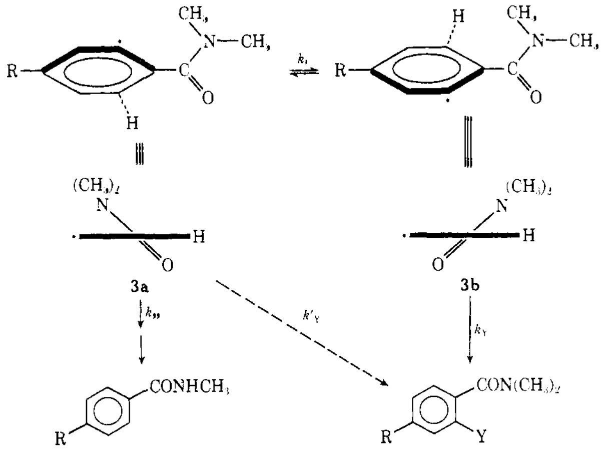
hydrogen transfer must then be close to the extreme of case A.

The large decreases in apparent isotope effects for 2 and 3 are not due to surprisingly large substituent and solvent influences, respectively, on the actual isotope effect for hydrogen transfer, since the corresponding diazonium salts labeled with two deuterium atoms in each methyl group (d_4) exhibit isotope effects in the appropriate solvents which are identical, within experimental error, with that of the tetradeuterated **1** (R = H) in water.[3,8] These are thus examples which are intermediate between cases A and B. In each of these two examples, one species must be undergoing predominant or exclusive external transfer while another must be undergoing predominant internal hydrogen atom transfer.

The most likely pair of species is **3a** and **3b** (only one enantiomer of each is shown) which are probably the two stable conformers of the intermediate radical about the CC bond. This latter assertion is based on (a) the crystal structures of benzamide and some analogs in which the aryl rings are canted from the plane of the amido groups by angles of 26–38°,[9] (b) evidence that various benzamides are nonplanar from spectroscopy,[10] complexing studies,[11] and model construction (the Fisher–Hirschfelder model of the coplanar form of *N*,*N*-dimethylbenzamide cannot be constructed even when one ortho hydrogen is removed), and (c) the expectation that the conformer in which the plane of the ring is perpendicular to that of the amido group is at an energy maximum due to the loss of resonance stabilization.



When R = OMe in aqueous cupric chloride or R = H in methanol, internal H transfer occurs from **3a** (the rate constant k_H probably involves the constant for bond rotation into a planar or nearly planar form as well as that for actual atom transfer), whereas Cl or external H transfer occurs in **3b**, although some external transfer from the more hindered **3a** cannot be ruled out. In these two reactions k_r is apparently of the same order of magnitude as k_H. The conversion of **3a** to **3b** requires the attainment of the perpendicular form in which resonance interaction between the ring and carboxamido group is minimized. Thus, the electron-donating *p*-methoxy substituent, by increasing this resonance stabilization, may decrease k_r.[12] It may also increase k_H by increasing the ease of achieving coplanarity.[12] A related explanation of the effect of this substituent is that it may decrease the average angle between the planes, thus, by steric hindrance, decreasing the contribution of k'_Y to the external transfer.

Studies on solvent and substituent effects in this system are planned. The application of this type of isotope effect study to other systems is well under way.

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by a factor S^2. The secondary effect then has the value of 1.2, which is in agreement with other α-secondary deuterium isotope effects in which a quaternary carbon is being converted to a trigonal carbon at that temperature.[7]

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(13) National Science Foundation Trainee.

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The Question of the Divergent Behavior of Singlet and Triplet Excited States of β,γ-Unsaturated Ketones. An Explanation Based on Spin Distribution[1]

Sir:

It has been demonstrated in several studies that cyclic and acyclic β,γ-unsaturated ketones show different reactions on direct, as contrasted with triplet-sensitized photolysis.[2–4] On direct irradiation a [1,3]-sigmatropic shift of the acyl group occurs to give an isomeric β,γ-unsaturated ketone.[5] The efficiency at this reaction normally is not reduced in the presence of typical triplet quenchers.[2–4,6]

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(1) The Application of Simple Theoretical Methods to the Solution of Chemical Problems. V. Paper IV: G. R. Underwood and V. L. Vogel, *J. Amer. Chem. Soc.*, **93**, 1058 (1971). This is also Part XXX of "The Photochemistry of Ketones in Solution." Part XXIX: D. I. Schuster, K. V. Prabhu, S. Adcock, J. van der Veen, and H. Fujiwara, *J. Amer. Chem. Soc.*, **93**, 1557 (1971).

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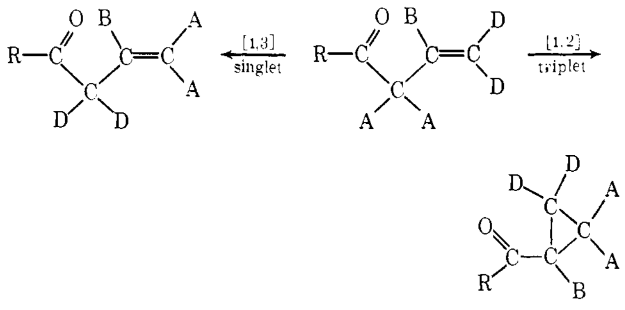
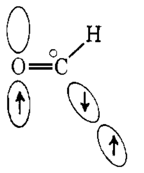
(5) This reaction has been known for some time, but only recently has it attracted mechanistic investigations. See, *e.g.*, G. Büchi and E. M. Burgess, *ibid.*, **82**, 4333 (1960); D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963); W. F. Erman and H. C. Kretschmar, *J. Amer. Chem. Soc.*, **89**, 3842 (1967).

(6) The sole exception appears to be a bicyclo[3.2.0]hept-6-en-2-one where quenching of the 1,3-sigmatropic shift is observed and triplet energy transfer has been established.[7] Since the Stern–Volmer plot levels off at high quencher concentrations, it has been proposed that this [1,3] rearrangement occurs from both singlet and triplet excited states.[7] However, it now seems probable that the triplet excited state does take a different course to produce a thermally unstable cyclopropane[3] which would not have been detected under the analytical conditions used in the earlier study.[7] In this case, unlike other β,γ-unsaturated ketones,[2–4] intersystem crossing to give triplets is a significant process.

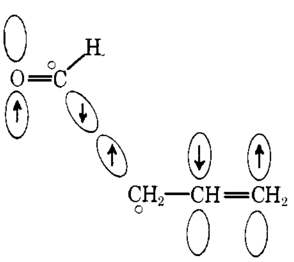
The triplet-sensitized photolysis of these systems, however, takes a different course resulting in a [1,2] shift of the acyl group and the formation of a substituted cyclopropane.[2-4] Givens[8] and Dauben[4] have pointed out the mechanistic relationship of this reaction to the di-π-methane rearrangement.[9] None of the cyclopropyl compound is formed on direct photolysis, indicating that there is negligible intersystem crossing in these compounds from the singlet to the triplet manifold.[6] Since no explanation has yet been given for the differences in behavior of the singlet and triplet excited states of these β,γ-unsaturated ketones, we have examined this equation in light of spin delocalization mechanisms developed in these laboratories[1,10] and elsewhere[11] and propose a possible explanation based upon a consideration of the spin density distribution.



Since the singly occupied π^* molecular orbital is orthogonal with the local σ framework and thus exerts a relatively small spin polarization effect on the latter, it is reasonable that spin polarization of the σ framework results primarily from interaction with the singly occupied p_y orbital on oxygen. The orientation of the C_{co}–C_α bond is optimal for a hyperconjugation spin delocalization mechanism to be operative. By arbitrarily assigning α electron spin to the p_y orbital, hyperconjugation results in the following partial spin distribution. This type of interaction is probably responsible for α cleavage reactions.[12]



The allyl residue is likewise spin polarized[13] with a small excess of β spin at C_β and an excess of α spin at C_α and C_γ. This type of spin distribution is well established from esr and theoretical studies of the allyl radical.[13,14] This description does not imply that there is a dissociation into two radicals, merely that these resonance structures contribute to the overall spin-density distributions of the species. In fact there is good experimental evidence against dissociation into two species.[8]



Having established the spin distribution in the noncarbonyl moiety of the excited state, we now include the π^* electron and, to account for the different products obtained from the singlet and triplet excited states, we make the following proposal: the new bond formed between the carbonyl carbon and the remainder of the molecule is formally produced by electron pairing between the π^* electron on the carbonyl carbon and electron spin density of opposite sign on one atom of the olefinic system. We do not suggest complete bond formation at this stage, merely that the reaction coordinate is influenced by the two relative spin densities and that the diradical is committed to reaction at either C_β or C_γ while still in the initial excited spin state. Thus if the carbonyl π^* electron is of α spin (triplet state), migration of the acyl group to C_β where there is an excess of β spin in the olefinic π orbital should be anticipated. During this process we envisage an increasing interaction between the p_y electron and one of the C_{co}–C_α electrons (of opposite spin) with consequent weakening of this bond. Ultimately this might be regarded as the new π bond. At some stage spin inversion to the singlet must occur, but at this point we can make no statement as to the timing of this process.

Likewise if the π^* electron is of β spin (singlet state) we would anticipate favored migration to C_γ.

To test the plausibility of these arguments we have performed INDO–MO calculations to determine spin density distributions in some relevant systems.[15] The p orbital spin densities are shown in Figure 1, where the + sign represents an excess of α spin density and − represents excess β spin. Because of certain computational difficulties we have not performed calculations on the singlet excited state. However, calculations on model structures B and C in Figure 1 serve well to illustrate our arguments.[16] The particular conformations used were chosen such that the carbonyl oxygen was as far away as possible from the C═C bond to reduce any direct interaction which would unjustifiably favor our argument. It will be noticed that the spin densities calculated for the triplet state are in excellent agreement

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(15) Standard bond lengths and bond angles of the ground-state molecules were used.

(16) The singlet diradical may be regarded as having a π^* electron of α spin and an unpaired n electron of β spin localized mostly on oxygen. Figure 1B demonstrates the expected spin distributions in the relevant orbitals which result from an α electron in π^*. Likewise from Figure 1C we can deduce what would be the effect on the electron spin distribution of an unpaired electron of β spin in the n orbital of oxygen: it would induce spins of opposite, like, opposite, and like sign, respectively (*viz.*, α, β, α, β) as we proceed along the chain. Consequently, both factors would produce the same effect and one which is in direct opposition to that obtained for the triplet state (Figure 1A). One could even note that in Figure 1A where the two electrons oppose one another, the spin densities are semiquantitatively what would be predicted from the simple summation of results of Figures 1B and 1C.

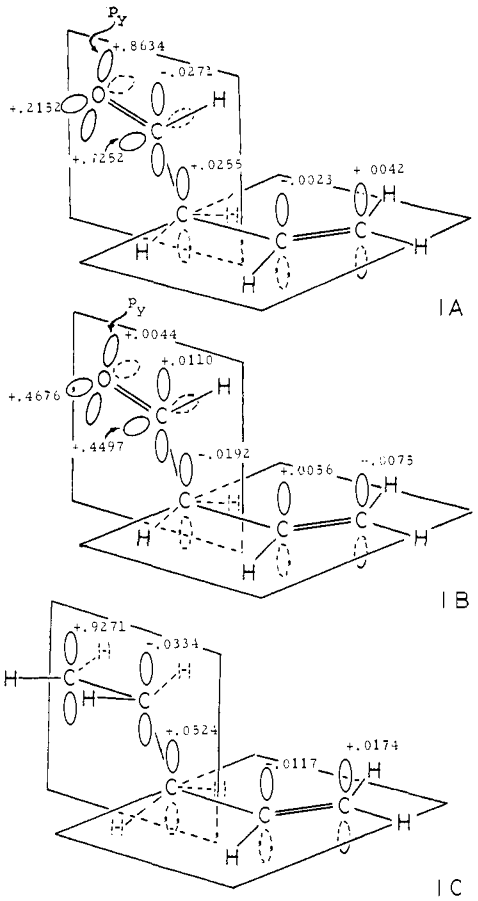

Figure 1. INDO p orbital spin densities calculated in (A) the triplet diradical, (B) the ketone radical anion, and (C) the pent-4-en-1-yl radical. Note that in 1A and 1B the nonbonding p orbital on oxygen is perpendicular to the O–C bond and is not exactly parallel with the p orbitals of the olefin system.

with those predicted by the simple arguments above and are also in accord with those calculated for the pent-4-en-l-yl radical (Figure 1C). This latter radical serves as our model for estimating the effect of an unpaired p electron on the spin distribution in the σ framework. In order to isolate the effect of a single carbonyl π^* electron on the spin distribution in the σ system, in the presence of a p_y electron pair on oxygen, calculations were also performed for the ketone radical anion. It is noted that in this case, the magnitude of spin density induced in the σ system is much reduced and the signs are in complete disagreement with the other systems.

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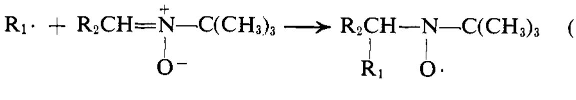
Spin Trapping of Short-Lived Free Radicals by Use of 2,4,6-Tri-*tert*-butylnitrosobenzene

Sir:

The detection and identification of short-lived free radicals by electron spin resonance trapping techniques ("spin trapping") has recently received wide attention. Stable nitroxide radicals ("spin adducts") can be formed by radical addition to *C*-nitroso compounds (eq 1)[1] and nitrones (eq 2)[2] ("spin traps"). Previously, we utilized reaction 1 to detect and identify free radicals as reaction

$$R_1\cdot + R_2N{=}O \longrightarrow R_1R_2NO\cdot \qquad (1)$$



$$R_1\cdot + R_2CH{=}\underset{\displaystyle |\atop O^-}{\overset{+}{N}}{-}C(CH_3)_3 \longrightarrow R_2\underset{\displaystyle |\atop R_1}{CH}{-}\underset{\displaystyle |\atop O\cdot}{N}{-}C(CH_3)_3 \qquad (2)$$

intermediates in nickel peroxide oxidations.[4] Janzen[3] made a comparison of the effectiveness of different spin traps and pointed out that of the spin traps used (nitroso compounds and nitrones) certain advantages and certain disadvantages exist for each. Of interest is a recent report[5] that α-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitrone is useful as a novel "bifunctional" trap.

We wish to report some of our observations on spin trapping using 2,4,6-tri-*tert*-butylnitrosobenzene (**1**), which was prepared by the oxidation of 2,4,6-tri-*tert*-butylaniline with *m*-chloroperbenzoic acid.[6] The purpose of this choice of spin trap was to get a simple spectrum for elucidation and to examine the steric effects in this reaction. The generation of radicals was achieved either by the abstraction of hydrogen from substrates by *tert*-butoxy radicals (formed by photolysis of di-*tert*-butyl peroxide or by thermolysis of di-*tert*-butyl peroxyoxalate) or by the abstraction of halogens from alkyl halides by the tri-*n*-butyltin radical.

The spin adducts produced with primary alkyl radicals were the same as those produced by the normal type of addition to ordinary nitroso spin traps. The values of the hyperfine splitting constants for nitroxides are shown in Table I (note that another spin adduct of isopropyl radical will be described later). Since the β-methylene hydrogen couplings vary with the kind of the group in the γ position, the structure of the attacking radical can be distinguished. Of interest is the finding that the order of the β-hydrogen couplings of the nitroxides is secondary > primary > methyl, in contrast to that found in the usual nitroxides,[7] presumably because of steric repulsion between the groups at the γ position and the *tert*-butyl groups of the benzene ring.

Upon heating azobisisobutyronitrile (AIBN) in benzene in the presence of **1**, the esr spectrum of a 1:1:1 triplet of 1:2:1 triplets was observed. This spectrum is different from those of the nitroxides because of the small *g* value, the small nitrogen coupling, and the large meta hydrogen coupling (see Table II). To help in the structural assignment of this spectrum, 2,4,6-tri-*tert*-butylaniline in benzene was oxidized with nickel per-

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