mm, $n^{22}D$ 1.6835) which solidified upon standing. Recrystallization from hexane afforded pure N,N'-disulfinyl-2,4,6-trichloro-*m*-phenylenediamine, m.p. 54–55°.

Anal. Calcd. for $C_6HCl_3N_2O_2S_2$: C, 23.73; H, 0.33; N, 9.23; S, 21.08. Found: C, 23.84; H, 0.50; N, 9.23; S, 20.86.

Treatment of 16 g. of N,N'-disulfinyl-2,4,6-trichloro-*m*-phenylenediamine with 50 ml. of 20% aqueous sodium hydroxide afforded 10 g. of pure 2,4,6-trichloro-*m*-phenylenediamine,[5] m.p. 140–141° (91% yield).

N,N'-Disulfinyl-2,3,5,6-tetrachloro-*p*-phenylenediamine (3).—An amount of 108 g. (1.0 mole) of *p*-phenylenediamine was added portionwise over a period of 30 min. to 600 ml. (983 g., 8.25 moles) of thionyl chloride with agitation. During the addition, the temperature of the reaction mixture was maintained at 50 to 65° by means of an oil bath kept at 50 to 55°. After stirring for additional 2 hr., an amount of 281 g. (7.92 moles) of chlorine was passed over a period of 4.5 hr. into the reaction mixture at 55 to 65°.

N,N'-Disulfinyl-2,3,5,6-tetrachloro-*p*-phenylenediamine precipitated slowly from the warm reaction mixture and was separated by filtration after the chlorination was completed (indicated by the presence of chlorine gas in the condenser), and the reaction mixture cooled to 0°. Recrystallization from carbon tetrachloride afforded 250 g. (75% yield) of compound **3**, m.p. 171–172°, in form of yellow needles.

Anal. Calcd. for $C_6Cl_4N_2O_2S_2$: C, 21.32; Cl, 42.00; N, 8.29; S, 18.93. Found: C, 21.60; Cl, 42.20; N, 8.20; S, 18.40.

Chlorination of N,N'-disulfinyl-*p*-phenylenediamine with sulfuryl chloride in thionyl chloride afforded compound **3** in a yield of 43%.

A nearly quantitative yield of 2,3,5,6-tetrachloro-*p*-phenylenediamine (**6**), m.p. 224–225°, was obtained by treatment of N,N'-disulfinyl-2,3,5,6-tetrachloro-*p*-phenylenediamine with either 15% aqueous sodium hydroxide at room temperature or with boiling hydrochloric acid.

Acknowledgment.—The authors are indebted to Mr. J. Pregler for technical assistance and to Dr. H. Agahigian for taking the n.m.r. spectra.

The Triacetyl-D-glucal Dichlorides

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Dihalogen addition products of the glycals and triacetyl glycals are formed quite readily by the direct addition of halogen to the unsaturated linkage. Inspection of I shows that carbon atoms 1 and 2 may become asymmetric and thus afford four different stereoisomers.

Fischer, Bergmann, and Schotte[1] reported that the chlorination of triacetyl-D-glucal (I) afforded a crystalline product of m.p. 92–94°, the optical rotation of which varied with the number of recrystallizations. Danilov and Gakhokidze[2] reported m.p. 89–92° for this material.

The addition of bromine to triacetyl-D-glucal has recently been studied by Lemieux and Fraser-Reid.[3] N.m.r. analysis of the sirupy product showed that it was a mixture of tri-*O*-acetyl-2-bromo-2-deoxyglycopyranosyl bromides containing about 60% and 30% of the compounds with the α-D-*gluco* and α-D-*manno* configurations, respectively.

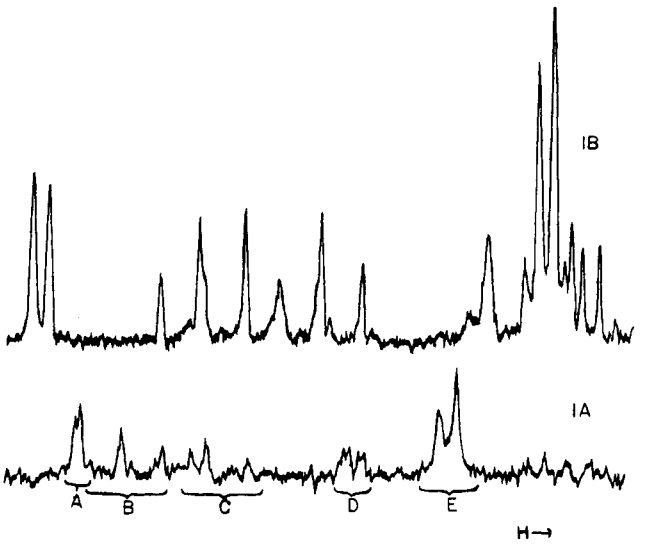
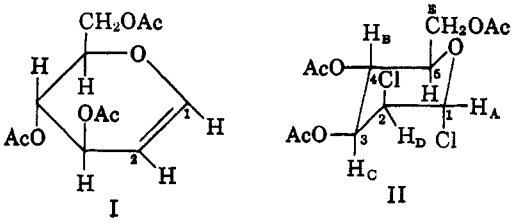
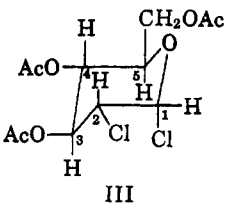


Figure 1.—The n.m.r. spectra of (A) tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranosyl chloride; and (B) the *gluco* stereoisomer

Experiments in our laboratories have been designed to separate and identify the isomers formed on chlorination of triacetyl-D-glucal. Two such compounds have been separated from the dichloro addition product and, by means of n.m.r. spectroscopy, have been shown to be triacetyl-2-chloro-2-deoxy-α-D-glucopyranosyl chloride (III) and triacetyl-2-chloro-2-deoxy-α-D-mannopyranosyl chloride (II).





The n.m.r. spectra of compound III (Figure 1B) showed a doublet at 6.08 p.p.m. with J = 3 c.p.s. and two triplets centered at 5.08 (J = 8 c.p.s.) and 5.42 p.p.m. (J = 8 c.p.s.).

Lemieux[4] has shown that the coupling constants between the vicinal hydrogen atoms of pyranose monosaccharides in diaxial, diequatorial, and axial-equatorial conformations are *ca.* 7, 3, and 3 c.p.s., respectively. Since the signal at 6.08 p.p.m. is assigned to the anomeric proton, it follows that III has the α-D-*gluco* configuration.

The n.m.r. spectrum of II (Figure 1A) showed a signal at 5.54 p.p.m. (labeled A) which is coupled to a proton whose resonance appears at about 4.52 p.p.m.

(1) E. Fischer, M. Bergmann, and H. Schotte, *Ber.*, **53**, 509 (1920).

(2) S. N. Danilov and A. M. Gakhokidze, *J. Gen. Chem. USSR*, **6**, 704 (1936); *Chem. Abstr.*, **30**, 633 (1936).

(3) R. U. Lemieux and B. Fraser-Reid, *Can. J. Chem.*, **42**, 532 (1964). This reference contains an excellent discussion of the stereochemical aspects of the halogenation reaction.

(4) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **81**, 6098 (1958).

with J = 1 c.p.s. This proton (labeled D) is in turn coupled to a second proton whose resonance appears at about 5.02 p.p.m. with J = 3 c.p.s. The group C at 5.02 p.p.m. is subsequently coupled to a proton whose signal appears at 5.38 p.p.m. (labeled B) with J = 9 c.p.s. The signal at 5.54 p.p.m. may be assigned to the proton geminal to both a chlorine and oxygen. Based on the magnitude of the coupling constants and going around the ring (structure II) protons 1 and 2 are equatorial, protons 3, 4, and 5 are axial.

This corresponds to an α-D-*manno* configuration. The material which both Fischer and Danilov obtained, therefore, was a mixture of tri-*O*-acetyl-2-chloro-2-deoxy-α-D-gluco and α-D-mannopyranosyl chlorides.

Experimental[5]

Reaction Procedure.—Triacetyl-D-glucal[6] was chlorinated in chloroform as described by Fischer, Bergmann, and Schotte except that a stoichiometric amount[7] of chlorine was used. The colorless oil obtained after removal of the solvent *in vacuo* was left in the refrigerator (4–5°) for 24 hr. A sample of the crystalline material (m.p. 59–70°) which had formed was subjected to t.l.c. The plate indicated that the material was a mixture of two major components of R_f 0.51 (III) and R_f 0.36 (II), and several trace components[8] of R_f 0.0–0.30. A densitometric scan[9] indicated that II and III had been formed in 58% yield in a ratio of *ca.* 1:4. Recrystallization twice from anhydrous ethyl ether afforded a material of m.p. 89–93° which consisted of only II and III (t.l.c.).

Isolation of II and III.—A slurry of 30 g. of silica gel containing 5% calcium sulfate (Brinkmann Instrument Co., Westbury, N.Y.) in 65 ml. of water was applied to the 20 × 20 cm. plates using a commercial spreader. The layer was about 250 μ thick. After air drying for 10 min. the plates were placed in the oven at 100–105° for 30 min. They were then stored in a desiccator containing anhydrous calcium chloride for at least 12 hr. before use.

The dichlorotriacetylglycal mixture (25 mg.) of m.p. 89–93° was applied to a plate with a micropipet so that 25 small spots were obtained.[10] The plate was allowed to develop (toluene–anhydrous ethyl ether, 2:1) without prior equilibration until the solvent was 16 cm. past the spotting point, and then air dried in a horizontal position. A strip 1.5 cm. wide was then removed from the plate by means of a good glass cutter. The spots on this strip could then be developed by spraying with a 5% solution of concentrated H_2SO_4 dissolved in 95% ethyl alcohol. The observed R_f values were found to vary somewhat from plate to plate, but the separation of spots was always reproducible and reliable. The developed strip showing only two spots was placed alongside the undeveloped plate and the appropriate areas scraped onto a glassine weighing paper by means of a spatula. The two fractions so obtained (from several plates) were extracted with hot chloroform. Separation of the silica gel by filtration and removal of the solvent *in vacuo* afforded 19.8 mg. of III, m.p. 95–95.5°, and 3.7 mg. of II, m.p. 139–140° (crystallization occurred after several hours in the refrigerator at 5°).

(5) Melting points were determined on a Fisher-Johns block and are uncorrected. Compounds II and III gave satisfactory carbon, hydrogen, and chlorine analysis which were performed by Drs. Weiler and Strauss, Microanalytical Laboratory, Oxford, England.

(6) P. T. Manolopoulous, M. Mednick, and N. N. Lichtin, *J. Am. Chem. Soc.*, **84**, 2203 (1962).

(7) We found that, if an excess of chlorine was used, the product which was obtained when analyzed by t.l.c. showed the presence of materials of low R_f. This is possibly the result of chlorination (of the acetyl groups) or partial deacetylation of the triacetyl-D-glucal. Immediately before use, 1 ml. of the chlorine solution was added to a solution of 2 g. of KI in 10 ml. of water. Ten milliliters of 0.2 *N* HCl was added and the mixture was titrated with 0.1000 *N* thiosulfate using 1 drop of starch solution as an indicator.

(8) If the β-*gluco* or β-*manno* isomers were present in the reaction mixture then their R_f's would have been identical with those of the α-*gluco* and α-*manno* dichlorides. The n.m.r. spectra eliminated this possibility.

(9) Concentrations were determined by means of a Photovolt recording densitometer and the appropriate areas were integrated planimetrically.

(10) The best separations were obtained under these conditions. A thicker layer of gel or more than 1.5 mg./spot gave considerable smearing.

N.m.r. Measurements.—The spectra were obtained using the Varian HA-60 spectrometer which is the HR-60 with a proton stabilization control added. The relative sensitivity of this instrument is slightly in excess of 20 to 1 for the HA-60 compared with a normal 6 or 7 for an A-60. Spectra of compound II were taken of a $CDCl_3$ solution contained in closed microcell plugs. Spectra were obtained on compound III dissolved in $CDCl_3$ contained in microcell tubes using the microcells gapped at approximately 7 mm. Data are reported in terms of the frequency-independent unit δ, using tetramethylsilane as an internal standard.

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Mass Spectrometry in Structural and Stereochemical Problems. LXVI.[1] Mass Spectral Fragmentation of 6,7-Dimethoxycoumarin[2]

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In a recent significant paper, Barnes and Occolowitz[3] recorded the mass spectra of numerous oxygen-containing heterocyclic systems and pointed out the potential utility of mass spectrometry in that field. Particular attention was paid[3,4] to coumarins, where the loss of the lactonic carbonyl function as carbon monoxide represents one of the most important processes. Methoxylated coumarins display a somewhat more complicated pattern, as is illustrated in Figure 1 by the mass spectrum[3] of 6,7-dimethoxycoumarin (I). The characteristic peaks at m/e 191 (M − CH_3), m/e 178 (M − CO), and m/e 163 (M − [CO + CH_3]) were interpreted[3] in terms of species *a*, *b*, and *c*.

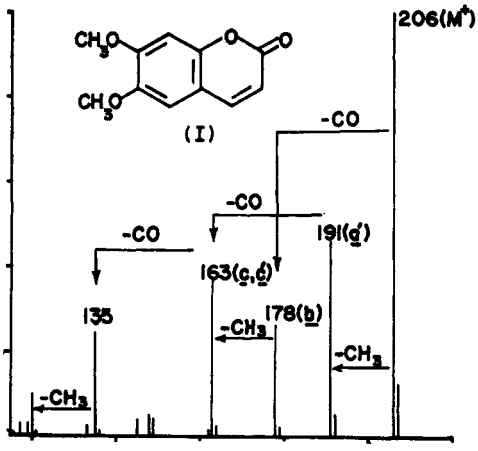

Figure 1.—Partial mass spectrum of 6,7-dimethoxycoumarin (I) (see ref. 3).

(1) For paper LXV, see C. Djerassi, G. von Mutzenbecher, J. Fajkos, D. H. Williams, and H. Budzikiewicz, *J. Am. Chem. Soc.*, **87**, 817 (1965).

(2) Supported by the National Institutes of Health of the U. S. Public Health Service (Grant No. GM 11309).

(3) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **17**, 975 (1964).

(4) N. S. Wulfson, V. I. Zaretskii, and V. G. Zyakoon, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2215 (1963).