Average Geminal and Vicinal Proton–Deuterium Coupling Constants in Variously Deuterated Ethanol, Propanol-2, and Toluene

W. C. LEWIS AND B. E. NORCROSS[1]

State University of New York at Binghamton,
Binghamton, New York

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In connection with several studies in progress at this laboratory, a number of variously deuterated compounds were submitted to high resolution proton magnetic resonance spectroscopic investigation. The resulting generally well-resolved spectra showed that the common assumption[2] that deuterium acts primarily as a line-broadening agent on the magnetic resonance absorption of geminal and vicinal hydrogens must be used with caution.

The coupling constants obtained in this study, as well as a selection of those available from other workers, are summarized in Table I. These couplings all fall within a range defined by the relationship[3] $J_{H-D} = J_{H-H}/6.55$ (J is the coupling constant in cycles per second), and support the statement[4] that, in general, "The absorptions of protons coupled with deutrons... are not appreciably broadened."

TABLE I

COUPLING CONSTANTS

Compound	J_{H-D}, c.p.s. Geminal	Vicinal	Reference
Monodeuteriomethane	1.19		*a*
Monodeuteriomethylene chloride	1.09		*b*
Monodeuteriomalononitrile	3.1		*b*
Monodeuterioacetylene		1.4	*a*
1-Deuterioethanol	1.7	1.1	This work
1,1-Dideuterioethanol		1.1	This work
α-Deuteriotoluene	2.2		This work
2-Deuteriopropanol-2		0.9	This work
1,1,1,3,3,3-Hexadeuteriopropanol-2		0.8	This work
α-Deuteriocumene		$\simeq$1.0	*c*
1-Deuterioindene	3.2		*d*
1-Deuterio-1-methylindene		0.9	*e*
3-Deuterio-1,1-dimethylallene	1.4		*f*

[a] M. Karplus, D. H. Anderson, R. C. Farrar, and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957). [b] Ref. 3. [c] This is NMR at Work", No. 32, Varian Associates, Palo Alto, Calif., 1956. [d] K. G. Flynn and G. Bergson, *Acta Chem. Scand.*, **18**, 2002 (1964). [e] G. Bergson and A. Weidler, *ibid.*, **18**, 1498 (1964). [f] E. L. Allred, D. M. Grant, and W. Goodlett, *J. Am. Chem. Soc.*, **87**, 673 (1965).

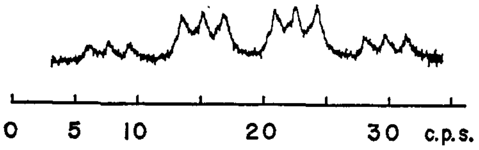

Figure 1.

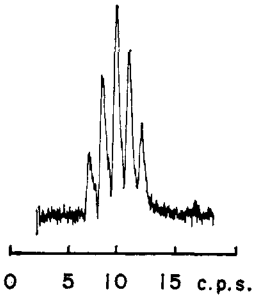

Figure 2.

The expected splittings are clearly evident in the spectra of the methylene hydrogen in 1-deuterioethanol (Figure 1) and the methyl hydrogens of 1,1-dideuterioethanol (Figure 2). The anticipated 13 peaks arising from the splitting of the α-hydrogen in 1,1,1,3,3,3,-hexadeuteriopropanol-2 by six adjacent equivalent deuterons [nuclear spin number (I) of 1; peak multiplicity given by $(2n_AI_A + 1)(2n_BI_B + 1)\ldots$, where n_A and n_B are the number of equivalent nuclei of spins I_A and I_B coupled to the observed nuclei] could not be clearly resolved, but the multiplet nature of the absorption is evident, and the coupling constant can readily be determined.

Experimental

Samples of α-deuteriotoluene,[5] 1,1-dideuterioethanol,[6] and 2-deuteriopropanol-2[7] were synthesized in moderate yields of high purity material by standard methods.

1-Deuterioethanol.—To a solution of 1.00 g. (0.0238 mole) of sodium borodeuteride[8] in 50 ml. of water, containing 1. pellet of potassium hydroxide, was added dropwise 4.28 g. (0.12 mole) of acetaldehyde. The resulting solution was heated at gentle reflux for 12 hr., neutralized with dilute hydrochloric acid, and distilled through a 15 × 170 mm. Helipak[9] column. The third fraction, b.p. 77.5–78.5° (746.7 mm.), amounting to 2.95 g. (52% yield), was used without further purification.

1,1,1,3,3,3-Hexadeuteriopropanol-2.—To a solution of 1.0 g. (0.106 mole) of lithium aluminum hydride in 150 ml. of ether was added dropwise a solution of 5.00 g. (0.078 mole) of hexadeuterioacetone[10] in 50 ml. of ether, over a period of 20 min. The resulting slurry was heated at reflux for 1 hr., cooled, and quenched with enough dilute hydrochloric acid to effect solution of all solid material.

The resulting two-phase mixture was reduced in volume by removing most of the ether through a 10-in. Vigreux column. This mixture was then fractionated through a 15 × 170 mm. Helipak column[9] at atmospheric pressure (737.2 mm.). A total yield of 4.1 g. (80%) of product was obtained, boiling at 79.0–79.5°. This material, containing about 5% water, was used without further purification for spectral measurements.

All samples were examined for homogeneity on two analytical vapor phase chromotography column packings of differing polarity, and were found to be pure (alcohol samples contained water).

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(1) To whom inquiries should be addressed.

(2) (a) J. D. Roberts, "An Introduction to the Analysis of Spin–Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 9; (b) R. U. Lemieux and J. Howard, *Can. J. Chem.*, **41**, 308 (1963); (c) E. Premuzic and L. W. Reeves, *J. Chem. Soc.*, 4817 (1964); (d) R. M. Silverstein and G. C. Bassler, "Spectrophotometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 81.

(3) H. S. Gutowsky, M. Karplus, and N. M. Grant, *J. Chem. Phys.*, **31**, 1683 (1959).

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(7) M. Farina and M. Peraldo, *Gazz. chim. ital.*, **90**, 973 (1960).

(8) Metal Hydrides, Inc., Beverly, Mass.

(9) Podbielniak, Inc., Chicago, Ill.

(10) Merck Sharp and Dohme of Canada, Ltd., Montreal, Canada.

Infrared[11] and mass[12] spectra were consistent with assigned structures, and with greater than 97% isotopic purity for all compounds.

Proton n.m.r. spectra were determined on a Varian A-60 high-resolution spectrometer on 10 ± 0.5% w./w. solutions in carbon tetrachloride or deuterium oxide (99.77%), except for samples of 1,1,1,3,3,3-hexadeuteriopropanol-2, which were 20% by weight. Chemical shifts were measured from internal tetramethylsilane (carbon tetrachloride solutions) or internal 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt monohydrate.[13] Probe temperature was 27 ± 1° during determinations (measured by ethylene glycol peak separation). All spectra were recorded under high resolution conditions: low radiofrequency field, broadest filter band width, and slow scan rate. Coupling constants were measured from the peak separations of at least three different spectra recorded at 100 c.p.s. chart width, and are accurate to ±0.1 c.p.s.

Acknowledgment.—We are grateful to the donors of the American Chemical Society Petroleum Research Foundation funds, to the Research Foundation of the State University of New York, and to the Harpur Foundation for making support available for those projects from which these compounds were obtained.

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[11] Determined on a Perkin-Elmer 521 spectrophotometer, in the gas phase, in a 10-cm. cell at room temperature.

[12] Determined on a Consolidated Electrodynamics Corporation 21-130 mass spectrometer by Mr. Stanley Raider, through the courtesy of the Department of Chemistry, State University of New York at Stony Brook. We are grateful to Mr. Raider for these spectra.

[13] Eastman Kodak, White Label.

Isomerization of the Butenyl Methyl Sulfides with Methanethiol

EARL S. HUYSER AND RICHARD M. KELLOGG[1]

Department of Chemistry, University of Kansas, Lawrence, Kansas

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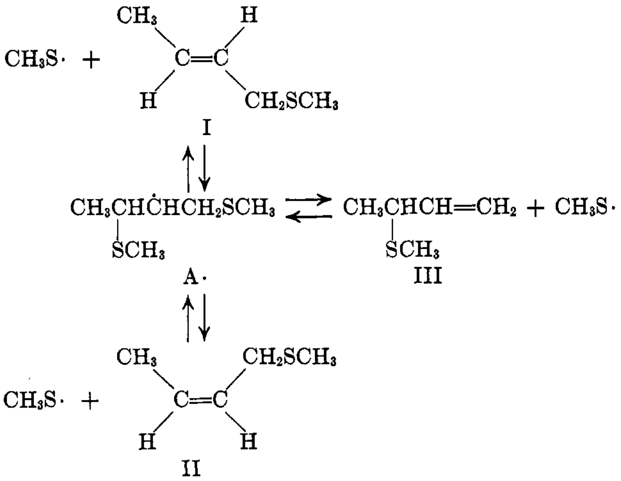
The rapid isomerization of either 1-bromo-2-butene or 3-bromo-1-butene to an equilibrium mixture of the two by hydrogen bromide in the presence of peroxides[2] has been suggested to be caused by the reversible addition of bromine atoms to unsaturated linkages.[3] The reversible addition of thiyl radicals to alkenes[4] suggests that similar isomerizations might occur in the free-radical reactions of the isomeric butenyl methyl sulfides with methanethiol. Addition of a methanethiyl radical ($CH_3S\cdot$) to *trans*-crotyl methyl sulfide (I), *cis*-crotyl methyl sulfide (II), and α-methallyl methyl sulfide (III) yields conformers of a common adduct radical A· from which, on elimination of a methanethiyl radical, a mixture of I, II, and III can result. Gas chromatographic analysis of the unreacted butenyl methyl sulfides resulting from the photoinduced reaction of I and III as well as a mixture of I, II, and III with methanethiol show that such isomerizations do indeed occur (Table I).

TABLE I

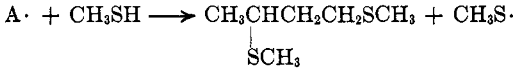
ISOMERIZATION OF BUTENYL METHYL SULFIDES IN PHOTOCHEMICAL REACTIONS WITH METHANETHIOL (23.5 hr. at 35°)

	Amounts, mmole				
	I	II	III	CH_3SH	Ratio of I:II:III
Before	0.01	0.01	0.75[a]	1.55	0.0:0.0:1.0
After	0.25	0.04	0.024	. . .	1.0:0.16:0.096
Before	0.01	0.01	0.77	1.54	0.0:0.0:1.0
After	0.33	0.047	0.024	. . .	1.0:0.14:0.088
Before	0.73	0.00	0.00	1.51	1.0:0.0:0.0
After	0.16	0.022	0.013	. . .	1.0:0.13:0.080
Before	0.79	0.00	0.00	1.51	1.0:0.0:0.0
After	0.13	0.022	0.008	. . .	1.0:0.17:0.061
Before	0.57	0.070	0.085	1.49	1.0:0.12:0.15
After	0.33	0.059	0.024	. . .	1.0:0.18:0.073
Before	0.58	0.072	0.089	1.58	1.0:0.12:0.15
After	0.44	0.071	0.031	. . .	1.0:0.16:0.070

[a] Purity of III was 98.4% with 1.4% contamination of the other isomers.



If the rates of elimination of $CH_3S\cdot$ from A· to yield I, II, and III are considerable faster than the reaction of A· with methanethiol to yield the addition product 1,3-di(methanethio)butane (IV), it is possible that



$$A\cdot + CH_3SH \longrightarrow \underset{\displaystyle SCH_3}{CH_3CH}CH_2CH_2SCH_3 + CH_3S\cdot$$

IV

an equilibrium mixture of the three isomers might be formed before all of the butenyl methyl sulfides have been consumed. The ratio of the three isomers found after 30–70% consumption of the butenyl methyl sulfides in the addition reaction is essentially the same starting with either I or III or with mixtures of the three isomers, suggesting that equilibration is very nearly attained well before the addition reaction is complete. The observed composition of the mixture is consistent with that which would be expected for an equilibrium mixture, namely, the internally unsaturated compounds I and II are more stable than the terminally unsaturated one (III) and the *trans* isomer I is more stable than the *cis* isomer II.[5]

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[1] National Science Foundation Cooperative Fellow, 1963–1965. The work described was taken from the thesis submitted by R. M. K. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas.

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[3] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 305.

[4] C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959); R. H. Pallen and C. Sivertz, *Can. J. Chem.*, **35**, 723 (1957).

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