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Rearrangement of 2-Aryl-3,3-dimethylmethylenecyclopropanes. Substituent Effects on a Nonpolar Radical-Like Transition State

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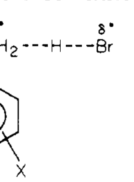
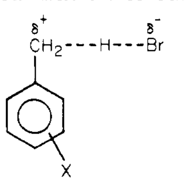
The effect of substituents on the thermal rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropanes, **4**, to 2-arylisopropylidenecyclopropanes, **5**, has been determined. This has allowed an evaluation of substituent effects on a free-radical-like transition state devoid of polar character. In general, no correlation of all the data could be obtained with Hammett σ values. Electronegative meta substituents slightly decreased rates ($\rho = -0.16$). Conjugating substituents such as CN and CO_2CH_3 in the para position increased rates. The effect of the *p*-CF_3 group was rate enhancing. The potential for C–F hyperconjugative stabilization is discussed as a radical-stabilizing feature. Thiomethyl and trimethylsilyl substituents in the para position increased rates. The possibility of radical-stabilizing interactions with vicinal σ^* and σ orbitals is discussed. *p*-Methoxy substitution increased rates while *p*-fluoro substitution slowed rates. Resonance delocalization involving charge-separated forms **10a** and **11** was suggested to be less favorable in the case of *p*-fluoro substitution. Delocalization involving an expanded octet accounted for increased rearrangement rates of *p*-Cl- and *p*-Br-substituted **4**.

The area of substituent effects on free radicals has continued to hold the interest of mechanistic chemists over the years. This is partly because the effect of substituents on radical stabilities is not as well understood as in carbocationic reactions. One problem is the separation of true radical-stabilizing effects from polar effects which are known to operate in many radical reactions. Because of the magnitude of polar effects, many radical reactions correlate with Hammett σ or Brown σ^+ values. Classic examples of this are free-radical brominations of substituted toluenes using bromine,[2] *N*-bromosuccinamide[2] or bromotrichloromethane,[3] all of which give correlations with σ^+. Hydrogen atom abstractions by alkoxy radicals,[4] chlorine atoms,[5] and peroxy radicals[5] also give correlations with σ^+. Pryor[6] has summarized much of the literature involving hydrogen atom abstractions from toluenes. Much of this literature data has been interpreted in terms of stabilization of a transition state with polar character as in **1b**. The free-radical bromination of substituted toluenes therefore does not give an accurate picture of true radical-stabilizing factors despite the intermediacy of a benzyl radical. It was felt that in order to gain truer insights into radical-stabilizing effects, such effects in a radical reaction which was devoid of significant polar character would have to be evaluated. We felt that alkyl radical abstractions from substituted toluenes should lack these large polar effects since the breaking C–H bond and the forming C–H bond have comparable polarities. Surprisingly, Pryor has reported that the reaction of substituted toluenes with isopropyl[7] and *tert*-butyl[7,8] radicals gives a correlation with σ and positive ρ values. Attempts to rationalize these polar effects must, however, be reevaluated in view of the recent criticisms of Pryor's conclusions by Tanner,[9] who suggests that the positive ρ values are an artifact of the measuring technique and the viscosity of the medium.

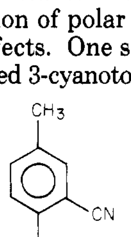


1a



1b

Others have tried to set up various free radical substituent constants in the form of $\sigma\cdot$ values with the goal of separation of polar factors from true free radical stabilizing effects. One such attempt[10] uses the reaction of 4-substituted 3-cyanotoluenes, **2**, with *N*-bromosuccinimide in an attempt to minimize polar contributions to this free-radical bromination. Another recent attempt[11] looks at substituent effects on thermal decomposition rates of dibenzyl mercury compounds, **3**. Both of these reactions give an improved evaluation of free radical substituent effects. However, polar effects are not completely absent, and one cannot be certain that the approaches used by these workers completely subtract out all such polar effects. We therefore sought to evaluate the effect of a wide range of substituents on the methylenecyclopropane rearrangement which involves fragmentation of a nonpolar carbon–carbon bond.[12] The transition state for this rearrangement has free-radical character[12d-k] and hence offers a chance to evaluate substituent effects on a free-radical-like transition state devoid of polar effects.



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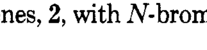

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[1] Alfred P. Sloan Fellow, 1977–1979.

[2] Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 354–5.

[3] Huyser, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 394–6.

[4] (a) Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6113–5. (b) Gilliom, R. D.; Ward, B. F., Jr. *Ibid.* **1965**, *87*, 3944–8. (c) Kennedy, B. R.; Ingold, K. U. *Can. J. Chem.* **1966**, *44*, 2381–5.

[5] Russell, G. A.; Williamson, R. C., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 2357–64.

[6] Pryor, W. A.; Lin, T. H.; Stanley, J. P.; Henderson, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 6993–8.

[7] Davis, W. H., Jr.; Pryor, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 6365–72.

[8] Pryor, W. A.; Davis, W. H., Jr.; Stanley, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 4754–6.

[9] Tanner, D. D.; Samal, P. W.; Ruo, T. C.-S.; Henriquez, R. *J. Am. Chem. Soc.* **1979**, *101*, 1168–75.

[10] Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* **1978**, *43*, 224–8.

[11] Dinctürk, S.; Jackson, R. A.; Townson, M. *J. Chem. Soc., Chem. Commun.* **1979**, 172–4.

[12] For a discussion of **1960**, general class of rearrangement, see: (a) Kon, G. A. R.; Nanji, H. R. *J. Chem. Soc.* **1932**, 2557–68. (b) Ettlinger, M. G. *J. Am. Chem. Soc.* **1952**, *74*, 5805–6. (c) Ullman, C. F. *Ibid.* **1960**, *82*, 505–6. (d) Chesick, J. P. *Ibid.* **1963**, *85*, 2720–3. (e) Shields, T. C.; Shoulders, B. A.; Krause, J. F.; Osborn, C. L.; Gardner, P. D. *Ibid.* **1965**, *87*, 3026–57. (f) Gajewski, J. J. *Ibid.* **1968**, *90*, 7178–9. (g) Noyari, R.; Takaya, H.; Nakanisi, Y.; Nozaki, H. *Can. J. Chem.* **1969**, *47*, 1242–5. (h) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 2168–9. (i) Doering, W. E.; Roth, H. D. *Tetrahedron* **1970**, 26, 2825–35. (j) Gajewski, J. J. *J. Am. Chem. Soc.* **1971**, 93, 4450–8. (k) Kirmse, W.; Marawski, H.-R. *J. Chem. Soc., Chem. Commun.* **1977**, 122–3.

0022-3263/80/1945-0280$01.00/0

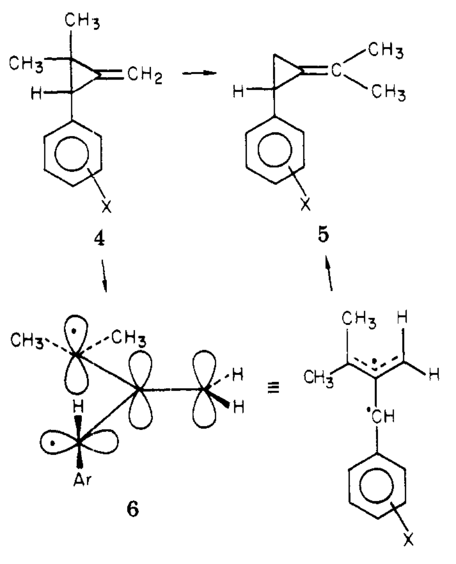
Table I. Rearrangement Rates[a] of 4 at 100 °C in Isooctane

substituent	10^4k, s^{-1}	substituent	10^4k, s^{-1}
p-CN	10.28	*m*-$SiMe_3$	3.87
p-SCH_3	9.53	*m*-CH_3	3.82
p-CO_2CH_3	8.09	*p*-H	3.58
p-OCH_3	6.16	*m*-OCH_3	3.40
p-$Si(CH_3)_3$	5.24	*m*-Cl	3.30
p-Br	4.88	*m*-F	3.17
p-*t*-Bu	4.78	*m*-CF_3	3.08
p-Cl	4.75	*p*-F	2.98
p-CH_3	4.65	3,5-Cl_2	2.87
p-CF_3	4.25	*m*-CN	2.69
3,5-$(CH_3)_2$	4.23		

[a] Maximum standard deviation ±0.07 s^{-1}.

Results and Discussion

The system chosen for an evaluation of free radical substituent effects was the thermal rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropanes, 4, to 2-arylisopropylidenecyclopropanes, 5. We have found[13] that 4 rearranges quantitatively to 5 in isooctane at 100 °C in a reaction easily monitored by gas chromatography or NMR. The mechanism of this and other related methylenecyclopropane rearrangements is suggested to involve a biradical such as 6.[12d-k,13] In the transition state for rearrangement of 4, radical character develops at the benzylic carbon as the cyclopropane bond fragments. It was felt that charge separation in this transition state should be minimal[14] and should allow an evaluation of true radical-stabilizing effects.



An extensive study of substituent effects on the rearrangement rate of 4 has been carried out. Data are given in Table I. While rate constants do not show the wide range that many cationic reactions do, nonetheless there are real and discernible differences. The first thing apparent from the data (Figure 1) is that there is no single substituent constant that correlates all or even most of the data. All substituents do not enhance the rate of this reaction. Attempts to correlate the data in Table I with recently derived free radical substituent constants of Fisher[10] and Jackson[11] gave low correlation coefficients. Neither were attempts at correlation with E_R[15] or E_D[16] values more fruitful. This was due in part to a lack of a significant number of similar substituents, especially in the meta position. However, a discussion of several points concerning the present reaction is in order.

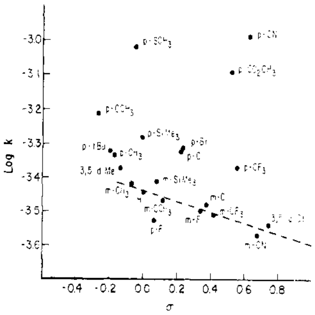
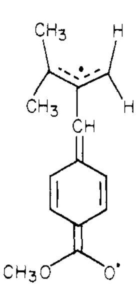


Figure 1. Plot of log *k* for the rearrangement of 4 to 5 at 100 °C in isooctane vs. *σ*.

Electronegative Meta Substituents. As can be seen from Figure 1, meta substituents with positive *σ* values all lead to slower rearrangement rates than unsubstituted 4. The least-squares line (correlation coefficient 0.97) using eight meta substituents is shown in Figure 1. Although the effect is small ($\rho = -0.16$), it is nonetheless real. This suggests that 6 behaves as an electron-deficient species,[17] being slightly destabilized by nonconjugating electron-withdrawing groups. The same trend was seen in the decomposition of dibenzyl mercury compounds 3 and was interpreted in terms of ground-state stabilization of 3 by electronegative substituents—due to the polar nature of the C–Hg bond.[11] Our results show that there is some rate retardation due to electronegative substituents even when the bond fragmenting is nonpolar.

Cyano and Carbomethoxy Substituents. These substituents in the para position lead to relatively large rate enhancements. In fact the largest rate difference is between the *m*-CN and the *p*-CN substituents. This behavior is easily rationalized in terms of *π* bond conjugation effects of the cyano and carbonyl groups as illustrated in 7. This conjugation effect is well documented in other radical reactions.[19]



7

Methyl Substituent. *p*-Methyl substitution leads to a modest rate enhancement over the unsubstituted 4 or the *m*-methyl derivative. The conclusion is, therefore, that methyl does indeed weakly stabilize a radical and that this stabilization is a resonance effect. The importance of

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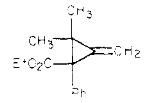
[13] Creary, X. *J. Org. Chem.* **1978**, *43*, 1777-83.

[14] In support of this we have found that rearrangement rates of i show no significant differences in methanol, chloroform, or isooctane.



i

[15] Yamamoto, T.; Otsu, T. *Chem. Ind. (London)* **1967**, 787-9.

[16] Sakurai, H.; Hayaski, S.; Hosomi, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1945-9.

[17] The electrophilic nature of many radicals is apparent. The $S_{RN}1$ reaction[18] is a prime example of such electrophilic behavior.

[18] For a review and leading references, see: Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413-20.

[19] Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957.

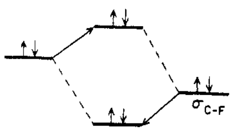


Figure 2. Interaction between a doubly occupied orbital and a vicinal C–F σ orbital.

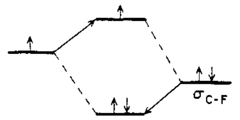


Figure 3. Interaction between a singly occupied orbital and a vicinal C–F σ orbital.

hyperconjugation as a radical-stabilizing feature is therefore weakly supported by our data. This conclusion is in conflict with Fisher's σ· value[10] of −0.02 for methyl, a value indicative of little stabilizing influence of a methyl group.

Trifluoromethyl Substituent. The *p*-trifluoromethyl substituent leads to a rate enhancement relative to the unsubstituted and the *m*-trifluoromethyl derivatives of **4**. As a rationale, the possibility of C–F hyperconjugation comes to mind. The question of C–F hyperconjugation has been a controversial issue since Roberts first suggested such a possibility.[20] The importance of forms such as **8a**

$$\underset{\mathbf{8}}{{}^-CH_2{-}CF_3} \leftrightarrow \underset{\mathbf{8a}}{CH_2{=}CF_2\ F^-}$$

in stabilizing **8** has been disputed. From a molecular orbital point of view, it has been pointed out that C–F hyperconjugation as a mode of anion stabilization is fundamentally different from cation stabilization via hyperconjugation.[21] Qualitatively, this is shown in Figure 2. There is no net stabilization since all resultant molecular orbitals are filled. Hence σ C–F hyperconjugation is not considered important as an anion-stabilizing feature.[22]

The situation is different in the case of a radical, as shown in Figure 3. A net stabilization should occur since the higher energy molecular orbital is only singly occupied. We are not certain of the magnitude of this interaction represented in Figure 3. We simply call attention to qualitative differences between anion and radical C–F hyperconjugation, which are in line with enhanced rates due to *p*-CF_3 substitution in **4**.

Thiomethyl and Trimethylsilyl Substituents. The thiomethyl and trimethylsilyl groups in the para position both give increased reactivity in **4**. The *p*-thiomethyl rate is greater than that of the *p*-methoxy rate, being exceeded only by the *p*-cyano rate. Methyl vinyl sulfide copolymerization data[23a] and azo pyrolysis data[23b] also suggest a radical-stabilizing effect of adjacent sulfur. This effect has been discussed[23a] in terms of expansion of the sulfur octet in a valence-bond description. More recently, it has been suggested[24] that stabilization is a result of interaction of the radical center with a doubly occupied nonbonding MO of the heteroatom as shown in Figure 4. A net stabilization should result. The larger stabilization of sulfur relative to oxygen was interpreted in terms of a smaller energy difference between the interacting orbitals in the case of sulfur. While the type of interaction shown in Figure 4 may be of some importance, it does not rationalize all the data. Similar arguments would predict a greater stabilizing influence on carbocations by adjacent thiomethoxy than by methoxy. This is *not* the case as reflected by σ^+ values.[25] Some other factor must therefore be involved in the explanation of *p*-thiomethyl radical stabilization.

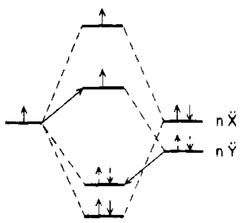


Figure 4. Interactions between a singly occupied orbital and doubly occupied heteroatom nonbonding orbitals of differing energies.

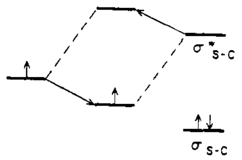


Figure 5. Interaction between a singly occupied orbital and a vicinal S–C σ* orbital.

In attempting to rationalize the origin of thiomethyl stabilization, one should keep in mind the known stabilizing influence of sulfur on an adjacent anion. The origin of this anion stabilization has also been a controversial area. Suggested reasons have varied from d-orbital interactions[26] to sulfur polarizability[27] and, more recently, the vicinal S–C σ* orbital.[28] This latter factor, if important in the stabilization of an anion, could also be important in stabilizing a radical as shown in Figure 5. Further interaction with the S–C σ orbital could result in further stabilization. It is felt that some factor, other than simple interaction with the sulfur lone pair, must be incorporated to account for the increased ability of sulfur, relative to oxygen, and chlorine to stabilize the radical center in **6**.

The *p*-trimethylsilyl substituent also shows a radical-stabilizing influence. This effect has been previously demonstrated by Wilt[29] and has been suggested to have its origin in (d-p) π overlap. While we have no evidence either supporting or ruling out this interpretation, we simply call attention to the possibility of a stabilizing interaction involving the Si–C vacant σ* orbital as in Figure 5.[30] More work is necessary to pinpoint the origin of

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(20) Roberts, J. D.; Webb, R. L.; McElhill, E. A. *J. Am. Chem. Soc.* **1950**, *72*, 408–11.

(21) Holty, D. "Progress in Physical Organic Chemistry"; Streitweiser, A., Jr., Taft, R. W., Eds; Wiley: New York, 1971; Vol 8, pp 1–74.

(22) The importance of C–F hyperconjugation employing the σ^*_{C-F} orbital has been discussed. See: Bingham, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 6743–6.

(23) (a) Price, C. C.; Zomfefer, J. *J. Am. Chem. Soc.* **1950**, *72*, 14–7. (b) Timberlake, J. W.; Garner, A. W.; Hodges, M. L. *Tetrahedron Lett.* **1973**, 309–12.

(24) Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whango, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 469–78.

(25) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 7663–7.

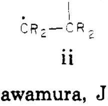
(26) Coffen, D. L. *Rec. Chem. Prog.* **1969**, *30*, 275–88.

(27) (a) Streitwieser, A., Jr.; Ewing, S. R. *J. Am. Chem. Soc.* **1975**, *97*, 190–1. (b) Streitwieser, A., Jr.; Williams, J. E., *Ibid.* **1975**, *97*, 191–2.

(28) (a) Epiotis, N. D.; Yates, R. L.; Bernardi, F.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 5435–9. (b) Barbarella, G.; Dembeck, P.; Garbesi, A.; Bernardi, F.; Bottoni, A.; Fava, A. *Ibid.* **1978**, *100*, 200–3.

(29) Wilt, J. W.; Aznavoorian, P. M. *J. Org. Chem.* **1978**, *43*, 1285–6.

(30) A β-trimethylsilyl group in ii is also radical stabilizing. This has also been rationalized in terms of hyperconjugative delocalization of the odd electron to the vicinal C–Si σ bond. See ref 31.



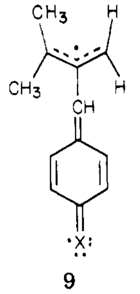
$$\dot{C}R_2{-}\overset{\displaystyle SiMe_3}{\overset{|}{C}}R_2$$

ii

(31) (a) Kochi, J. K.; Kawamura, J. *J. Am. Chem. Soc.* **1972**, *94*, 648–50. (b) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Org. Chem.* **1969**, *34*, 1764–8.

radical stabilization by second-row elements such as sulfur and silicon, which could be due to 3d, 3p, vicinal σ, or vicinal σ^* orbital interactions or any combination thereof.

Halogen Substituents. Our results suggest that p-chloro and p-bromo substituents stabilize a radical center, but the effect of the p-fluoro substituent is destabilizing. These conclusions contrast with those based on decomposition of dibenzylmercury compounds, **3**,[11] but are in agreement qualitatively with Fisher's[10] results. A valence-bond description, as illustrated in **9**, has been used to account for this halogen-stabilizing effect.[10] This type of delocalization results in an expanded octet and is not possible with fluorine. With the p-fluoro substituent, inductive destabilization of the radical center now becomes important, accounting for decreased rates. From a qualitative molecular orbital viewpoint, halogen stabilization of a radical could result in interaction with either a vacant 3d or a filled 3p orbital.



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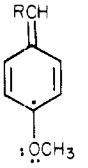
Methoxy Substituent. Previous work on alkoxy substituents has led to varying conclusions. Alkoxy substitution has been interpreted as largely radical stabilizing,[11,15,16,32] only slightly stabilizing,[33] and even destabilizing.[10] Our results indicate that the p-methoxy substituent is indeed radical stabilizing. Kirmse[12k] has also seen a similar effect in a methylenecyclopropane rearrangement. How, then, do we rationalize the stabilizing influence of the p-methoxy substituent in light of the destabilizing p-fluoro substituent? From a valence-bond viewpoint, we cannot suggest delocalization analogous to **9**. However, it is suggested that **10** can derive some stabilization from forms such as **10a**.[34] The analogous form for the p-fluoro-substituted system, **11**, would be of less importance because of the greater electronegativity of fluorine. This valence-bond description would account for the stabilizing p-methoxy influcence vs. the destabilizing p-fluoro influence.



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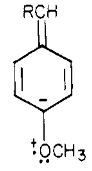
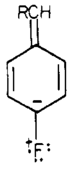


10a



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From a molecular orbital viewpoint, stabilization by methoxy could be derived from an interaction of the radical center with a filled oxygen nonbonding orbital as in Figure 4. The previous suggestion[24] that less stabilization results as the nonbonding orbital energy is lowered seems applicable here. Less stabilization is seen for the p-fluoro substituent due to the lower energy of the filled 2p fluorine orbitals relative to the oxygen 2p orbitals.

Table II. NMR Spectra (δ) of 4 in CCl_4

compd	Ar	CH_2	HCAr	CH_3	other
4 (p-SCH_3)	7.4-7.0	5.58	2.42	1.37, 0.87	2.46
4 (p-$SiMe_3$)	7.6-7.0	5.57	2.43	1.36, 0.87	0.24
4 (p-t-Bu)	7.5-7.0	5.59	2.45	1.33, 0.87	1.31
4 (3,5-$(CH_3)_2$)[a]	7.2-6.8	5.66	2.42	1.36, 0.88	2.33
4 (m-$SiMe_3$)	7.4-7.0	5.57	2.43	1.36, 0.85	0.25

[a] $CDCl_3$.

Conclusions

The effect of substituents on thermal methylenecyclopropane rearrangement can be rate enhancing or rate retarding. Hammett σ values cannot correlate all of the data. The intermediate biradical is slightly destabilized by electronegative groups in the meta position but is stabilized by conjugating or second-row elements in the para position. Valence-bond or qualitative molecular orbital theory can account for these rate-enhancing effects in terms of delocalization of radical density involving σ^*, σ, π, p, or d orbitals of the substituent. It is felt that the present data present a more accurate picture of free radical stabilizing effects.

Experimental Section

Preparation of 2-Aryl-3,3-dimethylmethylenecyclopropanes, 4. Methylenecyclopropanes **4** were prepared by addition of the corresponding carbenes (carbenoids) to 1,1-dimethylallene by procedures previously described.[13,35] The preparations of compounds **4** (X = p-SCH_3, p-$SiMe_3$, p-t-Bu, 3,5-$(CH_3)_2$ and m-$SiMe_3$) have not been described and are described below.

Preparation of 4 (X = SCH_3). A solution of lithium tetramethylpiperidide (LiTMP), prepared from 8.2 mL of 1.4 M methyllithium in ether and 1.70 g of tetramethylpiperidine, was added dropwise to a solution of 1.00 g of p-(thiomethoxy)benzyl chloride in 5 mL of 1,1-dimethylallene at room temperature. After 30 min, water was added and a standard aqueous workup followed. The organic phase was washed with dilute HCl and dried over $MgSO_4$. Much insoluble material was present, and 50 mL of Skelly F was added. The mixture was filtered, and the solvents were removed by a rotary evaporator. The yellow semisolid residue was slurried with Skelly F, and the washings were concentrated by a rotary evaporator. The residue was chromatographed on 13 g of silica gel with Skelly F elution. The yield of **4** (p-SCH_3) after chromatography was 0.16 g (14%). The NMR shows about 13% of **5** (p-SCH_3) to be present in the product. Spectral data are given in Table II.

Preparation of 4 (X = p-$SiMe_3$). A solution of LiTMP prepared from 8.5 mL of 1.6 M methyllithium and 1.60 g of tetramethylpiperidine was added dropwise to a solution of 1.60 g of p-(trimethylsilyl)benzyl bromide in 6 mL of 1,1-dimethylallene and 1 mL of ether at room temperature. After 30 min, a standard aqueous workup followed. After the mixture was dried over Na_2SO_4, the solvents were removed by a rotary evaporator. The entire residue was chromatographed on 20 g of silica gel with Skelly F elution. A mixture of **4** and **5** (p-$SiMe_3$) eluted first and weighed 0.76 g (50%). The ratio of **4** to **5** was about 4:1 by NMR. An acetylene product, 3,3-dimethyl-4-[4-(trimethylsilyl)-phenyl]-1-butyne (0.09 g, 6%), eluted last. Spectral data for **4** (p-$SiMe_3$) are given in Table II.

Preparation of 4 (X = p-t-Bu). A solution of LiTMP prepared from 6.2 mL of 1.6 M methyllithium and 1.50 g of tetramethylpiperidine was added dropwise to a solution of 1.20 g of p-*tert*-butylbenzyl chloride in 6 mL of 1,1-dimethylallene and 3 mL of ether. After 1 h, a standard aqueous workup followed. After the mixture was dried over Na_2SO_4 and the solvent removed by a rotary evaporator, the entire residue was chromatographed on 20 g of silica gel with Skelly F elution. A mixture of **4** and **5** (X = p-t-Bu) eluted first and weighed 0.80 g (57%). The ratio of **4** to **5** was about 4:1 by NMR. An acetylene product, 3,3-di-

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[32] Walling, C.; Mintz, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1515-9.

[33] (a) Timberlake, J. W.; Hodges, M. L. *Tetrahedron Lett.* **1970**, 4147-50. (b) Ohno, O.; Ohnishi, Y. *Ibid.* **1969**, 4405-8.

[34] It has been previously suggested that forms such as **10a** are not very important. See ref 19, p 122.

[35] Creary, X., accepted for publication in *J. Am. Chem. Soc.*

methyl-4-(4-*tert*-butylphenyl)-1-butyne (0.08 g, 6%) eluted last. Spectral data for 4 (*p*-*t*-Bu) are given in Table II.

Preparation of 4 (X = 3,5-$(CH_3)_2$). A solution of LiTMP prepared from 8.2 mL of 1.6 M methyllithium and 1.90 g of tetramethylpiperidine was added dropwise to a solution of 1.30 g of 3,5-dimethylbenzyl bromide in 6 mL of 1,1-dimethylallene and 3 mL of ether. After 30 min, a standard aqueous workup followed. After the organic phase was dried over Na_2SO_4, the solvent was removed by a rotary evaporator. The residue was chromatographed on 20 g of silica gel with Skelly F elution. A mixture of 4 and 5 (X = 3,5-$(CH_3)_2$) eluted first and weighed 0.47 g (37%). The ratio of 4 to 5 was about 3:1 by NMR. An acetylene product, 3,3-dimethyl-4-(3,5-dimethylphenyl)-1-butyne (0.18 g, 14%), eluted last. Spectral data for 4 (3,5-$(CH_3)_2$) are given in Table II.

Preparation of 4 (X = *m*-$SiMe_3$). A solution of LiTMP prepared from 9.6 mL of 1.4 M methyllithium and 1.90 g of tetramethylpiperidine was added dropwise to a solution of 1.60 g of *m*-(trimethylsilyl)benzyl bromide in 6 mL of 1,1-dimethylallene. After 30 min, a standard aqueous workup followed. After the mixture was dried over Na_2SO_4, the solvents were removed by a rotary evaporator. The entire residue was chromatographed on 18 g of silica gel. A mixture of 4 and 5 (X = *m*-$SiMe_3$) eluted first and weighed 0.61 g (40%). The ratio of 4 to 5 was approximately 4:1 as determined by NMR. An acetylene product, 3,3-dimethyl-4-[3-(trimethylsilyl)phenyl]-1-butyne (0.07 g, 5%), elutes last. Spectral data for 4 (*m*-$SiMe_3$) are given in Table II.

Thermal Rearrangement of 4. Kinetics Procedure. Approximately 100 mg of 4 was dissolved in isooctane and sealed in an NMR tube under nitrogen. The tube was heated in a constant-temperature bath for a given amount of time and periodically analyzed for remaining 4 by integration of the olefinic signal at δ 5.5–5.7. Rate constants were calculated by the method of least squares. Correlation coefficients were in all cases greater than 0.999 and in most cases greater than 0.9999. For product analyses, samples of 5 were isolated by preparative gas chromatography or by distillation of the thermolysis products after 10 half-lives.

In the cases of some of the more volatile methylenecyclopropanes (*p*-H, *p*-F, *m*-CF_3, *p*-CF_3), kinetics were monitored by gas chromatography by analysis for unreacted 4 vs. an internal standard (biphenyl). A 20-mg sample was dissolved in 2 mL of isooctane with 35 mg of biphenyl, and portions were sealed in tubes under nitrogen. The tubes were immersed in a constant-temperature bath, and at appropriate time intervals, the contents of the various tubes were analyzed by gas chromatography on a 5-ft, 5% SE 30 column. Rate constants were calculated by standard procedures.

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Registry No. 4 (X = *p*-CN), 72138-30-8; 4 (X = *p*-SCH_3), 72138-31-9; 4 (X = *p*-CO_2CH_3), 72138-32-0; 4 (X = *p*-OCH_3), 65108-27-2; 4 (X = *p*-$Si(CH_3)_3$), 72138-33-1; 4 (X = *p*-Br), 65354-66-7; 4 (X = *p*-*t*-Bu), 72138-34-2; 4 (X = *p*-Cl), 65354-61-2; 4 (X = *p*-CH_3), 65108-26-1; 4 (X = *p*-CF_3), 72138-35-3; 4 (X = 3,5-$(CH_3)_2$), 72138-36-4; 4 (X = *m*-$SiMe_3$), 72138-37-5; 4 (X = *m*-CH_3), 72138-38-6; 4 (X = H), 65108-25-0; 4 (X = *m*-OCH_3), 65354-64-5; 4 (X = *m*-Cl), 65354-63-4; 4 (X = *m*-F), 65354-65-6; 4 (X = *m*-CF_3), 72138-39-7; 4 (X = *p*-F), 72138-40-0; 4 (X = 3,5-Cl_2), 72138-41-1; 4 (X = *m*-CN), 72138-42-2; 5 (X = *p*-SCH_3), 72138-43-3; 5 (X = *p*-$SiMe_3$), 72138-44-4; 5 (X = *p*-*t*-Bu), 72138-45-5; 5 (X = 3,5-$(CH_3)_2$), 72138-46-6; 5 (X = *m*-$SiMe_3$), 72138-47-7; *p*-(thiomethoxy)benzyl chloride, 874-87-3; 1,1-dimethylallene, 598-25-4; *p*-(trimethylsilyl)benzyl bromide, 17903-42-3; 3,3-dimethyl-4-[4-(trimethylsilyl)phenyl]-1-butyne, 72152-04-6; *p*-*tert*-butylbenzyl chloride, 19692-45-6; 3,3-dimethyl-4-(4-*tert*-butylphenyl)-1-butyne, 72138-48-8; 3,5-dimethylbenzyl bromide, 27129-86-8; 3,3-dimethyl-4-(3,5-dimethylphenyl)-1-butyne, 72138-49-9; *m*-(trimethylsilyl)benzyl bromide, 17903-42-3; 3,3-dimethyl-4-[3-(trimethylsilyl)phenyl]-1-butyne, 72138-50-2.

Proximity Effects on Nitrogen-15 Chemical Shifts of 8-Substituted 1-Nitronaphthalenes and 1-Naphthylamines[1a]

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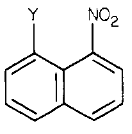
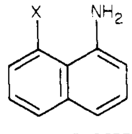
^{15}N chemical shifts of several 8-substituted 1-nitronaphthalenes and 8-substituted 1-naphthylamines have been determined and, in general, the substituent effects are unexpectedly small. The high-field shift of the amine nitrogen of 8-nitro-1-aminonaphthalene may indicate a degree of σ complexing between the amino group and the proximate substituents of the type suggested by Dunitz. The smallness of the other substituent effects may be the result of mutual cancellation of opposing larger effects.

Although the steric interactions of proximate alkyl groups are generally well understood and, in fact, often are reliably predictable by molecular mechanics calculations, the interactions of proximate polar groups are less well understood because of the possibility of complex electrical interactions in addition to simple steric effects.

We report here the ^{15}N chemical shifts of 1,8-disubstituted naphthalenes 1 and 2 where it is well established that large proximate effects are to be expected.[2] In the absence of proximity effects, the ^{15}N shifts of these compounds are reasonably expected to correlate with the electronic properties of the substituents X and Y which occupy "meta-like" positions. Large deviations of the ^{15}N shifts from those expected can be assumed to be the result of



1, Y = H, Cl, I, NH_2, NO_2, CN



2, X = H, Cl, Br, I, NH_2, NO_2, CN

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[2] For a review, see V. Balasubramaniyan, *Chem. Rev.*, 66, 567–641 (1966).

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