was detected by the spontaneous evolution of carbon dioxide. After remaining overnight at room temperature an additional 6 g. (0.06 mole) of phosgene was added, rendering the mixture acidic. Following a nitrogen flushing until no phosgene could be detected,[9] insoluble inorganic salts were separated by filtration, washed once with toluene, and finally with a toluene–water mixture. Vacuum distillation gave 33.5 g. (0.18 mole, 71% yield) of diisopropyl dicarbonate collected at 44–46°/0.3 mm., n^{25}_D 1.3982. Forecuts contained traces of isopropyl chloroformate with no evidence for the presence of diisopropyl carbonate. Redistillation of the major fractions gave a constant boiling product (85°/5 mm.), n^{25}_D 1.3986 (lit., b.p. 196°/atm., n^{20}_D 1.4015). An infrared spectrum of this ester showed strong double peaks at 1765 and 1820 cm.$^{-1}$, typical of dicarbonates.

By a similar procedure 56 and 76% yields, respectively, of dimethyl and diethyl dicarbonates were obtained.

Di-*t*-butyl Dicarbonate.—In the present synthesis, conducted similarly to that described for diisopropyl dicarbonate, phosgene was added to potassium *t*-butyl carbonate in toluene over 0.5 hr. at −80°. Subsequently, the mixture was warmed slowly to room temperature over a 5-hr. period and after remaining overnight was worked up as described previously. Rapid fractionation of the isolated organic phase gave di-*t*-butyl dicarbonate, b.p. 56–57°/0.5 mm., n^{25}_D 1.4078, m.p. 21–22°.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.0; H, 8.26. Found: C, 55.4; H, 8.31.

A special titration technique with diisobutylamine[10] indicated a purity of 97% while an infrared spectrum pointed out the typical double dicarbonate absorption peaks in the range of 1750–1850 cm.$^{-1}$.

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[9] Phosgene detector crayon No. 1, Aromil Chem. Co., was used to indicate the presence of phosgene, becoming pink in color upon exposure to p.p.m. of phosgene. This crayon was found useful in detecting small amounts of a number of alkyl chloroformates, becoming orange-brown in color upon exposure to their vapors.

[10] W. Thoma and H. Rinke, *Ann.*, **624**, 30 (1959).

Urea Formation *via* Oxidative Carbamylation

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Recently we described a new method for peptide synthesis *via* the oxidation of acyl hydrazides in the presence of free amino groups.[2] We have now found that a similar carbamyl activation can also be demonstrated. Carbohydrazide, and 4-substituted semicarbazides if oxidized in the presence of free amino groups, yields symmetrical and unsymmetrical ureas, respectively.

The symmetrical ureas were obtained after several minutes by the oxidation of one mole of carbohydrazide with four moles of iodine in the presence of ten moles of amine (or two moles of the amine and eight moles of triethylamine) using dimethylacetamide as solvent.

$$NH_2NHCONHNH_2 + 4I_2 + 10\,RNH_2 \longrightarrow RNHCONHR + 8RNH_3{}^+I^- + 2N_2$$

At the end of the reaction small amounts of unchanged iodine were removed with sodium thiosulfate. Upon addition of four volumes of water to the reaction mixture the symmetrical ureas precipitated; after crystallization 60–85% yields of various ureas were obtained.

In a similar manner the oxidation of 4-phenylsemicarbazide hydrochloride with two moles of iodine and six moles of amine (or one mole of the amine and five moles of triethylamine) gave unsymmetrical ureas in yields of about 90%.

$$RNHCONHNH_3{}^+Cl^- + 2I_2 + 6R'NH_2 \longrightarrow RNHCONHR' + 4R'NH_3{}^+I^- + R'NH_3{}^+Cl^- + N_2$$
$$R = C_6H_5—$$

TABLE I

UREAS OBTAINED *via* OXIDATIVE CARBAMYLATION

Urea	Yield, %	M.P.	Nitrogen, % Calcd.	Nitrogen, % Found
1,3-Diphenyl	88	238–239[a]	13.21	13.64
1,3-Dibenzyl	84	169–170[a]	11.66	11.98
1,3-Dicyclohexyl	87	216–218[b]	12.49	11.99
1,3-Dibutyl	61	70[b]	16.26	16.54
1-Benzyl-3-phenyl	90	171–172[c]	12.38	12.32
1-Cyclohexyl-3-phenyl	89	150[d]	12.83	12.76

[a] M.p. of 241–242° for the 1,3-diphenylurea and 170° for the 1,3-dibenzylurea is given by P. A. Boivin, W. Bridgeo, and J. L. Boivin, *Can. J. Chem.*, **32**, 242 (1954). [b] M.p. of 216–217° for the 1,3-dicyclohexylurea and 67–68° for the 1,3-dibutylurea is given by E. Junod, *Helv. Chim. Acta*, **35**, 1667 (1952). [c] M.p. of 172° is given by R. N. Lacey, *J. Chem. Soc.*, 845 (1954). [d] M.p. of 149–150° is given by W. B. Bennet, J. H. Saunders, and E. E. Hardy, *J. Am. Chem. Soc.*, **75**, 2101 (1953).

Experimental

Symmetrical Ureas.—A 900-mg. sample of carbohydrazide (10 mmoles) and 100 mmoles of amine were dissolved in 20 ml. of dimethylacetamide. To the ice-cold solution 10 g. of solid iodine (40 mmoles) was added with mixing. After 5 min. excess of iodine was removed with dilute solution of sodium thiosulfate. The product was precipitated by addition of about 80 ml. of water, filtered off, air-dried, and crystallized.

Unsymmetrical Ureas.—A 1.86-g. sample of 4-phenylsemicarbazide hydrochloride (10 mmoles) and 60 mmoles of amine were dissolved in 20 ml. of dimethylacetamide. To the ice cold solution 5 g. of solid iodine (20 mmoles) was added with mixing. After 5 min. excess of iodine was removed with a dilute solution of sodium thiosulfate and the urea was precipitated by the addition of 80 ml. of water, filtered off, air-dried, and crystallized.

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[1] On leave of absence from the Weizmann Institute of Science.

[2] (a) Y. Wolman and P. M. Gallop, *Bull. Research Council Israel*, **10A**, 43 (1961); (b) Y. Wolman, P. M. Gallop, and A. Patchornik, *J. Am. Chem. Soc.*, **83**, 1263 (1961); (c) Y. Wolman, P. M. Gallop, A. Patchornik, and A. Berger, *ibid.*, in press.