Methylenecyclopropane Rearrangement as a Probe for Free Radical Substituent Effects. $\sigma^{\bullet}$ Values for Commonly Encountered Conjugating and Organometallic Groups

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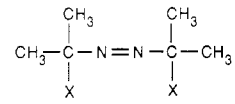
A series of 3-aryl-2,2-dimethylmethylenecyclopropanes, **8**, with NO_2, NMe_2, vinyl, isopropenyl, phenyl, cyclopropyl, CH_2SiMe_3, $SiMe_3$, $SnMe_3$, $-\overline{BOCH_2CH_2O}$, and HgCl substitution in the para position of the aromatic ring have been prepared. All rearrange thermally to the corresponding isopropylidenecyclopropanes **9** at rates that are substitutent dependent. These commonly encountered substituents all enhance rearrangement rates relative to the unsubstituted analogue with *p*-NMe_2 being the most effective. The rate enhancements are interpreted in terms of stabilization of the biradical intermediate by the para substituent. Rate data have allowed the assignment of $\sigma^{\bullet}$ values for these groups, which have not been previously determined. The nitro group in the para position is also quite effective in increasing the rearrangement rate, which contrasts with the effect of this group on many other free radical reactions. Vinyl is somewhat more effective as a radical stabilizing group than is isopropenyl or phenyl, possibly due to steric interactions in the planar conformations necessary for conjugative stabilization by isopropenyl or phenyl. Trimethylsilyl, trimethylstannyl, and HgCl all enhance the methylenecyclopropane rearrangement rate, but only to a moderate extent. Boron containing substituents, where boron can act as an acceptor group, are among the more effective radical stabilizing groups, as implied by their effect on the rearrangement rate of **8**. The cyclopropyl and CH_2SiMe_3 groups, which also enhance the rearrangement rate of **8** to a moderate extent, become even more effective radical stabilizing groups when present in conjunction with the carbethoxy group. These two conjugating groups are therefore capable of acting as donor groups in captodative radical stabilization.

Free radicals remain one of the reactive intermediates of fundamental importance in organic chemistry. As such, interest has continued in the factors that promote their stability or instability.[1] Evaluating such effects on free radicals is not a trivial process since polar effects often operate in free radical reactions and can overwhelm true free radical effects. Recently we and others have attempted to quantitatively describe substituent effects on free radicals. The pyrolysis studies of Timberlake and others[2] on **1** and related systems have been of fundamental importance in providing insight into the relative abilities of certain groups to stabilize free radicals. Various $\sigma^{\bullet}$ scales have also been developed that attempt to measure substituent effects on benzylic type radicals in the absence of polar effects. Among these are Jackson's $\sigma^{\bullet}$ scale based on pyrolysis rates of the dibenzylmercurials **2**.[3] The $\sigma^{\bullet}$ scale of Fisher is based on an attempt to minimize polar contributions in the free radical bromination of **3**.[4] Jiang's $\sigma^{\bullet}$ scale is based on relative cyclodimerization rates of **4**.[5] Unlike many previous methods, Arnold's $\sigma_{\alpha}^{\bullet}$ scale is a nonkinetic measure of radical stabilizing effects based on hyperfine coupling constants in the benzylic radical **5**.[6] The recent ΔAOP values of Bordwell[7] are based on pK_a differences in the conjugate acids of **6** and oxidation potential differences in the anions **6** (and related anions). These ΔAOP values also provide a nonkinetic measure of free radical stabilizing effects in **6** and related systems. A molecular orbital computational approach has been used by Pasto to evaluate the effect of the substituent X directly attached to the radical center in **7**.[8]



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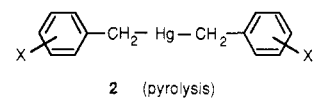
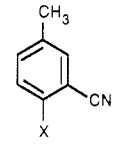
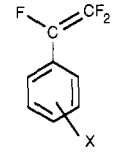


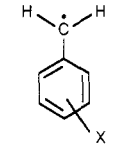
2 (pyrolysis)



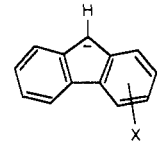
3 (bromination)



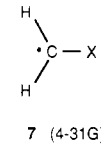
4 (dimerization)



5 (α-hyperfine)



6 (Δ AOP)



7 (4-31G)

Our $\sigma^{\bullet}$ scale is based on the thermal rearrangement rate of substituted methylenecyclopropanes **8** to the isopropylidenecyclopropanes **9**.[9] This rearrangement is a radical process that is devoid of significant polar character in the transition state leading to the intermediate **10**. This rearrangement serves as a probe for the stabilizing effect

(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.; Reidel Publishing Co., Dordrecht, Holland, 1986.

(2) 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*, 1753-1756. (f) Luedtke, A. E.; Timberlake, J. W. *J. Org. Chem.* **1985**, *50*, 268-270.

(3) (a) Dinçtürk, S.; Jackson, R. A.; Townson, M. *J. Chem. Soc., 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.

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

(5) Jiang, X.-K.; Ji, G.-Z.; Yu, C.-X. *Acta Chim. Sin. (Engl. Ed.)* **1984**, 82-85.

(6) (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.

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

(8) Pasto, D. J. *J. Org. Chem.*, in press. We thank Professor Pasto for informing us of his results prior to publication.

(9) A $\sigma^{\bullet}$ scale has been defined on the basis of rearrangement rates of **8**.[6a] $\sigma_C^{\bullet} = \log k_{rel}$ (for rearrangement of **8**). See: (a) Creary, X. *J. Org. Chem.* **1980**, *45*, 280-284. (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*, 1110-1114.

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of various groups on the benzylic radical center in **10**. Arnold's $\sigma_\alpha^\bullet$ scale correlates reasonably well with rearrangement rates of **8**. The major advantage of the methylenecyclopropane rearrangement probe lies in its simplicity and versatility. We can readily prepare a wide variety of substrates **8** and easily monitor substituent effects *not easily determined by other methods*. We have now used our methylenecyclopropane rearrangement probe to determine new $\sigma^\bullet$ values for the commonly encountered NO_2 and NMe_2 groups. We have also measured $\sigma^\bullet$ values for the conjugating vinyl, 2-propenyl, phenyl, and cyclopropyl groups. In an attempt to gain further insights into the effect of metals on free radicals, we have also determined $\sigma^\bullet$ values based on rearrangements of the organometallic systems **8** containing the CH_2SiMe_3, $SiMe_3$, $SnMe_3$, $-\overline{BOCH_2CH_2O}$, and HgCl groups in the para position. Reported also is the effect of *p*-cyclopropyl and *p*-CH_2SiMe_3 substitution on the analogous rearrangement of the methylenecyclopropanes **11** to **12**. The effect of these groups (which are well-established as carbocation stabilizing) in the potential captodative systems **11** is compared to the effect in the "parent" system **8**.

Results and Discussion

Synthetic Aspects. The general synthetic method used for the preparation of methylenecyclopropanes **8** involves the addition of carbenes to 1,1-dimethylallene.[9] Our previous attempts[10] to prepare *m*- and *p*-NO_2 substituted systems **8** by photochemical carbene additions were unsuccessful. Irradiation of *m*- and *p*-nitrophenyldiazomethane, **13**, in the presence of 1,1-dimethylallene gave only the isopropylidenecyclopropanes **9**, presumably via a mechanism involving the triplet nitrophenylcarbenes. In an attempt to avoid this singlet to triplet interconversion of the nitrophenylcarbenes, metal-catalyzed carbene additions were now attempted. Rhodium(II) acetate catalyzed decomposition of **13** in 1,1-dimethylallene gave mainly the corresponding stilbenes **14**,[11] with only small amounts of the methylenecyclopropane products. However $Cu(OTf)_2$-catalyzed decomposition of **13** led to the desired 8-*m*-NO_2 and 8-*p*-NO_2. These reactions presumably involve the copper carbenoid which prevents the intersystem crossing to the triplet state that is seen in the free carbenes.

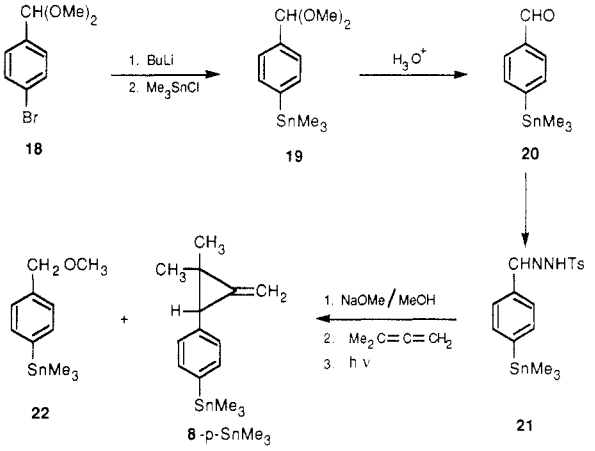
Preparation of 8-*p*-NMe_2 presented a different challenge since [*p*-(dimethylamino)phenyl]diazomethane, **17**, has not been reported to date. This diazo compound is predicted to be relatively unstable due to the potent electron-donating group substituted on the aromatic ring.[12] In an attempt to generate this diazocompound in situ, and to add the corresponding carbene to 1,1-dimethylallene, the tosylhydrazone salt **15** was prepared by treatment of the tosylhydrazone with sodium methoxide in methanol. Photochemical decomposition of a solution of this salt dissolved in a large excess of 1,1-dimethylallene containing small amounts of methanol (allene/methanol molar ratio = 8.6) gave only the methanol addition product **16** and none of the desired product 8-*p*-NMe_2. The methanol solvent was therefore removed from **15** under high vacuum and the solid salt **15** was suspended in 1,1-dimethylallene. Heating this mixture in sealed tube in a bomb at 95 °C for short periods of time gave some of the desired product 8-*p*-NMe_2, along with the rearranged product 9-*p*-NMe_2.

(10) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611–1618.
(11) In a related study, rhodium acetate catalyzed aryldiazomethane decompositions in the absence of alkenes also led to *cis*-stilbenes as major products. See: Shankar, B. K. R.; Schechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277–2280.
(12) This expectation is based on our qualitative unpublished observations that electron-withdrawing groups (NO_2, CN, CF_3, etc.) enhance the thermal stability of aryldiazomethanes while electron-donating groups such as methoxy decrease thermal stability. More quantitative studies show that methoxy substitution increases the unimolecular decomposition rate of diphenyldiazomethanes. See: Miller, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7920–7927.

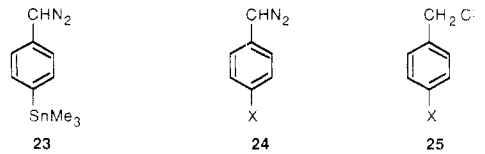
Table I. Rearrangement Rates of 8 in C_6D_6 at 80 °C

substituent	k, s^{-1}	k_{rel}	σ_C^+
m-NO_2	4.29×10^{-5}	0.77	−0.11
p-NO_2	2.09×10^{-4}	3.76	0.57
p-NMe_2	4.39×10^{-4}	7.88	0.90
p-$CH{=}CH_2$	2.60×10^{-4}	4.67	0.67
p-$C(CH_3){=}CH_2$	1.90×10^{-4}	3.41	0.53
p-C_6H_5	1.60×10^{-4}	2.87	0.46
p-cyclopropyl	9.57×10^{-5}	1.72	0.24
p-CH_2SiMe_3	1.04×10^{-4}	1.87	0.27
p-$SiMe_3$	8.50×10^{-5}	1.53	0.18
p-$SnMe_3$	7.56×10^{-5}	1.36	0.13
p-HgCl	8.27×10^{-5}	1.48	0.17
p-$\overline{BOCH_2CH_2O}$	1.06×10^{-4}	1.90	0.28
p-boronic anhydride	1.23×10^{-4}	2.21	0.34
p-H	5.57×10^{-5}	1.00	0.00

The preparation of 8-p-$SnMe_3$ was complicated by destannylation during the synthetic sequence. The aldehyde **20** was prepared by lithium–halogen exchange on the dimethyl acetal of p-bromobenzaldehyde, **18**, followed by stannylation of the aryllithium reagent. Careful hydrolysis of **19** gave the aldehyde **20**, which was converted to the tosylhydrazone **21**. We were unable to prepare the necessary diazo compound **23** completely free from the destannylated material, phenyldiazomethane, by pyrolysis of the salt of tosylhydrazone **21**. Photolysis of the mixture



of **23** and phenyldiazomethane led to formation of 8-p-$SnMe_3$ containing some of the destannylated methylenecyclopropane 8-p-H. This byproduct could not be chromatographically separated from the desired product 8-p-$SnMe_3$ due to further destannylation of 8-p-$SnMe_3$ during silica gel chromatography. Consequently a solution of the sodium salt of **21** in a 1,1-dimethylallene–methanol mixture was irradiated directly. The in situ generated diazo compound **23** leads to the desired 8-p-$SnMe_3$, free of 8-p-H, along with the methanol addition product **22**. The benzyl ether **22** does not interfere with the kinetic studies by NMR and, in fact, can be used as an internal standard in determination of rearrangement rates of 8-p-$SnMe_3$.



The substrates 8-p-$CH{=}CH_2$, 8-p-cyclopropyl, and 8-p-CH_2SiMe_3 were prepared in straightforward fashion by direct photolysis of the appropriate aryldiazomethane, **24**, dissolved in 1,1-dimethylallene. 8-p-phenyl and 8-p-2-propenyl were prepared by reaction of the appropriately substituted benzyl chloride, **25**, in 1,1-dimethylallene with lithium tetramethylpiperidide.

Table II. Additional σ^+ Values for Various Groups

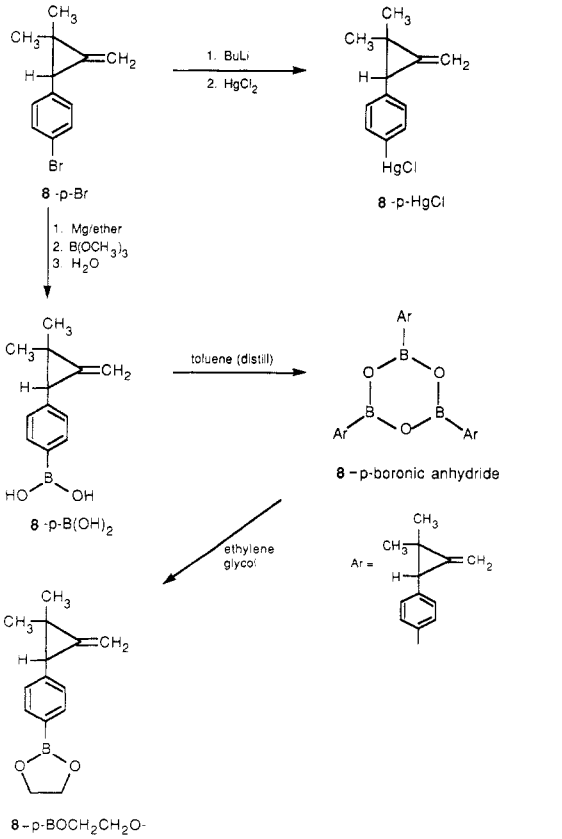
substituent	σ_C^+	substituent	σ_C^+
p-CN	0.46[a]	m-$SiMe_3$	0.03[a]
p-SCH_3	0.43	m-CH_3	0.03[a]
p-CO_2Et	0.39	m-$SOCH_3$	0.01
p-CO_2CH_3	0.35[a]	m-OCH_3	−0.02[a]
p-$PS(OEt)_2$	0.29	m-SCH_3	−0.03
p-OCH_3	0.24[a]	m-Cl	−0.04[a]
p-SO_2CH_3	0.18	m-F	−0.05[a]
p-$SOCH_3$	0.18	m-$PS(OEt)_2$	−0.06
p-$PO(OEt)_2$	0.18	m-SO_2CH_3	−0.07
p-Br	0.13[a]	m-CF_3	−0.07[a]
p-t-Bu	0.13[a]	p-F	−0.08[a]
p-Cl	0.12[a]	3,5-Cl_2	−0.10[a]
p-CH_3	0.11[a]	m-$PO(OEt)_2$	−0.11
p-CF_3	0.08[a]	m-CN	−0.12[a]
3,5-$(CH_3)_2$	0.07[a]		

[a] Value in isooctane at 100 °C (ref 9a).

Table III. Rearrangement Rates of 11 in Isooctane at 50 °C

substituent	k, s^{-1}	k_{rel}
p-CH_2SiMe_3	1.95×10^{-3}	3.48
p-cyclopropyl	1.35×10^{-3}	2.41
p-H	5.62×10^{-4}	1.00

Incorporation of a boron-containing substituent in the para position was accomplished by conversion of 8-p-Br to the Grignard reagent. Reaction with trimethyl borate followed by hydrolysis gave the boronic acid 8-$B(OH)_2$, which could be dehydrated to give the trimeric anhydride, 8-boronic anhydride, by azeotropic distillation of water. Esterification to give 8-p-$\overline{BOCH_2CH_2O}$ proceeded smoothly on treatment with ethylene glycol. Finally, 8-p-HgCl was prepared from 8-p-Br by lithium–halogen exchange followed by reaction with $HgCl_2$.



Rearrangements of Methylenecyclopropanes 8. Rearrangement rates of 8 to **9** were determined by NMR in C_6D_6 by monitoring the disappearance of the olefinic

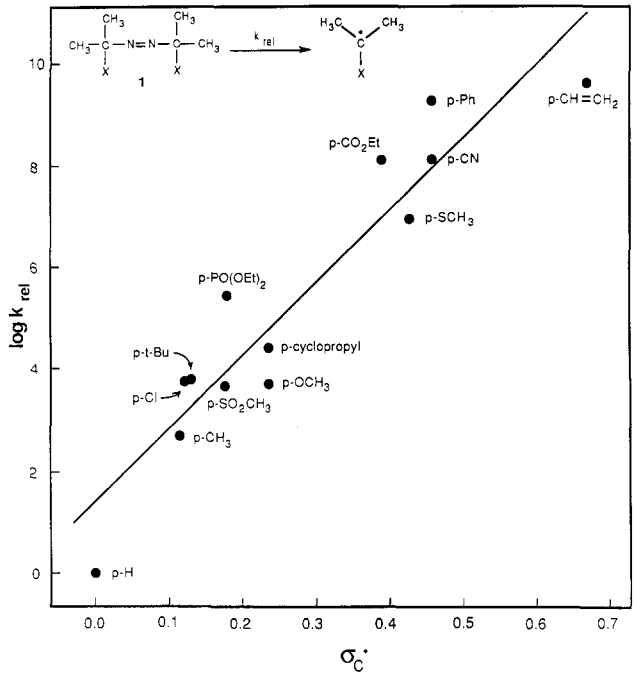


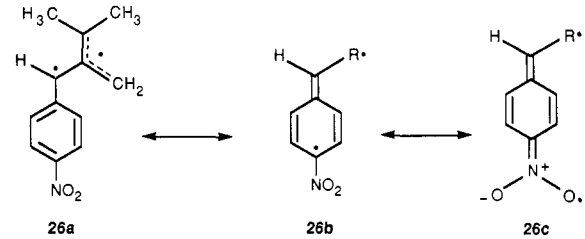
Figure 1. Plot of log k for thermolysis of azopropanes 1 vs. $\sigma_C^{\bullet}$.

signal of 8. Data are given in Table I. Tables I and II also give pertinent $\sigma^{\bullet}$ values, derived from rearrangement rates of 8. Figure 1 shows an attempt to correlate rearrangement rates of 8 with rate data for pyrolysis of azo compounds 1.[2] The correlation is fairly good (r = 0.940) when one considers the vastly different nature of the substrates 8 and 1. The Timberlake azo pyrolysis data, where the substituent is directly attached to the developing radical center, covers rates over a range of 10^9 while our rate range is quite small (only a factor of 5 in Figure 1). This is undoubtedly due to the fact that the developing radical center in 9 is insulated from the substituent by the aromatic ring. Nonetheless, the correlation further supports the use of the methylenecyclopropane rearrangement as a free radical probe despite the relatively small effects.

Despite the importance of the nitro group, its effect on free radicals in the absence of complicating polar factors has not been definitively established. Many free radical reactions are slowed by the nitro group because of a complicating polar effect due to charge separation in the transition state.[13] However the E_R value[14] for NO_2, which is based on an attempt to subtract our polar effects in hydrogen atom abstraction reaction, suggests that NO_2 is radical stabilizing by a resonance interaction. Jackson[3a,b] has reported data on the pyrolysis of 2, where Ar = p-$NO_2C_6H_4$. The rate was 1.9 times faster than the unsubstituted system but not as fast as the p-methyl analogue. However, by "factoring out" the polar component of this reaction, Jackson has derived a $\sigma^{\bullet}$ value for NO_2 which indicates that this group is substantially radical stabilizing.

The rearrangement of 8-m-NO_2 is retarded somewhat by the m-NO_2 substituent. We have seen this effect before[9] in rearrangements of 8 substituted with strong electron-withdrawing groups in the meta position (CN, CF_3, etc.) and there is a fair correlation of rate data with σ_{meta} values for these electron-withdrawing groups. To account for this effect, we have proposed that a benzylic radical (which is a neutral but electron deficient species) can be *slightly* destabilized inductively by a potent electron-withdrawing meta substituent. A more detailed explanation of this inductive meta effect on benzylic radicals has been put forth by Arnold who has observed analogous effects as manifested in $\sigma_{\alpha}^{\bullet}$ values for electronegative meta substituents. Arnold[6c] has suggested that inductive electron withdrawal by electronegative meta substituents leads to a decrease in spin delocalization in benzylic radicals (or an increase in spin localization at the benzylic position) due to decreased overlap between the radical center and the aromatic ring. Electronegative meta substituents lower the energy of the aromatic π-system and results in poorer overlap with the radical center. A third alternative explanation for this small rate retardation by electronegative meta substituents may lie in the nature of the methylenecyclopropane rearrangement. If there is some *small* charge separation (polar character) in the transition state for the methylenecyclopropane rearrangement (as is observed in other radical reactions), then electronegative meta substituents would slighly retard the rearrangement rate.

In contrast to the behavior of 8-m-NO_2, 8-p-NO_2 is one of the faster rearranging substrates studied to date. The rearrangement rate is even faster than that of 8-p-CN, 8-p-CO_2Et, 8-p-SCH_3, or 8-p-Ph, where these substituents are among the most effective radical stabilizing groups. We conclude that NO_2 in a conjugating position is quite effective at stabilization of a benzylic radical, presumably by spin delocalization as in **26c**. This conjugative stabilization more than offsets any radical destabilizing inductive effect of the p-NO_2 group.



26a 26b 26c

This conclusion contrasts somewhat with the recent computational data of Pasto[8] based on the isodesmic reactions of methyl radical with substituted methanes.

$$\cdot CH_3 + CH_3{-}NO_2 \rightleftharpoons CH_4 + \cdot CH_2{-}NO_2 \qquad \Delta E = -1.73 \text{ kcal/mole}$$

$$\cdot CH_3 + CH_3{-}CH_3 \rightleftharpoons CH_4 + \cdot CH_2{-}CH_3 \qquad \Delta E = -3.27 \text{ kcal/mole}$$

$$\cdot CH_3 + CH_3{-}CN \rightleftharpoons CH_4 + \cdot CH_2{-}CN \qquad \Delta E = -5.34 \text{ kcal/mole}$$

$$\cdot CH_3 + CH_3{-}CH{=}CH_2 \rightleftharpoons CH_4 + \cdot CH_2{-}CH{=}CH_2 \qquad \Delta E = -7.80 \text{ kcal/mole}$$

Nitro appears to be only slightly radical stabilizing relative to hydrogen, but less stabilizing than the methyl group, and considerably less stabilizing than cyano or vinyl. What is the origin of this apparent discrepancy with our data which suggests than NO_2 is one of the *most effective* radical stabilizing groups? In qualitative terms, this could be due to the inductive effect of the potent electron withdrawing nitro group. This inductive effect of NO_2 should be more effective at radical destabilization when directly attached to a radical center in $^{\bullet}CH_2NO_2$. Our study on 8-m-NO_2 supports the notion that nitro should destabilize radicals by an inductive process. The inductive destabilization in $^{\bullet}CH_2NO_2$ is offset by a conjugative interaction with the net result being *slight* overall NO_2 stabilization of $^{\bullet}CH_2NO_2$ relative to the methyl radical. In 10-p-NO_2, the benzylic radical center is insulated from the inductive effect of the nitro group by the aromatic ring and therefore the inductive destabilizing effect should be

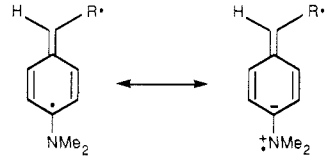
(13) A classic example is the pyrolysis of peresters of the type $ArCH_2CO_3$-t-Bu, which involves benzylic radicals. See: Bartlett, P. D.; Rüchardt, C. *J. Am. Chem. Soc.* **1960**, *82*, 1756–1762. For related studies, see also: Rüchardt, C.; Böck, H. *Chem. Ber.* **1971**, *104*, 577–592.

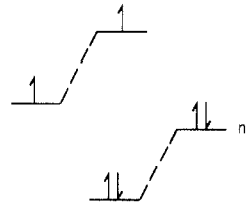
(14) Yamamoto, T.; Otsu, T. *Chem. Ind. (London)* **1967**, 787–789.

smaller. The conjugative stabilizing effect of the nitro group should also fall off in **10**-*p*-NO_2 but it is our suggestion that the inductive effect falls off more rapidly. Therefore the nitro group is more stabilizing in a benzylic radical than might be predicted based on its effect on a methyl radical.

Alternatively, a reviewer has suggested that the difference between the effect of the nitro group in $^{\bullet}CH_2NO_2$ (as in the isodesmic reaction) and a nitro group on the aromatic ring (as in **26**) could be due to the intact bond of CH_3NO_2 being affected to a greater extent than is the intact bond of the methylenecyclopropane. In other words, the nitro group has an effect on the intact C–H bond of CH_3NO_2 as well as on the radical. The isodesmic reaction includes CH_4 and CH_3NO_2 as well as $^{\bullet}CH_3$ and $^{\bullet}CH_2NO_2$. If the C–H bond in CH_3NO_2 is not the same as in CH_4, then the isodesmic reaction may not give an accurate picture of the ability of the nitro group to stabilize a radical.

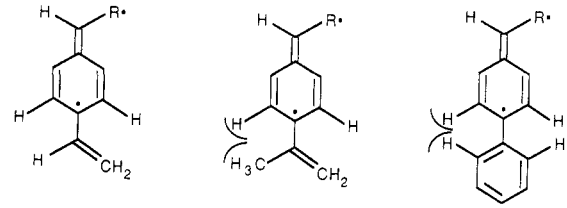
The methylenecyclopropane 8-*p*-NMe_2 is the most reactive of the systems studied, suggesting that the dimethylamino group is the best radical stabilizing group encountered to date. This is consistent with Bordwell's ΔAOP values,[7] Pasto's calculated radical stabilization energy,[8] rates of hydrogen atom abstraction from amines,[15] and heats of formation data,[16] all of which suggest that the dimethylamino is one of the best radical stabilizing groups. This is undoubtedly due to spin delocalization as in **27b** involving the nonbonding electron pair associated with nitrogen. A PMO description of this interaction involves a "three electron bond". The dimethylamino group is substantially better than methoxy as a radical stabilizing group due to the greater electronegativity of oxygen relative to nitrogen. This renders forms analogous to **27b** less important in methoxy-substituted radicals. In PMO terms, the lower energy of the oxygen nonbonding electrons (relative to nitrogen nonbonding electrons) results in a less favorable interaction with the singly occupied carbon orbital.



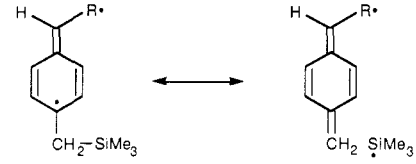


Radical stabilization by non-bonding electrons

Comparison of the substrates 8-*p*-cyclopropyl, 8-*p*-CH=CH_2, 8-*p*-2-propenyl, and 8-*p*-phenyl, which contain "unsaturated" groups, is informative. The *p*-cyclopropyl groups is the least effective radical stabilizing group of this set. It is nonetheless more effective than simple alkyl groups or halogen as a radical stabilizing group and comparable to the methoxy group. This moderate stabilizing effect of cyclopropyl has been previously noted in azo pyrolysis reactions.[2a,17] by way of contrast, the ability of the vinyl group[18] to enhance the methylenecyclopropane rearrangement rate is exceeded only by that of the dimethylamino group. It appears to be a slightly more effective benzylic radical stabilizing group than the related 2-propenyl group using our $\sigma^{\bullet}$ probe. This could be due to a slightly greater steric interaction in the conformation **29** than in **28**, which are necessary for stabilizing conjugative interactions to occur. The greater stabilizing ability of vinyl relative to *p*-phenyl could also be a result of a similar unfavorable steric interaction between ortho hydrogens as in **30**.



Effect of Organometallic Groups. Attention was next turned to the effect of certain organometallic groups on the rearrangement of **8**. The (trimethylsilyl)methyl group is recognized as a very effective carbocation stabilizing group via a hyperconjugative mechanism.[19] Studies by Kochi[20] and Sakurai show that the β-trimethylsilyl group is also an effective radical stabilizing group. Our present study on 8-CH_2SiMe_3 verifies the radical stabilizing ability of CH_2SiMe_3, which, in a more quantitative sense, is comparable to that of OCH_3 in enhancing the rearrangement rate of **8**. This radical stabilization is presumably due to a conjugative mechanism as shown in **31b**, and is supported by Kochi's EPR studies.[20]

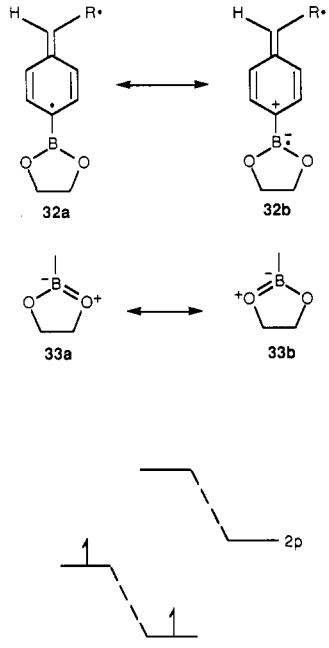


Our previous study[9a] on 8-*p*-$SiMe_3$ in isooctane suggested that the trimethylsilyl group is radical stabilizing, in agreement with findings based on other methods. We have now determined the effect of the related $SnMe_3$ group and redetermined the effect of *p*-$SiMe_3$ in the common solvent, C_6D_6. The rate enhancing effect of *p*-$SnMe_3$ is slighly smaller than that of $SiMe_3$, but the difference is minimal. Consequently, in the series CMe_3, $SiMe_3$, and $SnMe_3$, there is no large effect on replacing carbon with a more elec-

(15) Griller, D.; Howard, J. A.; Marriot, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619–623.
(16) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586–1587.
(17) For further examples of the effect of the cyclopropyl group on radical centers, see: (a) Bauld, N. L.; McDermed, J. D.; Hudson, C. E.; Rim, Y. S.; Zoeller, J.; Gordon, R. D.; Hyde, J. S. *J. Am. Chem. Soc.* **1969**, *91*, 6666–6676. (b) Russell, G. A.; Malkus, H. *Ibid.* **1967**, *89*, 160–162.
(18) The radical stabilizing ability of the vinyl group is well-documented. For leading references, see: (a) Golden, D. M.; Rodgers, A. S.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 3196–3198. (b) Golden, D. M.; Gac, N. A.; Benson, S. W. *Ibid.* **1969**, *91*, 2136–2137. (c) Engel, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 2148–2149. (d) Rossi, M.; Golden, D. M. *Ibid.* **1979**, *101*, 1230–1235. (e) Korth, H.-G. Trill, H.; Sustmann, R. *Ibid.* **1981**, *103*, 4483–4489.
(19) For representative examples and leading references, see: (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496–1500. (b) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020–2022. (c) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761–786. (d) Davis, D. D.; Gray, C. E. *J. Org. Chem.* **1970**, *35*, 1303–1307. (e) Jarvie, A. W. P.; Holt, A. Thompson, *J. Chem. Soc. B* **1969**, 852–855.
(20) Kochi, J. K.; Kawamura, J. *J. Am. Chem. Soc.* **1972**, *94*, 648–650.
(21) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Org. Chem.* **1969**, *34*, 1764–1768.

tropositive element. All of these groups appear to stabilize benzylic radicals to a comparable extent. Along these lines, *p*-HgCl also appears to be only a modest radical stabilizing group, enhancing the rate of formation of the biradical intermediate **9** to about the same extent as $SiMe_3$. This stabilization by *p*-$SiMe_3$, *p*-$SnMe_3$, and *p*-HgCl can be viewed as a result of interaction of the radical with some unoccupied orbital associated with the metal center, i.e., the metal acts as an acceptor group.[22]

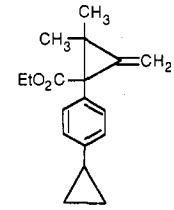
Both of the boron-containing substrates, 8-boronic anhydride and 8-*p*-$\overline{BOCH_2CH_2O}$, rearrange substantially faster than the unsubstituted analogue 8-*p*-H, suggesting that boron in the para position is quite effective in radical stabilization. In line with this conclusion is the observation that free radicals α to boron are readily generated from organoboranes,[23a] borinate,[23b] and boronate esters[23b] during bromination of these substrates. Radical stabilization by boron can be viewed as resulting from an interaction of the radical center with the vacant p orbital associated with boron. This stabilization mechanism involves boron acting as an acceptor group. A valence bond representation of this stabilization is given in **32b** and an equivalent PMO description is also shown.



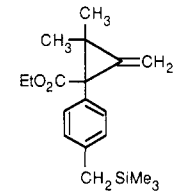
Radical stabilization by vacant boron 2p orbital

8-boronic anhydride rearranges somewhat faster than the ester 8-*p*-$\overline{BOCH_2CH_2O}$. This could be a reflection of the availability of the vacant p orbital on boron for interaction with the radical center. In the ester there are two oxygen atoms with nonbonding electrons that can interact with the vacant p orbital on boron (as in **33**) and thereby reduciing the availability for interaction with the radical center. In the anhydride, the ratio of oxygen atoms to boron atoms is one. Therefore there is, on the average, only one oxygen to interact with boron. Interaction of the radical center with boron is therefore more favorable in the anhydride, since the vacant orbital is not as "tied up" as in the ester.

Captodative Effects. The captodative effect is a free radical stabilizing feature in which the combination of electron donor substituents (such as NR_2, OR) and electron acceptor substituents (such as CN, COR) attached to a radical center exert a synergistic stabilizing effect.[24] The stability of such radicals is suggested to be greater than the simple sum of the stabilizing effect of the donor group and the stabilizing effect of the acceptor group. We have previously shown[25] that the methylenecyclopropanes **11**, which contain the acceptor carbethoxy group, undergo a thermal rearrangement to **12**. Rates are also subject to substituent effects on the aromatic ring. Furthermore, we have shown that the captodative effect can operate in rearrangement of **11** when the substituent on the aromatic ring is a donor group. Donor groups such as *p*-OCH_3 and *p*-SCH_3 enhance the rearrangement rate of **11** to a greater extent than they enhance the rearrangement rate of **8** due to the captodative effect.



11-p-cyclopropyl



11-p-CH_2SiMe_3

In order to gain further insights into the radical stabilizing effects of the *p*-cyclopropyl and the *p*-(trimethylsilyl)methyl groups, **11**-*p*-cyclopropyl and **11**-*p*-CH_2SiMe_3 were prepared and thermally rearranged to **12**-*p*-cyclopropyl and **12**-*p*-CH_2SiMe_3, respectively. This rearrangement presumably involves the intermediacy of the biradical **34**. The cyclopropyl group enhances the rearrangement rate of **11**-*p*-cyclopropyl by a factor of 2.41 relative to **11**-*p*-H. This is somewhat larger than the enhancing factor of 1.72 seen in rearrangement of 8-*p*-cyclopropyl. The rate enhancing factor in **11**-*p*-CH_2SiMe_3 is 3.48, but only 1.87 in 8-*p*-CH_2SiMe_3. These greater rate enhancements in **11**-*p*-cyclopropyl and **11**-*p*-CH_2SiMe_3 are attributed to the captodative effect in which the cyclopropyl and CH_2SiMe_3 groups become better donor groups when placed in conjunction with the acceptor carbethoxy group. In terms of a valance bond rationalization, forms such as **35** and **36** have increased importance in radical stabilization due to the cation stabilizing ability of cyclopropyl and CH_2SiMe_3. The cyclopropyl and CH_2SiMe_3 groups therefore are capable of radical stabilization by a donor type of mechanism.

We have previously shown[25] that rearrangement rates of **11** correlated fairly well with σ^+ values when the substituent on the aromatic ring is a donor group. Figure 2 shows this plot of rearrangement rates of **11** vs. σ^+ where data for cyclopropyl[26] and CH_2SiMe_3[27] have now been

(22) For related examples of radical stabilization by α-$SiMe_3$ and leading references, see: (a) Wilt, J. W.; Aznavoorian, P. M. *J. Org. Chem.* **1978**, *43*, 1285–1286. (b) Paquette, L. A.; Hoppe, M.; Johnston, L. J.; Ingold, K. U. *Tetrahedron Lett.* **1986**, *27*, 411–414.

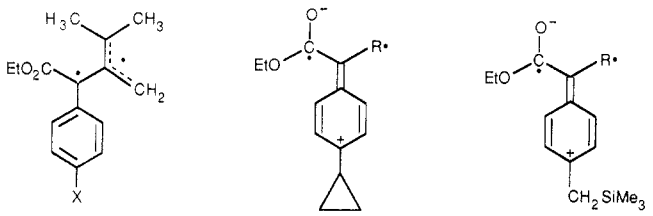
(23) (a) Lane, C. F.; Brown, H. C. *J. Am. Chem. Soc.* **1970**, *92*, 7212–7213. (b) Pasto, D. J.; McReynolds, K. *Tetrahedron Lett.* **1971**, 801–804.

(24) For a review of the captodative effect, which is also called merostabilization or "push-pull" stabilization, and leading references, see: (a) Viehe, H. G.; Janousek, Z.; Merényi, R. *Acc. Chem. Res.* **1985**, *18*, 148–154. (b) Baldock, R. W.; Hudson, P.; Katritzky, A. R.; Soti, F. *Heterocycles* **1973**, 67. (c) Baldock, R. W.; Hudson, P.; Katritzky, A. R.; Soti, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1422–1427. (c) Katritzky, A. R.; Soti, F. *J. Chem. Soc., Perkin-Trans. 1* **1974**, 1427–1432. (d) Negoita, N.; Baican, R.; Balaban, A. T. *Tetrahedron Lett.* **1973**, 1877–1878. (e) Balaban, A. T.; Istratoiu, R. *Tetrahedron Lett.* **1973**, 1879–1880.

(25) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 2664–2668.

(26) (a) Brown, H. C.; Cleveland, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 2051–2052. (b) Hahn, R. C.; Corbin, T. F.; Shechter, H. *Ibid.* **1968**, *90*, 3404–3015.

(27) Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 293–299.



34 35 36

included. Rearrangement rates of these substrates also correlate with σ^+. This can be rationalized by the fact that σ^+ values are one measure of the increased donor ability of cyclopropyl and CH_2SiMe_3 under conditions of increased electron demand. These observations support our use of systems **11** as a very sensitive probe for captodative effects, despite the fact that this effect can be quite small.

Summary and Conclusions

Methylenecyclopropanes **8**, which contain the commonly encountered donor group NMe_2, the acceptor group NO_2, the conjugating groups vinyl, 2-propenyl, phenyl, and cyclopropyl, and the organometallic groups CH_2SiMe_3, $SiMe_3$, $SnMe_3$, $-BOCH_2CH_2O$, and HgCl, have been prepared and thermally rearranged to **9**. The donor group NMe_2 is the best radical stabilizing substituent encountered to date as judged by its ability to enhance the rearrangement rate of **8**. The nitro group is also a very effective radical stabilizing group, being exceeded only by the NMe_2 and the vinyl group. Vinyl is slighly more effective than 2-propenyl or phenyl in stabilization of benzylic radicals, presumably due to unfavorable steric interactions in the later two groups in the conformation necessary for conjugative stabilization. The radical stabilizing ability of CH_2SiMe_3 is comparable to that of methoxy. This group, as well as the cyclopropyl group, can act as an acceptor group and become involved in captodative radical stabilization. The organometallic groups $SiMe_3$, $SnMe_3$, and HgCl are "moderate" radical stabilizing groups, presumably via interaction of the radical center with a vacant metal orbital. Boron containing substituents are even more effective radical stabilizing groups, also due presumably to interaction of the radical center with a vacant orbital (2p) associated with boron.

Experimental Section

Preparation of 8-*p*-NO_2 and 8-*m*-NO_2. A solution of 20 mg of $Cu(OTf)_2$ in 1 mL of 1,1-dimethylallene was stirred at room temperature as a solution of 100 mg of (*p*-nitrophenyl)diazomethane[28] in 26 mL of 1,1-dimethylallene was added dropwise. Nitrogen evolution was instantaneous. After completion of the addition the 1,1-dimethylallene solvent was removed under reduced pressure. The residue was chromatographed on 5 g of silica gel and eluted with 2% ether in hexanes. Solvent removal using a rotary evaporator gave 78 mg (62%) of a mixture of 8-*p*-NO_2 and 9-*p*-NO_2 in a 10:1 ratio as determined by NMR. NMR of 8-*p*-NO_2 ($CDCl_3$) δ 8.1 and 7.4 (AA'BB' quartet, 4 H, aromatic), 5.640 (d, J = 2.3 Hz, 1 H), 5.577 (d, J = 1.2 Hz, 1 H), 2.539 (m, 1 H), 1.386 (s, 3 H), 0.869 (s, 3 H).

8-*m*-NO_2 was prepared in an analogous fashion (38% yield) by addition of 95 mg of (*m*-nitrophenyl)diazomethane in 1.5 mL of ether to 10 mg of $Cu(OTf)_2$ in 1 mL of 1,1-dimethylallene.

Preparation of 8-*p*-NMe_2. A suspension of 1.86 g of tosylhydrazine in 15 mL of methanol was swriled as 1.49 g of *p*-(dimethylamino)benzaldehyde was added in one portion. After a few moments, the tosylhydrazone began to crystallize. After 1 h the red-orange mixture was cooled in an ice bath. The solid was collected, washed with a small amount of cold methanol, and dried under vacuum to give 1.97 g (62%) of *p*-(dimethylamino)benzaldehyde tosylhydrazone: mp 165 °C dec; NMR ($CDCl_3$) δ 7.85 and 7.46 (AA'BB' quartet, 4 H, aromatic), 7.69 (s, 1 H), 7.47 (s, 1 H), 7.29 and 6.64 (AA'BB' quartet, 4 H, aromatic), 3.00 (s, 6 H), 2.39 (s, 3 H). Anal. Calcd for $C_{16}H_{19}N_3O_2S$: C, 60.55; H, 6.03. Found: C, 60.80; H, 6.04.

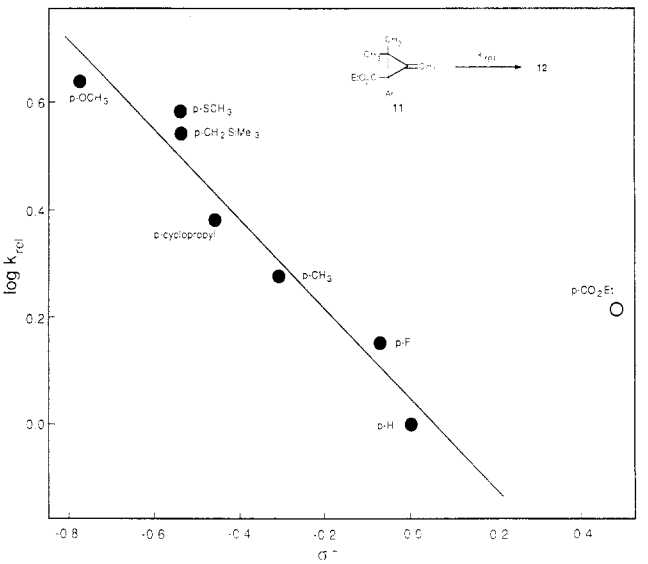


Figure 2. Plot of k_{rel} for rearrangement of **11** vs. σ^+.

The tosylhydrazone (0.80 g) was treated with 5.05 mL of 0.5 M $NaOCH_3$ in methanol. The solvent was removed on a rotary evaporator and the solid residue **15** (under nitrogen) was crushed into a powder. The powder was evacuated at 15 mm pressure for an additional 2 h on the rotary evaporator. The solid **15** was transferred to 4 test tubes and 4 mL of 1,1-dimethylallene was added to each tube. The tubes were sealed under nitrogen. The tubes were shaken to disperse the suspended solid and one of the sealed tubes was placed in a steel bomb containing 75 mL of ether. The bomb was sealed and placed in a water bath at 95 °C for a total of 60 min. At 15-min intervals the bomb was briefly removed from the bath and rolled on the side in an attempt to further disperse the solid. The bomb was then cooled and opened and the tube was removed. The contents of the tube were centrifuged and filtered through a cotton plug, and the excess allene was removed under reduced pressure. The residue was chromatographed on 2 g of silica gel and eluted with 8% ether in hexanes. Two fractions containing the product were collected. The first fraction contained 8-*p*-NMe_2 and 9-*p*-NMe_2 in a 1.33:1 ratio. The second fraction contained 8-*p*-NMe_2, 9-*p*-NMe_2, and the benzyl ether **16** in a 1:2.4:2.1 ratio. NMR of 8-*p*-NMe_2 (C_6D_6): δ 7.23 and 6.62 (AA'BB' quartet, 4 H, aromatic), 5.64 (m, 2 H, olefin), 2.526 (s, 6 H), 1.286, (s, 3 H), 0.984 (s, 3 H). NMR of 9-*p*-NMe_2 (C_6D_6): δ 7.13 and 6.64 (AA'BB' quartet, 4 H, aromatic), 2.526 (s, 6 H), 1.894 (q, J = 1.5 Hz, 3 H), 1.854 (q, J = 1.5 Hz, 3 H), 1.56 (m, 1 H), 1.11 (m, 1 H).

A separate run under identical conditions, followed by silica gel chromatography, gave 4.9 mg (4% based on the amount of **15** pyrolyzed) of a mixture of 8-*p*-NMe_2 and 9-*p*-NMe_2 in a 1.0:2.0 ratio, followed by 2.2 mg (2%) of the benzyl ether **16**, which could also be prepared as described below.

Photolysis of 15 in 1,1-Dimethylallene/Methanol Solution. *p*-(Dimethylamino)benzaldehyde tosylhydrazone (40 mg) was dissolved in 0.26 mL of 0.5 M $NaOCH_3$ in methanol. 1,1-Dimethylallene (5.2 mL) was added and the homogeneous solution was transferred to a Pyrex tube. The solution was irradiated with Pyrex-filtered light from a Hanovia 450-W medium pressure lamp for 9 min. A slight purple color remained. After an additional 14 min of irradiation, the solution was light yellow. The excess allene was removed under reduced pressure and the residue was taken up into ether and water. The organic phase was washed with saturated NaCl solution and dried over $MgSO_4$. Solvent removal by rotary evaporator gave 20 mg of the benzyl ether **16** with no trace of the methylenecyclopropane 8-*p*-NMe_2. NMR of **16** ($CDCl_3$): δ 7.19 and 6.63 (AA'BB' quartet, 4 H, aromatic), 4.33 (s, 2 H), 3.32 (s, 3 H), 2.94 (s, 6 H).

(28) Davies, H. W.; Schwarz, M. *J. Org. Chem.* **1965**, *30*, 1242–1244.

Preparation of p-(Trimethylstannyl)benzaldehyde (20). A solution of 1.742 g of p-bromobenzaldehyde dimethylacetal in 18 mL of dry tetrahydrofuran was cooled to −78 °C and 3.6 mL of 2.5 M n-butyllithium in hexane was added. After 25 min at −78 °C, a solution of 1.788 g of trimethyltin chloride in 4 mL of THF was added. The mixture was then warmed to room temperature. After 2 h at room temperature, water was added and the mixture was transferred to a separatory funnel with ether. The organic phase was washed with saturated NaCl solution, dried over $MgSO_4$ and filtered, and the solvent was removed by using a rotary evaporator. The crude residue **19** (3.195 g) was dissolved in 14 mL of THF and 12 mL of 1% $KHSO_4$ was added. The two-phase mixture was vigorously stirred for 12 h and then taken up into ether. The organic phase was washed with dilute Na_2CO_3 and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was distilled by using a short path distillation head. After a small forerun, 1.450 g (72%) of p-(trimethylstannyl)benzaldehyde (**20**)[29] was collected, bp 74–76 °C. NMR of **20** ($CDCl_3$): δ 10.00 (s, 1 H), 7.81 and 7.68 (AA'BB' quartet, 4 H, aromatic), 0.34 (s with ^{117}Sn and ^{119}Sn satellites at ±26.7 Hz and ±27.9 Hz, 9 H, $SnMe_3$ group).

Preparation of p-(Trimethylstannyl)benzaldehyde Tosylhydrazone (21). A suspension of 330 mg of tosylhydrazine in 4 mL of methanol was swirled as 449 mg of aldehyde **20** was added. The mixture became homogeneous. After 30 min at room temperature the methanol was removed from the solution on a rotary evaporator and 8 mL of hexanes was added. The mixture was cooled at −20 °C and the product **21** slowly crystallized. The hexane was decanted and the solid residue was slurried with a small amount of cold methanol. The solid was collected and dried under vacuum, giving 536 mg (73%) of tosylhydrazone **21**, mp 144–148 °C. NMR of **21** ($CDCl_3$): δ 7.86 and 7.30 (AA'BB' quartet, 4 H, aromatic), 7.75 (br. s, 1 H), 7.72 (s, 1 H), 7.51 (AA'BB' quartet, 4 H, aromatic), 2.40 (s, 3 H), 0.29 (s with ^{117}Sn and ^{119}Sn satellites at ±26.7 Hz and ±27.9 Hz, 9 H, $SnMe_3$ group).

Preparation of 8-p-$SnMe_3$. Tosylhydrazone **21** (162 mg) was dissolved in 0.68 mL of 0.49 M $NaOCH_3$ in methanol and 3.5 mL of 1,1-dimethylallene was added. The homogeneous solution was transferred to a Pyrex tube and the solution was irradiated with Pyrex-filtered light from a Hanovia 450-W lamp for 140 min. The solvents were removed under reduced pressure and the residue was taken up into hexanes and water. The organic phase was washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was removed on a rotary evaporator with the last traces being removed on a vacuum pump at 0.1 mm. The crude residue (100 mg) consisted of 8-p-$SnMe_3$, 9-p-$SnMe_3$, and the benzyl ether **22** in a 47:14:39 ratio. Gas chromatography showed none of the destannylated 8-p-H (which can interfere with rate measurements). In a separate run, attempted chromatography on silica gel led to partial destannylation of 8-p-$SnMe_3$. The rearrangement rate of 8-p-$SnMe_3$ was therefore determined by using this crude product mixture. NMR of 8-p-$SnMe_3$ ($CDCl_3$): δ 7.5–7.1 (AA'BB' quartet, 4 H, aromatic), 5.57 (dd, J = 2.5, 1.0 Hz, 1 H), 5.51 (m, 1 H), 2.43 (br s, 1 H), 1.33 (s, 3 H), 0.87 (s, 3 H), 0.26 (s, with ^{117}Sn and ^{119}Sn satellites at ±26.3 Hz and ±27.7 Hz, 9 H, $SnMe_3$ group). NMR of **22** ($CDCl_3$): δ 7.5–7.1 (AA'BB' quartet, 4 H, aromatic), 4.45 (s, 2 H), 3.38 (s, 3 H), 0.28 (s with ^{117}Sn and ^{119}Sn satellites at ±26.4 Hz and ±27.7 Hz, 9 H, $SnMe_3$ group).

Preparation of p-(Chloromethyl)cumyl Alcohol. A Grignard reagent prepared from 1.02 g of magnesium and 5.95 g of methyl iodide in 50 mL of ether was added to a solution of 5.89 g of p-(chloromethyl)benzoyl chloride in 50 mL of ether at −78 °C. The reaction mixture was allowed to warm to 0 °C and NH_4Cl solution was added. The organic phase was separated, washed with saturated NaCl solution, and dried over $MgSO_4$. After solvent removal on a rotary evaporator, the residue was distilled to give 4.79 g (83%) of p-(chloromethyl)cumyl alcohol, bp 85–92 °C (0.05 mm). NMR of p-(chloromethyl)cumyl alcohol ($CDCl_3$): δ 7.47 and 7.35 (AA'BB' quartet, 4 H, aromatic), 4.57 (s, 2 H), 2.03 (s, 1 H), 1.56 (s, 6 H).

Preparation of 2-[p-(Chloromethyl)phenyl]propene. A mixture of 1.50 g of p-(chloromethyl)cumyl alcohol, 47 mg of $KHSO_4$, and 5 mg of hydroquinone was placed in a flask and a short path distillation head was attached. The mixture was slowly heated to 160 °C under aspirator pressure and a mixture of water and 2-(p-(chloromethyl)phenyl)propene distilled. The distillate was taken up into ether, washed with saturated NaCl solution, and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was distilled to give 1.05 g (78%) of 2-(p-(chloromethyl)phenyl)propene, bp 82–85 °C (0.4 mm). NMR of 2-(p-(chloromethyl)phenyl)propene ($CDCl_3$): δ 7.49 and 7.37 (AA'BB' quartet, 4 H, aromatic), 5.41 (m, 1 H), 5.14 (pentuplet, J = 1.5 Hz, 1 H), 4.62 (s, 2 H), 2.18 (dd, J = 1.5 Hz and J = 0.7 Hz, 3 H).

Preparation of 8-p-Isopropenyl. Reaction of 1.00 g of 2-(p-(chloromethyl)phenyl)propene in 6 mL of 1,1-dimethylallene with lithium tetramethylpiperidide[30] prepared from 1.70 g of tetramethylpiperidine and 8.0 mL of 1.5 M methyllithium, using a procedure analogous to that previously described,[9a] gave, after silica gel chromatography, 0.75 g (67%) of a mixture of 8-p-isopropenyl and 9-p-isopropenyl in a 4.5:1 ratio. NMR of 8-p-isopropenyl ($CDCl_3$): δ 7.37 and 7.14 (AA'BB' quartet, 4 H, aromatic), 5.570 (m, 1 H), 5.531 (br s, 1 H), 5.351 (br s, 1 H), 5.035 (m, 1 H), 2.455 (br s, 1 H), 2.137 (br s, 3 H), 1.344 (s, 3 H), 0.865 (s, 3 H).

8-p-phenyl was prepared by an analogous procedure[9a] starting with p-phenylbenzyl chloride.

Preparation of p-[(Trimethylsilyl)methyl]benzaldehyde. A solution of 6.994 g of p-[(trimethylsilyl)methyl]bromobenzene[31] in 35 mL of THF was cooled to −78 °C and 14.8 mL of 2.5 M butyllithium in hexane was added dropwise. After 20 min at −78 °C, this solution was transferred (using a positive pressure of nitrogen and a double headed needle) to a solution of 6.34 g of dimethylformamide in 35 mL of THF at −78 °C. The mixture was allowed to warm to 0 °C and water was added. The organic phase was separated, washed with water and saturated NaCl solution, and dried over $MgSO_4$. Gas chromatographic analysis showed the presence of p-[(trimethylsilyl)methyl]benzaldehyde as well as small amounts of benzyltrimethylsilane and p-$C_4H_9C_6H_4CH_2SiMe_3$. The solvent was removed on a rotary evaporator and the residue was chromatographed in two portions on 24 g of silica gel and eluted with 2% ether in hexanes. The solvent was removed from the fractions containing p-[(trimethylsilyl)methyl]benzaldehyde on a rotary evaporator, and the residue was distilled by using a short path distillation head. After a small forerun, 3.849 g (70%) of p-[(trimethylsilyl)methyl]-benzaldehyde was collected, bp 64–66 °C (0.1 mm). NMR of p-[(trimethylsilyl)methyl]benzaldehyde ($CDCl_3$): δ 9.912 (s, 1 H), 7.73 and 7.13 (AA'BB' quartet, 4 H, aromatic), 2.197 (s, 2 H), 0.000 (s, 9 H). Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38. Found: C, 68.49; H, 8.41.

Preparation of 8-p-CH_2SiMe_3. Following the procedure of Reese,[32] [(triisopropylphenyl)sulfonyl]hydrazine (1.81 g) was suspended in 20 mL of methanol and 1.02 g of p-[(trimethylsilyl)methyl]benzaldehyde was added with vigorous stirring. An additional 10 mL of methanol was added to the mixture and stirring was continued for 30 min. The mixture was cooled to −20 °C and the solid was collected on a Buchner funnel, washed with a small amount of cold methanol, and dried under vacuum to give 2.23 g (84%) of p-[(trimethylsilyl)methyl]benzaldehyde [(triisopropylphenyl)sulfonyl]hydrazone, mp 190–191 °C dec. NMR ($CDCl_3$): δ 7.70 (br s, 2 H), 7.41 and 6.95 (AA'BB' quartet, 4 H, aromatic), 7.18 (s, 2 H), 4.27 (heptet, J = 7 Hz, 2 H, CH of ortho isopropyl groups), 2.89 (heptet, J = 7 Hz, 1 H, CH of para isopropyl group), 2.08 (s, 2 H), 1.31, (d, J = 7 Hz, 2 H), 1.24 (d, J = 7 Hz, 6 H), −0.04 (s, 9 H). Anal. Calcd for $C_{26}H_{40}N_2O_2SSi$: C, 66.06; H, 8.53. Found: C, 66.43; H, 8.64.

Sodium metal (188 mg) was dissolved in 20 mL of ethylene glycol and 1.005 g of p-[(trimethylsilyl)methyl]benzaldehyde [(triisopropylphenyl)sulfonyl]hydrazone was added. The mixture

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was heated to 50 °C with vigorous stirring for 10 min, cooled to room temperature, and extracted with 10 mL of hexanes. The mixture was reheated to 50 °C for 10 min and again extracted with hexanes. After a third cycle, the combined hexane extracts were washed with water, 10% NaOH solution, and saturated NaCl solution and dried over $MgSO_4$. Solvent removal gave a red oil with some insoluble white solid. Seven milliliters of 1,1-dimethylallene was added and the red solution containing [*p*-(trimethylsilyl)methyl]phenyldiazomethane was decanted from the white solid. This solution was irradiated at room temperature with Pyrex-filtered light from a Hanovia 450-W medium pressure lamp for 3 h, during which time the red color completely disappeared. The excess allene was removed under reduced pressure and the residue was chromatographed on 7 g of silica gel and eluted with hexanes. Solvent removal gave 90 mg (17%) of a mixture of 8-*p*-CH_2SiMe_3 and 9-*p*-CH_2SiMe_3 in an 11:1 ratio. NMR of 8-*p*-CH_2SiMe_3 ($CDCl_3$): δ 7.03 and 6.88 (AA'BB' quartet, 4 H, aromatic), 5.55 (m, 1 H), 5.52 (br s, 1 H), 2.416 (m, 1 H), 2.034 (s, 2 H), 1.323 (s, 3 H), 0.834 (s, 3 H), −0.02 (s, 9 H).

8-***p***-$CH{=}CH_2$ and 8-*p*-cyclopropyl were prepared in an analogous fashion from the corresponding diazo compounds (prepared respectively from the [(triisopropylphenyl)sulfonyl]-hydrazones of *p*-vinylbenzaldehyde[33] and *p*-cyclopropylbenzaldehyde,[34] which were prepared by reaction of the appropriate organolithium reagent with dimethylformamide as described above).

Preparation of 8-*p*-HgCl. A solution of 300 mg of 8-*p*-Br and 9-*p*-Br in a 6:1 ratio (prepared by reaction of *p*-bromobenzyl bromide with lithium tetramethylpiperidide in 1,1-dimethylallene)[10] in 1 mL of THF was cooled to −78 °C and 0.56 mL of 2.5 M *n*-butyllithium in hexane was added. The mixture was kept at −78 °C for 55 min and then transferred (using a positive pressure of nitrogen and a double headed needle) to a solution of 375 mg of $HgCl_2$ in 2 mL of THF at −78 °C. The mixture was slowly warmed to room temperature and after 20 min at room temperature, water was added. The mixture was transferred to a separatory funnel with a small amount of THF and the organic phase was washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the solid residue was slurried with hexanes and collected, giving 306 mg (62%) of 8-*p*-HgCl and 9-*p*-HgCl in a 5 to 1 ratio. NMR of 8-*p*-HgCl ($CDCl_3$): δ 7.21 and 7.20 (AA'BB' quartet, 4 H, aromatic), 5.59 (m, 1 H), 5.53 (m, 1 H), 2.47 (m, 1 H), 1.35 (s, 3 H), 0.85 (s, 3 H). Mass spectrum (EI): *m/e* 204–198 (Hg^+ in pattern expected for Hg isotopes), 157 (100%) (M^+ − HgCl). No parent ion was observed in the EI mode. Mass spectrum (CI, isobutane): 399–391 (M + 1 in a pattern calculated for $C_{12}H_{14}HgCl^+$), 361–355 (M − Cl in a pattern calculated for $C_{12}H_{13}Hg^+$), 157 (100) (M^+ − HgCl). The spectrum also shows a cluster of variable intensity at *m/e* 404–397 in a pattern calculated for $C_{15}H_{19}Hg^+$ (9-*p*-$HgCMe_2$)$^+$.

Preparation of 8-*p*-Boronic Anhydride. This compound was prepared by using modifications of published procedures.[35] A Grignard reagent was prepared from 668 mg of a mixture of 8-*p*-Br and 9-*p*-Br (6:1 ratio) in 12 mL of ether. The reaction was initiated by the addition of a small amount of ethylene dibromide and by sonication. When the starting bromide was consumed (as indicated by gas chromatographic analysis of a quenched sample) the Grignard reagent was added to a solution of 770 mg of trimethylborate in 5 mL of ether at −30 °C. The mixture was then stirred at room temperature for 20 min and quenched with aqueous NH_4Cl solution. The organic extract was then dried over $MgSO_4$ and the solvent was removed on a rotary evaporator. The crude residue (478 mg) was chromatographed in two portions on a total of 8 g of silica gel and eluted with ether in hexanes. About 70 mg of dehalogenated material, 8-*p*-H, eluted with 5% ether in hexanes. A mixture of 8-$B(OH)_2$ and the dehydrated material, 8-boronic anhydride (263 mg) (40:60 ratios as determined by NMR), eluted with 20% ether in hexanes.

A solution of 123 mg of the mixture of 8-$B(OH)_2$ and 8-boronic anhydride in 5 mL of toluene was distilled at approximately 2 mm. The last traces of toluene were removed at 0.1 mm. 8-boronic anhydride (118 mg) remained as a viscous oil. This anhydride contained about 15% of rearranged aryl groups where the para substituent is the isopropylidenecyclopropane group. NMR ($CDCl_3$): δ 8.2–7.1 (4 H, aromatic), 5.7–5.5 (m, 2 H, olefinic), 2.55 (m, 1 H), 1.39 (s, 3 H), 0.89 (s, 3 H).

Preparation of 8-*p*-$\overline{BOCH_2CH_2O}$. A solution of 97 mg of 8-boronic anhydride obtained above in 1.5 mL of hexanes was stirred at room temperature and 64 mg of ethylene glycol was added. After 90 min, NMR analysis of the hexane phase showed about 70% conversion to product. The bottom phase was removed and an additional 70 mg of ethylene glycol was added with continued stirring for an additional 90 min. The hexane phase was separated and the solvent was removed under reduced pressure, leaving 87 mg (73%) of 8-*p*-$\overline{BOCH_2CH_2O}$ as a clear oil. About 12% of the rearranged isomer 9-*p*-$\overline{BOCH_2CH_2O}$ was also present. NMR of 8-*p*-$\overline{BOCH_2CH_2O}$ ($CDCl_3$): δ 7.72 and 7.21 (AA'BB' quartet, 4 H, aromatic), 5.59 (m, 1 H), 5.55 (m, 1 H), 4.36 (s, 4 H), 2.48 (m, 1 H), 1.35 (s, 3 H), 0.84 (s, 3 H). Exact mass calcd for $C_{14}H_{17}BO_2$: *m/e* 228.1322. Found: 228.1327.

Preparation of 11-*p*-CH_2SiMe_3. A solution of 3.314 g of *p*-[(trimethylsilyl)methyl]bromobenzene in 15 mL of THF was cooled to −78 °C and 6.5 mL of 2.5 M butyllithium in hexane was added dropwise. After 10 min at −78 °C, this solution was transferred (using a positive pressure of nitrogen and a double headed needle) to a solution of 3.7 g of diethyl oxalate in 15 mL of THF at −78 °C. The mixture was allowed to warm to 0 °C and then taken up into ether and water. The organic phase was separated, washed with water and saturated NaCl solution, and dried over $MgSO_4$, and the solvents were removed on a rotary evaporator. The excess diethyl oxalate and lower boiling impurities were removed by distillation through a 15-cm Vigreux column at 0.4 mm. The Vigreux column was removed and the remaining residue was distilled, giving 1.919 g (53%) of the keto ester *p*-$Me_3SiCH_2C_6H_4COCO_2Et$, bp 113–119 °C (0.08 mm). NMR ($CDCl_3$): δ 7.76 and 7.10 (AA'BB' quartet, 4 H, aromatic), 4.42 (q, *J* = 7 Hz, 2 H), 2.19 (s, 2 H), 1.40 (t, *J* = 7 Hz, 3 H), −0.01 (s, 9 H). Anal. Calcd for $C_{14}H_{20}O_3Si$: C, 63.60; H, 7.62. Found: C, 63.57; H, 7.83.

A mixture of 0.704 g of tosylhydrazine in 7 mL of methanol was stirred as 1.000 g of *p*-$Me_3SiCH_2C_6H_4COCO_2Et$ was added. The mixture became homogeneous and after 15 min 7.0 mL of 0.534 M $NaOCH_3$ in methanol was added. The solvent was removed on a rotary evaporator and 15 mL of ethylene glycol was added to the solid residue. The solution was heated to 50 °C for about 10 min and then extracted with ether. The ether was decanted and the process was repeated after heating to 65 °C. The combined ether extracts were washed with water, 10% NaOH solution, and saturated NaCl solution, and dried over $MgSO_4$. Solvent removal on a rotary evaporator gave 0.744 g (71%) of the diazo ester *p*-$Me_3SiCH_2C_6H_4CN_2CO_2Et$. NMR ($CDCl_3$): δ 7.32 and 7.02 (AA'BB' quartet, 4 H, aromatic), 4.32 (q, *J* = 7 Hz, 2 H), 2.07 (s, 2 H), 1.33 (t, *J* = 7 Hz, 3 H), −0.02 (s, 9 H).

A solution of 210 mg of *p*-$Me_3SiCH_2C_6H_4CN_2CO_2Et$ in 7 mL of 1,1-dimethylallene was irradiated with Pyrex-filtered light from a Hanovia 450-W medium pressure lamp for 90 min at room temperature. The unreacted allene was removed under reduced pressure and the residue was chromatographed on 4 g of silica gel and eluted with 4% ether in hexanes. Solvent removal using a rotary evaporator gave 200 mg (83%) of 11-*p*-CH_2SiMe_3 and 12-*p*-CH_2SiMe_3 in a 1:1 ratio. NMR of 11-*p*-CH_2SiMe_3 ($CDCl_3$): δ 7.29 and 6.91 (AA'BB' quartet, 4 H, aromatic), 5.760 (s, 1 H), 5.561 (s, 1 H), 4.13 (m, 2 H), 2.045 (s, 2 H), 1.362 (s, 3 H), 1.212 (t, *J* = 7 Hz, 3 H), 0.835 (s, 3 H), −0.03 (s, 9 H).

11-*p*-cyclopropyl was prepared by an analogous sequence starting with *p*-(bromocyclopropyl)benzene.[26b]

Rearrangements of 8. Kinetics Procedures. Kinetics procedures for thermal rearrangement of 8 in C_6D_6 were analogous to those previously described.[9c] The disappearance of the olefinic signal of 8 at δ 5.50–5.64 was periodically monitored by 300-MHz NMR by using dimethyl maleate as an internal standard. In the

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case of 8-NMe_2 or 8-*p*-$SnMe_3$, the methylene signal of the methyl ethers **16** and **22** could be used as the internal standard. Rate constants were calculated by the method of least squares. Correlation coefficients were greater than 0.999. Rate constants given represent the average of at least two runs.

Rearrangement of 11-*p*-CH_2SiMe_3 and 11-*p*-cyclopropyl. Kinetics Procedures. Rearrangements rates of these substrates in isooctane were monitored in sealed cuvettes by ultraviolet spectroscopy as previously described.[25] The absorbance change for 11-*p*-CH_2SiMe_3 was monitored at 245 nm and 11-*p*-cyclopropyl was monitored at 246 nm. After 10 half-lives, an infinity reading was taken. Rate constants were calculated by standard methods and represent an average of at least 2 runs.

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Alkylations of Tetracarbonyl(phosphine)chromium and Pentacarbonylchromium Carbene Complexes and Their Reactions with Selected Acetylenes

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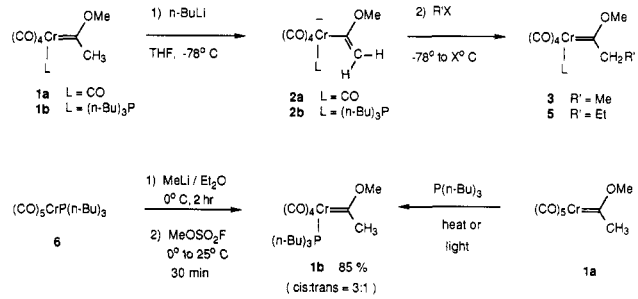
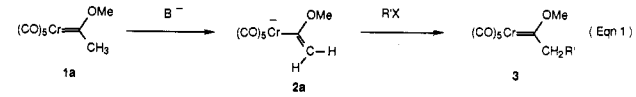
The thermodynamic acidity of (methylmethoxymethylene)tetracarbonyl(tri-*n*-butylphosphine)chromium (**1b**) was found to be 6 orders of magnitude less than that of (methylmethoxymethylene)pentacarbonylchromium (**1a**). The anion **2b** is generated from **1b** by deprotonation with *n*-butyllithium. The difference in acidity of **1a** and **1b** is reflected in an increase in the reactivity of **2b** with alkyl halides and sulfonate esters that is sufficient to allow for the efficient preparation of elaborated carbene complexes from simple precursors. Since the anion **2a**, generated from pentacarbonyl complex **1a**, can only be effectively alkylated with trifluoromethanesulfonate esters, methods are developed for the conversion of tetracarbonyl phosphine carbene complexes to pentacarbonyl carbene complexes such that the former can serve as synthons for the latter. Several reactions of tetracarbonyl phosphine carbene complexes were investigated, including the benzannulation reaction with acetylenes, the reaction of acetylenes with alkyl-substituted complexes to produce stable vinylketenes, and two-alkyne annulations with 1,6-heptadiyne that provide for the first time selective synthesis of bicyclo[4.3.0]nonadien-2-ones.

Shortly after it was discovered[1] that the protons on carbons α to the carbene carbon in several transition-metal Fischer carbene complexes are acidic, the chemistry of stoichiometrically generated anions of alkyl carbene complexes (such as **2a**) was investigated.[2] From an examination of the equilibrium of the bis(triphenylphosphine)nitrogen(1+) salt of **2a** with various phenols, it was established that the pK_a of **1a** was approximately 8.[3] Given the acidity of **1a**, it is to be expected that its conjugate base **2a** would be relatively unreactive with most electrophiles, and the extensive studies by Casey reveal that this is indeed the case.[2] Methyl iodide and primary halides either give very poor yields or fail to give detectable amounts of alkylated products in their reactions with anion **2a**.[2f,j,k] Methyl fluorosulfate gives moderate yields with **2a** but ethyl tosylate fails to alkylate **2a**.[2j] Alkylations with allylic and benzylic halides give improved yields but this is offset by severe problems with dialkylation.[2f] Condensation products can be obtained from the reaction of **2a** with nonenolizable aldehydes but under the same conditions ketones do not react.[2b,e,g,i-k] Certain electrophiles such as epoxides[2h] α-bromo esters,[2h] and α-chloro ethers[2g] give moderate yields of interesting and/or synthetically useful carbene complexes.

Scheme I





Due to the increasing value of transition-metal carbene complexes in organic synthesis,[4,5] there is consequently a

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