Table I. Effect of 1 on Enantiotropic Protons of RCH_2OH[a]

R	PS,[b] ppm	Mole ratio (1/ RCH_2OH)	J_{AB}, Hz	$\Delta\nu_{AB}$,[c] ppm
Ph	6.63	0.15	13.0 ± 0.2	0.13
Ph	10.03	0.21	13.0 ± 0.2	0.19
Ph	11.72	0.28	12.9 ± 0.2	0.22
Ph	15.29	0.38	12.5 ± 0.3	0.26
4-CNPh	12.18	0.30	14.5 ± 0.5	0.12
4-CF_3Ph	10.58	0.27	14.0 ± 0.2	0.15
4-FPh	10.21	0.26	13.2 ± 0.2	0.08
4-CH_3Ph	9.48	0.23	12.8 ± 0.2	0.15
4-CH_3OPh	11.31	0.22	13.0 ± 0.4	0.11
4-$N(CH_3)_2$Ph	8.74	0.22	12.5 ± 0.4	0.09
t-Bu	11.06	0.27	12.0 ± 0.5	0.12

[a] All spectra were measured on a Varian HA-100 spectrometer at 26° using 0.2 *M* solutions of the alcohol in CCl_4. Coupling constants are reported as the average of at least eight determinations with the quoted uncertainty representing the standard deviation. [b] PS represents the upfield shift induced by addition of 1. [c] $\Delta\nu_{AB}$ represents the nonequivalence of the enantiotropic protons.

The 12.0-Hz geminal coupling constant in neopentanol is 1.6 Hz larger than the value of 10.4 Hz calculated[8] from the 1.6-Hz H–D coupling constant in α-deuterioneopentanol.[9] This descrepancy can result from residual effects of deuterium relaxation,[10] an isotope effect on J_{H-D},[8] or both. From the line width (>1 Hz) in the published spectra it appears likely that relaxation effects are influencing their measurement of J_{H-D}.

In order to determine the isotope effect of deuterium substitution on ^2J, we have examined the nmr spectrum of a 1:3 mixture of benzyl methyl sulfoxide and its stereoselectively labeled[11] α-deuterio derivative in acetone. The effect of nuclear quadrupole relaxation on the H–D splittings was shown to be nil by measuring[6] J_{H-D} at 34 and 45°. At both temperatures the line widths for the triplet were 0.6 Hz and J_{H-D} was 1.92 ± 0.01 Hz. The value for J_{H-H} was 12.97 ± 0.02 Hz. Thus, the discrepancy between J_{H-H} (measured) and J_{H-H} (calculated, *i.e.* 1.92 × 6.514 = 12.51 Hz) is 0.46 Hz. This value represents an accurate assessment (±0.2 Hz) of the isotope effect on J_{H-H}. This effect, though probably constant, must be investigated further.

Addition of 1 to solutions of benzylamine, dibenzylnitrosamine, and allyl alcohol failed to effect a resolution of the signals for the enantiotropic protons. However, in the only two cases studied, enantiotropic methyl groups were distinguishable. The methyl groups of dimethyl sulfoxide showed a nonequivalence of 0.17 ppm in the presence of 0.34 equiv of 1 while those of 2-propanol possessed a nonequivalence of 0.04 ppm in the presence of 0.27 equiv of 1, both measured in CCl_4. It can be concluded from the above results that chiral shift reagents offer a potent method for distinguishing nmr signals of internally enantiotropic groups.

It seems likely that 1 and future chiral reagents of improved potency will be of great use in the determination of geminal coupling constants and in the solution of complex stereochemical problems.

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Robert R. Fraser,* Michel A. Petit, Maurice Miskow
Department of Chemistry, University of Ottawa
Ottawa, Canada K1N 6N5

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son with those previously measured in conformationally fixed benzyl ethers [R. R. Fraser and R. Renaud, *Can. J. Chem.*, **49**, 755 (1971)] is evidence that the dominant conformation about the CH_2–Ph bond is the one in which the oxygen atom lies in or nearly in the plane of the benzene ring.

(8) It has generally been assumed that a geminal J_{H-H} can be determined by isotopic substitution of one H by D in which case the measurable J_{H-D} multiplied by γ_H/γ_D (6.514) equals J_{H-H} (see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 188). This assumption neglects changes in electron distribution resulting from the isotopic substitution.

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Nitrogen-Centered Free Radicals. IV. An Electron Spin Resonance Study of Transient Dialkylaminium Radical Cations[1]

Sir:

Transient dialkylaminium radical cations, $R_2\dot{N}H^+$, are of interest to chemists not only because they are isoelectronic with alkyl radicals but also because these species are finding increasing use as chain-carrying intermediates in novel synthetic applications.[2–5] We presently wish to report the high-resolution electron spin resonance (esr) spectra of several dialkylaminium radical cations generated by photolysis of sulfuric acid solutions of the corresponding *N*-chloramines directly in the cavity of the esr spectrometer.[6,7] Results are reported in Table I along with the corresponding neutral dialkylamino radicals which we have reported previously.[9] Representative spectra are shown in Figure 1; satisfactory computer simulations have been obtained for all radicals.

$$R_2NCl \xrightarrow[H_2SO_4]{h\nu} R_2\dot{N}H^+$$

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(6) A PEK AH6-2B, 2000-W, high-pressure mercury capillary lamp was utilized in conjunction with a suitable lens system.

(7) Neta and Fessenden have recently postulated the formation of dimethylaminium and aziridinium radical cations by high-energy electron irradiation of acidic solutions of trimethylamine and dimethylamine, respectively,[8] Although the coupling constants attributed to $(CH_3)_2\dot{N}H^+$ differ considerably from the values herein reported, subsequent investigations by these workers revealed a misinterpretation of spectra and that $(CH_3)_3\dot{N}^+$ and $(CH_3)_2\dot{N}H^+$ were instead being produced from the respective amines (private communication from R. W. Fessenden).

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Table I. Hyperfine Splitting Constants and g Values for Dialkylaminium Radical Cations in 90% Sulfuric Acid Solution at 31 ± 1°[a]

Radical	a^N	a_{NH}^H	a_β^H	a_γ^H	g value[b]
$(CH_3)_2NH^+$	19.28	22.73	34.27		2.0036
$(CH_3CH_2)_2\dot{N}H^+$	18.65	22.24	37.19	c	2.0036
$(CH_3CH_2CH_2)_2\dot{N}H^+$	18.58	21.81	32.41	c	2.0036
$[(CH_3)_2CH]_2\dot{N}H^+$	18.7	22.5	21.7	0.80	2.0036
$(CH_3)_3CN\overset{+}{H}CH_3$	19.2	22.2	34.5	0.71	2.0036
$(CH_3)_2ND^{+}$[d]	19.3	3.52[e]	34.5	c	2.0036
$(CH_3CH_2)_2\dot{N}D^{+}$[d]	18.7	3.44[e]	37.5	c	2.0035
$(CH_3)_2N\cdot$[f]	14.78		27.36		2.0044
$(CH_3CH_2)_2N\cdot$[f]	14.27		36.90	c	2.0044
$[(CH_3)_2CH]_2N\cdot$[f]	14.31		14.31	0.66	2.0042

[a] Hyperfine splitting constants and g values relative to Fremy's salt taken as 13.091 G and 2.0055, respectively. Accuracy of coupling constants limited to an estimated ±0.7% by reproducibility of V4502 spectrometer under experimental conditions. [b] Corrected for second-order effects; estimated accuracy ±0.0001. [c] Not resolved; <0.2 G. [d] 90% D_2SO_4–10% D_2O solvent. [e] Deuterium coupling. [f] Reference 9; spectra obtained at −90°.

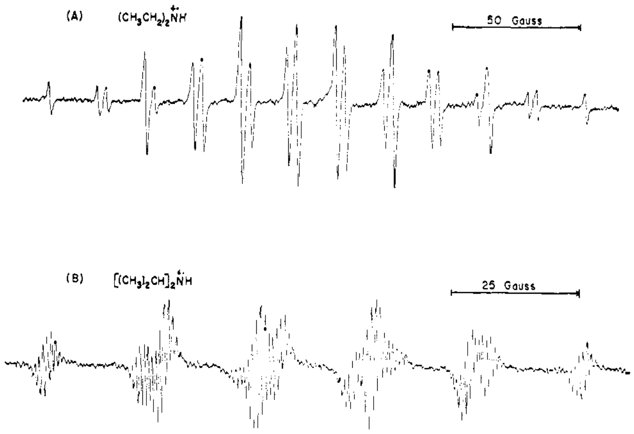
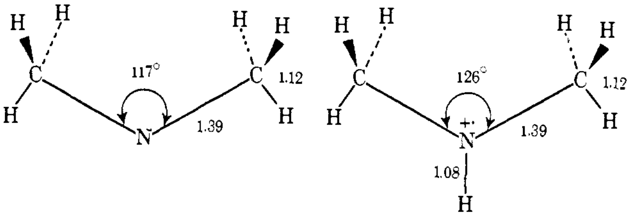


Figure 1. Esr spectra of (A) diethylaminium radical cation and (B) diisopropylaminium radical cation in 90% H_2SO_4 solution at room temperature.

Several features may be noted when dialkylaminium radical cations are compared to the corresponding neutral dialkylamino radicals. (a) The nitrogen coupling is significantly larger in the radical cations. A similar effect was noted for $\cdot NH_2$ *vs.* $\dot{N}H_3^+$ and several different explanations have been advanced.[10,11] The enhanced a^N values for the cation radicals do not appear to result from any degree of nonplanarity, however. It has been concluded that $\dot{N}H_3^+$ is planar[12,13] and INDO calculations predict a planar structure for $(CH_3)_2\dot{N}H^+$ (see below). Moreover, the a^N/a_{NH}^H ratio for the present radicals is reasonably constant at 0.84 ± 0.02 which is quite similar to the 0.76 ratio observed for $\dot{N}H_3^+$[12] and the value of 0.84 obtained for a variety of diarylaminium radical cations.[14] It is anticipated that this ratio should be quite sensitive to the configuration of these radicals and increase with increasing deviation from planarity. It may be noted that the deuterium coupling, a_{ND}^D, is within experimental error of that expected from a_{NH}^H when allowing for the different nuclear moments and spin. The a^N is not affected within experimental limits by deuteration, although a^N decreases by *ca.* 2 G in going from $\dot{N}H_3^+$ to $\dot{N}D_3^+$.[10] A much attenuated effect is anticipated in the present dialkylaminium radicals because the relatively massive alkyl groups do not allow an out-of-plane bending vibration to contribute significantly to a^N.

(b) The methyl hyperfine interaction in $(CH_3)_2\dot{N}H^+$ is significantly larger than the corresponding interaction in $(CH_3)_2N\cdot$. This result can be understood in terms of the relationship developed by Bolton, Carrington, and McLachlan to explain the variation in $Q_{CCH_3}^H$ between various aromatic radical cations and anions.[15] Basically, β-hydrogen hyperconjugation is more effective in a positively charged radical because of a better matching of the energies of the 2p orbital possessing the unpaired spin and the appropriate C–H orbital. Our studies of simple nitrogen-centered radicals suggest Q_{NCH}^H values of 32.7 and 42.9 G for neutral dialkyamino radicals and dialkylaminium radical cations, respectively, for the relationship $a_\beta^H = Q_{NCH}^H \cdot \rho_N$.[16]

(c) The β-hydrogen coupling constants in the diethyl- and diisopropylaminium radicals differ by only +9 and −37%, respectively, from that observed for the freely rotating methyl groups in the dimethylaminium radical cation. These may be compared with analogous differences of +35 and −48% for the neutral diethyl- and diisopropylamino radicals indicating a less pronounced conformational preference in the charged radicals. The reason for the lower barrier to rotation about the C–N bond in the aminium radical cations is apparent from a comparison of the INDO energy-minimized structures for $(CH_3)_2N\cdot$ and $(CH_3)_2\dot{N}H^+$.



It is noted that the CNC angle is 9° larger in the charged radical allowing for greater ease of rotation in the case of the diethyl- and diisopropylaminium radicals and bringing the time-averaged a_β^H values closer to the value for the freely rotating methyl group.[17] The INDO calculations predict $a^N = 16.7$, $a_{NH}^H = -25.2$, and $a_{CH_3}^H = 28.7$ G for $(CH_3)_2\dot{N}H^+$ in reasonable agreement with experiment.

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(16) These values are calculated from the observed methyl splittings in the dimethylamino radical and the dimethylaminium radical cation and the INDO calculated nitrogen 2p spin densities for these radicals (0.8370 and 0.7996, respectively).

(17) This requires the reasonable assumption that similar changes in the CNC angles occur for the diethyl and diisopropyl species. The higher temperature at which the spectra of the radical cations were recorded would also tend to diminish the difference between the β hydrogens for this series. We have shown, however, that the β-hydrogen coupling in the diisopropylamino radical is practically invariant over the temperature range −120 to +30°.

We are presently investigating a wide variety of aminium radical cations.

Acknowledgments. We are indebted to Professor N. C. Deno of Pennsylvania State University for suggesting this method of generating the dialkylaminium radicals. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. PRF 5579-AC4), for support of this work. Thanks are also due to Kansas State University for assistance in defraying computing costs.

Wayne C. Danen,* Robert C. Rickard
Department of Chemistry, Kansas State University
Manhattan, Kansas 66502
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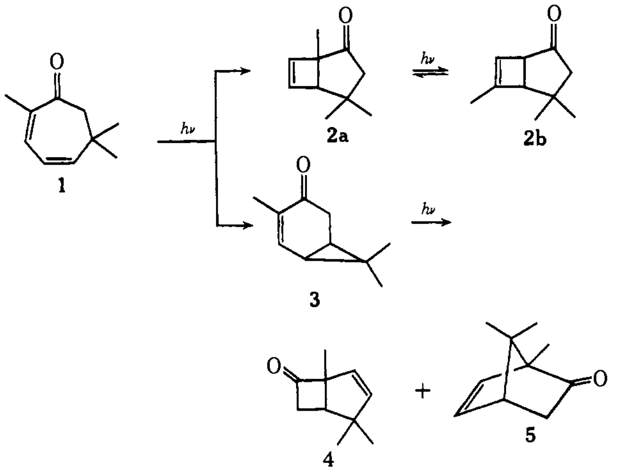
Photoisomerization of 2,7,7-Trimethyl-2,4-cycloheptadienone

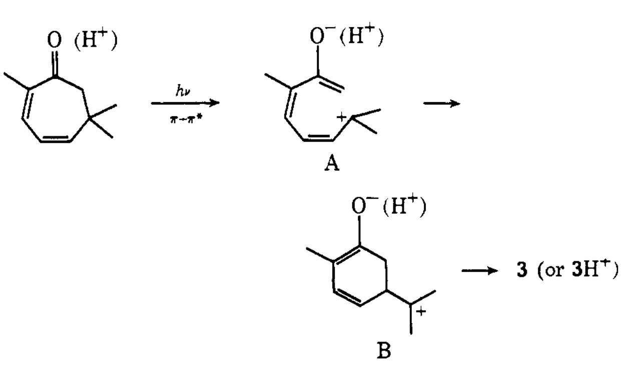
Sir:

We wish to report a previously unobserved type of photoisomerization of conjugated cycloheptadienones, and to call attention to the important role which alkyl substituents may play in determining product structure.

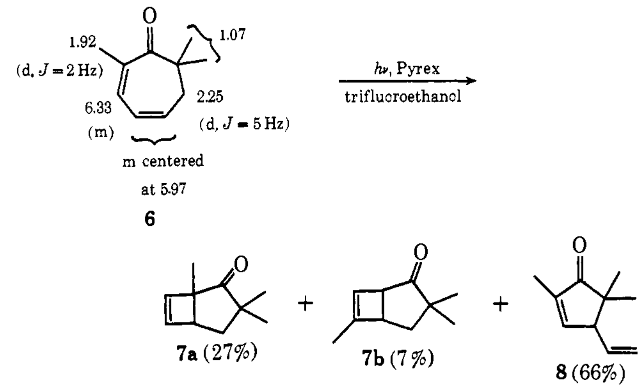
Eucarvone (**1**), long considered the prototype for cycloheptadienone photoisomerizations,[1] rearranges primarily by two paths as shown.[1e] Nonpolar solvents favor **2a** and **2b**, whereas polar solvents favor **3**–**5** suggesting that these two sets of products are derived from two close-lying excited states, n–π^* and π–π^*, respectively. Credibility was lent to this suggestion by the finding[1f] that protonated **1** (1H$^+$), which of necessity reacts from a π–π^* excited state, gave mainly 3H$^+$.



Plausible mechanisms[1e,1f] for the formation of **3** (or 3H$^+$) from **1** (or 1H$^+$) involve intermediates (such as A and B) which place a positive charge on the carbon which bears the *gem*-dimethyl group. It seemed possible that **3** and related products were therefore not necessarily characteristic of all cycloheptadienones, but only of those with substituents at C-6 which stabilize carbonium ions. To test this possibility, we synthesized and irradiated a cycloheptadienone with a *gem*-dimethyl group at C-7, rather than at C-6.



2,7,7-Trimethyl-2,4-cycloheptadienone (**6**) was synthesized from cycloheptanone in an unexceptional manner.[2] Irradiation of **6** in cyclohexane through Pyrex (450-W Hanovia lamp) was slow, and gave a mixture of three products, **7a**, **7b**,[3] and **8**,[4] each of which was isomeric with the starting material. No products resulting from α cleavage were observed, despite the



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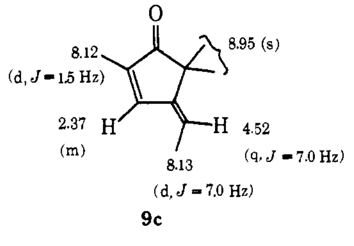
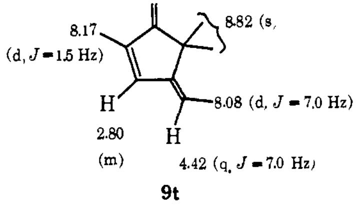
[2] Synthetic, structural, and analytical details will be presented in a full paper.

[3] The structures of **7a** and **7b** rest on their spectra and on their photochemical interconversion.

[4] Ir 1705, 1640 (cyclopentenone), 930 cm^{-1} (terminal methylene); uv 344 nm (ϵ 45), 330 (60), 317 (50), 275 (143), 225 (93,700); nmr δ 0.87, 1.07 (s, 3 H each, *gem*-dimethyls), 1.75 (d of d, 3, J = 1.8, 2.5 Hz, allylic methyl split by protons at C-3 and C-4, respectively), 3.03 (d split into quintets, 1, J = 8.0, 2.5 Hz, methine split by the adjacent proton of the C-4 vinyl group and by the C-2 methyl and C-3 vinyl protons, respectively), 4.6–6.0 (m, 3, protons of the C-4 vinyl group), 6.98 (m, 1, C-3 vinyl proton). Splittings were verified by decoupling. Treatment of **8** with base (1 M NaOCH$_3$ in CH$_3$OH) caused isomerization to the fully conjugated dienones **9c** and **9t**.[2]



9c



9t