on ice; a dirty yellow product separated which was dissolved in 5% sodium bicarbonate solution and filtered. The filtrate on acidification with ice-cold hydrochloric acid gave a yellow precipitate. This was dissolved in excess of water and then just acidified with concd. sulfuric acid. On allowing it to stand 0.99 g. of 2,4-dinitrophenylbenzoylacetic acid, yellow needles, m.p. 106°, was obtained.

Anal. Calcd. for $C_{15}H_{10}N_2O_7$: C, 54.54; H, 3.03. Found: C, 54.19; H, 2.98.

Ethyl (2-Chloro-4,6-dinitrophenyl)benzoylacetate.—To a suspension of sodio derivative of ethyl benzoylacetate (2.8 g.) in ether was added 1,2-dichloro-4,6-dinitrobenzene (2.37 g.). By adopting a procedure as for compound Ic, a dirty yellow solid was obtained which on recrystallization from acetic acid gave ethyl (2-chloro-4,6-dinitrophenyl)benzoylacetate, lemon-yellow needles, m.p. 128°.

Anal. Calcd. for $C_{17}H_{13}N_2O_7Cl$: Cl, 9.04. Found: Cl, 8.87.

2-(Chloro-4,6-dinitrophenyl)dibenzoylmethane.—To a suspension of potassio derivative of dibenzoylmethane in ether prepared from 3.3 g. of the latter was added 1,2-dichloro-4,6-dinitrobenzene (2.37 g.). By adopting a procedure as for compound Ib, a pale yellow solid was obtained which on recrystallization from acetic acid gave 2-chloro-4,6-dinitrophenyldibenzoylmethane, pale yellow needles, m.p. 179°. (Total yield 53.1%.)

Anal. Calcd. for $C_{21}H_{13}N_2O_6Cl$: Cl, 8.36. Found: Cl, 8.15.

2-Chloro-4,6-dinitrophenylbenzoylmethane. Method A.—A solution of 2-chloro-4,6-dinitrophenylbenzoylacetylmethane in concd. sulfuric acid was heated on a water bath for 1 hr. On cooling and dilution, a dirty white precipitate was obtained which on purification with activated charcoal and recrystallization from dilute acetic acid gave 81% of 2-chloro-4,6-dinitrophenylbenzoylmethane, colorless needles, m.p. 104°.

Anal. Calcd. for $C_{14}H_9N_2O_5Cl$: Cl, 11.07. Found: Cl, 10.89.

Method B. It was prepared by using 2-chloro-4,6-dinitrophenyldibenzoylmethane and concd. sulfuric acid as in method A above (yield 85%).

Method C.—It was prepared by using ethyl (2-chloro-4,6-dinitrophenyl)benzoylacetate and concd. sulfuric acid as in method A above (yield 76%). The mixed melting points of compounds prepared by methods A, B, C remained undepressed.

An Improved Synthesis of Dicarbonates[1]: Di-*t*-butyl Dicarbonate

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Since 1939 a number of alkyl and mixed alkyl aryl dicarbonates (pyrocarbonates) have been prepared and characterized. These diesters were first synthesized in a solvent by the reaction of alkyl chloroformates with potassium hydroxide in the presence of the alkaloid, emetine,[2,3] and more recently by the anhydrous reaction of metal alkyl carbonates with alkyl chloroformates.[4-6]

A convenient, one-step synthesis of dicarbonates by the direct reaction of phosgene with the sodium or potassium salt of the desired carbonic acid ester was developed and is illustrated as follows:

$$\mathrm{ROCO}\left\{\begin{matrix}\mathrm{Na}\\ \mathrm{K}\end{matrix}\right. + \mathrm{COCl_2} \longrightarrow \mathrm{ROCOCOR} + \mathrm{CO_2}\uparrow + \left\{\begin{matrix}\mathrm{Na}\\ \mathrm{K}\end{matrix}\right\}\mathrm{Cl}$$

This process eliminates the necessity of preparing and isolating the intermediate chloroformates, some of which are too unstable to isolate and store readily. Generally, over-all yields of the dicarbonates prepared thus far have been improved over those described in the literature, with little or no formation of by-product dialkyl carbonate as a contaminant.[2]

It is of interest, also, to report the preparation and isolation in low yield (5%) of di-*t*-butyl dicarbonate by this direct phosgenation technique. An unsuccessful attempt to synthesize and isolate this ester by a different method has been reported[6] previously. Although the yield of di-*t*-butyl dicarbonate was low, it was felt that improvement could be made by a shorter work-up time and a more carefully controlled reaction temperature. This ester was found to decompose slowly at room temperature and rapidly above 100°. The stability of di-*t*-butyl dicarbonate may be compared to that of *t*-butyl chloroformate, found to be thermally unstable above 10°. In contrast, di-*t*-butyl carbonate was reported to be a very stable solid which sublimes readily.[7]

Experimental

Diisopropyl Dicarbonate.—The following synthesis of diisopropyl dicarbonate is typical. Initially a solution of sodium isopropoxide was prepared by treating 55 g. (2.4 moles) of sodium with 1085 g. (18.0 moles) of isopropyl alcohol at reflux. Carbonation of this solution for 4 hr. at 87–88° and subsequently for 2 hr. at room temperature gave a thick paste-like gel. Following filtration, vacuum drying gave 242 g. of sodium isopropyl carbonate with above 90% purity as determined by acid-base titration and measurement of carbon dioxide liberated by acid hydrolysis. Subsequently, a solution of 25.8 g. (0.26 mole) of phosgene in 200 ml. of cooled dry toluene was added dropwise to a stirred slurry of 63 g. (0.5 mole) of sodium isopropyl carbonate at 0–5° over a 4-hr. period.[8] Evidence of reaction

(1) The term "dicarbonate" is apparently preferred to "pyrocarbonate" when referring to these diesters, according to the Committee on Publications of the IUPAC [*J. Am. Chem. Soc.*, **82**, 5541 (1960)].

(2) T. Boehm and D. Mehta, *Ber.*, **71B**, 1797–1802 (1938).

(3) L. N. Parfentev and A. A. Shamshurin, *Sbornik Rabot Khim.*, **15**, 67–74 (1939); *Chem. Abstr.*, **35**, 4351 (1941).

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(5) V. I. Kovalenko, *J. Gen. Chem. U.S.S.R. Eng. Trans.*, **22**, 1587–1590 (1952); *J. Gen. Chem. U.S.S.R. Eng. Trans.*, **24**, 1039–1040 (1954); *Chem. Abstr.*, **48**, 4442a (1954); *Chem. Abstr.*, **50**, 6296g (1956).

(6) L. A. Carpino, *J. Am. Chem. Soc.*, **82**, 2725–2727 (1960).

(7) A. R. Choppin and J. W. Rodgers, *J. Am. Chem. Soc.*, **70**, 2967 (1948).

(8) An acetone–Dry Ice condenser was used to contain the phosgene within the reaction mixture.

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 $C_{10}H_{18}O_6$: 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.$^{-1}$.

(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.	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.

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