Table II. Disproportionation Equilibrium Constants Standardized for Cation Concentration

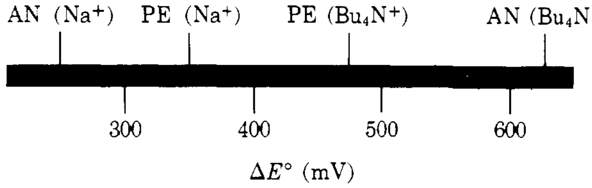
Compound	Solvent	Cation[a]	(C.V.)[b]	Pot. tit[c]
Perylene	THF	Na^+	7.2×10^{-7}	6.9×10^{-7}
		Bu_4N^+	2.8×10^{-9}	—
	DME	Na^+	5.5×10^{-10}	2.1×10^{-10}
		Bu_4N^+	1.9×10^{-9}	—
	DMF	Na^+	2.4×10^{-10}	—
		Bu_4N^+	3.7×10^{-10}	—
Anthracene	THF	Na^+	1.9×10^{-5}	7.4×10^{-6}
		Bu_4N^+	1.1×10^{-11}	—
	DME	Na^+	9.8×10^{-9}	8.6×10^{-9}
		Bu_4N^+	1.4×10^{-11}	—
	DMF	Bu_4N^+	6.4×10^{-13}	—

[a] Cation concentration 0.02 *M*. [b] K_{disp} calculated from cyclic voltammetry, temperature 11°C. [c] K_{disp} from potentiometric titrations, temperature 25°C, data from ref 2.

was found to be almost independent of salt concentration in DMF.

In DMF, K_{disp} for both AN^- and PE^- is nearly the same when the cation is Na^+ or Bu_4N^+. In THF but not DME, K_{disp} for both PE^- and AN^- is greater in the presence of Na^+ than in the presence of Bu_4N^+. The latter is brought out dramatically by Scheme I. For PE in THF, ΔE^0 changed by only 135 mV in going from Bu_4N^+ to Na^+ while a change of 350 mV was observed in ΔE^0 for AN with the cation change. Changes have previously been observed in ΔE^0 for both PE and AN in the presence of Li^+, Na^+, and K^+ and have been attributed to changes in the degree of solvation of the cations in the presence of the radical ions.[2] The previous discussion[2] assumed that both dianions, AN^{2-} and PE^{2-}, bring about the desolvation of sodium ions which are solvated in THF in the presence of the corresponding anion radicals. If the increase in disproportionation equilibrium constants in THF and DME as compared to DMF is indeed due to the increased interaction between dianions and cations as compared to the anion radical–cation interaction in the less polar solvents, then the interaction must be greater for AN^{2-} and Na^+ than for PE^{2-} and Na^+. The latter is of course reasonable since the degree of interaction of dianions with cations is expected to increase as the dianion becomes smaller.[5]

Scheme I



The effect of electrolyte concentration on the degree of disproportionation of radical ions must be due to an effective increase in the dielectric constant of the medium as the salt concentration is increased. This is indicated by the following: (i) the magnitude of the effect decreases with increasing dielectric constant of the solvent, DME = THF ≫ DMF; (ii) the magnitude of the effect is essentially independent of the radical anion, $AN^- = PE^-$; and (iii) the effect is the same for Na^+ as for Bu_4N^+. Thus, it seems highly unlikely that the origin of the effect lies in any specific equilibria involving the organic anions and the cations. It follows from the above discussion that reactions involving a disproportionation (eq 3) of a radical ion to a reactive dianion (in DMF or THF) followed by product forming reactions of the dianion (eq 4) should decrease in rate as the salt concentration is increased due to the decrease in K_3 accompanying the salt concentration change.

$$2\pi\cdot^- \rightleftarrows \pi + \pi^{2-} \tag{3}$$

$$\pi^{2-} \rightarrow \text{products} \tag{4}$$

For example, a 100-fold increase in salt concentration brings about a change of 8×10^{-3} in disproportionation equilibrium constants of PE and AN radical anions. Thus, kinetic studies which involve measurements at various salt concentrations would be of great value in evaluating possible disproportionation mechanisms. The kinetics of protonation of aromatic hydrocarbon anion radicals have been the subject of several recent studies,[6-11] some of which have resulted in the conclusion that disproportionation is an important contribution to the overall mechanisms. In such cases, further work involving kinetic studies with variable salt concentrations should prove decisive in establishing mechanisms.

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The Electron Paramagnetic Resonance Spectra of α-Substituted Nitrotoluene Anion Radicals. The Influence of Electron-Withdrawing Substituents on the Coupling Constants for β-Hydrogen Atoms

Sir:

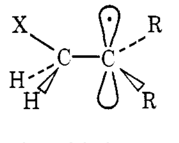
We have obtained new experimental and theoretical information which indicates that electron-withdrawing substituents importantly diminish the magnitude of spin delocalization to β-hydrogen atoms in radicals. These substituent effects are so large that the EPR coupling constants for β-hydrogen atoms, $a_{\beta\text{-H}}$, cannot be used without correction to estimate conformational preferences, to detect structural changes such as bridging (distortion), or to guide the experimental assessment of B_2 parameters for other β-atoms, such as fluorine.

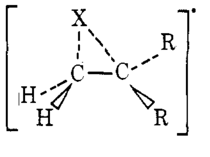
Radicals with electronegative substituents often exhibit unusually low values of $a_{\beta\text{-H}}$.[1] Such results have often been interpreted as evidence for bridging (distortion at C_β) by X.[1,2] However, according to the concept of hyperconjugation,[3] electron-withdrawing substituents should diminish the donor properties of the β-carbon–hydrogen bonds. Thus, as pointed out by Symons and his associates,[4] hyperconjugation alone may provide a satisfactory explanation for the influence of electronegative groups on $a_{\beta\text{-H}}$.

Table I. EPR Coupling Constants for 4-Substituted Nitrobenzene Anion Radicals in Acetonitrile

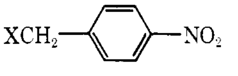
4-Substituent	Temp	Coupling constant, G				
		a_N	a_2-H	a_3-H	a_{β}-H	a_{β}-X
H[b]	Amb	10.32	3.39	1.09	3.97	–
CH_3[a]	Amb	10.70	3.39	1.11	3.98	–
CH_2CH_3[a]	Amb	10.71	3.37	1.11	2.96	–
$CH_2C(CH_3)_3$	Amb	10.73	3.33	1.12	2.14	–
$CH_2C(CH_3)_3$	−35°	10.96	3.40	1.10	2.06	–
$CH_2N(CH_3)_2$	Amb	12.38	3.33	1.19	2.62	1.20[c]
$CH_2N(C_6H_5)_2$	Amb	10.70	3.30	1.13	2.75	1.06[c]
CH_2OH[d]	Amb	13.70	3.40	1.15	2.75	–
CH_2F[e]	−35°	9.65	3.35	1.02	1.75	25.73[f]
$CH_2N(CH_3)_3^+$	−35°	11.21	3.31	1.00	1.52	2.85[c]

[a] Reference 7. [b] For 4-H. [c] For β-nitrogen. [d] Reference 5. [e] Line broadening is observed between −40 and −5°. [f] For β-fluorine.





To examine this issue, we studied a series of nitrotoluenes with alkyl, hydroxyl,[5] amino, fluoro, and trimethylammonium substituents. These derivatives were selected for study because bridging is unlikely and because there are ample data to ensure that the variations in $a_{\beta\text{-H}}$ do not result from changes in spin density at the 4 position.[6] These molecules



were converted to their anion radicals by conventional techniques.[7] The anion radicals with fluoro and trimethylamino substituents were unstable at ambient temperature. However, these radicals could be examined at −35°. The results are summarized in Table I.

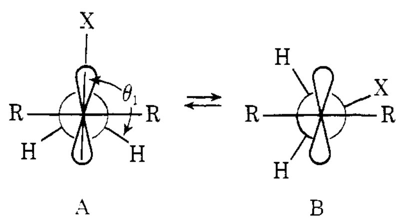
The $a_{\beta\text{-H}}$ values are customarily analyzed on the basis of eq 1

$$a_{\beta\text{-H}} = \rho_C^{\pi}(B_0 + B_2 \langle\cos^2\theta\rangle) \quad (1)$$

where ρ_C^{π} is the spin density at the 4 position, B_0 and B_2 are constants near -1.5[8] and 50 G, respectively, and $\langle\theta\rangle$ is the average dihedral angle. Often, it is assumed that B_0 is negligible and that ρ_C^{π} and B_2 are essentially constant for the substituted (XCH_2–) and unsubstituted (CH_3–) radicals. Under these circumstances, $a_{\beta\text{-H}}$ for the substituted radical is related to a_{CH_3} by eq 2

$$a_{\beta\text{-H}} = (\cos^2\theta_1 + \cos^2(\theta_1 + 120°))a_{CH_3} \quad (2)$$

This expression predicts that the minimum value of $a_{\beta\text{-H}}$, 2 G, is realized when the nitrotoluene anion radical adopts Conformation A.



The experimental $a_{\beta\text{-H}}$ values are all appreciably smaller than the constant for toluene. The values for the radicals with the most electron-withdrawing substituents are actually less than the minimum allowable value based on eq 2. Clearly, the result for the saturated trimethylammonium derivative which exhibits the smallest $a_{\beta\text{-H}}$ value in this series cannot be attributed to bridging.[9] This finding suggests that the electronegative groups localize electron density in the carbon–hydrogen bonds with a consequent reduction in the interaction between the aromatic π electron system and the carbon–hydrogen bonds as predicted by qualitative models based on hyperconjugation.[3] This theory also accounts for the fourfold energy barrier, about 5 kcal, between the A and B conformations of the anion radical derived from 4-nitrobenzyl fluoride.

Table II. Calculated Values of $a_{\beta\text{-H}}$ for β-Substituted Ethyl Radicals[a]

Radical	Coupling constant, $a_{\beta\text{-H}}$, G	
	Conformation A	Conformation B
$CH_3–CH_2CH_2\cdot$	15.3	42.3
$H–CH_2CH_2\cdot$	15.0	41.0
$H_2N–CH_2CH_2\cdot$[b]	11.8	43.5
$F–CH_2CH_2\cdot$	9.4	44.5
$H_3N^+–CH_2CH_2\cdot$[b]	8.9	40.4

[a] Conventional bond distances and angles for sp^3 and sp^2 hybridization were used. [b] Equivalent results were obtained for several conformations of the amino and ammonium groups.

A quantitative theoretical analysis, Table II, based on the INDO approach[10] yields the same conclusion.

The theoretical results suggest that $a_{\beta\text{-H}}$ is virtually independent of a substituent effect when the radicals adopt conformation B. In contrast, these results also indicate that $a_{\beta\text{-H}}$ depends quite significantly on the polar character of the C–X bond when the radicals adopt conformation A.

In conclusion, both the experimental and the theoretical treatments suggest that the reduced $a_{\beta\text{-H}}$ values result, for the most part, from electronic substituent effects rather than from serious structural deformations. These substituent interactions and the negative B_0 value, -1.5 G, considerably alter the hyperfine constants. Thus, the values of $\langle\theta\rangle$ and, more important, the energy barriers deduced from eq 1 or 2 on the basis of unadjusted $B_2{}^H$ parameters are subject to important error. Consequently, rather thorough analyses of the experimental data are necessary before the $a_{\beta\text{-H}}$ values can be related, with confidence, to novel structural or conformational effects.[11]

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(6) The $a_{2\text{-H}}$ and $a_{3\text{-H}}$ values are virtually constant. In addition, the relative a_C values for the ring positions deduced from NMR studies on the nickel acetylacetonate complexes of the related anilines do not differ significantly even for the 4-methyl and 4-trifluoromethyl substituents. L. M. Stock and M. R. Wasielewski, unpublished results.
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(12) Fannie and John Hertz Foundation Fellow at the University of Chicago.

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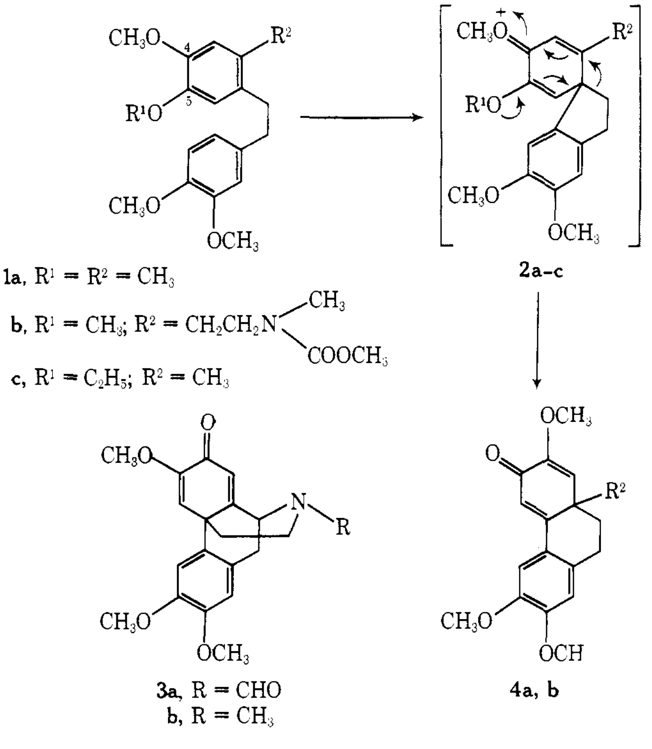
On the Mechanism of Formation of Spirodienone Products of Nonphenol Oxidative Coupling[1,2]

Sir:

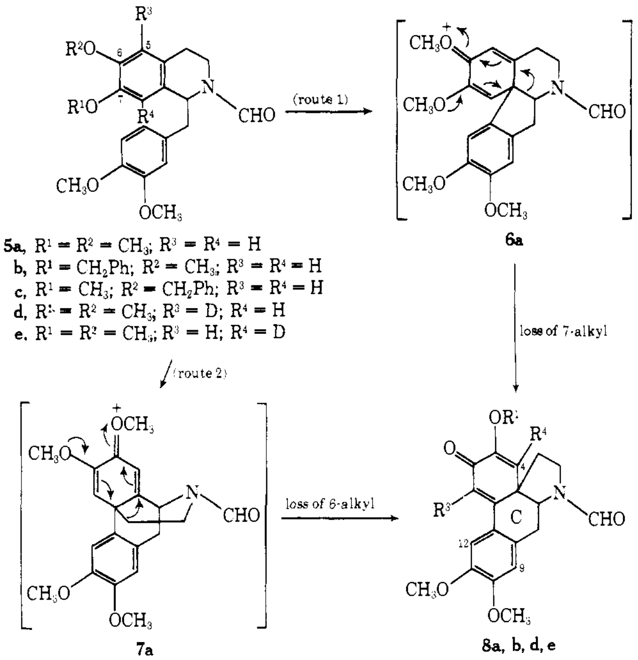
Nonphenol oxidative coupling reactions which yield spirodienone intermediates and products are currently subjects of great interest.[3-7] The first practical syntheses of this type involved electrooxidative coupling of 1-benzylisoquinolines to morphinandienones,[3-5] and the anodic cyclization of an isochroman-3-one derivative was also reported.[6] We have subsequently reported the novel chemical intramolecular coupling of nonphenolic benzylisoquinolines with vanadium oxytrifluoride in trifluoroacetic acid and have demonstrated the usefulness of the reaction for the synthesis of (±)-glaucine and the neospirinedienone **8a**.[7,8] We report herein evidence that the VOF_3–TFA oxidations of *N*-acylnorlaudanosines **5a–e** to neospirinedienones **8a–e** proceed via the intermediacy of morphinandienone intermediates. This finding has important implications for the biosynthesis of dibenzazonine and aporphine alkaloids, and facile biomimetic alkaloid syntheses based on these considerations are reported in the accompanying communication.[9]

In an extension of our studies of chemical intramolecular coupling of nonphenolic substrates, oxidation of bibenzyl **1a** with VOF_3 in TFA (Scheme I) gave the dihydrophenanthrone **4a**[10] (76%), and oxidation of **1b**[11,12] gave **4b** (68%; mp 196–198°; uv $\lambda_{\max}^{\text{EtOH}}$ (log ε) 240 (4.00), 265 (4.04), 289 (3.97), 352 (4.10) nm; ir $\lambda_{\max}^{\text{KBr}}$ 5.92, 6.06, 6.10 μ; NMR (TFA) δ 7.25, 7.09, 6.82, and 6.27 (all s, 4 H, Ar*H* and olefinic *H*), 3.96, 3.93, 3.80, and 3.67 (all s, 12 H, 4-OCH_3), 2.68 (s, 3 H, N-CH_3)). When the bibenzyl **1c**[10] was oxidized with VOF_3 in TFA, dihydrophenanthrone **4a** (75%) was obtained, an indication that these chemical coupling reactions proceed through the five-membered ring spiro intermediates **2a–c** followed by rearrangement and loss of the 5-alkyl group to give **4a** and **b**. The proposed intermediates **2a–c** are similar to the proerythrinadienone-type system (e.g., **6a**) and the rearrangement of **2a** to **4a** resembles the demonstrated acid-catalyzed rearrangement of proerythrinadienones to neospirinedienones (e.g., **8**).[13] These facts led us to consider the possibility that the formation of neospirinedienone **8a** by VOF_3–TFA oxidation of *N*-formylnorlaudanosine may occur via route 1 (**5a** → **6a** → **8a**).[7] However, route 2, via a morphinandienone-type intermediate **7a**, could not be precluded. The sequel relates the experimental evidence which demonstrates that route 2, via **7a**, is, indeed, correct.

Scheme I



Scheme II



The consequences for the two plausible routes (Scheme II) from the acylnorlaudanosines (**5a–e**) to the acylneospirinedienones (**8a, b, d, e**) differ in two significant respects: (a) route 1, via the acylproerythrinadienone intermediate, requires loss of the 7-alkyl group, whereas route 2, via the acylmorphinandienone intermediate, requires loss of the 6-alkyl group; (b) route 1 requires that the hydrogen atoms at C-5 and C-8 of the precursor **5a** be attached at C-4 and C-1, respectively, in **8a**, whereas route 2 requires that the attachment be at C-1 and C-4, respectively, in **8a**. When the 7-benzyloxy (**5b**)[14] and 6-benzyloxy (**5c**)[15] analogs of *N*-formylnorlaudanosine (**5a**) were oxidized with VOF_3–TFA, the product from **5c** was **8a** (77% yield, identical with the product obtained from **5a**). In contrast, the structure of the product (**8b**, mp 232–235°, 30% yield) obtained from **5b** showed that the benzyloxy group had been retained, indicative that both oxidations had followed route 2.

Confirmation of the intermediacy of the morphinandienone intermediate **7a** in the route from **5a** to **8a** was achieved by a study of the oxidation of the specifically deuterated analogs **5d** and **5e**.[16-19] The characterization of the