[Contribution from the Division of Industrial and Cellulose Chemistry, Pulp and Paper Research Institute of Canada and McGill University]

Isolation of Penta- and 1,2,4,5-Benzenetetracarboxylic Acids from Wood Lignins Oxidized with Alkaline Permanganate[1]

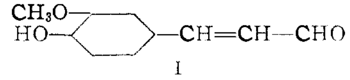
By D. E. Read and C. B. Purves

The following samples, after exhaustive oxidation with alkaline potassium permanganate, gave the above crude benzenepolycarboxylic acids in the amounts noted: solvent-extracted sprucewood (0.14% on the lignin), the periodate, Willstätter and Klason lignins therefrom (0.8, 1.0 and 2.4%, respectively), and a commercial alkali lignin from poplar (3.6%). The alkali lignin was the only sample to yield mellitic acid (0.2%). These results suggested that aromatic units in lignin underwent an increasing amount of nuclear condensation as the conditions of isolation from the wood became more drastic.

Introduction

In connection with extensive research on the drastic oxidation of coals with hot, alkaline potassium permanganate, Randall, Benger and Groocock[2] studied the action of the same reagent on sixty simpler compounds. Their results showed that the products of the oxidation were never more complex than the original substance, and that the production of benzenepolycarboxylic acids originated in benzene rings unsubstituted by oxygen but repeatedly substituted by carbon atoms. The appearance of increasing amounts of the higher benzenepolycarboxylic acids from lignites and coals of increasing maturity was accordingly considered[3,4] to indicate the presence in these substances of fused benzene rings. Juettner[5] interpreted his recovery of mellitic acid from the drastic nitric acid oxidation of cokes, graphite and anthracite to primary systems of the 9,10-benzophenanthrene type, and studies employing hydrogenation[6] and X-ray diffraction[7] were not inconsistent with this view.

Apart from a few substances like diphenyl oxide, diphenylene oxide and benzophenone, which were unaffected by alkaline permanganate, compounds consisting of benzene rings directly substituted by oxygen atoms yielded no benzenepolycarboxylic acids, but were completely degraded to carbon dioxide, oxalic acid, acetic acid and similar substances. Since coniferyl alcohol (I) was shown to behave in this way,[2] and since the structures currently entertained for softwood lignins were based on building units closely resembling (I),[8-11] it was to be expected that lignin would yield no higher benzenepolycarboxylic acids by oxidation with alkaline permanganate. Nevertheless, Bone and co-workers[3] claimed to have isolated crude 13.6 and 15.8% yields of these acids from lignins prepared from silver fir and from poplar by the fuming hydrochloric acid (Willstätter[12]) method. Larger-scale oxidations of the Willstätter lignins from Scotspine and beech enabled them to identify 1,2,4,5-benzene-tetracarboxylic (pyromellitic) acid, together with the penta- and hexacarboxylic acids, among the products, but no yields were stated. No succinic or benzene di- or tricarboxylic acid, and no position isomers of the tetracarboxylic acid, were found. The importance of these results for the structure of lignin made it desirable to confirm them, and the present article had this objective. The first sample chosen for examination was a solvent-extracted spruce woodmeal, the lignin in which was obviously close to its original state, and whose cellulose content was known[3] to yield no benzenepolycarboxylic acids on oxidation. Three lignins isolated from the same meal by methods of increasing chemical severity, and a commercial alkali lignin, were also examined. The conditions used for the oxidation were those of Bone and co-workers,[3] but the products were isolated and separated by means of partial esterification with acid methanol as described in another article.[13]



I

Experimental

Materials.—A 140-year old, newly felled log of black spruce, freed of knots, was the source for woodmeal of 40–80 mesh. This meal was exhaustively extracted in all-glass apparatus for 60 hours with constant-boiling (1:2) alcohol-benzene; then for four hours with 95% ethanol and finally for four hours with hot water. The product was dried in air, thoroughly mixed and kept in glass-stoppered bottles.

A 510-g. portion of the woodmeal was alternately oxidized with sodium periodate, at *p*H 4.15 and room temperature, and extracted with boiling water near *p*H 6, substantially as described elsewhere.[14] After five of these oxidation–hydrolysis cycles, which were attended with considerable mechanical loss, the product was dried *in vacuo* at 55° for 20 hours; yield 114 g., or 22.4%. Approximately 96% dissolved when pulped for six hours at 135° in a calcium bisulfite liquor containing 4.9% free and 0.9% combined sulfur dioxide.

Anal. Found: OCH_3, 11.3, 11.6; Klason lignin, 87.2, 87.2; apparent holocellulose, less than 2%.

The woodmeal, 100 g., was immersed for two hours at 0° in 2 l. of fuming hydrochloric acid (d. 1.22), the Willstätter lignin was recovered,[12] and dried to constant weight *in vacuo* at 55°; yield from four preparations 110 g., or 22.5%.

Anal. Found: OCH_3, 14.4, 14.6; Klason lignin, 90.3, 90.2.

The Klason lignin was prepared by adapting a standard method[15] to a larger scale. The meal, 100 g., was digested

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[1] Presented before Section 15 of the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951. Abstracted from a Ph.D. Thesis submitted by D. E. Read, October, 1949.

[2] R. B. Randall, M. Benger and C. M. Groocock, *Proc. Roy. Soc.* (*London*), **A165**, 432 (1938).

[3] W. A. Bone, L. G. B. Parsons, R. H. Sapiro and C. M. Groocock, *ibid.*, **A148**, 492 (1935).

[4] W. A. Bone, L. Horton and S. G. Ward, *ibid.*, **A127**, 480 (1930).

[5] B. Juettner, This Journal, **59**, 1472 (1937).

[6] B. S. Biggs, *ibid.*, **58**, 484, 1020 (1936).

[7] W. R. Ruston, *Fuel*, **26**, No. 3, 74 (1948).

[8] H. Hibbert, *Ann. Rev. Biochem.*, **11**, 183 (1942).

[9] H. Erdtman, *Svensk. Papperstidn.*, **44**, 243 (1941). Translation in *Pulp & Paper Mag. Can.*, **43**, 253 (1942).

[10] K. Freudenberg, *Ann. Rev. Biochem.*, **8**, 88 (1940).

[11] F. E. Brauns, *Tech. Assoc. Papers*, **24**, 612 (1941).

[12] R. Willstätter and L. Kalb, *Ber.*, **55**, 2637 (1922).

[13] D. E. Read and C. B. Purves, This Journal, **74**, 116 (1952).

[14] P. F. Ritchie and C. B. Purves, *Pulp & Paper Mag. Can.*, **48**, 74 (1947).

[15] G. J. Ritter, R. M. Seborg and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1942).

with 2 l. of 72% sulfuric acid (by weight) for two hours at 20°. To avoid the large increase in volume that a direct dilution to 3% acid would occasion, the crude product was recovered on sintered glass and suspended, without prior drying or washing, in sufficient water to give a supernatant liquor containing 3% of sulfuric acid. This suspension was boiled under reflux for three hours, and after recovery the lignin was washed thoroughly with water and dried as in the other cases; yield 82.1 g. from three runs, or 27.4%.

Anal. Found: OCH_3, 15.0, 15.1.

The alkali lignin, a brown powder prepared commercially from poplar,[16] was used as received.

Anal. (by Mr. I. Cabott). Found: OCH_3, 19.7, 19.4; ash, 0.55, 0.64; moisture, 2.5, 2.4.

Oxidation with Alkaline Potassium Permanganate.[3]—The oxidation was similar in all cases, and was carried out in an open enamelled iron vessel of 10-l. capacity, heated externally and fitted with an efficient mechanical stirrer.

A 50-g. or 30-g. sample of the lignin, or 100 g. of the woodmeal, was suspended in about 8 l. of 1% aqueous potassium hydroxide. External heating was commenced as solid potassium permanganate was added in 20-g. portions as fast as the preceding portion had been completely reduced. The alkali lignin, 50 g., was soluble in the alkali and reduced about 200 g. of the permanganate almost immediately and an additional 200 g. within three hours. The other lignins required about 45 minutes to reduce 200 g. and the 100 g. of woodmeal consumed 400 g. of the permanganate in this time. After three hours, when the rapid oxidation was over and the temperature had risen to 75 to 80°, an additional 100 g. of permanganate was added in portions during the next five hours. Thereafter the mixture was kept at the oxidation temperature for a further 14 hours, or until the rate of oxidation had become inappreciable. Water was added periodically to replace that lost by evaporation. The actual consumption of permanganate was between 450 and 480 g. for 50-g. samples of the four lignins, or corresponded to the utilization of one gram atom of oxygen by 10–11 g. of lignin. The woodmeal required nearly 400 g. on the 50-g. basis.

Any residual permanganate was decomposed by the addition of a few cc. of ethanol, the manganese dioxide was removed, washed thoroughly with water, and discarded. After being acidified to *p*H 2–3 with strong hydrochloric acid to decompose carbonates, the filtrate and washings were concentrated under reduced pressure from 12 to 2 liters. At this stage the concentrates from the Klason and alkali lignins were pale yellow in color, that from the Willstätter lignin very pale yellow, while those from the periodate lignin and the woodmeal were colorless. All concentrates became golden yellow when made alkaline (*p*H 10.4) with aqueous potassium hydroxide. The addition of a hot solution of 120 g. of barium chloride dihydrate to the hot alkaline concentrate then caused the separation of a voluminous precipitate which was digested in the mother liquor for 30 minutes before being recovered and dried to constant weight at 105°. This precipitation separated oxalic and benzenepolycarboxylic acids quantitatively or nearly so[13] as snow-white barium salts (Table I, column 2).

Separation of Benzenepolycarboxylic Acids.[13]—A solution of the dry barium salt in 10 volumes of 1 *N* hydrochloric acid was mixed with the exact amount of 3 *N* sulfuric acid to precipitate all barium as the sulfate. Evaporation of the filtrate under diminished pressure, alternated with periods at 0°, made it possible to eliminate successive crops of crystalline oxalic acid dihydrate (Table I). Before being rejected, each crop was shown to have the correct m.p. 100–102°, a neutralization equivalent correct to ±1%, and therefore to be free of benzenepolycarboxylic acids.

The filtrate and washings from the last crystallization of oxalic acid were carefully evaporated, at first on a hot-plate and then to constant weight (Table I) in an evacuated desiccator with solid potassium hydroxide to remove traces of hydrochloric acid. The residual oxalic acid, together with any other α-ketoacid, was then destroyed by boiling the residue for two hours with 50 cc. of concentrated nitric acid. Evaporation of the pale green-yellow solution to dryness and constant weight, finally in a desiccator containing solid potassium hydroxide to absorb nitric acid, left a crystalline mixture of benzenepolycarboxylic acids and inorganic material (Table I, column 5).

TABLE I

OXIDATIONS WITH ALKALINE POTASSIUM PERMANGANATE

Substance	Sample wt., g.	Crude Ba salts, g.	Oxalic acid,[a] g.	Acidic residues g.[b]	Acidic residues g.[c]
Woodmeal	100	185.4	85.5	4.86	1.81
Lignins					
Periodate	50	101.1	45.0	4.50	2.03
Willstätter	50	81.8	34.3	5.14	1.53
Klason	30	64.6	25.8	4.24	1.49
Alkali[d]	50	72.2	27.2	5.84	2.93

[a] As the pure dihydrate, m.p. 99 to 102°. [b] Prior to digestion with nitric acid to decompose residual oxalic acid. [c] After digestion with nitric acid. [d] A commercial lignin from poplar. Other lignins from spruce.

The crude mixture was heated, under reflux and in all-glass equipment, for six hours with about 20 volumes of 3% methanolic hydrogen chloride. A portion, presumably silica, resisted solution. Sufficient methanol was then evaporated to reduce the volume to 20 cc. and the addition of 100 cc. of half-saturated sodium bicarbonate solution increased the *p*H of the mixture to 8. Four successive extractions with 50-cc. volumes of ether removed the neutral tetramethyl ester of pyromellitic acid, which was recovered as crystals embedded in a thick sirup (yields in Table II). Removal of the sirup between layers of filter paper, followed by recrystallization from a few cc. of aqueous methanol, gave the pure tetramethyl ester. Although the method of separation differentiated this ester from those of the other benzenepolycarboxylic acids, the identity was checked in each case by the accuracy of the m.p., 142 to 143.5°, undepressed by admixture with authentic tetramethyl pyromellitate.[13]

After the above extractions with ether, the alkaline aqueous residue was acidified to *p*H 1 with 16 cc. of 6 *N* hydrochloric acid and re-extracted with ether in an attempt to remove the acidic trimethyl ester of 1,2,3,5-benzenetetracarboxylic acid. This substance was not found in preliminary tests, and the ether extracts were united with four subsequent extractions of the aqueous residue made with 50-cc. volumes of ethyl acetate. The extracts were dried and evaporated and the residues, which might have contained both the acidic dimethyl ester of 1,2,3,4-benzenetetracarboxylic acid and the ill-defined acidic ester of the pentacarboxylic acid,[13] were completely esterified by two treatments with diazomethane. The crude products partly crystallized (Table II) and when recrystallized twice from aqueous methanol yielded pure pentamethyl benzenepentacarboxylate with the correct m.p., 147–148°, undepressed by admixture with an authentic sample.[13] No trace of the crystalline tetramethyl ester of 1,2,3,4-benzenetetracarboxylic acid was found.

TABLE II

RECOVERIES OF NEUTRAL METHYL BENZENEPOLYCARBOXYLATES

Substance	1,2,4,5-Tetra ester, g. Crude	1,2,4,5-Tetra ester, g. Pure[a]	Penta ester,[b] g. Crude	Penta ester,[b] g. Pure[c]	Hexa ester[b] Crude, g.
Woodmeal	0.039[e]	...	0.048[d]	...	0.028[e]
Lignin					
Periodate	.102	0.001	.385	0.038	.084[e]
Willstätter	.125	.02	.494	.016	.028[e]
Klason	.136	.03	.755	.056	.040[e]
Alkali	.323	.029	1.97	.259	.109[f]

[a] M.p. 139–143.5° in the different samples. Mixed m.p. correct. [b] After complete methylation with diazomethane. [c] M.p. 146–149° in the different samples. Mixed m.p. correct. [d] M.p. 138–141°; mixed m.p. 141–147°. [e] No crystals obtainable. [f] Crystals, 0.019 g., separated with m.p. 176–183°. Mixed m.p. 182–186°.

The aqueous residue from the above extractions would contain any mellitic acid, which would not have been esterified.[13] After being warmed to 60°, the addition of 10 cc. of a barium chloride solution caused the precipitation of barium salts. Barium was removed from a solution of these salts

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(16) The authors are indebted to Dr. G. H. Tomlinson, II, and the Howard Smith Paper Mills, Cornwall, Ontario, for the gift of this material.

in *N* hydrochloric acid as barium sulfate; the free acids after recovery were twice methylated with diazomethane and a trace of gelatinous precipitate was removed from the methanol–ether solution. Extraction of the methylated product with methanol gave fine unfilterable dispersions of a gelatinous substance, and evaporation of the extract gave crystals only in the case of the alkali lignin. Although recrystallization was omitted because of their small amount, their m.p. and mixed m.p., together with their method of separation, showed them to be hexamethyl mellitate (Table II).

Results and Discussion

Correction of the data in columns 1, 3 and 5 of Table II from a neutral ester to a free acid basis yielded the percentage amount by weight of the original lignin that was recovered as benzenepolycarboxylic acids (Table III). These crude yields were preferred to the pure yields in columns 2 and 4 of Table II because the process of purification to constant melting point was very wasteful. Crude products that failed to produce any crystalline ester, however, were omitted from Table III. Although Table III exaggerated the amounts of the acids actually isolated, their separation from each other was by no means quantitative, and their formation by the oxidation even of simple substances sometimes proceeded in quite low (20–30%) yield. For these reasons the precursors of the benzenepolycarboxylic acids might possibly account for considerably greater fractions of the original lignin. The absence of 1,2,3,4- and 1,2,3,5-benzenetetracarboxylic acids, the presence of the 1,2,4,5 isomer and of the pentacarboxylic acid among the oxidation products from Willstätter lignin confirmed the results of Bone and his collaborators,[3] but the crude yields were less by a factor of at least ten. The earlier yields, however, were based on uncrystallized products that in all probability were not efficiently freed from oxalic and α-ketoacids. Contrary to expectation,[3] mellitic acid could not be isolated from the oxidation products of the Willstätter, periodate and Klason lignins, or from the woodmeal itself.

TABLE III

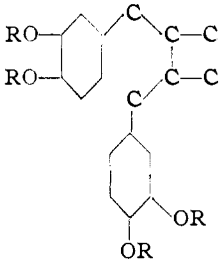
PERCENTAGE YIELDS OF BENZENEPOLYCARBOXYLIC ACIDS

Substance	1,2,4,5-Tetra, %	Penta, %	Hexa, %	Total, %
Woodmeal	..	0.14[a]	..	0.14
Lignin				
Periodate	0.17	0.62	..	0.8
Willstätter	.21	0.76	..	1.0
Klason	.37	2.04	..	2.4
Alkali[b]	.46	3.20	0.17	3.8

[a] Approximate. Based on Klason lignin content. [b] From a commercial cook.

The almost zero yield of benzenepolycarboxylic acids from the spruce woodmeal was not inconsistent with the view that nearly 100% of lignin *in situ* was based upon structural units analogous to (I), which certainly would not survive the drastic oxidations as an aromatic substance. Neither could benzenepolycarboxylic acids have been produced from any resins left in the solvent-extracted woodmeal, nor from the conditions of the permanganate and nitric acid oxidations. It followed that the positive results for the spruce lignins depended upon changes brought about during their isolation from the wood, and that these changes increased from periodate to Willstätter and Klason lignin as the severity of the conditions of isolation increased. The results for alkali lignin emphasized the trend but were not closely comparable because they referred to another wood (poplar) that presumably had not been freed of resins before use. This lignin was also peculiar in yielding a small amount of mellitic acid.

The present work was not inconsistent with the suggestion[17–20] that wood lignins contained oxygenated phenylpropane units resembling those of the crystalline lignans (structure II) in being directly linked through the β-carbon atoms. Many lignans readily underwent intramolecular condensation and dehydrogenation to 1-phenylnaphthalenes of the general type (III) under the influence of hot methanolic hydrogen chloride,[21b] fuming hydrochloric acid at 100–110°,[22] dehydrogenation by palladium at 230–240°,[22] or of mild oxidizing agents like iodine[23] or lead tetraacetate at room temperature.[21a] The cyclization to (III) produced a new benzene ring (A), fivefold substituted by carbon but unsubstituted by oxygen, that would be expected to produce some benzenepentacarboxylic acid when oxidized with alkaline permanganate.[24] The pentacarboxylic acid was the dominant product from the lignins, and the minor product, pyromellitic acid, would arise from naphthalene structures corresponding to (III) with the phenyl substituent deleted.



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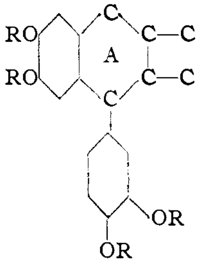

III

R variable, even in the same lignan

Fischer and his co-workers[25a] drastically oxidized 2 kilograms of a commercial Willstätter lignin suspended in dilute caustic soda by air at 200° and 55 atmospheres pressure. Among the five different fatty and nine different benzenecarboxylic acids which the product yielded were benzenepentacarboxylic acid (1.65%), pyromellitic acid (0.28%), mellitic acid (0.38%) and 1,2,3,4- or 1,2,3,5-ben-

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[17] L. E. Wise, "Wood Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, p. 349.

[18] R. D. Haworth, *J. Chem. Soc.*, 448 (1942).

[19] R. D. Haworth, *Ann. Repts. Chem. Soc.*, **33**, 266 (1936).

[20] (a) H. Richtzenhain, *Svensk. Papperstidn.*, **20**, 644 (1950); (b) *Ber.*, **83**, 488 (1950).

[21] (a) R. D. Haworth and T. Richardson, *J. Chem. Soc.*, 633 (1935); (b) *ibid.*, 348 (1936).

[22] E. Späth, F. Wessely and L. Kornfeld, *Ber.*, **65**, 1536 (1932).

[23] R. D. Haworth, C. R. Mavin and G. Sheldrick, *J. Chem. Soc.*, 1423 (1934).

[24] Späth and co-workers (ref. 22) heated one lignan, podophyllotoxin, with concentrated hydrochloric acid and isolated an unstated yield of pyromellitic acid by oxidizing the resulting brown resin. Dehydrogenation followed by oxidation gave some benzenepentacarboxylic acid.

[25] (a) F. Fischer, H. Schrader and A. Friedrich, *Ges. Abhandl. Kenntnis Kohle*, **6**, 1 (1921); (b) *ibid.*, **6**, 22 (1921).

zenetetracarboxylic acid (0.12% and called "prehnitic" acid). Since the same conditions produced none of these aromatic acids from cellulose, but 0.83% of the pentacarboxylic acid from a solvent-extracted sprucewood,[25b] the authors suggested that the immediate precursors existed as such in the wood. The present almost negative result for sprucewood suggests that the pentacarboxylic acid they found was an artifact from the alkalinity and high temperature used in their oxidation, and was therefore comparable in origin to that now derived from alkali lignin itself (Table III). In the same way, Horn's[26] isolation of perhaps 0.4% of mellitic acid from a Willstätter lignin might have owed its success to the condensing action of the fuming hydrochloric acid used to prepare the lignin, and to the boiling concentrated nitric acid employed for the oxidation.

The effect of acid reagents upon lignin was recently demonstrated by Richtzenhain,[20] who recovered up to 1.3% of 4,5-dimethoxyphthalic (metahemipinic) acid from methylated samples of Willstätter lignin, ethanol lignins and lignosulfonic acid, but none from methylated sprucewood, by oxidation with hot potassium permanganate solution kept near *p*H 7. Structure (I) must have undergone a nuclear condensation in position 6 to produce the precursor yielding metahemipinic acid. Treatment of the Willstätter lignin with 70% potassium hydroxide at 170° prior to methylation caused the yield of this acid to decrease, and none was isolated from the oxidation of a methylated alkali lignin. These observations might have been connected with further nuclear condensation to the precursors of the benzenepolycarboxylic acids discussed in the present article. It was interesting to note that the same treatment increased Richtzenhain's recoveries of 2,3-dimethoxy-*m*-phthalic (isohemipinic) acid from 0.9% in sprucewood to 6.65% in the alkali lignin, and that some of the lignin in sprucewood was presumably substituted in the fifth position of the structural unit (I). Such a substitution would also explain the origin of 3.9% of *m*-toluic acid isolated after the electrochemical oxidation of a butanol lignin from western hemlock,[27] although, of course, the requisite precursor might have been formed only during the extraction of the lignin with aqueous butanol near 160°.

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[26] O. Horn, *Brennstoff-Chem.*, **10**, 364 (1929).

[27] A. Bailey and H. M. Brooks, THIS JOURNAL, **68**, 445 (1946).

MONTREAL, CANADA RECEIVED JULY 2, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XV. Preparation and Properties of the 1,2,3-Trichloropropenes[1]

BY LEWIS F. HATCH, JOHN J. D'AMICO[2a] AND EDWARD V. RUHNKE[2b]

The two isomers of 1,2,3-trichloropropene have been prepared, characterized and their relative reactivities have been determined with potassium iodide in acetone and with sodium ethoxide in ethanol. No relationship between reactivity and configuration was noted for the reaction with sodium ethoxide but with potassium iodide the isomer with the vinyl chlorine atom and the chloromethyl group in the *cis* position was appreciably more reactive. In addition to the 1,2,3-trichloropropenes the following compounds were prepared and characterized: *cis*- and *trans*-3-bromo-1,2-dichloro-1-propene and *cis*- and *trans*-2,3-dichloro-2-propen-1-ol.

1,2,3-Trichloropropene has been reported in the literature as having been prepared by the dehydrochlorination of 1,2,2,3-tetrachloropropane,[3,4] the dehydrobromination of 2-bromo-1,2,3-trichloropropane[4] and by the decarboxylation and dehydrochlorination of $\alpha,\beta,\beta,\gamma$-tetrachlorobutyric acid.[5] With all of these methods of preparation it would be possible to obtain a mixture of both *cis*- and *trans*-1,2,3-trichloropropene, but in no case was any mention made of the separation and identification of these isomers. The present paper describes the preparation and characterization of these two isomeric trichlorides and two closely related pairs of geometrical isomers. The following equations represent the reactions employed in this study.

$$\mathrm{CHCl{=}CClCH_3 + N\text{-bromosuccinimide} \longrightarrow CHCl{=}CClCH_2Br} \quad \text{(I)}$$

$$\mathrm{CHCl{=}CClCH_2Br + H_2O \xrightarrow{Na_2CO_3} CHCl{=}CClCH_2OH} \quad \text{(II)}$$

$$\mathrm{CHCl{=}CClCH_2OH + PCl_3 \xrightarrow{C_5H_5N} CHCl{=}CClCH_2Cl} \quad \text{(III)}$$

$$\mathrm{CHCl{=}CClCH_2Cl + LiAlH_4 \longrightarrow CHCl{=}CClCH_3} \quad \text{(IV)}$$

In reaction I both *cis*- and *trans*-1,2-dichloro-1-propene was brominated separately but for each reaction the product consisted of a mixture of both *cis*- and *trans*-3-bromo-1,2-dichloro-1-propene. The isomerization of the 3-bromo-1,2-dichloro-1-propenes was sufficiently slow, however, to permit their separation and hydrolysis to give good yields of the corresponding dichloroalcohol. The isomers of both 2,3-dichloro-2-propen-1-ol and 1,2,3-trichloropropene did not isomerize.

The configuration of the isomers of 1,2,3-trichloropropene was assigned by relating the trichloride to the corresponding 1,2-dichloro-1-propene of known structure[6] (reaction IV). With each

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[1] For number XIV of this series see L. F. Hatch and J. J. D'Amico, THIS JOURNAL, **73**, 4393 (1951).

[2] (a) Monsanto Chemical Co., Nitro, West Virginia; (b) Agricultural and Mechanical College of Texas, College Station, Texas.

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[5] G. Oestermann, *ibid.*, 254 (1949).

[6] W. H. King and H. A. Smith, THIS JOURNAL, **72**, 3459 (1950); H. J. Bernstein and J. Powling, *ibid.*, **73**, 1843 (1951).