

τ for α -hydrogens and no signal around 8.5 τ for β -hydrogens. II should show a broad doublet ($J \sim 7.4$ c.p.s.) or two triplets around 6.6 τ and a multiplet around 8.5 τ , the ratio of 6.6 τ to 8.5 τ signals being 2.

A solution of 29.58 g. (0.181 mole) of 97.5% 1-propylammonium-1,1,2,2- d_4 perchlorate and 2.5% 1-propylammonium-1,1,2- d_3 perchlorate⁷ (m.p. 168–169°; lit. value 167°) in 26 ml. of 35% aqueous perchloric acid was treated with a solution of 27.6 g. (0.4 mole) sodium nitrite in 40 ml of water, at room temperature. The product was treated as before⁴ yielding 4.21 g. (36.4%) propanols. The mixture consisted of 30% 1-propanol and 70% 2-propanol (v.p.c. determination). The two propanols were separated and purified with a Beckman Megachrom, and analyzed with a Varian Associates A-60 n.m.r. spectrometer.

The 1-propanol (40% solution in carbon tetrachloride) gave signals at 9.14 τ (methyl), 6.58 τ (α -hydrogens) and 5.41 τ (hydroxyl). The 6.58 τ signal is a single broad peak with a half-width of about 6 c.p.s. A weak signal (multiplet) appears at 8.5 τ with an integrated area corresponding to about 20% of the area of the 6.58 τ ; however, because of the interference of spinning bands from the methyl signal in this area the 20% value is considered to be a maximum value.

On the basis of the above results we conclude that the rearrangement is mainly, if not exclusively,⁸ due to a 1,3-hydride shift. The amount of I in 1-propanol is 11.8%. Corroborative evidence that the rearrangement occurs *via* a 1,3-shift and not *via* successive 1,2-shifts is obtained by examining the spectrum of 2-propanol. Successive 1,2-shifts should introduce hydrogen at C-2 of 2-propanol. The amount of hydrogen at C-2 was found to be 1% (originally there was 2.5% hydrogen at C-2 as indicated previously). The less than 2.5% found probably is due to a kinetic isotope effect (k_H/k_D 1). That the 2-propyl cation does not rearrange to the 1-propyl cation is supported further by the fact that 2-propylamine gave 2-propanol without a trace of 1-propanol.

In summary, the above and previous data⁵ suggest the following with respect to the rearrange-

(7) The labeled perchlorate was prepared from the corresponding amine which in turn was prepared by reduction of propionitrile-2,2- d_2 with lithium aluminum deuteride. The propionitrile-2,2- d_2 was prepared according to L. C. Leitch, *Can. J. Chem.*, **35**, 345 (1957), and was found by n.m.r. (integration of the methylene signal at 7.67 τ against the natural abundance C^{13} -satellites of the methyl group) to be 97.5% dideuterated species and 2.5% monodeuterated species. All integrations involving weak signals were made against natural abundance C^{13} -satellites of strong signals. Details will be published later.

(8) The 20% value of the 8.5 τ signal could be construed as indicative of the fact that the rearrangement occurs 60% *via* a 1,3-shift and 40% *via* successive 1,2-shifts. If such were the case the 6.58 τ signal would not have been a clean singlet. We could easily detect from the 6.58 τ signal a 10% rearrangement *via* successive 1,2-shifts.

ments of the 1-propyl cation under the experimental conditions: The 1-propyl cation rearranges irreversibly to the 2-propyl cation; it undergoes a 1,3-hydride shift; protonated cyclopropanes are not intermediates in the formation of the propanols; methyl migration does not occur.⁵

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VIBRONIC INTERACTION IN POTASSIUM *o*-XYLENIDE¹

Sir:

The possibility of vibronic mixing in paramagnetic negative ions with nearly degenerate ground states has been discussed recently in connection with apparent positive spin densities around para carbon atoms in monoalkylated benzenides.² This discussion further pointed to the possibility of observing a temperature dependence in the proton hyperfine splittings in the electron spin resonance (e.s.r.) absorption spectra of these compounds. Such a temperature dependence has been reported in the e.s.r. absorption spectra of a series of monoalkylated benzenides.³ We present evidence here to support the contention that vibronic mixing is also important in alkylated benzenides.

The e.s.r. absorption spectrum of potassium *o*-xylene in 1,2-dimethoxyethane solution at -80° has been observed to consist of three groups of seven lines. Each of these twenty-one lines is further split into six. The corresponding spectrum of potassium *o*-xylene- $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'-d_6$ also has three main lines each made up of at least fifteen components. The data on these spectra are summarized in Table I. In comparing the

TABLE I

HYPERFINE COUPLINGS IN POTASSIUM <i>o</i> -XYLENIDE	A ^a	B ^b
	Two ring protons	6.95
Methyl protons	2.01	0.41 ^c
Two ring protons	ca. 0.2	...
Potassium	ca. 0.2	...

^a Potassium *o*-xylene hyperfine couplings. ^b Potassium *o*-xylene- d_6 hyperfine couplings. ^c Smaller coupling for *o*-xylene- d_6 .

data for the two spectra we see that the substitution of six deuteriums on the methyl groups has the expected effect of collapsing the seven line structure on each of the three main components, but we also see an unexpected amplification of about 11% in the large proton splitting. Considering the evidence previously presented for near degeneracy in the ground states of closely allied compounds, this redistribution of electron spin, on changing essentially nothing but mass through

(1) This work has been supported in part by the National Science Foundation.

(2) J. R. Bolton, A. Carrington, A. Forman and J. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

(3) T. R. Tuttle, Jr., *J. Am. Chem. Soc.*, **84**, 1492 (1962).

isotopic substitution, is very strong evidence for the breakdown of the Born-Oppenheimer approximation.

In a previous communication we reported a similar deuterium isotope effect in potassium *p*-deuteriotoluenide as a natural partner of temperature dependent proton couplings.³ This view is supported by the above interpretation according to which deuterium substitution has a substantial effect on the energy gap between ground and excited state. However, part of the isotope effect observed in the spectrum of potassium *p*-deuteriotoluenide probably can be attributed to vibronic mixing. In cases of near degeneracy we expect, in general, two sources of isotopic shifts: (1) a difference in the energy gap and (2) a difference in vibronic mixing. For potassium *o*-xylenide-*d*₆ the principal source of the isotope effect must be (2) since we observe no temperature dependence of proton splittings in its e.s.r. absorption spectrum. In principal, the effect always may be apportioned between the two causes through extrapolation of data on the temperature dependence to very high or very low temperatures using equation 1 in reference three. In practice this may not be possible because of the small differences involved.

We also have observed the e.s.r. absorption spectra of potassium *p*-xylenide and potassium *p*-xylenide- $\alpha, \alpha, \alpha, \alpha', \alpha', \alpha'-d_6$. The large proton coupling which we measured in each case is substantially the same as that previously reported,⁴ and is independent of temperature. The lack of a deuterium isotope effect suggests little vibronic mixing in the ground state. This suggestion accords with the fact that the methyl proton splittings are rather small.^{2,4,5} However, since the situation with respect to vibronic mixing can be rather complicated it is not at all clear that under certain circumstances a substantial amount of vibronic mixing may give rise to little or no isotope effect. We are now planning experiments which will help us eliminate some of the possibilities involved in vibronic interaction in these and other free radical anions and allow us to make a firmly founded correlation between isotope effect and degree of vibronic mixing.

(4) R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).

(5) The spectrum of potassium *p*-xylenide-*d*₆ contains small temperature dependent alkali metal splittings. This fact leaves some question about the value of the methyl proton coupling constant assignment given in reference 4.

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TERPENES. I. THE ABSOLUTE CONFIGURATION OF (-)-UMBELLULONE AND THE THUJANE TERPENES

Sir:

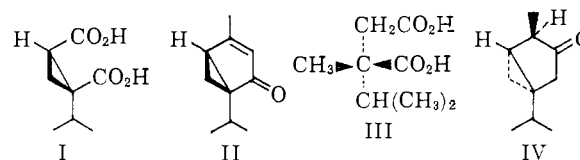
Recently Walborsky and co-workers¹ reported the asymmetric synthesis of (-)-*cis*-umbellularic acid, a degradation product of the thujane terpene (-)-umbellulone.² On the basis of this synthesis,

(1) H. M. Walborsky, T. Sugita, M. Ohno and Y. Inouye, *J. Am. Chem. Soc.*, **82**, 5255 (1960).

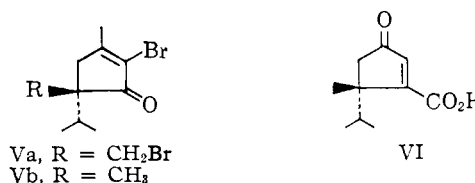
(2) F. Tutin, *J. Chem. Soc.*, **89**, 1104 (1906).

they assigned the absolute configuration of this acid as I, and thus the absolute configuration of (-)-umbellulone as II. Since the configuration of (-)-umbellulone has been related³ to those of the other members of the thujane group, the absolute configurations of these terpenes may also be assigned.

In connection with our current interest in optically active amines⁴ and the thujylamines⁵ in particular, we sought a verification of these assignments of absolute configurations, and we now wish to report a degradation of (-)-umbellulone to (S)-(+)- α -methyl- α -isopropylsuccinic acid, the absolute configuration of which has been established⁶ as III. This degradation follows the elegant route utilized by Eastman and Oken⁷ in the establishment of the structure of (+)-umbellulone dibromide (Va). It confirms Walborsky's assignment of the absolute configuration of I and, in addition, definitively fixes the absolute configuration of (-)-umbellulone as II and thus also the absolute configurations of the other members of the thujane group of terpenes,³ notably that of (-)-thujone as IV,^{3a} the relative configuration of the methyl group having been recently assigned by Walborsky¹ contrary to that assumed previously.^{3a,8}



Bromination of II, $[\alpha]^{22D} -40^\circ$ (neat), yielded Va which on reduction with zinc in acetic acid gave (-)-bromodihydroumbellulone (Vb). Oxidation of Vb with buffered aqueous potassium permanganate followed by treatment of the product with concentrated aqueous sodium hydroxide gave (-)-1-carboxy-3-keto-5-methyl-5-isopropylcyclopentene (VI). The latter three compounds were found to



have all physical properties identical with those reported by Eastman and Oken.⁷ Although these workers were able to oxidize VI to III in very small yield (5%), they did not record the rotatory power of this acid and, for our purpose, their

(3) (a) J. L. Simonsen, "The Terpenes," Cambridge University Press, Cambridge, England, Second Edition, Vol. II, 1949, pp. 5-60; D. H. R. Barton, "Chemistry of Carbon Compounds," Edited by E. H. Rodd, Elsevier Publishing Co., New York, Vol. IIB, 1953, pp. 547-557; (b) J. W. Daly, F. C. Green and R. H. Eastman, *J. Am. Chem. Soc.*, **80**, 6330 (1958).

(4) H. E. Smith, M. E. Warren, Jr., and A. W. Ingersoll, *ibid.*, **84**, 1513 (1962).

(5) H. L. Dickison and A. W. Ingersoll, *ibid.*, **61**, 2477 (1939).

(6) (a) J. Porath, *Arkiv Kemi*, **1**, 385 (1949); (b) K. Freudenberg and W. Lwowski, *Ann.*, **587**, 213 (1954).

(7) R. H. Eastman and A. Oken, *J. Am. Chem. Soc.*, **75**, 1029 (1953).

(8) R. H. Eastman and A. V. Winn, *ibid.*, **82**, 5908 (1960).