Substituent Effects at the Origin of a Free-Radical 1,2-Aryl Migration and in the Related Disproportionation Reaction of 10-Hydro-9-*p*-X-phenyl-9-phenanthryl Radicals

Richard N. Goerner, Jr., Philip N. Cote, and Bruno M. Vittimberga*

Chemistry Department, University of Rhode Island, Kingston, Rhode Island 02881

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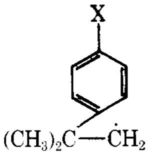
A series of (9-*p*-X-phenyl-9-fluorenyl)acetaldehydes (**5**) (X = H, F, Cl, OCH_3, SCH_3, $SOCH_3$, SO_2CH_3, and CH_3) have been synthesized, characterized, and decarbonylated in the presence and absence of benzyl mercaptan to yield (9-*p*-X-phenyl-9-fluorenyl)carbinyl radicals (U·). In the presence of mercaptan, these radicals rearranged to yield 9,10-dihydro-9-*p*-X-phenylphenanthrenes (**7**) and 9-*p*-X-phenyl phenanthrenes (**6**), and abstracted hydrogen from the mercaptan to yield 9-methyl-9-*p*-X-phenylfluorenes (**8**). The relative percentages of these products were determined by NMR integration, and were used to calculate relative rearrangement rate constants (rel k_R). An excellent linear correlation was found between log rel k_R and Hammett's σ_p ($\rho = 0.39$, $r = 0.988$, $s = \pm 0.05$). The methylthio substituted compound showed a strong deviation in the direction of rate enhancement. In the absence of mercaptan the rearranged 10-hydro-9-*p*-X-phenyl-9-phenanthryl radicals (R·) were found to undergo a disproportionation reaction yielding **6** and **7** as the sole products. The relative percentages of these products were used to calculate relative disproportionation rate constants (rel k_D). Separate correlations were obtained between log rel k_D and σ_R or $\sigma_R{}^\circ$ for the sulfur-containing substituents and for the non-sulfur-containing substituents. Evidence is presented which indicates that the substituent on the abstracting radical (R·) exerts the controlling influence on the rate of disproportionation.

Free-radical carbon rearrangements in solution have been under investigation since their initial discovery by Urry and Kharasch[1] in 1944. Yet, in spite of three decades of research in this area, until a short time ago little was known concerning the nature of the transition state for vicinal aryl migration, or the effects of substituents upon its stability.

Early work[2–5] implied a gross order of migratory abilities for substituted phenyl groups: $p\text{-}O_2NC_6H_4 > p\text{-}H_3CC_6H_4 \simeq C_6H_5 > p\text{-}H_3COC_6H_4$. Unfortunately, these results were qualitative, and the systems studied were sufficiently sterically dissimilar to make conclusions drawn from comparison of the results highly tentative.

The first comprehensive and quantitative treatment of substituent effects in free-radical aryl migrations was carried out by Rüchardt and his co-workers,[6–10] who studied the rearrangement of the 2-methyl-2-phenylpropyl (e.g., neophyl) radical as a function of substitution in the migrating aromatic nucleus. Their results showed that electron-withdrawing groups in the migrating ring facilitate the rearrangement process, and that strong electron-withdrawing groups (e.g., *p*-CN or *p*-NO_2) enhance the rate of rearrangement anomalously. To explain these results, they postulated a hybrid rearrangement transition state having polar character due to charge separation (resonance structures **1–4** below). Further, they have suggested that the extent of polar contribution (e.g., forms **3** and **4**) to the migration transition state is substituent dependent, apparently increasing as the extent of electron withdrawal by the substituent increases.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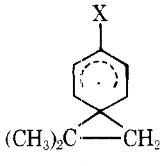
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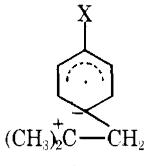
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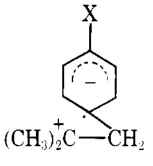
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Recently, we reported some preliminary findings[11,12] on the rearrangement of the (9-*p*-X-phenyl-9-fluorenyl)carbinyl radical systems (U·) (X = H, OCH_3, CH_3, or Cl). In this radical, only the phenylene ring of the fluorenyl ring system undergoes rearrangement,[13] thus permitting the unique opportunity to observe substituent effects at the origin of a radical rearrangement. We now wish to report our findings for the rearrangement of this radical (U·) for a spectrum of substituents ranging from electron donating to strongly electron withdrawing[14] and for the disproportionation of the resultant 9,10-dihydro-9-*p*-X-phenyl-9-phenanthryl radicals (R·).

Results and Discussion

The (9-*p*-X-phenyl-9-fluorenyl)acetaldehydes (**5**, X = H, CH_3, Cl, F, OCH_3, or SCH_3)[15] were synthesized from fluorenone and the appropriately substituted phenylmagnesium bromide by a procedure analogous to that described by Nesmeyanov et al.[16] and by Curtin and Hurwitz[4] in an average overall yield of 45%.

The methyl sulfoxide and the methyl sulfone substituted acetaldehydes were obtained by controlled oxidation of the methyl sulfide substituted acetaldehyde, using *m*-chloroperoxybenzoic acid in a procedure adapted from that employed by McIntosh et al.[17] for the oxidation of thiatane derivatives.

The desired (9-*p*-X-phenyl-9-fluorenyl)carbinyl radicals were generated by peroxide-induced decarbonylation of the corresponding aldehydes under identical experimental conditions in the presence of benzyl mercaptan. In each case, 20 mol % of the mercaptan was added to a 0.5 M solution of the aldehyde in purified 1,2-dichlorobenzene. The solution was degassed to remove oxygen, and then it was maintained at 140 ± 0.01 °C with agitation as two quantities, each 20 mol % of di-*tert*-butyl peroxide, were added initially and after 120 min. Each reaction was run for a total of 330 min and the rates of carbon monoxide evolution were monitored by measuring the slopes of various sections of the graphs of volume of gas evolved vs. time for each run.[18] All of the aldehydes were found to undergo decarbonylation to the same extent, and at the same rate, indicating that the rate-determining step is probably the homolysis of the peroxide.

It is notable that the presence of benzyl mercaptan results in a consistent increase in the rate of gas evolution over that observed in similar experiments in which benzyl mercaptan was absent. The effect of mercaptan, as observed earlier by Harris and Waters,[19] is a consequence of aldehydic hydrogen atom abstraction by benzylthiyl radicals in addition to the normally observed hydrogen atom abstraction by *tert*-butoxy radicals. From the average volume of gas evolved it was calculated that approximately 78% decarbonylation had oc-

Table I. Product Percentages[a] Calculated from NMR Integrations

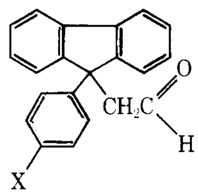
				% 6/% 7	
Substituent (X)	% 6 + % 7	% 6 − % 7	% 8	Mercaptan present	Mercaptan absent
OCH_3	77.0	36	23.0	2.35	2.13
CH_3	80.0	12	20.0	2.08	1.27
H	81.0	8	19.0	1.93	1.17
F	84.0	22	16.0	4.25	1.56
Cl	85.0	20	15.0	1.74	1.50
$SOCH_3$	87.0	20	13.0	3.14	1.50
SCH_3	88.5	38	11.5	4.71	2.23
SO_2CH_3	89.5	10	10.5	1.71	1.22

[a] Each datum is the average of at least two runs. The error is less than 1%.

curred, indicating a chain length of less than or equal to unity.[20-22]

The products from the decarbonylation reaction of the aldehydes were isolated by a combination of column and preparative layer chromatography, and were characterized by standard physical and spectral procedures. In each reaction the products were found to be 9-(*p*-X-phenyl)phenanthrenes (**6**), 9,10-dihydro-9-(*p*-X-phenyl)phenanthrenes (**7**), and 9-methyl-9-(*p*-X-phenyl)fluorenes (**8**) (X = H, CH_3, Cl, F, OCH_3, SCH_3, $SOCH_3$, or SO_2CH_3).

Also obtained, though in low yield, were compounds **9** and **10**. Benzyl disulfide is presumed to arise through dimerization of benzylthiyl radicals. The structure of compound **10** (X = H) was assigned on the basis of elemental analysis, its reaction with bromine in carbon tetrachloride, and its NMR spectrum. This compound most likely arises from a reaction between aldehyde and benzyl mercaptan with subsequent dehydration, a process which has been observed for other aldehydes[23,24] and ketones,[25] but under different reaction conditions. In each instance compounds **9** and **10** together accounted for less than 5% by weight of the overall product mixture. Neither of these compounds was characterized further, since they should be formed in proportionate amounts and to the same extent in each reaction.[26]



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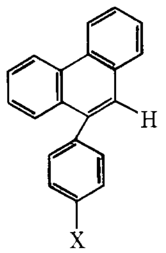

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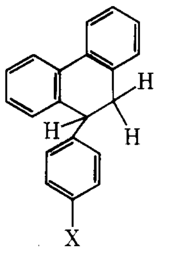

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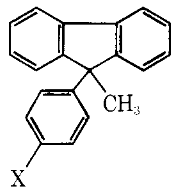

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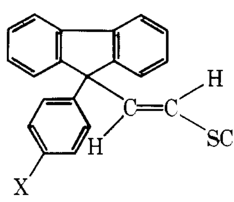
$(C_6H_5CH_2S\text{-})_2$

9



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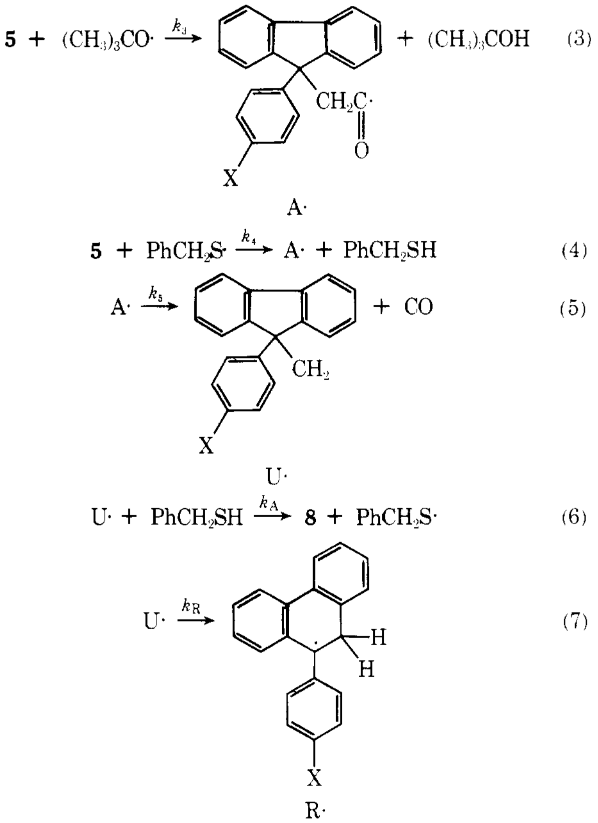
The relative percentages (Table I) of the decarbonylation products[27] were determined from the NMR integrations of the characteristic peaks at δ 1.78–1.82 (s, CH_3 of compound **8**), 3.12–3.18 (d, $-CH_2-$ of compound **7**), 3.95–4.01 (t, Ar_2CH- of compound **7**), and 8.67–8.73 (m, for the 4,5 aromatic H's of compound **6**). Each series of compounds showed these NMR peaks as well as those corresponding to the remaining aromatic hydrogens. All other NMR signals were consistent with hydrogen-bearing substituents on the molecules.

These results are in accord with the reaction mechanism shown in eq 1–13 of Scheme I.

Scheme I

$$(CH_3)_3CO{-}OC(CH_3)_3 \xrightarrow[\Delta]{k_1} 2(CH_3)_3CO\cdot \quad (1)$$

$$PhCH_2SH + (CH_3)_3CO\cdot \xrightarrow{k_2} PhCH_2S\cdot + (CH_3)_3COH \quad (2)$$



$$R\cdot + \mathbf{5} \xrightarrow{k_6} \mathbf{7} + A\cdot \quad (8)$$

$$2R \xrightarrow{k_7} \mathbf{7} + \mathbf{6} \quad (9)$$

$$R\cdot + (CH_3)_3CO\cdot \xrightarrow{k_8} \mathbf{6} + (CH_3)_3COH \quad (10)$$

$$R\cdot + PhCH_2SH \xrightarrow{k_9} \mathbf{7} + PhCH_2S\cdot \quad (11)$$

$$R\cdot + PhCH_2S\cdot \xrightarrow{k_{10}} \mathbf{6} + PhCH_2SH \quad (12)$$

$$2PhCH_2S\cdot \xrightarrow{k_{11}} PhCH_2SSCH_2Ph \quad (13)$$

Using the rate constants and mechanism depicted in Scheme I, one can readily derive the expression for the ratio of rearranged (R = % **6** + % **7**) to unrearranged (U = % **8**) products as shown in eq 14, where k_R and k_A are the rate constants for rearrangement (7) and hydrogen atom abstraction (6), respectively.

$$R/U = d(R)/d(U) = k_R/k_A\,(PhCH_2SH) \quad (14)$$

In view of the insulation of the substituent (X) from the

Table II. Product Ratios and Relative Rate Constants

Substituent (X)	$(R/U)_X$	Rel k_R	Log rel k_R
OCH_3	3.35	0.785	−0.105
CH_3	4.00	0.938	−0.028
H	4.26	1.000	0.000
F	5.12	1.202	0.080
Cl	5.67	1.329	0.124
$SOCH_3$	6.70	1.570	0.196
SCH_3	7.72	1.818	0.259
SO_2CH_3	8.55	2.010	0.303

radical center, it seems reasonable to assume that the rate constant for hydrogen atom abstraction, k_A, is independent of the substitution on the 9-phenyl moiety. Thus, eq 15 can be readily developed, permitting the calculation of relative rate constants for the rearrangement step.

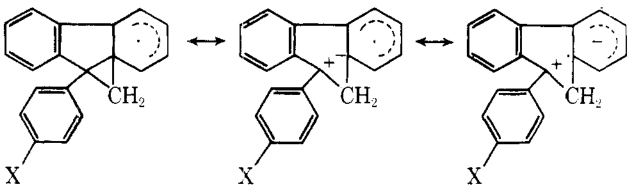
$$\frac{(R/U)_X}{(R/U)_H} = \frac{(k_R)_X/(k_A)_X(PhCH_2SH)}{(k_R)_H/(k_A)_H(PhCH_2SH)} = \frac{(k_R)_X}{(k_R)_H} = \text{rel } k_R \qquad (15)$$

where $(R/U)_X$ = (% **6** + % **7**)/(% **8**) for substituted compounds, $(R/U)_H$ = (% **6** + % **7**)/(% **8**) for unsubstituted compounds, $(k_R)_X$ = rate constant for rearrangement of substituted radical, $(k_R)_H$ = rate constant for rearrangement of the unsubstituted radical, $(k_A)_X$ = rate constant for hydrogen atom abstraction from a substituted radical, $(k_A)_H$ = rate constant for hydrogen atom abstraction from an unsubstituted radical.

Table II shows the results of applying the product percentage data of Table I to eq 15.

The degree of correlation between the log relative k_R data of Table II and σ_p,[28] σ_m,[28] $\sigma_p{}^+$,[28] σ_I,[29] $\Delta\sigma$,[30] F,[26] R,[28] σ_R,[29] or $\sigma_R{}^\circ$[29] was evaluated by means of the subprogram "linear regression analysis" of the IBM computer program STATPACK.[31] Bulk correlation was low in each instance. Inspection of the scatter plots indicated that data case X = SCH_3 represented the largest source of deviation. Accordingly, the calculations were repeated with this data case omitted. An excellent linear correlation with Hammett's σ_p was then obtained, in which $\rho = 0.392$, $s = 0.027$, and $r = 0.988$[32] (Figure 1, X = SCH_3 included for reference).

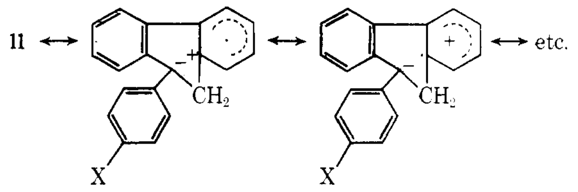
Assuming that the rearrangement is an isoentropic reaction, based on these results, it can be argued that the transition state for the rearrangement is essentially nonpolar in character. If the transition state for rearrangement of the (9-phenyl-9-fluorenyl)carbinyl radical were a hybrid having polar contributions similar to those suggested by Ruchardt et al. for the neophyl radical (cf. **3** and **4**), then canonical structures **11**, **12**, **13**, etc., would be appropriate. Our observation that electron-withdrawing substituents facilitate the rearrangement process clearly militates against hybrids such as **12** and **13** which show development of partial positive character at the migration origin.



11 **12** **13**

⟷ etc.

Alternatively, one might suggest the rearrangement transition state to be a polar hybrid with the charges reversed from those shown in **12** and **13** as shown in **14** and **15**. Such a hybridization scheme would place partial negative charge where it could most effectively be stabilized by the electron-withdrawing groups.



14 **15**

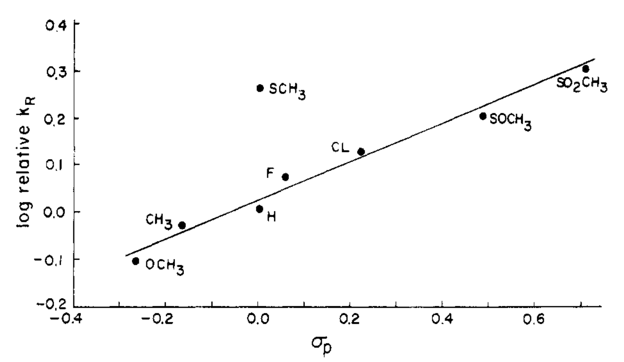


Figure 1. Hammett correlation of log rel k_R vs. σ_p for the rearrangement of the (9-*p*-X-phenyl-9-fluorenyl)carbinyl radical.

Curtin and Kauer[5] have examined the related rearrangement of the 2,2-diphenyl-2-(*p*-nitrophenyl)ethyl radical and estimated that the *p*-nitrophenyl moiety displays a migratory aptitude at least eightfold greater than that of the unsubstituted phenyl group. In the present work if charge separation developed as indicated in **14** and **15**, then partial negative charge would be placed at the migration origin and partial positive charge on the migrating ring. If this were the case, however, in the Curtin and Kauer experiment the unsubstituted phenyl group should have shown a migratory aptitude greater than that of the *p*-nitrophenyl group. The similarity of this rearrangement to that of (9-*p*-X-phenyl-9-fluorenyl)-carbinyl radical would lead one to conclude that structures with this type of polarization probably do not contribute to the transition state of either reaction.

Even if an isokinetic relationship were to exist for this rearrangement, it seems unlikely that ρ would vary far from zero. The small magnitude of the reaction constant is more in keeping with the general trend observed for nonpolar reactions.[33]

The rather striking deviation of the *p*-methylthio substituted radical from the Hammett correlation (Figure 1) indicates a greater participation of this group in stabilizing the rearrangement transition state than is accountable for in terms of inductive influence alone and must also involve electron-pair conjugation of the sulfur atom with radical center. This explanation is compatible with the results of a wide variety of reactions involving this group.[34] The importance of this type of resonance interaction has also been implicated for other substituents[35,36] such as the nitro and cyano groups.

On the basis of the results obtained in the present study and the considerations mentioned above, we conclude that the transition state for the reaction involving substituent effects at the origin of a free-radical aryl migration is essentially radical in character and that polar effects are negligible.

In order to gain further insight into the nature of this rearrangement the decarbonylation reactions were also carried out in the absence of benzyl mercaptan with some interesting results. Under these conditions the intermediate benzyl radicals (R·) were found to undergo disproportionation, allowing the first observations of substituent effects in such a reaction.[37,38]

Column chromatography on neutral alumina separated the mixture of products **6** and **7** from aldehyde **5** and the products of the reaction of **5** on the absorbent surface.[26] None of the unrearranged product, **8**, could be detected. Relative percentages of products were determined as previously described by NMR and these data were cross checked, when possible, by comparing the averaged NMR integrations for the hydrogen bearing substituents on **6** and **7** and were, in each instance, found to be in agreement with the product percentage data obtained from the skeletal framework hydrogens. These data are shown in Table I.

The products **6** and **7** were then separated by multiple development preparative thin layer chromatography, or chemically converted into previously characterized mixtures, and then separated.

In the presence of oxygen[11] only 9-phenylphenanthrene was observed as a product from the decarbonylation reaction of **5** (X = H). Most likely under these conditions disproportionation is not competitive with abstraction by oxygen of a hydrogen atom α to the radical center in the rearranged radical R·. In each instance it was observed that more of **6** than **7** was formed. If these reactions were chain processes, the expected result would have been the formation of more **7** and less of **6**. On the other hand, if all **7** were formed from the disproportionation reaction, an equal amount of **6** would have been anticipated. Clearly there must be an additional source of **6**.[39]

A logical explanation for this excess is that exclusion of oxygen permits a competition to develop between disproportionation reactions of R· to form **6** and **7**, and H-atom abstraction reactions of R· with *tert*-butoxy radical to form additional amounts of **6** (eq 16). Indeed, Trecker and Foote[40] reported a similar reaction

$$\mathrm{R\cdot} + t\text{-BuO}\cdot \xrightarrow{k_E} \mathbf{6} + t\text{-BuOH} \qquad (16)$$

of 2-carbomethoxy-2-propyl radical with *tert*-butoxy radical and calculated that the reaction is thermodynamically favorable. It is obvious from the higher ratio of % **6**/% **7** obtained in the presence of mercaptan (Table I) that benzylthiyl radical also participates in this type of reaction.

While **7** may be formed in two separate reactions, propagation (eq 17) and disproportionation (eq 18), based on the amount of peroxide required for the decarbonylation, the rate data, and the product ratios, it seems likely that little or no chain propagation is occurring.

$$\mathrm{R\cdot} + \mathbf{5} \rightarrow \mathbf{7} + \mathrm{A\cdot} \qquad (17)$$

$$\mathrm{R\cdot} + \mathrm{R\cdot} \rightarrow \mathbf{6} + \mathbf{7} \qquad (18)$$

These results are consistent with the mechanism, K_1, K_3, K_5, K_D (eq 19), and K_E (eq 20). Other, less probable reactions to form **6** and **7** have been excluded from the mechanism.

$$\mathrm{R\cdot} + \mathrm{R\cdot} \xrightarrow{k_D} \mathbf{6} + \mathbf{7} \qquad (19)$$

$$\mathrm{R\cdot} + \mathrm{RO\cdot} \xrightarrow{k_E} \mathbf{6} + \mathrm{ROH} \qquad (20)$$

Accordingly, it seems reasonable to assume that essentially all of **7** is formed in the disproportionation reaction. Since there should also be an equivalent amount of **6** formed in this reaction, the excess of **6** over **7** can be calculated as the difference between the total amount of **6** formed in all reactions and the amount of **6** formed in the disproportionation reaction. The results of these calculations are shown in Table I under column % **6** − % **7**.

Table III. Product Ratios and Relative Rate Constants

Substituent	(DH)/(P_E)	Rel k_D	Log rel k_D
H	5.750	1.000	0.000
SO_2CH_3	4.500	0.783	−0.106
CH_3	3.667	0.638	−0.195
Cl	2.000	0.348	−0.458
$SOCH_3$	2.000	0.348	−0.458
F	1.770	0.304	−0.517
OCH_3	0.889	0.155	−0.810
SCH_3	0.815	0.142	−0.851

It is clear from these data that the substituents have a definite effect on the relative amounts of products formed. The exothermicity of the H-atom exchange reaction would be expected to be high and by the Hammond principle[41,42] the transition state for such a reaction would be expected to occur early along the reaction coordinate. Thus, the H-atom exchange reaction should involve little C–H bond breaking in the transition state, which will bear a close resemblance to the starting radical R·. The rate constant for hydrogen atom exchange, k_E, should be essentially independent of the substituent X, while the stability of radical R· does affect the abstraction reaction and is substituent dependent. Hence, while k_E is independent of the substituent X, k_D is not. The different distribution of products is, therefore, considered to be the result of a substituent effect in the disproportionation step.

In the present study disproportionation occurs to the exclusion of dimerization, a fact which is probably due to steric hindrance to dimerization and to the relative stabilities of the rearranged radicals. This system, therefore, provides a unique opportunity to examine substituent effects on a disproportionation reaction without competition from a dimerization reaction, and without the complication of a substituent dependent hydrogen atom exchange reaction.

An equation (21) can be developed which relates product ratios to the rate constants for disproportionation and hydrogen atom exchange. Comparison of eq 21 for a substituent X against the standard (X = hydrogen) yields eq 22.

$$(\mathrm{DH})/(P_E) = d(\mathrm{DH})/d(P_E) = k_D\,(\mathrm{R\cdot})/k_E\,(\mathrm{RO\cdot}) \qquad (21)$$

(DH) = total amount of **7**)
(P_E) = amount of **6** formed in eq 16 (i.e., % **6** − % **7**)
(RO·) = concentration of *tert*-butoxy radicals
(R·) = concentration of R·
k_D = rate constant for the disproportionation
k_E = rate constant for the hydrogen atom exchange

$$\frac{[(\mathrm{DH})/(P_E)]_X}{[(\mathrm{DH})/(P_E)]_H} = \frac{(k_D)_X}{(k_D)_H} = \text{rel } k_D \qquad (22)$$

$[(\mathrm{DH})/(P_E)]_X$ = product ratio for substituted case
$[(\mathrm{DH})/(P_E)]_H$ = product ratio for hydrogen substituted case
$(k_D)_X$ = rate constant for disproportionation of the substituted radical
$(k_D)_H$ = rate constant for disproportionation of the hydrogen substituted radical

The results of applying the data from Table I to eq 22 are shown in Table III. It is noteworthy that all of the substituents studied are rate retarding relative to the hydrogen substituted standard, a behavior which parallels that observed for the relative stabilities of benzyl and benzyl-type radicals.

The degree of correlation between the log rel k_D data of Table III and a variety of substituent constants[28-30] was evaluated by means of the subprogram "linear regression analysis" of the IBM computer program STATPACK.[31] Linear correlations were obtained between log rel k_D and Tafts[29] σ_R or $\sigma_R°$ constants in two sets (Table IV). One set (A) is comprised of the non-sulfur-containing substituents (X = H, F, Cl, OCH_3, CH_3), while the other set (B) is comprised of the substituents containing sulfur (X = SCH_3, $SOCH_3$, SO_2CH_3). Plots of data for sets A and B (log rel k_D) against $\sigma_R°$ are shown in Figure 4. It is both unusual and interesting that two separate correlations were observed with each of the substituent parameters. It is not surprising, however, that the observed substituent effect on the rate of

Table IV. Correlation Data for the Disproportionation Reaction

Parameter	Set A vs. σ_R	Set B vs. σ_R	Set A vs. σ_R°	Set B vs. σ_R°
Intercept	−0.060	−0.368	−0.010	−0.413
Regression coefficient (ρ)	1.206	1.586	1.718	2.276
Correlation coefficient (r)	0.966	0.975	0.988	0.994
Standard error (s)	0.093	0.117	0.059	0.059

the radical disproportionation reaction follows an order similar to those observed for benzyl-type radical stabilizations[43,44] since the disproportionation step involves a benzyl-type radical.

Most reactions which correlate with Hammett's σ values involve a ground state reactant whose potential energy is affected very little (or not at all) by the substituent; thus the major influence of the substituent is in its ability to stabilize the transition state of the reaction. This disproportionation reaction, however, involves as a reactant a benzyl-type radical the stability of which should be substituent dependent.

The effects of the two substituents in the transition state of the disproportionation reaction must be considered separately. In the hydrogen exchange reaction (eq 20), the substituent on the hydrogen donor radical will have nearly the same effect in the transition state as it does in the initial radical R·. 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 stabilizing effect of the substituent is, consequently, diminished. The overall effect is a lesser stabilization of the transition state relative to the ground state. Thus, the greater the benzyl radical stability the slower the rate of the disproportionation reaction. The present results accordingly reflect the effects of substituents on a reaction step in which the energy barrier is more strongly influenced by the raising or lowering of the energy of the initial state than it is by energy changes in the transition state.

The magnitude of the reaction constants led us to consider the possibility of charge separation in the transition state of this reaction. However, since the reaction constant is merely a measure of the sensitivity of the reaction center to variations in the substituent, other things being equal, it did not seen reasonable to base the assignment of polar character to the transition state solely on the magnitude of ρ_R or ρ_R°. This reaction is particularly sensitive to the stability of the benzyl-type initial radical, which is, in turn, strongly dependent on the substituent. Then too, as was mentioned earlier, the transition state should bear a closer resemblance to the starting radical than to products. Though a definite conclusion cannot be reached at this time, these factors tend to support a mechanism that is radical in character and a reaction which has a substantial ρ constant.

Experimental Section

All melting points (corrected) were determined on a Thomas-Hoover capillary melting point apparatus. The nuclear magnetic resonance (NMR) spectra were recorded on a Japan Electron Optics Laboratory, high-resolution, C60HL NMR spectrometer, or on a Varian A-60 spectrometer using tetramethylsilane as the internal reference and $CDCl_3$ as the solvent. Mass spectra were recorded on a C. E. C. Du Pont type 490-B single focusing mass spectrometer, using a mass marker and perfluorokerosene for reference. Infrared spectra were determined on a Perkin-Elmer 700, a Beckman IR-8, or a Baird-Atomic KM-1 spectrometer (with polystyrene film reference), employing potassium bromide wafers for solids and matched sodium chloride liquid cells or sodium chloride plates (Wilk's Scientific Co.) for solutions and neat liquids. The combustion analyses were performed by Micro Analysis, Inc., Wilmington, Del.

Thin layer chromatography was performed on either Polygram Sil G/UV$_{254}$ or Polygram Sil N-HR/UV$_{254}$, 20 × 20 cm × 0.25 mm precoated, plastic TLC plates (Machery-Nagel and Co., through Brinkman Instruments, Inc.) Preparative thin layer chromatography was performed on either 125–1000 μ gradient, glass TL plates (Kontes' Glass Co.), or on normal glass plates spread to the desired thickness with a Desaga spreader (Brinkman Instruments, Inc.), using an aqueous slurry of silica gel 60 PF-254 (E. M. Reagents, for preparative layer chromatography). Dry column chromatography was performed with 35 mm i.d. Nylon tubing, using Woelm silica gel, dry column grade (activity III/30 mm), containing 0.5% inorganic (uv$_{254}$) fluorescent indicator. Both TLC plates and dry columns were visualized with a UVSL-25, multiband, Mineralight ultraviolet lamp (short–long wave, from Ultraviolet Products, Inc., San Gabriel, Calif.); all thin layer plates were visualized, additionally, in a glass chamber saturated with iodine.

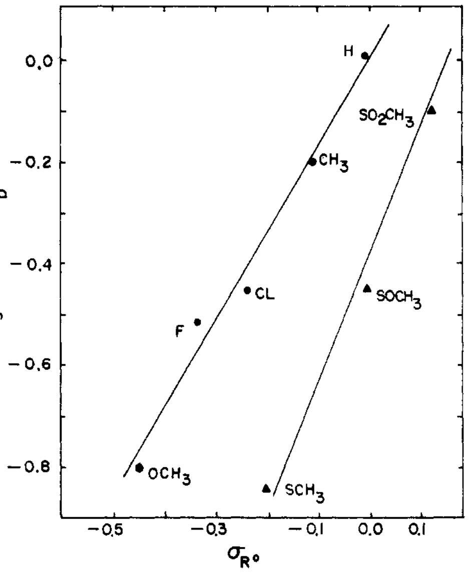


Figure 4. Hammett-type correlation of log rel k_D vs. σ_R° for the disproportionation of the 10-hydro-9-*p*-X-phenyl-9-phenanthryl radical.

Column chromatography was performed in 10 mm (qualitative), or 22 mm (preparative) i.d. glass columns (Kontes' Glass Co.). The adsorbents used were silica gel, 0.05–0.2 mm (70–325 mesh ASTM for column chromatography, E. M. Reagents), or alumina (aluminum oxide, Woelm, neutral, activity grade I).

All gas chromatography was conducted on a Perkin-Elmer 820 gas chromatograph, employing dual 5 ft × 0.5 in. columns of 15% Dexsil 300 GC on 90–100 mesh Anakrom Q, DMCS (Analabs, Inc., North Haven, Conn.), or on a 20 × 0.25 in. column containing molecular sieve 5A. All spectral data were consistent with the assigned structures.

Materials. Technical grade fluorenone was purified by distillation [bp 341.5 °C (760 mm)], followed by recrystallization from hexane (mp 82–84 °C) prior to use; 98+% fluorenone (mp 82–84 °C), Aldrich Chemical Co., Inc.) was employed without further purification. Bromobenzene, *p*-bromothioanisole, 4-bromotoluene, 4-bromofluorobenzene, *p*-bromoanisole, and *p*-bromochlorobenzene were obtained from Aldrich Chemical Co., Inc.; each was distilled prior to use. Hydrogen chloride gas was obtained from the Matheson Coleman and Bell Co. Ether was dried over sodium metal prior to use, and benzene was distilled (bp 80 °C), then dried over metallic sodium prior to use. Mercuric acetate (Fischer Scientific Co.) and *m*-chloroperoxybenzoic acid (mp 92–94 °C dec), 85% (Aldrich Chemical Co., Inc.) were used without further purification. Vinyl acetate (Eastman Kodak Co.) with 0.2% diphenylamine inhibitor was distilled (bp 72–73 °C) immediately prior to use.

Preparation of 9-*p*-X-Phenyl-9-fluorenols (X = H, CH_3, Cl, OCH_3, F, or SCH_3). The 9-*p*-X-phenyl-9-fluorenols (X = H, CH_3, Cl, OCH_3, F, or SCH_3)[45] were prepared from fluorenone and the appropriately substituted *p*-X-bromobenzenes by a Grignard reaction according to a procedure similar to one described by Curtin and Hurwitz.[4]

9-Phenyl-9-fluorenol was obtained in 80% yield, mp 108–109 °C (lit.[46] 108–109 °C) on recrystallization from benzene–petroleum ether (bp 30–60 °C).

9-*p*-Methylphenyl-9-fluorenol was obtained in 86% yield, mp 73–79 °C (lit.[47,48] 86–87 °C).

9-*p*-Chlorophenyl-9-fluorenol was obtained in 84% yield, mp 81–85 °C (lit.[48] 91–92 °C).

9-*p*-Methoxyphenyl-9-fluorenol was obtained in 64% yield. mp 76–81 °C (lit.[49] 87–88 °C).

9-*p*-Fluorophenyl-9-fluorenol was obtained in 69% yield: mp 100.5–102 °C; ir 3355, 3050, 1601, and 1195 cm^{-1}: NMR δ 2.55 (s, –OH, broad, 1), 7.12 (m, aryl, 10), and 7.61 (m, aryl, 2).

Anal. Calcd for $C_{19}H_{13}FO$: C, 82.54; H, 4.42; F, 6.79. Found: C, 82.67; H, 4.32; F, 6.71.

9-*p*-Methylthiophenyl-9-fluorenol was obtained in 80% yield: mp 60.5–62 °C; ir (KBr) 3420, 3050, 1601, and 1185 cm^{-1}; NMR δ 2.40 (s, $-SCH_3$, 3), 2.60 (s, –OH, broad, 1), 7.27 (m, aryl, 2).

Anal. Calcd for $C_{20}H_{16}OS$: C, 78.91; H, 5.30; S, 10.53. Found: C, 78.68; H, 5.41; S, 10.32.

Preparation of 9-Chloro-9-*p*-X-phenylfluorenes (X = H, CH_3, Cl, OCH_3, F, or SCH_3). The 9-chloro-9-*p*-X-phenylfluorenes (X = H, CH_3, Cl, OCH_3, F, or SCH_3) were prepared from the corresponding 9-*p*-X-phenyl-9-fluorenols by a procedure similar to one described by Curtin and Hurwitz.[4]

9-Chloro-9-phenylfluorene was obtained in 95% yield, mp 73–75 °C (lit.[50] 78–79 °C) on recrystallization from petroleum ether (bp 80–110 °C).

9-Chloro-9-*p*-methylphenylfluorene was obtained in 63% yield, mp 64–68 °C (lit.[51] 96–97 °C).

9-Chloro-9-*p*-chlorophenylfluorene was obtained in 63% yield, mp 74–76 °C (lit.[48] 79.5–80.5 °C).

9-Chloro-9-*p*-methoxyphenylfluorene was obtained in 85% yield, mp 148–150 °C (lit.[52] 149–151 °C).

9-Chloro-9-*p*-fluorophenylfluorene was obtained in 80% yield: mp 120.5–121 °C after recrystallization from dichloromethane–petroleum ether; ir 3055, 1600, and 1185 cm^{-1}; NMR aryl complex multiplets between 6.95 and 7.88 (aryl, 12).

Anal. Calcd for $C_{19}H_{12}ClF$: C, 77.49; H, 4.20; F, 6.73. Found: C, 77.42; H, 4.11; F, 6.45.

9-Chloro-9-*p*-methylthiophenylfluorene was obtained in 94% yield: mp 100–100.5 °C; ir (KBr) 3050, 2940, 1601, and 1190 cm^{-1}; NMR δ 2.48 (s, SCH_3, 3), 7.30 (m, aryl, 10), and 7.69 (m, aryl 2).

Anal. Calcd for $C_{20}H_{15}ClS$: C, 74.41; H, 4.68; S, 9.93. Found: C, 74.45; H, 4.65; S, 9.70.

Preparation of Chloromercuriacetaldehyde. The procedure employed was that of Curtin and Hurwitz,[4] which is a modification of that used by Nesmeyanov.[16] The chloromercuriacetaldehyde was obtained in 65% viel, mp 129–132 °C dec (lit.[4] 129–130 °C).

Preparation of (9-*p*-X-Phenyl-9-fluorenyl)acetaldehydes (X = H, Cl, F, CH_3, OCH_3, SCH_3, $SOCH_3$, SO_2CH_3). The aldehydes were prepared by the method of Curtin and Hurwitz[4] as modified by Vittimberga.[13] In a typical procedure 0.12 mol of 9-chloro-9-*p*-X-phenylfluorene was placed in a 500-ml three-necked flask equipped with mechanical stirrer, glass stopper, and reflux condenser fitted with anhydrous calcium chloride drying tube. After complete dissolution of the solid in 200 ml of anhydrous benzene, 34.9 g (0. 25 mol) of chloromercuriacetaldehyde was added and the mixture was stirred at ambient temperature for 18 h. The mixture was then heated at reflux for 2 h on a steam bath, cooled to room temperature, and filtered to remove insoluble mercury salts.

The benzene solution was then washed repeatedly with 10% aqueous sodium carbonate solution until all red-brown mercury salts, precipitated by the washings, were removed (usually 4 × 150 ml of 10% aqueous sodium carbonate). Following this, the benzene layer was washed several times with water and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the benzene was evaporated in vacuo to yield a solid (X = Cl, CH_3, OCH_3, or SCH_3), or a viscous amber liquid (X = H or F), which yielded an amorphous solid on standing overnight. Recrystallization from benzene–petroleum ether gave pure aldehyde in the cases of X = Cl, CH_3, OCH_3, or SCH_3, but failed in the cases of the hydrogen and fluoro-substituted compounds.

The aldehydes (X = H or F) were obtained in pure form by conversion to their respective diethyl acetals, followed by reconversion (after purification) to the aldehyde form by a procedure adapted from Vogel.[53] To accomplish this, the aldehydes were heated at reflux for 15 min in an excess of absolute ethyl alcohol, followed by cooling to crystallize the acetals. The purified acetals were then reconverted to their respective aldehydes by heating at reflux for 2 h in an acidic dioxane solution. The aldehydes were extracted from the crude reaction mixtures with diethyl ether, and, after drying, the drying agent and solvent were removed as usual. The residual powdered aldehydes were then recrystallized to yield pure aldehydes.

(Phenyl-9-fluorenyl)acetaldehyde was obtained in 80% yield, mp 114.5–115 °C (lit.[13] 114–115 °C).

(9-*p*-Methylphenyl-9-fluorenyl)acetaldehyde was obtained in 76% yield: mp 112–113 °C; ir (KBr) 1715, 1447, 807, 750, 733, and 680 cm^{-1}; NMR δ 2.22 (s, $-CH_3$, 3), 3.27 (d, $-CH_2-$, 2, $J = 2.5$ Hz), 7.17 (m, aryl, 10), 7.68 (m, aryl, 2), and 8.91 (t, –CHO, 1, $J = 2.5$ Hz).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.41; H, 5.98.

(9-*p*-Chlorophenyl-9-fluorenyl)acetaldehyde was obtained in 91% yield: mp 109–110 °C; ir (KBr) 1718, 1486, 1445, 1087, 1006, 752, 730, and 674 cm^{-1}; NMR δ 323 (d, $-CH_2-$, 2, $J = 2.5$ Hz), 7.15 (m, aryl, 10), 7.69 (m, aryl, 2), and 8.85 (t, –CHO, 1, $J = 2.5$ Hz).

Anal. Calcd for $C_{21}H_{15}OCl$: C, 79.12; H, 4.74; Cl, 11.12. Found: C, 78.98; H, 4.99; Cl, 10.89.

(9-*p*-Methoxyphenyl-9-fluorenyl)acetaldehyde was obtained in 92% yield: mp 133–134 °C; ir (KBr) 1712, 1447, 1253, 1186, 1030, 828, 755, and 739 cm^{-1}; NMR δ 3.22 (d, $-CH_2-$, 2, $J = 2.5$ Hz), 3.63 (s, $-OCH_3$, 3), 6.64 (d, aryl, 2, $J = 9$ Hz), 6.97 (d, aryl, 2, $J = 9$ Hz), 7.27 (m, aryl, 6), 7.73 (m, aryl, 2), and 8.99 (t, –CHO, 1, $J = 2.5$ Hz).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.82. Found: C, 84.04; H, 5.55.

(9-*p*-Fluorophenyl-9-fluorenyl)acetaldehyde was obtained in 88% yield: mp 99.5–100.5 °C on recrystallization from diethyl ether–petroleum ether (bp 30–60 °C); ir (KBr) 3055, 2950, 2850, 2755, 1715, 1601, and 1195 cm^{-1}; NMR δ 3.32 (d, $-CH_2-$, 2, $J = 2.5$ Hz), 7.03 (m, aryl, 4), 7.33 (m, aryl, 6), 7.76 (m, aryl, 2), and 8.70 (t, –CHO, 1, $J = 2.5$ Hz).

Anal. Calcd for $C_{21}H_{15}FO$: C, 83.43; H, 5.00; F, 6.28. Found: C, 83.19; H, 4.90; F, 6.34.

(9-*p*-Methylthiophenyl-9-fluorenyl)acetaldehyde was obtained in 62% yield: mp 99–100 °C (benzene–petroleum ether); ir (KBr) 3055, 2955, 2855, 2760, 1715, 1600, and 1185 cm^{-1}; NMR δ 2.24 (s, $-SCH_3$, 3), 3.24 (d, $-CH_2-$, 2, $J = 2.5$ Hz), 6.92 (m, aryl, 4), 7.27 (m, aryl, 6), and 7.63 (m, aryl, 2), and 8.75 (t, –CHO, 1, $J = 2.5$ Hz).

Anal. Calcd for $C_{22}H_{18}OS$: C, 79.97; H, 5.48; S, 9.70. Found: C, 79.79; H, 5.27; S, 9.66.

Preparation of (9-*p*-Methylsulfinylphenyl-9-fluorenyl)acetaldehyde (X = $SOCH_3$). This aldehyde was prepared by adaption of the method of McIntosh, Goodbrand, and Masse[17] for the oxidation of thiatane derivatives. (9-*p*-Methylthiophenyl-9-fluorenyl)acetaldehyde (9.90 g, 3×10^{-2} mol) was dissolved in 50 ml of dichloromethane at 0 °C in a 500-ml three-necked flask equipped with magnetic stirrer, pressure-equalizing dropping funnel, condenser fitted with anhydrous calcium chloride drying tube, and thermometer. At 0 °C, 6.72 g (3.3×10^{-2} mol) of *m*-chloroperoxybenzoic acid was dissolved in 150 ml of dichloromethane. This ice-cold solution was charged into the dropping funnel and added to the aldehyde solution over a 15-min period at a rate such as to maintain the temperature of the mixture between 0 and 5 °C. The mixture was then stirred at 0 °C for 3 h.

The solution was diluted with 100 ml of cold dichloromethane and extracted with 4 × 250 ml of 10% aqueous sodium carbonate and 2 × 250 ml of distilled water. After drying over anhydrous sodium sulfate, the solution was filtered and solvent was removed in vacuo to give an amber-colored solid (X = $SOCH_3$).

(9-*p*-Methylsulfinylphenyl-9-fluorenyl)acetaldehyde was obained in 87% yield: mp 160–160.5 °C (benzene); ir (KBr) 3050, 2940, 2850, 2750, 1715, 1600, 1190, and 1070 cm^{-1}; NMR δ 2.60 (s, $-SOCH_3$, 3), 3.37 (d, $-CH_2-$, 2, $J = 2.5$ Hz), 7.30 (m, aryl, 10), 7.73 (m, aryl, 2), and 8.83 (t, –CHO, 1, $J = 2.5$ Hz).

Anal. Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24; S, 9.26. Found: C, 76.47; H, 4.97; S, 9.20.

Preparation of (9-*p*-Methylsulfonylphenyl-9-fluorenyl)acetaldehyde (X = SO_2CH_3). The aldehyde (X = SO_2CH_3) was also prepared by an adaptation of the methods employed by McIntosh and co-workers[17] for the oxidations of thiatane derivatives. (9-*p*-methylthiophenyl-9-fluorenyl)acetaldehyde (15.000 g, 4.54×10^{-2} mol) was dissolved in 100 ml of dichloromethane at 0 °C in a 500-ml three-necked flask equipped with magnetic stirrer, dropping funnel, thermometer, and reflux condenser fitted with anhydrous calcium chloride drying tube. At 0 °C, 20.760 g (1.21×10^{-1} mol) of *m*-chloroperoxybenzoic acid was dissolved in 200 ml of dichloromethane. The latter ice-cold solution was charged into the dropping funnel, and added to the aldehyde solution over a period of 30 min, at a rate such as to maintain the solution temperature between 0 and 5 °C. The mixture was then stirred at 0 °C for 3 h and, finally, at ambient temperature for 3 h.

After dilution with 200 ml of dichloromethane, the reaction mixture was extracted with 4 × 250 ml of 10% aqueous sodium carbonate solution and 2 × 250 ml of distilled water. The dichloromethane solution was dried over anhydrous sodium sulfate. Subsequently, the drying agent was removed by filtration and the solvent by evaporation under vacuum leaving a thick amber colored oil as residue, which crystallized on standing overnight.

(9-*p*-Methylsulfonylphenyl-9-fluorenyl)acetaldehyde (X = SO_2CH_3) was obtained in 66.5% yield: mp 161.5–162 °C (benzene–petroleum ether); ir (KBr) 3055, 2940, 2920, 2840, 2750, 1712, 1600, 1320, and 1160 cm^{-1}; NMR δ 2.83 (s, $-SO_2CH_3$, 3), 3.32 (d, $-CH_2-$, 2, J = 2.5 Hz), 7.13 (m, aryl, 10), 7.58 (m, aryl, 2), and 8.79 (t, -CHO, 1, J = 2.5 Hz).

Anal. Calcd for $C_{22}H_{18}O_3S$: C, 72.91; H, 5.01; S, 8.85. Found: C, 73.15; H, 5.14; S, 8.85.

Materials, Equipment, and Procedure Used in the Decarbonylations. *o*-Dichlorobenzene (Matheson Coleman and Bell) was purified by successive washing with concentrated sulfuric acid, 10% sodium carbonate solution, and distilled water. Drying over anhydrous calcium chloride and distillation gave pure *o*-dichlorobenzene (bp 178.5–179 °C). Di-*tert*-butyl peroxide (K & K Laboratories, Inc.) was distilled before use, bp 55–56 °C (120 mm). Benzyl mercaptan (Aldrich Chemical Co., Inc.) was used without further purification.

For the decarbonylations, the reaction vessel used was a 50-ml Claisen distilling flask with the side arm removed. One neck of the flask was fitted with a rubber serum stopper (through which the peroxide was injected), and the other neck, immediately prior to immersion of the flask in the oil bath, was connected to the gas measuring system by means of Latex rubber tubing.

The constant temperature bath, shaking apparatus, and gas measuring system are shown in Figure 2 (see paragraph at end of paper regarding supplementary material). The glass, constant temperature bath (Lab-Line Instruments, Inc.; 800 W), containing hydrogenated cottonseed oil (Arthur H. Thomas Co.) was maintained at 140 ± 0.1 °C with a Lux Scientific Corp. vertical relay, and a Jumo contact thermometer.

In the standard decarbonylation reaction procedure, 12 ml of a 0.5 M solution of the aldehyde in *o*-dichlorobenzene was pipetted into the reaction vessel; the solution was degassed through five successive freeze–vacuum–thaw cycles, and then dry nitrogen was introduced in order to provide an inert atmosphere. When the decarbonylations were conducted in the presence of benzyl mercaptan, 0.14 ml (0.0012 mol, 20 mol %) of this compound was introduced prior to the degassing procedure. The reaction vessel was then quickly attached to the gas measuring system (prepurged with dry nitrogen gas).

The reaction vessel (Figure 3) (see paragraph at end of paper regarding supplementary material) was supported at H by means of a swivel clamp so that the flask was immersed in the oil bath up to the mark M, and attached at point J to a shaker arm K, so that the vessel could be rocked back and forth at 80 swings per minute through an arc of 6 in. After immersion in the oil bath, all connections were tightly secured and the mixture was equilibrated for 10 min. The expansion gas escaping from the reaction vessel during this time (at L) was passed through a water-cooled spiral condenser, and allowed to escape at C after having entered at A. Following the equilibration period, 0.225 ml (0.0212 mol, 20 mol %) of di-*tert*-butyl peroxide was injected through serum cap I into the reaction vessel, and the shaker was started. The decarbonylation gas was allowed to enter buret E through port A with stopcock B open to the reaction vessel, buret E, and leveler G, with the stopcock D open to B but closed to C. When a reading was to be made, stopcock B was closed to A and left open to E and G. Water was quickly drained from buret F so that the water level in leveler G was quickly adjusted. The gas volume was read; and then stopcock B was reopened to the reaction vessel. After 120 min of reaction time, the shaker was halted, an additional 0.225 ml of di-*tert*-butyl peroxide was injected through I, and the shaker was restarted. The decarbonylation reaction was carried out for a total of 330 min. At the end of each run, the reaction solution was quenched by immediately cooling the reaction vessel in ice, and retained for the product analysis.

Isolation of the Products from the Decarbonylation Reactions. In a typical isolation procedure (X = H, CH, Cl, OCH_3, F, or SCH_3), the reaction solution was concentrated in vacuo to remove the *o*-dichlorobenzene and the resulting residue was chromatographed on a 22 × 350 mm column containing 120 g of alumina (Woelm, neutral, activity I). Elution with mixtures of petroleum ether–benzene–ether–methanol in increasing polarity (average flow rate 40 ml/6 min) separated the products from unreacted aldehyde. In each case, the course of chromatography was monitored by analytical, simultaneous TLC run side by side on a Polygram Sil G/UV_{254} precoated plastic TLC plate, using benzene–petroleum ether (3:1) as the developer, and visualizing with uv light and iodine. The yellow oils obtained in these chromatographic fractions have been found to be the result of an oxidation–reduction reaction of the aldehyde on the absorbent surface.[26] After combination of the product aromatic hydrocarbon containing fractions, the NMR spectrum ($CDCl_3$) of the product mixture was recorded. From knowledge of the chemical shifts and numerous integrations, the percentages of the components in the product mixtures were calculated.

In the cases of the decarbonylation of the methylsulfinyl and methylsulfonyl substituted aldehydes (X = $SOCH_3$ or SO_2CH_3) the same general procedure was followed; however, silica gel 0.05–0.20 mm (70–325 mesh ASTM, E. M. Reagents) was used as the absorbent in place of alumina, and elution was carried out with mixtures of petroleum ether, ether, and methanol in increasing polarity. Again, the course of the chromatography was monitored by TLC; appropriate fractions were combined, and numerous integrations of the NMR spectra ($CDCl_3$) permitted calculation of the respective percentages of products of the decarbonylation reactions. Fractional recrystallization proved ineffective toward the separation and isolation of the components of these product mixtures. Attempts were made to separate the mixture components using a Perkin-Elmer 820 gas chromatograph employing matched 5 ft × 0.25 in. columns of 15% Dexsil 300 GC on 90–100 mesh Anakrom Q DMCS (Analabs). Separation of product mixtures was effected in the cases of the aldehydes where X = H, F, and CH_3SO_2. However, none of the products could be isolated by this method.

Unless otherwise stated, small samples of **8** were obtained by column chromatography on neutral alumina. Separation of **6** and **7** was effected by techniques of preparative thin layer chromatography on silica gel. In both methods mixtures of petroleum ether and benzene were used as eluents. Bands were carefully scraped from the plate and the organic compounds were then recovered by extraction with chloroform. Drying and evaporation of the solvent left a residue which was further purified by recrystallization from an appropriate solvent system.

Attempts to transfer these procedures to dry column chromatography using Woelm dry column grade silica gel (activity III, 30 mm) in 35-mm i.d. Nylon tubing, and the developer which gae a separation in PLC, failed to provide a useful separation of the mixture components. This method was therefore abandoned. Separation of products was made by chromatography as usual and relative percent yields determined by NMR.

Thermal Stability of (9-Phenyl-9-fluorenyl)acetaldehydes. The decarbonylation procedure was carried out as previously described, but without di-*tert*-butyl peroxide. After 330 min of heating, the *o*-dichlorobenzene was removed in vacuo. The NMR spectrum ($CDCl_3$) of the resulting paste was identical with that of starting material. Column chromatography of this residue on neutral alumina yielded only the starting aldehyde, and a yellow oil resulting from the reaction of the aldehyde on the alumina surface.[26] Similar results were obtained with 3 ml of 0.5 M solutions of the other aldehydes used in this study.

Product Stability under Reaction Conditions. A mixture consisting of 25% (by mole) **7** (X = H), 25% **8** (X = H), and 50% **6** (X = H) and weighing 240 mg was dissolved in 5 ml of *o*-dichlorobenzene. The solution was degassed, 0.04 ml (2.1 × 10^{-4} mol) of di-*tert*-butyl peroxide was added, and the mixture was heated at 140 °C for 330 min. The percentages of **6**, **7**, and **8** (X = H) redetermined by integration of the NMR spectrum, after removal of solvent, and also after column chromatography on neutral alumina, were found to be unchanged. Repetition of this experiment in the presence of 0.07 ml (1.2 × 10^{-4} mol) of benzyl mercaptan also showed the product percentages to be unaffected by the reaction conditions, or chromatographic workup.

Calculation of Percentages from NMR Spectra. Accuracy Test. A mixture of **6** (x , och_3) and **7** (X = OCH_3) was prepared gravimetrically from pure samples so that the percentages were 46.7 and 53.3%, respectively. The mixture was dissolved in deuteriochloroform, the NMR spectrum recorded, and the product percentages calculated from the averaged integrations. The average value for the percentage of **7** (X = OCH_3) was 53.8% so that the error is assumed to be not more than ±1%. Similar results were obtained with X = H.

Decarbonylations in the Presence of Benzyl Mercaptan. Products from the Decarbonylation of 5 (X = H). The hydrocarbon mixture consisted of 53% 9-phenylphenanthrene (**6**, X = H), 28% 9,10-dihydrophenylphenanthrene (**7**, X = H), and 19% 9-methyl-9-phenylphenanthrene (**8**, X = H).

9-Phenylphenanthrene was recrystallized from petroleum ether (bp 30–60 °C), mp 104–105 °C (lit.[11] mp 104–105 °C).

9,10-Dihydro-9-phenylphenanthrene was recrystallized from petroleum ether (bp 30–60 °C), mp 78.5–80 °C (lit.[54] mp 79–80 °C).

9-Methyl-9-phenylfluorene was recrystallized from petroleum ether, mp 84.5–85 °C (lit.[55] mp 84–85 °C).

Products from the Decarbonylation of 5 (X = CH_3). The hydrocarbon mixture consisted of 54% 9-*p*-methylphenylphenanthrene (**6** X = CH_3), 26% 9,10-dihydro-9-*p*-methyphenylphenanthrene (**7**, X = CH_3), and 29% 9-methyl-9-*p*-methylphenylfluorene (**8**, X =

CH_3). Samples of compounds **6** and **7** were obtained by preparative layer chromatography. The sulfur containing compounds **9** and **10** (X = CH_3)[56] were isolated by thin layer chromatography on silica gel using petroleum ether–benzene (10:1) as the solvent. These products were then characterized as dibenzyl disulfide, **9**, and *trans*-1-(9-*p*-methylphenyl-9-fluorenyl)-4-phenyl-3-thia-1-butene (**10**, X = CH_3).

9-*p*-Methylphenylphenanthrene was recrystallized from petroleum ether, mp 91.5–92.5 °C (lit.[57] mp 90–91 °C).

9,10-Dihydro-9-*p*-methylphenylphenanthrene was recrystallized from petroleum ether: mp 78–79.5 °C; ir (KBr) 1443, 812, 766 and 746 cm^{-1}; NMR δ 2.26 (s, -CH_3, 3), 3.12 (d, -CH_2, 2, J = 7.5 Hz), 4.12 (t, -$CHAr_2$, 1, J = 7.5 Hz), 7.14 (m, aryl, 10), and 7.80 (m, aryl, 2).

Anal. Calcd for $C_{21}H_{18}$: C, 93.27; H. 6.71. Found: C, 93.08; H, 6.61.

9-Methyl-9-*p*-methylphenylfluorene was recrystallized from ethanol: mp 57.5–58.5 °C; ir (KBr) 1443, 1018, 800, 768, 746, and 733 cm^{-1}; NMR δ 1.78 (s, -CH_3, 3), 2.20 (s, ArCH_3, 3), 6.85 (m, aryl, 4), 7.15 (m, aryl, 6), and 7.62 (m, aryl, 2).

Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.44; H, 6.75.

Dibenzyl disulfide was obtained as a viscous liquid (lit.[58] mp 69–70 °C). The infrared spectrum (film), almost identical with that of a pure sample, showed major absorptions at 1493, 1453, 763, and 695 cm^{-1}. The NMR spectrum showed bands at δ 3.51 (s, -CH_2-, 4) and 7.18 (s, aryl, 10).

trans-1-(9-*p*-Methylphenyl-9-fluorenyl)-4-phenyl-3-thia-1-butene was obtained as a viscous liquid which would not crystallize: ir (film) 3049, 3030, 1508, 1493, 1449, 945, 823, 749, and 698 cm^{-1}; NMR δ 2.16 (s, -CH_3, 3), 3.60 (s, -CH_2, 2), 5.67 (d, -CH=CH, 1, J = 15 Hz), 6.16 (d, -CH=CH, 1, J = 15 Hz), 6.75 (s, aryl, 5), 7.07 (m, aryl, 10), and 7.55 (m, aryl, 2).

Anal. Calcd for $C_{29}H_{24}S$: C, 86.10; H, 5.98; S, 7.92. Found: C, 86.05; H, 5.78; S, 8.07.

Products from the Decarbonylation of 5 (X = Cl). The hydrocarbon mixture consisted of 54% 9-*p*-chlorophenylphenanthrene (**6**, X = Cl), 31% 9,10-dihydro-9-*p*-chlorophenylphenanthrene (**7**, X = Cl), and 15% 9-methyl-9-*p*-chlorophenylfluorene (**8**, X = Cl).

9-*p*-Chlorophenylphenanthrene was recrystallized from petroleum ether: mp 131–133 °C; ir (KBr) 1488, 1087, 1013, 833, 822, 769, 750 and 727 cm^{-1}; NMR δ 7.67 (m, aryl, 11) and 8.71 (m, aryl, 2).

Anal. Calcd for $C_{20}H_{13}Cl$: C, 83.19; H, 4.54; Cl, 12.28. Found: C, 83.30; H, 4.28; Cl, 12.43.

9,10-Dihydro-9-*p*-chlorophenylphenanthrene was recrystllized from petroleum ether: mp 108–109.5 °C; ir (KBr) 1488, 1087, 1012, 836, 818, 776, 752, 739, and 724 cm^{-1}; NMR δ 3.13 (d, -CH_2-, 2, J = 7.5 Hz), 4.15 (t, -$CHAr_2$, 1, J = 7.5 Hz), 7.16 (m, aryl, 10), and 7.84 (m, aryl, 2).

Anal. Calcd for $C_{20}H_{15}Cl$: C, 82.61; H, 5.20; Cl, 12.19. Found: C, 82.64; H, 4.98; Cl, 12.28.

9-Methyl-9-*p*-chlorophenylfluorene was recrystallized from petroleum ether: mp 111–113 °C; ir (KBr) 1488, 1443, 1089, 1011, 766, 758, and 736 cm^{-1}; NMR δ 1.80 (s, -CH_3, 3), 7.15 (m, aryl, 10), and 7.64 (m, aryl, 2).

Anal. Calcd for $C_{20}H_{15}Cl$: C, 82.61; H, 5.20; Cl, 12.19. Found: C, 82.62; H, 5.37; Cl, 12.08.

Products from the Decarbonylation of 5 (X = OCH_3). The hydrocarbon mixture consisted of 54% of 9-*p*-methoxyphenylphenanthrene (**6**, X = OCH_3), 23% of 9,10-dihydro-9-*p*-methoxyphenylphenanthrene (**7**, X = OCH_3), and 23% of 9-methyl-9-*p*-methoxyphenylfluorine (**8**, X = OCH_3).

9-*p*-Methoxyphenylphenanthrene was recrystallized from petroleum ether–benzene, mp 156–157.5 °C (lit.[59] mp 155.5–156 °C).

9,10-Dihydro-9-*p*-methoxyphenylphenanthrene was recrystallized from petroleum ether: mp 106–107 °C; ir (KBr) 1511, 1449, 1247, 1176, 1031, 870, 824, 767, and 752 cm^{-1}; NMR δ 3.14 (d, -CH_2-, 2, J = 7.5 Hz), 3.72 (s, -OCH_3, 3), 4.12 (t, $CHAr_2$, 1, J = 7.5 Hz), 7.09 (m, aryl, 10), and 7.82 (m, aryl, 2).

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.94; H, 6.18.

9-Methyl-9-*p*-methoxyphenylfluorene was recrystallized from petroleum ether: mp 138–140 °C; ir (KBr) 1504, 1439, 1247, 1179, 1031, 766, 749, and 736 cm^{-1}; NMR δ 1.81 (s, -CH_3, 3), 3.69 (s, -OCH_3, 3), 6.70 (d, aryl, 2, J = 8.5 Hz), 7.05 (d, aryl, 2, J = 8.5 Hz), 7.18 (m, aryl, 6), and 7.71 (m, aryl, 2).

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.01; H, 6.35.

Products from the Decarbonylation of 5 (X = F). The hydrocarbon mixture consisted of 68% 9-*p*-fluorophenylphenanthrene (**6**, X = F), 16% 9,10-dihydro-9-*p*-fluorophenylphenanthrene (**7**, X = F), and 16% 9-methyl-9-*p*-fluorophenylfluorene (**8**, X = F).

9-*p*-Fluorophenylphenanthrene was recrystallized from absolute methanol: mp 148.5–149 °C; ir ($CHCl_3$) 3140, 1605, 1510, 1440, and 1220 cm^{-1}; NMR δ 7.65 (m, aryl, 11) and 8.73 (m, aryl, 2).

Anal. Calcd for $C_{20}H_{13}F$: C, 88.21; H, 4.81; F. 6.98. Found: C, 88.12; H, 4.68; F, 7.20.

9,10-Dihydro-9-*p*-fluorophenylphenanthrene was recrystallized from absolute methanol: mp 89.5–90 °C; ir ($CHCl_3$) 3145, 2955, 2880, 1600, and 1450 cm^{-1}; NMR δ 3.09 (d, -CH_2-, 2, J = 7.5 Hz), 4.09 (t, -$CHAr_2$, 1, J = 7.5 Hz), 6.98 (m, aryl, 10), and 7.69 (m, aryl, 2).

Anal. Calcd for $Cinfc_{20}H_{15}F$: C, 87.56; H, 5.51; F, 6.93. Found: C, 87.42; H, 5.37; F. 7.21.

9-Methyl-9-*p*-fluorophenylfluorene was recrystallized from petroleum ether (bp 30–60 °C): mp 113–113.5 °C; ir (KBr) 3050, 2940, 1600, and 1460 cm^{-1}; NMR δ 1.80 (s, -CH_3, 3), 6.97 (m, aryl, 10), and 7.59 (m, aryl, 2).

Anal. Calcd for $C_{20}H_{15}F$: C, 87.56; H, 5.51; F, 6.93. Found: C, 87.58; H, 5.51; F, 6.77.

Products from the Decarbonylation of 5 (X = SCH_3). The hydrocarbon mixture consisted of 73% 9-*p*-methylthiophenylphenanthrene (**6**, X = SCH_3), 15.5% 9,10-dihydro-9-*p*-methylthiophenylphenanthrene (**7**, X = SCH_3), and 11.5% 9-methyl-9-*p*-methylthiophenylfluorene (**8**, X = SCH_3).

9-*p*-Methylthiophenylphenanthrene was recrystallized from absolute methanol: mp 139.5–140.5 °C; ir ($CHCl_3$) 3050, 3020, 2940, 1600, 1500, 1460, 1440, and 1210 cm^{-1}; NMR δ 2.49 (s, -SCH_3, 3), 7.45 (m, aryl, 11), and 8.67 (m, aryl, 2).

Anal. Calcd for $C_{21}H_{16}S$: C, 83.96; H, 5.37; S, 10.67. Found: C, 83.86; H, 5.44; S, 10.67.

9,10-Dihydro-9-*p*-methylthiophenylphenanthrene was recrystallized from absolute methanol: mp 99.5–100.5 °C; ir ($CHCl_3$) 3050, 3020, 2950, 2880, 1600, 1500, 1440, and 1230 cm^{-1}; NMR δ 2.33 (s, -SCH_3, 3), 3.07 (d, -CH_2-, 2, J = 7.5 Hz), 3.93 (t, -$CHAr_2$, 1, J = 7.5 Hz), 6.93 (m, aryl, 10), and 7.56 (m, aryl, 2).

Anal. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00; S, 10.60. Found: C, 83.19; H, 5.56; S, 10.26.

9-Methyl-9-*p*-methylthiophenylfluorene was recrystallized from petroleum ether: mp 101–103 °C dec; ir ($CHCl_3$) 3055, 3025, 2950, 2880, 1600, 1500, and 1450 cm^{-1}; NMR δ 1.77 (s, -CH_3, 3), 2.33 (s, -SCH_3, 3), 7.13 (m, aryl, 10), and 7.63 (m, aryl, 2). The amount of pure material available was insufficient for combustion analysis; however, mass spectrometry showed a parent peak at *m/e* 302. Other fragmentation peaks consistent with the assigned structure were also observed.

Products from Decarbonylation of 5 (X = $SOCH_3$). The hydrocarbon mixture consisted of 66% 9-*p*-methylsulfinylphenylphenanthrene (**6**, X = $SOCH_3$), 21% 9,10-dihydro-9-*p*-methylsulfinylphenylphenanthrene (**7**, X = $SOCH_3$), and 13% 9-methyl-9-*p*-methylsulfinylphenylfluorene (**8**, X = $SOCH_3$). Repeated efforts to separate the hydrocarbon mixture into pure **6**, **7**, and **8** by preparative thin layer, or dry column, or normal column chromatography on Florisil, on silica gel, or on alumina failed to give homogeneous samples. However, a small sample of **6** could be isolated by preparative thin layer chromatography.

9-*p*-Methylsulfinylphenylphenanthrene was recrystallized twice from petroleum ether, followed by twice from methanol: mp 124–125 °C; ir ($CHCl_3$) 3055, 2905, 1600, 1400, 1450, and 1075 cm^{-1}; NMR δ 2.73 (s, -$SOCH_3$, 3), 7.56 (m, aryl, 11), and 8.63 (m, aryl, 2).

Anal. Calcd for $C_{21}H_{16}SO$: C, 79.71; H, 5.10; S, 10.13. Found: C, 79.43; H, 5.28; S, 10.02.

It was possible to further demonstrate the identity of the mixture by reduction with lithium aluminum hydride using an adaptation of the general procedure of Djerassi and co-workers.[60] In a 50-ml flask fitted with reflux condenser and anhydrous calcium chloride drying tube were placed 80 mg (2.07 mmol) of lithium aluminum hydride and 4 ml of dry tetrahydrofuran. To this was added, portionwise over 10 min, a solution of 200 mg of the hydrocarbon mixture in 10 ml of dry tetrahydrofuran. The mixture was heated at reflux for 2 h, cooled to room temperature, and quenched by careful titration with distilled water. The resultant paste was diluted with 30 ml of diethyl ether, filtered, and washed with 20 ml of ether. The combined ether layers were extracted with 3 × 60 ml of distilled water and dried over anhydrous sodium sulfate. Removal of the drying agent by filtration, followed by evaporation of the solvent in vacuo, gave 193 mg of white amorphous solid.

The infrared spectrum of the starting mixture showed a strong sulfoxide SO band at 1060 cm^{-1}, which was absent in the infrared spectrum ($CHCl_3$ solution) of the reduced mixture. The NMR spectrum of the starting mixture showed signals at δ 1.81 (s, CH_3), 2.58 (s, $SOCH_3$), 2.73 (s, $SOCH_3$), 3.11 (d, -CH_2-, J = 7.5 Hz), 4.09 (t, -$CHAr_2$,

J = 7.5 Hz), 7.05 (m, aryl), 7.57 (m, aryl), and 8.67 (m, aryl), indicating a mixture consisting of 66% **6**, 21% **7**, and 13% **8** (X = $SOCH_3$). The NMR spectrum ($CDCl_3$) of the mixture after treatment with lithium aluminum hydride and workup showed signals at δ 1.74 (s, $-CH_3$), 2.35 (s, $-SCH_3$), 2.47 (s, $-SCH_3$), 3.10 (d, $-CH_2-$, J = 7.5 Hz), 4.13 (t, $-CHAr_2$, J = 7.5 Hz), 7.09 (m, aryl), 7.74 (m, aryl), and 8.59 (m, aryl), indicating a mixture consisting of 67% **6**, 20% **7**, and 13% **8** (X = SCH_3). The character of the reduced mixture was further confirmed by chromatographic separation in the manner described above for the decarbonylation of **5** (X = SCH_3).

Products from the Decarbonylation of 5 (X = SO_2CH_3). The hydrocarbon mixture consisted of 56.5% 9-*p*-methylsulfonylphenylphenanthrene (**6**, X = SO_2CH_3), 33% 9,10-dihydro-9-*p*-methylsulfonylphenylphenanthrene (**7**, X = SO_2CH_3), and 10.5% 9-methyl-9-*p*-methylsulfonylphenylphenanthrene (**8**, X = SO_2CH_3). Attempts to isolate **6**, **7**, and **8** by means of preparative thin layer chromatography, dry column chromatography, or normal column chromatography on silica gel, Florisil, or neutral alumina all failed to yield homogeneous samples. The NMR spectrum displayed signals at δ 1.79 (s, $-CH_3$, **8**), 2.92 (s, $-SO_2CH_3$, **7** and **8**), 3.04 (s, $-SO_2CH_3$, **6**), 3.13 (d, partially overlapped by the singlet at 3.04, $-CH_2-$, **7**), 4.09 (t, $-CHAr_2$, J = 7.5 Hz, **7**), 7.15 (m, aryl), 7.91 (m, aryl), and 8.62 (m, aryl, **6**) in agreement with a mixture of **6**, **7**, and **8** (X = SO_2CH_3).

Decarbonylation of **5** (X = SO_2CH_3) in the absence of benzyl mercaptan led to a mixture of **6** and **7**, and no **8**. Samples **6** and **7** were separable from this mixture by means of preparative thin layer chromatography on silica gel [20 mg of mixture per 1000-μ plate, 16 successive developments with benzene–chloroform (5:1) each].

9-*p*-Methylsulfonylphenylphenanthrene was recrystallized from absolute methanol: mp 163.5–164.5 °C; ir ($CHCl_3$) 3050, 2950, 1600, 1500, 1470, 1320, and 1160 cm^{-1}; NMR ($CDCl_3$) δ 3.07 (s, $-SO_2CH_3$, 3), 7.64 (m, aryl, 11), and 8.67 (m, aryl, 2).

Anal. Calcd for $C_{21}H_{16}SO_2$: C, 75.88; H, 4.85; S, 9.65; O, 9.62. Found: C, 75.59; H, 4.71; S, 9.68; O, 9.85.

9,10-Dihydro-9-*p*-methylsulfonylphenylphenanthrene was recrystallized from absolute methanol: mp 127.5–129.5 °C; ir 3050, 3020, 2950, 2900, 1600, 1315, and 1160 cm^{-1}; NMR δ 2.92 (s, $-SO_2CH_3$, 3), 3.17 (d, $-CH_2-$, 2, J = 7.5 Hz), 4.13 (t, $-CHAr_2$, 1, J = 7.5 Hz), 7.05 (m, aryl, 10), and 7.71 (m, aryl, 2). The amount of material available was insufficient for a combustion analysis; however, mass spectrometry showed a parent peak at *m/e* 334. Other fragmentation peaks consistent with the assigned structure were also observed.

Registry No.—**5** (X = H), 5043-46-9; **5** (X = CH_3), 31462-50-7; **5** (X = Cl), 60253-20-5; **5** (X = OCH_3), 31462-49-4; **5** (X = F), 60253-21-6; **5** (X = SCH_3), 60253-22-7; **5** (X = $SOCH_3$), 60253-23-8; **5** (X = SO_2CH_3), 60253-24-9; **6** (X = H), 844-20-2; **6** (X = CH_3), 37842-68-5; **6** (X = Cl), 37842-69-6; **6** (X = OCH_3), 37842-67-4; **6** (X = F), 60253-25-0; **6** (X = SCH_3), 60253-26-1; **6** (X = $SOCH_3$), 60253-27-2; **6** (X = SO_2CH_3), 60253-28-3; **7** (X = H), 5235-80-3: **7** (X = CH_3), 37842-71-0; **7** (X = Cl), 37842-72-1; **7** (X = OCH_3), 37842-70-9; **7** (X = F), 60253-01-2; **7** (X = SCH_3), 60253-02-3; **7** (X = $SOCH_3$), 60253-03-4; **7** (X = SO_2CH_3), 60253-04-5; **8** (X = H), 56849-83-3; **8** (X = CH_3), 60253-05-6; **8** (X = Cl), 60253-06-7; **8** (X = OCH_3), 60253-07-8; **8** (X = F), 60253-08-9; **8** (X = SCH_3), 60253-09-0; **8** (X = $SOCH_3$), 60253-10-3; **8** (X = SO_2CH_3), 60253-11-4; **9**, 150-60-7; **10** (X = CH_3), 60253-12-5; U· (R = H), 60253-13-6; U· (R = CH_3), 60253-14-7; U· (R = Cl), 60253-15-8; U· (R = OCH_3), 60253-16-9; U· (R = F), 60253-17-0; U· (R = SCH_3), 60253-18-1; U· (R = $SOCH_3$), 60253-19-2; U· (R = SO_2CH_3), 60252-86-0; R· (X = H), 60252-87-1; R· (X = CH_3), 60252-88-2; R· (X = Cl), 60252-89-3; R· (X = OCH_3), 60252-90-6; R· (X = F), 60252-91-7; R· (X = SCH_3), 60252-92-8; R· (X = $SOCH_3$), 60252-93-9; R· (X = SO_2CH_3), 60252-94-0; bromobenzene, 108-86-1; *p*-bromothioanisole, 104-95-0; *p*-bromochlorobenzene, 106-39-8; 4-bromotoluene, 106-38-7; 4-bromofluorobenzene, 460-00-4; *p*-bromoanisole, 104-92-7; 9-phenyl-9-fluorenol, 25603-67-2; 9-*p*-methylphenyl-9-fluorenol, 57028-28-1; 9-*p*-chlorophenyl-9-fluorenol, 60252-95-1; 9-*p*-methoxyphenyl-9-fluorenol, 57028-27-0; 9-*p*-fluorophenyl-9-fluorenol, 2284-44-8; 9-*p*-methylthiophenyl-9-fluorenol, 60252-96-2; 9-chloro-9-phenylfluorene, 25022-99-5; 9-chloro-9-*p*-methylphenylfluorene, 60252-97-3; 9-chloro-9-*p*-chlorophenylfluorene, 60252-98-4; 9-chloro-9-*p*-methoxyphenylfluorene, 60252-99-5; 9-chloro-9-*p*-fluorophenylfluorene, 1994-55-4; 9-chloro-9-*p*-methylthiophenylfluorene, 60253-00-1; chloromercuriacetaldehyde, 5321-77-7; benzyl mercaptan, 100-53-8.

Supplementary Material Available. Figure 2, showing the gas collecting and measuring apparatus, and Figure 3, showing the reaction vessel (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944); see also F. W. Frey, *J. Org. Chem.*, **26**, 5187 (1961). Radical rearrangements of other types and in the gas phase were known long before 1944 (for a review see J. W. Wilt in "Free Radicals", Vol. 1, J. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 8).

(2) W. H. Urry and N. Nicolaides, *J. Am. Chem. Soc.*, **74**, 5163 (1952).

(3) S. Winstein and F. H. Seubold, *J. Am. Chem. Soc.*, **69**, 2916 (1947).

(4) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).

(5) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).

(6) C. Rüchardt, *Chem. Ber.*, **94**, 2599, 2609 (1961).

(7) C. Rüchardt and S. Eichler, *Chem. Ber.*, **95**, 1921 (1962).

(8) C. Rüchardt and R. Hecht, *Chem. Ber.*, **98**, 2460, 2471 (1965).

(9) C. Rüchardt and H. Trautwein, *Chem. Ber.*, **96**, 160 (1963).

(10) C. Rüchardt and H. Trautwein, *Chem. Ber.*, **98**, 2478 (1965).

(11) B. M. Vittimberga, *Tetrahedron Lett.*, 2383 (1965).

(12) P. N. Cote and B. M. Vittimberga, *J. Am. Chem. Soc.*, **93**, 276 (1971).

(13) Interaction of the 9-phenyl's ortho hydrogens with the C-1 and C-8 hydrogens of the fluorenyl ring causes the 9-phenyl moiety to assume an unfavorable geometry for orbital overlap with the radical center and subsequent migration. See ref 11 for a further discussion of this restricted rotation and the review article by J. W. Wilt in ref 1 for other references on rotationally restricted rearrangements.

(14) R. N. Goerner, Jr., and B. M. Vittimberga, Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1976, No. 118.

(15) The acetaldehydes (**5**, X = CN and CF_3) were prepared during the course of this work. Unfortunately, the low yields and extreme difficulties involved in purification of both compounds precluded their application to this study.

(16) A. N. Nesmeyanov, I. F. Lutsenko, and Z. M. Tumanva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 601 (1949).

(17) J. M. Mcintosh, H. B. Goodbrand, and G. M. Masse, *J. Org. Chem.*, **39**, 202 (1974).

(18) The apparatus for carborn monoxide dilatometry was fashioned after that employed by Schubert in a study of the rate of decarboxylation of mesitoic acid and was connected directly to the reaction vessel [see W. M. Schubert, *J. Am. Chem. Soc.*, **71**, 2639 (1949)].

(19) E. F. R. Harris and W. A. Waters, *Nature* (*London*), **170**, 212 (1952).

(20) Chain length is defined as the rate of carbon monoxide evolution divided by the rate of initiation. See K. E. J. Barrett and W. A. Waters, *Discuss. Faraday Soc.*, **14**, 221 (1953).

(21) The VPC analysis of the gases produced in the decarbonylation was carried out using a Perkin-Elmer Model 154 vapor fractometer equipped with a 20 × 0.25 in. column containing molecular sieve 5A. The analysis was carried out at room temperature with a helium carrier gas flow rate of 3 ml/min in order to confirm the presence of carbon monoxide as a reaction product.

(22) For examples of other decarbonylation reactions which are believed to have degenerated to nonchain processes, see ref 4.

(23) I. T. Strukov, *Zh. Obshch. Khim.*, **30**, 2701 (1960); *Chem. Abstr.*, **55**, 154466*e* (1961).

(24) T. M. Voronkina, I. T. Strukov and M. F. Shastakovskii, *Zh. Obshch. Khim.*, **32**, 3877 (1962); *Chem. Abstr.*, **58**, 111340*d* (1963).

(25) E. E. Campaigne and J. R. Leal, *J. Am. Chem. Soc.*, **76**, 1272 (1954).

(26) In each case the last few fractions of the chromatograms contained a small amount of yellow oil which was characterized as column catalyzed oxidation–reduction products of the individual aldehydes. See F. A. Lamb, P. N. Cote, B. Slutsky, and B. M. Vittimberga, *J. Org. Chem.*, **39**, 2796 (1974).

(27) The product percentages were determined for product mixtures which had been chromatographically separated from unreacted aldehyde, **9**, and **10** after it was established that column chromatography does not alter the ratio of products formed.

(28) C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968); see also A. R. Katritzky and R. D. Topsom, *J. Chem. Educ.*, **48**, 427 (1971).

(29) S. Ehrenson, R. W. Taft, and R. T. C. Brownlee, *Prog. Phys. Org. Chem.* **10**, 1 (1973).

(30) C. C. Price, *Chem. Rev.*, **29**, 37 (1941).

(31) Call/360: Statistical Package (STATPACK), Version 2, 2d ed, G320-1009-1, International Business Machines Corp., New York, N.Y., 1970.

(32) s = standard deviation; r = correlation coefficient, H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(33) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, p 220 ff; Yu. L. Spirin, *Russ. Chem. Rev.* (*Engl. Transl.*), **38**, 529 (1969); see particularly Table I.

(34) C. C. Price and H. Morita, *J. Am. Chem. Soc.*, **75**, 4747 (1953); A. Streitwieser, Jr., and C. Perrin, *ibid.*, **86**, 4938 (1964); H. B. Stegmann, K. Scheffler, and E. Muller, *Justus Liebigs Ann. Chem.*, **657**, 5 (1962); **677**, 59 (1964); E. A. C. Lucken and B. Poncioni, *Helv. Chim. Acta*, **55**, 2673 (1972); I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, **28**, 867 (1972).

(35) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals", Academic Press, New York, N.Y., 1968, pp 62–66.

(36) W. A. Pryor, W. H. Davis, Jr., and J. H. Gleaton, *J. Org. Chem.*, **40**, 2099 (1975).

(37) Presented in part at the 170th National Meeting of the American Chemical Society, Chicago, Ill., August 1975.

(38) P. N. Cote and B. M. Vittimberga, *Tetrahedron Lett.*, 2397 (1972).

(39) That the products **6** and **7** are stable under the reaction conditions has been demonstrated by heating known, degassed mixtures of **6** and **7** at 140 °C in the presence of di-*tert*-butyl peroxide in *o*-dichlorobenzene for 3.5 h. In each case, the mixture was found to be unchanged with respect to material balance or product ratio. Similar results were obtained with regard

to column chromatography on neutral alumina and preparative thin layer chromatography on silica gel.

(40) D. J. Trecker and R. S. Foote, *J. Org. Chem.*, **33**, 3527 (1968).

(41) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(42) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(43) C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.*, **75**, 4750 (1953).

(44) J. E. Hodgkins and E. D. Megarity, *J. Am. Chem. Soc.*, **87**, 5322 (1965). See also C. S. Marvel, J. Whitson, and H. N. Johnson, *ibid.*, **66**, 415 (1944); R. I. Benyon and T. S. Bowden, *J. Chem. Soc.*, 4259 (1957), and papers therein; M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3353 (1952).

(45) See F. G. Bordwell and H. M. Anderson, *J. Am. Chem. Soc.*, **75**, 6019 (1953), for preparation and purification of *p*-bromothioanisole.

(46) W. E. Bachman, *J. Am. Chem. Soc.*, **52**, 3287 (1930).

(47) A. Kovache, *Ann. Chim. (Paris)*, **10**, 205 (1918).

(48) C. Eaborn, R. C. Golesworthy, and M. N. Lilly, *J. Am. Chem. Soc.*, **83**, 3052 (1961).

(49) M. Gomberg and C. C. Buchler, *J. Am. Chem. Soc.*, **45**, 207 (1923).

(50) A. Kliegl, *Chem. Ber.*, **38**, 284 (1905).

(51) L. E. Schniepp and C. S. Marvel, *J. Am. Chem. Soc.*, **57**, 1635 (1935).

(52) W. Schlenk, *Justus Liebigs Ann. Chem.*, **394**, 198 (1912).

(53) A. I. Vogel, "Practical Organic Chemistry", 3d ed, Longmans, Green and Co., New York, N.Y., 1970, pp 327–328.

(54) W. L. Dilling, *Tetrahedron Lett.*, 939 (1966).

(55) E. Bergmann and A. Bondi, *Chem. Ber.*, **64**, 1455 (1931).

(56) The sulfur containing compounds were not isolated from the reaction mixtures resulting from decarbonylation of the other aldehydes (**5**, X = H, Cl, OCH_3, F, SCH_3, $SOCH_3$, or SO_2CH_3). However, based on the appearance of characteristic bands in the NMR spectrum, these compounds are assumed to be present and similar to those found in the decarbonylation of **5** (X = CH_3).

(57) C. K. Bradsher and A. K. Schneider, *J. Am. Chem. Soc.*, **60**, 2960 (1938).

(58) O. Hinsberg, *Chem. Ber.*, **45**, 2339 (1912).

(59) C. K. Bradsher and R. S. Kittila, *J. Am. Chem. Soc.*, **72**, 277 (1950).

(60) J. Romo, M. Romero, C. Djerrasi, and G. Rosenkranz, *J. Am. Chem. Soc.*, **73**, 1528 (1951).

1-Ethynylcyclopropyl Tosylate Solvolysis. 2.[1] *p*-Aryl Substituent Effect upon Rate and Product Distribution

J. Salaün

Laboratoire des Carbocycles, Bât. 420, Université de Paris-Sud, 91405 Orsay, France

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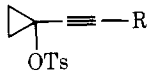
1-*p*-Tolylethynylcyclopropyl tosylate (**4**) and 1-*p*-anisylethynylcyclopropyl tosylate (**5**) have been prepared. Their rates of reaction and the resulting products of solvolysis in various solvents were compared with those of 1-phenylethynylcyclopropyl tosylate (**3**). The relative rates (k_{rel}) in 50% ethanol (70 °C) are **3**, $k_{rel} = 1$; **4**, $k_{rel} = 7.5$; and **5**, $k_{rel} = 152$. The rate enhancements over the parent system **3** due to *p*-methyl (**4**) and *p*-methoxy substitution (**5**), the solvent effects ($m = 0.583$–0.505), and the ρ value (-2.98) are clearly consistent with a $S_N'i$ ionization process involving anchimeric assistance of the triple bond (k_Δ), and leading to the mesomeric cation **11**, which is highly stabilized by further delocalization of the positive charge through the adjacent aryl ring. A cyclopropyl tosylate solvolysis, involving no ring opening at all, is reported.

In a previous solvolytic investigation, we reported the behavior of a variety of substituted 1-ethynylcyclopropyl tosylates **1**.[1]



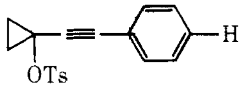
1

The solvolytic reactions of simple cyclopropyl derivatives usually afford, in the absence of steric[2] or direct conjugative interaction,[3] only allyl products[4] through concerted ionization and disrotatory ring opening.[5] On the other hand, it has been shown that the resonance-stabilized cation **2** does not undergo such a ring opening.

2

However, the formation of **2** as an intermediate in the solvolysis of 1-ethynylcyclopropyl tosylates **1** appeared to be strongly dependent upon the nature of the substituent R, as evidenced from product distribution and kinetic data. Thus, for instance, the products of aqueous ethanolysis of **1** (R = CH_3) were only allylic derivatives from opening of the cyclopropane ring while unrearranged cyclopropanols (or derivatives) were obtained from **1** (R = cyclopropyl) in high yield.[1] Therefore, the stabilization of the positive charge of **2**, by delocalization over the three carbons of the mesomeric propargyl allenyl system, entails a powerful electron-releasing substituent at the allenyl end.

We report here the solvolysis reactions of the 1-*p*-arylethynyl 1-tosyloxy cyclopropanes **3**, **4**, and **5** in order to determine the increase in the stabilization of the intermediate mesomeric cations induced by the increased electron-releasing effect of the para substituents H, CH_3, OCH_3.



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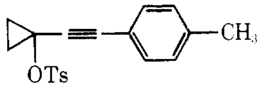

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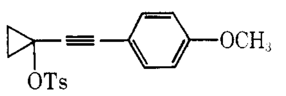
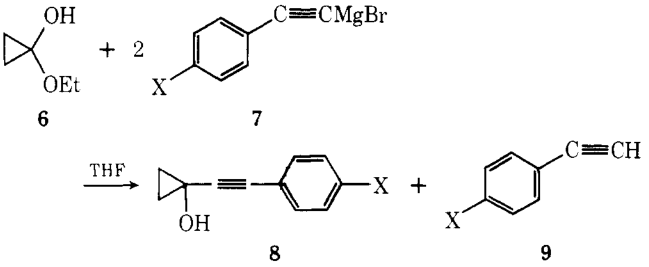


5

Syntheses. The reaction of the hemiketal of cyclopropanone **6**[6] with 2 equiv of the acetylenic magnesium bromides **7** provides the 1-*p*-arylethynylcyclopropanols **8** in high yield.



75–86%

X = H, CH_3, OCH_3

The hemiketal **6** is now readily available from ethyl 3-chloropropanoic ester;[1] the para arylacetylenic compounds which give the Grignard reagents **7** by exchange with ethylmagnesium bromide[7] were prepared from the suitable para-