

Novel Route to 1,1,1,2,2,3-Hexachloropropane

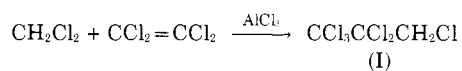
MAX M. BOUDAKIAN

Chemicals Division, Olin Mathieson Chemical Corp., Rochester, N. Y. 14601

A one-step, low-yield route to 1,1,1,2,2,3-hexachloropropane by the aluminum chloride-catalyzed reaction of methylene chloride and tetrachloroethylene is described. Previously published procedures to this compound required five- or six-step sequences based on carbon tetrachloride-ethylene or allyl chloride, respectively.

PREVIOUSLY published routes to 1,1,1,2,2,3-hexachloropropane, (I), involve five- or six-step sequences based on carbon tetrachloride-ethylene (4, 6) or allyl chloride (2, 18, 20), respectively.

A one-step route to (I) would be the aluminum chloride-catalyzed alkylation of tetrachloroethylene with methylene chloride.



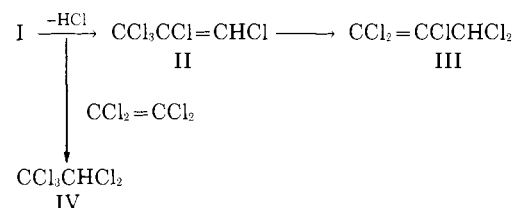
However, the aluminum chloride-catalyzed addition of methylene chloride with chlorinated olefins such as tetrachloroethylene could not be effected by Prins (7). The inertness of methylene chloride under these conditions prompted its use as a solvent in ionic reactions involving other haloalkanes with halolefins (8-17). This behavior of methylene chloride is to be contrasted with numerous examples of the alkylation of aromatics by this reagent (19), as well as its addition to olefins under free radical conditions (1, 3).

Lehmann and Bayer (5) reported that the aluminum chloride-catalyzed addition of methylene chloride to 1,2-dichloroethylene (isomer unspecified) gave 1,1,2,3-tetrachloropropane in 24% yield. Accordingly, a reinvestigation of the corresponding reaction of methylene chloride with tetrachloroethylene, a less-reactive halogenated olefin in such alkylation reactions, was undertaken.

Contrary to previously published observations (7), it was demonstrated that addition could be effected under mild conditions (40° to 50° C.) to give (I) in 4% uncorrected yield. Gallium chloride catalyst was ineffective. There was no evidence of 1,1,2,2,3,3-hexachloropropane, $\text{HCCl}_2\text{CCl}_2\text{-CCl}_2\text{H}$, in the main distillation fraction. The proton chemical shift of (I) confirmed the value predicted by White (21) for this compound. This prediction was based on the observed linear dependence of the chloromethyl chemical shift with increasing chlorine substitution in the series, $\text{ClCH}_2\text{CCl}_2\text{CH}_x\text{Cl}_{3-x}$.

Higher temperatures (75° to 80° C.) do not increase the yield of (I); instead, side reactions occur to give 1,2,3,3,3-

pentachloropropene-1, (II), and/or 1,1,2,3,3-pentachloropropene-1, (III), pentachloroethane, (IV), and unidentified high boilers.



The dehydrohalogenation of I by aluminum chloride in refluxing carbon tetrachloride to give II, followed by an allylic shift to form III, has been reported (15).

EXPERIMENTAL

A mixture consisting of tetrachloroethylene (Eastman Kodak, 0.50 mole; 89.2 grams), methylene chloride (Matheson, Coleman and Bell, 1.5 moles; 127.5 grams), and aluminum chloride (Baker and Adamson, 0.1 mole; 13.34 grams) was heated to reflux at 40° to 50° C. for 26.8 hours. Ice (100 grams) was then added; the organic layer was separated and washed twice with 100-ml. portions of water. Distillation of the dried (magnesium sulfate) organic layer provided recovery of the bulk of starting materials and isolation of a product (4.7 grams, 3.7% uncorrected yield), b.p. 72-4° C., 2.8 mm. of Hg; m.p. 23-5° C., n_D^{25} 1.5278. Reported for I: b.p. 75-6° C., 4 mm. of Hg (4), m.p. 25-6° C. (4); n_D^{25} 1.5282 (2); 1.5288 (4). Anal. Calcd. for $\text{C}_3\text{Cl}_6\text{H}_2$: C, 14.37; H, 0.80; Cl, 84.83. Found C, 14.53; H, 0.87; Cl, 84.95. Mass spectral assay—scanned from m/e 13 to 400; single-focusing mass spectrometer, Consolidated Electrodynamical Corp., Model 21-103-C—disclosed a fragmentation pattern consistent with I; fragments were noted at m/e 117 (loss of $-\text{CCl}_2\text{CH}_2\text{Cl}$); 131 (loss of CCl_3-), and 199 (loss of $-\text{CH}_2\text{Cl}$). Other fragments were noted at m/e 83, 143, 164, 177, and 213.

NMR. The ^1H NMR spectrum of a deuteriochloroform solution of I was obtained using a Varian A-60 NMR

spectrometer. Only one sharp resonance line was observed: 4.42 p.p.m. referenced to internal tetramethylsilane (TMS). White (21) had predicted a chemical shift value of 4.44 p.p.m. (from TMS) for I. Isomeric 1,1,2,2,3,3-hexachloropropane exhibits a chemical shift of 6.35 p.p.m. (from TMS) (21).

IR. NaCl plates (neat) using a Perkin-Elmer Model 137 spectrophotometer showed absorptions (μ) at: 3.32 (vw); 7.00 (m); 7.72 (vw); 8.25 (w); 9.45 (w); 9.80 (vw); 10.10 (vw); 10.30 (s); 11.78 (s); 12.30 (vs); 12.90 (vs); 13.35 (m); 13.70 (vs); and 14.85 (vs). The characteristic frequencies of the Raman spectrum of I have been reported (2).

VPC. F and M Chromatograph, Model 300: 1 meter, 0.25-inch O.D. aluminum column, packed with 5% Igepal on Chromosorb ABS (80- to 100-mesh); injection port temp., 250°C.; detector block temp., 280°C.; helium flow rate, 75 ml. per minute; column temp. programmed 9°C. per minute from 75° to 225°C. Retention time of I, 7.0 minutes.

The distillation residue (0.95 gram) consisted of a viscous liquid (n_D^{25} 1.575) which was not characterized.

When the above reaction was conducted in a glass-lined rocking autoclave—75°C., 24 to 60 hours; 5 moles of methylene chloride, 1 mole of tetrachloroethylene, and 0.2 mole of aluminum chloride—the yield of I decreased to 2.5%. Mass spectral and infrared analysis indicated that a low-boiling fraction, b.p. 42–7°C., 4.5 mm. of Hg, consisted of II and/or III and IV. The distillation residue (maximum temp., 183°C., 4 mm. of Hg) was not identified.

Tetrachloroethylene (1.79 moles), methylene chloride (5.37 moles), and gallium chloride (0.057 mole; Alfa Inorganics) were heated at reflux for 22 hours. VPC indicated the presence of starting materials only.

ACKNOWLEDGMENT

The author acknowledges stimulating discussions with J.S. Babiec, H.D. Hoberecht, and G.D. Vickers of the Analytical Department, Olin Research Center.

LITERATURE CITED

- (1) Colebourne, N., Stern, E.S., *Chem. Ind. (London)* **1964**, p. 2127.
- (2) Gerding, H., Haring, H.G., *Rec. Trav. Chim.* **74**, 841 (1955).
- (3) Harmon, J., Ford, T.A., Hanford, W.E., Joyce, R.N., *J. Am. Chem. Soc.* **72**, 2213 (1950).
- (4) Haszeldine, R.N., *J. Chem. Soc.* **1953**, p. 3371.
- (5) Lehmann, W., Bayer, O. (to I.G. Farbenindustrie A.G.), Ger. Pat. **715,069** (Nov. 20, 1941); *CA* **38**, 2051 (1944).
- (6) Nesmeyanov, A.N., Freidlina, R.K., Firstov, V.I., *Izv. Akad. Nauk SSSR. Otd. Khim. Nauk* **1951**, p. 505; *CA* **46**, 7034 (1952).
- (7) Prins, H.J., *Rec. Trav. Chim.* **51**, 1065 (1932).
- (8) *Ibid.*, **54**, 249 (1935).
- (9) *Ibid.*, **56**, 779 (1937).
- (10) *Ibid.*, **57**, 659 (1938).
- (11) *Ibid.*, **65**, 455 (1946).
- (12) *Ibid.*, **68**, 217 (1949).
- (13) *Ibid.*, **68**, 419 (1949).
- (14) *Ibid.*, **72**, 253 (1953).
- (15) *Ibid.*, **72**, 867 (1953).
- (16) *Ibid.*, **73**, 479 (1954).
- (17) *Ibid.*, **75**, 1347 (1956).
- (18) Raulet, C., Levas, M., *Bull. Soc. Chim. France*, **1963**, p. 2147.
- (19) Thomas, C.A., "Anhydrous Aluminum Chloride in Organic Chemistry," p. 10, Reinhold, New York, 1941.
- (20) Whaley, A.M., Ph.D. dissertation, The Ohio State University, Columbus, Ohio, 1941.
- (21) White, H.F., *Anal. Chem.* **36**, 1291 (1964).

ANNOUNCEMENT

Infrared Spectra of Monosaccharides Related to Glycolipids in the Range 800–200 Cm.^{-1}

ANDREW E. GAL and FRANK J. FASH

Laboratory of Neurochemistry, National Institute of Neurological Diseases and Blindness, National Institutes of Health, Bethesda, Maryland 20014

INFORMATION is available on the infrared spectra of the following monosaccharides in the range of 800 to 200 cm.^{-1} : α -D-Galactose, α -D-glucose, α -D-mannose, α -D-fucose, D-ribose, β -lactose, N-acetylneuraminic acid, D-galactosamine-HCl, D-glucosamine-HCl, D-mannosamine-HCl, N-acetyl-D-galactosamine, N-acetyl-D-glucosamine, and N-acetyl-D-mannosamine. The majority of the spectra were recorded as suspension of the compounds in Nujol injected into a disposable or demountable polyethylene cell. Some spectra were recorded using pellets made from cesium iodide powder, which was obtained by lyophilization. The spectra were recorded with 2 to 20 mg. of the saccharides, using a Perkin-Elmer 621 Spectrophotometer. Expanded fre-

quency scale and ordinate expansion was used. The spectra are quite different and can be used for the identification of these compounds.

The complete spectral data and techniques for sample preparation employing cesium iodide pellets of Nujol suspensions in polyethylene cells may be obtained as NAPS Document NAPS-00427 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, New York 10001; remit \$1.00 for microfiche or \$3.00 for photocopies.

RECEIVED for review September 12, 1968. Accepted February 10, 1969.