

SUBSTITUENT EFFECTS IN A RADICAL DISPROPORTIONATION REACTION

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Little is known about the nature of the transition state in benzyl-type radical disproportionation reactions. We wish to report the first data on substituent effects in such a reaction which show that the transition state is radical in character with essentially no ionic contribution.

The peroxide-induced decarbonylations of a series of substituted 9-(p-X-phenyl-9-fluorenyl)acetaldehydes (1, X = OCH<sub>3</sub>, CH<sub>3</sub>, H or Cl) in the presence of benzyl mercaptan have recently been reported.<sup>1</sup> We have found that if these decarbonylation reactions are carried out in the absence of benzyl mercaptan only the rearranged products 9-(p-X-phenyl)phenanthrenes 2, and 9,10-dihydro-9-(p-X-phenyl)phenanthrenes 3 are formed. The product percentages, determined by nmr, are shown in Table I.

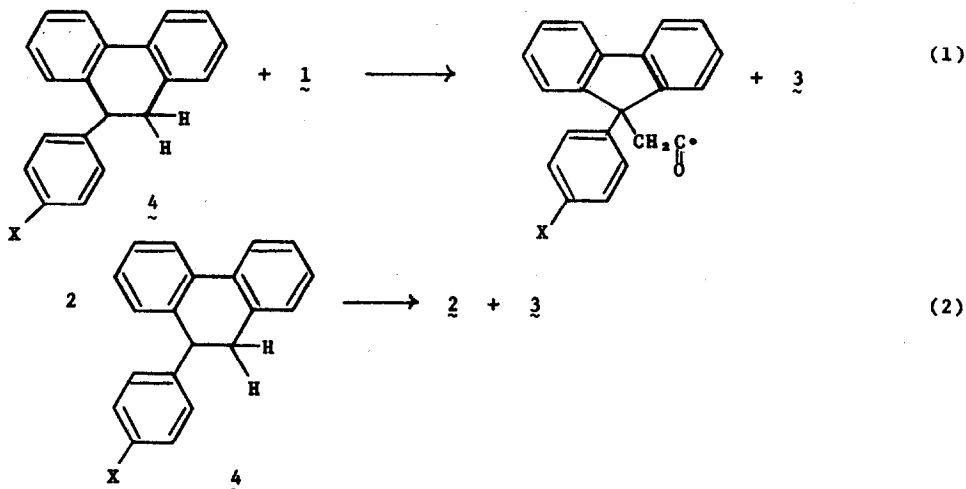
Table I. Product Percentages<sup>a</sup>

Substituent	% <u>2</u>	% <u>3</u>	% excess <u>2</u> <sup>b</sup>
OCH <sub>3</sub>	68	32	36
CH <sub>3</sub>	56	44	12
H	54	46	8
Cl	60	40	20

<sup>a</sup>Error is ±1%

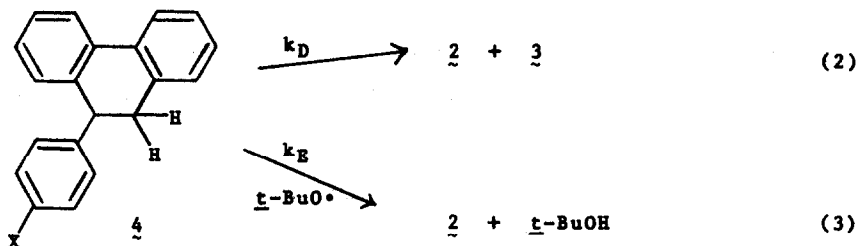
<sup>b</sup>%2 - %3

The two possible routes to the formation of 3 are via chain propagation (eq. 1) and disproportionation (eq. 2).



All available evidence indicates, however, that little or no chain propagation occurs in these decarbonylation reactions.<sup>2</sup> In the absence of chain propagation the amounts of 2 and 3 formed should be equal (eq. 2). The fact that 2 is always the major product clearly indicates that an additional amount of this compound is formed in a competing reaction which involves a hydrogen atom exchange between a rearranged radical and a tert-butoxy radical (eq. 3, Scheme I). The products, 2 and 3, have been found to be stable under the reaction conditions.<sup>3</sup>

Scheme 1



The exothermicity of reaction (3) is predicted to be high<sup>4</sup> and according to the Hammond principle<sup>5,6</sup> the transition state for such a reaction will occur very early on the reaction coordinate and will involve little C-H bond breaking. Consequently, the transition state will bear a close resemblance to the starting radical 4 and the rate constant for hydrogen atom exchange,  $k_E$ , will be independent of the substituent X. An equation, (4), can be developed which allows the calculation of the relative rate constants for the disproportionation reactions.

$$\text{relative } k_D = \frac{\left( \frac{\%3}{\% \text{ excess } 2} \right)_X}{\left( \frac{\%3}{\% \text{ excess } 2} \right)_H} = \frac{(k_D)_X}{(k_D)_H} \quad (4)$$

The product ratios and the relative disproportionation rate constants are shown in Table II.

Substituent	Dispropor. Product Exchange Product	Relative $k_D$
OCH <sub>3</sub>	0.89	0.155
CH <sub>3</sub>	3.67	0.638
H	5.75	1.000
Cl	2.00	0.348

Although a plot of log relative  $k_D$  vs. Hammett's  $\sigma$  value failed to give a straight line, excellent linear correlations were obtained using Taft's  $\sigma_R$  ( $\rho=+1.64$ ;  $r=0.995$ ;  $s=0.045$ )<sup>7</sup> and  $\sigma_R^\circ$  ( $\rho=+2.00$ ;  $r=0.998$ ;  $s=0.022$ ) values.<sup>8</sup> These results show that the rate of disproportionation is retarded to a large degree by substituents which can undergo resonance interactions with the ring.

It is well established that nearly all substituents (both electron donating and withdrawing) increase the relative stability of *p*-benzyl-type radicals.<sup>9-17</sup> The high exothermicity of the disproportionation reaction requires that the transition state closely resemble the starting radicals.<sup>5</sup> The effects of the two substituents in the transition state will be different and must be considered separately. As in the hydrogen exchange reaction (eq. 3), the substituent on the hydrogen donor radical will have nearly the same effect in the transition state as it does in the initial radical 4. Therefore, the substituent on the abstracting radical clearly exerts the controlling influence in this reaction. In the transition state the  $sp^2$  character of the abstracting benzylic-type carbon atom is decreased and the resonance stabilizing effect of the substituent is, consequently, diminished. The overall effect is a lesser stabilization of the transition state relative to the initial radical. Thus, the greater the radical stability the slower the rate of the disproportionation reaction. The correlations with  $\sigma_R$  and  $\sigma_R^\circ$  are the results of the resonance stabilizing effects of the substituents.<sup>18</sup> This precludes any inductive influence of the substituents and indicates that this disproportionation transition state is of radical character with no contributing polar effects.

Additional work is in progress with this system and a complete report is forthcoming.

R E F E R E N C E S

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