[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

The Stereospecific Cleavage of Vinylic Sulfides. Observance of a Solvent Effect in Metal–Amine Systems[1,2]

BY WILLIAM E. TRUCE AND JEROME J. BREITER[3]

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The stereospecific reductive cleavage of vinylic sulfides has been accomplished by the use of sodium or lithium in liquid ammonia. Reductive cleavage of vinylic sulfides with lithium in methylamine was shown to be non-stereospecific and this fact is attributed to a solvent effect.

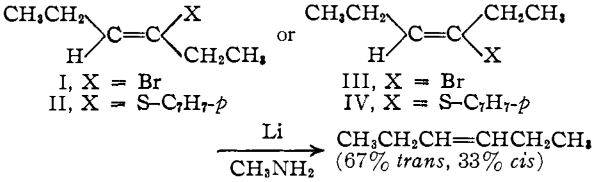
As part of our study on the reductive cleavage of sulfides and sulfones,[4] it appeared of interest to study the stereochemistry of the cleavage of vinylic sulfides. Since Boord[5] had reported that reductive cleavage of vinylic chlorides with sodium in liquid ammonia occurred with retention of configuration, it was thought that cleavage of vinylic sulfides with lithium in methylamine would also occur with retention of configuration.

The compounds chosen for this study were the *cis*- and *trans*-3-*p*-tolylmercapto-3-hexenes because the cleavage products, *cis*- and *trans*-3-hexene, were well known and easily separated and identified by vapor-phase chromatography. The 2-*p*-tolylmercapto-2-butene system was avoided, although these compounds had been prepared previously,[6] because of the difficulty of separating the very volatile 2-butenes from the amine solvent.

The synthesis of the vinylic sulfides was accomplished in the manner which follows. Addition of HBr to 3-hexyne gave 94% *trans*- and 6% *cis*-3-bromo-3-hexene (I), which on treatment with lithium in ether followed by *p*-tolyl disulfide gave 80% *trans*- and 20% *cis*-3-*p*-tolylmercapto-3-hexene (II). The reaction of a vinyllithium compound with a disulfide has been shown by Bordwell[6] to occur with retention of configuration. Reduction of 3-hexyne with sodium in ammonia gave *trans*-3-hexene. which on addition of bromine gave *meso*-3,4-dibromohexane. Dehydrohalogenation of the *meso*-dibromide with piperidine gave >99% *cis*-3-bromo-3-hexene (III), which on treatment with lithium in ether followed by *p*-tolyl disulfide gave 84% *cis*- and 16% *trans*-3-*p*-tolylmercapto-3-hexene (IV).

Cleavage of II or IV with lithium or sodium in ammonia resulted in the formation of the corresponding 3-hexene with greater than 90% retention of configuration. In addition, cleavage of I or III with lithium or sodium in ammonia also resulted in the formation of the corresponding 3-hexene with greater than 90% retention of configuration, thereby substantiating the results of Boord.[5]

However, when I, II, III or IV was cleaved with lithium in methylamine, the same mixture of 67% *trans*- and 33% *cis*-3-hexene was obtained.



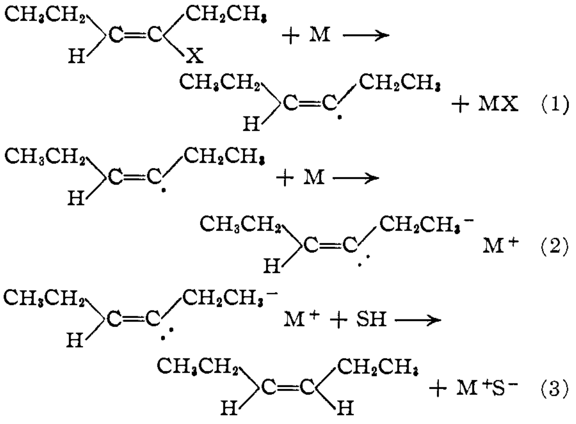
I, X = Br
II, X = S–C_7H_7-*p*

or

III, X = Br
IV, X = S–C_7H_7-*p*

$\xrightarrow[CH_3NH_2]{Li}$ $CH_3CH_2CH{=}CHCH_2CH_3$ (67% *trans*, 33% *cis*)

Since it was shown that III was not isomerized under the reaction conditions and *trans*-3-hexene was not affected by lithium methylamide, the non-stereospecificity observed with the lithium-methylamine system is attributed to a solvent effect. These results also suggest a stepwise electron transfer rather than a two-electron transfer for the cleavage,[7] (1) → (3). By analogy to the work of Curtin,[8]



the alkenyl carbanion should be configurationally stable under these conditions, and since the starting material was not isomerized under the reaction conditions, the observed isomerization is believed to occur at the radical stage, *i.e.*, after the transfer of one electron. In some way, then, reaction 2 is sufficiently retarded in methylamine and not in ammonia, thus allowing isomerization to occur. At this time, the exact nature of this solvent effect is not apparent but could be due to the increase in the size of the solvent in going from ammonia to methylamine.[9] Solvent effects have also been ob-

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(2) Taken from the Ph.D. Thesis of J. J. B.

(3) Continental Oil Co. Fellow, 1960–1961.

(4) W. E. Truce, D. P. Tate and D. N. Burdge, *J. Am. Chem. Soc.*, **82**, 2872 (1960); W. E. Truce and J. J. Breiter, *ibid.*, **84**, 1621 (1962).

(5) M. C. Hoff, K. W. Greenlee and C. E. Boord, *ibid.*, **73**, 3329 (1951).

(6) F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957).

(7) For a discussion of one- or two-electron transfer in reductive cleavages, see for example: A. J. Birch, *Quart. Revs.*, **4**, 69 (1950); E. Grovenstein and R. W. Stevenson, *J. Am. Chem. Soc.*, **81**, 4850 (1959); J. Van Schooten, J. Knotnerus, H. Boer and Ph. M. Duinker, *Rec. trav. chim.*, **77**, 935 (1958).

(8) D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958); D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716 (1951).

(9) It has been suggested by a referee that perhaps the carbanion is formed rapidly in both solvents, but that methylamine somehow facilitates the isomerization of the carbanion. However, it is believed that these carbanions would be configurationally stable at the temperature of the reaction (−75°).

served in the reduction of aromatic hydrocarbons by lithium in amines.[10]

In a preliminary communication, Adams and Wallis[11] reported that cleavage of optically active 12-phenyl-12-β-benzoxanthenethioglycolic acid with sodium in liquid ammonia ruptured the C–S bond and gave a deep orange-brown sodium triarylmethyl. After reaction with a slight excess of ammonium bromide, the resulting trisubstituted methane was found to be optically active. However, this claim was shown by Wittig[12] to be erroneous.

TABLE I

CLEAVAGE OF VINYLIC SULFIDES AND HALIDES

Compound	System	3-Hexene % *cis*	% *trans*	Yield, %
I	$Na-NH_3$	9	91	..
I	$Li-NH_3$	10	90	..
I	$Li-CH_3NH_2$	32	68	..
II	$Na-NH_3$	24	76	70
II	$Li-NH_3$	20	80	60
II	$Li-CH_3NH_2$	33	67	81
III	$Na-NH_3$	91	9	..
III	$Li-NH_3$	90	10	..
III	$Li-CH_3NH_2$	34	66	..
IV	$Na-NH_3$	77	23	72
IV	$Li-NH_3$	82	18	60
IV	$Li-CH_3NH_2$	33	67	52

Experimental[13]

Preparation of *trans*-3-Bromo-3-hexene.—In a flask fitted with a gas dispersion tube and reflux condenser was placed 41 g. (0.5 mole) of 3-hexyne and 500 ml. of pentane. The flask was cooled to 0° and 39 g. (0.48 mole) of anhydrous HBr was added. The solvent and excess acetylene were removed and the product was distilled under reduced pressure to give 46.9 g. (60%) of 94% *trans*- and 6% *cis*-3-bromo-3-hexene,[14] b.p. 47–48° (23 mm.), $n^{25}\mathrm{D}$ 1.4608 (lit.[15] for 3-bromo-3-hexene, b.p. 34° (16 mm.), $n^{21}\mathrm{D}$ 1.459).

Proof of Structure of *trans*-3-Bromo-3-hexene.—To a suspension of 0.36 g. (0.0576 g.-atom) of lithium in 100 ml. of anhydrous ether was added slowly 4.2 g. (0.0258 mole) of 91% *trans*- and 9% *cis*-3-bromo-3-hexene. The mixture was refluxed under nitrogen for 3 hours and then cooled to 0° in an ice-bath. Methanol was added slowly and the lithium bromide was filtered off and the ether solution was analyzed by vapor-phase chromatography.[16] The mixture contained 87 mole % *trans*-3-hexene and 13 mole % *cis*-3-hexene.[17]

Preparation of *trans*-3-Hexene.—3-Hexyne (41 g., 0.5 mole) was reduced with 24.32 g. (1.05 g.-atoms) of sodium in 500 ml. of ammonia to *trans*-3-hexene in 76% yield, b.p. 66.5°, $n^{25}\mathrm{D}$ 1.3927 (lit.[18] b.p. 67.15°, $n^{20}\mathrm{D}$ 1.3941).

Preparation of *meso*-3,4-Dibromohexane.—To 26.5 g. (0.315 mole) of *trans*-3-hexene was added dropwise 51.5 g. (0.315 mole) of bromine at 0°. The product was distilled under reduced pressure to give 74.9 g. (96%) of *meso*-3,4-dibromohexane, b.p. 90–91° (23 mm.), $n^{25}\mathrm{D}$ 1.5045 (lit.[19] for 3,4-dibromohexane, b.p. 64.5–65° (6 mm.), $n^{20}\mathrm{D}$ 1.5090).

Preparation of *cis*-3-Bromo-3-hexene.—In a flask was placed 34.5 g. (0.141 mole) of *meso*-3,4-dibromohexane and 200 g. (2.35 moles) of piperidine. The mixture was refluxed for 4 hours and then poured into excess ice-cold 25% HCl. The organic layer was separated and dried over anhydrous magnesium sulfate. Distillation gave 18 g. (64%) of *cis*-3-bromo-3-hexene, b.p. 50–51° (28 mm.), $n^{25}\mathrm{D}$ 1.4623.

Preparation of *cis*-3-*p*-Tolylmercapto-3-hexene.—In a flask was placed 50 ml. of anhydrous ether and 0.7 g. (0.1 g.-atom) of lithium. To this was added slowly at 0° 8.15 g. (0.05 mole) of *cis*-3-bromo-3-hexene and the mixture was stirred until all of the lithium dissolved. The mixture was then cooled to −50° by means of a Dry Ice–acetone-bath and 12.3 g. (0.05 mole) of *p*-tolyldisulfide in 60 ml. of anhydrous ether was added slowly. The mixture was stirred for 1 hour and then filtered through a glass-wool plug into 300 ml. of water. The organic layer was separated, washed with 10% sodium hydroxide and dried over anhydrous magnesium sulfate. The ether was removed and the residue was distilled under reduced pressure to give 6.4 g. (60%) of 84% *cis*- and 16% *trans*-3-*p*-tolylmercapto-3-hexene, b.p. 93–94° (0.7 mm.), $n^{25}\mathrm{D}$ 1.5474.

Anal. Calcd. for $C_{13}H_{18}S$: C, 75.76; H, 8.73; S, 15.53. Found: C, 75.76; H, 8.98; S, 15.40.

Preparation of *trans*-3-*p*-Tolylmercapto-3-hexene.—The procedure used was identical to that described above. From 8.15 g. (0.05 mole) of 94% *trans*- and 6% *cis*-3-bromo-3-hexene, 0.7 g. (0.1 g.-atom) of lithium and 12.3 g. (0.05 mole) of *p*-tolyl disulfide was obtained 5.3 g. (50%) of 80% *trans*- and 20% *cis*-3-*p*-tolylmercapto-3-hexene, b.p. 92–93° (0.6 mm.), $n^{25}\mathrm{D}$ 1.5480.

Procedure for the Cleavage of Vinylic Sulfides and Bromides.—The procedure used was similar to that described by Boord.[5] The solvent was condensed into a 100-ml. flask and then the appropriate amount of alkali metal (6 g.-atoms per mole of compound) was added. After the metal had completely dissolved, the flask and contents were cooled to about −75° by means of a Dry Ice–acetone-bath and the compound to be cleaved (dissolved in about five times its volume of methylcyclohexane) was added dropwise. After all of the compound had been added, the mixture was stirred at −75° for about 15 minutes and then the excess metal was decomposed by the addition of methanol. The cold bath was removed and 50 ml. of water was added slowly. The mixture was then poured into 300 ml. of water and the methylcyclohexane layer was separated, dried over anhydrous magnesium sulfate, and analyzed by vapor-phase chromatography, using a column of adiponitrile on Celite to determine the relative amounts of *cis*- and *trans*-3-hexene produced. When vinylic sulfides were cleaved, yields were based on the amount of *p*-toluenethiol obtained on acidification of the aqueous solution. The results of the cleavages are summarized in Table I.

Reduction of 3-Hexyne with Lithium in Methylamine.—3-Hexyne (1.23 g., 0.015 mole) in 4 ml. of methylcyclohexane was reduced with 0.21 g. (0.03 g.-atom) of lithium in 40 ml. of methylamine. The only olefin present was *trans*-3-hexene, thus showing that the final product is stable to this system.

Treatment of *cis*-3-Bromo-3-hexene with One Equivalent of Lithium in Methylamine.—Using the procedure described above, 3.5 g. (0.0215 mole) of 98% *cis*- and 2% *trans*-3-bromo-3-hexene in 10 ml. of methylcyclohexane was cleaved with 0.15 g. (0.0215 g.-atom) of lithium in 50 ml. of methylamine. The bromide which was recovered was found not to be isomerized, while the 3-hexenes were produced in the proportions of 66% *trans*, 34% *cis*.

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(10) R. A. Benkeser, R. K. Agnihotri and M. L. Burrous, *Tetrahedron Letters*, **16**, 1 (1960).

(11) F. H. Adams and E. S. Wallis, *J. Am. Chem. Soc.*, **54**, 4753 (1932).

(12) G. Wittig, F. Vidal and E. Bohnert, *Ber.*, **83**, 359 (1950).

(13) All melting points and boiling points are uncorrected. Microanalysis was performed by C. S. Yeh.

(14) Determined by vapor-phase chromatography.

(15) Lespieau and Wiemann, *Bull. soc. chim. France*, **45**, 632 (1929).

(16) A Perkin–Elmer model 154-C vapor fractometer was used for this purpose and the resulting curves were integrated by means of a compensating polar planimeter.

(17) We are indebted to Dr. H. C. Brown for authentic samples of these compounds.

(18) P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg and F. L. Howard, *J. Research Natl. Bur. Standards*, **52**, 59 (1954).

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