An Electron Spin Resonance Study of the Conjugative Ability of the Oxiryl Group in Radical Anions[1]

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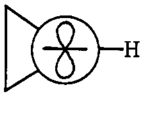
Abstract: The radical anions of a variety of substituted oxiranes as well as appropriate model compounds were generated and studied by electron spin resonance spectroscopy. Hammett substituent constants for the various substituents were determined from the magnitude of the nitrogen hyperfine coupling constant in the *p*-nitrophenyl group used as the spin label. The oxiryl group appears to be somewhat electron withdrawing, $\sigma = +0.14$, but the effect is not greatly dependent upon the conformational alignment of the three-membered ring. A comparison of the radical anions derived from *p*-nitrostilbene oxide and *p*-methoxy-*p'*-nitrostilbene oxide reveals that the oxiryl group does not allow sufficiently effective transmission of conjugation between the two aromatic rings to produce a difference in the nitrogen coupling constant in these paramagnetic species.

There has been much interest in recent years in the electronic properties and conformational requirements for conjugative interaction of three-membered rings with adjacent π systems. The cyclopropyl substituent has received the most attention and substantial evidence has been obtained which indicates the cyclopropyl group adopts the bisected, **1**, over the perpendicular, **2**, conformation when attached to an electron-deficient carbon atom such as a carbonium ion or carbonyl carbon.[2] However, the evidence is not nearly as conclusive concerning the corresponding cyclopropylcarbinyl radical[2a,3] and anion.[2a,4] In general, it appears that a cyclopropyl group adjacent to a free-radical site prefers the bisected conformation I[3b–d] and imparts at least some stabilizing influence[3a] but that the effect is greatly attenuated as compared to the corresponding cation. Although in his review Charton cites some evidence that a cyclopropyl group can stabilize an adjacent carbanion,[2a] more recent evidence suggests that the effect is very weak;[4] only scanty evidence is available concerning conformational effects in carbanionic systems.[2a,3b,3c,4]



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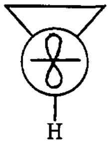

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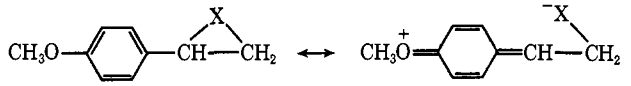
A considerable amount of effort has been expended in attempts to differentiate between the ability of a three-membered ring to *extend* a conjugated system and the ability to *transmit* conjugation from one unsaturated group to another.[2a,5] Ultraviolet absorption spectroscopy studies appear to indicate a capability for both effects in cyclopropane derivatives at least in the excited state species but extrapolation of such results to ground-state molecules is not warranted.[5i] Ground-state studies are somewhat ambiguous but in general indicate that the cyclopropyl group can indeed both extend and transmit conjugation although the effectiveness of the latter appears less than that of the vinylene group.[2a,5i]

While a large amount of data in the literature has dealt with the cyclopropane ring, the electronic properties of heterocyclic three-membered rings have received considerably less attention. Resonance structures such as **3b** have been postulated to account for the apparent electron-withdrawing effect of the oxiryl and thiiryl groups in the excited states of para-substituted styrene oxides and sulfides,[5d] but ^{19}F nmr studies indicate that these groups exhibit an electron-donating resonance interaction in the ground state.[2f] Transmission of conjugation in the excited state *via* contributing resonance structures such as **4a** and **4b** has been invoked to account for the ultraviolet absorption spectra of variously substituted stilbene oxides.[5c] A recent nmr study[6] has indicated that the oxirane ring is similar to the cyclopropane ring in efficiency of transmission



3a, X = O, S **3b**, X = O, S

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF No. 1123-Gl), and the Bureau of General Research, Kansas State University, for support of this work.

[2] (a) M. Charton, "The Chemistry of Alkenes," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, Chapter 10, has compiled a rather extensive summary of much of the work relating to the olefinic properties of cyclopropanes; (b) J. C. Martin and B. R. Ree, *J. Amer. Chem. Soc.*, **91**, 5882 (1969); **92**, 1660 (1970); (c) F. R. Jensen and B. E. Smart, *ibid.*, **91**, 5686 (1969); (d) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966); (e) L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965); (f) R. G. Pews, *J. Amer. Chem. Soc.*, **89**, 5605 (1967); (g) W. H. Sachs and C. Rappe, *Tetrahedron Lett.*, 2317 (1968).

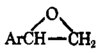
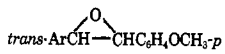
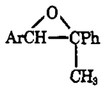
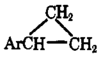
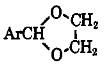
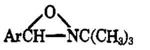
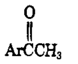
[3] (a) J. C. Martin and J. W. Timberlake, *J. Amer. Chem. Soc.*, **92**, 978 (1970), and references cited therein; (b) N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967); (c) N. L. Bauld, J. C. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, *ibid.*, **91**, 6666 (1969); (d) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1877 (1969).

[4] H. J. Perkins and P. Ward, *Chem. Commun.*, 1134 (1971).

[5] (a) E. N. Trachtenberg and G. Odian, *J. Amer. Chem. Soc.*, **80**, 4018 (1958); (b) J. M. Stewart and G. K. Pagenkopf, *J. Org. Chem.*, **34**, 7 (1969); (c) L. A. Strait, D. Jambotkar, R. Ketcham, and M. Hrenoff, *ibid.*, **31**, 3976 (1966); (d) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Amer. Chem. Soc.*, **86**, 4628 (1964); (e) C. H. Heathcock and S. R. Poulter, *ibid.*, **90**, 3766 (1968), and references cited therein; (f) M. J. Jorgenson and T. Leung, *ibid.*, **90**, 3769 (1968); (g) J. P. Pete, *Bull. Soc. Chim. Fr.*, 357 (1967); (h) M. M. Baizer, J. L. Chruma, and P. A. Berger, *J. Org. Chem.*, **35**, 3569 (1970), and references cited therein; (i) R. G. Pews and N. D. Ojha, *J. Amer. Chem. Soc.*, **91**, 5769 (1969); (j) R. C. Hahn, P. H. Howard, and G. A. Lorenzo, *ibid.*, **93**, 5816 (1971).

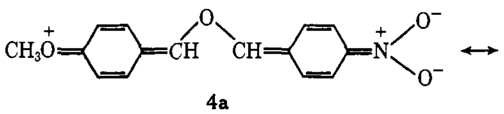
[6] A. B. Turner, R. E. Lutz, N. S. McFarlane, and D. W. Boykin, Jr., *J. Org. Chem.*, **36**, 1107 (1971).

Table I. Hyperfine Splitting Constants and Calculated σ Values for Substituted Oxiryl and Related Radical Anions[a]

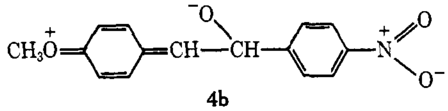
Compound ($\mathrm{Ar} = p\text{-}\mathrm{NO_2C_6H_4}$)	No.	a^N	a_o^H	a_m^H	a_α^H	a_β^H	$\sigma_p{}^b$
	**7**	9.50	3.32	1.05	1.05	c	+0.14
	**6**	9.26	3.37	1.04	1.04	0.41	+0.23
	**4**	9.26	3.37	1.04	1.04	0.41	+0.23
	**8**	9.48	3.27	1.06	3.02		+0.15
	**5**	10.20	3.35	1.10	1.10	0.26[d]	−0.10
$\mathrm{ArCH(CH_3)_2}$	**9**	10.34	3.35	1.07	1.85	c	−0.14
$\mathrm{ArCH_2OCH_3}$	**10**	9.65	3.33	1.03	2.57		+0.09
	**11**	9.34	3.29	1.05	1.05		+0.20
	**12**	8.31	3.18	e	e	e	+0.55
 $\mathrm{Ar}\overset{\overset{O}{\|}}{C}\mathrm{CH_3}$	**13**	6.23	3.15	0.68		0.68[f]	g

[a] All spectra in DMSO solution at room temperature. Estimated a^N accuracy ±0.05 G. [b] Calculated from eq 1. [c] Not resolved. [d] Either two or four hydrogens; see text. [e] Hyperfine splittings due to meta and α hydrogens and oxaziryl nitrogen not unambiguously assigned. [f] Three equivalent (methyl) hydrogens. [g] More appropriately considered a σ^- value.[9]

of substituent effects, while a more quantitative assessment by a ^{19}F chemical shift study revealed that the oxirane ring is *ca.* 26% as effective as a double bond in ability to transmit conjugation in the ground state.[7]



4a



4b

In this paper we wish to report an esr study of the radical anions of a number of substituted oxiranes as well as several appropriate model compounds. Esr spectroscopy is ideally suited for the study of electronic effects in paramagnetic species since detailed information concerning the delocalization of the unpaired electron can be obtained. In the present study we have utilized the *p*-nitrophenyl substituent as the spin label in order to take advantage of the well-known stabilizing influence this group possesses for radical anions. Moreover, a determination of the magnitude of the nitrogen hyperfine interaction in such compounds will allow an assignment of a Hammett σ value to the substituent group.[8–10] As discussed by Janzen,[9] the main effect of the substituent in such radical anions is not to delocalize the unpaired electron but to exert a polar effect on the spin distribution within the nitro group.

Results

The radical anions of the compounds listed in Table I were generated by electrolytic reduction at a mercury pool cathode directly within the cavity of the esr spectrometer at room temperature. Purified dimethyl sulfoxide (DMSO) was utilized as a solvent in all cases. Cyclic voltammograns for the majority of the compounds studied exhibited nicely reversible behavior indicating that the radical anions were sufficiently stable for esr investigation (*vide infra*).

We have shown in a previous study[8] that there is a quite good correlation between $a_X{}^N/a_H{}^N$ (the nitrogen hyperfine interaction of the substituted nitrobenzene radical anion divided by the nitrogen hyperfine coupling constant of nitrobenzene radical anion, 9.92 G) and Hammett substituent constants.[11] This Hammett-type correlation[9,10] exhibits a slope (ρ value) of −0.297 (correlation coefficient = 0.993) and can be described by eq 1. From this relationship it is possible to obtain

$$\sigma = 3.369(1.00 - a_X{}^N/a_H{}^N) \qquad (1)$$

the substituent constants listed in Table I for the groups investigated. From the nine experimental points used to obtain eq 1, a standard error in the estimate of σ of ±0.046 is calculated assuming σ is the dependent variable.

Discussion

The first point worthy of note is that the radical anions of the oxiranes **4**, **6**, and **8** are quite stable and produce intense, well-resolved esr spectra (Figure 1). This stability is predicted by the reversible nature of the cyclic voltammograms but contrasts the somewhat

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(7) R. G. Pews and N. D. Ojha, *Chem. Commun.*, 1033 (1970).
(8) W. C. Danen and C. T. West, *Tetrahedron Lett.*, 219 (1970).
(9) E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969).
(10) (a) E. T. Strom and J. R. Norton, *J. Amer. Chem. Soc.*, **92**, 2327 (1970); (b) E. T. Strom, A. G. Bluhn, and J. Weinstein, *J. Org. Chem.*, **32**, 3853 (1967).
(11) D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

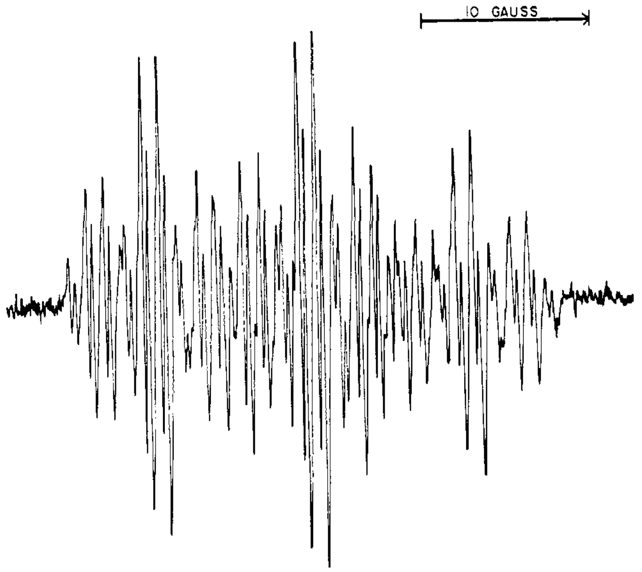


Figure 1. Electron spin resonance spectrum produced by the electroreduction at −1.10 V (sce) of 4 × 10^{-3} *M trans-p*-nitrostilbene oxide in DMSO at room temperature. See Table I for assignments of hyperfine coupling constants.

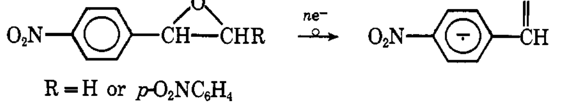
analogous systems in which either an unpaired electron (eq 2) or a lone pair of electrons (eq 3) is localized on a


(2)


(3)

center adjacent to an oxiryl group.[12] In both of these cases the three-membered ring is opened to give the rearranged allyloxy radical or anion. Although it has not been determined whether ring opening is concerted with formation of the radical species, rearrangement occurs faster than facile hydrogen transfer from tin hydride[12b] since no propylene oxide is observed as a product in the reaction of epibromohydrin with organotin hydrides. The enhanced stability of the substituted oxirane radical anions generated in the present study presumably results from the rather extensive delocalization of the unpaired electron and the diminished radical and ionic character at the aromatic carbon to which the three-membered ring is attached.

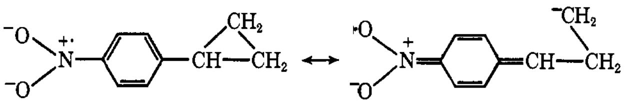
It was noted, however, that several of the oxiranes under investigation are indeed unstable and undergo decompositional fragmentation. Although the esr spectrum of the radical anion of *p*-nitrostyrene oxide, **7**, can be obtained if one records the spectrum immediately after initiating the electrolytic generation, the radical


(4)

R = H or $p\text{-}O_2NC_6H_4$

anion gradually decomposes and the characteristic spectrum[13] of the *p*-nitrobenzaldehyde radical anion appears. Attempted generation of the corresponding radical anions from either *cis-* or *trans-p,p'*-dinitrostilbene oxide in DMSO likewise produces a strong signal due to *p*-nitrobenzaldehyde radical anion. Although it might be suspected that the known albeit weak oxidizing ability of the DMSO solvent may be playing a role in these decompositions, it was found that similar results are obtained when dimethylformamide (DMF) is utilized as the solvent.

An examination of the σ values obtained in the present study (Table I) reveals results similar to those of Strait, *et al.*,[5d] in that the *p*-oxiryl group is electron withdrawing. The −0.10 σ value observed for the cyclopropyl group can be compared with the range of values, −0.14 to −0.24,[14] obtained from other studies. The value obtained in the present study is quite similar to that found for the isopropyl group, $\sigma_p = -0.14$ (lit.[11] $\sigma_p = -0.151$), but indicates that the cyclopropyl substituent is not as electron donating in a radical anion as would be predicted from the substituent constants derived in other studies. This is in agreement with the conclusion that the cyclopropyl group exhibits strong electron-donating characteristics only when a sufficiently electron-deficient center is present.[2f,g] Furthermore, the cyclopropyl substituent, unlike a carbon–carbon double bond, apparently cannot readily accept electrons when adjacent to an unsaturated center *via* resonance structures such as **5b** which is analogous to **3b**, X = CH_2.[5d,15]



5a **5b**

Our results indicate that the *p*-oxiryl group on the other hand is somewhat electron withdrawing with $\sigma_p = +0.14$. This result concurs qualitatively with that of Strait, *et al.*,[5d] but contrasts somewhat with that of Pews[2f] who concluded that the oxiranyl ring is weakly electron withdrawing inductively ($\sigma_I = +0.07$) and weakly electron donating *via* resonance ($\sigma_R{}^0 = -0.04$).[16] Pews rationalized the discrepancy between his results and those of Strait, *et al.*, as being due to differences in the conjugative ability of the three-membered rings in the ground state *vs.* the excited state species. The present esr study involves radical anions which are formed by placing an electron in the lowest unoccupied molecular orbital of the neutral parent molecule. Although this orbital is likewise populated in the photochemically excited species, the radical anions are expected to exhibit ground-state properties as evidenced by good linear free energy correlations with substituent constants[9] in contrast to the lack of any reasonable correlation of ultraviolet (excited state) $\Delta\lambda$ values with σ constants.[17]

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(12) (a) S. K. Pradhan and V. M. Girijavallabhan, *Tetrahedron Lett.*, 3103 (1968); (b) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

(13) A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

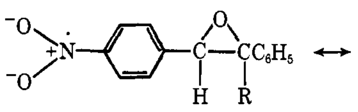
(14) Values obtained from Table 29, ref 2a. The −0.14 value was calculated from the ionization constant for *p*-cyclopropylbenzoic acid in 50% aqueous ethanol assuming a Hammett ρ value of 1.52.[15]

(15) R. D. Hahn, T. F. Corbin, and H. Shechter, *J. Amer. Chem. Soc.*, **90**, 3404 (1968).

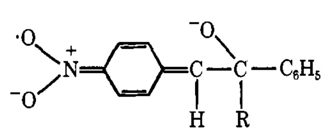
(16) Charton believes that σ_I values obtained from ^{19}F nmr chemical shift measurements are always too low (ref 2a, p 554). The discrepancy between the present value and that of Pews[2f] would be less pronounced if the estimate of σ_I is indeed too low by *ca.* 0.1 unit.

(17) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 259.

A comparison of oxiranes **6** and **8** is especially revealing. An examination of molecular models demonstrates that the methyl group in the oxirane **8** causes a rather severe restriction to rotation of the *p*-nitrophenyl ring forcing this ring and the C–O bond of the oxiryl ring to approach coplanarity. Such a conformational alignment is not conducive to electron delocalization in the radical anion as indicated in **8b** since such interaction requires the C–O bond of the three-membered ring[18] to align itself more or less parallel to the *p* orbital on the para carbon of the *p*-nitrophenyl ring while in **8** the C–O bond is almost orthogonal to this orbital. This conformational ordering is also evident from the rather large change in the α hydrogen hyperfine interaction, a quantity known to follow a $\cos^2\theta$ relationship where θ is the dihedral angle between the C–H bond and the axis of the adjacent *p* orbital.[19] The tripling in magnitude from 1.04 G in **6** to 3.02 G in **8** is indicative of a conformational change from an alignment of the C–H bond approaching the nodal plane of the *p* orbital in **6** to a more nearly parallel alignment in **8**. The increase in the nitrogen hyperfine interaction in going from **6** to **8** represents a change in σ values from +0.23 to +0.15, respectively, for the two differently substituted oxiryl groups. These results at first glance suggest that the oxiryl ring is at least weakly capable of extending conjugation by electron withdrawal *via* contributing resonance structures in which the C–O bond of the oxiryl ring is aligned with the *p* orbital of the aromatic system. However, the methyl group in **8** not only affects the conformational alignment of the oxiryl group but also introduces an electron-donating inductive effect which would be expected to shift the nitrogen coupling constant in the same direction as anticipated due to the conformational change. By comparing compounds **6**, **7**, and **8** and estimating the inductive effect of the respective phenyl, hydrogen, and methyl groups from their σ^* values,[20] it can be estimated that approximately one-half of the 0.08 change in σ in going from **6** to **8** can be attributed to the inductive effect of the added methyl group. It, therefore, appears that the electronic effect of the oxiryl group in these radical anions is not extremely sensitive to conformational alignment and that resonance structures such as **6b** probably contribute only in a minor way to the description of the resonance hybrid in the ground state.

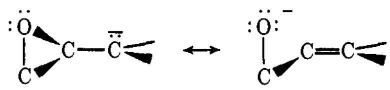


6a, R = H
8a, R = CH$_3$



6b, R = H
8b, R = CH$_3$

In the following paper[21] we report a rather extensive study of the conformational preferences of the isobutyl, cyclopropylcarbinyl, and oxirylcarbinyl cations, radicals, and anions as determined by INDO method calculations. It is shown that the oxiryl group is indeed at least somewhat effective in the anion in delocalizing excess charge onto the oxygen atom when in the lower energy "bisected" conformation **16**. On the other hand, the cyclopropyl anion is calculated to prefer the perpendicular conformation but by an energy difference of only 1.48 kcal/mol. However, the 8.88 kcal/mol calculated energy difference between the bisected and perpendicular conformations of the oxirylcarbinyl anion is quite small compared to the differences of 31.15 and 41.15 kcal/mol for the oxirylcarbinyl and cyclopropylcarbinyl cations, respectively (the bisected conformation being lower in energy in both cases). The present esr results appear to be in qualitative agreement with the calculations.



16

In order to circumvent the necessity of estimating the inductive effect of the methyl group in comparing **6** and **8**, *cis-p*-nitrostilbene oxide was synthesized to compare directly with the trans isomer **8** to determine the effect of conformational alignment on electron delocalization. Electroreduction of the cis isomer yielded an esr spectrum identical with that observed for the trans radical anion indicating an apparent isomerization. Such an isomerization is analogous to that observed upon generation of the radical anions of *cis*-stilbene and *cis*-azobenzene[22] and indicates that opening of the oxiryl ring as depicted in eq 2 and 3 must take place allowing bond rotation to the more stable trans isomer.

In spite of the apparent absence of a dramatically preferred conformational alignment, a comparison of the hyperfine coupling constants for the α hydrogens in the **5** and **7** with that of the isopropyl substituent, **9**, reveals somewhat smaller values for the three-numbered ring substituents which is reasonable if these groups, on the time average, adopt a more nearly bisected conformational alignment.[23] A splitting of 0.26 G was noted for the β-cyclopropyl hydrogens in **5** but the lack of resolution did not permit an unambiguous choice of assignment between two equivalent hydrogens (1:2:1 intensity ratio) and four equivalent hydrogens (1:4:6:4:1 intensity ratio but with the wing peaks not being observed). There is no reason, however, to expect all four β hydrogens to be equivalent. Although the esr spectrum of the cyclopropylcarbinyl radical[3d] exhibits splittings of comparable magnitude for the syn and anti β hydrogens, 2.01 and 2.98 G, respectively, our INDO calculations for this system[21] indicate that these splittings are of opposite sign in the preferred bisected conformations. In rotating from the bisected to the symmetrical alignment, however, the anti hydrogens are calculated to changeover in sign

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[18] The electron density of the C–O bond is not, of course, symmetrical about a line connecting the two atoms.

[19] C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

[20] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 222.

[21] W. C. Danen, *J. Amer. Chem. Soc.*, **94**, 4835 (1972).

[22] C. S. Johnson, Jr., and R. Chang, *J. Chem. Phys.*, **43**, 3183 (1965).

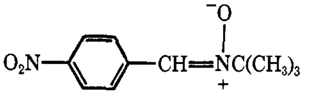
[23] This assumes, of course, that the hyperfine couplings of the methine hydrogens in the cyclopropyl, oxiryl, and isopropyl substituents follow a ($\beta_0 + \beta\cos^2\theta$) relationship with the β_0 and β terms similar for the three groups.[21]

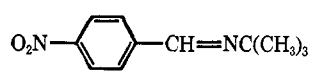
of spin density from positive to negative; the syn hydrogens remain negative throughout. It is not unreasonable to expect that at some intermediate conformational alignment, the two anti β hydrogens would have vanishingly small hyperfine interactions.

A comparison of the oxiryl group in **7** to other oxygen-containing substituent groups such as **10** and **11** reveals that it is intermediate in electron-withdrawing ability between substituent groups with one and two oxygen atoms. The somewhat enhanced effect as compared to the methoxymethyl group in **10** may be due to a conjugative interaction as discussed above or an increased s character in the phenyl–oxiryl ring bond resulting from the unique hybridization of the atoms constituting the three-membered ring. The oxiryl substituent does not, however, even approach the keto group (*cf.* **13**) in ability to delocalize negative charge.

A comparison of the radical anions of **4** and **6** reveals that the methoxy substituent has no observable effect on the magnitude of the nitrogen hyperfine coupling constant and it can be concluded either that inductive effects or transmission of conjugation by contributing resonance structures **4a** and **4b** is of no importance in these paramagnetic species or that the present esr probe is not sufficiently sensitive to detect such an effect. It was thought that the small difference in inductive effect ("modified substituent effect"[5i]) between a phenyl and a *p*-methoxyphenyl group might be sufficient to cause a slight but perceptible change in the nitrogen coupling constant. To this end and to minimize experimental variables, we electroreduced an equimolar mixture of **4** and **6** and obtained an esr spectrum indistinguishable from either **4** or **6** separately. It appears most probable that the effect of the *p*′-methoxy substituent on the nitrogen hyperfine interaction in the radical anion of **4** is of too low magnitude to detect in the present esr experiment. The nmr investigations[6,7] mentioned above clearly demonstrate that substituents are indeed capable of exerting their influence through an oxiryl linkage. The measurement of the ^{19}F nmr shielding parameters is sufficiently sensitive to detect the electron-donating or withdrawing effect of a substituent even in *p*-fluoro-para′-substituted bibenzyls.[6,7] On the other hand, the effect of substituents on the esr nitrogen coupling constant in nitroaromatic radical anions is severely attenuated even in going from substituted nitrobenzenes to substituted stilbenes in which the nitro and substituent groups are in different rings.[9,24] The nmr results indicate that the transmission of substituent effects through the vinyl linkage in stilbene compounds should be significantly more effective than transmission through the oxiryl linkage.

We have also briefly investigated the *tert*-butyl-substituted oxazirane **12** and from the σ value of $+0.55$ it can be seen that the introduction of both an oxygen and nitrogen into a three-membered ring results in a quite strongly electron-withdrawing group. This value differs with the results of Pews[2f] from which a much smaller σ value can be estimated for the oxaziryl group. Although the esr spectrum of the radical anion produced upon electroreduction of **12** was not completely analyzed, we are quite confident that the spectrum is indeed attributable to this species. The cyclic voltammogram of **12** produced a reversible cathodic wave and electroreduction of **14** and **15** produced esr spectra which were not at all similar to that formed from **12**.


14


15

In conclusion, it appears that the oxiryl and substituted oxiryl substituents are fairly effective electron-withdrawing groups in the radical anions studied but that this behavior must be primarily inductive in nature as there is little conformational preference for the effect; transmission of conjugation such as depicted in **4a** and **4b** for these species which are presumably exhibiting ground-state behavior is not detected in the present study.

Experimental Section

The esr spectra were obtained on a Varian V-4502 electron spin resonance spectrometer equipped with 100-kc field modulation, dual cavity, and Fieldial scanning unit. The radical anions were generated *in situ* at a mercury pool cathode in purified dimethyl sulfoxide as solvent with 0.10 *M* tetra-*n*-butylammonium perchlorate or tetra-*n*-propylammonium perchlorate as supporting electrolyte; the initial concentration of the compound was *ca.* 10^{-3}–10^{-4} *M*. The cyclic voltammograms were obtained at either a hanging mercury drop or platinum botton electrode as described in detail elsewhere;[25] electrogeneration of the radical anions for esr investigation was performed at an applied potential *ca.* 0.10 V more cathodic than the peak obtained from cyclic voltammetric studies. All spectra were recorded at room temperature and calibrated against a solution of Fremy's salt taken as 13.091 G[26] held in the second cavity. All solutions were degassed by thoroughly purging with dry, oxygen-free nitrogen and kept under a nitrogen atmosphere during the esr experiment.

The DMSO was purified by distilling from calcium hydride under reduced pressure and was stored over Linde Type 4A molecular sieves. Compounds **5**,[27] **6**,[28] **7**,[28] **9**,[29] **10**,[27] **12**,[30] **14**,[30] and **15**[30] were synthesized according to the indicated literature reference. Compound **8**, mp 137–138°, was prepared from α'-methyl-4-nitrostilbene *via* the bromohydrin according to the general procedure described by Strait, *et al.*[5c] The α'-methyl-4-nitrostilbene, mp 107–108°, was synthesized by the Wittig reaction of (α-methylbenzyl)triphenylphosphonium bromine with *p*-nitrobenzaldehyde in a manner analogous to that described by McDonald and Campbell.[31] *p*-Nitrobenzaldehyde ethylene acetal (**11**) was prepared in a manner identical with that utilized for the ortho isomer.[32] *cis-p*-Nitrostilbene oxide, mp 75–77°, was formed in 73% yield by the peracetic acid oxidation[33] of *cis-p*-nitrostilbene;[34] this procedure is to be preferred over synthesis *via* the bromohydrin[5c] as the yield is enhanced and no trans isomer is observed.

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[24] L. S. Degtyarev and Yu. A. Kruglyak, *Teor. Eksp. Khim.*, **2**, 184 (1966); *Chem. Abstr.*, **65**, 12089*d* (1966). There is a decrease of only 0.3 G in the nitro group hyperfine coupling constant in going from the *p*-nitrostilbene to the *p*-amino-*p*′-nitrostilbene radical anion.

[25] D. E. Bartak, W. C. Danen, and M. D. Hawley, *J. Org. Chem.*, **35**, 1206 (1970).

[26] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, **47**, 2462 (1967).

[27] R. Fuchs and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **76**, 1631 (1954).

[28] E. Bergmann and J. Hervey, *Ber.*, **62**, 893 (1929).

[29] H. C. Brown and W. H. Bonner, *J. Amer. Chem. Soc.*, **76**, 605 (1954).

[30] W. D. Emmons, *ibid.*, **79**, 5739 (1957).

[31] R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, **24**, 1969 (1959).

[32] H. E. Baumgarten, D. L. Pedersen, and M. W. Hunt, *J. Amer. Chem. Soc.*, **80**, 1977 (1958).

[33] A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *ibid.*, **80**, 2844 (1958).

[34] P. Schmid, *U. S. At. Energy Comm.*, UCRL-8883 (1959); *Chem. Abstr.*, **54**, 7647*b* (1960).