trated in vacuo, giving a solid, which was subjected to flash alumina chromatography to afford 0.011 g (30%) of the desired ester **67** as a white solid (mp 204.5–206.0 °C, acetone): ^{1}H NMR 1.94 (d, J = 15.5 Hz, 1 H, H-8 eq), 2.23 (br m, 1 H, H-8a), 2.36 (ddd, J = 15.5, 6.6, 3.7 Hz, 1 H, H-8 ax), 2.82 (ddd, J = 12.9, 5.2, 1.6 Hz, 1 H, H-1 eq), 2.91 (s, 3 H, NCH_3), 3.11 (td, J = 5.3, 1.3 Hz, 1 H, H-4a), 3.47 (s, 3 H, CO_2CH_3), 3.66 (s, 3 H, 6-OCH_3), 3.68 (m, J = 5.2, 1.8 Hz, 1 H, H-5), 3.83 (dd, J = 2.3, 1.8 Hz, 1 H, H-6), 3.86 (s, 6 H, aromatic 3,5-OCH_3), 3.89 (s, 1 H, aromatic 4-OCH_3), 3.96 (t, J = 12.9 Hz, 1 H, H-1 ax), 5.37 (dd, J = 3.7, 2.6 Hz, 1 H, H-7), 7.46 (s, 2 H, aromatic H), 7.52 (s, 1 H, H-3); ^{13}C NMR 26.9 (C-8), 27.4 (C-4a or C-8a), 29.0 (C-4a or C-8a), 29.9 (C-5), 42.8 (NCH_3), 49.5 (C-1), 50.5 (CO_2CH_3), 56.5 (aromatic 3-OCH_3, 5-OCH_3), 57.5 (6-OCH_3 or aromatic 4-OCH_3 or 6-OCH_3), 60.8 (6-OCH_3 or aromatic 4-OCH_3), 68.3 (C-7), 76.3 (C-6), 93.5 (C-4), 107.6 (aromatic C-2 and C-6), 120.6 (CN), 124.4 (aromatic C-1), 142.7 (aromatic C-4), 148.1 (C-3), 153.2 (aromatic C-3 and C-5), 165.4 (O(C=O)Ar), 167.9 (CO_2CH_3); IR ($CHCl_3$) 1685, 1650, 1590 cm^{-1}; mass spectrum, m/e (relative intensity) 474 (P, 11), 459 (6), 294 (12), 279 (8), 263 (19), 240 (47), 222 (26), 195 (58), 166 (72), 152 (100); high-resolution mass spectrum, m/e 474.1977 ($C_{24}H_{30}N_2O_8$ requires 474.2002).

Acknowledgment. This research was supported by a grant from the NIH (GM-29016).

Registry No. (±)-**14**, 87371-63-9; (±)-**15**, 120230-10-6; (±)-**16**, 120230-11-7; (±)-**18** (isomer 1), 120328-40-7; (±)-**18** (isomer 2), 120230-09-3; (±)-**19**, 120230-13-9; (±)-*exo*-**21**, 120328-39-4; (±)-*endo*-**21**, 120328-41-8; (±)-*exo*-**22**, 120328-42-9; (±)-*endo*-**22**, 120230-14-0; (±)-*exo*-**23**, 120328-43-0; (±)-*endo*-**23**, 120230-15-1; (±)-*exo*-**24**, 120328-44-1; (±)-*endo*-**24**, 120230-16-2; **30**, 3061-65-2; **31**, 57956-33-9; (±)-**32** (*exo*-CN), 120328-45-2; (±)-**32** (*endo*-CN), 120230-17-3; (±)-**33**, 120230-18-4; (±)-**34**, 120230-19-5; (±)-**35**, 120230-20-8; (±)-**36**, 120230-21-9; (±)-**37**, 120230-22-0; (±)-**38**, 120230-23-1; (±)-**39** (R = *t*-Bu), 120230-28-6; (±)-**45**, 120262-54-6; (±)-**46**, 120230-30-0; (±)-**47**, 119594-50-2; (±)-**48**, 120328-46-3; (±)-**49**, 120328-47-4; (±)-**51**, 120230-25-3; (±)-**52**, 120230-26-4; (±)-**53**, 120230-27-5; (±)-**54**, 120230-29-7; (±)-**55**, 120328-48-5; (±)-**55a**, 119594-57-9; (±)-**56**, 120230-31-1; (±)-**57**, 120230-32-2; (±)-**58**, 120230-24-2; (±)-**59**, 120230-33-3; (±)-**62**, 120230-34-4; (±)-**63**, 120230-35-5; (±)-**64**, 120230-36-6; (±)-**64** (diol), 120230-37-7; (±)-**65**, 120230-39-9; (±)-**66**, 120230-38-8; (±)-**67**, 120230-40-2; $MeO_2CC{\equiv}CH$, 922-67-8; $EtO_2CC{\equiv}CH$, 623-47-2; *t*-$BuO_2CC{\equiv}CH$, 13831-03-3.

A Comparison of the Radical-Stabilizing Ability of Aromatic Groups. $\gamma^\bullet$ Values for Aromatic Groups

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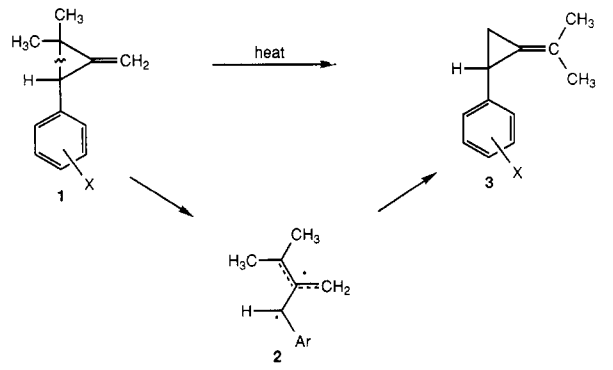
A series of 15 2-aryl-3,3-dimethyl-1-methylenecyclopropanes, **1**, have been prepared and thermally rearranged in C_6D_6 to the corresponding 2-aryl-1-isopropylidenecyclopropanes, **3**. Rearrangement rates give a measure of the ability of various aromatic groups to stabilize the transition state leading to a biradical intermediate. The 4-pyridine *N*-oxide group was found to be the most effective of the aromatic groups in stabilizing the radical intermediate. This has been rationalized by considering the mode of spin delocalization in such radicals. Resonance interactions result in an intermediate which is stabilized due to nitroxide radical character. The 2-furanyl and 2-thienyl groups are also very effective radical stabilizing groups. Rearrangement rates of **1** were converted to $\gamma^\bullet$ values, which are a quantitative measure of the relative abilities of various groups to stabilize free radicals.

Interest in the chemistry of free radicals has remained high over the years.[1] We[2] and others[3-9] have developed quantitative methods of probing the factors that promote their stability. $\sigma^\bullet$ substituent constants[2d,4-7] have been developed that factor out polar effects, which can often dominate free-radical reactions. These substituent constants attempt to measure the pure radical stabilizing ability of substituents on benzylic radicals. Our $\sigma^\bullet$ sub-

Scheme I



(1) For discussions of many current aspects of free-radical chemistry, see: *Substituent Effects in Free Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1986.

(2) (a) Creary, X. *J. Org. Chem.* **1980**, 45, 280. (b) Creary, X.; Benage, B.; Mehrsheikh-Mohammadi, M. E.; Bays, J. P. *Tetrahedron Lett.* **1985**, *26*, 2383–2386. (c) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 1110, 2664. (d) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254. (e) Creary, X.; Mehrsheikh-Mohammadi, M. E. *Tetrahedron Lett.* **1988**, *29*, 749.

(3) For leading references, see: (a) Martin, J. C.; Timberlake, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 978–983. (b) Timberlake, J. W.; Hodges, N. L. *Tetrahedron Lett.* **1970**, 4147–4150. (c) Timberlake, J. W.; Garner, A. W.; Hodges, M. L. *Ibid.* **1973**, 309–312. (d) Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 5856–5862. (e) Dube, M. F.; Timberlake, J. W. *Tetrahedron* **1980**, *36*, 1753–56. (f) Luedtke, A. E.; Timberlake, J. W. *J. Org. Chem.* **1985**, *50*, 268–270.

(4) (a) Dinçtürk, S.; Jackson, R. A.; Townson, M. *Chem. Commun.* **1979**, 172–174. (b) Dinçtürk, S.; Jackson, R. A.; Townson, M.; Agirbas, 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) Agirbas, H.; Jackson, R. A. *Ibid.* **1983**, 739–742.

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

(6) Jiang, X.-K.; Ji, G.-Z.; Yu, C.-X. *Acta Chimica Sinica (English Edition)* **1984**, 82–85.

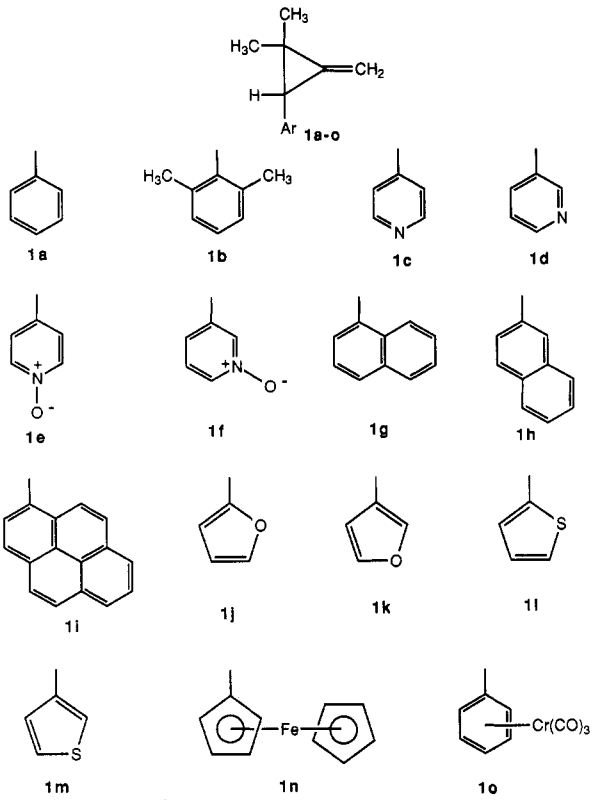
(7) (a) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221–1227, 6531. (b) Wayner, D. D.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164–1168. (c) Wayner, D. D.; Arnold, D. R. *Ibid.* **1985**, *63*, 2378–2383.

(8) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985.

(9) Pasto, D. J. *J. Org. Chem.* **1987**, *52*, 3062.

0022-3263/89/1954-2904$01.50/0

Chart I



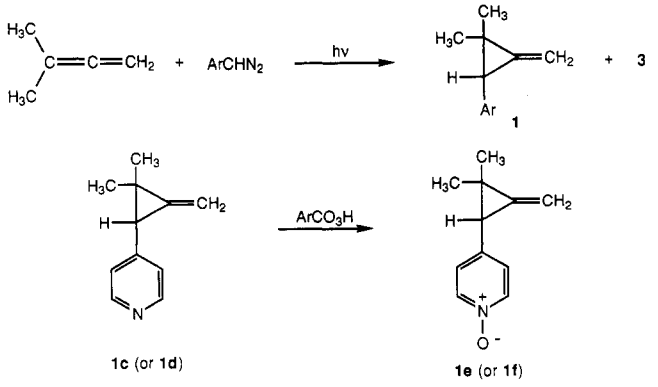
stituent constant[2] is based on the thermal rearrangement rate of the substituted methylenecyclopropanes **1** (Scheme I). The advantages and disadvantages of this probe have been previously discussed.[2d] To date we have reported $\sigma^{\bullet}$ substituent constants for 43 meta and para substituents.

We have been interested in the relative abilities of the various aromatic groups to stabilize free radicals when directly attached to such radical centers. We have therefore prepared a series of methylenecyclopropanes **1** (Chart I), substituted with various aromatic groups, and applied our methylenecyclopropane rearrangement probe to these systems. Rearrangement rates of **1** give a quantitative measure of the relative ability of the aromatic group to stabilize the intermediate biradical **2**. These rates can be converted to $\gamma^{\bullet}$ values,[10] which are group $\sigma^{\bullet}$ values. These $\gamma^{\bullet}$ values are analogous to γ^{+} values (group σ^{+} values),[11] which measure the relative abilities of aromatic groups to stabilize carbocations. Reported here are results of studies which give a quantitative measure of the stabilizing effect of various aromatic groups when directly attached to a radical center.

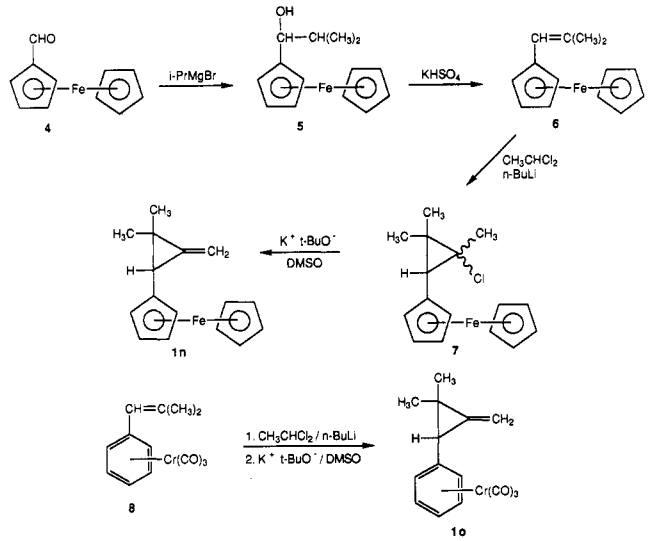
Results and Discussion

Synthetic Aspects. The synthesis of most of the methylenecyclopropanes **1** was accomplished using our previously developed methodology involving arylcarbene additions to 1,1-dimethylallene.[2,12] Aryldiazomethanes (via photolyses) served as carbene precursors for the substrates **1b–d,h–m**, while the reaction of 1-(chloromethyl)-naphthalene with lithium tetramethylpiperidide[12] served as a carbene source in the preparation of **1g**. The pyridine *N*-oxides **1e** and **1f** were prepared by peracid oxidation of

Scheme II



Scheme III



the corresponding pyridines **1c** and **1d** (Scheme II).

Ferrocenyldiazomethane and the chromium tricarbonyl complex of phenyldiazomethane could, in principle, serve as precursors in **1n** and **1o**, respectively. However, these diazocompounds are presently unknown. Therefore the systems **1n** and **1o** were prepared by an alternative method[14] developed for the synthesis of methylenecyclopropanes. The ferrocene derivative **6** was prepared in straight-forward fashion from ferrocenecarboxaldehyde. Addition of methylchlorocarbene to the ferrocene derivative **6** gave the cyclopropane **7**, which could be dehydrohalogenated to give the desired methylenecyclopropane **1n**. An analogous procedure was used to prepare the chromium tricarbonyl derivative **1o** (Scheme III).

Rearrangement of 1a and the Ortho-Substituted System 1b. Thermodynamic Considerations. The ortho-disubstituted system **1b** was rearranged in C_6D_6 at 80 °C, and the reaction was monitored by NMR spectroscopy. Rate data for this and other substrates are given in Table I. The rate of **1b** is slower than that of the parent unsubstituted system **1a**, despite the expectation that 2,6-dimethyl substitution should stabilize a benzylic radical. This implies that steric factors are important in determining the rearrangement rate of ortho-substituted systems and that our methylenecyclopropane rearrangement probe may not be valid for hindered systems such as **1b**. Therefore the $\gamma^{\bullet}$ value for 2,6-dimethylphenyl may not give an accurate indication of the radical-stabilizing ability of this group.

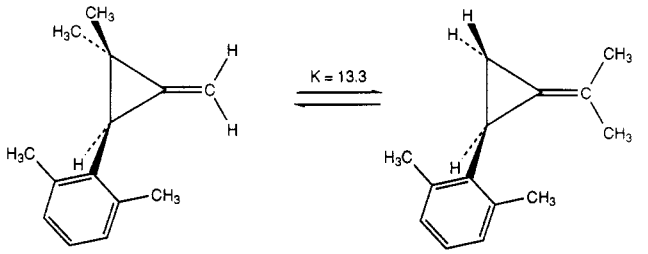
(10) $\gamma^{\bullet}$ for the 4-pyridyl group is defined by log (k_{1c}/k_{1a}).
(11) (a) Peters, E. N. *J. Am. Chem. Soc.* **1976**, *98*, 5627. (b) Peters, E. N. *J. Org. Chem.* **1977**, *42*, 1419.
(12) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611.
(13) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 581.
(14) Orora, S.; Binger, P. *Synthesis* **1974**, 801.

Table I. Rearrangement Rates of 1 in C_6D_6 at 80.0 °C

aryl group	k, s^{-1}	k_{rel}	$\gamma^\bullet$
phenyl (**1a**)	5.57×10^{-5}	1.00	0.00
2,6-$(CH_3)_2C_6H_3$ (**1b**)	2.37×10^{-5}	0.42	−0.37
4-pyridyl (**1c**)	2.95×10^{-5}	0.53	−0.28
3-pyridyl (**1d**)	4.39×10^{-5}	0.79	−0.10
4-pyridyl *N*-oxide (**1e**)	4.20×10^{-3} [a]	75	1.88
	1.40×10^{-4} (50.0°)		
	2.01×10^{-5} (35.0°)		
3-pyridyl *N*-oxide (**1f**)	2.86×10^{-5}	0.51	−0.29
1-naphthyl (**1g**)	9.51×10^{-5}	1.71	0.23
2-naphthyl (**1h**)	1.74×10^{-4}	3.12	0.49
3-pyrenyl (**1i**)	5.27×10^{-4}	9.46	0.98
2-furanyl (**1j**)	2.43×10^{-3} [a]	43.7	1.64
	1.68×10^{-4} (55.0°)		
	2.75×10^{-5} (40.0°)		
3-furanyl (**1k**)	4.31×10^{-5}	0.77	−0.11
2-thienyl (**1l**)	2.78×10^{-3} [a]	49.9	1.70
	1.72×10^{-4} (55.0°)		
	2.62×10^{-5} (40.0°)		
3-thienyl (**1m**)	6.71×10^{-5}	1.21	0.08
ferrocenyl (**1n**)	8.90×10^{-5}	1.60	0.20
$C_6H_5Cr(CO)_3$ (**1o**)	1.82×10^{-5}	0.33	−0.49

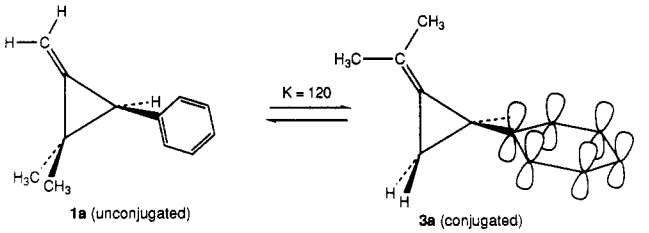
[a] Extrapolated value.

The rearrangement of **1b** is reversible, and the ratio of **1b** to **3b** is 7.5:100 at equilibrium at 100 °C as determined by NMR. This corresponds to an equilibrium constant of 13.3 and a free energy difference between **1b** and **3b** of 1.9 kcal/mol at 100 °C. The majority of this energy difference is attributed to the dimethyl substitution on the exocyclic double bond of **3b**, which, as expected, leads to a more stable alkene.



1b **3b**

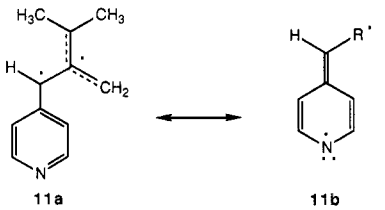
Careful re-examination of the rearrangement of **1a** shows that a trace of unrearranged **1a** (0.8%) remains at equilibrium at 100 °C. The equilibrium constant of 120 corresponds to a free energy difference of 3.5 kcal/mol between **1a** and **3a**. This compares to a free energy difference of 1.9 kcal/mol for the **1b**, **3b** pair. Examination of the NMR spectrum of **1a** shows that the phenyl group is in an "unconjugated" conformation.[15] In the rearranged product **3a**, the phenyl group becomes "conjugated" with the cyclopropane ring,[16] presumably as a result of placing the hindering methyl groups on the exocyclic double bond of **3a** and away from the phenyl ring. On the other hand, Brown has shown that *o*-dimethyl substitution forces an aryl group to adopt an unconjugated conformation with respect to a cyclopropane ring.[17] Therefore, the aromatic ring in **3b** should remain in the "unconjugated" position with respect to the cyclopropane ring presumably due to the *o*-dimethyl substitution. Hence the free energy difference between **1b** and **3b** (1.9 kcal/mol) is due essentially to the additional methyl substition on the double bond in **3b**. The free energy difference between **1a** and **3a** is due not only to exocyclic methyl substitution (~1.9 kcal/mol) but also the phenyl "conjugation" with the cyclopropane ring of **3a**. We estimate that this conjugation of the phenyl group with the cyclopropane contributes an additional 1.6 kcal/mol to the stability of **3a**.



1a (unconjugated) **3a** (conjugated)

Pyridine and Pyridine *N*-Oxide Systems. Rate data in Table I indicate that both the 4-pyridyl and the 3-pyridyl systems **1c** and **1d** rearrange less readily than the parent system **1a**. The $\gamma^\bullet$ values for these systems are in agreement with hyperfine coupling constant data, which indicate that spin delocalization is less in the 3- and 4-pyridyl radicals than in the benzyl radical.[18] The decreased stability of 3-pyridyl-substituted radicals can be attributed to the presence of the electronegative nitrogen atom in the 3-position. The small destabilizing effect of electronegative groups in this position has been seen before and has been discussed in some detail.[2d] The electron-withdrawing nature of the 4-pyridyl group may also contribute to the decreased rate of the 4-pyridyl system **1c**. The rate of the 3-pyridyl *N*-oxide system **1f** is also retarded due to the electron-withdrawing *N*-oxide group in the meta position.

In the case of 4-pyridyl analogue **1c**, another factor may be involved in slowing the rearrangement rate relative to **1a**. Resonance interactions in the biradical intermediate, as represented by **11b**, place spin density on the nitrogen atom. Forms such as **11b** may have less importance due to the expected lower intrinsic stability of nitrogen-centered versus carbon-centered radicals.[19]



11a **11b**

The rearrangement rate of the 4-pyridyl *N*-oxide **1e** stands in sharp contrast to the rearrangement rate of the pyridine systems **1c** and **1d** and the 3-pyridine *N*-oxide system **1f**. It is the fastest rearranging system studied to date, being 142 times faster than the unoxidized 4-pyridyl system **1c** and 75 times faster than the phenyl analogue **1a**. This rate enhancement is considered a truly enormous effect in view of previously observed substituent effects. For example, the best radical stabilizing substituent that

(15) This unconjugated conformation of **1a** is a result of the cis methyl group which, as Closs and Moss have shown, forces the phenyl group to adopt the conformation **1a** (unconjugated) as the minimum energy conformation. See: Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042.

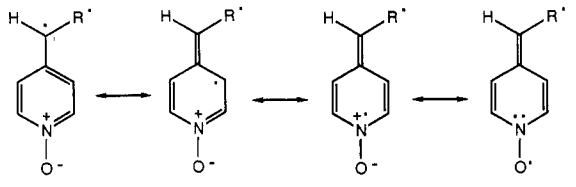
(16) The conformation **3a** (conjugated) is the preferred conformation where the aromatic ring can best interact with the bent bonds of the cyclopropane ring. In **3a**, the ortho hydrogens are shifted upfield to δ 7.08. Previous estimates of stabilization due to this conjugation range from 1.4 to 2.0 kcal/mol. See: (a) Closs, G. L.; Klinger, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3265. (b) Parr, W. J. E.; Schaefer, T. *J. Am. Chem. Soc.* **1977**, *99*, 1033.

(17) Brown, H. C.; Cleveland, J. D. *J. Org. Chem.* **1976**, *41*, 1792.

(18) Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1985**, 121.

(19) This expectation is based on electronegativity considerations where a simple periodic trend suggests that radical stability order should be $^\bullet F < ^\bullet OR < ^\bullet NR_2 < ^\bullet CR_3$. Qualitative data support this contention. The nitrogen centered succimidyl radical readily abstracts hydrogen atom from hydrocarbons in a very nonselective process. See: (a) Traynham, J. G.; Lee, Y.-S. *J. Am. Chem. Soc.* **1974**, *96*, 3590. (b) Day, J. C.; Lindstrom, M. J.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5616.

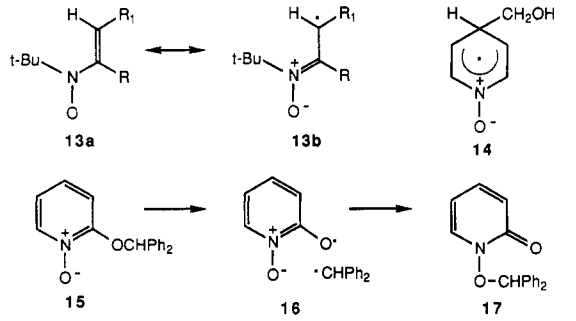
we have previously seen is the *p*-NMe_2 group, which enhances the rearrangement rate of **1a** by a factor of 7.9.[2a] We attribute the extraordinarily rapid rearrangement rate of the 4-pyridyl *N*-oxide system, **1e**, to a potent radical stabilizing effect of the *N*-oxide function as rationalized by the resonance interactions shown in **12a–d**. Spin



12a **12b** **12c** **12d**

density can be placed on nitrogen as in **12c** and further delocalized to oxygen as in **12d**. This later form is recognizable as a nitroxide radical, a radical of unusually high kinetic (and presumably thermodynamic) stability. Hence the intermediate involved in the thermal rearrangement of **1e** has nitroxide radical character and is formed quite readily. The $\gamma^{\bullet}$ value for the 4-pyridyl *N*-oxide system of 1.88 far exceeds those of the *p*-(dimethylamino)phenyl, *p*-vinylphenyl, and *p*-nitrophenyl groups, which are among the best radical stabilizing groups known.

Radicals related to **12** have been suggested in the past. Pertinent examples include the vinyl nitroxide radical **13** (where R_1 is CO_2CH_3 or SO_2Ph), which has been generated and studied by ESR techniques.[20] There is significant spin density on the β-carbon in this nitroxide radical. The delocalized radical **14** is formed on addition of the hydroxymethyl radical to pyridine *N*-oxide.[21] INDO calculations show substantial spin density on nitrogen and oxygen in **14**, as well as on the appropriate ring carbons. The radical pair **16** is a proposed intermediate in the thermal rearrangement of **15** to the *N*-alkoxy-2-pyridone **17**.[22] Such intermediates suggest, and our own studies confirm, that the 4-pyridyl *N*-oxide group is an extraordinary radical-stabilizing group.



13a **13b** **14**

15 **16** **17**

The fact that **1e** is best represented by a zwitterionic structure suggests that there may be a solvent effect on its rearrangement rate. Figure 1 shows that there is no correlation with the solvent polarity parameter E_T.[23] However, the ability of the solvent to hydrogen bond to **1e** appears to have an effect on the rate. The rearrangement rate of **1e** is slower in methanol than in C_6D_6. In acetic acid, the rearrangement rate is the slowest. We attribute this to hydrogen bonding of methanol and acetic acid to **1e** (the ground state), which decreases the ability of the oxygen nonbonding electron pair to interact with

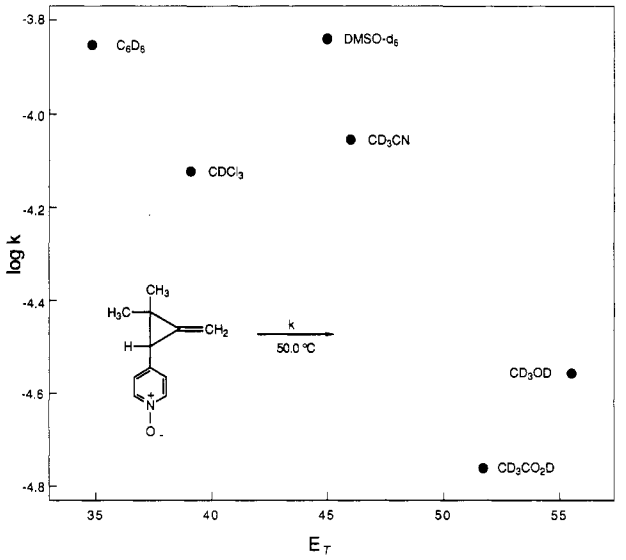


Figure 1. A plot of log *k* for rearrangement of **1e** versus E_T.

Table II. Solvent Effects on the Rearrangement Rates of 1e and 1f

solvent	*k* for **1e** (50 °C), s^{-1}	*k* for **1f** (80 °C), s^{-1}
C_6D_6	1.40×10^{-4}	2.86×10^{-5}
$CDCl_3$	7.57×10^{-5}	2.99×10^{-5}
$(CD_3)_2SO$	1.45×10^{-4}	
CD_3CN	8.85×10^{-5}	2.51×10^{-5}
CD_3OD	2.77×10^{-5}	2.61×10^{-5}
CD_3CO_2D	1.74×10^{-5}	2.81×10^{-5}

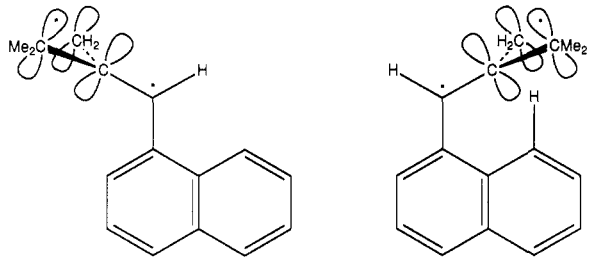
the unpaired electron, i.e. forms such as **12d** have decreased importance. In acetic acid-d_4 solvent, **1e** is probably substantially protonated,[24] and hence nitroxide radical character in the transition state is of less importance. However, in the polar aprotic solvents DMSO and CD_3CN, this effect is not observed.

In contrast to the behavior of **1e** in protonating solvents, the effect of such solvents on the rearrangement rate of the 3-pyridyl *N*-oxide system **1f** is negligible. Data in Table II show that rearrangement rates of **1f** are comparable in benzene, chloroform, acetonitrile, methanol, and acetic acid. This supports the view that the decreased rearrangement rates of **1e** in protic solvents are not due simply to a lowering of the ground state energy of **1e** as a result of hydrogen bonding. The decreased ability of the oxygen to stabilize the transition state leading to **12**, as a result of hydrogen bonding, is the likely cause of decreased rearrangement rates of **1e** in protic solvents.

Polycyclic Aromatic Systems. Both the 1- and the 2-naphthyl derivatives **1g** and **1h** as well as the pyrenyl system **1i** rearrange faster than the parent system **1a**. This is attributed to increased spin delocalization into the added aromatic ring(s) with the tetracyclic pyrenyl system providing the greatest delocalization. However, unexpectedly, the 2-naphthyl system is somewhat more reactive than the 1-naphthyl derivative. This is contrary to expectations based on simple valence bond theory in which spin delocalization is expected to be more favorable in the intermediate derived from the 1-naphthyl system. This expectation is based on arguments analogous to those used to explain the preference for electrophilic aromatic sub-

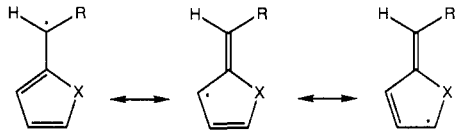
(20) Aurich, H. G.; Hahn, K.; Stork, K. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 551.
(21) Quaegebeur, J. P.; Perly, B.; Surpateanu, G.; Lablanche-Combier, A. *Can. J. Chem.* **1977**, *55*, 3442.
(22) Schöllkopf, U.; Hoppe, I. *Tetrahedron Lett.* **1970**, 4527.
(23) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1. There is also no correlation with Kosower *Z* values. See: Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253.
(24) The H_0 value for acetic acid is 0.00[25] and the pK_a of 4-methylpyridine *N*-oxide is 1.29.[26] If the pK_a of **1e** is comparable to that of 4-methylpyridine *N*-oxide, then **1e** would be approximately 95% protonated in HOAc.
(25) Milyaeva, N. M. *Russ. J. Inorg. Chem.* **1958**, *3*, 27.
(26) Jaffe, H. H.; Doak, G. O. *J. Am. Chem. Soc.* **1955**, *79*, 4441.

stitution at the 1-position of naphthalene as opposed to the 2-position.[27] This suggests that steric factors may be important in the rearrangement of **1g**, and the rearrangement rate of this "ortho-substituted" system may not be a true reflection of the radical stabilizing ability of the 1-naphthyl group. We suggest that the thermal rearrangement of **1g** occurs with the naphthyl group rotating in only one of two possible directions to give the less hindered biradical **18a** (and not the more hindered system **18b**). The 2-naphthyl derivative is not subject to such complicating steric factors, and hence rearranges faster than the 1-naphthyl derivative. Increased spin delocalization in the pyrenyl derivative more than offsets an analogous rate retarding steric effect of the ortho fused ring.



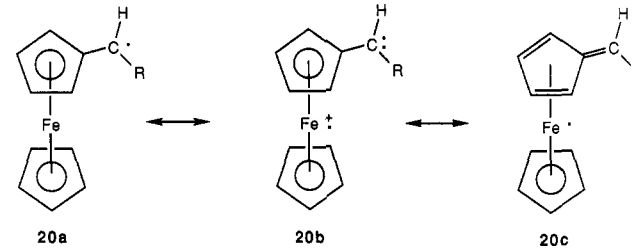
18a 18b

Thienyl and Furanyl Systems. The 2-furanyl and the 2-thienyl derivatives **1j** and **1l** are among the fastest rearranging systems studied, being exceeded only by the 4-pyridine *N*-oxide system **1e**. These heteroaromatic groups are therefore significantly better radical-stabilizing groups than phenyl presumably due to extensive spin delocalization as in **19**. The 3-furanyl and 3-thienyl derivatives **1k** and **1m** show reduced rates relative to **1j** and **1l**. Additional spin delocalization in the biradicals derived from **1j** and **1l** (as represented by **19c**) is not available in the 3-isomers. These simple resonance considerations account for the enhanced rearrangement rates of **1k** and **1m** relative to the 3-isomers. Similar arguments account for the preference of furan and thiophene to undergo electrophilic aromatic substitution at the 2-position rather than at the 3-position.[28]



19a (X = O, S) 19b 19c

Organometallic Aromatic Systems 1n and 1o. Although ferrocenyl type radicals have been suggested in the past[29] as intermediates in certain transformations, no quantitative data is available concerning their relative stability. Our study on the rearrangement of the ferrocenyl derivative **1n** shows that the ferrocenyl group is a very effective radical-stabilizing group. This system rearranges somewhat faster than the phenyl analogue **1a**, but its reactivity does not approach that of the *N*-oxide or the 2-thienyl and 2-furanyl systems. While the ferrocenyl group is much more effective at carbocation stabilization than is the phenyl group,[30] its radical stabilizing ability does not surpass that of the phenyl group by a great deal. The extent of spin delocalization involving iron is uncertain, although forms such as **20b** (an Fe(III) ferricenium form) and **20c** (an Fe(I) η^4 form) would account for the ability of the ferrocenyl group to stabilize radicals.



20a 20b 20c

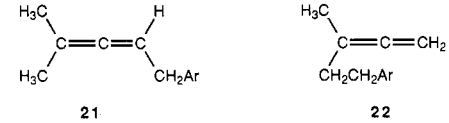
Complexation of a chromium tricarbonyl fragment to the phenyl group reduces reactivity, and the substrate **1o** rearranges at only one-third the rate of the unsubstituted system **1a**. Spin delocalization by the $C_6H_5(Cr(CO)_3)$ group therefore appears to be reduced somewhat relative to delocalization by C_6H_5. Reasons for this are unclear, although it is known that $Cr(CO)_3$ complexation renders an aromatic ring electron deficient and hence susceptible to nucleophilic aromatic substitution.[31] As such, the aromatic ring in **1o** may simply be acting as very electron deficient aromatic group and therefore slows the rearrangement rate relative to unsubstituted **1a**.

Summary and Conclusions

A variety of aryl-substituted methylenecyclopropanes, **1**, have been prepared. These substrates all thermally rearrange via biradical intermediates. All of the aromatic groups can be considered radical stabilizing. The 4-pyridine *N*-oxide group is the most effective radical-stabilizing group. This is attributed to effective spin delocalization and resultant nitroxide radical character in the biradical derived from **1e**. The 2-furanyl and 2-thienyl groups are also among the most effective radical-stabilizing groups. A $\gamma^{\bullet}$ scale has been established which allows a quantitative comparison to be made on the relative abilities of these aromatic groups to stabilize radicals.

Experimental Section

Preparation of Methylenecyclopropanes 1 from Aryldiazomethanes and 1,1-Dimethylallene. General Procedure. This general reaction has been previously described.[2d,12] A solution of the appropriate aryldiazomethane in 1,1-dimethylallene was irradiated with Pyrex-filtered light from a Hanovia 450-W medium-pressure lamp in a water-cooled apparatus until the color of the diazocompound disappeared. The excess 1,1-dimethylallene solvent was recovered by removal at aspirator pressure with the receiver flask cooled to −78 °C. The crude residue, which contained **1** and smaller amounts of **3**, was chromatographed on silica gel. In certain cases, small amounts of the allenes **21** and **22** were also produced (by carbene insertion reactions). These products, which are difficult to remove by chromatography, do not interfere with kinetic studies and were therefore not removed. Representative examples are given below. NMR spectral data are shown in Table III.



21 22

Preparation of 1b. A solution of 108 mg of 2,6-dimethylphenyldiazomethane[32] in 9 mL of 1,1-dimethylallene was irradiated

(27) March, J. In *Advanced Organic Chemistry*; Wiley: New York, 1985; pp 461–462.
(28) Marino, G. *Adv. Heterocycl. Chem.* **1971**, *13*, 235.
(29) Baker, C.; Horspool, W. M. *J. Chem. Soc., Perkin Trans, 1* **1979**, 1862, 2294.
(30) (a) Watts, W. E. *J. Organomet. Chem. Libr.* **1979**, *7*, 399. (b) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304.
(31) Pearson, A. J. In *Metallo-organic Chemistry*: Wiley: New York, 1985; pp 350–360.
(32) Creary, X. *Org. Synth.* **1986**, *64*, 207.

Table III. NMR Spectral Data for Methylenecyclopropanes 1 in $CDCl_3$

substrate	aromatic	olefinic	H_2	methyl
1a	7.28–7.15	5.58 and 5.55	2.47	1.343 and 0.849
1b	6.9–7.1	5.62 and 5.55	2.28	1.391 and 0.787
1c	8.44 and 7.05	5.62 and 5.54	2.42	1.368 and 0.881
1d	8.42, 7.5–7.1	5.62 and 5.57	2.44	1.367 and 0.856
1e	8.08 and 7.08	5.64 and 5.56	2.41	1.365 and 0.896
1f	8.08, 7.22–7.04	5.64 and 5.58	2.37	1.360 and 0.907
1g	8.2–7.2	5.72 and 5.67	2.81	1.539 and 0.726
1h	7.85–7.30	5.65 and 5.64	2.62	1.393 and 0.863
1i	8.6–7.6	5.85 and 5.76	3.11	1.629 and 0.729
1j	7.33, 7.18, 6.26	5.46	2.14	1.29 and 0.94
1k	7.33, 7.18, 6.25	5.46 and 5.44	2.15	1.291 and 0.939
1l	7.10, 6.91, 6.76	5.56 and 5.53	2.52	1.319 and 0.954
1m	7.22, 6.94, 6.91	5.51	2.40	1.313 and 0.897
1n	4.16, 4.14, 4.07, 4.00	5.50 and 5.46	2.15	1.228 and 0.886
1o	5.48–5.10	5.61	2.12	1.31 and 1.02

for 90 min. After removal of the excess allene, the residue was chromatographed on 4.5 g of silica gel. Elution with hexane gave 100 mg (73%) of a mixture of **1b**, **3b**, and **21** (Ar = 2,6-di-CH_3-C_6H_3) in a 74:14:12 ratio, respectively, as determined by NMR. Exact mass calcd for $C_{14}H_{18}$ m/e 186.14085, found 186.14086.

Preparation of 1c and 1d. A solution of 420 mg of 4-pyridyldiazomethane[33] in 33 mL of 1,1-dimethylallene was irradiated with Pyrex-filtered light from a Hanovia 450-W lamp for 45 min. The solution was filtered to remove the insoluble precipitate, and the solution was irradiated again for an additional 45 min. The color of the 4-pyridyldiazomethane had faded, but much of the diazo compound still remained. After filtering again, the excess 1,1-dimethylallene was removed under reduced pressure (15 mm). The crude residue was chromatographed on 5 g of silica gel and eluted with increasing amounts of ether in hexanes. A mixture of **1c**, **3c**, **21** (Ar = 4-pyridyl), and **22** (Ar = 4-pyridyl) in a 42:34:15:9 ratio eluted with about 35% ether in hexanes. The combined yield of these products was 153 mg (25%): exact mass calcd for $C_{11}H_{13}N$ m/e 159.1048, found 159.1046.

By a similar procedure, irradiation of 280 mg of 3-pyridyldiazomethane[29] in 27 mL of 1,1-dimethylallene gave, after chromatography on silica gel, 233 mg (62%) of **1d**, **3d**, and **21** (Ar = 3-pyridyl) in a 67:28:5 ratio: exact mass calcd for $C_{11}H_{13}N$ m/e 159.1048, found 159.1041.

Preparation of *N*-Oxides 1e and 1f. A solution of 153 mg of the mixture of **1d** prepared above in 2 mL of CH_2Cl_2 was cooled in a 15 °C bath, and 195 mg of *m*-chloroperbenzoic acid was added in 1 portion. The mixture was kept at this temperature for 10 min and then allowed to warm to room temperature. After being stirred for 6.5 h at room temperature, the mixture was taken up into ether and washed with a cold solution of aqueous KOH containing some $Na_2S_2O_3$ and NaI. The organic extract was then dried over $MgSO_4$, and the solvent was removed with a rotary evaporator. The NMR spectrum of the crude residue showed about 30% unreacted **1c** along with the *N*-oxide **1e**. The crude product was chromatographed on 6 g of silica gel and eluted initially with 50% ether in hexanes. The unreacted **1c** eluted with this solvent. The column was then eluted successively with 100% ether, 50% CH_2Cl_2 in ether, 100% CH_2Cl_2, and then 5% methanol in CH_2Cl_2. The *N*-oxide **1e**, along with **3e**, **21** (Ar = 4-pyridyl *N*-oxide), and **22** (Ar = 4-pyridyl *N*-oxide), eluted with 5% methanol in CH_2Cl_2 in a 63:26:6:5 ratio. The total yield was 66.6 mg (40%): exact mass calcd for $C_{11}H_{13}NO$ m/e 175.0997, found 175.0997.

By a similar procedure, reaction of 156 mg of **1d** with in 2 mL of CH_2Cl_2 with 215 mg of *m*-chloroperbenzoic acid gave, after chromatography on 5 g of silica gel and elution with 5% methanol in CH_2Cl_2, 93 mg (54%) of the *N*-oxide **1f** containing **3f** and **21** in an 82:15:3 ratio: exact mass calcd for $C_{11}H_{13}NO$ m/e 175.0997, found 175.0997.

Preparation of 1j and 1k. These substrates were prepared from the corresponding diazocompounds, which were prepared in low yield by MnO_2 oxidation of the corresponding hydrazones.[33] The diazocompounds decomposed readily on removal of the ether solvent used for the oxidation of the hydrazones.

Preparation of 3-Thiophenecarboxaldehyde Triisopropylbenzenesulfonhydrazone. Via the procedure of Reese,[34] a suspension of 2.94 g of 2,4,6-triisopropylbenzenesulfonhydrazine in 20 mL of methanol was stirred as 1.10 g of 3-thiophenecarboxaldehyde was added. The mixture became homogeneous for a few seconds, and then crystals began to form. After being stirred for 1 h at room temperature, the mixture was cooled to 0 °C, and the solid was collected, washed with cold methanol, and dried under vacuum. The yield of 3-thiophenecarboxaldehyde triisopropylbenzenesulfonhydrazone, mp 201 °C dec, was 3.36 g (84%): NMR of 3-thiophenecarboxaldehyde triisopropylbenzenesulfonhydrazone ($CDCl_3$) δ 7.804 (br, 2 H), 7.422 (d of d, J = 2.9, 1 Hz, 1 H), 7.349 (d of d, J = 5.1, 1 Hz, 1 H), 7.262 (d of d, J = 5.1, 2.9 Hz, 1 H), 7.177 (br, 2 H), 4.254 (heptet, J = 6.7 Hz, 2 H), 2,896 (heptet, J = 6.7 Hz, 1 H), 1.304 (d, J = 7 Hz, 12 H), 1.247 (d, J = 7 Hz, 6 H).

Preparation of 1m. Sodium metal (52 mg) was dissolved in 16 mL of ethylene glycol, and 0.54 g of 3-thiophenecarboxaldehyde triisopropylbenzenesulfonhydrazone was added. The mixture was warmed to 60 °C for 5 min, cooled to room temperature, and extracted with 7 mL of 1,1-dimethylallene. The red solution of 3-thienyldiazomethane in 1,1-dimethylallene was decanted, and the pyrolysis–extraction procedure was repeated two more times. The combined allene extracts were washed with 2 portions of cold water and saturated sodium chloride solution and dried over $MgSO_4$. After filtration, the red solution of 3-thienyldiazomethane in 1,1-dimethylallene was irradiated for 50 min. The red color was discharged, and, after removal of the solvent, the residue was chromatographed on 5.5 g of silica gel. Elution with hexanes gave 45 mg (21% based on hydrazone) of a mixture of **1m** and **3m** in a 7.6:1 ratio as determined by NMR: exact mass calcd for $C_{10}H_{12}S$ m/e 164.0660, found 164.0658.

Preparation of 1-Ferrocenyl-2-methylpropene, 6. This compound has been previously prepared by a related procedure.[35a] A Grignard reagent was prepared from 23.5 g of 2-bromopropane and 3.5 g of magnesium in 150 mL of ether. The solution of 2-propylmagnesium bromide was cooled to 0 °C, and a solution of 10.05 g of ferrocenecarboxaldehyde in 50 mL of ether was added dropwise. The mixture was warmed to room temperature and after 6 h the mixture was poured into a mixture of 100 mL of water, 100 g of ice, and 15 mL of concentrated sulfuric acid. The mixture was then transferred to a separatory funnel with ether, and the aqueous phase was discarded. The ether extract was washed with dilute $NaHCO_3$ solution and saturated NaCl solution and dried over $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator. Crushed $KHSO_4$ (50 mg) was added to the residue, and a short path distillation head was attached to the flask. The pressure was lowered to 0.2 mm, and the flask was heated to about 75 °C in an oil bath for 90 min. After the bubbling ceased, the pot temperature was increased and the product was distilled, giving 10.57 g (94%) of **6** as a red oil: bp 93–94 °C (0.17 mm); NMR of **6**[35b] ($CDCl_3$) δ 5.890 (m, 1 H), 4.250

(33) Maas, G.; Hummel, C. *Chem. Ber.* **1980**, *113*, 3679.

(34) Dudman, C. C.; Reese, C. B. *Synthesis* **1982**, 419–421.

(35) (a) Berger, K. R.; Biehl, E.; Reeves, P. C. *J. Org. Chem.* **1974**, *39*, 477. (b) Horspool, W. M.; Sutherland, R. G. *Can. J. Chem.* **1968**, *46*, 3453.

(t, J = 1.8 Hz, 2 H), 4.135 (t, J = 1.8 Hz, 2 H), 4.088 (s, 5 H), 1.802 (m, 3 H), 1.787 (m, 3 H).

Preparation of 1n. A preliminary reaction of **6**, with 1.1 equiv of CH_3CHCl_2 and *n*-BuLi led to about 80% recovery of unreacted **6**. Therefore a large excess of CH_3CHCl_2 and *n*-BuLi was used in the preparation of **7**. A solution of 1.002 g of 1-ferrocenyl-2-methylpropene, **6**, and 2.569 g of 1,1-dichloroethane in 5 mL of ether was cooled to −35 °C. *n*-Butyllithium (8.9 mL of 2.5 M in hexanes) was added dropwise over a 20-min period. The mixture was warmed to 0 °C, water was added, and the mixture was transferred to a separatory funnel. The organic phase was washed with saturated NaCl solution and dried over $MgSO_4$, and the solvent was removed with a rotary evaporator. Evacuation of the residue for 3 h at 0.03 mm removed most of the lower boiling volatile components leaving 1.05 g (83%) of crude **7** as a red oil. Attempted distillation of a small portion of the crude residue led to decomposition. Standing for prolonged periods at room temperature also led to decomposition of the crude **7**.

Potassium *tert*-butoxide (333 mg) was dissolved in 10 mL of dry dimethyl sulfoxide, and 502 mg of the crude chloride **7** was added. The mixture was warmed to 40 °C for 90 min. The mixture was taken up into ether, washed with water, and saturated NaCl solution, and dried over $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator, leaving 440 mg (99%) of the methylenecyclopropane **1n** as a red oil: exact mass calcd for $C_{16}H_{18}Fe$ 266.0758, found 266.0757.

Preparation of the Chromium Tricarbonyl Complex of 1-Phenyl-2-methylpropene, 8. A mixture of 3.00 g of chromium hexacarbonyl, 6.0 g of 1-phenyl-2-methylpropene, and 5 mL of tetrahydrofuran in 40 mL of dry di-*n*-butyl ether was refluxed under nitrogen for 28 h. Periodically the $Cr(CO)_6$, which sublimed into the condenser, was scraped back into the reaction mixture. The mixture was then diluted with 100 mL of diethyl ether, and the yellow solution was filtered through Celite. The ether was removed with a rotary evaporator, and the butyl ether and unreacted 1-phenyl-2-methylpropene were removed by distillation at reduced pressure. The yellow oil was again taken up into ether and refiltered through Celite. The ether was again removed with a rotary evaporator, and hexane was added to the residue. The yellow solid **8** which formed was collected, washed with hexane, and dried under vacuum. The yield of **8**, mp 50–52 °C, was 2.28 g (62%): NMR of **8** ($CDCl_3$) δ 5.86 (br, 1 H), 5.40 (t, J = 6 Hz, 2 H), 5.28 (d, J = 6 Hz, 2 H), 5.20 (t, J = 6 Hz, 1 H), 1.88 (m, 6 H). Anal. Calcd for $C_{13}H_{12}CrO$: C, 58.21; H, 4.51. Found: C, 58.03; H, 4.60.

Preparation of 1o. The preparation of **1o** from the chromium tricarbonyl complex **8** was analogous to the preparation of **1n** from **7**. The addition of chloromethyl carbene to **8** was an inefficient reaction. Reaction of 6 equiv of 1,1-dichloroethane and *n*-butyllithium with **8**, followed by dehydrohalogenation with potassium *tert*-butoxide, gave a mixture of unreacted **8** and **1o** in a 1.5:1 ratio. This mixture was not further separated since attempts at careful chromatography led to decomposition of **1o**.

Thermal Rearrangements of 1. Kinetics Procedure. Kinetics procedures for thermal rearrangement of **1** in C_6D_6 were analogous to those previously described.[2c] A solution of the appropriate methylenecyclopropane **1** in C_6D_6 containing a small amount of dimethyl maleate was sealed in an NMR tube under nitrogen. The tube was immersed in a constant temperature bath at the appropriate temperature, and the disappearance of the olefinic signal of **1** in the region from δ 5.4–5.9 was periodically monitored by 300-MHz NMR with dimethyl maleate as an internal standard. In the case of **1g**, methyl benzoate was used as the internal standard, while dimethyl fumarate was used as the internal standard in the case of **1i**. In the rearrangement of **1o**, the olefinic signal of the unreacted **8** was used as the internal standard. Rates for the *N*-oxides **1e** and **1f** in solvents other than C_6D_6 were determined by completely analogous procedures. Rate constants were calculated by the method of least squares. Correlation coefficients were greater than 0.999. Rate constants given represent the average two runs. Maximum standard deviations were ±3% and most standard deviations were approximately ±1%.

Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **1a**, 65108-25-0; **1b**, 120361-08-2; **1c**, 118674-95-6; **1d**, 118674-93-4; **1e**, 118674-96-7; **1f**, 118674-94-5; **1g**, 65354-62-3; **1h**, 120361-09-3; **1i**, 120361-10-6; **1j**, 120361-11-7; **1k**, 120361-12-8; **1l**, 120361-13-9; **1m**, 120361-14-0; **1n**, 120410-33-5; **1o**, 120410-34-6; **3b**, 120361-15-1; **3c**, 118674-97-8; **3d**, 118674-98-9; **3e**, 118674-99-0; **3f**, 118675-00-6; **3m**, 120361-27-5; **4**, 12093-10-6; **6**, 33040-03-8; **7**, 120410-35-7; **8**, 120410-36-8; **21** (Ar = 2,6-di-CH_3-C_6H_3), 120361-16-2; **21** (Ar = 4-pyridyl), 120361-17-3; **21** (Ar = 3-pyridyl), 120361-19-5; **21** (Ar = 4-pyridyl *N*-oxide), 120361-20-8; **21** (Ar = 3-pyridyl *N*-oxide), 120361-22-0; **22** (Ar = 4-pyridyl), 120361-18-4; **22** (Ar = 4-pyridyl *N*-oxide), 120361-21-9; $(CH_3)_2C{=}C{=}CH_2$, 598-25-4; 2,6-$(CH_3)_2C_6H_3CH{=}N_2$, 74998-89-3; 2,4,6-(iso-$C_3H_7)_3C_6H_3SO_2NHNH_2$, 39085-59-1; $(CH_3)_2CHBr$, 75-26-3; $(CH_3)_2CHMgBr$, 920-39-8; CH_3CHCl_2, 75-34-3; $C_6H_5CH{=}C(CH_3)_2$, 768-49-0; 4-pyridyldiazomethane, 26363-69-9; 3-pyridyldiazomethane, 26364-06-7; 2-furancarboxaldehyde hydrazone, 31350-00-2; 3-furancarboxaldehyde hydrazone, 120361-23-1; 2-furyldiazomethane, 5919-15-3; 3-furyldiazomethane, 120361-24-2; 3-thiophenecarboxaldehyde, 498-62-4; 3-thiophenecarboxaldehyde 2,4,6-triisopropylbenzenesulfonhydrazone, 120361-25-3; 3-thienyldiazomethane, 120361-26-4.