alkyl pentachlorophenylcarbonate as the alkyloxycarbonyl donor and *N*-trimethylsilylacetamide to promote *in situ* silyl ester formation[4] and to scavenge pentachlorophenol produced in the alkyloxycarbonylation reaction. Work-up of the reaction mixture is simplified by the ready hydrolysis of silyl esters and ethers, the high solubility of lithium acetate in absolute ethanol, and the ready precipitation of the crystalline lithium salts of II and closely related derivatives from ethanolic lithium acetate solution without coprecipitation of lithium pentachlorophenoxide. Other derivatives that have been prepared by the procedure are N^{α}-*p*-methoxybenzyloxycarbonyl-$N^{G,G}$-dibenzyloxycarbonyl-L-arginine (IV),[5] N^{α}-benzoyl-$N^{G,G}$-dibenzyloxycarbonyl-L-arginine (VI), and $N^{\alpha},N^{G,G}$-tri-*p*-methoxybenzyloxycarbonyl-L-arginine (VIII). The latter two derivatives are new compounds, and their use in peptide synthesis will be reported elsewhere.

Experimental Section[6]

Lithium $N^{\alpha},N^{G,G}$-Tribenzyloxycarbonyl-L-arginate (I). To 210 ml of dry DMF were added 20.88 g (0.12 mol) of L-arginine and 160 g (0.4 mol) of benzyl pentachlorophenylcarbonate.[7] The resulting suspension was stirred and heated to 60°. *N*-Trimethylsilylacetamide (78.6 g; 0.6 mol) was added to the mixture and the mixture was stirred for 60 hr at 60°.

After addition of 20 ml of water to the reaction mixture the DMF was evaporated *in vacuo*. The resulting residue was dissolved in absolute ethanol and the solution was added to a hot saturated solution of 50 g of lithium acetate in ethanol. The resulting mixture was cooled slowly to room temperature and then maintained at 4° overnight. A precipitate formed and was filtered. The collected solid was triturated with hot ethyl acetate and then was recrystallized from a minimum volume of boiling methanol. The solid was recovered by filtration and dried *in vacuo* to obtain 39 g (56%) of the title compound, mp 153–155°. An analytical sample was recrystallized from a mixture of methanol and acetone, mp 156–157°; $[\alpha]^{24}D$ +10.6 (*c* 1.5, methanol).

Anal. Calcd for $C_{30}H_{31}N_4O_8Li$: C, 61.85; H, 5.36; N, 9.62; mol wt 582.52. Found: C, 61.75; H, 5.50; N, 9.34.

$N^{\alpha},N^{G,G}$-tribenzyloxycarbonyl-L-arginine (II). Lithium $N^{\alpha},N^{G,G}$-tribenzyloxycarbonyl-L-arginate (10.0 g; 0.017 mol) was suspended in ethyl acetate. The suspension was neutralized by addition of 2% aqueous sulfuric acid. The ethyl acetate layer was separated, dried ($MgSO_4$), and evaporated *in vacuo*. The resulting residue was recrystallized from ethyl acetate to afford, after drying *in vacuo*, 9.1 g (92%) of the title compound: mp 138–139°; $[\alpha]^{25}D$ +15.1 (*c*, 1.5, chloroform) (lit.[2] mp 138–139°; $[\alpha]^{25}D$ +15.5 (*c* 1.5, $CHCl_3$)).

Anal. Calcd for $C_{30}H_{32}N_4O_8$: C, 62.49; H, 5.59; N, 9.72; mol wt 576. Found: C, 62.21; H, 5.80; N, 9.43.

Lithium N^{α}-*p*-Methoxybenzyloxycarbonyl-$N^{G,G}$-dibenzyloxycarbonyl-L-arginate (III). The title compound was prepared from N^{α}-*p*-methoxybenzyloxycarbonyl-L-arginine[5] as described in the procedure for I, except that the reaction time was limited to 34 hr. III was obtained in 63% yield: mp 209–210°; $[\alpha]^{24}D$ +9.9 (*c* 1.5, methanol).

Anal. Calcd for $C_{31}H_{33}N_4O_9Li$: C, 60.78; H, 5.43; N, 9.15; mol wt 612.55. Found: C, 60.51; H, 5.67; N, 9.08.

N^{α}-*p*-Methoxybenzyloxycarbonyl-N^{G},N^{G}-dibenzyloxycarbonyl-L-arginine (IV). Neutralization of III with 0.75 *N* aqueous citric acid gave the title compound in 91% yield: mp 139–141°; $[\alpha]^{25}D$ +16.6 (*c* 1.5, chloroform) (lit.[5] mp 135–136°; $[\alpha]^{25}546$ +14.0° (*c* 1.5, EtOH)).

Anal. Calcd for $C_{31}H_{34}N_4O_9$: C, 61.38; H, 5.65; N, 9.24; mol wt 606.63. Found: C, 61.65; H, 5.88; N, 9.46.

Lithium N^{α}-Benzoyl-$N^{G,G}$-dibenzyloxycarbonyl-L-arginate (V). The title compound was prepared from N^{α}-benzoyl-L-arginine[8] as described in the procedure for I, except that the reaction time was limited to 48 hr. V was obtained in 50% yield: mp 207–209°; $[\alpha]^{25}D$ +28.3 (*c* 1.5, chloroform).

Anal. Calcd for $C_{29}H_{29}N_4O_7Li$: C, 63.03; H, 5.29; N, 10.14; mol wt 552.49. Found: C, 62.80; H, 5.13; N, 10.29.

N^{α}-Benzoyl-N^{G},N^{G}-dibenzyloxycarbonyl-L-arginine (VI). Neutralization of V with 0.75 *N* aqueous citric acid gave the title compound in 83% yield: mp 172–173°; $[\alpha]^{25}D$ +20.0 (*c* 1.5, DMF).

Anal. Calcd for $C_{29}H_{30}N_4O_7$: C, 63.73; H, 5.53; N, 10.25; mol wt 546.58. Found: C, 63.59; H, 5.25; N, 10.07.

Lithium $N^{\alpha},N^{G,G}$-Tri-*p*-methoxybenzyloxycarbonyl-L-arginate (VII). The title compound was prepared exactly as described in the procedure for I. VII was obtained in 50% yield: mp 146–148°; $[\alpha]^{25}D$ +17.5 (*c* 1.0, DMF).

Anal. Calcd for $C_{33}H_{37}N_4O_{11}Li$: C, 58.93; H, 5.55; N, 8.33; mol wt 672.60. Found: C, 58.70; H, 5.76; N, 8.54.

$N^{\alpha},N^{G,G}$-Tri-*p*-methoxybenzyloxycarbonyl-L-arginine (VIII). Neutralization of VII with 0.5 *N* sulfuric acid gave the title compound in 80% yield: mp 125–128°; $[\alpha]^{25}D$ +1.9 (*c* 1, DMF).

Anal. Calcd for $C_{33}H_{38}N_4O_{11}$: C, 59.45; H, 5.75; N, 8.40; O, 26.40; mol wt 666.68. Found: C, 59.15; H, 5.84, N, 8.45; O, 26.57.

Registry No.—I, 52748-08-0; II, 52795-86-5; III, 52748-09-1; IV, 52748-10-4; V, 52748-11-5; VI, 52748-12-6; VII, 52748-13-7; VIII, 52748-14-8; L-arginine, 74-79-3; benzyl pentachlorophenylcarbonate, 13795-28-3; *p*-methoxybenzyl pentachlorophenylcarbonate, 52795-87-6.

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Ethylene Iminocarbonate

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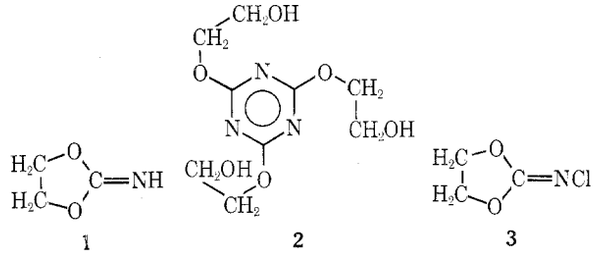
We wish to record here a preparation and characterization of ethylene iminocarbonate (**1**), and its spontaneous conversion to a trimer (**2**). Although the hydrochloride of **1** was described some time ago,[2] neither **1** itself nor **2** have apparently been reported previously.



1 **2** **3**

Ethylene chloriminocarbonate (**3**), easily available from ethylene glycol, potassium cyanide, and chlorine,[3] reacted with sodamide in liquid ammonia, slowly at −80°, vigorously at −50° to −60°. At the latter temperature, the reaction was complete in about 1 hr. Low-temperature work-up gave up to 25% yield of white crystals, mp 38–45° dec, assigned the structure of ethylene iminocarbonate based on spectral data. A by-product, white crystals of mp 117–120° (sintering), was isolated in 25–40% yield. From spectral evidence, it was assigned a trimer structure, most likely **2**.

After about 30 min at room temperature, the crystals of **1** started to melt and 2.5 hr after isolation, decomposition was extensive (effect of traces of base cannot be excluded). Upon further standing or trituration with acetonitrile, crystals of the trimer **2** were formed. On the other hand, the nmr spectrum of a solution of **1** in acetonitrile-d_3 remained unchanged for more than 2 weeks at room temperature.

To complete the characterization of **1**, it was converted at −80° to its hydrochloride, which had been prepared in a different way by Addor.[2] As described in ref 2, the hydrochloride rearranged into β-chloroethyl carbamate upon standing at room temperature.

Besides direct nucleophilic displacement on chlorine, which appears most likely, addition and elimination appears to be a possibility for the mechanism of formation of **1**.[4] It is interesting to note that a previous attempt to prepare **1** by reduction of **3** was unsuccessful.[3]

The trimerization of **1** most likely proceeds *via* ring opening to β-hydroxyethyl cyanate. Alkyl cyanates usually rearrange to isocyanates rather than trimerize, but electronegative substituents on the alkyl appear to slow down the isomerization so that trimerization can compete successfully, yielding trialkoxy-1,3,5-triazines.[5] A trimer similar to **2** was obtained upon basic treatment of 2-imino-1,3-oxathiane hydrochloride.[6]

Experimental Section

Ethylene Iminocarbonate (1). Into a 300-ml 3-neck flask fitted with Dry Ice–acetone condenser, mechanical stirrer, and gas inlet was condensed 200–250 ml of dry ammonia. To this was then added 2.5 g of sodium hydride washed 6–7 times with ether. A blue color resulted and disappeared after stirring for 6–10 hr, or upon addition of a small crystal of ferric nitrate (10–15 min. required). The mixture was cooled to −80° and 5 g of **3** were added. At −80°, the reaction proceeds to less than 50% after 2 hr. However, at −60° to −50°, it proceeds rapidly, often in a vigorously exothermic fashion. It was monitored by removing a small sample of the mixture, evaporating off the NH_3, triturating the residue with ice-cold pyridine and taking the nmr spectrum of the pyridine extract. The reaction was usually complete after 1 hr at −50 to −60° as evidenced by the loss of the nmr peak at δ 4.65, and the appearance of a singlet at δ 4.4. Ammonia was removed under reduced pressure (water aspirator) at −50 to −40°. The residue was triturated 3 times with ether at −20 to −30°. The ether extract was filtered and the ether removed on a rotary evaporator below 0°, leaving white crystals: mp 38–45°; yield varied from ~250 mg to 1 g (6–26%); ^1H nmr (acetonitrile-d_3) singlet at δ 4.4 (4 H), broad peak near δ 5.3 (1 H); ir (Nujol mull) 1700 and 3300 cm^{-1}; mass spectrum molecular ion peak at *m/e* 87, other peaks at 58, 44, and 43 (base peak) (a peak at *m/e* 58 is also seen in the mass spectrum of **3**).

2,4,6-Tris(β-hydroxyethoxy)-1,3,5-triazine (2). A. From Reaction Residue. Further extraction of the ether extracted sodamide residue with either acetonitrile or methylene chloride followed by filtration and evaporation of the solvent yielded a light yellow oil. Upon standing or triturating with acetonitrile, the oil gave white crystals, mp 113–117°. Yield 1.0–1.5 g. Analytical sample was crystallized from acetone: mp 117–120° (sintering); ^1H nmr (D_2O) A_2B_2 pattern centered at δ 3.7 and 4.2; ir (Nujol) 3300 (broad) and 1560 cm^{-1}; uv (acetonitrile) shoulder at 260 nm (ε 32), then strong rise in absorption but no maximum down to 205 nm; mass spectrum (electron impact ionization), no molecular ion at *m/e* 261, peaks at 244 ($M^+ - OH$, presumably bicyclic immonium ion), 231 ($M^+ - CH_2O$), 218, 201, 187, 174, 156, 143, 130 (base peak), 113, 87, 70; mass spectrum (chemical ionization) peak at *m/e* 262 ($M^+ + H$); high-resolution mass spectrum (Varian MAT 311, resolution 10,000), peak at nominal *m/e* 231 matched with PFK; 231.0852, for $C_8H_{13}N_3O_5$ calculated 231.0855.

B. From Ethylene Iminocarbonate (1). After standing at room temperature for several hours, ethylene iminocarbonate trimerized spontaneously, giving crystals of mp 114–118°, whose nmr and ir spectra were identical with those of the above-described trimer.

Ethylene Iminocarbonate Hydrochloride. Into 25 ml of dry ethylene glycol dimethyl ether (distilled from $LiAlH_4$) was placed ~20 mg of ethylene iminocarbonate. The solution was cooled to −80° (complete dissolution did not occur). A stream of dry HCl was bubbled into the mixture for 2 min. A cloudy suspension developed. The solid was collected on filter and washed with ether, giving fine white crystals: mp 73–75° (lit.[2] 77–78°); ir (Nujol mull) 1510, 1550, 1720, and a broad band at 2600–3400 cm^{-1}. Upon standing over the weekend, the hydrochloride rearranged to β-chlorethyl carbamate, mp 68–70° (lit.[2] 65–70°).

Registry No.—**1**, 6703-57-7; 1 HCl, 52699-47-5; **2**, 891-65-6; **3**, 22718-26-9.

References and Notes

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Ozonization of the 7-Phenylnorcaranes. Effects of Solvent and Temperature

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Recently we reported the first direct chemical evidence[1] supporting Closs',[2] Jensen's,[3] and Ledlie's[4] stereochemical assignments of *endo-* and *exo-*7-phenylnorcarane (**2a** and **2b**, respectively). This involved degrading **2a** and **2b** with ozone, employing the procedure of Shabarov,[5] producing the known *endo-* and *exo-*norcarane-7-carboxylic acids,[6,7] respectively, and a cyclopropane cleavage product, benzoic acid (**4**), all of which were isolated as their methyl esters. We then became interested in searching for other cleavage products and now wish to report the isolation and identification of the remaining compounds formed as **2a** and **2b** are ozonized, noting the effects of solvent and temperature on the product distribution. A modified procedure for the synthesis of **2a** is also discussed.

Jensen[3] has reported that triphenyltin hydride reduction of crude 7-chloro-7-phenylnorcarane (**1**), prepared by reaction of cyclohexene, benzal chloride, and potassium *tert*-butoxide,[8] yields, by vpc, 80% **2a**, 1% **2b**, and 19% olefin. Our observations indicate that the origin of the olefin arises not from the reduction of **1**, but occurs as a result of reduction of an olefinic product produced during the preparation of **1**. This olefinic impurity was removed with ozone. Purified **1** was then reduced with lithium aluminum hydride in diglyme furnishing a 65% yield of products which analyze (vpc) as 97% **2a**, 3% **2b**, and no olefin. Subsequent distillation of the reaction mixture yields a sample of **2a** that is 99% pure.[9]

Ozonization of **2a** in 95% acetic acid at 25°, followed by treatment of the ozonized material with hydrogen peroxide and subsequent methylation of the products, furnishes a mixture containing four volatile components. These were separated by preparative gas chromatography and labeled in order of increasing elution time as **3a**, **4**, **5**, and **6**. Compounds **3a** and **4** have previously been identified as *endo-*7-carbomethoxynorcarane and methyl benzoate, respectively.[1] Compound **5** was identified as dimethyl glutarate by comparison of its ir and nmr spectra with reference spectra, correct elemental analysis, and by saponification of **5** to glutaric acid. Compound **6** furnished a correct elemental analysis for dimethyl adipate, gave ir and nmr spectra identical with authentic material, and saponification of **6** furnished adipic acid. These materials, **3a**, **4**, **5**, and **6**, were formed in 13, 16, and 9 and 8% yields, respectively,