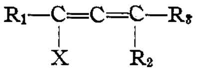
usually strong and occurs in a relatively unobscured infrared region. A number of new allenic compounds became available recently and the study of their spectra now reveals that the very strong allenic absorption band is near 1940 cm.$^{-1}$ and that it often splits into two strong bands near 1930 and 1950 cm.$^{-1}$, respectively. In Table I are listed the compounds studied and the position and intensities of the allenic absorption band(s). The upper curve in Fig. 1 is an example of a compound showing the doublet whereas the lower curve illustrates the single allenic absorption band.

With the exception of compounds I, VIII and XI the compounds studied are solids at room temperature. Their spectra were determined in carbon tetrachloride or nujol suspensions. It was observed that the doublet is especially noticeable when carbon tetrachloride was used as solvent, whereas it is not as apparent in nujol suspensions. We also found that compounds which often showed a broad band near 1940 cm.$^{-1}$ when studied with the Baird I. R. Spectrograph using a sodium chloride prism, showed a sharp doublet with a Perkin–Elmer instrument using a calcium fluoride prism. Thus we resolved the broad band near 1950 cm.$^{-1}$ of VIII in the recently published spectrum[2] into a doublet. We have also tried to determine the Raman spectrum of compound IV, but were unsuccessful due to absorption and (or) fluorescence in the region of 4358 Å.

TABLE I



$$\underset{X}{R_1—C}=C=\underset{R_2}{C}—R_3$$

Comp.	R_1	X	R_2	R_3	Synthesis reference	Allenic absorption band, cm.$^{-1}$ 1930	1940	1950
I	C_4H_9	H	H	H	*a*	−	++	−
II	H	CO_2H	H	H	*d*	+	−	+
III	C_3H_7	CO_2H	H	H	*b*	+	−	+
IV	C_4H_9	CO_2H	H	H	*b*	+	−	+
V	C_5H_{11}	CO_2H	H	H	*b*	+	−	+
VI	C_4H_9	CO_2H	H	CH_3	*c*	−	++	−
VII	C_4H_9	CO_2H	CH_3	CH_3	*c*	−	++	−
VIII	C_4H_9	CO_2CH_3	H	H	*b*	+	−	+
IX	C_3H_7	$CONH_2$	H	H	*b*	+	−	+
X	C_4H_9	$CONH_2$	H	H	*b*	+	−	+
XI	C_4H_9	CH_2OH	H	H	*e*	−	++	−

\+ Strong. ++ Very strong. − Missing. [a] H. Wotiz, THIS JOURNAL, **73**, 693 (1951). [b] Reference 2. [c] J. H. Wotiz and R. J. Palchak, THIS JOURNAL, **73**, 1971 (1951). [d] J. H. Wotiz, J. S. Matthews and J. A. Lieb, *ibid.*, **73**, 5503 (1915). [e] J. H. Wotiz and P. Mosso, unpublished results.

On the basis of the above listed findings we now have available a convenient method for the identification of compounds containing a carboxy, an amide or an ester grouping directly attached to an allenic bond. Such compounds containing a terminal allenic linkage show a doublet whereas the allenic bond inside the chain shows a single absorption band. The reason for such spectroscopic behavior is not apparent to us. We anticipate that other negative groups (electron attracting) will influence the allenic absorption band in the same manner as the groups listed above.

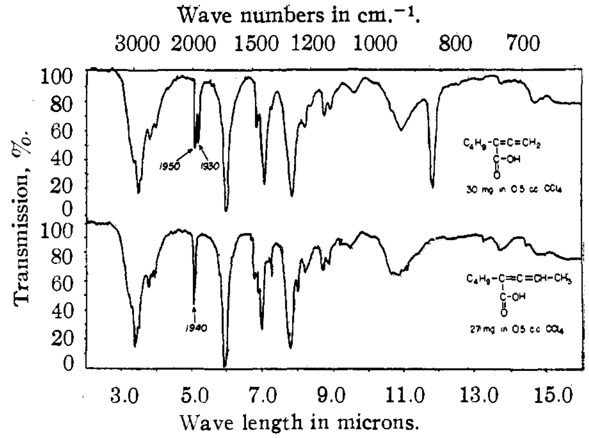


Fig. 1.

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[2] J. H. Wotiz, THIS JOURNAL, **72**, 1639 (1950)

The Reduction of Cyclohexanone Cyanohydrin by Lithium Aluminum Hydride

BY HAROLD R. NACE AND BILL B. SMITH[1]

RECEIVED NOVEMBER 12, 1951

The preparation of 1-aminomethyl-cyclohexanol by catalytic hydrogenation (Adams platinum) of cyclohexanone cyanohydrin has been reported by Tchoubar[2a,b] and Goldberg and Kirchensteiner.[2c] The hydrogenation was difficult to perform, and, consequently, unsatisfactory for the preparation of the aminoalcohol. Dauben, *et al.*,[3] developed a more convenient synthesis by reducing the corresponding nitroalcohol, 1-nitromethylcyclohexanol, to the aminoalcohol.

Difficulties with the hydrogenation of the cyanohydrin were also experienced in this Laboratory, and a second alternative synthesis, reduction of the cyanohydrin with lithium aluminum hydride, was developed.

Nystrom and Brown[4] reported the reduction of mandelonitrile (benzaldehyde cyanohydrin) in 48% yield using slightly more than one mole of hydride for two moles of cyanohydrin, and suggested that the use of a greater excess of hydride might improve the yield. Heusser, *et al.*,[5] reported the re-

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[1] Research Corporation Fellow, 1951–1952. This paper is based on a portion of the thesis to be submitted by Bill B. Smith in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

[2] (a) B. Tchoubar, *Compt. rend.*, **205**, 54 (1937). (b) B. Tchoubar, *Bull. soc. chim. France*, **216**, 160, 164, 169 (1949). (c) M. W. Goldberg and H. Kirchensteiner, *Helv. Chim. Acta*, **26**, 288 (1943).

[3] H. J. Dauben, H. J. Ringold, R. H. Wade and A. G. Anderson, THIS JOURNAL, **73**, 2359 (1951).

[4] R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948).

[5] H. Heusser, P. th. Herzig, A. Fürst and Pl. A. Plattner, *Helv. Chim. Acta*, **33**, 1093 (1950).

duction in unspecified yield (product isolated as oxazolidine) of $3(\beta),17(\beta)$-diacetoxy-17-iso-$\Delta^{5,6}$-etiocholenic acid nitrile with lithium aluminum hydride in ether. Amundsen and Nelson[6] found that maximum yields of amines from nitriles were obtained when the molar ratio of hydride to nitrile was one to one, lower yields being obtained when less hydride was used.

In the reduction reported here, the use of one and a half moles of hydride to one of cyanohydrin gave yields of 62–67%, and increasing the amount of hydride to two moles increased the yield to 76%. The method is convenient and requires no special equipment, and should prove to be a useful synthetic method for the preparation of aminoalcohols from cyanohydrins.

Experimental

1-Aminomethyl-cyclohexanol.—Cyclohexanone cyanohydrin was prepared from potassium cyanide and the bisulfite addition product of cyclohexanone according to the method of Tchoubar.[2b] Using 150 g. (1.53 moles) of cyclohexanone, the cyanohydrin (b.p. 112–115° (11 mm.)) was obtained in 70–79% yield.

A solution of 125 g. (1.0 mole) of cyclohexanone cyanohydrin in 200 ml. of absolute alcohol-free ether was added dropwise over a period of one hour to a well stirred slurry of 76 g. (2.0 moles) of lithium aluminum hydride (Metal Hydrides, Inc.) in 2 liters of ether in a three-necked, 5-liter flask (cooled in an ice-bath throughout the addition) fitted with an efficient reflux condenser, dropping funnel, and mercury-sealed Hershberg stirrer. After the addition, the mixture was stirred overnight at room temperature, and then the addition complex was decomposed by adding dropwise 50 ml. of water, 40 ml. of 20% sodium hydroxide solution, and finally 150 ml. of water. The resulting mixture was filtered, the filtrate dried over anhydrous sodium sulfate, the ether removed, and the residue distilled to yield 69 g. (53.5%) of 1-aminomethylcyclohexanol, b.p. 95–115° (22 mm.) (major portion 110–115°). The filter cake was digested with 600 ml. of hot benzene, and the benzene solution was dried and distilled to yield an additional 28.7 g. of aminoalcohol, b.p. 93–115° (20 mm.), total yield 97.7 g. (75.5%). The hydrochloride melted at 214.5–215.5° dec. (cor.) (reported[2] 215–216°) and the picrate at 169.5–171° (cor.) (reported[2] 168–170°).

The infrared spectra of the aminoalcohol prepared by the above method agreed in every respect with that of a sample of 1-aminomethylcyclohexanol prepared by the hydrogenation of cyclohexanone cyanohydrin. The strong band at 1700 cm.$^{-1}$ (unassigned) and the medium band at 2232 cm.$^{-1}$ ($C\equiv N$) of the cyanohydrin were absent in the aminoalcohol prepared above, thus assuring its purity. All spectra were taken on a modified Perkin–Elmer Model 12B infrared spectrometer in which a double beam rearrangement replaced the original single beam optical system.[7] Samples of the pure liquid were compressed between sodium chloride windows. A calcium fluoride prism was used.

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(6) L. H. Amundsen and L. S. Nelson, THIS JOURNAL, **73**, 242 (1951).

(7) D. F. Hornig, G. E. Hyde and W. A. Adcock, *J. Optical Soc. Am.*, **40**, 497 (1950).

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Comparative Ease of Cleavage of Some Phenyl Alkyl and Phenyl Aralkyl Sulfides

BY D. S. TARBELL AND DONALD P. HARNISH[1]

The present study was undertaken to find out how the ease of cleavage of the carbon–sulfur bond varies, in a series of phenyl alkyl and phenyl aralkyl sulfides, with the structure of the sulfide, and to obtain data for a comparison of the corresponding sulfur and oxygen compounds.[2]

The behavior of the sulfides listed in the table was examined toward a variety of agents of varying degrees of effectiveness; the results with aluminum bromide in chlorobenzene and with aqueous hydrobromic acid, which allow the most general comparison of activity, are tabulated. It is clear that, as would be expected, the rate of cleavage of the sulfides, C_6H_5SR, to form C_6H_5SH, follows the order $(C_6H_5)_3C > (C_6H_5)_2CH > C_6H_5CH_2 > C_6H_5CH_2CH_2$. This order is emphasized by further observations that $C_6H_5SC(C_6H_5)_3$ is converted by alcoholic iodine (even at room temperature) to triphenylcarbinol, diphenyl disulfide and ethyl trityl ether, but $C_6H_5SCH(C_6H_5)_2$ is unaffected by this reagent, even on boiling. The trityl sulfide is cleaved by aluminum bromide in ether or nitrobenzene, which, being strong donor solvents, completely prevent cleavage of benzyl phenyl sulfide by aluminum bromide.[2a] The trityl and benzhydryl sulfides are both cleaved by alcoholic silver nitrate.[3]

The slower rate of cleavage of sulfides in comparison with the corresponding ethers, is shown by the rapid splitting of benzyl phenyl ether by hydrogen bromide in acetic acid at room temperature,[4] and by the splitting of phenyl trityl ether by hydrogen chloride in acetic acid in the cold.[5] The deactivating effect toward electrophilic substitution in an aromatic ring of sulfur, compared to oxygen,[2d] is indicated by the isolation, after iodine oxidation of the reaction mixture, of diphenyl disulfide from the aluminum bromide catalyzed cleavage of the benzyl, benzhydryl and trityl phenyl sulfides; the analogous oxygen compounds give much nuclear alkylation under comparable conditions.[2a,6]

In the series C_6H_5SR, the ease of cleavage follows the expected order[7] $C(CH_3)_3 > CH(CH_3)_2 > CH_3$. *t*-Butyl phenyl sulfide is not, however, affected by alcoholic iodine or alcoholic silver nitrate, in contrast to the benzhydryl and trityl compounds. The thermal[8] and aluminum chloride[8,9] catalyzed cleavage of $C_6H_5OC(CH_3)_3$ lead to *p*-*t*-butylphenol, and the action of boron fluoride on isopropyl aryl ethers leads to isopropylphenols[10]; these carbon–oxygen cleavages appear to take place far more rapidly than the carbon–sulfur cleavages listed in the table. In agreement with this, it has been found[11] that ani-

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[1] Beaunit Mills Fellow, 1947–1948.

(2) Preceding papers on this topic: (a) D. P. Harnish and D. S. Tarbell, THIS JOURNAL, **70**, 4123 (1948); (b) *Anal. Chem.*, **21**, 968 (1949); (c) H. F. Wilson and D. S. Tarbell, THIS JOURNAL, **72**, 5200 (1950); (d) D. S. Tarbell and J. C. Petropoulos, *ibid.*, **74**, 244 (1952); (e) D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951).

(3) D. C. Gregg, H. A. Iddles and P. W. Stearns (*J. Org. Chem.*, **16**, 246 (1951)) found that phenyl trityl sulfide was cleaved by methanolic mercuric chloride at room temperature.

(4) B. W. Tronow and L. W. Ladigina, *Ber.*, **62**, 2844 (1929).

(5) A. Baeyer, *ibid.*, **42**, 2626 (1909).

(6) H. A. Iddles, *et al.*, THIS JOURNAL, **62**, 2757 (1940); **64**, 3154 (1942); J. Van Alphen, *Rec. trav. chim.*, **46**, 287, 803 (1927).

(7) J. F. Norris and G. W. Rigby, THIS JOURNAL, **54**, 2088 (1932), showed that the rates of cleavage of ethyl butyl ethers by concentrated hydrochloric acid followed the order *t*-butyl > *s*-butyl > *n*-butyl.

(8) R. A. Smith, *ibid.*, **55**, 3718 (1933).

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(10) F. J. Sowa, H. D. Hinton and J. A. Nieuwland, THIS JOURNAL, **54**, 2019 (1932); **55**, 3402 (1933).

(11) J. C. Petropoulos, unpublished observation.