrometer, as described previously.[6] The coupling constant reference was determined on a Bruker ESP 300 spectrometer at 21 °C. In each session, spectra of several different radicals were obtained one after the other and always including benzyl itself. At the end of each session, the cavity was allowed to warm up to room temperature and the spectrum of a manganese standard in SrO was obtained for calibration purposes.



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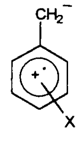

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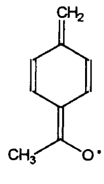

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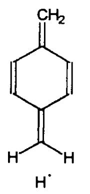

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Results and discussion

EPR spectra were obtained for 14 *para*-substituted benzyl radicals (**1**) on at least three separate occasions, and the coupling constants derived by MATCH were calibrated with reference to the $\alpha(CH_2)$ coupling constant of the unsubstituted benzyl radical whose spectrum had been run during the same session. The average standard deviation of the $\alpha(CH_2)$ coupling constants derived in this way was 0.019 G, and for all the measurable coupling constants 0.014 G. The absolute value of the $\alpha(CH_2)$ coupling constant for benzyl was determined as 16.27 ± 0.02 G with reference to the separation of the two central lines of a Mn^{2+} standard, determined as 83.74 G. This is slightly higher than the 16.25 G reported by Dust and Arnold,[2] but well within the uncertainty of the two sets of experiments.

The *p*-(methylsulfanyl)benzyl radical spectrum [from *p*-(methylsulfanyl)toluene] was obscured by a broad 1:2:1 triplet, $a_H = 16.12$ G, $\Delta g = +0.0015$ compared with the *p*-(methylsulfanyl)benzyl spectrum. This triplet was assigned as the *p*-tolylsulfanylmethyl radical. The coupling is similar to the value of 16.5 G reported,[7,8] for $C_6H_5SCH_2^{\bullet}$ and a higher *g* value is expected for a sulfur-substituted methyl radical than for the more remotely substituted *p*-(methylsulfanyl)benzyl radical (the *g* value[8] for $C_6H_5SCH_2^{\bullet}$ is 2.0042). When the simulated spectrum of the *p*-tolylsulfanylmethyl radical was subtracted from the experimental spectrum, the spectrum of the *p*-(methylsulfanyl)benzyl radical could be analysed satisfactorily.

On the whole, there is reasonable agreement with the extensive set of values obtained by Arnold and co-workers.[2,9] The most significant difference from Arnold's results is for the fluorine atoms in the CF_3 group of the *p*-trifluoromethylbenzyl radical where our value of 8.75 G is 1.87 G higher than Arnold's value. We have checked our assignment by MATCH[3] and by the Maximum Entropy Method[10] using an input pattern consisting of all the couplings except those due to the *para* CF_3 fluorine atoms; the output quartet confirms the higher value for this coupling.

The agreement with Arnold's results[2,9] for $\alpha(CH_2)$ coupling constants (on which most of the discussion about radical stabilization hinges) is good on the whole, but differences in coupling constants (relative to unsubstituted benzyl) of up to

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Table 1 EPR coupling constants for p-X–$C_6H_4CH_2^{\bullet}$(**1**)

X	Mean coupling constants/G				Standard deviations/G						
	α	o	m	p	α	o	m	p	$\sigma^{\bullet}_{\alpha}$ [a]	σ^{0} [b]	$\sigma^{\bullet}_{av}$ [c]
SMe	15.27	5.02	1.68	0.88	0.02	0.02	0.004	0.02	0.061	0.06	0.51
MeCO	15.30	5.05	1.79	—	0.03	0.04	0.01	—	0.059	0.47	0.66 [d]
PhCO	15.42	4.96	1.75	—	0.02	0.04	0.02	—	0.052	0.46	0.59 [d]
CN	15.60	5.09	1.80	0.89	0.01	0.01	0.02	0.02	0.041	0.71	0.55
CO_2Me	15.67	5.04	1.77	—	0.02	0.02	0.04	—	0.037	0.44	0.44
OMe	15.86	5.05	1.50	0.74	0.01	0.01	0.01	0.02	0.025	−0.12	0.27
Cl	16.03	5.20	1.81	0.55	0.01	0.01	0.01	0.004	0.015	0.24	0.18
Me	16.06	5.13	1.73	6.59	0.02	0.01	0.01	0.01	0.013	−0.14	0.18
$SiMe_3$	16.08	5.07	1.71	—	0.04	0.02	0.01	—	0.012	−0.07	0.13
Bu^t	16.10	5.08	1.74	0.20	0.01	0.01	0.03	0.001	0.011	−0.15	0.10
SO_3Me	16.14	5.10	1.71	—	0.03	0.02	0.003	—	0.008	0.90	0.24 [d]
OCOMe	16.25	5.23	1.76	—	0.01	0.003	0.003	—	0.001	0.16	0.04 [d]
H	16.27	5.15	1.77	6.19	—	0.01	0.005	0.01	0.000	0.00	0.00
CF_3	16.33	5.17	1.76	8.75	0.02	0.002	0.003	0.02	−0.004	0.53	0.10
F	16.41	5.27	1.72	14.39	0.01	0.002	0.004	0.01	−0.009	0.15	−0.02
Average sd					0.019	0.014	0.011	0.012			
Overall average sd					0.014						

[a] $\sigma^{\bullet}_{\alpha} = (a_H - a_X)/a_H$. [b] σ^0 Values from ref. 17. [c] $\sigma^{\bullet}_{av}$ See text. [d] EPR value only.

0.1 G were observed. The good correlation of Arnold's data with Creary's kinetic data on the ring-opening of methylidenecyclopropanes[11] [reaction(2)] is improved slightly if our results are used instead of those of Arnold *et al.*

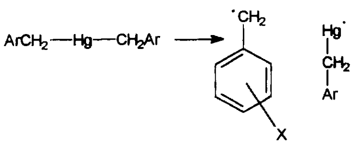
The EPR results are shown in Table 1. The fact that the large majority of *para* substituents reduce the $\alpha(CH_2)$ coupling constant is in line with the expectation that conjugating substituents, whether electron-withdrawing or electron-releasing, will provide additional delocalization of the unpaired electron, and will stabilize the radical. SMe, MeCO and PhCO groups have the smallest values; these groups are known to stabilize radicals in other systems. However, F and CF_3 substituents in the *para* position have values of the $\alpha(CH_2)$ coupling which are greater than that of unsubstituted benzyl by a small but significant amount. This suggests the possibility of radical destabilization, though this cannot be readily accounted for on the basis of stabilization by delocalization, for which the minimum stabilization would be expected to be zero when no additional delocalization takes place when a substituent is present. Evidence from some recent kinetic and equilibrium experiments on stabilization or destabilization caused by *para* F is equivocal, partly due to the difficulty of allowing for polar effects, with one[12] suggesting stabilization, two[11,13] destabilization and one[14] within experimental error of zero. *para* CF_3 is almost certainly stabilizing[11,15] although one source[14] makes the effect zero within experimental error.

There is a small but significant (at the 0.2% level) difference between the $\alpha(CH_2)$ coupling constants for *p*-methyl- and *p*-*tert*-butylbenzyl radicals, indicating that the methyl group is slightly more effective in hyperconjugatively delocalizing spin density.

There is a positive correlation ($R^2 = 0.63$) between the *ortho* and the $\alpha(CH_2)$ coupling constants of the *para*-substituted benzyl radicals; substituents which remove spin density from the α-position should also remove spin density from *ortho*-positions. However the variation in coupling constants is much smaller for the *ortho* hydrogens, and there is considerable scatter about the regression line. There is no discernible trend for *meta* coupling constants to follow polar or radical stabilizing parameters, and the differences between radicals are small. However, the value for *p*-methoxybenzyl seems to be significantly lower than the others; this may reflect the preference for the methoxy group to lie in the plane of the radical, and in this position there is the possibility for electronic interaction between the methyl group and the *meta* proton in close proximity.

The observed correlation of $\alpha(CH_2)$ coupling constants for *meta*[16] and 3,5-disubstituted[6] benzyl radicals with σ_m has already been noted, the correlation being better if a little $\sigma^{\bullet}$ component is included.[6] We have argued for the importance of charged contributors of type **2** to the structure of *meta*-substituted benzyl radicals; it seems likely that structures of this type will also contribute to *para*-substituted radicals, and that the coupling constants for both *meta* and *para*-substituted radicals will be predicted to depend on a two-component extended Hammett equation, which can be used to correlate EPR results with kinetic data.

Kinetic data are available for three decomposition and rearrangement reactions in which substantial benzylic radical character is expected to build up in the transition state, *viz.* dibenzylmercurials[12] [reaction (1)], methylidenecyclopropanes[11] [reaction (2)] and azo-compounds[13] [reaction (3)].



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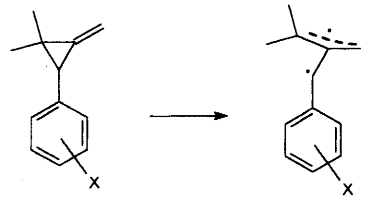

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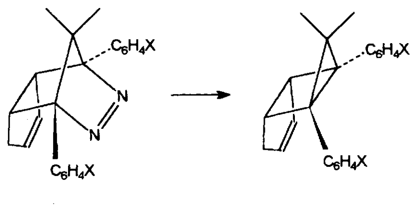

(3)

For reaction (2), an extensive set of rate data is available for *meta* substituted compounds, which shows a negative correlation with σ, with considerable scatter, but with no indication of enhanced rates of decomposition for substituents which are believed to stabilize benzylic radicals when situated in the *para* position. Accordingly, we have set up a model whereby the values of the $\alpha(CH_2)$ coupling constants in the EPR data and the logarithms of the rates of the decompositions are both

Table 2 Contribution of polar and radical components to EPR and rate data

System	ρ (Polar)	$\rho^{\bullet}$ (Radical)	Reference
EPR data	−0.18	1.02	This work and 6
Reaction (1)	−0.89	1	12
Reaction (2)	−0.12	0.91	11
Reaction (3)	0.34	0.51	13

expressed as two-component extended Hammett equations [eqns. (4) and (5)]. The polar component applies to both *meta* and *para* positions, but the 'radical stabilization component' $\rho^{\bullet}\sigma^{\bullet}$ applies only to *para* substituents. To avoid special pleading, we take σ^0 values[17] as representative of polar contributions in all cases; arguments in favour of this polar scale have already been advanced for the dibenzylmercury system.[12] The $\sigma^{\bullet}$ values are taken as variables, along with ρ factors for the polar and radical components of the two sets of EPR data (ref. 6 and this work) and the three sets of kinetic results.[11–13] The 'true' value of the unsubstituted compound is also taken as a variable for the kinetic results (the experimental value is not likely to be more reliable than that for any substituted compound). No such extra variable is needed for the EPR data, since all values are determined relative to the unsubstituted benzyl radical. Values for these variables are obtained by minimizing sums of squares of differences of predicted minus experimental values for all the experimental data, using eqn. (4) for the EPR data‡ and eqn. (5)

$$10 \times \sigma^{\bullet}_{\alpha} = \rho\sigma + \rho^{\bullet}\sigma^{\bullet}_{\mathrm{av}} \tag{4}$$

$$\log k_{\mathrm{X}} = \log k_{\mathrm{H}} + \rho\sigma + \rho^{\bullet}\sigma^{\bullet}_{\mathrm{av}} \tag{5}$$

for the kinetic data, utilizing a spreadsheet minimizing routine based on the quasi-Newton method. Primary $\sigma^{\bullet}_{\mathrm{av}}$ values are only derived if the *para*-substituent appears in at least two independent series. The system leaves us with 22 variables and 60 independent measurements for *meta*- and *para*-substituted compounds.

The final model gives a good overall fit to the experimental data. The average root mean square deviation for all the data is 0.05. The ρ (polar) and $\rho^{\bullet}$ (radical) values are shown in Table 2 and the best fitting $\sigma^{\bullet}_{\mathrm{av}}$ values are shown in the last column of Table 1. The value of $\rho^{\bullet}$ for the dibenzylmercury decomposition has been fixed at unity since this reaction almost certainly achieves the effectively complete fission of one Hg–C bond in the transition state.[12] Other reactions can thereby be calibrated for the amount of bond cleavage (or formation) by the $\rho^{\bullet}$ value, after correction for the temperature difference. On this basis, the methylidenecyclopropane ring openings[11] must involve near complete breakage of the C–C bond, whereas for the cyclic azo-compounds used by Nau *et al.*[13] the C–N bond appears to have only about half broken — the cyclic system may make it difficult for the full benzylic resonance to be achieved in the transition state. The polar effects in the kinetic series are as anticipated. There is only a very small polar effect on the methylidenecyclopropane ring opening, reflecting the C–C bond involved, whereas substantial polar effects in opposite directions are observed for the cleavage of C–Hg and C–N bonds. The former effect has been ascribed to the stabilization of the $^{\delta-}$C–Hg$^{\delta+}$ bond by electron-withdrawing substituents, a stabilization which is lost in the transition state. The effect will be expected to work in the opposite direction for $^{\delta+}$C–N$^{\delta-}$.

The radical delocalizing influence of the *para* substituents is seen to be much greater than that of *meta* substituents in reducing the α(CH_2) coupling constants of benzyl radicals, reflecting the greater importance of direct delocalization for example involving contributions from structures such as **3** or **4**, compared with reduction of the coupling constant by increasing the proportion of structures of type **2** to the benzyl structure; the polar contribution can act by increasing or decreasing the importance of these charged structures. It is by no means certain that these two factors have an equal effect on the stabilization energy for the same increase or reduction in coupling constant. If the 'delocalization' effect has a greater influence on stabilization than the polar effect, the stabilizing effect of CF_3, accompanied by a reduction of the α(CH_2) coupling constant is satisfactorily accounted for. The small positive $\sigma^{\bullet}$ for CF_3 increases stabilization of the benzylic radical and therefore makes decompositions go faster, whereas for the coupling constant, this effect is outweighed by the strong electron-withdrawing character of the group.

Fluorine remains the only substituent to appear both to have a (small) destabilizing effect, compared with hydrogen, on a benzyl radical, and to increase the α(CH_2) coupling constant. The transfer of spin density onto a *para*-hydrogen in a benzyl radical by polarization presumably involves a small stabilization (the negative[18] *p*-H coupling constant of −6.19 G and the nuclear isotropic hyperfine coupling constant[19] of 507 G corresponds to *ca.* 1.2% spin density). However, in *p*-fluorobenzyl, $a_{\mathrm{F}} = +14.4$ (ref. 20), arising mainly[21] from a component from the spin density in the F $2p_{\pi}$ orbital. If $Q_{\mathrm{FF}}{}^{\mathrm{F}} = 264$ (ref. 22); this corresponds to 5.5% spin density in the F $2p_{\pi}$ orbital. This is a minimum value since there will be a negative component arising from spin polarization from the spin density on the *para*-carbon atom. It is difficult, however, to reconcile a fluorine spin density of this magnitude with an increase in spin density at the α-carbon atom (and also at the *ortho* positions). It is possible that the electronegativity of fluorine may cause a slight change of preferred hybridization of the 4-carbon atom towards sp^3, thereby slightly diminishing the conjugation in the aromatic ring and thus leaving more of the unpaired spin density on the α-carbon atom.

The $\sigma^{\bullet}_{\alpha}$ scale remains a useful practical scale for assessing potential radical stabilization by substituents. Since it is dimensionless, accurate values for new substituents can be readily obtained individually by a direct comparison of the α(CH_2) coupling constant with that of unsubstituted benzyl under standard conditions. However, calculations at the Hückel level indicate that stabilization and changes in α(CH_2) coupling constant in benzyl radicals are not necessarily linearly related,[12] and it has been pointed out that for the analogous phenoxyl radicals, stabilization by *para* substituents (as evidenced by barriers to rotation) can take place both for phenoxyl radicals and for the parent phenols to different extents depending on the substituents involved.[23] Thus the relationship of the α(CH_2) coupling to thermodynamic stabilization remains open; to resolve this matter, further accurate kinetic (or preferably thermodynamic) data are needed on reactions of known mechanisms involving a substantial build-up or destruction of radical character, and preferably involving a large number of substituents, both *meta* and *para*.

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‡ $10 \times \sigma^{\bullet}_{\alpha}$ Is used in eqn. (4) because of the small values of $\sigma^{\bullet}_{\alpha}$ to give numbers of comparable magnitude to the differences between the log k_{X} and the log k_{H} values in eqn. (5), thereby ensuring similar weighting of the EPR and the kinetic experiments in arriving at the $\sigma^{\bullet}_{\mathrm{av}}$ scale.

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