**Table I.** Intramolecular Distribution of Tritium in Pentenes from CHT Reactions with *trans*-2-Butene

| Pressure, torr | Butene/ketene ratio | Wave-length, A | Total $C_5$ yield, % | Alkyl-tritium, % |
|---|---|---|---|---|
| | | Product 3-Methyl-1-butene | | |
| 25 | 30 | 3660 | 3.9 ± 0.3 | 52 ± 3 |
| 150 | 30 | 3660 | 2.0 ± 0.5 | 71 ± 2 |
| 294 | 49 | Mixed[a] | 2.5 ± 0.1 | 75 ± 3 |
| 294 | 49 | 3660 | 1.6 ± 0.1 | 85 ± 4 |
| 400 | 49 | 3660 | 1.0 ± 0.1 | 88 ± 3 |
| | | Product *cis*-2-Pentene | | |
| 25 | 30 | 3660 | 2.5 ± 0.3 | 97 ± 3 |
| 150 | 30 | 3660 | 1.3 ± 0.2 | 100 ± 2 |
| 294 | 49 | 3660 | 0.9 ± 0.2 | 99 ± 2 |
| 400 | 75 | 3660 | 0.7 ± 0.3 | 100 ± 2 |

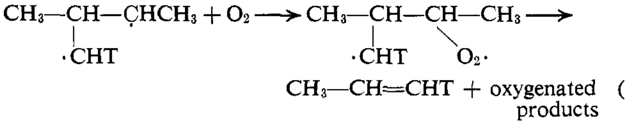
[a] Major bands are 3130 and 3660 A.

have not been unequivocally confirmed in alkyl monoradical reactions,[14] the additional driving force of the formation of the double bond should more readily permit such shifts for 1,3-diradicals. The increase in yield at lower pressures for the $(CH_3)_2CHCH{=}CHT$ may indicate that the 1,2 shift occurs more readily for the diradical still excited from the exothermic reaction (1).[15]

*cis*-2-Pentene shows no olefinic tritium activity in this pressure range within the limits of measurement, and therefore shows no evidence for the ring-closure–reopening mechanism.

The alkyl-*t* activity in *cis*-2-pentene is consistent with the 1,2-methyl shift mechanism, but could also be formed by radical combination. Similarly, the alkyl-*t* activity in 3-methyl-1-butene has two possible sources, and cannot be definitely assigned to a particular mechanism.

When oxygen is present, 3-methyl-1-butene is not observed and propylene appears as a product.[1] These changes can occur through the oxygenation of the diradical from reaction 1 and its subsequent decomposition, as shown in (2). The propylene-*t* formed by



$$CH_3{-}\underset{\cdot CHT}{\underset{|}{CH}}{-}\dot{C}HCH_3 + O_2 \longrightarrow CH_3{-}\underset{\cdot CHT}{\underset{|}{CH}}{-}\underset{O_2\cdot}{\underset{\diagdown}{CH}}{-}CH_3 \longrightarrow CH_3{-}CH{=}CHT + \text{oxygenated products} \qquad (2)$$

this sequence in triplet CHT reactions with *trans*- or *cis*-2-butene should be entirely $CH_3CH{=}CHT$, and actual observations of propylene-*t* formed in the presence of 3% oxygen indicate no alkyl-*t* activity within the limits of accuracy (about ±3%).

Propylene formation with all of the tritium activity in olefinic positions is certainly consistent with the sequence given in (2), but does not represent firm evidence for any structure of the addition product of the diradical and oxygen. It is, however, clear evidence that the oxygen does not completely scavenge the CHT itself, but instead reacts much of the time after the prior reaction of CHT with the olefinic substrate. These results indicate that the rate of reaction of triplet CHT with a double bond is competitive with its reaction with $O_2$, and that the 1,2-methyl shift of the diradical is slow compared to reaction of the diradical with $O_2$. The specific rate constant for the 1,2-methyl shift cannot exceed about $10^8$ $sec^{-1}$ in these experiments.

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(14) C. Walling, "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 416.

(15) Measurements of the isomerization rates of excited dimethylcyclopropanes indicate that isomerization to the pentenes is negligible even at 25 mm. The yields of *cis*-1,2-dimethylcyclopropane, the highest yield isomerization product, confirm that these reactions are not important at these pressures.[3]

## Nitroxides. XIX. Norpseudopelletierine-N-oxyl, a New, Stable, Unhindered Free Radical

*Sir:*

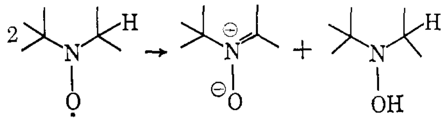
The "stability" of organic free radicals is generally considered to arise from a "delocalization" of the unpaired electron over a conjugated system or in other words from the presence of mesomeric structures.

Nitroxide radicals have recently been prepared[1,2] in which the unpaired electron is part of a two-center three-electron bond without further delocalization. Their stability has been attributed to steric hindrance,[2–4] bulky groups preventing the formation of the dimer.

However, the situation is certainly not very different from the NO or $NO_2$ molecules in which there is no steric hindrance to prevent dimerization. The stability of the paramagnetic monomer is then attributed to some particularities of the three-electron N–O bond.[2,5]

Organic unhindered nitroxides, such as dimethyl nitroxide[6] or diethyl nitroxide,[7] are also known, but these compounds are "unstable." This instability does not seem to be due to dimerization but rather to a decomposition of the free radical. To our knowledge, only two decompositions of nitroxide radicals have been studied (N,N-diphenyl nitroxide[8] and N-*t*-butyl-N-phenyl nitroxide[4,9]), suggesting a bimolecular dismutation of these aromatic nitroxides. On the other hand, the oxidation of hydroxylamines, known to give nitrones,[10] has been shown to involve unstable nitroxide radicals.[6,11]

This suggests that "unstable" nitroxide free radicals, *e.g.*, I, may decompose by dismutation to a nitrone (II) and a hydroxylamine (III), or, at least, that the nitrone



I II III

may be an important intermediate in their decomposition.

We wish to report the synthesis of a stable unhindered

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(1) O. L. Lebedev and S. N. Kazarnovskii, *Tr. po. Khim. i Khim. Tekhnol.*, 2, 649 (1959).

(2) A. K. Hoffmann and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).

(3) R. Brière, H. Lemaire, and A. Rassat, *Tetrahedron Letters*, 1775 (1964).

(4) A. R. Forrester and R. H. Thomson, *Nature*, 203, 74 (1964).

(5) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961).

(6) G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, **11**, 3283 (1965).

(7) G. M. Coppinger and J. D. Swallen, *J. Am. Chem. Soc.*, **83**, 4900 (1961).

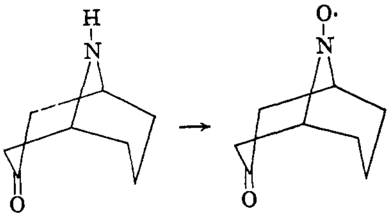
(8) H. Wieland and K. Roth, *Ber.*, **53B**, 210 (1920).

(9) G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 444 (1965).

(10) *Cf.* G. R. Delpierre and M. Lamchen, *Quart. Rev.* (London), **19**, 333 (1965).

(11) E. De La Mare and G. M. Coppinger, *J. Org. Chem.*, **28**, 1068 (1963).

nitroxide free radical, in which any nitrone formation would be prohibited by Bredt's rule. Treatment[12] of 1.5 g of norpseudopelletierine (IV) in 15 ml of water by 1.8 ml of 30% hydrogen peroxide in the presence of 10 mg of phosphotungstic acid gave, after ether extraction, chromatography on aluminum oxide, and recrystallization from ether, 308 mg (30% yield) of V, mp 120–121° (*Anal.* Found for $C_8H_{12}NO_2$: C, 62.12; H, 7.78; N, 9.28). The ultraviolet, infrared, and esr spectra are consistent with the nitroxide structure, showing the characteristic ultraviolet absorption[2,3,12] at 462 $m\mu$ ($\epsilon$ 8.5) in chloroform, blue shifted to 445 $m\mu$ ($\epsilon$ 6.4) in methanol, the carbonyl infrared absorption in $CCl_4$ at 1715 $cm^{-1}$, and the classical esr triplet, with a nitrogen splitting increasing with the solvent polarity,[3,12] going from 17.55 oersteds in benzene solution to 18.45 oersteds in water.[13]



IV V

This radical, although stable in the solid state and in benzene or water solution, is very reactive, much more than the related di-*t*-butyl nitroxide or 2,2,6,6-tetramethylpiperidine-N-oxyl; for instance, the ultraviolet or esr absorption disappears rapidly in acid or in basic solution.

The existence of V suggests that nitroxides are resistant to dimerization but that they are "stable" only when no double bond can be formed between the nitrogen and the adjacent carbon. Bis(trifluormethyl) nitroxide[14,15] may be another example of this rule.

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[12] *Cf.* R. Brière, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, **11**, 3273 (1965).

[13] In deoxygenated benzene solution, each component of the triplet is divided into at least 17 lines separated by 0.66 oersted and attributed to different protons of the molecule.

[14] W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, **87**, 802 (1965).

[15] S. P. Makarov, A. I. Iakubovich, S. S. Dubov, and A. N. Medvedev, *Dokl. Akad. Nauk SSSR*, **160**, 1319 (1965).

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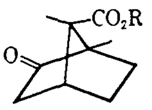
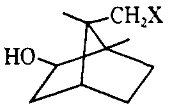
## Deuterium and the Octant Rule

*Sir:*

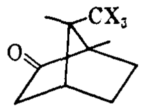
D-(+)-Isoketopinic acid (I) has been prepared from D-(+)-camphor by $\alpha$ bromination, $\pi$ bromination, $\alpha$ debromination, displacement of the $\pi$ bromine by acetate, saponification, and oxidation.[1] The corresponding methyl ester II is converted to the 2,9-diol III by lithium aluminum hydride, and selective 9-*p*-toluenesulfonation followed by lithium aluminum hydride reduction and Sarrett oxidation affords D-(+)-camphor. The molecular amplitudes of the Cotton effects of starting camphor and product camphor are identical, +62.89 ± 0.31 and + 62.56 ± 0.54°, respectively,[2] showing that optical purity is retained throughout the synthetic sequence. When the two lithium aluminum hydride reductions are replaced by lithium aluminum deuteride reductions, D-(+)-camphor-9,9,9-$d_3$ (at least 97.9% $d_3$ by mass spectral analysis) is obtained. The molecular rotations of this product are smaller in magnitude than those of camphor at both the peak (312 $m\mu$) and the trough (274 $m\mu$) of the Cotton effect, which as a result has a molecular amplitude of only +60.92 ± 0.23°,[2] 3% less than that of the protio counterpart.



I, R = H
II, R = $CH_3$



III, X = OH
IV, X = $OSO_2C_7H_7$
V, X = H



VI, X = H
VII, X = D

The 9-methyl group of camphor lies in a positive octant,[3] but the atomic refractivity of deuterium is less than that of hydrogen (the polarizability of a C–D bond is less than that of a C–H bond).[4-6] Thus deuterium (like fluorine[3,7]) should be expected to produce a contribution to the Cotton effect of sign opposite that predicted by the general octant rule, as is observed. Streitwieser[8] recently showed that compounds whose sole optical activity results from the difference between hydrogen and deuterium have normal (plain) rotatory dispersion properties, and thus that "deuterium behaves as an ordinary substituent so far as optical activity is concerned." We feel that the present result suggests[9] that deuterium is also a normal substituent so far as the octant rule is concerned, so long as its atomic refractivity properties are not overlooked. The magnitude of our observed effect, however, seems remarkably large.[9,10]

**Acknowledgment.** We are grateful to the National Science Foundation for Grant GB-1606 which partially supported this work, to Dr. Joseph Wolinsky and Mr.

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[1] E. J. Corey, S. W. Chow, and R. A. Scherrer, *J. Am. Chem. Soc.*, **79**, 5773 (1957); E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *ibid.*, **81**, 6305 (1959).

[2] Rotatory dispersion measurements were obtained at 24° with a Durrum-Jasco ORD/UV-5 recording spectropolarimeter. Methanol solutions (*ca.* 1 mg/ml) were prepared from two samples of each of three independently synthesized batches of camphor and camphor-$d_3$, and two ORD spectra were obtained from each solution. All measurements were made within a continuous 18-hr period, and the solutions were examined in random sequence.

[3] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

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[5] W. Fickett, *J. Am. Chem. Soc.*, **74**, 4204 (1952).

[6] J. H. Brewster, *ibid.*, **81**, 5475 (1959); *Tetrahedron Letters*, No. **20**, 23 (1959).

[7] C. S. Barnes and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1962 (1962).

[8] A. Streitwieser, Jr., L. Verbit, and S. Andreades, *J. Org. Chem.*, **30**, 2078 (1965).

[9] The deuteriomethyl group is smaller than a methyl group [*cf.* A. Horeau, A. Nouaille, and K. Mislow, *J. Am. Chem. Soc.*, **87**, 4957 (1965), and references therein]. Consequently when deuterium replaces hydrogen at C-9 there could be a decrease in nonbonded interactions between C-9 substituents and the remainder of the molecule, thereby producing a small conformational change in the ring system. That such a conformational distortion, rather than the atomic refractivity difference between D and H, is responsible for part or all of the osberved diminution of Cotton effect amplitude cannot be excluded as a possibility in the present example.

[10] C. Djerassi and B. Tursch, *J. Am. Chem. Soc.*, **83**, 4609 (1961), found no difference in the amplitudes of the Cotton effects of 3$\beta$-acetoxycholestan-7-one and 3$\beta$-acetoxy-6$\beta$-deuteriocholestan-7-one, and observed no (<42°) rotation at 322 $m\mu$ for 3-deuteriocyclopentanone, both of which results suggested that the effect of deuterium would be small if observable at all. In our camphor-$d_3$, of course, three deuterons have replaced protons in a positive octant, and in addition they are differently located in the octant (farther from the carbonyl, however) than those in the Djerassi compounds.