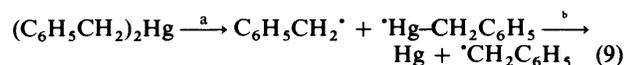




$\Delta H_f(\text{C}_6\text{H}_5\text{CH}_3) = 8 \text{ kcal mol}^{-1}$ ]. If we apply a similar increment for the change  $\text{C}_6\text{H}_5\text{CH}_2\text{HgC}_6\text{H}_5 \longrightarrow (\text{C}_6\text{H}_5\text{CH}_2)_2\text{Hg}$ , we obtain  $\Delta H_f[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Hg}]$  82 kcal mol<sup>-1</sup>. By using the known activation energy<sup>5</sup> of reaction (9),  $\Delta H_f(\text{HgCH}_2\text{C}_6\text{H}_5)$  76 and  $\Delta H(9b) - 16 \text{ kcal mol}^{-1}$ .



This implies that in contrast to  $\text{C}_6\text{H}_5-\text{Hg}^*$ ,  $\text{CH}_3-\text{Hg}^*$ , and  $\text{C}_2\text{H}_5-\text{Hg}^*$  (bond dissociation energies of 9, 3, and 3 kcal mol<sup>-1</sup> respectively, as estimated above with additional kinetic data from ref. 9),  $\text{C}_6\text{H}_5\text{CH}_2-\text{Hg}^*$  has a negative bond dissociation energy. There is considerable uncertainty in these figures, but it is very unlikely that the true value of  $D(\text{C}_6\text{H}_5\text{CH}_2-\text{Hg}^*)$  is positive, although there could still be a barrier to its decomposition.

We have also been able to compare the rate of decomposition at 155.4 °C of unsubstituted benzylphenylmercury with those of the *m*-chloro and *p*-methyl derivatives, substituted in the benzyl ring. Rates are:  $8.3 \times 10^{-5}$  (unsubstituted),  $2.0 \times 10^{-5}$  (*m*-Cl), and  $24 \times 10^{-5} \text{ s}^{-1}$  (*p*-CH<sub>3</sub>). The decrease caused by the substitution of a chlorine atom in the *meta* position is in line with the polar effects found for the decompositions of substituted dibenzylmercurials,<sup>2</sup> and would correspond to  $\rho -1.7$  compared with  $\rho -0.6$  for  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Hg}$ . Using the unsubstituted and *m*-chloro substituted benzylphenylmercury rate figures to predict the rate for the *para*-methyl compound shows that the methyl compound is decomposing 1.7 times faster than expected on the basis of the polar effect, providing evidence for stabilization of the incipient benzyl radical by the *para* methyl group; with only three points an extended Hammett-type treatment of the results is not justified.

### Experimental

The mixed benzylphenylmercury compounds were prepared from phenylmagnesium bromide and the appropriate benzylmercury(II) chloride in ether.<sup>10</sup> Benzylphenylmercury had  $\delta(\text{CDCl}_3)$  2.63 [s,  $J(\text{Hg}-\text{H})$  139 Hz, CH<sub>2</sub>].

*p*-Methylbenzylphenylmercury was recrystallized twice from ether as crystals, m.p. 38–40 °C,  $\delta(\text{CDCl}_3)$  2.64 [s,  $J(\text{Hg}-\text{H})$  137 Hz, CH<sub>2</sub>] and 2.33 (s, CH<sub>3</sub>) (Found: C, 43.7; H, 3.7. C<sub>14</sub>H<sub>14</sub>Hg requires C, 43.9; H, 3.7%).

*m*-Chlorobenzylphenylmercury was prepared as a yellow liquid, purified by t.l.c. (silica gel),  $\delta(\text{CDCl}_3)$  2.57 [s,  $J(\text{Hg}-\text{H})$  139 Hz, CH<sub>2</sub>] (Found: C, 39.2; H, 3.1. C<sub>13</sub>H<sub>11</sub>ClHg requires C, 38.7; H, 2.8%).

Kinetic experiments were carried out on degassed ampoules containing solutions of the mercurial in toluene ( $7-10 \times 10^{-3} \text{ M}$ ) with pentadecane, octadecane, or eicosane as internal standards. The mercurial remaining after a particular time was monitored by g.l.c. Results from first order plots over 1–3 half-lives (substituent: temp;  $10^5 k_1/\text{s}^{-1}$  values) were: unsubstituted: 140.4 °C; 1.25, 1.38, 1.02; 155.4 °C; 8.34, 8.30; 170.4 °C; 34.0, 34.8, *p*-methyl: 155.4 °C; 24.5, 23.0; *m*-chloro: 155.4 °C; 2.04, 1.93.

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