the free amino acid in pure form has not been recorded in the literature.[1] In connection with studies in which S^{35} was employed we had occasion to synthesize pure *d,l*-cysteine hydrochloride and wish to report our data at this time.

An optically inactive mixture of *d,l*-cystine and *meso*-cystine[2] was prepared from elementary sulfur by way of benzylmercaptan, benzylthiomethyl chloride, benzylthiomethylphthalimidomalonic ester and S-benzylcysteine by Seligman's[3] modification of the procedure of Wood and du Vigneaud.[4] Reduction of the mixed product with tin and hydrochloric acid afforded *d,l*-cysteine hydrochloride, m. p. 140–141.5° (dec.) in 62% yield. The sulfhydryl content of the product as determined by iodine titration was 98.7% of the theoretical value.

Experimental[5]

d,l-**Cysteine Hydrochloride.**—Optically inactive cystine (418 mg.) was dissolved in 5 ml. of 4.0 *N* hydrochloric acid; 400 mg. of granulated tin was added, and the reaction mixture was allowed to stand at room temperature in an atmosphere of nitrogen. At the end of four hours the tin had dissolved, and the solution was evaporated to dryness under reduced pressure to remove excess hydrochloric acid. The residue was dissolved in water, and the tin removed by saturation with hydrogen sulfide followed by filtration. The filtrate was then concentrated to dryness in vacuum. The crude product was finally washed with ethyl acetate, which removed a small amount of oil, and crystallized from absolute ethanol-ether; yield 340 mg. (62%), m. p. 140–141.5° (dec.). An additional 60 mg. of less pure material, m. p. 137–140° (dec.), was obtained from the mother liquor. All operations were conducted under nitrogen.

Anal. Calcd. for $C_3H_7O_2NS{\cdot}HCl$: C, 22.86; H, 5.11; N, 8.89; S, 20.34; Cl, 22.50. Found: C, 23.00; H, 5.20; N, 8.88; S, 20.66; Cl, 22.56.

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[1] Crude, uncharacterized material has been obtained by Schöberl and Wagner, *Naturwissenschaften*, **34**, 189 (1947), and presumably also by Farlow, U. S. Patent 2,406,362 (1946).

[2] Loring and du Vigneaud, *J. Biol. Chem.*, **102**, 287 (1933).

[3] Seligman, Rutenberg and Banks, *J. Clinical Investigation*, **22**, 275 (1943).

[4] Wood and du Vigneaud, *J. Biol. Chem.*, **131**, 276 (1939).

[5] Microanalyses were performed by Mr. S. M. Nagy of M. I. T.

NEW COMPOUNDS

N,N'-Bis-(trichloromethylmethylol)-melamine

12.6 g. (0.1 mole) of pure melamine[1] was added to a stirred solution of 132 g. (0.8 mole) of chloral hydrate in 125 cc. of water at 70–80°. The melamine was completely dissolved within two minutes and a granular solid began to precipitate. After five minutes heating the suspension was cooled, the product filtered off and washed well with water. It weighed 35 g. (83% yield). On larger scale runs yields were usually 90% of theoretical. *Anal.* Calcd. for $C_3H_6N_6{\cdot}2C_2HOCl_3$: N, 19.95; Cl, 50.6. Found: N, 19.9, 20.2; Cl, 50.5, 50.7.

When heated on a spatula the substance did not melt but evolved chloral. It did not react with boiling formalin. It was stable to dilute sodium hydroxide at room temperature but hydrolyzed rapidly on the steam-bath, liberating chloroform; pure melamine crystallized as the solution cooled.

We have observed that the reaction of chloral with melamine–formaldehyde mixtures or with water soluble methylolmelamines results in the formation of gels; this is attributed to the hydrolysis of chloral which lowers the reaction mixture to *p*H 4.

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[1] Salley and Gray, THIS JOURNAL, **70**, 2650 (1948).

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COMMUNICATIONS TO THE EDITOR

SIMULTANEOUS VICINAL DICHLORINATION

Sir:

Iodine trichloride, postulated as the reagent when iodine is a carrier in direct chlorination,[1] has been neglected as a chlorinating agent. Crepaz[2] obtained *p*-chloroacetanilide when acetanilide was treated with $KICl_4$. Spring and Winssinger[3] heated sulfonic acids with iodine trichloride and obtained various products. Thus ethanesulfonic acid with excess reagent heated to 150° for seven hours produced hexachloroethane and chlorosulfonic acid, but with a smaller amount of reagent apparently 1,2-dichloroethanesulfonic acid was produced. On the other hand, 1-propanesulfonic acid yielded 1,1,1-trichloropropane and chlorosulfonic acid with excess iodine trichloride. The latter case suggests a normal ionic substitution mechanism, but the former is more difficult to interpret. Ingold and Ingold[4] suggest that iodine trichloride acts as a chlorinating agent by dissociating to iodine monochloride and two active chlorine atoms

$$ICl_3 \rightleftarrows ICl + 2Cl$$

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[1] Fieser and Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 174.

[2] Crepaz, *Atti ist. veneto sci.*, **94**, 555 (1934–1935); *C. A.*, **31**, 6209 (1937).

[3] Spring and Winssinger, *Ber.*, **15**, 445 (1882); **16**, 326 (1883).

[4] Ingold and Ingold, *J. Chem. Soc.*, 1314 (1926).

When one mole of iodine trichloride was added gradually to eleven moles of benzene with stirring, the initial reaction was almost explosive. After refluxing and working up by distillation and crystallization, 27% of pure *o*-dichlorobenzene, identified by its constants, analyses, and 4,5-dinitro derivative,[5] was obtained. *No p-dichlorobenzene was isolated!* In addition, 7% of monochlorobenzene, 6% of 1,2,4,5-tetrachlorobenzene, and 3% of hexachlorobenzene were isolated. When 0.1 mole of iodine trichloride was mixed with 0.1 mole of benzene in carbon tetrachloride, 61% of *o*-dichlorobenzene and 9% of monochlorobenzene were the only isolated products. When 0.4 mole of iodine trichloride and 0.1 mole of benzene were allowed to react in carbon tetrachloride, 67% of *o*-dichlorobenzene and 32% of 1,2,4,-5-tetrachlorobenzene were obtained. The 1,2,4,5-tetrachlorobenzene was apparently uncontaminated by other isomers, and was identified by melting point (139–40°) and mononitro-derivative (m. p. 94–96°).[6]

Similar results were obtained with anisole, which would be expected to yield 2,4-dichloro- or 2,4,6-trichloroanisole. When 0.1 mole of anisole was refluxed with 0.2 mole of iodine trichloride in carbon tetrachloride, 40% of 3,4-dichloroanisole, (b. p. 200–204°, m. p. −7°[7]) identified by conversion to 3,4-dichlorophenol (m. p. 64°) and its mononitro derivative, m. p. 72–74°,[8] was obtained. In addition 54% of unreacted anisole was recovered.

When aliphatic acid chlorides are chlorinated in the presence of iodine, light being absent, only alpha-substituted derivatives are obtained.[9] When 0.2 mole of *n*-butyryl chloride was refluxed with 0.4 mole of iodine trichloride in carbon tetrachloride, 16% of 2,3-dichlorobutyryl chloride, identified by analysis, conversion to 2,3-dichlorobutyric acid, m. p. 74–75°, and to 2,3-dichlorobutyramide, m. p. 122–124°, was obtained: 55% of unsubstituted butyryl chloride was recovered.

The above products indicate that iodine trichloride must bring about substitution of adjacent carbon atoms simultaneously. This adjacent disubstitution occurs apparently in aromatic and aliphatic compounds. We have tentatively termed this phenomenon "Simultaneous Vicinal Dichlorination." Geometrical considerations suggest that a transitory cyclic intermediate, perhaps I_2Cl_6, is involved.

We are now engaged in determining the extent and limitations of "simultaneous vicinal disubstitution," both in aliphatic and aromatic compounds. It will be interesting to know whether iodine tribromide, iodine trinitrate, etc., can take part in this reaction. These results may also throw some light on the nature of iodine trichloride.

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RECEIVED NOVEMBER 16, 1949

SUBSTITUTED CYCLOÖCTATETRAENES

Sir:

An attempt to prepare phenylcycloöctatriene by addition of phenyllithium to cycloöctatetraene has led to discovery of a direct route to substituted cycloöctatetraenes. The products isolated were phenylcycloöctatetraene and a mixture of 1,3,5- and 1,3,6-cycloöctatrienes, formed by a process equivalent to hydrogen transfer between the initial adduct and cycloöctatetraene. The mixture of cycloöctatrienes was identified by infrared and ultraviolet absorption spectra, and by preparation of a known maleic anhydride adduct of the 1,3,5-isomer, which was formed in larger amount.

Phenylcycloöctatetraene (I) was isolated in 14–19% yield as a yellow liquid, b. p. 92–93° (0.2 mm.); $n^{25}D$ 1.6182; d^{25}_4 1.0335 (*Anal.* Calcd. for $C_{14}H_{12}$: C, 93.34; H, 6.66. Found: C, 93.24; H, 6.83). Treatment of I with one equivalent of powdered silver nitrate in boiling absolute ethanol yielded a yellow-green complex, m. p. 144.5° (dec.) (*Anal.* Calcd. for $C_{14}H_{12}\cdot AgNO_3$: C, 48.02; H, 3.46. Found: C, 48.11; H, 3.54). Hydrogenation of I in methanol in the presence of a palladium catalyst required 99% of four molar equivalents of hydrogen and formed phenylcycloöctane, $n^{25}D$ 1.5300, m. p. 8.2–8.7°, which did not depress the m. p. of an authentic sample. Reaction of I with maleic anhydride in benzene yielded a colorless adduct, m. p. 173–174° (*Anal.* Calcd. for $C_{18}H_{14}O_3$: C, 77.67; H, 5.07. Found: C, 77.69; H, 5.42). Likewise a yellow benzoquinone adduct was obtained, m. p. 191.5–192° (*Anal.* Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.41; H, 5.79).

Reaction of cycloöctatetraene with *p*-dimethylaminophenyllithium yielded *p*-dimethylaminophenylcycloöctatetraene (II) (13–25%), yellow-orange leaflets with m. p. 90–90.5° (*Anal.* Calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.68; N, 6.27. Found: C, 86.34; H, 7.75; N, 6.27). II absorbed 97–99% of four molar equivalents of hydrogen in the presence of palladium in methanol and formed *p*-dimethylaminophenylcycloöctane (III), a colorless liquid, b. p. 145–147° (0.3 mm.), $n^{25}D$ 1.5520, which was characterized as the picrate, m. p. 149–150° (dec.) (*Anal.* Calcd. for $C_{22}H_{28}N_4O_7$: C, 57.38; H, 6.13; N, 12.17. Found: C, 57.20; H, 6.31; N, 12.32). III was identified by an independent synthesis. Coupling of 3-bromocycloöctene with *p*-dimethylaminophenyllithium yielded 3-(*p*-dimethylaminophenyl)-cycloöctene (IV) (34%), a colorless liquid, b. p. 134–

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[5] Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 794, 796, 1077, 1081.

[6] Reference 5, pp. 367, 471.

[7] Holleman, *Rec. trav. chim.*, 37, 102 (1918).

[8] Hodgson and Kershaw, *J. Chem. Soc.*, 2922 (1929).

[9] Ash and Brown, *Rec. Chem. Prog.*, 9, 85 (1948).