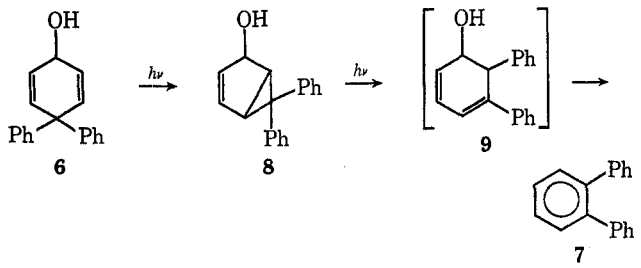

to a second intermediate **9** which, in turn, could dehydrate to the observed product. The alcohol **8** was prepared from the ketone **2** by lithium aluminum hydride reaction. The alcohol was unstable upon silica gel and alumina and so was characterized by spectral properties; oxidation of it gave back the starting ketone.

Direct irradiation of **8** in ethanol with a Vycor filter yielded the expected *o*-terphenyl. A dark control reaction yielded no *o*-terphenyl. The rate of photoinduced disappearance was three times as rapid as that of **6**; such a result is required since no buildup of an intermediate had been detected. Thus, the involvement of the cyclopropane alcohol **8** is not only feasible but possible. As with other related compounds with the 4,4-diphenyl-2-cyclohexenyl chromophore,[5] the reaction of **8** proceeds *via* the triplet state, the reaction being sensitized by acetophenone.

Experimental Section

Preparation of 4,4-Diphenyl-2,5-cyclohexadienone (1).—2,3-Dichloro-5,6-dicycano-1,4-benzoquinone (DDQ, 5.8 g, 0.026 mol) and 4,4-diphenyl-2-cyclohexanone[3] (5.8 g, 0.024 mol) were dissolved in 50 ml of dioxane and refluxed for 15 hr. After work-up, the product was recrystallized from a methylene chloride–hexane solution to give 3.1 g (48%) of 1, mp 122–123° (lit.[3] mp 121–123°).

Preparation of 1-Hydroxy-4,4-diphenyl-2,5-cyclohexadiene (6).—4,4-Diphenyl-2,5-cyclohexadienone (1.35 g) and sodium borohydride (0.2 g) were dissolved in 50 ml of ethanol and stirred overnight at room temperature. Upon work-up, the residue (1.05 g, 78%) crystallized on standing. Compound **6** has the following properties: mp 82–84°; uv max (95% EtOH) 260 nm (ε 420); ir (CCl_4) 3430 and 695 cm^{-1}; nmr (CCl_4) δ 6.97 (s, 10, phenyl), 5.6–6.0 (m, 4, CH=CH), 4.23 (s, 1, CHOH), 2.92 (s, 1, CHOH); mass spectrum *m/e* 248, 231, 230, 229, 228, 215, and 202.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.85; H, 6.53.

Irradiation of 1-Hydroxy-4,4-diphenyl-2,5-cyclohexadiene (6).—A solution of 235 mg of 1-hydroxy-4,4-diphenyl-2,5-cyclohexadiene (1) in 235 ml of absolute ethanol was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp and a Vycor filter (λ >210 nm). The progress of the irradiation was followed by thin layer chromatography. After 30 min the irradiation was halted, the solvent was removed by rotary evaporation, and the photomixture was separated by silica gel column chromatography. Two fractions were isolated, 31 mg of starting alcohol and 81 mg (43% based on reacted alcohol) of an aromatic hydrocarbon. The remainder of the photomixture was high molecular weight. The photoproduct was identified as *o*-terphenyl by comparison of spectra with those of the known compound. A dark control run parallel with the photoreaction showed no reaction.

Preparation of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-ol (8).—A solution of 100 mg of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**2**)[3] in 100 ml of anhydrous ether was added, dropwise, to a suspension of 128 mg of lithium aluminum hydride in 150 ml of anhydrous ether. The reaction mixture was stirred for 1 hr, water was carefully added, and the ethereal layer was separated and dried. The solvent was rotary evaporated. The crude **8** had the following properties: ir (CCl_4) 3420 and 1120 cm^{-1}; nmr (CCl_4) δ 7.12–7.17 (m, 10, phenyl), 6.02 (m, 2, CH=CH), 4.7 (m, 1, CHOH), 3.68 (s, 1, CHOH), 2.0–2.6 (m, 2, cyclopropyl); mass spectrum *m/e* 248, 230, 215, 202. Oxidation of the alcohol with chromic acid in pyridine[6] yielded the starting ketone.

Irradiation of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-ol (8).—A solution of 100 mg of **8** in 235 ml of absolute ethanol was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp and a Vycor filter. After 30 min, the irradiation was stopped, the solvent was rotary evaporated, and the photomixture was separated by silica gel column chromatography. *o*-Terphenyl (79 mg) was isolated and identified by comparison with an authentic sample.

Sensitized Irradiation of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-ol (8).—A solution of 370 mg of **8** in 230 ml of benzene, 15 ml of methanol, and 7 ml of acetophenone was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp and a Nonex filter (λ >310 nm). After 20 min, the irradiation was stopped, the benzene and methanol were rotary evaporated, and the acetophenone was distilled at reduced pressure. The residue was chromatogaphed on 70 g of basic Woelm alumina (activity III) and 84 mg of *o*-terphenyl eluted with 5% ethyl acetate–hexane. A dark control reaction showed no reaction.

Registry No.—**6**, 29765-37-5; **8**, 29765-38-6.

(5) W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 5817 (1970).

(6) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

Synthesis of 5,6-Dihydropyrido[2,3-*d*]pyrimidine Derivatives Directly from Acyclic Precursors

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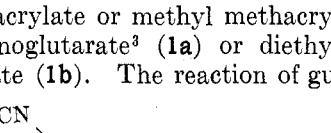
Received December 31, 1970

Existing methods for the synthesis of 5,6-dihydropyrido[2,3-*d*]pyrimidines involve several steps including production and isolation of one or more pyrimidine[1] or piperidine[1a,2] derivatives and subsequent ring closure. We wish to report a method by which several members of this class of compounds may be prepared in a single synthetic step starting with acyclic precursors.

Ethyl cyanoacetate sodium salt was caused to react with methyl acrylate or methyl methacrylate forming diethyl 2-cyanoglutarate[3] (**1a**) or diethyl 2-cyano-4-methylglutarate (**1b**). The reaction of gunaiidne with



1a, R = H
b, R = CH_3

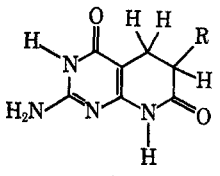
1a and **1b** in ethanol afforded 2-amino-5,6-dihydropyrido[2,3-*d*]pyrimidine-4,7(3*H*,8*H*)-dione (**2a**) and its 6-methyl analog **2b**, respectively. A similar reaction of **1a** with benzamidine afforded **3**. The pmr spectrum of

(1) (a) W. J. Irwin and D. G. Wibberley, *Advan. Heterocycl. Chem.*, **10**, 149 (1969); (b) J. Biggs and P. Sykes, *J. Chem. Soc.*, 1849 (1959); (c) L. Suranyi and L. Schuler, German Patent 1,100,030 (1961); *Chem. Abstr.*, **57**, 2231 (1962); (d) B. R. Baker and P. I. Almaula, *J. Heterocycl. Chem.*, **1**, 263 (1964); (e) V. Papesch, U. S. Patents 3,235,554 and 3,235,555 (1966); *Chem. Abstr.*, **64**, 14198 (1966); (f) B. Blank and W. T. Caldwell, *J. Org. Chem.*, **24**, 1137 (1959).

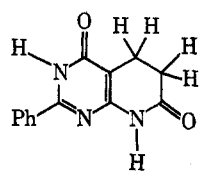
(2) J. DeGraw and L. Goodman, *Can. J. Chem.*, **41**, 3137 (1963).

(3) (a) C. F. Koelsch, *J. Amer. Chem. Soc.*, **65**, 2458 (1943); (b) L. Ruzicka, A. Borgesde Almeida, and A. Brack, *Helv. Chim. Acta*, **17**, 183 (1934); (c) P. C. Guha and D. D. Gupta, *J. Indian Inst. Sci., Sect. A*, **22**, 255 (1939); (d) L. Barthe, *C. R. Acad. Sci.*, **118**, 1268 (1894).

(4) C. K. Ingold, *J. Chem. Soc.*, **119**, 329 (1921).



2a, R = H
b, R = CH_3

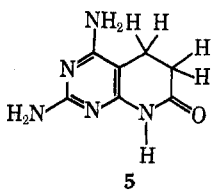


3

2b run in basic D_2O showed its C_6-methyl protons at τ 8.88 as a singlet and C_5 protons at τ 7.52 (J = 15 Hz) as an AB quartet. Mass spectral analysis of **2a** showed a molecular ion peak at m/e 180.

These results are in contrast to the reported isolation of 4-amino-5-ethoxycarbonylmethyl-6-hydroxy-2-methylpyrimidine and its 2-phenyl analog,[5] but in agreement with the more recent observation that methyl β-(4-hydroxy-2-methyl-5-pyrimidyl)propionate, when treated with methanolic ammonia at 110°, gave 2-methyl-5,6-dihydropyrido[2,3-*d*]pyrimidine-7(8*H*)-one.[1b]

Ethyl 4,4-dicyanobutyrate (**4**), prepared from the sodium salt of malononitrile[6] and ethyl 3-bromopropionate, undergoes an analogous condensation with guanidine forming 2,4-diamino-5,6-dihydropyrido[2,3-*d*]pyrimidin-7(8*H*)-one (**5**).



5

Experimental Section

Uv spectra were determined using a recording Beckman DB-G spectrophotometer. Pmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane or 3-trimethylsilylpropane sulfonic acid sodium salt as internal references. Analyses were performed by Galbraith Analytical Laboratories, Knoxville, Tenn. Melting points are uncorrected.

Diethyl 2-Cyano-4-methylglutarate (1b).—This material was prepared by the method of Koelsch,[3a] using ethyl cyanoacetate (18.8 g, 0.167 mol) and methyl methacrylate (16.7 g 0.167 mol). The oil obtained after work-up was distilled giving 15 g (39%) of **1b**, bp 105–120° (0.20 mm) [lit.[4] bp 160–162° (24 mm)].

2-Amino-5,6-dihydropyrido[2,3-*d*]pyrimidine-4,7(3*H*,8*H*)-dione (2a).—Guanidine carbonate (0.89 g, 5.0 mmol) was added to a solution prepared by addition of 40 ml of ethanol to sodium (0.23 g, 0.010 g-atom). The mixture was treated with **1a** (2.13 g, 0.010 mol) and stirred for 2 days at room temperature. The precipitate was collected by filtration and washed thoroughly with water, ethanol, and ether giving 0.33 g of **2a** as an off-white powder. An additional 0.10 g was obtained from the concentrated filtrate. The total yield was 0.43 g (24%). Recrystallization from boiling acetic acid gave a white powder: mp >400°; uv max (H_2O) 299 mμ ($\epsilon \times 10^{-3}$ 7.8), uv min 258 (1.1); uv max (pH 1) 292 (8.2), uv min 257 (2.4); uv max (pH 13) 290 (5.4), uv min 261 (2.1); pmr (D_2O containing NaOH) τ 7.45 (m).

Anal. Calcd for $C_7H_8N_4O_2$: C, 46.64; H, 4.48; N, 31.11. Found: C, 46.77; H, 4.43; N, 31.04.

Compound **2a** was converted to a derivative, **2-benzamido-5,6-dihydropyrido[2,3-*d*]pyrimidine-4,7(3*H*,8*H*)-dione**. A mixture of benzoic anhydride (4.5 g, 0.020 mol) and **2a** (1.0 g, 5.5 mmol) was heated gradually to 180–190°. After 15 min of heating, 50 ml of ethanol was added and the mixture refluxed for 10 min, cooled to room temperature, filtered, and washed with ethanol giving 0.90 g (58%) of tan solid. Recrystallization from 500 ml of boiling DMF gave a white powder, mp 376–378°.

Anal. Calcd for $C_{14}H_{12}N_4O_3$: C, 59.15; H. 4.25; N, 19.71. Found: C, 59.05; H, 4.41; N, 19.79.

2-Amino-6-methyl-5,6-dihydropyrido[2,3-*d*]pyrimidine-4,7(3*H*,8*H*)-dione (2b).—This material was prepared from **1b** using the same procedure and the same scale of reactants as used for **2a** giving 0.72 g (36%) of tan solid. Recrystallization from 600 ml of acetic acid gave a white powder: mp >400°; uv max (H_2O) 299 mμ ($\epsilon \times 10^{-3}$ 8.3), uv min 258 (0.9); uv max (pH 1) 293 (8.5), uv min 258 (2.4); uv max (pH 13) 291 (5.7), uv min 262 (1.9).

Anal. Calcd for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 29.25. Found: C, 49.62; H, 5.19; N, 29.02.

2-Phenyl-5,6-dihydropyrido[2,3-*d*]pyrimidine-4,7(3*H*,8*H*)-dione (3).—Benzamidine hydrochloride hydrate (7.2 g, 0.046 mol) was added to a solution prepared by adding 50 ml of ethanol to sodium (1.0 g, 0.046 g-atom). Sodium sulfate (2.0 g) was added and the mixture was filtered. The filtrate was treated with **1a** (9.74 g, 0.046 mol) and the solution was refluxed 12 hr. Work-up was handled as for **2a** giving 1.3 g (11%) of **3** as a light tan powder: mp >400°; uv max (95% EtOH) (pH 8) 313 and 244 mμ, uv min 279 and 223; uv max (pH 1) 312 and 247 mμ, uv min 278 and 212; uv max (pH 13) 294 mμ (sh, $\epsilon \times 10^{-3}$ 6.5), 288 (sh, 7.2), and 260 (sh, 14.4); pmr (D_2O containing NaOH) τ 7.32 (m, 2, CH_2CD_2CO), 2.48 (m, 3, C_6H_5).

Anal. Calcd for $C_{13}H_{11}H_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.72; H, 4.54; N, 17.37.

Ethyl 4,4-Dicyanobutyrate[7,8] (4).—The sodium salt of malononitrile was prepared by the method of Krapcho and Huyffer.[6] A solution of malononitrile (66.06 g, 1 mol) in 500 ml of dimethoxyethane was added dropwise during 1 hr to a stirred mixture of 55.9% sodium hydride (22.00 g, 0.52 mol) in mineral oil in 200 ml of dimethoxyethane. After 15 min, a solution of ethyl 3-bromopropionate (90.52 g, 0.50 mol) in 100 ml of dimethoxyethane was added dropwise during 30 min to the stirred mixture. After 12 hr of stirring at room temperature, the mixture was poured into a mixture of 1 l. of benzene and 1 l. of acidified saturated aqueous NaCl solution. The organic layer was washed with two 500-ml portions of saturated aqueous NaCl solution, dried (Na_2SO_4), filtered, and concentrated to give the product layer covered with mineral oil. The mineral oil was removed using a separatory funnel. Failure to remove the oil resulted in its co-distillation with the product fractions. The crude product mixture was fractionally distilled giving 33.6 g of **4** (57%): bp 118–120° (0.10 mm); pmr (CCl_4) τ 8.73 (t, 3, OCH_2CH_3), 7.57 (m, 4, $CHCH_2CH_2CO$), 5.82 (quartet, 2, OCH_2CH_3), and 5.80 (t, 1, $CHCH_2$), with the latter two signals overlapping but discernible; ν_{max}^{film} 2250 cm^{-1} (CN).

Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.61; H, 6.02; N, 16.71.

The higher boiling fraction consisted of 18 g of diethyl 4,4-dicyanopimelate: bp 140–144° (0.08 mm); pmr (CCl_4) τ 8.71 (t, 6, OCH_2CH_3), 6.53 (m, 8, $CHCH_2CH_2CO$), and 5.85 (quartet, 4, OCH_2CH_3).

Anal. Calcd for $C_{13}H_{18}N_2O_4$: C, 58.63; H, 6.81; N, 10.52. Found: C, 58.44; H, 6.58; N, 10.43.

2,4-Diamino-5,6-dihydropyrido[2,3-*d*]pyrimidin-7(8*H*)-one (5).—This material was prepared in 50% yield from guanidine carbonate and **4** using the method for **2a** above. Recrystallization from boiling acetic acid gave **5** as a white powder: mp 373–375°; uv max (95% EtOH) 292 mμ, uv min 261; uv max (pH 1) 305 mμ, uv min 261; uv max (pH 13) 298 mμ ($\epsilon \times 10^{-3}$ 8.2), uv min 264 (2.4); pmr[9] (D_2O containing NaOH) τ 7.75 (m, CH_2CD_2CO).

Anal. Calcd for $C_7H_9N_5O$: C, 46.90; H, 5.06; N, 39.10. Found: C, 47.14; H, 4.96; N, 38.94.

Registry No.—**2a**, 29668-91-5; **2b**, 29668-92-6; **3**, 29784-74-5; **4**, 29668-93-7; **5**, 29668-94-8; 2-benzamido-

(5) (a) I. G. Farbenindustrie, German Patent 671,787 (1939); (b) Z. Foldi, G. v. Foder, I. Demjen, H. Szekens, and I. Holmes, *Ber.*, **75**, 755 (1942).

(6) A. P. Krapcho and P. S. Huyffer, *J. Org. Chem.*, **28**, 2461 (1963).

(7) E. M. Gal, F. Fung, and D. M. Greenberg, *Cancer Res.*, **12**, 565 (1952), reported the preparation of **4** without accompanying spectral or analytical data.

(8) Pure samples of **4** were obtained by reacting malononitrile and ethyl 3-bromopropionate with NaH in dimethoxyethane.[6] The procedure using sodium ethoxide and ethanol also gave **4** along with imino ether contaminants. Malononitrile and its derivatives form imino ethers in the presence of alcohols and acidic or basic catalysts. See B. C. Hesse, *Amer. Chem. J.*, **18**, 723 (1896).

(9) Compound **5** is unstable in aqueous base.

5,6-dihydropyrido[2,3-*d*]pyrimidine-4,7-(3*H*,8*H*)-dione, 29668-95-9; diethyl 4,4-dicyanopimelate, 29668-96-0.

Acknowledgments.—A Summer Research Fellowship from the Research Council of the University of Colorado in partial support of this work is appreciated. Thanks are extended to Mr. James D. Specht for his aid in checking much of the work and for the preparation of **3**.

The Direct Preparation of *tert*-Butyl Azidoformate

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Received January 19, 1971

The carbo-*tert*-butoxy (BOC) function has achieved a role of major importance as a blocking group, particularly in peptide chemistry.[2] The "carbo-*tert*-butoxylating" agent of choice is *tert*-butyl azidoformate (**3**).[3] The value of the carbo-*tert*-butoxy group and the rather high cost of the reagent created a demand for a better and more convenient synthesis of **3**.

The instability of *tert*-butyl chloroformate (**1**) prevented its use as a direct precursor of **3** by displacement *via* the usual "azide method" and the azido group had to be built by the hydrazide–nitrosation route (eq 1).

$$\underset{\mathbf{2}}{H_2NNHCO_2(CH_3)_3} \xrightarrow{HONO} \underset{\mathbf{3}}{N_3CO_2C(CH_3)_3} \not\leftarrow \quad \overset{N_3^-\ (aq)}{\underset{ClCO_2C(CH_3)_3}{+}} \quad (1)$$
$$\mathbf{1}$$

Thus, most attempts at improving Carpino's method centered on the precursor of **3**, *tert*-butyl carbazate (**2**).[4] The several routes to **2** which have been published differ from Carpino's original procedure and each other only in the nature of the group being displaced by hydrazine (X in **4**).[5]

$$\underset{\mathbf{4}}{XCO_2C(CH_3)_3} + H_2NNH_2 \longrightarrow \underset{\mathbf{2}}{H_2NNHCO_2C(CH_3)_3} \quad (2)$$

Our general interest in azides[6] and in selective protective groups[7] provided a strong impetus to the search for an improved synthesis of *tert*-butyl azidoformate. In 1966, Papa[8] reported the synthesis of guanidinium azides which are ionic and *soluble* in organic solvents. Since *tert*-butyl chloroformate (**1**) is easily prepared in high yield from the reaction of *tert*-butyl alcohol and phosgene at −78°,[9] it was felt that the reaction of tetramethylguanidinium azide (TMGA) (**5**) with **1** might provide a more convenient and direct synthesis of *tert*-butyl azidoformate.

$$\underset{\mathbf{1}}{ClCO_2C(CH_3)_3} + \underset{\mathbf{5}}{N_3^-H_2\overset{+}{N}=C(NMe_2)_2} \longrightarrow$$
$$\underset{\mathbf{3}}{N_3CO_2C(CH_3)_3} + Cl^-H_2\overset{+}{N}=C(NMe_2)_2$$

The results of the experiment exceeded our expectations. The reaction of *tert*-butyl chloroformate with TMGA gave a near-quantitative yield of *tert*-butyl azidoformate, isolated as an amber liquid, *without distillation*. Its purity as judged from comparison of its infrared spectrum with that of a commercial sample appeared to be better than 98%. Phenyl and *tert*-amyl azidoformates[10] were obtained in 97 and 84% yields, respectively.

Tetramethylguanidinium azide is prepared very simply in high yields (86%)[8,11] by the addition of an ethereal solution of hydrazoic acid to tetramethylguanidine.[12] Although it is hygroscopic and thus immediate use is recommended, TMGA can be kept in a desiccator in the cold for long periods of time. *tert*-Butyl chloroformate was prepared by the addition of phosgene to *tert*-butyl alcohol at −78° in the presence of pyridine. The reaction of **1** with TMGA was carried out at 0° in ether with pyridine as the base. The ease and high yields of this procedure coupled with the ready availability of the required starting materials recommend it as a convenient and direct source of *tert*-butyl azidoformate and related azides.

Experimental Section

***tert*-Butyl Azidoformate.**—*tert*-Butyl chloroformate was prepared in solution as follows. Dry phosgene was introduced into a solution of 18 g (0.24 mol) of *tert*-butyl alcohol in 500 ml of anhydrous ether until about 52 g (0.5 mol) had been absorbed and the mixture was cooled in a Dry Ice–acetone bath. Then a solution of 20 g (0.25 mol) of pyridine in 200 ml of anhydrous ether was added dropwise with vigorous stirring. The reaction mixture was stored overnight in a Dry Ice box. The precipitated pyridine hydrochloride was filtered and the volume of the filtrate was reduced to ~70 ml at reduced pressure with cooling in an ice–water bath.[13] This cold solution of *tert*-butyl chloroformate was added over 30 min to a vigorously stirred solution of 31.6 g (0.2 mol) of tetramethylguanidinium azide in 200 ml of chloroform;[8,14] the temperature was kept at 0° throughout the addition. The bath was removed and the reaction mixture stirred for an additional hour and then poured into 500 ml of ice water containing ~2 ml of acetic acid. Extraction with two 60-ml portions of ether followed by careful evaporation of the dried (magnesium

(1) Alfred P. Sloan Fellow.

(2) M. Bodansky and M. A. Ondetti, "Peptide Synthesis," Interscience, New York, N. Y., 1966, p 29 ff.

(3) L. A. Carpino, *et al.*, *Org. Syn.*, **44**, 20 (1964).

(4) See, however, M. A. Insalaco and D. S. Tarbell, *ibid.*, **50**, 9 (1970); and H. Yajima and H. Kawatani, *Chem. Pharm. Bull.*, **16**, 183 (1968); **18**, 850 (1970).

(5) (a) L. A. Carpino, *J. Amer. Chem. Soc.*, **79**, 98 (1957); (b) G. W. Anderson and A. C. McGregor, *ibid.*, **79**, 6180 (1957); (c) F. Eloy and C. Moussebois, *Bull. Soc. Chim. Belg.*, **68**, 409 (1959); (d) W. Klee and M. Brenner, *Helv. Chim. Acta*, **44**, 2151 (1961); (e) M. Muraki and T. Misoguchi, *Chem. Pharm. Bull.*, **18**, 217 (1970).

(6) For the latest paper in this general area, see K. Sakai, N. Koga, and J.-P. Anselme, *Tetrahedron Lett.*, 4553 (1970).

(7) N. Koga and J.-P. Anselme, *Org. Prep. Proced.*, **2**, 125 (1970).

(8) A. J. Papa, *J. Org. Chem.*, **31**, 1426 (1966).

(9) (a) S. Sakakibara, *et al.*, *Bull. Chem. Soc. Jap.*, **38**, 1522 (1965); **40**, 2415 (1967); (b) R. B. Woodward, *et al.*, *J. Amer. Chem. Soc.*, **88**, 852 (1966).

(10) TMGA was *not* isolated and weighed in this case and thus the actual yield of this reaction is probably nearly quantitative also.

(11) Dr. Papa has informed us that he has prepared TMGA on a molar scale about a dozen times without incident although he *strongly* urges the usual *extreme* caution that must be observed with *any* azide. Of course, the toxic and explosive properties of hydrazoic acid are well known and should be respected.

(12) Tetramethylguanidine is available from American Cyanamid Co. whom we thank for a sample.

(13) It is advisable as a cautionary measure to purge the reaction mixture of any excess phosgene by bubbling nitrogen through the *cold*, stirred reaction mixture. Carbonyl azide which would be formed during the reaction with TMGA is an extremely potent explosive.

(14) Concentrated hydrochloric acid was used instead of concentrated sulfuric acid to generate hydrazoic acid. The product obtained was used without purification.