Captodative Rate Enhancements in the Methylenecyclopropane Rearrangement

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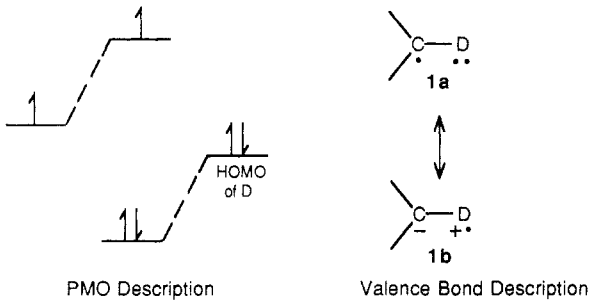
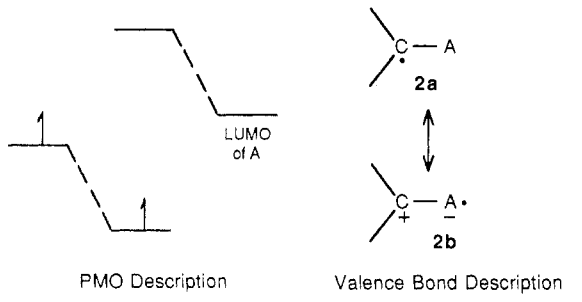
A series of 2-aryl-2-carbethoxy-3,3-dimethylmethylenecyclopropanes, **7**, with substitution in the para position of the aromatic ring, have been prepared. These substrates rearrange thermally to 2-aryl-2-carbethoxyisopropylidenecyclopropanes, **8**, by fragmentation of the cyclopropane bond which gives a biradical intermediate. Rates of this rearrangement are substituent-dependent. Electron-donor substituents such as *p*-OCH_3 and *p*-SCH_3 enhance the rearrangement rate to a greater extent than that predicted by their rate-enhancing effect on the "parent" system, 3-aryl-2,2-dimethylmethylenecyclopropane (**4**). This enhanced rearrangement rate is attributed to the captodative effect in which the acceptor carbethoxy group and the donor group on the aromatic ring exert a synergistic stabilizing effect on the benzylic portion of the biradical intermediate. *p*-Fluoro and *p*-methyl substituents are also capable of acting as true donor groups in captodative systems. Rearrangement rates of **7** containing electron-donor groups correlate with σ^+ values, which are a measure of the donor abilities of various groups. The captodative effect has been used as a probe for the mechanism of stabilization of free radicals by the sulfinyl group, $SOCH_3$. No captodative rate enhancement is observed when **7**-*p*-$SOCH_3$ is rearranged. This implies that stabilization of free radicals by the sulfinyl group does not involve utilization of the sulfur nonbonding electron pair in a donor fashion, but probably involves this group acting as an acceptor group.

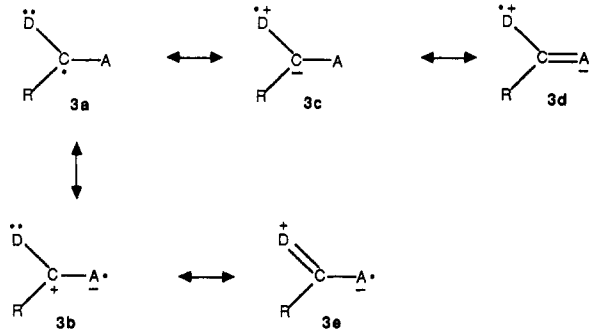
The captodative effect is a free radical stabilizing feature reviewed by Viehe[1] in which the combination of electron-donor and electron-acceptor substituents attached to a radical center exert a synergistic stabilizing effect. Donor substituents (such as NR_2, OR) stabilize a free radical by interaction of the nonbonding electron pair of the donor group with the radical center (as in **1b**), while electron-acceptor substituents can also stabilize by interaction of a vacant acceptor orbital with the radical center (as in **2b**). As Viehe has shown,[1] the actual effect of having both donor and acceptor groups attached to the same radical center is greater than the sum of the individual effects. This captodative effect has been rationalized in terms of a PMO approach in which the donor ability of the group D is enhanced because of the presence of the acceptor group A, and vice versa. A valence bond rationalization leads to the same conclusion. A captodative radical receives enhanced stabilization as reflected in resonance forms **3d** and **3e**. The donor ability of D, as reflected by form **3c**, is enhanced due to the presence of the electron-acceptor group, as reflected in **3d**. The acceptor ability of the group A, as reflected by form **3b**, is enhanced by the presence of the donor group, as reflected in **3e**.



Free radical stabilization by a donor group D



Free radical stabilization by an acceptor group A



We[2-4] and others[5-9] have been interested in the quantitative ability of various groups to stabilize (or destabilize) free radicals in the absence of polar effects. in this regard, we have studied the thermal methylenecyclopropane rearrangement of **4** to **5** as a probe for stabilizing effects of various groups on a benzylic radical center.[2-4] This rear-

(1) For a review and leading references, see: Viehe, H. G.; Janousek, Z.; Merényi, R. *Acc. Chem. Res.* **1985**, *18*, 148-154. The captodative effect is also referred to as merostabilization or "push-pull" stabilization. For further leading references, see: Leigh, W. J.; Arnold, D. R.; Humphreys, R. W. R.; Wong, P. C. *Can J. Chem.* **1980**, *58*, 2537-2549.

(2) Creary, X. *J. Org. Chem.* **1980**, *45*, 280-284.

(3) Creary, X.; Benage, B.; Mehrsheikh-Mohammadi, M. E.; Bays, J. P. *Tetrahedron Lett.* **1985**, *26*, 2383-2386.

(4) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 1100-1115.

(5) Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* **1978**, *43*, 224-228.

(6) (a) Dinçtürk, S.; Jackson, R. A.; Townson, M. *Chem. Commun.* **1979**, *172*-174. (b) Dinçtürk, S.; Jackson, R. A.; Townson, M.; Ağirbaş, H.; Billingham, N. C.; March, G. *J. Chem. Soc. Perkin Trans. 2*, **1981**, 1121-1126. (c) Dinçtürk, S.; Jackson, R. A. *Ibid.* **1981**, 1127-1131. (d) Ağirbaş, H.; Jackson, R. A. *Ibid.* **1983**, 739-742.

(7) (a) Timberlake, J. W.; Hodges, N. L. *Tetrahedron Lett.* **1970**, 4147-4150. (b) Timberlake, J. W.; Garner, A. W.; Hodges, M. L. *Ibid.* **1973**, 309-312. (c) Dube, M. F.; Timberlake, J. W. *Tetrahedron* **1980**, *36*, 1753-1756. (d) Luedtke, A. E.; Timberlake, J. W. *J. Org. Chem.* **1985**, *50*, 268-270.

(8) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1211-1221, 6531.

(9) Jiang, Xi-Kui.; Ji, Guo-Zhen.; Yu, Chong-Xi *Acta Chimica Sinica (Engl. Ed.)* **1984**, 82-85.

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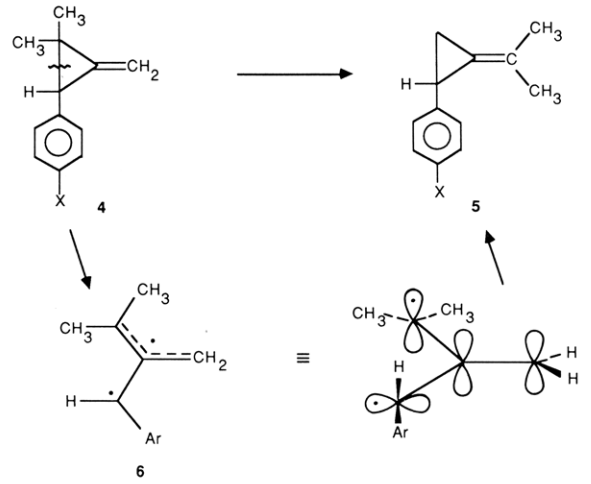


rangement is suggested to proceed via thermal fragmentation of the cyclopropane bond, with the transition state resembling the singlet perpendicular biradical **6**.[10] Substituents on the aromatic ring can, in principle, stabilize or destabilize the transition state leading to **6** and we have used rates of this reaction as a quantitative measure of free radical stabilizing effects. This is a kinetic method for assessing the influence of substituents on benzylic free radical stability and one could therefore suggest numerous *potential* problems with this method. Reversibility in the formation of **6**, i.e., **6** returning to **4** faster than it closes to the product **5**, may complicate the interpretation of the kinetic data.[11] Ground-state effects could be of importance. Rate effects are rather small due to the fact that the substituent effect is insulated from the radical center by the aromatic ring. Despite these potential problems, a reasonable correlation exists between our methylenecyclopropane rearrangement rates and the σ_α·-free radical substituent constant later developed by Arnold and Dust.[8] This free radical substituent constant, σ_α·, is based on benzyl radical hyperfine coupling constants, and the correlation with rearrangement rates of **4** strongly supports the validity of using this rearrangement as a true probe for benzyl radical stabilizing effects. Potential problems with our kinetic method therefore are not real problems. The real advantages of our method, in terms of the wide variety of substituents which can be studied by a facile and accurate method, make it an attractive method for studying free radical substituent effects.

We have now prepared a series of related methylenecyclopropanes **7** and monitored their rearrangement to the isopropylidenecyclopropanes **8**. In this rearrangement, the carbethoxy group, as well as the aromatic ring substituent can, in principle, interact with the developing benzylic radical center. Groups such as carbethoxy and cyano are considered acceptor groups. If the ring substituent is a donor group, then the potential for captodative stabilization of the intermediate biradical exists. Reported here are the effects of captodative substitution on the rearrangement rates of **7** to **8**.

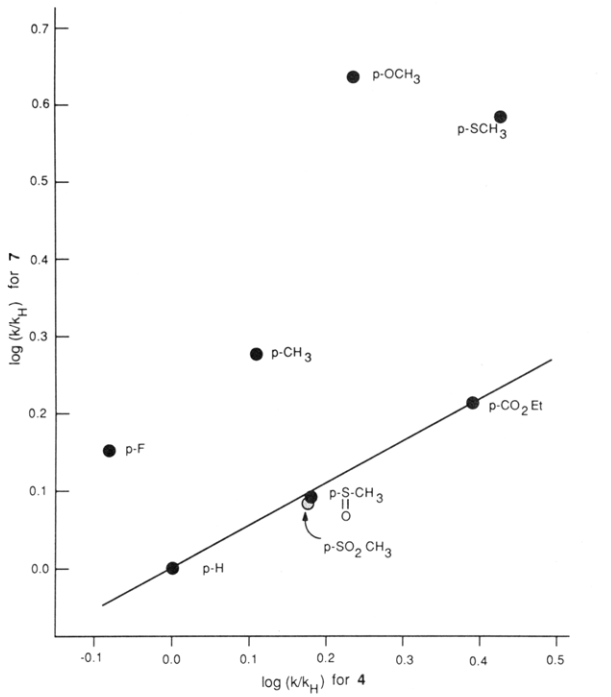


Figure 1. Plot of log (k/k_H) for rearrangement of **7** vs. log (k/k_H) for rearrangement of **4**.

Table I. Rearrangement Rates of 7 in Isooctane at 50.0 °C

substituent	k, s^{-1}	k_{rel} for **7**	k_{rel} for **4**
p-H	$(5.62 \pm 0.06) \times 10^{-4}$	1.00	1.00
	$(3.61 \pm 0.03) \times 10^{-5}$ [a]		
p-CO_2Et	$(9.18 \pm 0.11) \times 10^{-4}$	1.63 ± 0.04	2.45[b]
p-CH_3	$(1.06 \pm 0.01) \times 10^{-3}$	1.89 ± 0.03	1.30[c]
p-OCH_3	$(2.44 \pm 0.03) \times 10^{-3}$	4.35 ± 0.09	1.72[c]
p-SCH_3	$(1.38 \pm 0.11) \times 10^{-4}$ [a]	3.83 ± 0.33[a]	2.67[b]
p-F	$(7.99 \pm 0.12) \times 10^{-4}$	1.42 ± 0.04	0.83[c]
p-$SOCH_3$	$(4.41 \pm 0.10) \times 10^{-5}$ [a]	1.22 ± 0.04[a]	1.52[b]
p-SO_2CH_3	$(4.21 \pm 0.10) \times 10^{-5}$ [a]	1.17 ± 0.03[a]	1.50[b]

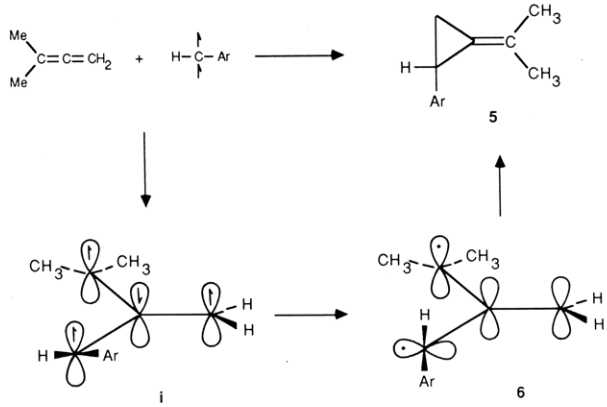
[a] Rate in C_6D_6 at 25 °C. [b] Relative rate in C_6D_6 at 80 °C. [c] Relative rate in isooctane at 100 °C; see ref 2.

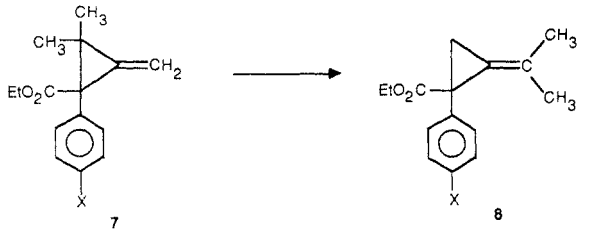
Results and Discussion

The requisite substrates **7** were prepared by addition of the appropriate carbenes to 1,1-dimethylallene, with the

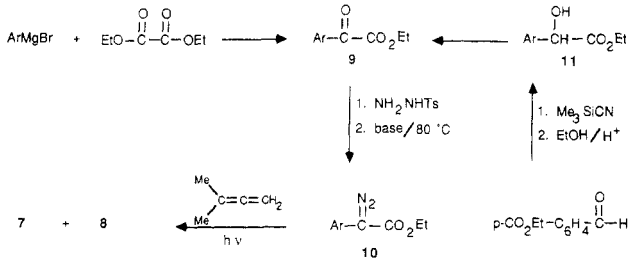
(10) For a discussion of this general class of rearrangement, see: (a) Kon, G. A. R.; Nanji, H. R. *J. Chem. Soc.* **1932**, 2557–2568. (b) Ettlinger, M. G. *J. Am. Chem. Soc.* **1952**, *74*, 5805–5806. (c) Ullman, C. F. *Ibid.* **1960**, *82*, 505–506. (d) Chesick, J. P. *Ibid.* **1963**, *85*, 2720–2723. (e) Shields, T. C.; Shoulders, B. A.; Krause, J. F.; Osborn, C. L.; Gardner, P. D. *Ibid.* **1965**, *87*, 3026–3037. (f) Gajewski, J. J. *Ibid.* **1968**, *90*, 7178–7179. (g) Noyari, R.; Takaya, H.; Nakanisi, Y.; Nozaki, H. *Can. J. Chem.* **1969**, *47*, 1242–1245. (h) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 2168–2169. (i) Doering, W. E.; Roth, H. D. *Tetrahedron* **1970**, *26*, 2825–2835. (j) Gajewski, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 4450–4458. (k) Kirmse, W.; Marawski, H.-R. *J. Chem. Soc., Chem. Commun.* **1977**, 122–123. (l) Hehre, W. J.; Salem, L.; Willcott, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 4328–4330.

(11) Our related studies have shown that triplet carbene additions to 1,1-dimethylallene result in the formation of only **5**. We have interpreted this in terms of initial formation of the triplet trimethylenemethane **i**. Presumably ring closure occurs, after spin inversion and rotation, via the singlet biradical **6** (which is the same intermediate suggested in the thermal methylenecyclopropane rearrangement). The fact that only **5** is formed from triplet carbene additions implies that closure of **6** to give **5** is faster than closure to give **4**. Reversibility in formation of **5** in the thermal rearrangement of **4** therefore does not appear to be a complicating feature. See: Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611–1618.



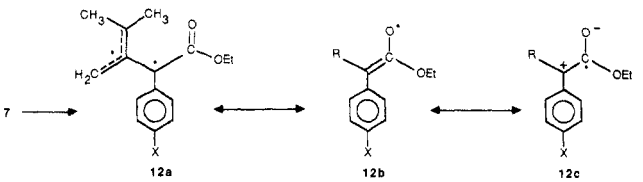


diazo compounds **10** serving as the carbene precursors.

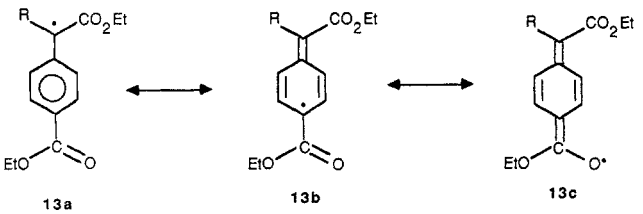


Rates of thermal rearrangement of **7** to **8** in isooctane were monitored spectrophotometrically. In the cases of 7-*p*-SCH_3, 7-*p*-$SOCH_3$, and 7-*p*-SO_2CH_3, the absorbance change was not large enough to permit accurate rate determinations. Therefore rates of these substrates were monitored by NMR spectroscopy (in C_6D_6) by observing the disappearance of the olefinic methylene signal.

Rearrangement rates of **7** to **8** as a function of substituent are given in Table I. This rearrangement proceeds presumably via the biradical **12**. In principle, the demand



for stabilization by the substituent X in **12** should be *less than* in the "parent" system **6** since the benzylic radical center in **12** is additionally stabilized by the directly attached CO_2Et group.[12,13] Figure 1 shows an attempt to correlate rearrangement rates of **7** with those of **4**. The correlation is quite poor. Consider first the effect of the *p*-CO_2Et substituent. The rearrangement rate of 7-*p*-CO_2Et is enhanced by a factor of 1.63 relative to 7-*p*-H. This enhancement is no doubt due to further stabilizing interactions of the *p*-CO_2Et group as shown in **13**. The



rate enhancement in 7-*p*-CO_2Et is somewhat less than the factor of 2.45 seen in the parent system 4-*p*-CO_2Et (Table I). This behavior is not unexpected since the demand for CO_2Et stabilization in 6-*p*-CO_2Et should be larger than

(12) The carbethoxy group is free radical stabilizing. See: Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957. See also ref 2 and ref 8.

(13) Form **12b** shows carbonyl stabilization by a standard conjugative mechanism while form **12c** emphasizes the acceptor properties of the carbonyl group. From a molecular orbital viewpoint, the interaction of the radical nonbonding orbital with the carbonyl π^* orbital is more effective than with the π orbital. Hence the carbonyl group can also stabilize a free radical by an acceptor type of mechanism.

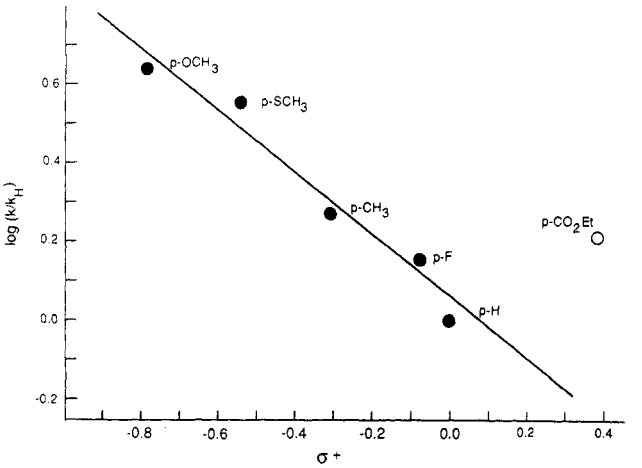
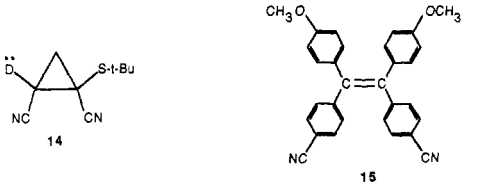
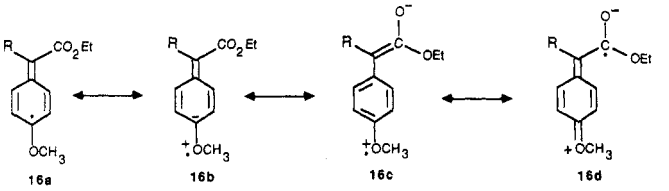


Figure 2. Plot of log (k/k_H) for rearrangement of **7** vs. σ^+.

that in **12**. The rate behavior of 7-*p*-CO_2Et is therefore considered quite "normal". A line has therefore been arbitrarily drawn between the *p*-H and *p*-CO_2Et substituents in Figure 1.

Rates for 7-*p*-OCH_3 and 7-*p*-SCH_3 show relatively large positive deviations from "normal" behavior as defined by the line in Figure 1. The rate-enhancing effect of *p*-OCH_3 and *p*-SCH_3 substitution in **7** is greater than that in **4**, despite the expected decreased demand for radical stabilization in **7**. This is suggestive of enhanced transition-state stabilization and is presumably due to the captodative effect. Analogous rate-enhancing captodative effects were observed earlier by Viehe[14] in the thermal cis–trans isomerization of cyclopropanes **14** and by Arnold[15] in the thermal cis–trans isomerization of the tetraphenylethylene **15**. This effect is apparently also manifested in the methylenecyclopropane rearrangement, as depicted in **16c** and **16d**, despite the fact that the donor group is insulated from the radical center by the aromatic ring.

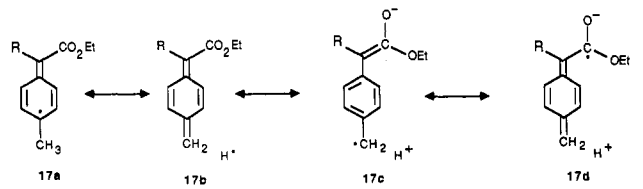




The rate of 7-*p*-CH_3 also deviates from the arbitrary line in Figure 1, i.e., *p*-CH_3 substitution is more effective in stabilization of **12** than stabilization of **6** despite the decreased demand for stabilization in **12**. This suggests that the methyl group, in conjunction with carbethoxy, is capable of captodative stabilization. To account for this observation, the methyl group must be behaving as a true donor group in a captodative sense. A valence bond description would require the involvement of forms such as **17c** and **17d**, and not simply the more standard forms such as **17a** and **17b**, to account for this increased stabilization. The substrate 7-*p*-F rearranges faster than 7-*p*-H. This

(14) Merényi, R.; DeMesmaeker, A.; Viehe, H. G. *Tetrahedron Lett.* **1983**, *24*, 2765–2768.

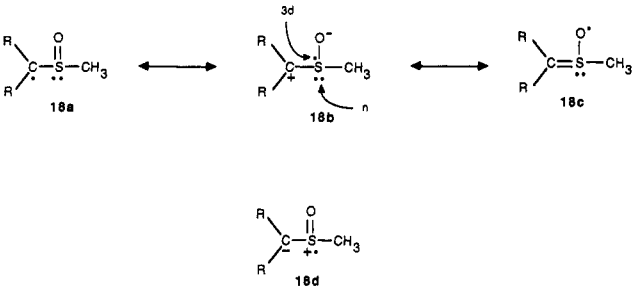
(15) Leigh, W. J.; Arnold, D. R. *Can. J. Chem.* **1981**, *59*, 609–620.



trend is opposite that which is observed in the parent system 4, where a *p*-F substituent is slightly rate-retarding.[16] These data indicate that fluorine is also capable of involvement in captodative stabilization, as are the less electronegative elements oxygen and sulfur.

Figure 2 shows that rates of rearrangement of 7, where captodative stabilization is postulated, correlate reasonably well ($\rho = 0.82$; $r = 0.98$) with σ^+ values. This can be viewed as evidence in support of the suggested captodative stabilization by OCH_3, SCH_3, CH_3, and F. σ^+ values are one measure of the increased donor ability of various substituents under conditions of electron demand. Since the donor ability of various substituents is enhanced in captodative systems, it is not surprising that some correlation is observed with the σ^+ substituent constant.

Attention was next turned to the substrate 7-*p*-$SOCH_3$. We have previously reported that the sulfinyl group, $SOCH_3$, enhances the rate of rearrangement of 4 by a factor of 1.52. Arnold's σ_α value for $SOCH_3$[17] also indicates that this group is free radical stabilizing relative to hydrogen. However a question concerns the source of this stabilization. Are the sulfur nonbonding electrons of great importance in this stabilization (as a donor group), as they presumably are in stabilization by the SCH_3 group? Such a suggestion has been made.[17] In order to probe the donor properties of $SOCH_3$, the rearrangement rate of 7-*p*-$SOCH_3$ has been measured and the effect in this potential captodative system has been compared to the effect in the "parent" system 4. The substrate 7-*p*-$SOCH_3$ rearranges only 1.22 times faster than 7-*p*-H. These data suggest that there is no unusual rate enhancement in the potentially captodative system 7-*p*-$SOCH_3$. The $SOCH_3$ group therefore does not exhibit increased donor capabilities despite the sulfur nonbonding electron pair, i.e., forms such as **18d**, which utilize the nonbonding electron pair, do not



appear to have much importance in stabilization of α-sulfinyl radicals. We conclude that this group stabilizes free radicals by an acceptor type of mechanism. Utilization of vacant sulfur d orbitals, as in **18b** and **18c**, would account for the stabilizing properties of this acceptor group.

Finally, attention was focused on the sulfonyl group, SO_2CH_3, which has been shown to increase the rearrangement rate of 4 by a factor of 1.50.[4] Stabilization of the transition state leading to 6 by the sulfonyl group is presumably via an acceptor type of mechanism. The rate behavior of 7-*p*-SO_2CH_3 is quite similar to that of 7-*p*-$SOCH_3$. Both substrates react at essentially the rates predicted by the line in Figure 1. This is consistent with the fact that there can be no captodative stabilization in the rearrangement of 7-*p*-SO_2CH_3. It also supports our contention that no captodative stabilization operates for $SOCH_3$ and that $SOCH_3$ therefore does not stabilize radicals by a donor mechanism.

Conclusions

The captodative effect can be demonstrated kinetically in the methylenecyclopropane rearrangement of 7 even though the donor substituent is insulated from the developing radical center by an aromatic ring. *p*-Methoxy and *p*-thiomethoxy substitution in 7 give larger rate enhancements than in the parent system 4. *p*-Methyl and *p*-fluoro substituents also appear to be capable of enhanced captodative stabilization. The *p*-fluoro substituent, which destabilizes the transition state for rearrangement of 4, can become a free radical stabilizing group in captodative systems. σ^+ values provide some measure of the ability of donor substituents to provide captodative stabilization. Finally, the $SOCH_3$ group is radical stabilizing but the mechanism of this stabilization does not appear to utilize the donor properties of the sulfur nonbonding electron pair.

Experimental Section

Preparation of $ArCOCO_2Et$ (9). General Procedure. A Grignard reagent in ether was prepared from the appropriately substituted bromobenzene. The corresponding Grignard reagent, ArMgBr, was then added dropwise to a mechanically stirred solution of approximately 3 equiv of diethyl oxylate in ether at −78 °C. The mixture was then allowed to warm to room temperature and satd. NH_4Cl solution was added. The organic phase was separated, washed with water and saturated NaCl solution, and then dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the excess diethyl oxylate was removed by distillation through a 15-cm Vigreux column at 15 mmHg pressure. The products 9 were isolated in yields ranging from 60 to 79% by distillation using a short path distillation head. Details for the specific preparation of 9 (Ar = *p*-$CH_3OC_6H_4$) are given below.

A mixture of 0.19 mmol of (*p*-methoxyphenyl)magnesium bromide in 180 mL of ether (this Grignard reagent forms a two-phase system with the bottom phase having a higher concentration of the Grignard reagent) was added dropwise to a mixture of 71 g of diethyl oxylate in 200 mL of ether at −78 °C. After workup as described above, distillation gave 24.9 g (63%) of 9 (Ar = *p*-$CH_3OC_6H_4$):[18] bp 110–115 °C (0.05 mm); NMR ($CDCl_3$) δ 8.08 (2 H, d, J = 8 Hz), 7.00 (2 H, d, J = 8 Hz), 4.46 (2 H, q, J = 7 Hz), 3.88 (3 H, s), 1.40 (3 H, t, J = 7 Hz).

Preparation of 9 (Ar = *p*-$CO_2EtC_6H_4$). A mixture of 5.80 g of *p*-carbethoxybenzaldehyde and 3.26 g of freshly distilled trimethylsilyl cyanide was stirred in an ice bath and about 20 mg of anhydrous ZnI_2 was added. The mixture was then allowed to stand at room temperature for 30 min. Distillation using a short path distillation head gave 8.57 g (95%) of the corresponding silylated cyanohydrin, *p*-$CO_2EtC_6H_4CH(OSiMe_3)CN$: bp 115–125 °C (0.04 mm); NMR ($CDCl_3$) δ 8.2–7.4 (4 H, AA'BB' quartet), 5.49 (1 H, s), 4.32 (2 H, q, J = 7 Hz), 1.34 (3 H, t, J = 7 Hz), 0.18 (9 H, s).

A solution of 4.68 g of *p*-$CO_2EtC_6H_4CH(OSiMe_3)CN$ in 10 mL of absolute ethanol was cooled in an ice bath and hydrogen chloride gas was bubbled through the mixture for about 7 min. The flask was stoppered and left standing at room temperature for 16 h. At this point, a white precipitate had formed and the excess ethanol was removed on a rotary evaporator. Twenty milliliters of water was added to the residue and solid Na_2CO_3

(16) Free radicals, which are intrinsically electron-deficient species, should be inductively destabilized by electronegative elements such as fluorine. This inductive effect apparently offsets any donor effect in the intermediate 6.

(17) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164–1168.

(18) Adams, D. L.; Vaughan, W. R. *J. Org. Chem.* **1972**, *37*, 3906–3913. (b) Nimitz, J. S.; Mosher, H. S. *Ibid.* **1981**, *46*, 211–213.

was added to the mixture until the solution became slightly basic. The mixture was then stirred at room temperature for 24 h and extracted with ether, and the ether extract was dried over $MgSO_4$. The solvent was removed on a rotary evaporator leaving 2.50 g (59%) of crude **11** (Ar = p-$CO_2EtC_6H_4$) which was oxidized without further purification.

Pyridine (8.80 g) was added to a stirred mixture of 5.18 g of CrO_3 in 100 mL of CH_2Cl_2. After 15 min, 2.20 g of ethyl p-carbethoxymandelate (**11**) was added. The mixture, which became difficult to stir, was swirled for 15 min and then filtered through Celite. The filtrate was washed with water, 10% HCl solution, Na_2CO_3 solution and saturated NaCl solution and then dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was distilled on a short path distillation head. The fraction boiling at greater than 115 °C (0.04 mm) was collected and weighed 1.58 g. Gas chromatographic analysis showed that this fraction contained the product **9**, along with about 10% of two unidentified lower boiling impurities. Redistillation gave 1.30 g (60%) of **9** (Ar = p-$CO_2EtC_6H_4$), bp >115 °C (0.04 mm) which contained about 5% of a lower boiling impurity. NMR ($CDCl_3$) δ 8.22–8.04 (4 H, AA'BB' quartet), 4.47 (2 H, q, J = 7 Hz), 4.42 (2 H, q, J = 7 Hz), 1.44 (3 H, t, J = 7 Hz), 1.42 (3 H, t, J = 7 Hz). Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.32; H, 5.78.

Preparation of 9 (Ar = p-$SOCH_3C_6H_4$). A solution of 1.60 g of **9** (Ar = p-$CH_3SC_6H_4$) in 10 mL of CH_2Cl_2 was cooled in an ice bath and a solution of 1.55 g of 85% m-chloroperbenzoic acid in 14 mL of CH_2Cl_2 was added dropwise. After warming to room temperature for 15 min, the mixture was taken up into ether and washed with a solution of 0.40 g of NaOH in 20 mL of water. The organic phase was washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was removed on a rotary evaporator leaving 1.45 g (85%) of **9** (Ar = p-$SOCH_3C_6H_4$) as a clear oil: NMR ($CDCl_3$) δ 8.25–7.75 (4 H, AA'BB' quartet), 4.48 (2 H, q, J = 7 Hz), 2.78 (3 H, s), 1.44 (3 H, t, J = 7 Hz). Reaction with 1.1 equiv of tosylhydrazine in ethanol gave the corresponding tosylhydrazone, mp 155–156 °C. Anal. Calcd for $C_{18}H_{20}N_2O_5S_2$: C, 52.93; H, 4.93. Found: C, 52.82; H, 4.94.

Preparation of 9 (Ar = p-$SO_2CH_3C_6H_4$). A solution of 1.25 g of **9** (Ar = p-$CH_3SC_6H_4$) in 25 mL of CH_2Cl_2 was cooled in an ice bath and 2.39 g of 85% m-chloroperbenzoic acid was added in small portions. After completion of the addition, the mixture was stirred at room temperature for 4 h. The mixture was taken up into ether and washed with a solution of 0.62 g of NaOH in water containing 0.20 g of NaI and 0.23 g of $Na_2S_2O_3$. The organic phase was then washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give 1.25 g (87%) of **9** (Ar = p-$CH_3SO_2C_6H_4$), mp 69–72 °C. Recrystallization from ether–hexane (60:40) gave an analytical sample: mp 75–77 °C; NMR ($CDCl_3$) δ 8.4–8.1 (4 H, AA'BB' quartet), 4.50 (2 H, q, J = 7 Hz), 3.10 (3 H, s), 1.42 (3 H, t, J = 7 Hz). Anal. Calcd for $C_{11}H_{12}O_5S$: C, 51.55; H, 4.72. Found: C, 51.72; H, 4.74.

Preparation of Diazo Compounds 10. General Procedure.[19] A suspension of 1.1 equiv of (p-toluenesulfonyl)hydrazine in 10 parts methanol or ethanol was stirred at room temperature and 1.0 equiv of the appropriate keto ester **9** was added in one portion. After about 3 h at room temperature, the solvent was removed on a rotary evaporator and a solution of 1.05 equiv of sodium dissolved in ethylene glycol was added to the viscous residue. The mixture was cooled and ether was added. The ether extract of the diazo compounds **10** was decanted and this procedure of heating at 70–80 °C and ether extraction was repeated 4 times. The combined ether extracts were washed with dilute NaOH solution and saturated NaCl solution and dried over $MgSO_4$. In the cases of diazo compounds **10** (Ar = p-$SOCH_3C_6C_4$ and p-$SO_2CH_3C_6H_4$), the corresponding tosylhydrzones were treated with 1.1 equiv of sodium ethoxide in ethanol and the ethanol solution was heated at 65–75 °C for 15 min. The ethanol was removed by rotary evaporator, water was added, and the mixture was extracted with ether. Solvent removal using a rotary evaporator gave the corresponding diazo compounds **10**. Details for the specific preparation of **10**, Ar = p-$CH_3C_6H_4$, are given below.

Reaction of 1.50 g of **9** (Ar = p-$CH_3C_6H_4$) with 1.52 g of tosylhydrazine in 13 mL of methanol for 2 h at room temperature gave the crude tosylhydrazone. The methanol was removed on a rotary evaporator and a solution of 0.18 g of sodium in 35 mL of ethylene glycol was added. After heating at 70–75 °C as described above, and periodic ether extractions, solvent removal gave 1.28 g (80%) of the red diazo compound **10** (Ar = p-$CH_3C_6H_4$): NMR ($CDCl_3$) δ 7.6–7.1 (4 H, AA'BB' quartet), 4.32 (2 H, q, J = 7 Hz), 2.32 (3 H, s), 1.31 (3 H, t, J = 7 Hz). This diazo compound was stored at −20 °C.

Photolyses of Diazo Compounds 10 in 1,1-Dimethylallene. Preparation of 7. A solution of approximately 200–500 mg of the appropriate diazo compound **10** in 8 mL of 1,1-dimethylallene was irradiated in a water cooled (approximately 15 °C) Pyrex tube with a Hanovia 450-W medium pressure mercury lamp until the red-orange color disappeared (approximately 2–5 h). The excess allene was removed at 15 mm pressure and the residue containing **7** and **8** was rapidly filtered through about 5 g of silica gel with 2–5% ether in Skelly F. Solvent removal using a rotary evaporator left a mixture of **7** and **8** which was used directly for kinetic studies. These products were stored at −20 °C. Details for the specific preparation of **7**-p-F and **8**-p-F are given below.

A solution of 439 mg of **10** (Ar = p-F-C_6H_4) in 8 mL of 1,1-dimethylallene was irradiated for 5 h. Solvent removal and filtration through 7 g of silica gel gave 353 mg (67%) of a mixture of **7**-p-F and **8**-p-F in a ratio of 2.5:1 as determined by NMR. NMR of **7**-p-F ($CDCl_3$): 7.5–6.9 (4 H, m), 5.77 (1 H, s), 5.59 (1 H, s), 4.13 (2 H, m), 1.38 (3 H, s), 1.22 (3 H, t, J = 7 Hz), 0.84 (3 H, s). NMR of **8**-p-F ($CDCl_3$): δ 7.5–6.9 (4 H, m), 4.13 (2 H, m), 2.33 (1 H, m), 1.95 (3 H, t, J = 2 Hz), 1.92 (3 H, t, J = 1.5 Hz), 1.18 (3 H, t, J = 7 Hz). Anal. Calcd for $C_{15}H_{17}FO_2$: C, 72.56; H, 6.90. Found: C, 72.73; H, 6.97.

Rearrangement of 7 to 8. Kinetics Procedures. Twenty microliters of a solution of about 10 mg of the appropriate mixture of **7** and **8** in 1 mL of isooctane was injected into 3 mL of isooctane in a cuvette equilibrated at 50.0 °C. This initiated the kinetic run. The absorbance change of the solution was monitored by ultraviolet spectroscopy after allowing 4 min for re-equilibration of the temperature in the cuvette. For certain runs, the cuvette was sealed under nitrogen before beginning measurements. The following wavelengths were used for kinetic measurements: p-H, 237 nm; p-CH_3, 240 nm; p-CH_3O, 249 nm; p-F, 230 nm; p-CO_2Et, 247 nm. After 10 half-lives, an infinity reading was taken. Rate constants given in Table I were calculated by the method of least squares and represent an average of at least 2 runs.

Absorbance changes in the ultraviolet were not large enough to permit accurate determination of rearrangement rates of **7**-p-SCH_3, **7**-p-$SOCH_3$, and **7**-p-SO_2CH_3 in isooctane. Rearrangement rates of **7**-p-SCH_3, **7**-p-$SOCH_3$, **7**-p-SO_2CH_3 in C_6D_6, and **7**-p-H in C_6D_6 at 25 °C were therefore determined by NMR by monitoring the disappearance of the olefinic methylene signal. Dimethyl maleate was used as an internal standard. As before, rate constants given in Table I were calculated by the method of least squares and represent an average of at least 2 runs.

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