differences are better described with correlation than at the Hartree–Fock level. Table IV also reports the enthalpy for the isomerization reaction involving 1-methylimidazole and 4-methylimidazole for which no experimental data are available. The computed results predict that 4-methylimidazole is the more stable isomer by 6.6 kcal/mol.

Conclusions

In this study, the following experimental gas phase proton affinities (in kcal/mol) for a series of azoles have been determined: isoxazole, 202.3; oxazole, 207.8; 1,2,4-triazole, 212.4; pyrazole, 212.8; thiazole, 213.2; imidazole, 222.1; 4-methylimidazole, 224.8; and 1-methylimidazole, 228.0. Ab initio protonation enthalpies for first-row azoles computed at the MP2/6-31G(d,p) level of theory reproduce the above order but tend to overestimate the experimental values, the largest difference being 8.9 kcal/mol for the proton affinity of 4-methylimidazole. These calculations show that the protonation sites are N_3 in imidazole and oxazole and N_4 in 1,2,4-triazole, the alternate protonation sites of N_1, O, and N_2, respectively, being less favorable by 53, 57, and 13 kcal/mol.

These calculations also indicate a correlation between lone pair n orbital energies and proton affinities for those azoles in which the lone pair is localized at the protonation site. The methyl substituent effect on the proton affinity of imidazole and the differences in the proton affinities of the isomeric pairs oxazole and isoxazole and imidazole and pyrazole are reproduced by these calculations. Computed isomerization energies for pyrazole and imidazole and oxazole and isoxazole are in excellent agreement with the experimental values.

Acknowledgment. J.E.D.B. thanks the National Institutes of Health, National Institute of General Medical Sciences for partial support of this work through Grant GM27955 and the Youngstown State University Computer Center for computational support and assistance.

Registry No. 1-Methylimidazole, 616-47-7; 4-methylimidazole, 822-36-6; imidazole, 288-32-4; thiazole, 288-47-1; pyrazole, 288-13-1; 1,2,4-triazole, 288-88-0; oxazole, 288-42-6; isoxazole, 288-14-2.

Supplementary Material Available: STO-3G and 3-21G structures of neutral and protonated azoles (34 pages). Ordering information is given on any current masthead page.

Methylenecyclopropane Rearrangement as a Probe for Free Radical Substituent Effects. Effect of Sulfur in Various Oxidation States

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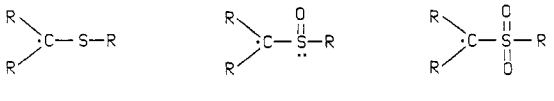
A series of 3-aryl-2,2-dimethylmethylenecyclopropanes **4** with the sulfur-containing substituents SCH_3, $SOCH_3$, SO_2CH_3, and $PS(OEt)_2$ in the para and meta positions have been prepared. These substrates undergo thermal rearrangement at 80 °C in C_6D_6 to give the corresponding 2-arylisopropylidenecyclopropanes **5** at rates which vary as a function of substituent. The para-substituted substrates all rearrange at faster rates than the unsubstituted system. Comparison with the meta isomers suggests that the rate-enhancing effect is conjugative in nature. The singlet trimethylenemethane biradical intermediate is suggested to be stabilized by *p*-SCH_3, *p*-$SOCH_3$, and *p*-SO_2CH_3 substituents, with *p*-SCH_3 providing the greatest stabilization. The *p*-$PS(OEt)_2$ substituent is also quite effective at increasing rate. These rate effects are considered in terms of interaction of the nonbonding electron pair of SCH_3 with the developing benzylic radical center. A further stabilizing interaction involving vacant d orbitals is considered to account for the greater stabilizing effect of SCH_3 relative to OCH_3, as well as the relatively large stabilizing effects of $SOCH_3$, SO_2CH_3, and $PS(OEt)_2$ on the transition state for this methylenecyclopropane rearrangement.

The effect of sulfur-containing groups on free radicals is an area of current interest. Neighboring sulfide substituents are thought to stabilize free radicals. Evidence for this comes from a variety of studies including vinyl sulfide copolymerization data,[1] azocumene pyrolyses,[2] hydrogen atom abstraction data,[3a] and ESR data.[4] The effect of sulfur in oxidized forms (as in sulfoxides and sulfones) is not as clear. While α-sulfinyl[3b] as well as α-sulfonyl radicals[3c] have been generated in the past, the effect of these substituents on radical stability is not as well understood. We wanted a more quantitative comparison of the effect of sulfide, sulfoxide, and sulfone on free radicals such as **1**–**3**.



1 **2** **3**

Large polar effects are often observed in reactions leading to free radicals. Hydrogen atom abstraction reactions are a classic example and rate data for such processes often reflect the polar nature of the transition state which can overwhelm any true radical stabilizing effects.[5] We therefore sought a reaction which was devoid of significant polar character to evaluate true free radical stabilizing effects. A number of years ago we suggested[6] that the methylenecyclopropane rearrangement of **4** to **5** could

(1) Price, C. C.; Zomfefer, J. *J. Am. Chem. Soc.* **1950**, *72*, 14–17.
(2) (a) Timberlake, J. W.; Garner, A. W.; Hodges, M. L. *Tetrahedron Lett.* **1973**, 309–312. (b) Ohno, A.; Kito, N.; Ohnishi, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 463–467.
(3) For a summary, see: (a) Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; p 183; (b) 194–195; (c) pp 196–198.
(4) Biddles, I.; Hudson, A.; Wiffen, J. T. *Tetrahedron* **1972**, *28*, 867–874.
(5) For pertinent examples, see: (a) Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 354–355. (b) Huyser, E. S. *Ibid.* **1960**, *82*, 394–396. (c) Walling, C.; Jacknow, B. B. *Ibid.* **1960**, *82*, 6113–6115. (d) Gilliom, R. D. *Ibid.* **1965**, *87*, 3944–3948. (e) Kennedy, B. R.; Ingold, K. U. *Can. J. Chem.* **1966**, *44*, 2381–2385. (f) Russell, G. A.; Williamson, R. C., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 2357–2364.
(6) Creary, X. *J. Org. Chem.* **1980**, *45*, 280–284.

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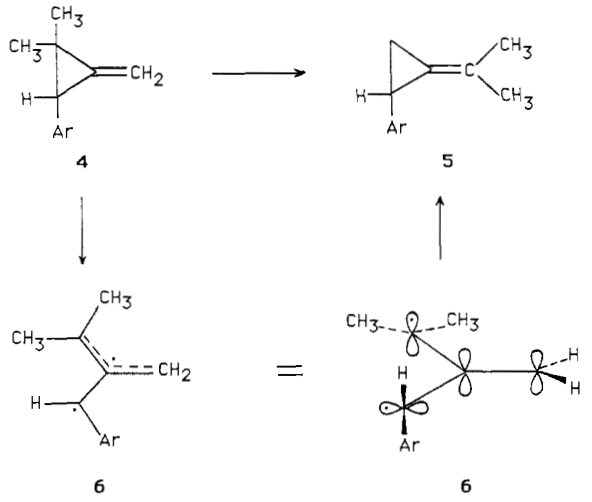
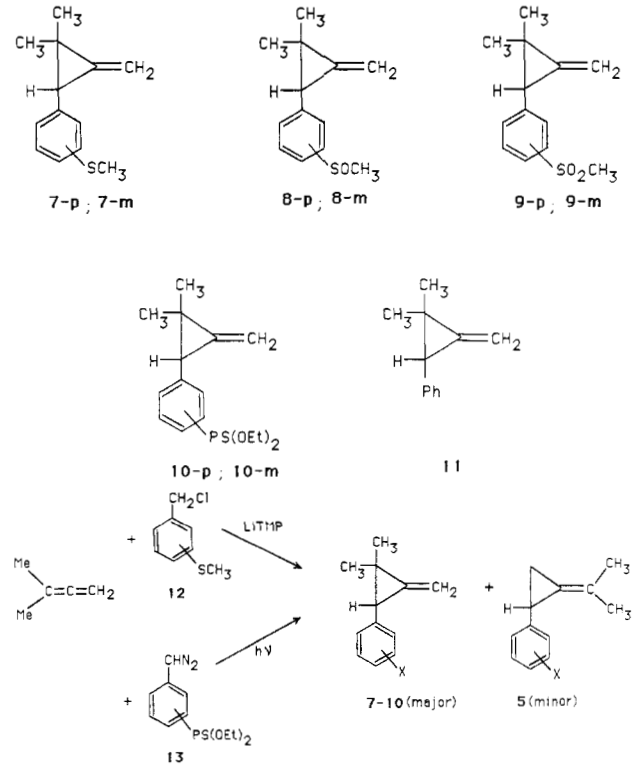


give a quantitative measure of the ability of various groups to stabilize a free radical in the absence of overwhelming polar effects. The rearrangement of **4** to **5**, which proceeds in high yield and can be monitored quite easily and accurately by NMR spectroscopy, presumably occurs by way of the singlet trimethylenemethane **6**. The rate of this reaction was substituent-dependent with free radical stabilizing groups lending increased stability to the transition state leading to **6**. This is a kinetic method for evaluating radical stabilizing effects which does not take into account ground-state effects. Another problem associated with the use of this rearrangement as a probe for free radical substituent effects is the rather small rate effects (due to the fact that the substituent is insulated from the radical center by the aromatic ring). Despite these limitations, correlation with the $\sigma\cdot$ substituent constant later developed by Arnold and Dust[7] (based on benzyl radical hyperfine coupling constants) was good. This lent further support to the validity of use of this rearrangement as a true probe for free radical stabilizing effects. Despite the potential problems associated with the methylenecyclopropane rearrangement probe, this method has proven to be ammenable to study of a wide variety of substituents by a facile and accurate kinetic method.

We have now prepared a series of substituted methylenecyclopropanes (**7–9**) (meta and para isomers) which allow one to compare the effect of sulfur in various oxidation states on the methylenecyclopropane rearrangement. We now report how these rates correlate with the recently reported $\sigma\cdot$ values for these groups as determined by Arnold[8] and the recent azocumene pyrolysis data of Timberlake.[9] We have also prepared the sulfur-containing thiophosphoryl system **10** for comparison with our recently reported data[10] on the *O*-phosphoryl analogues. These data on benzylic type radicals **6** (where the substituent is insulated from the radical center by an aromatic ring) should give some insights as to the effect of these substituents when attached directly to a radical center as in **1–3**.

Results and Discussion

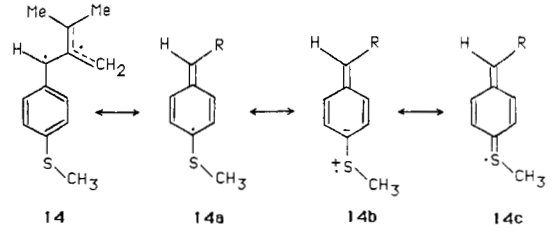
The requisite methylenecyclopropanes **7–10** were prepared by the addition of the appropriate carbene to 1,1-dimethylallene. In the preparation of **7**, the reaction of



lithium tetramethylpiperidide with the appropriate thiomethyl-substituted benzyl chlorides **12** generated the necessary carbenic intermediate. In the preparation of **8–10**, the corresponding diazo compounds **13** served as carbene precursers. Also produced were smaller amounts of the isopropylidenecyclopropanes **5** which result from the addition to the less substituted double bond of the allene.

Table I gives rate data for rearrangement of the substrates **7–10** to the corresponding isopropylidenecyclopropanes **5**. The first thing that is apparent from the data is that the para isomers all rearrange faster than the meta isomers, as well as the parent unsubstituted system **11**. The thiomethyl substituent in the meta position slightly retards the rate relative to the unsubstituted analog **11**. This is in line with our earlier studies[6] (in isooctane) where electronegative substituents in the meta position slightly decreased rates. This was attributed to the fact that a free radical is still an electron-deficient intermediate and, as such, should be slightly destabilized by a purely electron-withdrawing substituent.

The **7**-p/**7**-m rate ratio of 2.83 verifies that the radical stabilizing effect of the thiomethyl group is a conjugative effect. Our earlier study[6] on **7**-p and Arnold's $\sigma\cdot$ value[8] also support this conjugative stabilization. This stabilization has been discussed in terms of interaction of the radical center with the doubly occupied nonbonding molecular orbital of the sulfur.[11] A net stabilizing interaction occurs. An equivalent valence bond description of spin delocalization by sulfur is shown in **14a,b**. Our study, as well as



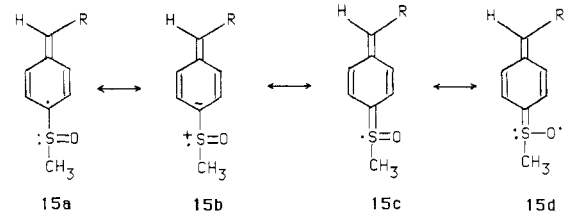
(7) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1211–1227.
(8) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164–1168.
(9) Luedtke, A. E.; Timberlake, J. W. *J. Org. Chem.* **1985**, *50*, 268–270.
(10) Creary, X.; Benage, B.; Mehrsheikh-Mohammadi, M. E.; Bays, J. P. *Tetrahedron Lett.* **1985**, *26*, 2283–2286.
(11) (a) Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whango, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 469–478. See also: (b) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2378–2383.

Table I. Rearrangement Rates of 7-11 in C_6D_6 at 80.0 °C

substitutent	k, s^{-1}	k_{rel}
p-SCH_3(7-p)	$(1.49 \pm 0.00) \times 10^{-4}$	2.67 ± 0.04
m-SCH_3 (7-m)	$(5.25 \pm 0.08) \times 10^{-5}$	0.94 ± 0.03
p-$SOCH_3$ (8-p)	$(8.47 \pm 0.21) \times 10^{-5}$	1.52 ± 0.07
m-$SOCH_3$ (8-m)	$(5.69 \pm 0.14) \times 10^{-5}$	1.02 ± 0.05
p-SO_2CH_3 (9-p)	$(8.35 \pm 0.12) \times 10^{-5}$	1.50 ± 0.05
m-SO_2CH_3 (9-m)	$(4.79 \pm 0.08) \times 10^{-5}$	0.86 ± 0.03
p-$PS(OEt)_2$ (10-p)	$(1.09 \pm 0.00) \times 10^{-4}$	1.95 ± 0.04
m-$PS(OEt)_2$ (10-m)	$(4.93 \pm 0.08) \times 10^{-5}$	0.88 ± 0.03
p-H (11)	$(5.57 \pm 0.10) \times 10^{-5}$	1.00

Arnold's $\sigma\cdot$ value, and earlier studies[2] show that thiomethoxy is much more effective than methoxy as a radical stabilizing group. The greater stabilization of sulfur relative to oxygen has been rationalized in terms of a more favorable interaction of the sulfur nonbonding electron pair with the radical center.[11] However, an unanswered question concerns the importance of sulfur d orbitals in radical stabilization. Theoretical calculations have questioned the importance of d orbitals in spin delocalization.[12] If interaction of the radical center with the heteroatom nonbonding electron pair were the only stabilizing factor, then thiomethoxy should also be much more effective than methoxy in stabilization of cationic centers. This is not the case. Experimental data suggest that, in solution, methoxy-substituted cations are more stable than their thiomethoxy analogues.[13,14] The ability of a carbon 2p orbital to interact with sulfur and oxygen nonbonding electron pairs therefore does not explain both radical and carbocation stabilization trends. While the sulfur nonbonding electron pair is undoubtedly important, some other factor, such as spin delocalization involving sulfur d orbitals (as depicted in **14c**), may also be involved in radical stabilization. It is also possible that delocalization involving an adjacent antibonding C–S σ^* orbital may be involved. An analogous interaction has been suggested to account for stabilization of anions by adjacent sulfur.[15]

To further evaluate the importance of other factors (such as d-orbital delocalization) in radical stabilization by sulfur, attention was turned to more oxidized substrates **8** and **9**. The sulfoxide **8**-p is more reactive than either **8**-m or the unsubstituted analogue **11**. It is, however, less reactive than the sulfide **7**-p. This is again consistent with Arnold's $\sigma\cdot$ value for $SOCH_3$ which indicates that this group is radical-stabilizing. The mechanism of spin delocalization by $SOCH_3$ is uncertain, although Arnold[8] has suggested that this group behaves as a spin doner (i.e., **15** derives stabilization by interaction with the sulfur nonbonding pair as in **15b**). However, our preliminary unpublished data on α-sulfinyl carbocations indicate that the sulfinyl group

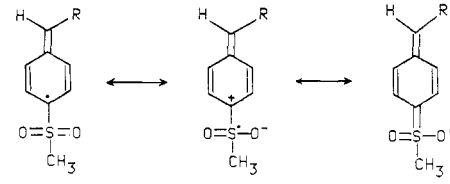


15a **15b** **15c** **15d**

is not particularly effective as a carbocation stabilizing group. This suggests that forms such as **15c** and **15d** (involving d-orbital delocalization) may well be more important than the nonbonding electron pair in sulfinyl stabilization of free radicals.

The rate of **8**-m is about the same as that of the unsubstituted system **11**. This is unexpected since the $SOCH_3$ is electron withdrawing and such substituents usually retard the rate of rearrangement of **4** to a small extent. The reasons for this slightly anomolous behavior of **8**-m are not understood.

The sulfonyl group, SO_2CH_3, in **9**-p also increases the rearrangement rate relative to **9**-m or the unsubstituted analogue **11**. The **9**-p/**9**-m ratio of 1.74 implies that the sulfonyl group is capable of substantial spin delocalization. This is contrary to the $\sigma\cdot$ value for this group which indicates only a very weak spin delocalizing ability. Our results imply that delocalization involving sulfur d orbitals (or some other form of transition-state stabilization) is important. Forms such as **16b** and **16c** would account for



16a **16b** **16c**

the stabilizing effect of the sulfonyl group in which there are no nonbonding electron pairs associated with sulfur. This implies that sulfur d-orbital effects (**14c**) may also be important in stabilization of the unoxidized sulfide system **14**. We do not understand the reason for the conflicting conclusions regarding the ability of SO_2CH_3 to stabilize benzylic radicals based on our present data and $\sigma\cdot$ values of Arnold.[16] Of the 18 substituents common to our studies, this is the first major discrepency. Our data is qualitatively in agreement with Timberlake's pyrolysis

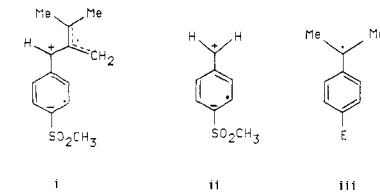
(12) (a) Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Tiecco, M.; Whangbo, M. H.; Wolfe, S. *Gazz. Chim. Ital.* **1974**, *104*, 1101–1108. See also: (b) Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel H. B.; Whangbo, M. H.; Wolfe, S. *J. Am. Chem. Soc.* **1975**, *97*, 2209–2218.

(13) σ^+ values support this contention. See: (a) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 7663–7667. (b) Brown, H. C.; Okamoto, Y.; Inukai, T. *Ibid.* **1958**, *80*, 4964–4968. See also: (c) McClelland, R. A.; Leung, M. *J. Org. Chem.* **1980**, *45*, 187–189. (d) McClelland, R. A. *Can. J. Chem.* **1977**, *55*, 548–551. (e) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476–1488. (f) Bohme, H.; Fisher, H.; Frank, R. *Justus Liebigs Ann. Chem.* **1949**, *563*, 54–72. (g) Jones, T. C.; Thornton, F. R. *J. Am. Chem. Soc.* **1967**, *89*, 4863–4867. (h) Modena, G.; Scorrano, G.; Venturello, P. *J. Chem. Soc.*; *Perkin Trans. 2* **1979**, 1–6.

(14) Theoretical calculations suggests that $^+CH_2SH$ is more stable than $^+CH_2OH$ (in contrast to most experimental data in solution). See: (a) Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; M. H.; Wolfe, S. *Can. J. Chem.* **1975**, *53*, 1144–1153. (b) Bernardi, F.; Csizmadia, I. G.; Epiotis, N. D. *Tetrahedron* **1975**, *31*, 3085–3088.

(15) (a) Epiotis, N. D.; Yates, D. L.; Bernardi, F.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 5435–5439. (b) Barbarella, G.; Dembech, P.; Garbesi, A.; Bernardi, F.; Bottoni, A.; Fava, A. *Ibid.* **1978**, *100*, 200–203.

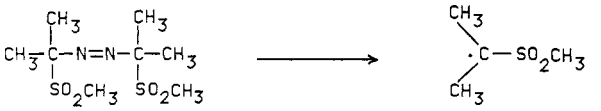
(16) A reviewer has suggested that the apparent discrepancy may be due to the fact that evaluations of the effect of SO_2CH_3 (by $\sigma\cdot$ and the methylenecyclopropane rearrangement) are based on different systems and hence the effect of SO_2CH_3 may not necessarily be the same. The reviewer has further suggested that our result may be an indication of merostabilization (captodative effect) due to the electron-withdrawing properties of SO_2CH_3, i.e., forms such as i may be more important in stabilization of **16** than in stabilization of the analogous benzyl radical ii. Such an effect has been suggested to influence the β-hyperfine coupling constant in cumyl radicals iii.[17] This suggestion requires that the R group (which is an allylic radical with its π-system perpendicular to the benzylic radical) in **16** have donor properties relative to hydrogen. This is not at all clear. Further studies are necessary to support or rule out this reviewer suggestion.



i **ii** **iii**

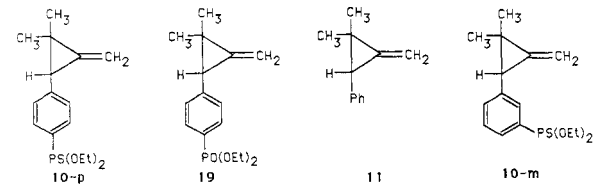
(17) Arnold, D. R.; Nicholas, A. M. De P.; Snow, M. S. *Can. J. Chem.* **1985**, *63*, 1150–1155.

study[9] on **17** where SO_2CH_3 appears to be capable of stabilizing the transition state leading to the radical **18**.



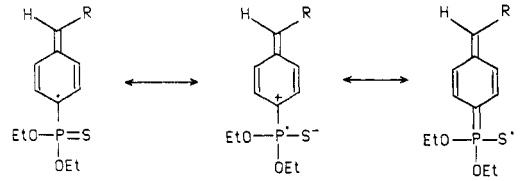
17 **18**

Attention was next turned to system **10** for comparison with our previously reported data[10] on the *O*-phosphoryl analogue **19**. The thermal rearrangement of **10-p** proceeds at a faster rate than that of **10-m** or **11**. The thio-



	10-p	**19**	**11**	**10-m**
rel rates	1.95	1.51	1.00	0.88

phosphoryl group is therefore quite radical-stabilizing. The thiophosphoryl system also rearranges 1.3 times faster than the *O*-phosphoryl analogue **19**. While this data is difficult to interpret precisely due to the relatively small rate differences, it may imply spin delocalization involving sulfur as in **20c**. Such delocalization would necessitate interaction of the radical center of **20** with a vacant phosphorus d orbital. The faster rate of **10-p** relative to the *O*-phosphoryl analogue **19** could be a result of the increased importance of **20c** relative to the oxygen analogue.



20a **20b** **20c**

Conclusions

The sulfur-containing substituents SCH_3, $SOCH_3$, SO_2CH_3, and $PS(OEt)_2$ in the para position of the aromatic ring all stabilize the transition state for the methylenecyclopropane rearrangement of **7–10**. Our present data were interpreted in terms of spin delocalization in the biradical intermediate. Interaction with the sulfur nonbonding electron pair as well as a vacant sulfur d orbital is necessary to account for the SCH_3 effect. This type of d-orbital interaction was also considered important in the case of the $SOCH_3$, SO_2CH_3, and $PS(OEt)_2$ substituents. Our rate data is in line with expectations based on $\sigma\cdot$ values for SCH_3 and $SOCH_3$. The SO_2CH_3 substituent stabilizes the transition state for the methylenecyclopropane rearrangement while Arnold's $\sigma\cdot$ value for this group suggests only a small stabilizing effect on benzylic radicals. The origin of this apparent conflict is uncertain.

Experimental Section

Preparation of *p*-(Thiomethoxy)benzaldehyde. A Grignard reagent was prepared from 26.3 g of *p*-bromothioanisole and 3.91 g of magmesium in 225 mL of ether. The reaction was initiated with a small amount of ethylene dibromide and the solution was refluxed for 2.25 h after completion of the addition of the bromide to ensure complete reaction. The two-phase Grignard reagent was transferred to an addition funnel and added dropwise to a mechanically stirred solution of 20.2 g of dimethyl formamide in 65 mL of ether at −78 °C. On completion of the addition, the mixture was brought to room temperature and quenched with an aqueous ammonium chloride solution. The organic phase was separated, washed with water and saturated NaCl solution, and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was distilled. A forrun of 2.12 g of thioanisole was collected followed by 12.9 g (65%) of *p*-(thiomethoxy)benzaldehyde,[18] bp 87–91 °C (0.1 mm): NMR (CCl_4) δ 10.17 (1 H, s), 7.9–7.1 (4 H, AA'BB' quartet), 2.52 (3 H, s).

m-(Thiomethoxy)benzaldehyde was prepared by an analogous procedure (61% yield) from *m*-bromothioanisole.

Preparation of *p*-(Thiomethoxy)benzaldehyde Dimethyl Acetal. A mixture of 7.14 g of *p*-(thiomethoxy)benzaldehyde and 6.17 g of trimethyl orthoformate in 100 mL of absolute methanol was treated with 165 mg of *p*-toluenesulfonic acid. After 1.5 h at room temperature, 1.9 mL of 0.5 M $NaOCH_3$ in methanol was added. The solvent was removed on a rotary evaporator and the residue was distilled to give 7.69 g (83%) of the dimethyl acetal of *p*-(thiomethoxy)benzaldehyde, bp 87–89 °C (0.1 mm): NMR ($CDCl_3$) δ 7.32 (4 H, AA'BB' quartet), 5.37 (1 H, s), 3.33 (6 H, s), 2.48 (3 H, s).

m-(Thiomethoxy)benzaldehyde dimethyl acetal was prepared in the same fashion in 93% yield starting with *m*-(thiomethoxy)benzaldehyde.

Preparation of *p*-(Methanesulfinyl)benzaldehyde. A solution of 1.46 g of *p*-(thiomethoxy)benzaldehyde dimethyl acetal in 10 mL of methylene chloride was cooled in an ice bath as 1.52 g of 85% *m*-chloroperbenzoic acid in 10 mL of methylene chloride were added dropwise. The solution was stirred at room temperature for 35 min and then transferred to seperatory funnel with ether. The mixture was washed with NaOH solution, followed by a NaI–NaOH–$Na_2S_2O_3$ solution and saturated NaCl solution. The organic phase was dried over $MgSO_4$ and the solvent was removed on a rotary evaporator. The residue was distilled to give 1.04 g (66%) of *p*-(methanesulfinyl)benzaldehyde dimethyl acetal, bp 124–125 °C (0.1 mm): NMR ($CDCl_3$) δ 7.62 (4 H, s), 5.42 (1 H, s), 3.37 (6 H, s), 2.70 (3 H, s).

A solution of 2.16 g of the acetal in 20 mL of tetrahydrofuran and 20 mL of 2% H_2SO_4 in water was stirred at room temperature for 1.5 h. Solid K_2CO_3 was added to neutralize the H_2SO_4. The mixture was taken up into ether and the organic phase was dried over $MgSO_4$. The solvent was removed on a rotary evaporator. The solid residue was slurried with ether and the ether was decanted with the last traces being removed under vacuum. The yield of *p*-(methanesulfinyl)benzaldehyde, mp 81–82 °C (lit.[19] mp 82–88 °C) was 1.54 g (91%): NMR ($CDCl_3$) δ 10.10 (1 H, s), 7.95 (4 H, AA'BB' quartet), 2.79 (3 H, s).

m-(Methanesulfinyl)benzaldehyde was prepared in the same fashion (86% overall yield) from *m*-(thiomethoxy)benzaldehyde dimethyl acetal.

Preparation of *p*-(Methanesulfonyl)benzaldehyde. The procedure was analogous to that described for preparation of the sulfoxide. Oxidation of 2.86 g of *p*-(thiomethoxy)benzaldehyde dimethyl acetal in 50 mL of CH_2Cl_2 with 6.16 g of 85% *m*-chloroperbenzoic acid for 13.5 h at room temperature gave 2.76 g (83%) of *p*-(methanesulfonyl)benzaldehyde dimethyl acetal, bp 134 °C (0.06 mm): NMR ($CDCl_3$) δ 7.80 (4 h, AA'BB' quartet), 5.48 (1 H, s), 3.38 (6 H, s), 3.06 (3 H, s).

A solution of 1.91 g of the acetal in 20 mL of tetrahydrofuran and 20 mL of 2% H_2SO_4 in water was stirred at room temperature for 5 h. During this time, the ether insoluble aldehyde precipitated. Solid Na_2CO_3 was added to neutralize the H_2SO_4. The mixture was taken up into CH_2Cl_2 and the organic phase was dried over $MgSO_4$. The solvent was removed on a rotary evaporator leaving 1.53 g (100%) of *p*-(methanesulfonyl)benzaldehyde, mp 156–158 °C (lit.[20] mp 158–159 °C): NMR ($CDCl_3$) δ 10.15 (1 H, s), 8.12 (4 H, AA'BB' quartet), 3.12 (3 H, s).

m-(Methanesulfonyl)benzaldehyde[20] was prepared in the same fashion (79% overall yield) from *m*-(thiomethoxy)benzaldehyde dimethyl acetal.

Preparation of *p*-(Diethylthiophosphono)benzaldehyde. A solution of potassium diethyl thiophosphite in liquid ammonia

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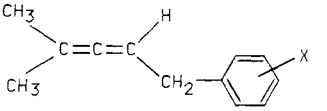
was prepared by the dropwise addition of 4.15 g of diethyl thiophosphite to a solution of 1.05 g of potassium metal in 200 mL of ammonia. The blue color disappeared on completion of the addition and 4.20 g of *p*-iodobenzaldehyde dimethyl acetal was then added. The resulting solution was irradiated in a Griffin–Srinivasan photochemical reactor using "350-nm" lamps for 3 h.[21] The ammonia was allowed to evaporate and an aqueous workup followed. The ether extract was dried over $MgSO_4$ and the solvent was removed on a rotary evaporator. The residue (which contained some unreacted *p*-iodobenzaldehyde dimethyl acetal) was dissolved in 25 mL of THF and 25 mL of 2% H_2SO_4 in water was added. The mixture was stirred for 2.5 h at room temperature and K_2CO_3 was then added. The mixture was taken up into ether and the organic phase was washed with water and saturated NaCl solution and dried over $MgSO_4$. After removing the solvent on a rotary evaporator, the residue was chromatographed on 25 g of silica gel. Increasing amounts of ether in Skelly F were used to elute. *p*-(Diethylthiophosphono)benzaldehyde, contaminated with a small amount of *p*-iodobenzaldehyde, eluted with 25% ether. Distillation gave 2.90 g (74%) of *p*-(diethylthiophosphono)benzaldehyde, bp 115–135 °C (0.05 mm): NMR ($CDCl_3$) δ 10.09 (1 H, s), 8.2–7.9 (4 H, m), 4.28–4.05 (4 H, m), 1.33 (6 H, t, J = 7 Hz).

m-(Diethylthiophosphono)benzaldehyde was prepared in the same fashion (43% yield) from *m*-iodobenzaldehyde dimethyl acetal.

Preparation of Aryldiazomethanes from Substituted Benzaldehydes. General Procedure. The aldehydes described above (approximately 1.2 g in 10 mL of methanol containing 1 drop of pyridine) were added to a suspension of 1.05 equiv of tosylhydrazine in methanol. After about 4 h, the precipitated tosylhydrazones were collected by using a Buchner funnel. When no solid formed, the methanol solvent was removed on a rotary evaporator. The solid tosylhydrazones or the residual oils were treated with 1.0 equiv of $NaOCH_3$ in methanol and the methanol was again removed on a rotary evaporator. About 15 mL of ethylene glycol was then added.

The diazo phosphonates **13** [X = *m*- and *p*-$PS(OEt)_2$] were prepared from the corresponding tosylhydrazones by using the ethylene glycol pyrolysis method (periodic extractions with ether) previously described.[22] The diazo compounds **13** (X = $SOCH_3$ and SO_2CH_3) were prepared by a slightly modified procedure. The sodium salts of the sulfoxide and sulfone tosylhydrazones in ethylene glycol were then heated in an oil bath (80 °C for sulfoxides; 65 °C for sulfones) for an appropriate time (10 min for sulfoxides; 15 min for sulfones). The mixtures were then taken up into water and extracted with three portions of CH_2Cl_2. The extracts were washed with dilute NaOH, water, and saturated NaCl solution. The solutions were dried by using $MgSO_4$. The solvent was removed on a rotary evaporator, leaving the crude diazo compounds **13** (X = $SOCH_3$ and SO_2CH_3), which were used without further purifcation.

Photolyses of Aryldiazomethanes 13 in 1,1-Dimethylallene. General Procedure. The procedure was analogous to that previously described.[23] A solution of the appropriate aryldiazomethane **13** (1 part) in 1,1-dimethylallene (50 parts) was irradiated in a water-cooled Pyrex tube with a Hanovia 450-W medium pressure mercury lamp until the red-orange color had substantially faded. In the case of **13** (X = $SOCH_3$ and SO_2CH_3), about 5–10% THF was added to increase the solubility of the diazo compound in the allene. On completion of the irradiation, the excess allene was removed at reduced pressure below room temperature. The residue was chromatographed on silica gel. The sulfoxides **8** were eluted with ether. The sulfones **9** were eluted with 1:1 ether/Skelly F and the thiophosphonates **10** were eluted with 2% ether in Skelly F. Small amounts of the allenes **21** were also present in the chromatographed products. The following procedure is representative.



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A solution of 540 mg of **13** (X = *p*-$PS(OEt)_2$) in 10 mL of 1,1-dimethylallene was irradiated for 6 h. After removal of the excess allene, the residue was chromatographed on 15 g of silica gel. Solvent removal gave 280 mg (44%) of a mixture of **10**-p, **5** (Ar = *p*-$PS(OEt)_2C_6H_4$), and **21** (X = *p*-$PS(OEt)_2$) in a 1.9:1:0.2 ratio as determined by 300-MHz NMR. This mixture was used in kinetic studies. NMR of **10**-p ($CDCl_3$) δ 7.9–7.1 (4 H, m), 5.596 (1 H, d, J = 2.2 Hz), 5.533 (1 H, d, J = 1.2 Hz), 4.2–4.0 (4 H, m), 2.48 (1 H, m), 1.357 (3 H, s), 1.305 (6 H, t, J = 7 Hz), 0.855 (3 H, s).

Preparation of 7-p and 7-m. The *p*-thiomethoxy derivative, **7**-p, was prepared from *p*-(thiomethoxy)benzyl chloride, 1,1-dimethylallene, and lithium tetramethylpiperidide as previously described. The *m*-thiomethoxy derivative, **7**-m, was prepared in an analogous fashion from *m*-(thiomethoxy)benzyl chloride. The yield of **7**-m and **5** (Ar = *m*-$CH_3SC_6H_5$) was 9% in a 5.4 to 1 ratio, respectively. These mixtures were used in kinetic studies. NMR of **7**-m ($CDCl_3$) δ 7.4–6.9 (4 H, m), 5.56 (2 H, m), 2.47 (3 H, s), 2.43 (1 H, m), 1.34 (3 H, s), 0.86 (3 H, s).

Thermal Rearrangements of 7–10. Kinetics Procedures. Approximately 5–10 mg of the appropriate substrate (which also contained some of the isomer **5** formed in the synthesis) and a small amount of an internal standard (dimethyl maleate) was dissolved in about 0.7 mL of C_6D_6. The solution was sealed in an NMR tube under nitrogen and the tube was immersed in a constant temperature bath for a given amount of time. The tube was periodically analyzed by 300-MHz NMR for remaining substrate by integration of the olefinic signal at δ 5.50–5.64 and the signal due to the internal standard at δ 5.68. 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. Standard deviations are given in Table I.

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