Relative Conjugative Abilities of Three-Membered Ring Heterocycles with Benzene Based on ^{13}C and ^{15}N NMR[1]

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Abstract: The conjugative ability of various three-membered rings with benzene was investigated by observing the sensitivity of β-carbon ^{13}C chemical shifts to para substituents. These Hammett ρ values were 2.0, 1.5, 1.0, and 0.9 ppm for arylcyclopropanes, *N*-methyl-2-arylaziridines, phenyloxiranes, and *N,N*-dimethyl-2-arylaziridinium fluorosulfonates, respectively. These values were intermediate to ones for para-substituted styrenes (6.5 ppm) and ethylbenzenes (−0.9 ppm), model compounds which were taken to represent extremes of conjugative ability. Similar results were found for ^{15}N chemical shifts of *trans*-3-aryloxaziridines, which had a slope of 2.1 ppm, intermediate to those for benzylimines (20.2 ppm) and benzylamines (−1.3 ppm). The order of conjugative ability, which decreases with increasing electronegativity of the hetero group, could not be explained by hybridization changes based on comparing open chain analogues with the above compounds or by conformational factors. The trend can, however, be interpreted qualitatively by perturbation theory which shows that more electronegative hetero groups decrease the extent of interaction between aryl-π and cyclopropane orbitals as well as cross ring conjugation.

Three-membered ring heterocycles, especially oxiranes and aziridinium salts, have significant practical importance as synthetic intermediates and in biological applications.[3] Long known for possessing a degree of unsaturated character,[4] three-membered rings have also received considerable theoretical attention due to the unusual electronic nature of the strained ring.[5] Recently, for example, various theoretical treatments[6] have concerned the apparent contradiction that three-membered rings stabilize a carbocation[7] but do not readily transmit charges.[8]

Table I. ^{13}C Chemical Shifts of Para-Substituted Ethylbenzenes and Propylbenzenes

para substituent	ethylbenzenes[a]		propylbenzenes[b]		
	C_α	C_β	C_α	C_β	C_γ
NH_2			37.26	24.98	13.79
OH			37.20	24.78	13.75
OCH_3	28.3	16.1	37.29	24.90	13.81
CH_3	28.8	15.9	37.78	24.78	13.86
H	29.3	15.8	38.21	24.66	13.85
Br	28.6	15.5	37.44	24.40	13.69
COOH			38.21	24.25	13.76
CHO			38.23	24.20	13.73
NO_2	29.2	15.1	37.93	24.11	13.68

[a] Data at 22.63 MHz with 3.6 M concentration in methylene chloride at ca. 45 °C. Shifts in ppm downfield from Me_4Si with uncertainty ±0.1 ppm. [b] Downfield shifts from internal Me_4Si in $CDCl_3$ at 1.8 M concentrations.

In a previous attempt to quantify conjugative effects of three-membered rings relative to vinyl and ethyl groups, ^{19}F NMR studies of *p*-fluoro-*p'*-substituted-1,2-diphenylcyclopropanes[9a] and 1,2-diphenylepoxides[9b] showed that cyclopropane and epoxide groups transmit conjugation 27 and 26% as well as vinyl. These values are lower than corresponding ones of 38 and 48% based on pK_a values in ethanol–water of *trans*-2-arylcyclopropanecarboxylic acids[10a] and *trans*-2,3-epoxy-3-arylpropionic acids[10b] relative to *trans*-cinnamic acids and 2-arylpropionic acids. However, the latter method was very sensitive to solvent, since in water the cyclopropane group showed *less* conjugative ability than a dimethylene group.[8a] No similar attempts have been made to quantify conjugative properties of aziridines or aziridinium salts,[11] probably because of synthetic and reactivity problems with these systems.

Continuing our synthetic and structural studies in three-membered ring heterocycles,[12] we were interested in carrying out a

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(2) (a) Georgetown University. (b) Naval Weapons Center.

(3) For a review of aziridinium salt chemistry, see: (a) Crist, D. R.; Leonard, N. J. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 962. (b) Crist, D. R.; Leonard, N. J. *Angew. Chem.* **1969**, *81*, 953.

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(11) See ref 8c for σ_R^0 values of cyclopropane, oxirane, aziridine, and oxaziridine groups interacting with a *p*-fluorophenyl group. However, in this study the conjugative character of a three-membered ring is obscured by an "internal inductive effect of the heteroatom".[8c]

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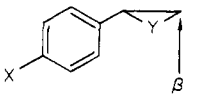
Table II. ^{13}C Chemical Shifts of Para-Substituted-Phenyl Three-Membered Ring Derivatives[a]

	cyclopropanes 1		aziridines 2		oxiranes 3		aziridinium salts 4[b]	
substituent	α	β	α	β	α	β	α	β
OCH_3	14.8	8.8	41.9	39.2	52.2	50.7		
CH_3	15.3	9.0	42.4	39.2	52.2	50.7	43.5	42.8
H	15.6	9.2	42.5	39.6	52.1	50.7	43.6	43.0
Br	15.1	9.3	41.6	39.6	51.7	50.9	43.6	43.1
NO_2	16.0	11.0	41.7	39.6	51.7	51.6	43.9	43.8

[a] Data at 22.63 MHz at 3.5 M concentration in methylene chloride at ca. 45 °C. Shifts in ppm downfield from internal Me_4Si with uncertainty ±0.1 ppm. [b] Concentration 3.0 M in acetone. Chemical shifts measured at ca. 10 °C in ppm downfield from acetone and converted to the Me_4Si scale using δ(acetone) = 30.4 ppm.

systematic study to determine how the nature of the hetero group affects the conjugative ability of three-membered rings with benzene. We now report our results on the series **1–4** which



1, Y = CH_2
2, Y = $\ddot{N}(CH_3)$
3, Y = $\ddot{O}$
4, Y = $N(CH_3)_2^+$

represent Y groups of different electron-withdrawing ability and different numbers of lone pairs.

The ^{13}C chemical shift sensitivity of the β position to X groups was taken as an estimate of the interactive ability of three-membered rings with benzene, with the β-carbon chemical shift of styrenes and ethylbenzenes serving as models for maximum and minimum interactions, respectively. The use of NMR as a probe of substituent effects is advantageous, since observed effects reflect the substituent's perturbation on the ground-state electronic distribution and polarizability rather than on that of a distorted species, a transition state, or an electronically excited state of molecule.[13]

By examining *differences* in δ among similar molecules with different substituents we are principally examining the perturbation of the electronic structure at the NMR sensitive nucleus caused by change of the remote substituent. The most important contribution to this perturbation in these systems is the transmission of π-electron distortion in the benzene ring to the Walsh orbitals of the three-membered ring.

Results

Sensitivity of β-Carbon Chemical Shifts to Para Substituents. The ^{13}C chemical shifts of β carbons of para-substituted styrenes[14] and ethylbenzenes listed in Table I and shown in Figure 1 gave slopes vs. σ of 6.5 ± 0.6 and −0.9 ± 0.1 ppm, respectively. The inverse substituent effect observed for ethylbenzenes was further investigated by determining ^{13}C chemical shifts of propylbenzenes (Table I). The α carbons, as might be expected from data on styrenes,[14] toluenes,[15] and phenylacetylenes,[16] showed only a very general correlation with more downfield shifts for more electron-withdrawing X (Figure 2a). The β carbons gave a similar result as ethylbenzenes with ρ = −0.69 ± 0.07 ppm (Figure 2b), while the γ carbon showed a near-zero (or possibly slight inverse) substituent effect of −0.09 ± 0.1 (Figure 2c). Data on various three-membered ring derivatives (Table II) gave slopes which were all positive as can be seen in Figure 3, with values of 2.0 ± 0.2,

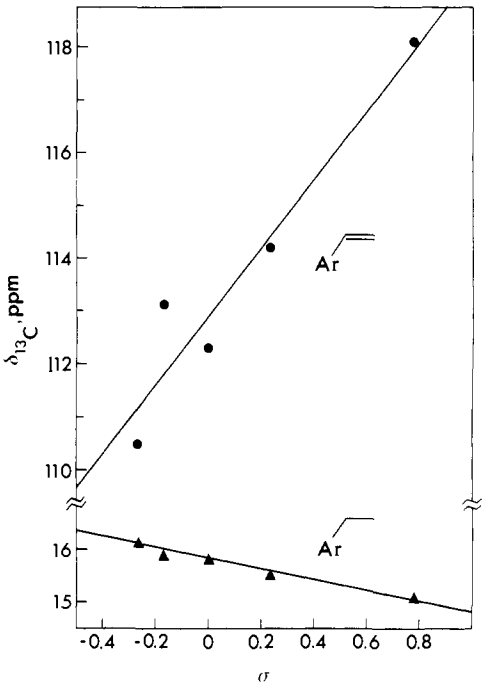


Figure 1. Substituent effects on ^{13}C chemical shifts of β carbons of para-substituted styrenes[14] (●) and ethylbenzenes (▲).

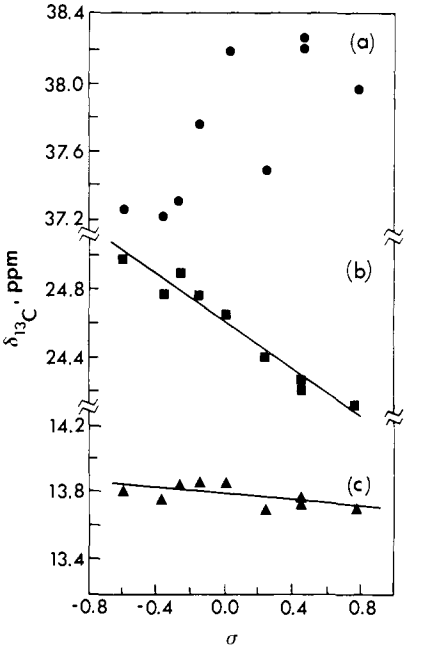


Figure 2. Substituent effects on ^{13}C chemical shifts of para-substituted propylbenzenes: (a) α carbons, (b) β carbons, (c) γ carbons.

(13) Although excited electronic states are important in calculations of chemical shifts, their use arises from the theoretical method of representing perturbed ground-state functions as mixtures of ground- and excited-state functions. The electrons in a molecule are polarized by the magnetic field but not excited to an excited electronic state by it (Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803. Pople, J. A. *Ibid.* **1962**, *37*, 53. Memory, J. D. "Quantum Theory of Magnetic Resonance Parameters"; McGraw Hill: New York, 1968; Chapters 5 and 6).

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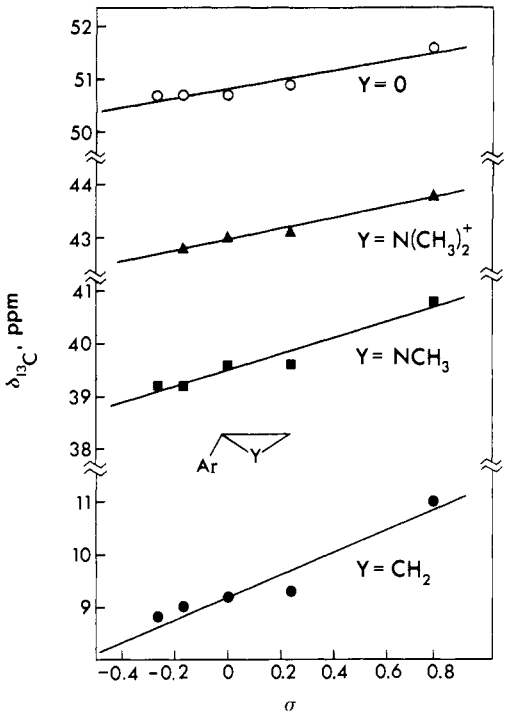


Figure 3. Substituent effects on ^{13}C chemical shifts of β carbons of three-membered ring derivatives: phenyloxirane (○), 2-aryl-1,1-dimethylaziridinium fluorosulfonates (▲), 2-aryl-1-methylaziridines (■), arylcyclopropanes (●).

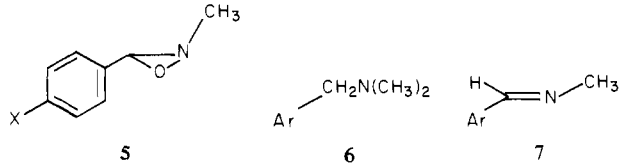
Table III. ^{15}N Chemical Shifts of Para-Substituted-Phenyl Derivatives[a]

substituent	benzylamines 6	benzylimines 7	oxaziridines 5[b] cis	oxaziridines 5[b] trans
$(CH_3)_2N$	−356.9	−77.9		
CH_3O	−356.5	−69.1	−227.9	−232.9
CH_3	−357.8	−64.7	−229.2	−233.3
H	−357.3	−61.2	−228.7	−232.2
Br	−358.2	−58.6	−228.2	−231.7
NO_2	−358.7	−45.4	−227.8	−231.0

[a] Values in ppm upfield from nitromethane and considered accurate to ±0.1 ppm. [b] Assignments based on relative intensities of ^{15}N signals and the isomer ratio as determined by ^1H NMR (see Experimental Section).

1.5 ± 0.2, 0.9 ± 0.1, and 1.0 ± 0.1 for **1**, **2**, **3**, and **4**, respectively.

Similar behavior was found for the ^{15}N chemical shifts (Table III) of *trans*-2-methyl-3-phenyloxaziridines **5** which showed a slope of 2.1 ± 0.4 ppm (Figure 4) intermediate to those for benzylamines **6** (ρ = −1.3 ± 0.4 ppm) and benzylimines **7** (20.2 ± 1.1 ppm).



5 **6** **7**

Data for cis isomers of **5** showed more scatter, with the *p*-OCH_3 derivative well off a line of other derivatives having a slope of 1.4 ± 0.3 ppm.

Effect of Ring Closure. To provide information on hybridization changes as well as other electronic effects, the ^{13}C shift of α carbons of phenyl-substituted, three-membered ring compounds was compared with open-chain analogues. As shown in Table IV this shift was more upfield for all three-membered rings with the aziridinium salt experiencing the largest $\Delta\delta$ value.

Preliminary UV studies also suggested more delocalized character to three-membered rings, with long-wavelength maxima[17a] in methylene chloride for *N*-methyl-2-phenylaziridine,

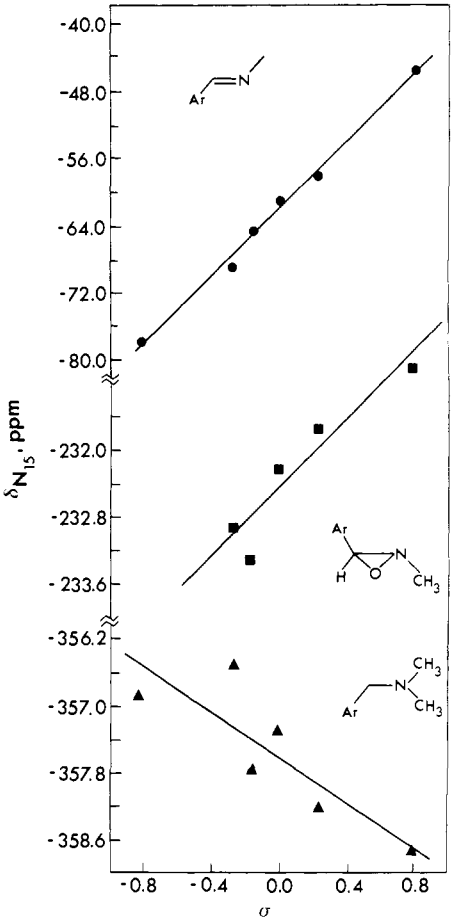
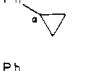
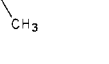
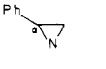
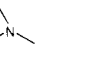
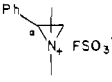
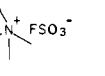
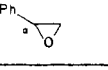
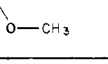


Figure 4. Substituent effects on the ^{15}N chemical shifts of para-substituted phenyl derivatives: *N*-methylbenzylimines (●), *trans*-2-methyl-3-aryloxaziridines (■), *N*,*N*-dimethylbenzylamines (▲).

Table IV. ^{13}C Chemical Shifts of Ring Carbons of 2-Aryl Three-Membered Rings and Model Compounds[a]

three-membered-ring compounds: compound	δ_α, ppm	model compounds: compound	δ_α, ppm	$\Delta\delta_\alpha$[b]
	15.6		38.2	22.9
	42.5		64.6	22.1
	43.6		69.3	25.7
	52.1		74.8	22.7

[a] Spectra recorded at 22.63 MHz at ca. 45 °C with uncertainty of ±0.1 ppm from internal Me_4Si. [b] δ of C_α of three-membered ring − δ of C_α of model compound.

phenylcyclopropane,[17b] and *N*,*N*-dimethyl-2-phenylaziridinium fluorosulfonate at 272, 271, and 270 nm compared to values for dimethylbenzylamine, isopropylbenzene,[17b] and trimethylbenzylammonium fluorosulfonate at 268, 268, and 269 nm, respectively. However, direct correlations from these data cannot be made, since only N → V transitions seem to be characteristic of extended conjugation,[17c] and the nature of excited electronic

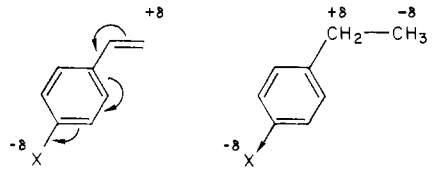
(17) (a) The most intense of the long-wavelength absorption bands was used for this comparison. (b) Data from ref 4b in cyclohexane. (c) see ref 4b where the long-wavelength maximum for methyl isopropyl ketone was at *longer* wavelength than that for methyl cyclopropyl ketone.

states will greatly affect the position of absorbance.

Discussion

Hybridization of Three-Membered Rings. Hybridization differences do not seem important in comparing 2-phenyl-substituted three-membered ring compounds. This is suggested by similar upfield shifts of the α carbon when a ring is formed from an open-chain model (Table IV). These $\Delta\delta$ values for cyclization to form phenyl-substituted cyclopropane, aziridine, and oxirane were 22.9, 22.1, and 22.7 ppm, respectively, with the value for forming an aziridinium salt, 25.7 ppm, somewhat higher. Although the similarity of values could conceivably be caused by cancellation of opposite effects, and granted that the $\Delta\delta$ value includes factors other than hybridization, the similarity of $\Delta\delta$ values certainly is suggestive of similar hybridization.

Conjugative Ability. In an empirical approach, it seems reasonable to consider para-substituted styrenes and ethylbenzenes as models for "100% conjugation" and "0% conjugation" of a β carbon with the benzene ring, respectively. As reported by Stothers,[14] the β carbon of styrene moves progressively downfield with electron-withdrawing groups because of expected resonance effects (**8**).



8 **9**

The inverse substituent effect for β carbons of ethylbenzenes, previously noted by others,[18] possibly represents a buildup of negative charge at the β carbon (see **9**), although one must be cautious in attributing ^{13}C chemical shift changes entirely to ground-state electron density changes.[7e,18a,19] Such charge alternation[20] along a carbon skeleton by inductive effects was favored as early at 1935 by Arndt and Eistert.[21] After Pople and Gordon[22] established this theory on an MO basis, it has received several applications in recent work.[18,23] A problem with this interpretation is that the γ carbon of propylbenzenes tended to suggest also a negative charge buildup (see Figure 2)[24a], although the slope was too small to be measured accurately (ρ = −0.09 ± 0.1 ppm). Conformation factors may be responsible for this inverse substituent effect as suggested from data on 2,2-dichlorocyclopropylbenzenes in which the CH_2 carbon (postulated to be nearly in the plane of the benzene ring) showed a normal substituent effect, while the CCl_2 carbon (nearly perpendicular to the benzene ring) showed an inverse effect.[18a] However, other factors are more important for the cyclopropyl system as shown by data on 5-substituted indans.[24b] Although more theoretical work on ^{13}C chemical shift dependence is necessary, it seems useful at the present time to take an inverse substituent effect at the β atom as characteristic of a saturated atom.

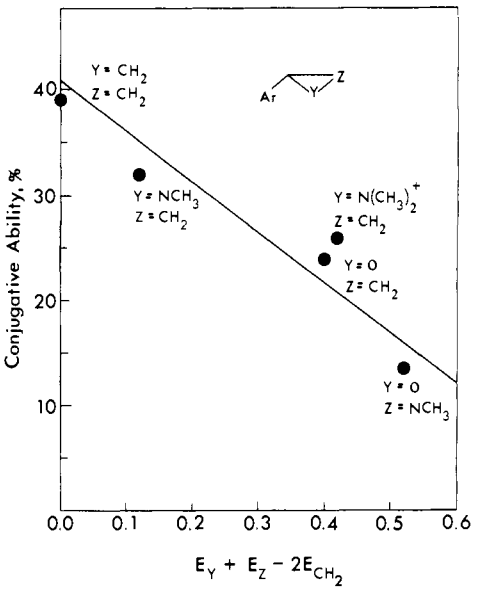


Figure 5. Conjugative ability as a function of electronegativity of ring hetero group. Following R. Radeglia (*Spectrochim. Acta, Part A* **1967**, *23*, 1677), the electronegativity effect of ring members Y and Z are normalized with respect to CH_2 and generalized to three-membered rings with two heteroatoms Y and Z by the function $E_Y + E_Z - 2E_C$. Group electronegativities of J. E. Huheey (*J. Phys. Chem.* **1965**, *69*, 3284) are used with E_Y values (Pauling scale) for ethyl, dimethylamino, methoxy, and trimethylammonium groups representing **1**, **2**, **3**, and **4**, respectively (E_Z that of ethyl), and E_Y and E_Z values for methoxy and dimethylamino representing oxaziridines.

The positive slopes for the substituent effect for all three-membered rings studied (Figures 3 and 4) show clearly that three-membered rings behave more like unsaturated compounds than saturated ones with respect to the chemical shift of the β atom. Since the main process by which the β atom is affected by a para substituent must involve an interaction between the benzene ring and the three-membered ring, it is tempting to take these slopes as a measure of the conjugative ability of the various three-membered rings. With this approach, the unsaturated model compounds of styrenes and imines vs. the ethylbenzenes and benzylamines could represent "100% vs. 0% conjugation". Relative slopes then show that "conjugative ability" decreases from cyclopropane, aziridine, aziridinium ion, to oxirane with values of 39, 32, 26, and 24%, respectively. Oxaziridine has a considerably lower conjugative ability of 16% in line with the added electronegativity effects of two heteroatoms (see below).

The present results for cyclopropane and oxirane cover a larger range (39 to 24%) compared to that derived from ^{19}F NMR data (27 to 26%).[9] Values for conjugative ability will obviously differ depending on the definition and criteria used and on the experimental method taken. The present **1–4** series, however, is the most extensive one studied in a systematic manner.

One explanation for the order of conjugative ability is that hybridization changes are responsible. However, this is unlikely owing to the nearly identical $\Delta\delta$ values on ring closure for cyclopropane, aziridine, and oxirane compounds. The somewhat larger $\Delta\delta$ value for the aziridinium salt would if anything suggest *more* three-ring character than for cyclopropane, but the aziridinium salt showed less unsaturated character from its substituent effect. Another explanation is that conformational factors are important, either by allowing different degrees of overlap of the π system with Walsh orbitals of the cyclopropyl groups or by varying the angle between the β carbon and the plane of the benzene ring. However, CNDO/2 calculations have shown that cyclopropylbenzene and *trans*-2-phenylaziridine have the same preferred conformation.[25] Similar MINDO/2 calculations for

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(19) (a) For review, see: Maciel, G. E. In "Topics in Carbon-13 NMR Spectroscopy"; Levy, G. C., Ed.; Wiley: New York, 1974; Vol. I, pp 53–77. (b) Günther, H.; Prestien, J.; Joseph-Nathan, P. *Org. Magn. Reson.* **1975**, 7, 339, and references therein.

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(24) (a) Direct application of the hyperconjugative γ effect will not explain this result, since we are not dealing with a lone-pair atom on the α carbon. (b) Unpublished work.

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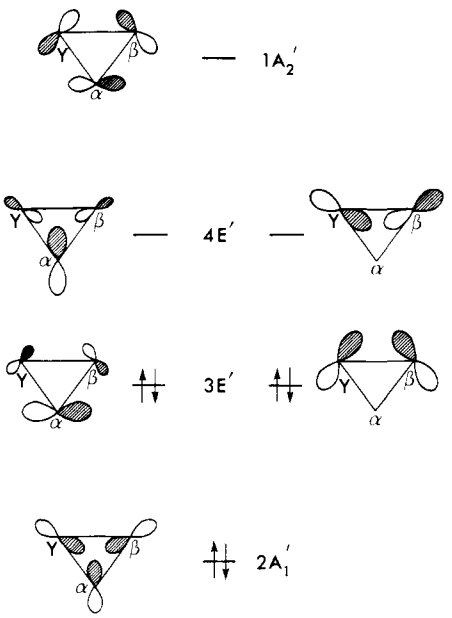

Figure 6. Orbital diagram of the Walsh orbitals in three-membered ring systems.[5d]

aziridinium salts support this conclusion.[26] Also, there does not appear to be a significant substituent effect on phenyl rotation for phenylcyclopropane and phenyloxirane, since curves of ΔH_f (calculated by MINDO/2) vs. phenyl rotation angle for *p*-nitro-substituted derivatives were virtually superimposable with those of unsubstituted compounds.[26]

The best explanation for the order of conjugative ability at this time appears to be the importance of the electronegativity of the three-membered ring group Y. That the relatively small differences in slopes for **1**, **2**, **3**, and **4** follow a definite trend with electronegativity of hetero groups(s), especially when oxaziridine data are included, can be clearly seen in Figure 5. This result contrasts with the effect of Y on coupling constant behavior,[12d] where the lone-pair characteristics of Y predominated over electronegativity effects.

The following perturbation argument can be used to explain the observed trends in conjugative ability. Insertion of a heteroatom in place of a carbon at Y (see Figure 6) will alter the transmission of substituent effects from the π system of an aryl group at the α position to the β carbon by perturbing the orbitals which result from mixture of the aryl π orbitals and the 3E' and 4E' orbitals on cyclopropyl. A heteroatom more electronegative than carbon will increase the atomic orbital contribution at position Y while decreasing the contributions at α and β. This alteration will decrease the amount of interaction between the cyclopropyl orbital and the aryl π system as well as decrease the transmission of substituent effects from α to β. Electropositive element insertion will have the opposite effect. This argument agrees with the order of group electronegativities O $\approx$ N^+ > N > C and conjugative abilities 39% (C) > 32% (N) > 26% (N^+) $\approx$ 24% (O) $\gg$ 16% (N *and* O in the oxaziridine ring).

Another approach is simply to observe that transmission of substituent effects is through electron density at C_α and C_β. Electronegative groups relative to carbon lower this electron density and hence reduce conjugative ability. The perturbation argument, however, shows how this can occur.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Varian Associates A-60 spectrometer or, if so noted, at 90 MHz on a Bruker HFX-90. Proton spectra on propylbenzenes were obtained on a Varian EM-360 spectrometer. Reagent grade solvents, with tetramethylsilane (Me_4Si) as an internal standard were used unless otherwise noted. IR spectra were recorded on a Perkin-Elmer Model 337 or 457 spectrometer. All melting points were determined on a Gallenkamp apparatus in sealed capillaries and were uncorrected. Boiling points were also uncorrected. MINDO/2 calculations were carried out at the Georgetown University Academic Computation Center on an IBM 360/40 computer.

Materials. Model Compounds. A. Open-Chain Analogues. *N,N,N*-Trimethylbenzylammonium fluorosulfonate was prepared by adding 2 g (0.02 mol) of *N,N*-dimethylbenzylamine to 10 g (0.090 mol) of methyl fluorosulfonate in 50 mL of dry ether at −70 °C. The resulting white solid was collected by filtration, washed with dry ether, and dried in vacuo giving 3.2 g (87%), mp 85–87 °C: IR (KBr) ν_{max} 3050 (w), 3005 (m), 2975 (w), 1500 (m), 1460 (m), 1300 (br, s), 1070 (s), 730 (s), 580 (s) cm^{-1}; NMR (D_2O) δ 3.10 [s, $N^+(CH_3)_3$, 9 H], 4.70 (s, $PhCH_2N^+$, 2 H), 7.65 (s, Ar-H, 5 H).

Benzyl methyl ether was prepared by reaction of sodium methoxide with benzyl chloride[27] in 85% yield, bp 60 °C (12 torr) (lit.[28] 59–60 °C (12 torr)).

B. Ethylbenzenes. 4-Ethylanisole was prepared by Wolff–Kishner reduction of *p*-methoxyacetophenone[29] in 59% yield, bp 83–84 °C (16 torr) (lit.[30] 83–84 °C (16 torr)).

C. Propylbenzenes. *p*-Nitro-*n*-propylbenzene was prepared by nitration of *n*-propylbenzene. To a mixture of concentrated sulfuric acid (66.6 mL), water (16.6 mL), and concentrated nitric acid (37.3 mL) at 0 °C was added *n*-propylbenzene (25 g, 0.21 mol). After stirring for 45 min the organic portion was removed and fractionated at 20 torr. The fraction (8 g) boiling at 145–148 °C was dissolved in ether and dried with $MgSO_4$. The ether was removed in vacuo and the residue redistilled through a 9-in. Vigreux column. The portion boiling at 147–148 °C (20 torr) (lit.[31] 154 °C (20 torr)) was saved (4 g, 11%) and the *p*-nitro-*n*-propylbenzene separated from the mixture of isomers by preparative gas chromatography: NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 8 Hz), 1.65 (m, 2 H), 2.79 (t, 2 H, J = 8 Hz), 7.33 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 8.16 ($H_{BB'}$, 2H).

p-Bromo-*n*-propylbenzene was prepared by bromination of *n*-propylbenzene. To *n*-propylbenzene (10 g, 0.08 mol) and iron filings (5 g) was added bromine (13.3 g, 0.08 mol). The mixture was stirred at room temperature overnight. Ether was added to the reaction mixture and the mixture filtered. The ether solution was washed with water and 5% aqueous $NaHCO_3$ and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was distilled through a 9-in. Vigruex column and the fraction (5 g, 30%) boiling at 109.5–111.0 °C (21 torr) (lit.[32] 225.0 °C) was collected. The para isomer was separated from the ortho isomer (ca. 10% of total) by preparative gas chromatography: NMR ($CDCl_3$) δ 1.90 (t, 3 H, J = 7 Hz), 1.58 (m, 2 H), 2.57 (t, 2 H, J = 7 Hz), 7.10 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.48 ($H_{BB'}$, 2 H).

n-Propyltoluene was prepared by Wolff–Kishner reduction of *p*-methylpropiophenone[29] in 18% yield, bp 179 °C (lit.[33] 183 °C).

D. Amines (6). *N,N*-Dimethyl-*p*-dimethylaminobenzylamine was prepared from *p*-dimethylaminobenzaldehyde[34] (29.8 g, 0.2 mol) by reductive amination with 25% aqueous dimethylamine (120 g, 0.67 mol) and 10% palladium on carbon (4 g) in a Parr hydrogen apparatus. When 1 equiv of hydrogen was absorbed, excess dimethylamine was removed in vacuo and the aqueous residue was extracted with ether which was dried with potassium carbonate. After removal of the solvent in vacuo, distillation through a 6-in. Vigreux column gave 21.5 g (60%) of *N,N*-dimethyl-*p*-dimethylaminobenzylamine, bp 67 °C (0.2 torr): IR (neat) ν_{max} 2990 (m), 2890 (m), 2810 (m), 2800 (m), 1620 (s), 1530 (s), 1460 (s), 1355 (s), 1170 (s), 1030 (s), 950 (m), 810 (s); NMR ($CDCl_3$) δ 2.15 (s, 6 H), 2.80 (s, 6 H), 3.28 (s, 2 H), 6.61 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.15 ($H_{BB'}$, 2 H).

N,N-Dimethyl-*p*-methoxybenzylamine was prepared from *p*-methoxybenzaldehyde as described above in 66% yield, bp 57 °C (0.2 torr): NMR ($CDCl_3$) δ 2.06 (s, 6 H), 2.15 (s, 3 H), 3.28 (s, 2 H), 6.95 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.20 ($H_{BB'}$, 2 H).

N,N-Dimethyl-*p*-methylbenzylamine was prepared from *p*-methylbenzyl bromide. To 40% aqueous dimethylamine (350 g, 3.1 mL) was added *p*-methylbenzyl bromide (25 g, 0.12 mol) in 75 mL of absolute ethanol. The mixture was stirred for 1 h and heated on a steam bath for 30 min. After the excess dimethylamine was removed in vacuo, the residue was extracted, washed with water, and dried with magnesium sulfate. The ether was removed in vacuo and the residue was distilled

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through a 6-in. Vigreux column to give 12.5 g (70%) of *N,N*-dimethyl-*p*-methylbenzylamine, bp 64 °C (8 torr): IR (neat) ν_{max} 2960 (m), 2890 (m), 2800 (m), 2770 (m), 1610 (w), 1510 (m), 1450 (s), 1360 (m), 1255 (m), 1180 (m), 1040 (s), 860 (s), 805 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.26 (s, 6 H), 2.36 (s, 3 H), 3.40 (s, 2 H), 7.28 (s, 4 H).

N,N-Dimethyl-*p*-bromobenzylamine was prepared from *p*-bromobenzyl bromide as previously described in 70% yield, bp 51 °C (0.2 torr): IR (neat) ν_{max} 2900 (m), 2800 (m), 2760 (m), 2740 (m), 1590 (w), 1475 (m), 1450 (m), 1395 (w), 1350 (w), 1065 (m), 1030 (m), 1005 (s), 855 (s), 800 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.12 (s, 6 H), 3.30 (s, 2 H), 7.23 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.48 ($H_{BB'}$, 2 H).

N,N-Dimethyl-*p*-nitrobenzylamine was prepared from *p*-nitrobenzyl bromide as previously described in 83% yield, bp 78 °C (0.2 torr): IR (neat) ν_{max} 2930 (m), 2800 (m), 2760 (m), 1600 (m), 1520 (s), 1450 (m), 1340 (s), 1260 (w), 1110 (m), 1040 (m), 865 (s), 840 (m), 810 (m), 745 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.25 (s, 6 H), 3.60 (s, 2 H), 7.62 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 8.25 ($H_{BB'}$, 2 H).

E. Imines (7). *N*-Benzylidenemethylamine was prepared from benzaldehyde[35] by adding 50 g (0.47 mol) to 77 g (1.0 mol) of 40% aqueous methylamine. After 30 min, potassium hydroxide pellets were added and the aqueous layer which separated was discarded. The organic layer was distilled through a 6-in. Vigreux column from fresh potassium hydroxide to give 16 g (30%) of *N*-benzylidenemethylamine, bp 64 °C (9 torr) (lit.[36] 69 °C (10 torr)): IR (neat) ν_{max} 3060 (w), 3040 (w), 2960 (w), 2900 (m), 2860 (m), 2790 (w), 1650 (s), 1580 (w), 1450 (s), 1410 (w), 1000 (m), 755 (s), 700 (s) cm^{-1}; NMR ($CDCl_3$) δ 3.50 (d, 3 H, J = 2 Hz), 7.64 (m, 3 H), 7.80 (m, 2 H), 8.42 (q, 1 H, J = 2 Hz).

N-(*p*-Methoxybenzylidene)methylamine was prepared from *p*-methoxybenzaldehyde as described above in 76% yield, bp 86 °C (2 torr): IR (neat) ν_{max} 3020 (w), 2950 (m), 2890 (m), 2850 (m), 1650 (m), 1620 (s), 1580 (m), 1520 (s), 1310 (s), 1250 (s), 1170 (s), 1025 (s), 835 (s) cm^{-1}; NMR ($CDCl_3$) δ 3.56 (d, 3 H, J = 2 Hz), 3.85 (s, 3 H), 6.97 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.75 ($H_{BB'}$, 2 H), 8.32 (q, 1 H, J = 2 Hz).

N-(*p*-Bromobenzylidene)methylamine was prepared from *p*-bromobenzaldehyde as previously described in 54% yield, bp 65 °C (0.15 torr): IR (neat) ν_{max} 3030 (w), 2940 (m), 2870 (m), 2840 (m), 1650 (s), 1590 (s), 1490 (m), 1460 (m), 1405 (m), 1300 (w), 1070 (s), 1005 (s), 860 (s), 820 (vs) cm^{-1}; NMR ($CDCl_3$) δ 3.50 (d, 3 H, J = 2 Hz), 7.68 (s, 4 H), 8.31 (q, 1 H, J = 2 Hz).

N-(*p*-Methylbenzylidene)methylamine was prepared from *p*-methylbenzaldehyde as described above in 75% yield, bp 50 °C (1 torr): IR (neat) ν_{max} 3020 (m), 2920 (m), 2870 (m), 2810 (m), 1650 (s), 1510 (m), 1450 (m), 1405 (m), 1180 (m), 1010 (s), 815 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.55 (d, 3 H, J = 2 Hz), 7.30 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.70 ($H_{BB'}$, 2 H), 8.32 (q, 1 H, J = 2 Hz).

N-(*p*-Nitrobenzylidene)methylamine was prepared from *p*-nitrobenzaldehyde[37] by adding 40 g (0.26 mol) to 400 g (3.7 mol) of 40% aqueous methylamine. The mixture was heated on a steam bath and crystals appeared after 30 min. Water (400 mL) was added to the mixture and the solid removed by filtration. The product was recrystallized from hexane to give 36 g (84%) of *N*-(*p*-nitrobenzylidene)methylamine, mp 106–108 °C: IR (KBr) ν_{max} 3100 (w), 2950 (w), 2890 (w), 2850 (w), 1650 (m), 1600 (m), 1520 (s), 1340 (s), 1280 (m), 1110 (m), 1000 (m), 853 (s), 835 (s), 745 (s) cm^{-1}; NMR ($CDCl_3$) δ 3.55 (d, 3 H, J = 2 Hz), 7.91 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 8.1 ($H_{BB'}$, 2 H), 8.35 (q, 1 H, J = 2 Hz).

N-(*p*-Dimethylaminobenzylidene)methylamine was prepared from *p*-methylaminobenzaldehyde as described above in 95% yield, mp 58–60 °C: IR (KBr) ν_{max} 2950 (w), 2850 (w), 1650 (m), 1610 (s), 1525 (m), 1370 (m), 1180 (m), 1000 (m), 815 (m) cm^{-1}; NMR ($CDCl_3$) δ 2.95 (s, 6 H), 3.40 (d, 3 H, J = 2 Hz), 6.70 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.65 ($H_{BB'}$, 2 H), 8.20 (br, s, 1 H).

Three-Membered Ring Compounds. A. Cyclopropanes (1). Phenylcyclopropane was prepared from cinnamaldehyde and hydrazine[38] in 13% yield, bp 171–173 °C (lit.[38] 172–174 °C). *p*-Bromophenylcyclopropane was prepared by bromination of phenylcyclopropane at −70 °C[39] in 66% yield, bp 107 °C (11 torr) (lit.[39] 116 °C (15 torr)). *p*-Methoxyphenylcyclopropane was prepared by reaction of *p*-methoxystyrene with diethylzinc and methylene iodide[40] in 54% yield, bp 96–97 °C (8 torr) (lit.[41] 223.5–224.0 (745 torr)). *p*-Methylphenylcyclopropane was prepared in a similar way[40] from *p*-methylstyrene in 36% yield, bp 194–195 °C (lit.[41] 194–194.5 °C).

p-Nitrophenylcyclopropane was prepared by nitration of phenylcyclopropane at −40 °C[33] giving a 46% yield of a mixture of *o*- and *p*-nitro isomers with bp 103–105 °C (4 torr) (lit.[33] 106 °C (5 torr)): IR (neat) ν_{max} 3090 (w), 1610 (m), 1525 (s), 1350 (s), 1030 (m), 850 (m), 780 (m), 745 (m) cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.5–1.2 (m, PhC$\overline{H-CH_2-CH_2}$, 4 H), 1.79 (m, *p*-NO_2-PhC$\overline{H-CH_2-CH_2}$, 0.2 H), 2.38 (m, *o*-NO_2- PhC$\overline{H-CH_2-CH_2}$, 0.8 H), 7.0–8.2 (m, Ar-H, 4 H). The mixture was considered to be 1:4 ratio of *p*- to *o*-nitrophenylcyclopropane by assuming that the upfield multiplet at 1.79 ppm is due to the protons in the para isomer while the more downfield one at 2.38 is due to the protons in the ortho isomer. Support for this assignment is found in ^{13}C spectra which showed six resonances in the aromatic region for the major isomer with the intensity of 1-C each: $\delta_{C\text{-}13}$ (16 scans) 124.2, 126.7, 127.9, 132.9, 138.1, and 151.5. The chemical shifts are in agreement with predictions using ^{13}C chemical shift additivity rules[42] assuming ortho substitution. The aromatic region of the minor isomer consists of four resonances with the following chemical shifts and ratios: $\delta_{C\text{-}13}$ 125.6 (1 C), 128.4 (1 C), 126.0 (2 C), 144.2 (1 C), in agreement with para substitution.

B. Aziridines (2). 1-Methyl-2-phenylaziridine and its 4′-methoxy, 4′-methyl, and 4′-bromo derivatives were prepared as previously reported.[12a]

The *p*-nitro derivative[43a] was made from an *N*-methyl-2-hydroxy-2-(4′-nitrophenyl)ethylamine precursor. 4′-Nitrophenyloxirane (63 g, 0.38 mol) and 100 g of 40% aqueous methylamine (1.25 mol) were refluxed until no more solid oxirane was present (ca. 30 min) in a flask equipped with a Dewar condenser containing dry ice. Excess methylamine and water were removed in vacuo and the residue was dissolved in hot methylene chloride. On cooling to 0 °C, the product crystallized out of solution and was recrystallized from methylene chloride to yield 61 g (82%) of *N*-methyl-2-hydroxy-2-(4′-nitrophenyl)ethylamine as a yellow solid, mp 95–98 °C: IR (KBr) ν_{max} 3300 (s), 3200–2600 (br), 1600 (m), 1525 (s), 1445 (m), 1350 (s), 1078 (m), 855 (s), 785 (s), 750 (s), 715 (s) cm^{-1}; NMR (Me_2SO-d_6) δ 2.28 (s, NCH_3, 3 H), 2.60 (d, PhC(OH)HCH_2NHCH_3, 2 H, J = 12 Hz), 3.67 (br s, PhC(O*H*)HCH_2N*H*CH_3, 2 H), 4.80 (t, PhC(OH)*H*CH_2NHCH_3, 1 H, J = 12 Hz), 7.64 ($H_{AA'}$ of AA'BB' pattern, Ar-H, 2 H, $J_{A'B'}$ = 8.0 Hz), 8.16 ($H_{BB'}$, Ar-H, 2 H). This hydroxy amine was converted to the corresponding bromo amine and cyclized to the aziridine by the method of Okado, Inchimura, and Sudo[43b] in 11% yield, bp 77 °C (0.01 torr): IR (neat) ν_{max} 3110 (w), 3050 (w), 2980 (m), 2960 (m), 2905 (w), 2860 (m), 2795 (w), 1605 (s), 1520 (s), 1350 (s), 1110 (m), 1070 (m), 1015 (m), 860 (s), 745 (s) cm^{-1}; NMR (CCl_4, 90 MHz) δ 1.67 (H_A of ABX pattern, PhC$\overline{H-CH_2}$–N (cis to phenyl), 1 H, J_{AB} = 1.5 Hz), 1.74 ($H_{B'}$, PhC$\overline{H-CH_2}$–N (trans to phenyl, 1 H), 2.30 (H_X, PhC$\overline{H-CH_2}$–N, 1 H, J_{AX} = 6.4 Hz, J_{BX} = 2.9 Hz), 2.45 (s, N-CH_3, 3 H), 7.31 ($H_{AA'}$ of AA'BB' pattern, Ar-H, 2 H, $J_{A'B'}$ = 8.9 Hz), 8.03 ($H_{BB'}$, Ar-H, 2 H).

C. Oxiranes (3). Phenyloxiranes containing *p*-methyl, *p*-methoxy, and *p*-bromo groups were prepared as previously reported.[12a] 4′-Nitrophenyloxirane was prepared by sodium borohydride reduction of 2-bromo-4′-nitroacetophenone and ring closure[44] in 92% yield, mp 80–81 °C (lit.[45] 84.2–85.4 °C).

D. Aziridinium Salts (4). 1,1-Dimethyl-2-phenylaziridinium fluorosulfonate and its *p*-methyl and *p*-bromo derivatives were made as previously reported. The *p*-nitro derivative was made from the corresponding aziridine in a similar way in 92% yield giving an oil which crystallized on trituration with ether. The white solid had mp 71–72 °C: IR (KBr) ν_{max} 3110 (w), 3040 (s), 3000–2800 (w), 1610 (m), 1520 (m), 1350 (s), 1300 (br, s), 1075 (m), 860 (m), 740 (s), 580 (s) cm^{-1}; NMR (D_2O) δ 2.55 (s, NCH_3 (cis to phenyl), 3 H), 3.15 (s, NCH_3 (trans to phenyl), 3 H), 3.62 (H_A of ABX pattern, $-\overline{CH-CH_2}-N^+$ (trans to phenyl), 1 H, J_{AB} = 5 Hz), 3.78 (H_B, PhC$\overline{H-CH_2}-N^+$ (cis to phenyl, 1 H), 4.75 (H_X, PhC$\overline{H-CH_2}-N^+$, 1 H, J_{AX} = 8 Hz, J_{BX} = 9 Hz), 7.88 ($H_{AA'}$ of AA'BB' pattern, Ar-H, 2 H, $J_{A'B'}$ = 9 Hz), 8.37 ($H_{BB'}$, Ar-H, 2 H).

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E. Oxaziridines (5). 2-Methyl-3-phenyloxaziridine was prepared from *N*-benzylidenemethylamine,[46] by adding to 14.6 g (0.12 mol) in 100 mL of CH_2Cl_2 dropwise a solution of *m*-chloroperoxybenzoic acid (25 g, 0.125 mol) in 250 mL of CH_2Cl_2. After addition was complete, the solid *m*-chlorobenzoic acid was removed by filtration. The reaction mixture was washed with 5% aqueous sodium sulfite and then 5% aqueous sodium carbonate and dried with anhydrous sodium carbonate. Removal of the solvent in vacuo and distillation through a 6-in. Vigreux column gave 10.6 g (65%) of 2-methyl-3-phenyloxaziridine, bp 44 °C (0.05 torr) (lit.[46] 45 °C (0.07 torr): IR (neat) ν_{max} 3050 (w), 2950 (m), 2910 (w), 1710 (w), 1600 (w), 1500 (w), 1460 (m), 1410 (s), 1390 (s), 1180 (w), 1000 (w), 850 (s), 760 (s), 700 (s) cm^{-1}, NMR ($CDCl_3$) δ 2.54 (s, 0.9 H), 2.98 (s, 2.1 H), 4.51 (s, 0.7 H), 5.3 (s, 0.3 H), 7.43 (s, 5 H); 30:70 ratio of cis to trans oxaziridine.[47]

2-Methyl-3-(*p*-methylphenyl)oxaziridine was prepared from *N*-(*p*-methylbenzylidene)methylamine as described above in 67% yield, bp 51 °C (0.4 torr) (lit.[48] 50 °C (0.5 torr)): IR (neat) ν_{max} 3000 (w), 2930 (m), 2900 (m), 1710 (vw), 1620 (m), 1520 (m), 1440 (s), 1380 (s), 1305 (s), 1180 (m), 1105 (m), 860 (m), 810 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.25 (s, 3 H), 2.33 (s, 0.9 H), 2.78 (s, 2.1 H), 4.36 (s, 0.7 H) 5.15 (s, 0.3 H), 7.10 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.30 ($H_{BB'}$, 2 H); 30:70 ratio of cis to trans oxaziridine.

2-Methyl-3-(*p*-methoxyphenyl)oxaziridine was prepared from *N*-(*p*-methoxybenzylidene)methylamine as described above in 47% yield, bp 35 °C (4×10^{-5} torr) (lit.[49] 80–110 °C (0.3 torr)): IR (neat) ν_{max} 2900 (m), 2800 (m), 1700 (w), 1610 (s), 1515 (s), 1390 (m), 1310 (s), 1260 (s), 1175 (m), 1040 (s), 860 (m), 830 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.43 (s, 0.75 H), 2.90 (s, 2.25 H), 4.47 (s, 0.75 H), 5.28 (s, 0.25 H), 6.95 ($H_{AA'}$ of AA'BB' pattern, 2 H, $J_{A'B'}$ = 8 Hz), 7.43 ($H_{BB'}$, 2 H); 25:75 ratio of cis to trans oxaziridine.

2-Methyl-3-(*p*-nitrophenyl)oxaziridine was prepared from *N*-(*p*-nitrobenzylidene)methylamine as described above to give a solid which was recrystallized from pentane in 61% yield 64–74 °C (lit.[36] 64.6 °C): IR (KBr) ν_{max} 3100 (w), 2990 (w), 2910 (w), 2850 (w), 1710 (vw), 1650 (w), 1600 (m), 1510 (s), 1340 (s), 1310 (m), 1110 (m), 830 (s), 750 (m) cm^{-1}; NMR ($CDCl_3$) δ 2.48 (s, 1.5 H), 2.96 (s, 1.5 H), 4.68 (s, 0.5 H), 5.38 (s, 0.5 H), 7.70 (m, 2 H), 8.39 (m, 2 H); 50:50 ratio of cis to trans oxaziridine.

2-Methyl-3-(*p*-bromophenyl)oxaziridine was prepared from *N*-(*p*-bromobenzylidene)methylamine as described above in 80% yield, mp 30–45 °C: (neat) ν_{max} 3000 (m), 2960 (m), 1710 (vw), 1600 (m), 1490 (m), 1440 (m), 1375 (m), 1305 (m), 1070 (m), 1020 (m), 850 (s), 810 (s), cm^{-1}; NMR ($CDCl_3$) δ 2.47 (s, 1.95 H), 2.92 (s, 1.05 H), 4.5 (s, 0.65 H), 5.24 (s, 0.35 H), 7.45 (m, 4 H); 35:65 ratio of cis to trans oxaziridine.

All materials not described above were used as obtained from commercial sources.

NMR Instrumentation. For ethylbenzenes and all three-membered ring derivatives, wide-band proton-decoupled ^{13}C NMR spectra were recorded on a Bruker HFX-90 spectrometer at 22.63 MHz using methylene chloride as a solvent and internal Me_4Si as a standard except for aziridinium salts whose spectra were recorded using acetone as a solvent and standard. A 10-mm sample tube was used with a coaxial tube containing external hexafluorobenzene for frequency locking on ^{19}F. Most spectra were recorded in a single scan. Multiple-scan spectra were accumulated on a Varian C-1025 time-averaging computer. All chemical shifts were in parts per million (ppm) downfield from internal Me_4Si; acetone was taken to be 30.4 ppm downfield from Me_4Si.[42]

For propylbenzenes, ^{13}C spectra were measured on a Varian XL-100-15 NMR spectrometer in the pulsed Fourier transform mode at 25.14 MHz and with ^1H noise decoupling. A 6.0-μs pulse was provided by a Transform Technology TT1010 pulse amplifier and controller, and the free induction decays were stored in a Nicolet Instrument Corp. 1085 computer using 16K data points. The free induction decay was transformed after about 700 accumulations to give an 8K transformed spectrum over a 5000-Hz spectrum width. Field/frequency stabilization was obtained from the deuterium resonance of the solvent ($CDCl_3$ or D_2O). Samples (3.6 mL) were prepared in 12-mm tubes as 1.8 M solutions in $CDCl_3$ with 3 to 4% Me_4Si as an internal standard.

All ^{15}N spectra were measured on a Varian XL-100-15 NMR spectrometer in the pulsed FT mode at 10.13 MHz and with ^1H noise decoupling. A 12-μs pulse was provided by a Transform Technology TT1010 pulse amplifier and controller and free induction decay signals were stored in a Nicolet Instrument Corp. unit using 16K data points. Signals were transformed after 7000 to 25 000 accumulations to give an 8K transformed spectrum over a 5000-Hz spectrum width. Field/frequency stabilization was obtained from the deuterium resonance of the solvent. Samples (3.6 mL) were prepared in 12-mm tubes as ca. 2 M solutions in acetonitrile-d_3 which served as a lock signal and internal standard. A relaxation agent chromium(III) tris(acetylacetone), 50 mg was added to each sample. ^{15}N chemical shifts were reported in ppm upfield from nitromethane with acetonitrile-d_3 taken at −137.2 ppm with respect to nitromethane.

^{15}N spectra of *p*-NO_2 and *p*-CH_3 oxaziridines and benzylamines were recorded with and without the relaxation agent (chromium(III) tris(acetylacetone)) in solutions as described above on a Nicolet NT-300-WB spectrometer at 30.4 MHz in a 20-mm tube using a broadband sideways-spinning probe equipped with a solenoidal observe coil. Shifts in the ^{15}N signals observed for the four compounds upon addition of relaxation agent were 0.1 ppm or less, values within experimental error.

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Registry No. 1 (X = OCH_3), 4030-17-5; **1** (X = CH_3), 6921-43-3; **1** (X = H), 873-49-4; **1** (X = Br), 1124-14-7; **1** (X = NO_2), 6921-44-4; **2** (X = OCH_3), 58777-95-0; **2** (X = CH_3), 58777-94-9; **2** (X = H), 4164-25-4; **2** (X = Br), 58777-93-8; **2** (X = NO_2), 66296-00-2; **3** (X = OCH_3), 6388-72-3; **3** (X = CH_3), 13107-39-6; **3** (X = H), 96-09-3; **3** (X = Br), 32017-76-8; **3** (X = NO_2), 6388-74-5; **4** (X = CH_3)·FSO_3^-, 58777-99-4; **4** (X = H)·FSO_3^-, 58777-98-3; **4** (X = Br)·FSO_3^-, 58777-97-2; **4** (X = NO_2)·FSO_3^-, 85720-65-6; *cis*-**5** (X = OCH_3), 82044-36-8; *trans*-**5** (X = OCH_3), 82044-37-9; *cis*-**5** (X = CH_3), 85761-27-9; *trans*-**5** (X = CH_3), 85761-28-0; *cis*-**5** (X = H), 39245-63-1; *trans*-**5** (X = H), 40264-03-7; *cis*-**5** (X = Br), 85720-66-7; *trans*-**5** (X = Br), 85720-67-8; *cis*-**5** (X = NO_2), 28944-73-2; *trans*-**5** (X = NO_2), 28958-67-0; **6** (Ar = *p*-$(CH_3)_2NC_6H_4$), 51227-15-7; **6** (Ar = *p*-$CH_3OC_6H_4$), 15175-54-9; **6** (Ar = *p*-$CH_3C_6H_4$), 4052-88-4; **6** (Ar = C_6H_5), 103-83-3; **6** (Ar = *p*-BrC_6H_4), 6274-57-3; **6** (Ar = *p*-$NO_2C_6H_4$), 15184-96-0; **7** (Ar = *p*-$(CH_3)_2NC_6H_4$), 877-79-2; **7** (Ar = *p*-$CH_3OC_6H_4$), 13114-23-3; **7** (Ar = *p*-$CH_3C_6H_4$), 17972-13-3; **7** (Ar = C_6H_5), 622-29-7; **7** (Ar = *p*-BrC_6H_4), 35003-56-6; **7** (Ar = *p*-$NO_2C_6H_4$), 877-80-5; *p*-ethylanisole, 1515-95-3; *p*-ethyltoluene, 622-96-8; ethylbenzene, 100-41-4; *p*-bromoethylbenzene, 1585-07-5; *p*-nitroethylbenzene, 100-12-9; *p*-*n*-propylaniline, 2696-84-6; *p*-*n*-propylphenol, 645-56-7; *p*-*n*-propylanisole, 104-45-0; *p*-*n*-propyltoluene, 1074-55-1; *n*-propylbenzene, 103-65-1; *p*-bromo-*n*-propylbenzene, 588-93-2; *p*-*n*-propylbenzoic acid, 2483-05-3; *p*-*n*-propylbenzaldehyde, 28785-06-0; *p*-nitro-*n*-propylbenzene, 10342-59-3; *N*,*N*,*N*-trimethylbenzylammonium fluorosulfonate, 85720-68-9; *p*-dimethylaminobenzaldehyde, 100-10-7; *p*-methylbenzyl bromide, 104-81-4; dimethylamine, 124-40-3; benzaldehyde, 100-52-7; methylamine, 74-89-5; *p*-methoxybenzaldehyde, 123-11-5; *p*-bromobenzaldehyde, 1122-91-4; *p*-methylbenzaldehyde, 104-87-0; *p*-nitrobenzaldehyde, 555-16-8; *o*-nitrophenylcyclopropane, 10292-65-6; *N*-methyl-2-hydroxy-2-(4'-nitrophenyl)ethylamine, 61192-64-1.

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