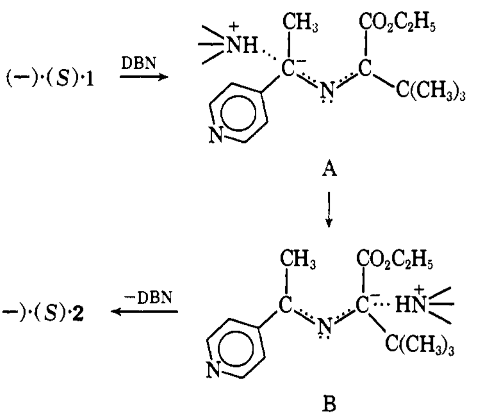

and *tert*-butyl groups maintained geometric homogeneity in **1**, **2**, A, and B. The $>$NH$^+$ group is visualized as being above the plane of the azaallylic system. (2) Isotopic exchange during isomerization dominated over intramolecularity by a factor of 4. (3) Imine **1** racemized with a large isoinversion component, probably by a conducted tour mechanism involving a symmetrical $>NH^+ \cdots N^-C_6H_4{=}C<$ stage.[7] (4) Imine **2** underwent isotopic exchange with high retention of configuration. A likely mechanism[12] involves these stages.

$$\overset{*}{R}H + RO^- \cdots DN^+< \rightleftharpoons R^- \cdots HOR \cdots DN^+< \xrightarrow[-HOR]{+DOR}$$

$$R^- \cdots DOR \cdots DN^+< \rightleftharpoons \overset{*}{R}D + RO^- \cdots DN^+<$$

The structural similarities between imines **1** and **2** and their biological analogs provide similar reaction pathways. The biological[3] and model systems both possess a stereospecific and intramolecular pathway for a *suprafacial* 1,3-proton transfer across an azaallylic anion. Both possess a stereospecific pathway for an isotopic exchange reaction (retention of configuration) between the α hydrogen of a derivative of an amino acid and the medium. The model differs from the biological system by providing competing stereochemical and isotope-labeling reaction pathways.

(12) (a) W. T. Ford and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 2606 (1968); (b) K. C. Chu and D. J. Cram, *ibid.*, **94**, 3521 (1972); (c) J. Almy, D. H. Hoffman, K. C. Chu, and D. J. Cram, *ibid.*, **95**, 1185 (1973).

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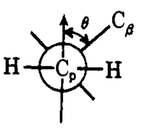
Angular Dependence of β-Carbon Atom Hyperfine Coupling Constants[1]

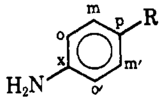
Sir:

The early observations of the epr constants, a_β^C, for β-carbon atoms in free radicals were related to carbon–carbon hyperconjugation.[2] Progress in the area has been slow, however, due to difficulties in the synthesis of ^{13}C-enriched compounds and in the spectroscopy of ^{13}C in natural abundance. Subsequent investigators have adopted eq 1 where ρ_p^π is

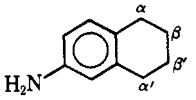


$$a_\beta^C = \rho_p^\pi(B_0^C + B_2^C\langle\cos^2\theta\rangle) \qquad (1)$$

the spin density in the adjacent p orbital, θ is the dihedral angle, and B_0^C and B_2^C are empirical constants for the analysis of their spectroscopic results.[2,3] In the absence of positive information, it has been assumed that B_0^C is near zero.[3] Curiously, the estimated values of B_2^C range from 10 to 20 G.[2c,3] The wide range may be due, in part, to reliance on data for molecules of uncertain conformation and difficulties in spectral interpretation. On the other hand, Russell and his associates have noted that the a_β^C data for semidiones do not conform to a simple $\langle\cos^2\theta\rangle$ relationship.[3b] The INDO theory[4] predicts that a_β^C for the *n*-propyl radical is linearly dependent on $\langle\cos^2\theta\rangle$, with $B_0^C = 1.1$ G and $B_2^C = 13.8$ G. These anomalies, the renewed interest in carbon–carbon hyperconjugation,[5] and the potential use of a_β^C for conformational analysis prompted us to study the contact chemical shifts of β-carbon nuclei resulting from the interaction of aniline derivatives, **1–8**, with nickel acetylacetonate[6] to establish the angular dependence in an unambiguous way.



α β
1, R = CH_2CH_3
2, R = $CH(CH_3)_2$
3, R = $CH(CH_2)_2$
4, R = $C(CH_3)_3$



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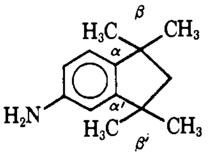

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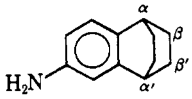

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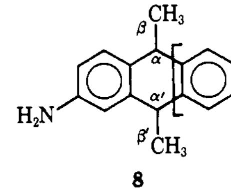

8

The resonance signals for **1–8** are readily assigned on the basis of known correlations.[7] The contact chemical shifts, σ_i^C, were measured in the usual way.[6] The shifts relative to the shift, σ_m^C, for the meta carbon atom are summarized in Table I.

The results for the aryl carbon atoms correspond well with prior work with negative values for a_x^C and

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(1) This research was supported by the National Science Foundation.

(2) (a) L. M. Stock and J. Suzuki, *Proc. Chem. Soc.*, 136 (1962); (b) M. C. R. Symons, *Tetrahedron*, **18**, 333 (1962); (c) H. Lemaire, A. Rassat, P. Servoz-Gavin, and G. Berthier, *J. Chim. Phys. Physicochim. Biol.*, 1247 (1962).

(3) (a) H. Lemaire, R. Ramasseul, and A. Rassat, *Mol. Phys.*, **8**, 557 (1964); (b) G. A. Russell, D. F. Lawson, H. L. Malkus, and P. R. Whittle, *J. Chem. Phys.*, **54**, 2164 (1971); (c) G. P. Laroff and R. W. Fessenden, *ibid.*, **55**, 5000 (1971).

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(5) (a) S. Fliszar, *ibid.*, **94**, 1068 (1972); (b) *ibid.*, **94**, 7386 (1972); (c) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *ibid.*, **94**, 6221 (1972).

(6) (a) L. M. Stock and M. R. Wasielewski, *ibid.*, **94**, 8276 (1972); (b) *ibid.*, **95**, 2743 (1973).

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Table I. Contact Chemical Shifts for Aniline Derivatives

Amine	Relative contact shifts[a]									
	C_x	C_o	$C_{o'}$	C_m	$C_{m'}$	C_p	C_α	$C_{\alpha'}$	C_β	$C_{\beta'}$
1	2.79	−1.82		1.00		−1.44	0.40		−0.77	
2	2.61	−1.46		1.00		−1.21	0.40		−0.48	
3	2.12	−1.74		1.00		−1.01	0.40		−0.56	
4	2.46	−1.48		1.00		−1.23	0.41		−0.34	
5	2.65	−1.65	−1.51	1.00	1.30	−1.41	0.46	−0.19	−0.16	0.08
6	2.65	−1.65	−1.62	1.00	1.06	−1.31	0.37	−0.15	−0.62	0.22
7		−1.52	−1.51	1.00	0.92	−1.26	0.37	−0.14	−0.65	0.22
8		−1.86	−1.58	1.00					0.016	−0.009

[a] The relative contact shifts σ_i^C/σ_m^C. The contact shift for the meta (m) carbon is positive in each case.

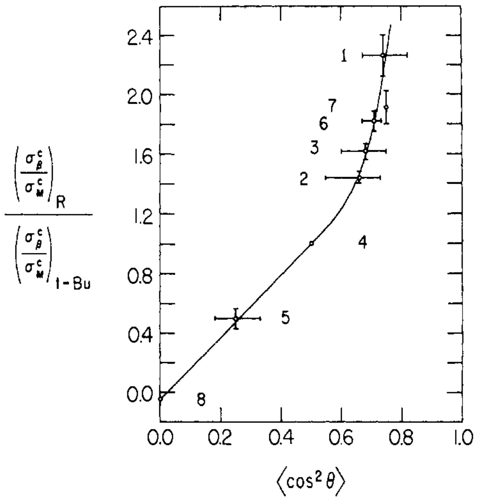

Figure 1. Relationship between contact shifts for the aniline derivatives and $\langle\cos^2\theta\rangle$ based on eq 3.

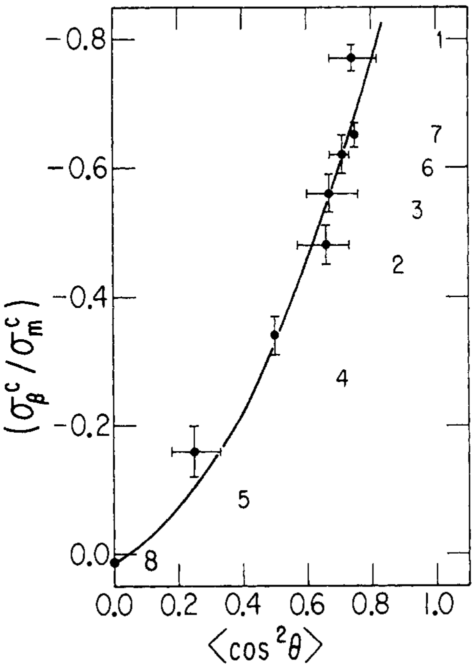

Figure 2. Relationship between contact shifts for the aniline derivatives and $\langle\cos^2\theta\rangle$ based on eq 4.

a_m^C and positive values for a_o^C and a_p^C.[8] Similarly, the negative a_α^C and positive $a_{\alpha'}^C$ are consistent with ideas concerning the spin polarization of electrons in the C_p–C_α bond by unpaired spin density in the π orbital on C_p.[9] The nickel reagent shifts the resonances of C_β in **1**–**7** downfield; thus a_β^C is positive in each case. However, in **8** C_β is shifted upfield and $C_{\beta'}$ is shifted downfield. Thus, a_β^C is negative and $a_{\beta'}^C$ is positive for $\theta = 90°$.

Two approaches have been used to test the linear dependence of the constants for the β-carbon atoms on $\langle\cos^2\theta\rangle$. Structural constraints fix θ for **5**–**8** ($30° \leq \theta \leq 90°$). For **4** θ is 45°. For **1**–**3**, $\langle\theta\rangle$ was calculated from geometrical factors based on σ_β^H. In one approach we adopted the procedure used by Geske.[10] In a first approximation, we neglect the small B_0^C term in eq 1 and adopt the view that ρ_p^π/ρ_m^π is unchanged in **1**–**8**. Thus

$$\frac{(\sigma_\beta^C/\sigma_m^C)_R}{(\sigma_\beta^C/\sigma_m^C)_{t\text{-Bu}}} = \frac{a_\beta^C}{a_{t\text{-Bu}}^C} = 2\langle\cos^2\theta\rangle \qquad (2)$$

The results are shown in Figure 1.

In the second approach, we compared the contact shifts of the β- and meta-carbon atoms. The hyperfine constant, a_m^C, is related to the spin density at the ortho, meta, and para positions and to the parameters $Q' = 32$ G and $Q'' = -14$ G, by eq 3.[11] Combination

$$a_m^C = \rho_m^\pi Q' + Q''(\rho_o^\pi + \rho_p^\pi) \qquad (3)$$

of this expression with eq 1 yields eq 4a. Data for a

$$\frac{\sigma_\beta^C}{\sigma_m^C} = \frac{\rho_p^\pi(B_0^C + B_2^C\langle\cos^2\theta\rangle)}{\rho_m^\pi Q' + Q''(\rho_o^\pi + \rho_p^\pi)} \qquad (4a)$$

$$\simeq \frac{B_2^C\langle\cos^2\theta\rangle}{-41} \qquad (4b)$$

variety of alkylanilines[6] suggest that $\rho_p^\pi \simeq \rho_o^\pi \simeq -2.3\rho_m^\pi$ to give eq 4b. The analysis based on this approach is shown in Figure 2.

Both analyses indicate that a simple linear $\langle\cos^2\theta\rangle$ dependence does not, in general, offer a satisfactory basis for the analysis of a_β^C data. Consequently, the discrepancies in the estimated values of B_2^C in earlier work stem, at least in part, from departures from eq 1. The application of eq 2 to the observations for the semidiones[3b] leads to the same conclusion.

Fessenden and Laroff have pointed out that there may be considerable torsional motions such that the estimate of $\langle\cos^2\theta\rangle$ for the β-carbon atom may be

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[8] I. Morishima, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **92**, 6651 (1970).

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[10] D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967).

[11] J. E. Wertz and J. R. Bolton, "Electron Spin Resonance Elementary Theory and Practical Applications," McGraw-Hill, New York, N. Y., 1972, p 126.

incorrect.[3c] They have also inferred that substituents may alter the value of $B_2{}^{C}$. Thus, the results for **1–4** may be influenced adversely. However, the observed relationship can also be accommodated by the view that the geometry of the alkyl group alters during rotation through angle θ. This suggestion is based on the fact that the values of $\langle\theta\rangle$ derived from $a_\beta{}^{H}$ for **1–4** do not, in general, correspond to conformations at potential energy minima. At the higher energy, steric interactions may increase the $C_pC_\alpha C_\beta$ bond angle, lengthen the C_p–C_α or C_α–C_β bond, or more likely result in some combination of these deformations to decrease $a_\beta{}^{C}$.[12] With these ideas in mind we reexamined the results shown in Figures 1 and 2. Structural constraints in **5–8** restrict C_β to conformations which minimize steric repulsions. The $a_\beta{}^{C}$ values for **5–8** very nearly conform to linear relationships. The data for **1–4** deviate from these relationships. However, these deviations may be related to structural deformations which are more significant for the cyclopropyl, isopropyl, and *tert*-butyl groups in **2–4** than for the ethyl group in **1**. Further study will be necessary to verify these suggestions.

(12) The $C_pC_\alpha C_\beta$ angle may decrease when θ is small. This decrease may be attributed to steric factors or to electron transfer mechanisms; see, *e.g.*, P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

(13) Fannie and John Hertz Foundation Fellow at The University of Chicago.

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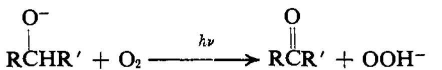
Oxidation of Alkoxides to Carbonyl Compounds by Singlet Oxygen[1]

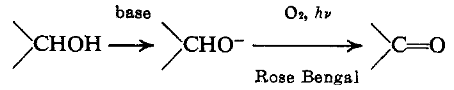
Sir:

Singlet oxygen has been shown to react with nucleophilic substrates such as olefins,[2] amines,[3] sulfides,[4] and carbanions,[5] to produce products which vary with the nature of the substrate. We have now found that primary and secondary alkoxide ions are readily converted to aldehydes and ketones by dye-sensitized photooxidation.[6,7] The results are summarized in Table I.



$$\mathrm{R\overset{O^-}{\overset{|}{C}}HR'} + O_2 \xrightarrow[\text{Rose Bengal}]{h\nu} \mathrm{R\overset{O}{\overset{\|}{C}}R'} + OOH^-$$

Table I. Photooxidation of Alkoxide Ions[a]



$$\rangle\mathrm{CHOH} \xrightarrow{\text{base}} \rangle\mathrm{CHO^-} \xrightarrow[\text{Rose Bengal}]{O_2,\ h\nu} \rangle\mathrm{C{=}O}$$

Product	Base	Temp, °C	Yield, %
Acetone	Na	6–8	100[b]
2-Butanone	*t*-BuOK	10	100[b]
Cyclohexanone	*t*-BuOK	25–27	97[c]
Benzophenone	KOH[d]	25–26	91[e]
Formaldehyde	NaOH	2–5	61[c]
Acetaldehyde	NaH	2–5	84[c]
Butyraldehyde	NaH	2–5	61[c]
Benzaldehyde	NaH	2–4	99[c]

[a] Except where noted, excess of corresponding alcohol used as a solvent, and moles O_2 used = moles base. [b] Nmr analysis. [c] Isolation as 2,4-dinitrophenylhydrazone; some loss of yield owing to solubility in aqueous methanol medium used. [d] Mole ratio, 2.0 KOH:1.0 benzhydrol:0.50 O_2, *t*-BuOH solvent. [e] Direct isolation.

In a typical reaction, a solution of 15.0 mmol of sodium isopropoxide in 115 ml of isopropyl alcohol containing 6 mg of Rose Bengal was irradiated internally by a 650-W DWY lamp operated at 100 V; 15.40 mmol of oxygen was absorbed within 55 min at 6–8°. Nmr analysis, using toluene as an internal standard, showed the presence of 15.0 mmol of acetone (2,4-DNP, mp 127–128°). The mixture was filtered under dry nitrogen, and the unstable, hygroscopic white residue was washed with isopropyl alcohol and dried *in vacuo* for 1 hr: Calcd for NaOOH: oxidation equivalent, 28.0; neutralization equivalent, 56.0. Found: oxidation equivalent, 31.9; neutralization equivalent, 59.4.

First-order dependence of the oxidation rate on isopropoxide ion was shown by a linear plot of log [(initial moles of RO^-) − (moles of O_2 consumed)] *vs.* time for a constant temperature run at 9°. The intermediacy of singlet oxygen was indicated by the fact that the initial rate of oxygen uptake by a 1.5×10^{-2} *M* isopropoxide solution containing either of the specific singlet oxygen quenchers β-carotene[8] (3×10^{-4} *M*) or 1,4-diazabicyclo[2.2.2]octane[8,9] (5×10^{-2} *M*) was 30–40% of the rate observed in the absence of added quenchers. Under our conditions, oxidations of alcohols were never observed in the absence of either base, light, or sensitizer.

While secondary alcohol solutions became neutral after absorption of 1 equiv of oxygen and uptake of oxygen diminished to a negligible rate, primary alcohol solutions remained basic and continued to be oxidized at a moderate rate. This behavior may be related to a higher solubility of the basic sodium hydroperoxide in the more acidic[10] primary alcohols.

Photooxidation of primary alkoxides was complicated by the second-stage chemical oxidation of the initially formed aldehydes in the peroxidic reaction mixture. High conversion to carboxylate salts was observed after reaction mixtures from methoxide and ethoxide were allowed to stand for a few hours. The yields of aldehydes reported in Table I were achieved by photooxidation at low temperatures, followed by quenching with acidic dinitrophenylhydrazine solution.

Considering the electrophilic nature of singlet oxygen,

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(1) Work done on sabbatical leave at Yale University, 1972.

(2) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, **90**, 975 (1968).

(3) W. F. Smith, Jr., *J. Amer. Chem. Soc.*, **94**, 186 (1972); M. H. Fisch, J. Gramain, and J. A. Oleson, *Chem. Commun.*, 663 (917); G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).

(4) C. S. Foote and J. W. Peters, *J. Amer. Chem. Soc.*, **93**, 3795 (1971).

(5) R. H. Young and H. Hart, *Chem. Commun.*, 827 (1967); R. H Young, *ibid.*, 704 (1970); D. Bethell and R. G. Wilkinson, *ibid.*, 1178 (1970).

(6) The oxidations are generally accompanied by the formation of a white precipitate of alkali metal hydroperoxide except in methanol in which the alkali metal hydroperoxides are soluble.

(7) Earlier related work (*e.g.*, G. O. Schenck and H. D. Becker, *Angew. Chem.*, 70, 504 (1958); G. O. Schenck, H. D. Becker, K. H. Schulte-Elte, and C. H. Krauch, *Ber.*, 509 (1963)) was concerned with photooxidation of alcohols using benzophenone as sensitizer. These studies were carried out in the absence of base and the products were α-hydroxy hydroperoxides. The mechanism, which seems to be well accepted, appears to involve reaction of oxygen with radicals produced by abstraction of hydrogen by triplet sensitizer.

(8) C. S. Foote, R. W. Denny, L. Weaver, Y. C. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, 171, 139 (1970).

(9) C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, 90, 6527 (1968); R. H. Young and R. L. Martin, *ibid.*, **94**, 5183 (1972).

(10) J. Hine and M. Hine, *J. Amer. Chem. Soc.*, **74**, 5266 (1952).