2,3,5,6,7,8-Hexahydro-1*H*,4*H*-3a,8a-etheno-*s*-indacene (12). Potassium *tert*-butoxide (18.5 g, 165 mmol) was added in one portion to a stirred solution of unpurified 11 (11.85 g, 41.4 mmol) in dry tetrahydrofuran (500 mL) cooled to 0 °C under nitrogen. The mixture was gradually heated to the reflux temperature of the solvent during several hours, where it was maintained for an additional 4 h. After being cooled, the mixture was treated with water (500 mL) and extracted with several portions of pentane. The combined organic layers were washed with water and brine, dried, and freed of solvent by distillation at atmospheric pressure. Distillation of the residue afforded 2.86 g of liquid (bp 124–134 °C, 10 mm), which was shown by VPC analysis (12% Carbowax 20M, 127 °C) to contain 77% of diene **12** (29% yield). An analytical sample was obtained by preparative VPC methods: ^{1}H NMR ($CDCl_3$) δ 5.67 (s, 2 H) and 2.48–1.43 (br m, 16 H).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 89.91; H, 9.89.

2,3,5,6,7,8-Hexahydro-*N*-phenyl-1*H*,4*H*-3a,8a-etheno-*s*-indacene-4,8-biimine-11,12-dicarboximide (14). A solution of bromine (23 μL, 0.423 mmol) in 1 mL of pentane (washed with H_2SO_4 and distilled) was added dropwise at −78 °C to a stirred solution of **12** (freshly purified; 75 mg, 0.043 mmol) in pentane (5 mL) under nitrogen. After 1 h, a solution of diazabicycloundecene (245 mg, 1.61 mmol) in dry tetrahydrofuran (5 mL) was introduced and the mixture was allowed to warm gradually to room temperature with stirring during 10 days. The resulting mixture was filtered down a short alumina (Act III) column with pentane elution. At this point, VPC analysis (10% SE-30, 119 °C) showed three components present in the ratio 22:55:23. Without being concentrated, this solution was cooled to −78 °C under nitrogen and *N*-phenyltriazolinedione (45.8 mg, 0.26 mmol) dissolved in ethyl acetate (2 mL) was added with stirring. After 48 h at room temperature, the product was purified by preparative thin-layer chromatography on silica gel (elution with 10% ether in pentane) and recrystallized from tetrahydrofuran–pentane. There was isolated 28 mg (36%) of **14**: mp 188–191 °C dec; IR (KBr) ν_{max} 1710 and 1400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60–7.24 (m, 5 H), 5.64 (s, 2 H), 4.78 (s, 2 H), 2.33–2.21 (m, 4 H), and 1.89–1.74 (m, 8 H); ^{13}C NMR $CDCl_3$ δ 156.6, 138.1 (2 C), 131.9, 129.0, 128.0, 125.4, 58.7, 58.4, 32.6, 28.5, 24.5, and 24.3; MS *m/e* 359.1640 (calcd 359.1634).

Anal. Calcd for $C_{22}H_{21}N_3O_2$: N, 11.69. Found: N, 11.59.

Tetrahydro-*N*-phenyl-1*H*,4*H*,5*H*,8*H*-3a,4a,7a-8a-ethanediylidene-*s*-indacene-4,8-biimine-11,12-dicarboximide (3). A solution of **14** (250 mg, 0.70 mmol) in acetone–benzene (1:1, 400 mL) was irradiated through Corex for 1 h with a medium pressure 450-W Hanovia lamp housed in an immersion well. The solvent was evaporated, and the residue was chromatographed on silica gel to give 150 mg (60%) of **3** as a viscous oil: ^{1}H NMR (CD_3COCD_3–C_6D_6) δ 7.72–7.24 (m, 5 H), 4.73 (s, 2 H), 2.38 (s, 2 H), and 1.87–1.62 (m, 12 H); ^{13}C NMR (C_6D_6) δ 151.1, 132.3, 129.0, 127.4, 125.3, 56.2, 53.9, 41.2, 30.1, and 27.1. Calcd for $C_{22}H_{21}N_3O_2$: *m/e* 359.1640. Found: *m/e* 359.1634.

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Registry No.—**3**, 67722-97-8; **6**, 3205-94-5; **7**, 20968-70-1; **8**, 67722-98-9; **9a**, 67722-99-0; **9b**, 67723-00-6; **10**, 67723-01-7; **11**, 67723-02-8; **12**, 67723-03-9; **13**, 67723-04-0; **14**, 67723-05-1; *N*-phenytriazolinedione, 4233-33-4; 1-chloro-5,6,7,8-tetrahydro-3*H*,4*H*-3a,8a-propane-1*H*-indeno[5,6-*c*]thiophene, 67723-06-2; methanesulfonyl chloride, 124-63-0; *N*-chlorosuccinimide, 128-09-6; sodium sulfide, 1313-82-2.

References and Notes

(1) Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. 37. Part 36: E. Chamot, A. K. Sharma, and L. A. Paquette, *Tetrahedron Lett.*, 1963 (1978).
(2) A. K. Cheng, F. A. L. Anet, J. Mioduski, and J. Meinwald, *J. Am. Chem. Soc.*, **96**, 2887 (1974).
(3) A. G. Anastassiou, E. Reichmanis, and J. C. Wetzel, *Tetrahedron Lett.*, 1651 (1975).
(4) (a) D. R. James, G. H. Birnberg, and L. A. Paquette, *J. Chem. Soc., Chem. Commun.*, 722 (1974); (b) L. A. Paquette, D. R. James, and G. H. Birnberg, *J. Am. Chem. Soc.*, **96**, 7465 (1974).
(5) (a) L. A. Paquette, W. E. Volz, M. A. Beno, and G. G. Christoph, *J. Am. Chem. Soc.*, **97**, 2562 (1975); (b) L. A. Paquette and W. E. Volz, *ibid.*, **98**, 2910 (1976).
(6) (a) L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Am. Chem. Soc.*, **94**, 4739 (1972); (b) R. K. Russell, L. A. Paquette, L. G. Greifenstein, and J. B. Lambert, *Tetrahedron Lett.*, 2855 (1973); (c) R. E. Wingard, Jr., R. K. Russell, and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 7474 (1974).
(7) (a) L. A. Paquette, R. K. Russell, and R. L. Burson, *J. Am. Chem. Soc.*, **97**, 6124 (1975); (b) L. A. Paquette and R. L. Burson, *Tetrahedron*, **34**, 1307 (1978).
(8) (a) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963); (b) E. Vogel, W. Maier, and J. Eimer, *ibid.*, 655 (1966).
(9) (a) L. A. Paquette and R. S. Beckley, *J. Am. Chem. Soc.*, **97**, 1084 (1975); (b) L. A. Paquette, R. S. Beckley, and W. B. Farnham, *ibid.*, **97**, 1089 (1975); (c) L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *ibid.*, **97**, 1101 (1975).
(10) J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *J. Chem. Soc., Chem. Commun.*, 40 (1971).
(11) L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Am. Chem. Soc.*, **93**, 4508 (1971).
(12) L. A. Paquette, *Org. React.*, **25**, 1 (1977).
(13) Reviews: (a) L. A. Paquette, *Synthesis*, 347 (1975); (b) L. A. Paquette, *Org. Chem., Ser. One, 1973*, **5**, 127 (1973); (c) K. C. Bishop, III, *Chem. Rev.*, **76**, 461 (1976).
(14) E. Chamot, A. K. Sharma, and L. A. Paquette, *Tetrahedron Lett.*, 1963 (1978).
(15) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).
(16) Unpublished work from this laboratory.
(17) For an early report on the fate of such diaza-1,8-bishomocubanes upon hydrolysis, see D. G. Farnum and J. P. Snyder, *Tetrahedron Lett.*, 3861 (1965).
(18) For a discussion of this dynamic situation, consult G. G. Christoph and M. A. Beno, *J. Am. Chem. Soc.*, **100**, 3156 (1978).
(19) R. Hoffman and W. D. Stohrer, *J. Am. Chem. Soc.*, **93**, 6941 (1971).
(20) L. Birladeanu, E. Chamot, W. E. Fristad, L. W. Paquette, and S. Winstein, *J. Org. Chem.*, **42**, 3260 (1977).
(21) P. D. Bartlett, A. S. Wingrove, and R. Owyang, *J. Am. Chem. Soc.*, **90**, 6067 (1968).
(22) S. C. Sen-Gupta, *J. Indian Chem. Soc.*, **17**, 183 (1940).

Notes

Synthesis of 1,3-Dialkyldiazetidinediones from *N,N'*-Dialkylaminocarbonylcarbamic Chlorides (2,4-Dialkylallophanoyl Chlorides)

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We describe here a synthesis of 1,3-dialkyldiazetidinediones (1) in which R may be primary, secondary, or tertiary. 1,3-Diaryldiazetidinediones are well-known and may be prepared readily by dimerization of aryl isocyanates under appropriate conditions.[1] 1,3-Dialkyldiazetidinediones have received far less study, primarily because they are not readily synthesized from the isocyanates. This conversion has been accomplished in good yield for benzyl isocyanates with 1,2-dimethylimidazole[2a] and in low yield for various other primary aliphatic isocyanates with tertiary phosphine or BF_3 catalysts.[2b,c] Antimony pentachloride has been used to induce dimerization of methyl (20%) and ethyl (30%) isocyanate, but the reaction failed with isopropyl isocyanate.[2d]

An attractive alternate route, that of the ring closure of the aminocarbonylcarbamic chlorides (2), has been effected by treating diarylaminocarbonylcarbamic chlorides with pyridine.[3] The procedure, however, was not successful in the dialkyl case tried (**2d**). Ring closure of the dialkyl derivatives

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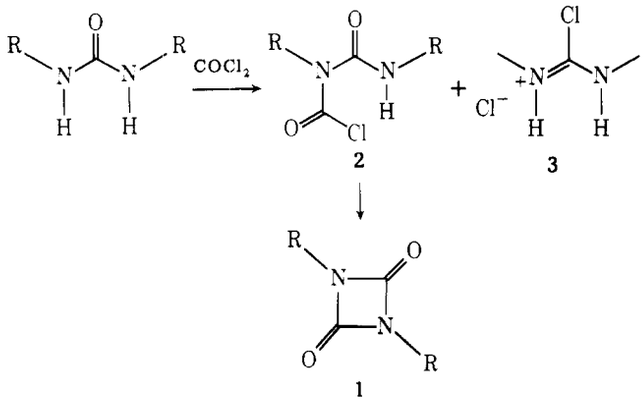
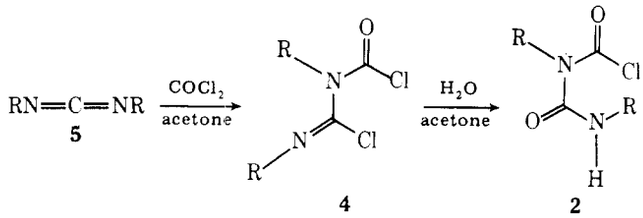


a, R = $(CH_3)_3C$; b, R = $(CH_3)_2CH$; c, R = c-C_6H_{11}; d, R = CH_3

with tertiary amines has been claimed in a patent, but no yields or physical data were reported.[4] The route has also been limited by the difficulty in synthesizing aminocarbonylcarbamic chlorides containing secondary R groups. Thus, while primary aminocarbonylcarbamic chlorides are available in approximately 70% yield from the reaction of *N,N'*-dialkylureas with phosgene, the secondary derivatives are formed only in 6–12% yield, the major product being the chloroformamidinium chloride salt (**3**).[5a] Tertiary aminocarbonylcarbamic chlorides may be synthesized by this route, but again in low (~15%) yields.[5b,c] Di-*tert*-butylurea forms the diazetidinedione **1a** directly when treated with phosgene and pyridine, presumably through **2a**.[6]

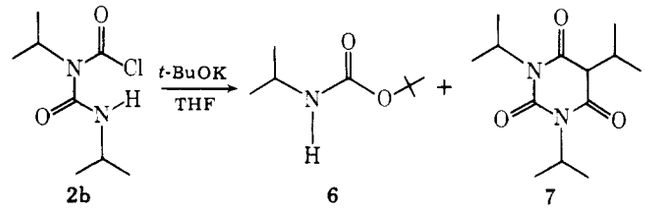
Although the aminocarbonylcarbamic chlorides are available in only low yield for R = *sec*- and *tert*-alkyl, the corresponding [chloro(alkylimino)methyl]carbamic chloride derivatives (**4**) may be synthesized in quantitative yield from the reaction of phosgene and the appropriate carbodiimides (**5**).[7]



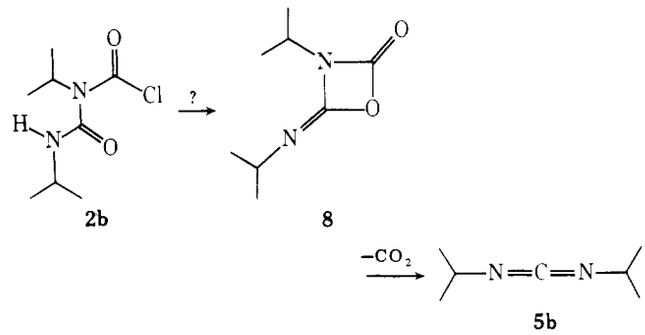
The known stability of carbamic chlorides in water,[8] coupled with the ease of hydrolysis of the imidoyl chloride moiety,[7b,9] suggested the hydrolysis of **4** as a route to **2**. The reaction is successful, producing **2** from **5** in overall yields of 60–80% (Table I).

Di-*tert*-alkylaminocarbonylcarbamic chlorides can also be made, but prove to be quite labile. Hydrolysis of [chloro(*tert*-butylimino)methyl]-*tert*-butylcarbamic chloride (**4a**) gave **2a**. Compound **2a** cyclized to **1a**[6] on standing at room temperature; heating a solution of **2a** converted it into **1a** and *tert*-butyl isocyanate. The facile ring closure is somewhat surprising, but may be ascribed in part to steric effects and perhaps in part to decreased conjugation of the nitrogen lone pairs.

Ring closure of **2** to **1** depends on the nature of the alkyl groups, but is also very sensitive to the nature of the base used. Treatment of **2b, 2c,** or **2d** with a solution of Dabco (1,4-diazabicyclo[2.2.2]octane) in ether resulted in rapid formation of the diazetidinedione in 55–84% yield (Table I). Stronger bases produced more side reactions. Potassium *tert*-butoxide in refluxing tetrahydrofuran converted **2b** to a mixture of



carbamate **6** and triazinetrione **7**. Sodium hydride effected little reaction of **2b** at room temperature, but upon refluxing in tetrahydrofuran a mixture of products including isocyanate, carbodiimide, diazetidinedione and triazinetrione was produced. The presence of carbodiimide may argue for some ring closure of **2b** through the oxygen rather than the nitrogen to give species **8**; loss of CO_2 would afford the carbodiimide **5b**.



Similar reactions have been noted in the addition of phosgene to thioureas[10] and in the synthesis of isocyanates from the reaction of aminocarbonylcarbamic chlorides with amines.[7a]

Hydrolysis of [chloro(alkylimino)methyl]carbamic chlorides thus provides a good route to aminocarbonylcarbamic chlorides which may be converted under mild conditions to 1,3-diazetidinediones.

Experimental Section

***tert*-Butyl[(*tert*-butylamino)carbonyl]carbamic Chloride (2a).** To a solution of di-*tert*-butylcarbodiimide (1.0 g, 6.5 mmol) in 15 mL of methylene chloride at 0 °C was added phosgene (2.2 g, 22.2 mmol) until the infrared spectrum showed no remaining carbodiimide stretch (2115 cm^{-1}), ca. 15 min. The solvent and phosgene were removed under vacuum to give a pale green oil (**4a**):[11] IR ($CHCl_3$) 1760 (s), 1690 (m), 1365 (w) cm^{-1}; NMR (CH_2Cl_2) δ 1.40 (s, 9 H), 1.51 (s, 9 H). Hydrolysis of an aliquot in methylene chloride, to which 3–4 drops of D_2O were added, was followed by NMR. During 20 min the peaks at δ 1.40 and 1.51 were replaced by new ones at δ 1.37 (s, 9 H) and 1.48 (s, 9 H). The infrared spectrum of the resulting product was similar to that described below for **2a**. Further standing at room temperature for 20 min gave an NMR spectrum containing a singlet at δ 1.37 (diazetidinedione, 70%) and a smaller singlet at δ 1.25 (isocyanate, 30%). The infrared spectrum showed bands at 1760 (diazetidinedione) and 2260 (isocyanate) cm^{-1}.

The major portion of the pale green oil, **4a**, was dissolved at 0 °C

Table I. Yields of Aminocarbonylcarbamoic Chlorides (2) and 1,3-Diazetidinediones

carbodiimide	registry no.	aminocarbonylcarbamoic chloride, % yield	registry no.	diazetidinedione, % yield	registry no.
di-*tert*-butyl	691-24-7	~80	13188-10-8	70	30885-14-4
diisopropyl	693-13-0	61	13188-12-0	55	67463-80-3
dicyclohexyl	538-75-0	67	13188-13-1	84	15234-14-7
(dimethyl)	4852-30-6	60[a]	13188-08-4	79	36909-44-1

[a] From dimethylurea and phosgene.[5a]

in 20 mL of acetone containing 0.2 mL of water and 1 g of $NaHCO_3$. The resulting solution was stirred for 25 min at 0 °C. Removal of solvent under vacuum gave a white solid, which was dissolved in 25 mL of hot ligroin and 25 mL of hot benzene. The solution was filtered, and the solvents were removed under vacuum to give 1.2 g (80%) of a white solid: IR ($CHCl_3$) 3400 (w), 1755 (s), 1720 (m), 1490 (m), 1455 (w), 1365 (m) cm^{-1}. Volhard titration for chlorine[12] gave 88.6 ± 2.1% of the theoretical value for **2a**. Recrystallization from pentane gave a white solid, mp 88–89 °C. Volhard titration was still low in chlorine (82.8 ± 1.3% of expected value) due to facile conversion of **2a** to the diazetidinedione.

Hydrolysis of **4a** under less carefully controlled conditions, or even leaving **4a** loosely stoppered for a few days at room temperature, gave diazetidinedione **1a** as the major product, isolated from the mixture by sublimation (75 °C, 0.1 torr): mp 88–90 °C (lit.[6] mp 89–90 °C); IR ($CHCl_3$) 1760 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (s).

Isopropyl[(isopropylamino)carbonyl]carbamic Chloride (2b). Phosgene was passed through a solution of diisopropylcarbodiimide in methylene chloride at 0 °C until the infrared spectrum showed no remaining carbodiimide stretch (2100 cm^{-1}), ca. 15 min. Removal of the volatile components under vacuum gave 88% of a pale green oil (**4b**):[7b] IR ($CHCl_3$) 1745 (s), 1665 (m) cm^{-1}. To 29.5 g (0.13 mol) of **4b** in 200 mL of acetone at 0 °C was added 20 mL of water, and the solution was stirred for 35 min. The solvents were removed under reduced pressure, and the residue was recrystallized from ligroin to give 16.4 g (61%) of white crystals: mp 61–64 °C (lit.[5a] mp 63 °C); IR ($CHCl_3$) 3430 (w), 3360 (w), 1725 (s), 1505 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.28 (d, 6 H, J = 7 Hz), 1.43 (d, 6 H, J = 7 Hz), 4.2 (m, 2 H), 6.5 (br, 1 H).

Cyclohexyl[(cyclohexylamino)carbonyl]carbamic Chloride (2c). Addition of phosgene to dicyclohexylcarbodiimide as for **4b** gave a quantitative yield of **4c**:[7a] IR ($CHCl_3$) 1735 (s), 1662 (m) cm^{-1}. A solution of **4c** (5.3 g, 17.4 mmol) in 30 mL of acetone and 25 mL of water was allowed to stand for 20 h. The resulting white needles were isolated by filtration: yield 1.70 g (34%); mp 122–123 °C [lit.[5a] mp 127–128 °C (hexane)]. An additional 1.66 g (33%), mp 120–121 °C, was obtained by extraction, solvent removal, and recrystallization from hexane. The total yield of recrystallized **2c** was 3.36 g (67%). Further recyrstallizations, either from hexane or acetone–water, did not raise the melting point above 122–123 °C: IR ($CHCl_3$) 3420 (w), 1715 (s), 1495 (m) cm^{-1}; NMR ($CHCl_3$) δ 1.0–2.1 (m, 20 H), 3.5–4.1 (m, 2 H), 6.0 (br, 1 H).

Anal. Calcd for $C_{14}H_{23}N_2O_2Cl$: C, 58.63; H, 8.08. Found: C, 58.90; H, 8.31.

1,3-Diisopropyldiazetidinedione (1b). Compound **2b** (2.63 g, 12.7 mmol) and 1.57 g (14.0 mmol) of Dabco in 50 mL ether were stirred for 1 h and filtered. Hydrogen chloride was bubbled through the filtrate, and the resulting suspension was again filtered. Removal of the ether gave 1.85 g (86%) of a clear oil, crystallized from pentane at −78 °C to give 1.19 g (55%) of white needles that melted to a clear oil below room temperature. The compound may also be distilled: bp 80–83 °C (14 torr); IR ($CHCl_3$) 1760 (s), 1450 (w), 1380 (m), 1315 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.33 (d, 12 H, J = 6 Hz), 3.7 (sept, 2 H, J = 6 Hz); mass spectrum m/e (relative intensity) 170 (M^+, 0.5), 155 (2), 86 (2), 85 (12), 84 (2), 71 (4), 70 (100).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29. Found: C, 56.28; H, 8.06.

1,3-Dicyclohexyldiazetidinedione (1c) was prepared as described for **2b**. Removal of the ether under vacuum and recrystallization of the residue from hexane at −15 °C gave an 84% yield of white crystals: mp 92–94 °C; IR ($CHCl_3$) 1750 (s), 1440 (w), 1390 (w), 1360 (w), 1340 (w) cm^{-1}; NMR ($CDCl_3$) δ 1.1–2.1 (m, 20 H), 3.1–3.4 (m, 2 H); mass spectrum, m/e (relative intensity) 250 (M^+, 6), 222 ($M^+ - CO$, 1), 207 (1), 169 (2), 168 ($M^+ - C_6H_{10}$, 5), 126 (41), 125 (M^+ - c-$C_6H_{11}NCO$, 100).

Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86. Found: C, 67.16; H, 8.94.

1,3-Dimethyldiazetidinedione (1d). Methyl[(methylamino)-carbonyl]carbamic chloride (**2d**) was prepared according to the procedure of Ulrich et al.:[5a] mp 31–32 °C (lit.[5a] mp 36 °C); IR ($CHCl_3$) 1730 (s), 1530 (m) cm^{-1}. Treatment of **2d** with Dabco as described for **2b**, removal of the solvent under vacuum, and recrystallization from hexane gave a 79% yield of white volatile plates: mp 96–98 °C (lit.[2d] mp 94–95 °C); IR ($CHCl_3$) 1780 (s), 1725 (w), 1440 (w), 1370 (w) cm^{-1}; NMR ($CDCl_3$) δ 2.86 (s); mass spectrum, m/e (relative intensity) 114 (M^+, 2), 86 (9), 70 (12), 59 (3), 58 (67), 57 (100).

Reaction of Isopropyl[(isopropylamino)carbonyl]carbamic Chloride (2b) with Potassium *tert*-Butoxide. Compound **2b** (2.06 g, 10 mmol) and potassium *tert*-butoxide (1.25 g, 11 mmol) were refluxed together in 12 mL of dry tetrahydrofuran under nitrogen for 10 h. The mixture was cooled to 0 °C, diluted with water, and extracted with pentane. The pentane was dried ($MgSO_4$) and removed under vacuum to give 2.74 g of an oil and solid. NMR analysis of the mixture was consistent with the presence of two products, *tert*-butyl isopropylcarbamate **6** (63%) and triisopropyltriazinetrione **7** (29%). The products were separated by GLC (15% SE 30 on Chromosorb W, 6 ft × 0.25 in., temperature programmed at 140–200 °C at 5 °C/min). The structure of **6** was confirmed by spectral comparison and a mixed melting point with an authentic sample. The triazinetrione **7** was a white solid: mp 103–104 °C; IR ($CHCl_3$) 1690 (s), 1470 (m), 1435 (s), 1425 (s), 1370 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.46 (d, 18 H), 5.0 (sept, 3 H); mass spectrum, m/e (relative intensity) 256 (6), 255 (M^+, 39), 240 (21), 214 (44), 198 (19), 172 (42), 171 (13), 170 (6), 57, (100).

***tert*-Butyl *N*-Isopropylcarbamate (6).** To 176 mg (2.1 mmol) of isopropyl isocyanate in 25 mL of ligroin at 0 °C was added a few milligrams of $SnCl_2 \cdot H_2O$[13] and 154 mg (2.1 mmol) of *tert*-butyl alcohol. The reaction was warmed to room temperature and then refluxed for 2.5 h. The warm reaction mixture was filtered and the filtrate taken to dryness under aspirator vacuum. The residue was sublimed at 14 torr to give 147 mg (45%) of white crystals:[14] mp 70.5–72.5 °C; IR ($CHCl_3$) 3440 (w), 1705 (s), 1495 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.13 (d, 6 H, J = 6 Hz), 1.47 (s, 9 H), 3.8 (m, 1 H), 4.3 (br, 1 H).

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Registry No.—**4a,** 55871-88-0; **4b,** 13829-15-7; **4c,** 13236-48-1; **6,** 51170-55-9; **7,** 67463-81-4; phosgene, 75-44-5; isopropyl isocyanate, 1795-48-8; *tert*-butyl alcohol, 75-65-0.

References and Notes

(1) H. Ulrich, "Cycloadditions of Heterocumulenes", Academic Press, New York, N.Y., 1967.
(2) (a) R. Richter and H. Ulrich, *Synthesis,* 463 (1975); (b) A. Etienne, G. Lonchambon, P. Giraudeau, and B. Jaubert, *C. R. Hebd. Seances Acad. Sci., Ser. C.* **280,** 995 (1975); (c) Farbenfabriken, Bayer A.-G., French Patent 1 532 054, 1968; *Chem. Abstr.,* **71,** 81328d (1969); (d) N. Kuhn, W. Schwarz, and A. Schmidt, *Chem. Ber.,* **110,** 1130 (1977).
(3) H. Helfert and E. Fahr, *Angew. Chem., Int. Ed. Engl.,* **9,** 372 (1970).
(4) H. E. Johnson (Union Carbide), U.S. Patent 3 671 500, 1972; *Chem. Abstr.,* **77,** P75833x (1972).
(5) (a) H. Ulrich, J. N. Tilley, and A. A. R. Sayigh, *J. Org. Chem.,* **29,** 2401 (1964); (b) U.S. Patent 3 337 621, 1967; *Chem. Abstr.,* **67** P9967In (1967); (c) U.S. Patent 3 275 669, 1966; *Chem. Abstr.,* **65,** P20006b (1966).
(6) J. C. Stowell, F. D. Greene, and W. R. Bergmark, *J. Org. Chem.,* **36,** 3056 (1971).
(7) (a) H. Ulrich and A. A. R. Sayigh, *J. Org. Chem.,* **28,** 1427 (1963); (b) K. Hartke and E. Palou, *Chem. Ber.* **99,** 3155 (1966).
(8) A. Queen, *Can. J. Chem.,* **45,** 1619 (1967).
(9) S. Patai, "The Chemistry of the Carbon–Nitrogen Double Bond", Wiley, New York, N.Y., 1970, p 630.
(10) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron,* **22,** 1565 (1966).
(11) C. J. Wilkerson and F. D. Greene, *J. Org. Chem.,* **40,** 3112 (1975).
(12) D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry", 2nd ed., Holt, Rinehart and Winston, New York, N.Y., 1969, p 233.
(13) S. R. Sandler and W. Karo, "Organic Functional Group Preparations", Vol. 2, Academic Press, New York, N.Y., 1971, p 223.
(14) T. Szirtes, E. Palosi, E. Ezer, L. Szporny and L. Kisfaludy, *Acta Pharm. Hung.,* **43,** 224 (1973); *Chem. Abstr.,* **80,** 103936r (1974).

1,1-Bis(acylthio)alkanes Formed by Base-Catalyzed Condensation of Thiol Acids

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As part of our continuing interest in using organosulfur-containing nucleophilic compounds as analytical reagents, the behavior of thiol acids was studied in basic solutions. Ether solutions containing equimolar quantities of thiolacetic acid and tertiary amine (pyridine or triethylamine) were unstable, as evidenced by the appearance of elemental sulfur (mp 116–117 °C) when the mixture was allowed to stand at room

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