light at 75°F. the solubility of the proteins was the same, within the range of experimental error (±1.0%) as at the beginning of the experiment for all samples of whole peanuts, shelled peanuts, and solvent extracted meals.

The solubility of the proteins in hydraulic meal showed no significant change when stored at 33°F. for three years; however, after one year in the dark and light at 75°F. the solubility dropped from 79.7 to 76.4 and 76.6%, and after three years to 72.9 and 70.5%, respectively. Although rancidity was observed in the samples showing changes in protein solubility, no further investigations were made. All other samples which did not change in protein solubility after storage were either not noticeably rancid or the proteins were extracted from oil-free meals; thus it is possible that changes in the residual lipids were responsible for the changes in solubility of proteins in the hydraulic meals stored at 75°F.

DEPARTMENT OF CHEMISTRY
GEORGIA AGR. EXPT. STA.
EXPERIMENT, GA.

RECEIVED JUNE 5, 1948

The Reaction of Thioglycolamide with Halomethyl Ketones

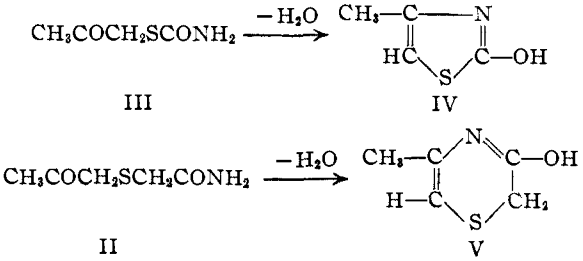
BY H. SOKOL[1] WITH JOHN J. RITTER

The unusual reactivity of the mercapto group in thioglycolamide was first noted by Klason and Carlson[2] when they observed the rapidity with which it was oxidized to the bis-disulfide on exposure to air. There do not however appear to be any other references in the literature to the lability of thioglycolamide.

We have found that thioglycolamide reacts with halomethyl ketones with striking vigor to liberate hydrogen halide. With chloroacetone, reaction occurred spontaneously on mixing the two reactants at room temperature; considerable heat was evolved. Reaction with phenacyl bromide was initiated by warming to 50°. Hydrogen bromide was evolved and S-phenacylthioglycolamide (I) was isolated in good yield. It was hydrolyzed to S-phenacylthioglycolic acid, which has been previously described.[3]

$$C_6H_5COCH_2Br + HSCH_2CONH_2 \longrightarrow \underset{\text{I}}{C_6H_5COCH_2SCH_2CONH_2} + HBr$$

The product obtained from the reaction of thioglycolamide and chloroacetone was not S-acetonylthioglycolamide (II). Analysis indicated the loss of a molecule of water with the formation of *anhydro*-S-acetonylthioglycolamide. This compound was soluble in cold dilute hydrochloric and acetic acids with cleavage to the open-chain compound, and liberated ammonia on boiling with 10% sodium hydroxide. In aqueous acid solution it formed a 2,4-dinitrophenylhydrazone which analyzed correctly for that of II. It is interesting to note that II is the next higher homolog of S-acetonylthiocarbamate (III) which readily loses one molecule of water to form 2-hydroxy-4-methylthiazole (IV).[4] By analogy a possible structure (V) is suggested for *anhydro*-S-acetonylthioglycolamide.



Experimental[5]

Thioglycolamide.—Anhydrous ammonia gas was bubbled slowly through 212 g. of methyl thioglycolate (b. p. 49–51° at 16 mm.) for twenty-four hours. The reaction mixture became warm and its viscosity increased markedly. It was transferred to a desiccator and the methanol removed under vacuum. There was obtained 175 g. (96%) of crude amide as a white amorphous powder. It was stored under nitrogen and used directly without purification.

S-Phenacylthioglycolamide.—A mixture of 20 g. of phenacyl bromide and 9 g. of thioglycolamide was warmed to 50°. A vigorous reaction occurred liberating copious quantities of hydrogen bromide. When evolution of the gas ceased, 100 g. of ice and water were added to the dark reaction mixture and a mass of brown crystals separated. The crude material was filtered and recrystallized from ethanol yielding 16 g. (76%) of sparkling white leaflets, m. p. 157–158°.

Anal. Calcd. for $C_{10}H_{11}O_2NS$: N, 6.70; S, 15.31. Found: N, 6.68; S, 15.39.

S-Phenacylthioglycolic Acid.—One gram of S-phenacylthioglycolamide was boiled for five minutes with 15 ml. of 20% hydrochloric acid; the solid dissolved slowly. The hot solution was filtered and cooled to give 0.7 g. of the acid. Recrystallization from water gave white needles, m. p. 100–101°.[3]

Anal. Calcd. for $C_{10}H_{10}O_3S$: S, 15.24; neut. equiv., 210. Found: S, 15.34; neut. equiv., 207.

Reaction of Chloroacetone with Thioglycolamide.—To 9 g. of thioglycolamide was added 9.3 g. of chloroacetone. A vigorous evolution of hydrogen chloride occurred spontaneously and a clear, viscous solution resulted. After five minutes, 50 g. of ice and water were added to the warm reaction mixture and the precipitate filtered and recrystallized from ethanol to give 12 g. (93%) of beautiful white platelets, m. p. 144°.

Anal. Calcd. for C_5H_7ONS: C, 46.50; H, 5.42; N, 10.85; S, 24.80. Found: C, 46.61; H, 5.48; N, 10.76; S, 24.85.

The 2,4-dinitrophenylhydrazone, prepared in aqueous solution, was recrystallized from ethanol, m. p. 159–161°.

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(1) Abstracted from a portion of the thesis submitted to The Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Klason and Carlson, *Ber.*, **39**, 763 (1906).

(3) Behaghel and Schneider, *Ber.*, **68**, 1591 (1935).

(4) Tcherniac, *J. Chem. Soc.*, **115**, 1076 (1919); Hantzsch, *Ber.*, **60**, 2537 (1927).

(5) Melting and boiling points uncorrected.

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

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
NEW YORK, N. Y.

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The Chlorination of Isophthaloyl and Terephthaloyl Chloride

BY NORMAN RABJOHN

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 $C_8H_3O_2Cl_3$, 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 $C_8O_2Cl_6$: 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 Holmberg[3] 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.

CONTRIBUTION NO. 152
RESEARCH DEPARTMENT
GOODYEAR TIRE & RUBBER CO.
AKRON, OHIO

RECEIVED MAY 27, 1948

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[1] Bradsher, Gross, Hobbs, Kittila, Rapoport, Tarrant and West, THIS JOURNAL, **70**, 1317 (1948).

[2] Semimicro analyses were carried out by W. C. Hukari.

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

Steroidal Sapogenins. II. New Derivatives of Kryptogenin[1]

BY G. ROSENKRANZ, ST. KAUFMANN, A. LANDA, J. J. CORONA AND A. OLALDE

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

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[1] For paper I in this series, see Kaufmann and Rosenkranz, THIS JOURNAL, **70**, 3502 (1948).

[2] F. C. Uhle and W. H. Jacobs, *J. Biol. Chem.*, **160**, 243 (1945); R. E. Marker, *et al.*, THIS JOURNAL, **69**, 2197 (1947).