

for $C_{11}H_{18}NO_5S_2K$: C 32.11; H 4.41; N 3.40; S 15.59).

Enzymatic hydrolysis. The synthetic potassium 3-butenylglucosinolate (136 mg), dissolved in a citrate buffer (pH 6.4) (3 ml), was subjected to enzymatic hydrolysis by adding a myrosinase solution (0.5 ml). Next day, the solution was extracted with ether. Ammonia-saturated methanol (0.5 ml) was added to the dried ether extract. After standing overnight, the solvents were removed, and the oily residue was purified by silica gel chromatography, with ethyl acetate as the eluting solvent. The thiourea-containing fractions were combined and concentrated to dryness. Upon recrystallization from water, colourless needles (6 mg) separated, m.p. 65°. They were identified as 1-(3-butenyl)-thiourea by comparison with an authentic specimen⁹ (undepressed mixed melting point and coinciding IR-spectra).

The authors are indebted to Professor F. W. Hougen for a sample of potassium *O*-tetraacetyl-3-butenylglucosinolate of natural origin.

1. Ettliger, M. G. and Kjær, A. In *Recent Advances in Phytochemistry*, vol. 1, (Editors: T. J. Mabry, R. E. Alston and V. C. Runeckles), Appleton-Century-Crofts, New York, N. Y. 1968, p. 100.
2. Kjær, A. *Fortschr. Chem. Org. Naturstoffe* **18** (1960) 122.
3. Josefsson, E. and Mühlenberg, C. *Acta Agric. Scand.* **18** (1968) 97.
4. Benn, M. H. and Ettliger, M. G. *Chem. Commun.* **1965** 445.
5. LaForge, F. B., Green, N. and Gersdorff, W. A. *J. Am. Chem. Soc.* **70** (1948) 3707.
6. Kornblum, N., Larson, H. O., Blackwood, R. K., Mooberry, D. D., Oliveto, E. P. and Graham, G. E. *J. Am. Chem. Soc.* **78** (1956) 1497.
7. Benn, M. H. *Can. J. Chem.* **41** (1963) 2836.
8. Ettliger, M. G. and Lundeen, A. J. *J. Am. Chem. Soc.* **79** (1957) 1764.
9. Kjær, A., Rubinstein, K. and Jensen, K. A. *Acta Chem. Scand.* **7** (1953) 518.

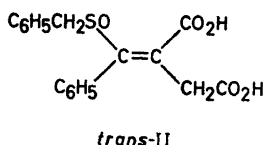
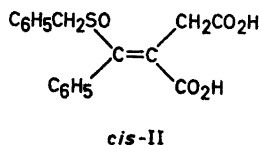
Received November 19, 1968.

A Note Concerning the NMR-Spectra of *cis*- and *trans*-1-Benzylsulfinyl-1-phenyl-1-propen-2,3-dicarboxylic Acid

STIG ALLENMARK and OVE BOHMAN

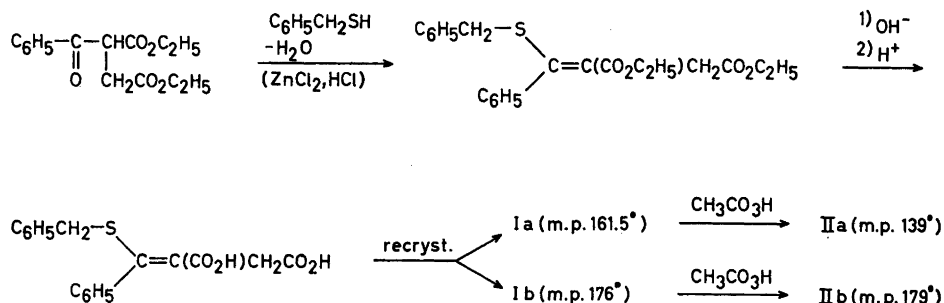
Chemical Institute, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

During the last few years much interest has been devoted to the study of proton magnetic non-equivalence originating from an adjacent asymmetric atom^{1,2} and it has been possible to demonstrate, by means of NMR-technique, a kinetic non-equivalence of diastereotopic methylene protons upon hydrogen exchange and to get information about the stereochemistry of transient asymmetric carbanions.³⁻⁸ Rather few examples of magnetically non-equivalent methylene protons located a great distance from the asymmetric atom can be found,⁷ however, and we will therefore make a contribution to this field by briefly reporting the synthesis and NMR-spectra of *cis*- and *trans*-II.



The acids were prepared according to the synthetic route on p. 3327.

In Table 1 the NMR-signals and their assignments to the various protons in IIa and IIb are given. It is found for each compound that both methylene groups appear as AB-quartets. We believe this is the first example of a long-range effect of a sulfoxide group giving rise to magnetic non-equivalence of methylene protons at such a great distance. Previously, how-



ever, we have noticed AB-quartets from the protons in methylene groups separated from the sulfoxide group by one carbon atom.⁸ The geminal coupling constants found in IIa and IIb, $|J_{AB}| = 12.5-13$ cps and $17-17.5$ cps, are typical for methylene protons in benzyl sulfoxides^{3,9,8} and adjacent to a carboxyl group in β, γ -unsaturated acids,⁸ respectively. That this non-equivalence is not due to restricted rotation in the molecules became evident from the spectra of the corresponding sulfides and sulfones, where the protons in question appeared as singlets.

An assignment of geometric configuration to the two series of compounds has not yet been made. The information obtained from NMR-spectra in this respect is of limited value, because an interpretation of chemical shift-differences originating from various anisotropy effects is very difficult in such a relatively flexible system as this. Further, the reduction rates of IIa and IIb in hydriodic acid⁹ give no answer to the question as both compounds react very slowly because of steric hindrance by the phenyl ring¹⁰ at C-1 to nucleophilic attack at the sulfur atom.

Table 1. NMR-spectral data for compounds IIa and IIb in methanol- d_4 .

Sulfoxide	Aromatic protons	Methylene protons					Assignment
		Centre of AB-quartet, ppm	J_{AB} cps	δ_A ppm	δ_B ppm	$(\delta_A - \delta_B)$ ppm	
IIa	7.40 ^a	4.25	12.5	4.57	3.92	0.65	benzyl-CH ₂ protons
	7.39	3.25	17.5	3.43	3.07	0.36	protons at C-3
IIb	7.41 ^b	3.93	13	4.16	3.70	0.46	benzyl-CH ₂ protons
	7.32	3.61	17	3.69	3.54	0.15	protons at C-3

^a Centre of multiplet. ^b Peak exhibiting fine-structure.

Experimental. Diethyl benzoylsuccinate was prepared according to Perkin.¹¹ B.p. 155°/0.2 mm, $n_D^{25}=1.5071$, (lit. values:¹² B.p. 159°/1 mm, $n_D^{27}=1.5012$).

1-Benzylthio-1-phenyl-1-propen-2,3-dicarboxylic acid (I) was obtained by thiol-addition to the carbonyl group according to Posner,¹³ a method which we have used earlier⁸ for the synthesis of enethiol ethers. Diethyl benzoylsuccinate, 27.8 g (0.1 mole), phenylmethanethiol 24.8 g (0.2 mole), and zinc chloride 9.1 g (0.067 mole) were mixed and saturated with dry hydrogen chloride. After 48 h at room temperature the mixture was diluted with ice-water and extracted with chloroform. The chloroform-phase was washed with water, dried, evaporated and distilled to remove excess thiol from the residue. This yielded 25.5 g of a crude product, which was hydrolyzed for 48 h at 50° with 11 g of sodium hydroxide in 90 ml of water + 20 ml of ethanol. Extraction with ether in order to remove any unchanged material was followed by acidification which yielded a brown oil. This was separated and washed with petroleum ether. Some benzoic acid was removed in this way. The rest constituted a semi-crystalline mass, which could be recrystallized from ethyl acetate-petroleum ether. In this way 2.4 g of a compound with m.p. 161–162° (Ia) was obtained. (Found: C 65.91; H 4.97; S 9.68. Calc. for $C_{18}H_{16}O_4S$: C 65.84; H 4.91; S 9.76). NMR (methylene protons, CD_3OD): 3.35 (s), 3.08 (s). The mother liquors from the recrystallizations were evaporated to dryness and the residue was recrystallized from a water-ethanol mixture. This yielded 1.5 g of the other geometric isomer with m.p. 175.5–176.5° (Ib). (Found: C 65.85; H 4.91; S 9.78. Calc. for $C_{18}H_{16}O_4S$: C 65.84; H 4.91; S 9.76). NMR (methylene protons, CD_3OD): 3.77 (s), 3.44 (s).

1-Benzylsulfinyl-1-phenyl-1-propen-2,3-dicarboxylic acid (II). Oxidation of Ia with peracetic acid in the way described earlier⁸ gave a product which after repeated recrystallization from ethyl acetate-petroleum ether had a m.p. of 138–140° (IIa). (Found: C 62.57; H 4.77; S 9.21. Calc. for $C_{18}H_{16}O_5S$: C 62.78; H 4.68; S 9.31).

Similarly, the oxidation of Ib yielded the other sulfoxide (IIb), which was recrystallized from acetone. M.p. 178.5–179.5°. (Found: C 62.84; H 4.78; S 9.27. Calc. for $C_{18}H_{16}O_5S$: C 62.78; H 4.68; S 9.31).

1-Benzylsulfonyl-1-phenyl-1-propen-2,3-dicarboxylic acid (III). Oxidation of Ia and Ib with peracetic acid in excess gave the corresponding sulfones (IIIa and IIIb). After a recrystallization from ethyl acetate-petroleum ether, IIIa had m.p. 163–165°. (Found: C 59.66; H 4.46; S 8.80. Calc. for $C_{18}H_{16}O_6S$: C 59.99; H 4.48; S 8.90). NMR (methylene protons, CD_3OD): 4.66(s), 3.20(s). IIIb, recrystallized from acetone, melted between 154 and 155°. (Found: C 59.68; H 4.64; S 8.83. Calc. for $C_{18}H_{16}O_6S$: C 59.99; H 4.48; S 8.90). NMR (methylene protons, CD_3OD): 4.33(s), 3.87(s).

The NMR-spectra were recorded with a Varian A-60 spectrometer. Chemical shifts are given in δ -values from TMS as an internal reference.

Acknowledgements. We are indebted to Professor Arne Fredga for his support to this work and to the *Swedish Natural Science Research Council* for a grant.

- Mislow, K. and Raban, M. In Allinger, N. L. and Eliel, E. L., (Eds.), *Topics in Stereochemistry*, Interscience, New York 1967, Vol. 1, p. 22.
- Raban, M. and Mislow, K. *Ibid.* Vol. 2, p. 216.
- Rauk, A., Buncel, E., Moir, R. Y. and Wolfe, S. *J. Am. Chem. Soc.* **87** (1965) 5498.
- Wolfe, S. and Rauk, A. *Chem. Commun.* **1966** 778.
- Bullock, E., Scott, J. M. W. and Golding, P. D. *Chem. Commun.* **1967** 168.
- Nishio, M. *Chem. Commun.* **1968** 562.
- Randall, J. C., McLeskey, J. J., Smith, P. and Hobbs, M. E. *J. Am. Chem. Soc.* **86** (1964) 3229.
- Allenmark, S. and Bohman, O. *Acta Chem. Scand.* **22** (1968) 1404.
- Allenmark, S. *Acta Chem. Scand.* **19** (1965) 2075.
- Allenmark, S., Hagberg, C.-E. and Bohman, O. *Arkiv Kemi* **30** (1968) 269.
- Perkin, W. H. *J. Chem. Soc.* **47** (1885) 273.
- Wiley, R. H. and Harrel, J. R. *J. Org. Chem.* **25** (1960) 903.
- Posner, T. *Ber.* **32** (1899) 2801.

Received November 23, 1968.