

The unsymmetrically substituted ureas I-XIX were formed by the reaction of nitro-urea with the corresponding secondary amines. This reaction is not complete with aromatic secondary amines having ortho-substitution. Ordinarily unreacted amine can be separated by partitioning between ether or benzene and about 6% hydrochloric acid. When, however, there is halogen substitution the basicity of the amine is too low for this separation. Steam-distillation from saturated sodium chloride solution (at about 110°) proved to be adequate for the removal of the unreacted amine and it was then possible to crystallize the secondary ureas reported here. The *n*-butyl derivative analogous to the ureas III and IV was not obtained in crystalline form. Tested physiologically as a crude preparation it showed considerable hypnotic activity.

The dibenzoyl urea XXII resulted from benzoylation of the known *N*-ethyl-*N*-*o*-ethyl phenyl urea either by the Schotten-Baumann method or by heating with benzoyl chloride in pyridine.

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RECEIVED DECEMBER 10, 1943

Di-*n*-butyl-*n*-propylamine

This compound was prepared by the hydrolysis of γ -di-*n*-butylaminopropylmagnesium chloride with aqueous hydrochloric acid, and by the interaction of 2 moles of di-*n*-butylamine and 1 mole of *n*-propyl iodide in a sealed tube at 120° for four hours, removing the residual secondary amine by shaking with benzoyl chloride and 10% sodium hydroxide.

Both methods gave an identical product, with the following constants: b. p. (754 mm.) 193°; b. p. (8 mm.) 73-75°; d_{20}^{20} , 0.7622; n_D^{20} 1.4248.

The picrate crystallized easily from 95% alcohol or from ether; m. p. 115.8-116.2°.

The picrate was analyzed for C and H. Calculated for $C_{17}H_{23}N_4O_7$: mol. wt., 400.42; C, 50.99; H, 7.05. Found: C, 50.90; H, 6.77.

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RECEIVED DECEMBER 23, 1943

o-Phenylene Dioxycetic Acid and its Ethyl Ester

The ethyl ester of *o*-phenylenedioxycetic acid was prepared by refluxing dichloroethyl acetate with catechol in absolute ethanol solution in the presence of 2 moles of sodium and in an atmosphere of nitrogen until neutral to litmus. The reaction mixture was diluted with water, the ester extracted with ether, washed with sodium hydroxide solution and water, and isolated by fractionation; boiling point 115-117° at 12.5 mm.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 61.86; H, 5.15; mol. wt., 194. Found: C, 61.09; H, 5.70; mol. wt. (Rast), 191.

The product gave no test for halogen nor phenolic hydroxyl.

The acid was prepared from its ester by hydrolysis with 1 *N* sodium hydroxide solution; melting point, 107-108° (uncor.) from ether-petroleum ether.

Anal. Calcd. for $C_8H_6O_4$: C, 57.84; H, 3.79. Found: C, 58.12; H, 3.91.

All attempts to effect direct preparation of *o*-phenylene dioxycetic acid by condensation between catechol and dichloroacetic acid failed.

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RECEIVED NOVEMBER 23, 1943

A New Ammine of Basic Copper Chromate

The salt which most commonly separates from ammoniacal copper chromate solutions is $Cu(NH_3)_4CrO_4$. Other ammines have been described.¹ However, from solutions deficient in chromium and containing a considerable excess of ammonium hydroxide, there separates a previously undescribed compound, having the composition $2CuO \cdot 4NH_3 \cdot CrO_3 \cdot H_2O$. In a typical experiment, the crystals were obtained by adding to a suspension of 14.3 g. of basic copper carbonate in 20 ml. of water, 20 ml. of a solution containing 220 g. of ammonium dichromate per liter; 50 ml. of concentrated ammonium hydroxide was added and the mixture shaken thoroughly. Solution was complete except for a few bluish flecks. On standing at room temperature for several days, crystals of the new compound will frequently deposit. Once a crop has been obtained, preparation of the material may be ensured by seeding the solution with the compound. Cooling should be avoided, as at low temperatures green needles of $Cu(NH_3)_4CrO_4$ tend to separate. The yield, after washing with ammonium hydroxide, alcohol and ether, and drying, is about 6 g. The crystals of the new compound are 0.05-1.0 mm. on a side, thickly tabular, almost cubic in habit, greenish-black by reflected light and deep blue-green by transmitted light. The material slowly loses ammonia on exposure to the air, and stoppered preparations have a noticeable odor. On ignition at low temperatures, the crystals decompose with mild deflagration. The crystalline substance becomes coated with an orange-brown discoloration on exposure to air, and water decomposes it to a yellow basic copper chromate. It is insoluble in alcohol, ether, benzene and carbon tetrachloride, and soluble in ammonium hydroxide and acids, being decomposed by the latter; d_{20}^{20} , 2.49.

Anal. Calcd. for $2CuO \cdot 4NH_3 \cdot CrO_3 \cdot H_2O$: CuO, 46.09; NH_3 , 19.73; CrO_3 , 28.96; H_2O , 5.22. Found: CuO, 46.21; NH_3 , 19.55; CrO_3 , 28.92; H_2O , 5.33.

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RECEIVED SEPTEMBER 29, 1943

(1) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1931, Vol. 11, pp. 261-262.