

Anal. Calcd. for $C_{11}H_{13}O_5N_5S$: N, 21.39. Found: N, 21.16.

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The Chlorination of Isophthaloyl and Terephthaloyl Chloride

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The chlorination of isophthaloyl and terephthaloyl chloride in the presence of iron leads to 5-chloroisophthaloyl chloride and 2,3,5,6-tetrachloroterephthaloyl chloride, respectively. The latter compound, due to its highly hindered structure, shows considerable stability toward reagents which are capable of attacking an acid chloride. The chlorinated phthaloyl chlorides have been converted to a number of derivatives.

Experimental

5-Chloroisophthaloyl Chloride.—A mixture of 144 g. of isophthaloyl chloride and 5 g. of iron filings was treated with chlorine at 95–100° until there was no further increase in weight. The reaction mixture was diluted with carbon tetrachloride and filtered. The filtrate was concentrated and distilled *in vacuo*. There was obtained 137 g. of material which boiled at 165–175° (22 mm.). This was redistilled through a 20" packed column; the main fraction boiled at 126–128° (4 mm.); *sapn. equiv. calcd.* for $C_8H_5O_2Cl$, 118.8; found, 118, 120.

5-Chloroisophthalic Acid.—A mixture of 16 g. of 5-chloroisophthaloyl chloride and 100 cc. of 10% sodium hydroxide solution was warmed on a steam-bath for five hours. The solution was filtered and acidified with concentrated hydrochloric acid. The white precipitate was removed by filtration and dried, weight 11 g. After crystallization from water it melted at 278–280° (lit.¹ 279–280°).

Dimethyl 5-Chloroisophthalate.—Five grams of 5-chloroisophthaloyl chloride was dissolved in 50 cc. of methanol. The initial heat of reaction was removed by cooling and then the reaction mixture was warmed on a steam-bath for one-half hour. The excess methanol was evaporated and the residue was crystallized from dilute methanol: m. p. 80–81° (lit.¹ 79–80°).

*Anal.*² Calcd. for $C_{10}H_9O_4Cl$: C, 52.52; H, 3.94. Found: C, 52.70; H, 4.01.

5-Chloroisophthalamide.—Ten grams of 5-chloroisophthaloyl chloride was mixed with 100 cc. of aqueous ammonia and an immediate reaction occurred. The reaction mixture was allowed to cool and the precipitate removed by filtration. It was washed with water and dried, weight 8 g. After crystallization from alcohol, the fine, white crystalline solid melted at 254–255°.

Anal. Calcd. for $C_8H_7O_2N_2Cl$: C, 48.36; H, 3.53. Found: C, 48.55; H, 3.69.

2,3,5,6-Tetrachloroterephthaloyl Chloride.—A mixture of 215 g. of terephthaloyl chloride and 5 g. of iron filings was heated at 175°. Chlorine was passed into the mixture until there was no further increase in weight. The reaction mixture was dissolved in carbon tetrachloride and filtered. The filtrate was treated with Norite and cooled; a pink colored solid resulted, m. p. 133–137°. The mother liquor was concentrated and more material was obtained. The total weight of product was 223 g. Recrystallization from carbon tetrachloride yielded a white crystalline solid

which melted at 144–145°. A small sample was sublimed for analysis.

Anal. Calcd. for $C_8O_2Cl_4$: C, 28.15; Cl, 62.46. Found: C, 28.40; Cl, 62.52.

2,3,5,6-Tetrachloroterephthalic Acid.—A mixture of 10 g. of 2,3,5,6-tetrachloroterephthaloyl chloride and 200 cc. of 10% sodium hydroxide solution was refluxed for twelve hours. The solution was filtered and acidified with concentrated hydrochloric acid. The white precipitate was removed by filtration and dried; weight 8.5 g. It was crystallized from water; m. p. 343–345° (dec.). Qvist and Holmberg³ have stated that 2,3,5,6-tetrachloroterephthalic acid melts with decomposition at about 330°. Neut. equiv. calcd. for $C_8H_2O_4Cl_4$: 152. Found: 153.

Dimethyl 2,3,5,6-Tetrachloroterephthalate.—A mixture of 10 g. of 2,3,5,6-tetrachloroterephthaloyl chloride and 300 cc. of methanol was refluxed for ten hours. After standing for four days at room temperature, a white crystalline precipitate had formed; m. p. 153–155°. The mother liquor was concentrated and a total of 9.3 g. of material was obtained. After crystallization from methanol, the ester was obtained in the form of long, white needles; m. p. 154–155°.

Anal. Calcd. for $C_{10}H_6O_4Cl_4$: C, 36.15; H, 1.81. Found: C, 36.31; H, 1.74.

2,3,5,6-Tetrachloroterephthalamide.—Ten grams of 2,3,5,6-tetrachloroterephthaloyl chloride was dissolved in 500 cc. of ether and treated with 200 cc. of ether which had been saturated with anhydrous ammonia. A white solid gradually precipitated from solution. More ammonia was added and the mixture was allowed to stand overnight. The ether was removed and the residue was washed with warm water. After drying there was obtained 8 g. of a white powder. It was crystallized from acetic acid; m. p. above 400°.

Anal. Calcd. for $C_8H_4O_2N_2Cl_4$: C, 31.79; H, 1.32. Found: C, 32.15; H, 1.62.

(3) Qvist and Holmberg, *Acta Acad. Aboensis Math. et Phys.*, **6**, No. 14, 3 (1932).

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Steroidal Sapogenins. II. New Derivatives of Kryptogenin¹

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At the beginning of our studies on the steroidal sapogenins very little was known about kryptogenin, so our first steps were to characterize this substance sufficiently and to prepare some functional derivatives. Some of the derivatives of kryptogenin have already been described: the diacetate, dioxime, and an amino compound which results from catalytic hydrogenation of the dioxime.²

Kryptogenin possesses a 1,4-diketone system and, as is known, the action of hydroxylamine leads to the formation of a dioxime. We have observed that there exists a considerable difference in the reactivity of the two carbonyl groups and that with ketonic reagents other than hydroxylamine mono derivatives are formed, in which

(1) For paper I in this series, see Kaufmann and Rosenkranz, *This Journal*, **70**, 3502 (1948).

(2) F. C. Uhlé and W. H. Jacobs, *J. Biol. Chem.*, **160**, 243 (1945); R. E. Marker, *et al.*, *This Journal*, **69**, 2197 (1947).

(1) Bradsher, Gross, Hobbs, Kittila, Rapoport, Tarrant and West, *This Journal*, **70**, 1317 (1948).

(2) Semimicro analyses were carried out by W. C. Hukari.