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.

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(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.

DEPARTMENT OF CHEMISTRY
BRANDEIS UNIVERSITY
WALTHAM 54, MASSACHUSETTS
T. R. TUTTLE, JR.

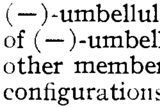
RECEIVED MAY 22, 1962

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

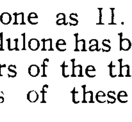
Sir:

Recently Walborsky and co-workers[1] reported the asymmetric synthesis of (−)-*cis*-umbellularic acid, a degradation product of the thujane terpene (−)-umbellulone.[2] On the basis of this synthesis, 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 related[3] to those of the other members of the thujane group, the absolute configurations of these terpenes may also be assigned.

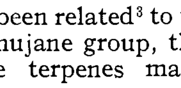
In connection with our current interest in optically active amines[4] and the thujylamines[5] in particular, we sought a verification of these assignments of absolute configurations, and we now wish to report a degradation of (−)-umbellulone to (S)-(+)-α-methyl-α-isopropylsuccinic acid, the absolute configuration of which has been established[6] as III. This degradation follows the elegant route utilized by Eastman and Oken[7] 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 Walborsky[1] contrary to that assumed previously.[3a,8]



I

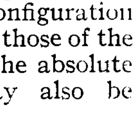


II



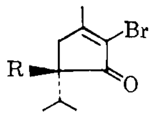
$$CH_3 \blacktriangleright \overset{CH_2CO_2H}{\underset{CH(CH_3)_2}{C}} \blacktriangleleft CO_2H$$

III

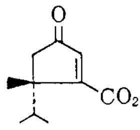


IV

Bromination of II, $[\alpha]^{22}D$ −40° (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



Va, R = CH_2Br
Vb, R = CH_3



VI

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

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(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).

(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).

method is unsatisfactory. However, ozonolysis of 0.240 g. of VI in ethyl acetate at −78°, treatment of the ozonide with hot aqueous 30% hydrogen peroxide and isolation of the acidic products yielded, after crystallization from benzene–cyclohexane, 0.134 g. (59%) of III, m.p. 132–133°. Two recrystallizations of this material from the same solvent and then sublimation (100°, 0.1 mm.) gave an analytical sample, m.p. 133–134°, $[\alpha]^{21}\text{D}$ +16° (*c* 2.9, ethanol).[9] *Anal.* Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10; neut. equiv., 87. Found: C, 54.97, 55.00; H, 8.14, 8.21; neut. equiv., 86. The infrared absorption spectrum (KBr pellet) of this material was found to be identical in all respects with that of an authentic sample of (+)-α-methyl-α-isopropylsuccinic acid, m.p. 128–130°, but definitely different in small details from that of an authentic sample of the racemic form, m.p. 154–155°.

We are grateful to the National Science Foundation for a grant (G14524) in support of this work, to Dr. Richard H. Eastman for a generous gift of umbellulone and to Dr. Arne Fredga for authentic samples of both the optically active and racemic forms of α-methyl-α-isopropylsuccinic acid.

[9] Reported (ref. 6a), m.p. 126.5–127°, $[\alpha]^{25}\text{D}$ +19° (*c* 1.57, ethanol).

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY HOWARD E. SMITH
NASHVILLE 5, TENN. ANNETTE WATERS GORDON

RECEIVED MAY 31, 1962

THE PHOTOSENSITITED DIMERIZATION OF CYCLOPENTADIENE[1]

Sir:

As was reported recently,[2] butadiene can be dimerized through the agency of a variety of photosensitizers. The sensitizers used are compounds believed to decay by way of triplet states after photoexcitation, The detailed mechanism of the dimerization may be written as (1) to (3) (where A is the sensitizer):

$$A_{S_0} \xrightarrow{h\nu} A_{S_1} \longrightarrow A_{T_1} \qquad (1)$$

$$A_{T_1} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow A_{S_0} + \cdot\overset{\downarrow}{C}H_2{-}CH{=}CH{-}\overset{\downarrow}{C}H_2\cdot \qquad (2)$$

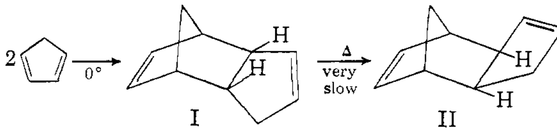
$$\overset{\downarrow}{\cdot}CH_2CH{=}CHCH_2\overset{\downarrow}{\cdot} + CH_2{=}CHCH{=}CH_2 \longrightarrow \begin{array}{l} CH_2{-}CH{\cdots}CH{\cdots}CH_2\downarrow \\ | \\ CH_2{-}CH{\cdots}CH{\cdots}CH_2\downarrow \end{array} \qquad (3)$$

$$\downarrow$$

$$\text{dimers}$$

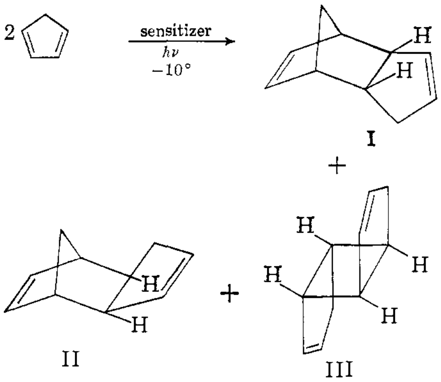
The composition of the mixture of dimers is rather different from that obtained by thermal dimerization of butadiene.[3] However, these results are difficult to compare since the two experiments were carried out at widely different temperatures. It seemed of interest to carry out a photosensitized dimerization under conditions which would also permit thermal dimerization. This experiment would be of particular interest because of the recent suggestions[4,5,6] that Diels–Alder reactions may involve transient intermediates in which one bond has been formed. One possible formulation of such an intermediate would be a triplet biradical of the type produced in reaction (3).

The dimerization of cyclopentadiene seemed appropriate for study since the diene undergoes the Diels–Alder reaction at 0° to give exclusively *endo*-dicyclopentadiene although on heating above 100° some *exo* isomer is formed.[7,8]



(4)

Cyclopentadiene containing acetophenone, benzophenone, fluorenone, mesityl oxide, acetone, benzil, or 2,3-pentadione when irradiated with a Hanovia 450-watt, quartz immersion lamp produces (after correction for the thermal reaction) *endo*-dicyclopentadiene (I), *exo*-dicyclopentadiene (II), and *trans*-(3,0,3,0)-tricyclo-2,8-decadiene (III) in approximately a 1:1:1 ratio, respectively. It is noteworthy that 9-anthraldehyde, which was incapable of sensitizing the isomerization of *cis*-piperylene,[9] is also inert as a photosensitizer for the dimerization of cyclopentadiene.



(5)

The reaction products were analyzed by vapor chromatography on a 7.3 m. length 6-mm. diameter column packed with 25% β,β′-oxydipropionitrile on 40/60 mesh firebrick. The products were separated by preparative vapor chromatography using first Apiezon J to separate *exo*- and *endo*-dicyclopentadiene from III and then using β,β′-oxydipropionitrile to separate *endo*- and *exo*-isomers.

The *exo*-dicyclopentadiene was identical in all respects with a sample of authentic material pre-

[1] Mechanisms of Photoreactions in Solution XI. Part X is G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

[2] G. S. Hammond, A. Fischer and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

[3] W. H. B. Reed, *J. Chem. Soc.*, 685 (1951).

[4] C. Walling and J. Peisch, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

[5] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[6] R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2198 (1961).

[7] K. Alder and G. Stein, *Ann*, **504**, 219 (1933).

[8] P. D. Bartlett and I. S. Goldstein, *J. Am. Chem. Soc.*, **69**, 2553 (1947).

[9] G. S. Hammond, P. A. Leermakers and N. J. Turro, *ibid.*, **83**, 2396 (1961).