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Cycloaddition of tert-butylcyanoketene to isocyanides

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filtrate was concentrated, dissolved in a small volume of 2-butanol-14 M formic acid (70:30), and flash chromatographed on silica gel (60 g, 3 × 15 cm, EM silica gel 60, 40-63 μm) eluted with the same solvent. Compounds **5a** and **5b** were eluted in the yellow fractions 15-35 mL after the void volume while **4a** and **4b** were eluted in the pale yellow fractions 35-80 mL after the void volume. The eluate containing **5a** and **5b** was concentrated, dissolved in water, cautiously basified to pH 6.0 with 1 M NaHCO₃, filtered through Dowex 2-X8 Cl⁻ (2 mL, 20-50 mesh), and extracted twice with ether. The aqueous phase was concentrated, triturated with 95% EtOH, filtered through Celite, and concentrated, redissolved in 95% EtOH (2 mL), treated with chloroform (2 mL), and filtered. The filtrate was concentrated to afford 100 mg (37% yield) of a reddish solid, a 1:1 mixture of **5a** and **5b**. LC, TLC, ¹H NMR, and ¹³C NMR revealed no impurities other than a small amount of formate.

cis-1,2,3,4-Tetrahydro-1,2-dimethyl-4,7,8-isoquinolinetriol Hydrochloride (5a). The mixture of **5a** and **5b** (40 mg) was applied to a column of C-18 Porasil B (37-75 μm, 120 × 0.78 cm) and eluted with 0.01 M KH₂PO₄ (5.0 mL/min). Compound **5a** was eluted between 50 and 100 mL. Ion exchange and EtOH trituration as before afforded 12 mg of **5a** as a yellow-brown solid: ¹H NMR (D₂O) δ 1.71 (3 H, d, *J* = 6.7, 1-CH₃), 3.07 (3 H, s, NCH₃), 3.52 (2 H, t, *J* = 5.7, NCH₂), 4.69 (1 H, q, *J* = 6.7, PhCH), 5.05 (1 H, t, *J* = 5, CHOH), 7.01 (2 H, s, arom); mass spectrum, *m/e* 194.0857 (100, M-CH₃, calcd 194.0817), 191 (6), 176 (68), 166 (5), 165 (12).

trans-1,2,3,4-tetrahydro-1,2-dimethyl-4,7,8-isoquinolinetriol Hydrochloride (5b). Continued elution of the Porasil column afforded **5b** in the next 100 mL. Ion exchange and EtOH trituration as before afforded 14 mg of **5b** as a yellow-brown solid: ¹H NMR (D₂O) δ 1.53 (3 H, d, *J* = 6.9, 1-CH₃), 3.05 (3 H, s, NCH₃), 3.42 (1 H, dd, *J* = 1.9, 14, NCH₂), 3.82 (1 H, dd, *J* = 3.5, 14, NCH₂), 4.65 (1 H, q, *J* = 6.9, PhCH), 5.00

H, dd, *J* = 1.9, 3.7, CHOH) 6.98 (2 H, s, arom); for the mass spectrum, see that for **5a**.

cis-1,2,3,4-Tetrahydro-6,7-dimethoxy-1,2-dimethyl-4-isoquinolinol (6a). Compound **4a** (35 mg, 0.14 mmol) in methanol (2 mL) was treated with ethereal diazomethane (3 mL, 0.25 M, 0.75 mmol, 500 mol %). After 5 h, the solvent was evaporated, methanol (2 mL) was added, and the pH was adjusted to 1-2 with conc HCl. More diazomethane (2 mL, 330 mol %) was added, and after 18 h the sample was concentrated, dissolved in water and saturated sodium carbonate, extracted into chloroform, and dried over magnesium sulfate. Evaporation of the solvent afforded 20 mg (60% yield) of **5a**. TLC (cyclohexane-chloroform-diethylamine, 50:40:10) *R_f* 0.18 (lit.¹⁰ *R_f* 0.48). The ¹H NMR was consistent with the literature.¹⁰

trans-1,2,3,4-Tetrahydro-6,7-dimethoxy-1,2-dimethyl-4-isoquinolinol (6b) was prepared from **4b** according to the above procedure; TLC *R_f* 0.15 (lit.¹⁰ *R_f* 0.39). The ¹H NMR was consistent with literature.¹⁰

Acknowledgment. We gratefully acknowledge support of this investigation by USPHS Biomedical Research Support Grant 5S07RR07067-11 to SUNY at Stony Brook and by the Stony Brook Research Development Fund, Research Foundation of SUNY. We thank David Yarmush for assistance with HDO suppression and Dr. Steven S. Miller and Professor Albert Haim for making the calculator-plotter available.

Registry No. 1, 51-43-4; 2, 79254-31-2; 2·HCl, 79254-32-3; 3, 79201-21-1; 3·HCl, 79201-22-2; 4a, 79201-23-3; 4a·HCl, 79201-24-4; 4b, 79201-25-5; 4b·HCl, 79201-26-6; 5a, 79201-27-7; 5a·HCl, 79201-28-8; 5b, 79201-29-9; 5b·HCl, 79201-30-2; 6a, 79254-33-4; 6b, 79254-34-5; formaldehyde, 50-00-0; acetaldehyde, 75-07-0.

Cycloaddition of *tert*-Butylcyanoketene to Isocyanides

Harold W. Moore* and Chih-Chou Yu

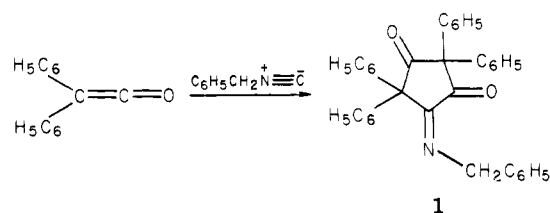
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Received May 5, 1981

The reaction of *tert*-butylcyanoketene with a series of isocyanides results in an unusual mode of addition involving the carbonyl bond of the ketene. The scope and mechanism of these cycloadditions are discussed.

Reported here is a study of the cycloaddition of *tert*-butylcyanoketene (TBCK) to isocyanides, a reaction which proceeds anomalously when compared to other ketene/isocyanide additions. Specifically, it is shown that 2 mol of the ketene react with 1 mol of isocyanide to give good yields of the previously unobserved imino lactones **5a-e**. Such products result from a reaction mode in which the cycloaddition takes place across the carbonyl bond of the ketene components. This is unusual since all other reported examples of ketene/isocyanide cycloadditions give products arising from reactions involving addition to the alkene bond of the cumulene. For example, the 1-imino-2,4-cyclopentanedione (**1**) was obtained in 90% yield when benzyl isocyanide was treated with diphenylketene at -20 °C.¹

The cycloadditions reported here were accomplished by the addition of a benzene solution of TBCK² to a slight



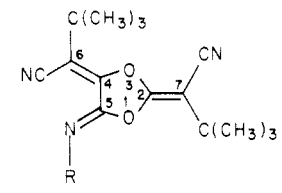
excess of the isocyanides at ambient temperature. The reactions were complete within a few minutes and the products isolated by standard methods. Although the yields differed slightly, the same products were obtained when the mode of addition was reversed or if the temperature of the reaction was maintained at -20 °C. In one case, the ketene was slowly added to an excess of neat *tert*-butylisocyanide in an attempt to obtain products incorporating more than 1 equiv of the isocyanide. However,

(1) I. Ugi and K. Rosendahl, *Chem. Ber.*, **94**, 2233 (1961).

(2) W. Weyler, Jr., W. G. Duncan, and H. W. Moore, *J. Am. Chem. Soc.*, **97**, 6187 (1975).

Table I. Spectral Data

compd	yield, %	mp, °C	IR (KBr), cm ⁻¹	¹ H NMR (CDCl ₃), δ
5a	97	150-151	2210 (C≡N), 1755 (C=N), 1675, 1640 (C=C)	1.45 (s), 1.4 (s), 1.33 (s)
5b	73	189-190	2210 (C≡N), 1755 (C=N), 1670, 1635 (C=C)	7.7-7.0 (m, 5 H), 4.83 (s, 2 H), 1.4 (s, 9 H), 1.3 (s, 9 H)
5c	70	82-83	2210 (C≡N), 1750 (C=N), 1675, 1640 (C=C)	3.8-3.5 (m, 2 H), 2.0-0.7 (m, 25 H), 1.4 (s), 1.3 (s)
5d	82	146-147	2210 (C≡N), 1745 (C=N), 1675, 1640 (C=C)	4.0-3.5 (br, 1 H, CH), 2.0-1.0 (m, 28 H), 1.4 (s), 1.3 (s)
5e	89	201-202	2210 (C≡N), 1745 (C=N), 1675, 1640 (C=C)	7.95-7.35 (4 H), 4.85 (s, 2 H), 2.45 (s, 3 H), 1.4 (s, 9 H), 1.3 (s, 9 H)
6	82	162-163	2200 (C≡N), 1815 (C=O)	1.55 (s), 1.33 (s), 1.28 (s)
7	95	123-124	3390 (NH), 2220 (C≡N), 1780 (C=O), 1630 (exocyclic C=C), 1590 (endocyclic C=C)	8.0-7.6 (br, 1 H), 1.63 (s, 9 H), 1.38 (s, 9 H)
9	49	119-120	2205 (C≡N), 1720 (C=N)	1.53 (s), 1.48 (s), 1.4 (s)

Table II. Characteristic ¹³C NMR Chemical Shifts for Compounds 5a-e


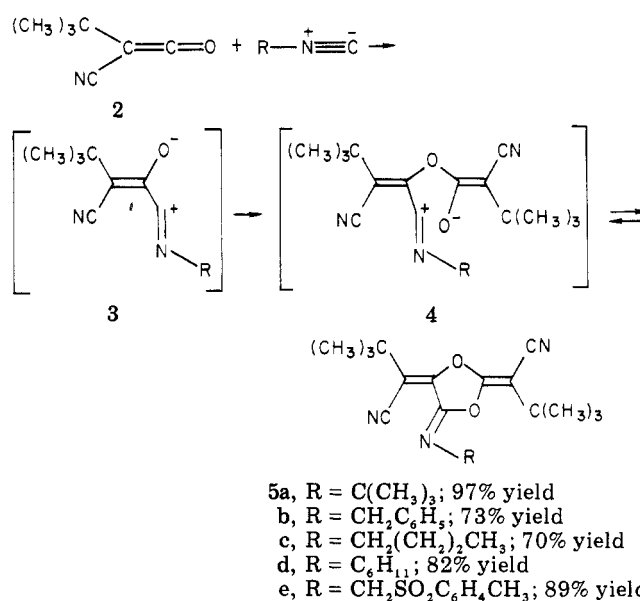
R	chemical shifts (CDCl ₃), δ				
	C ₂ , C ₄ , C ₅	C ₆	C ₇	C≡N	
C(CH ₃) ₃	135.0, 159.6, 144.6	103.9	97.8	114.2, 115.5	
CH ₂ C ₆ H ₅	141.1, 159.3, 144.1	105.0	76.1	114.2, 115.2	
CH ₂ (CH ₂) ₂ CH ₃	140.2, 159.5, 144.2	104.2	89.9	114.2, 115.4	
C ₆ H ₁₁	140.2, 159.5, 144.1	104.2	89.7	114.2, 115.4	
CH ₂ SO ₂ C ₆ H ₄ CH ₃	145.6, 158.6, 146.3	107.2	76.6	113.6, 114.6	

the only product observed was again the imino lactone. Although several stereoisomers are possible for **5a-e**, only one is formed in the cycloadditions. On the basis of steric arguments, the stereochemistry of these products is assumed to be that represented by structures **5a-e**.

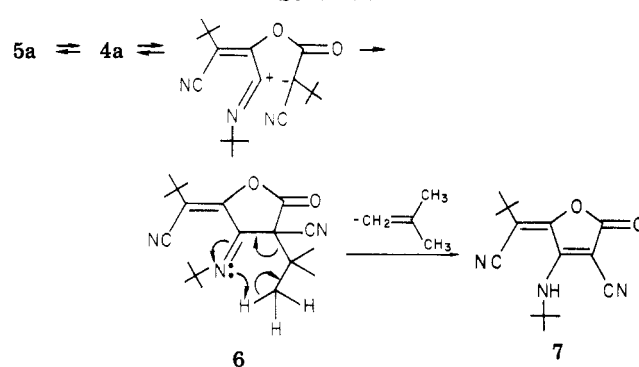
The structures of compounds **5a-e** are based primarily upon spectral and analytical data (Tables I and II). Their IR spectra all show a weak absorption between 1745 and 1755 cm⁻¹ for the strained imidate group. Also, strong absorptions for the conjugated nitriles appear at 2210 cm⁻¹, and the polar double bonds absorb between 1635 and 1675 cm⁻¹. Their ¹H NMR spectra all show the appropriate absorptions for the *tert*-butyl and R substituents, and their ¹³C NMR spectra reveal the required number of sp, sp², and sp³ carbon atoms. Finally, their mass spectra gave the appropriate molecular ion (M⁺) and an intense (100%) peak corresponding to M⁺ - TBCK.

The most reasonable explanation accounting for the formation of **5** involves the initial formation of zwitterion **3**. Interception of this by another molecule of the ketene, **2**, would give **4** as the penultimate precursor to **5** (Scheme I). It is noteworthy that an intermediate analogous to **3** was proposed in the previously mentioned cycloaddition of diphenylketene to isocyanides.¹ However, unlike the transformation of **3** to **4**, this zwitterion undergoes acylation at carbon rather than oxygen to afford ultimately the iminocyclopentanediones, e.g., **1**. That such a transformation is not observed with TBCK is most likely due to the steric congestion imparted by the bulky *tert*-butyl group.³

Scheme I



Scheme II

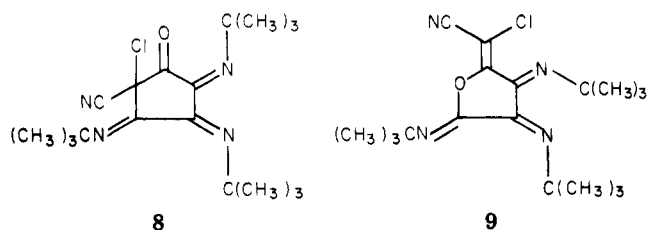


In order to investigate the possibility that **5** represents the kinetic products in these cycloadditions, we also studied the thermal chemistry of **5a**. Here it was observed that **5a** rearranges to **6** (82%) after 72 h in refluxing benzene. Clearly this must involve equilibration of **5a** with

(3) Addition to the carbonyl group of TBCK has been encountered in a number of its cycloaddition reactions. See, for example: A. Dondoni, A., Medici, C. Venturoli, L. Forlani, and V. Bertolasi, *J. Org. Chem.*, **45**, 621 (1980); E. Schaumann, H. Mrotzek, and F. Abmann, *Liebigs Ann. Chem.*, **334** (1979); E. Schaumann and H. Mrotzek, *Chem. Ber.*, **111**, 661 (1978); E. Schaumann, H. Mrotzek, and G. Adiwidjaja, *J. Chem. Soc., Chem. Commun.* 830 (1978); Z. Lysenko, M. M. Joulle, I. Miura, and R. Rodebaugh, *Tetrahedron Lett.*, 1705 (1977).

4a. The thermodynamically more stable **6** then results from C-iminolation of the enolate moiety of **4a** (Scheme II). A most interesting additional thermolysis pathway was observed when **6** was heated at 145 °C in *o*-dichlorobenzene for 50 min. Under these conditions, de-*tert*-butylation occurred to give the butenolide **7** in 95% yield. This is viewed as arising via a retroene reaction as outlined in Scheme II.

Finally, brief mention is made of a comparative study of the cycloaddition of chlorocyanoketene⁴ to *tert*-butyl isocyanide. This ketene, unlike its *tert*-butyl analogue, readily undergoes self-condensation and thus must be generated in situ. When this was accomplished by the thermolysis of 4-azido-3-chloro-5-methoxy-2(5*H*)-furanone in refluxing benzene containing an excess of *tert*-butyl isocyanide, an entirely different reaction course was encountered. Rather than imino lactone, butenolide, or iminocyclopentanedione products, a 3:1 adduct was isolated in 49% yield. The only reasonable structures that can be considered for a 3:1 adduct are **8** or **9**, and the latter is



avored on the basis of spectral data. The IR spectrum shows a conjugate nitrile absorption at 2205 cm^{-1} and the imine absorption as a multiplet at 1720 cm^{-1} . The ¹H NMR spectrum shows only absorptions for the three *tert*-butyl groups. The ¹³C NMR spectrum provides significant structural information in that it reveals the required 12 absorptions, and six of these are in the sp^2 region of the spectrum. Specifically, the absorptions for the *tert*-butyl groups appear at δ 60.5, 59.9, 56.8, 29.6, 28.8, and 28.7. The remaining sp^2 carbons appear at δ 157.4, 146.9, 144.0, 135.9, 114.6, and 87.1.

This adduct is presumably favored over the previously described examples since, under the conditions utilized, the ketene would be in very low concentration relative to that of the isocyanide. Thus, the initially formed zwitterion analogous to **3** reacts further with additional isocyanide rather than ketene. In any regard, the synthesis of analogues of **9** by this method appears limited in scope since complex product mixtures were obtained when chlorocyanoketene was generated in the presence of less bulky isocyanides, e.g., benzyl and (*p*-tolylsulfonyl)methyl isocyanide.

Experimental Section

Reaction of *tert*-Butylcyanoketene with *tert*-Butyl Isocyanide. A solution of 6 mmol of *tert*-butylcyanoketene was prepared by refluxing 0.906 g (3 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone in 25 mL of anhydrous benzene for 75 min. The benzene solution was cooled to room temperature and 1.494 g (18 mmol) of *tert*-butyl isocyanide was added dropwise. The reaction mixture was stirred for 10 min, and then the volatile components were removed in vacuo at room temperature. The crude reaction residue was chromatographed on silica gel, and 0.956 g (97%) of compound **5a** was obtained. Recrystallization in ether-hexane (20:80) afforded the analytical sample: mp 150–151 °C; mass spectrum (CI), m/e (relative intensity) 330 ($M + 1$, 15), 274 (6), 207 (22), 180 (23), 125 (14), 124 (100), 84 (22).

(4) H. W. Moore, L. Hernandez, and A. Sing, *J. Am. Chem. Soc.*, **98**, 3728 (1976).

Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}_2$: C, 69.30; H, 8.21. Found: C, 69.17; H, 8.20.

Reaction of *tert*-Butylcyanoketene with Benzyl Isocyanide. A solution of 6 mmol of *tert*-butylcyanoketene was prepared by refluxing 0.906 g (3 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone in 25 mL of anhydrous benzene for 75 min. The benzene solution was cooled to room temperature and then was added dropwise to 2.106 g (18 mmol) of benzyl isocyanide. The reaction mixture was stirred for 1 day. The volatile components were removed in vacuo, and the crude reaction residue was chromatographed on silica gel to give 0.797 g (73%) of compound **5b**. Recrystallization in hexane-chloroform provided the analytical sample: mp 189–190 °C; mass spectrum (CI), m/e (relative intensity) 364 ($M + 1$, 15), 241 (16), 214 (8), 180 (8), 125 (8), 124 (100), 92 (6), 91 (48).

Anal. Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_2$: C, 72.73; H, 6.89. Found: C, 73.01; H, 7.01.

Reaction of *tert*-Butylcyanoketene with *n*-Butyl Isocyanide. By use of the above method, compound **5c** was obtained in 70% yield. Recrystallization in hexane gave the analytical sample: mp 82–83 °C; mass spectrum (CI), m/e (relative intensity) 331 (13), 330 ($M + 1$, 60), 274 (8), 207 (10), 180 (19), 166 (8), 125 (13), 124 (100), 108 (8), 84 (68).

Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}_2$: C, 69.30; H, 8.21. Found: C, 69.42; H, 8.43.

Reaction of *tert*-Butylcyanoketene with Cyclohexyl Isocyanide. By using the same method, compound **5d** was obtained in 82% yield. Recrystallization in hexane-chloroform gave the analytical sample: mp 146–147 °C; mass spectrum (CI), m/e (relative intensity) 356 ($M + 1$, 6), 125 (8), 124 (100), 110 (22), 84 (10), 83 (32).

Anal. Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_2$: C, 70.99; H, 8.17. Found: C, 71.19; H, 8.41.

Reaction of *tert*-Butylcyanoketene with (*p*-Tolylsulfonyl)methyl Isocyanide. A solution of 6 mmol of *tert*-butylcyanoketene was prepared by refluxing 0.906 g (3 mmol) of 2,5-diazido-3,6-di-*tert*-benzoquinone in 25 mL of anhydrous benzene for 75 min. The benzene solution was cooled to room temperature and then was added dropwise to a solution of 0.585 g (3 mmol) of (*p*-tolylsulfonyl)methyl isocyanide in 15 mL of benzene. The reaction mixture was stirred for 1 h. After removal of the solvent, the reaction residue was chromatographed on silica gel to give 1.18 g (89%) of compound **5e**. Recrystallization in hexane-chloroform provided the analytical sample: mp 201–202 °C; mass spectrum (CI), m/e (relative intensity) 442 ($M + 1$, 10), 288 (5), 165 (13), 157 (84), 141 (5), 139 (17), 125 (9), 124 (100).

Anal. Calcd for $\text{C}_{23}\text{H}_{27}\text{N}_3\text{O}_4\text{S}$: C, 62.59; H, 6.12. Found: C, 62.62; H, 6.14.

Thermolysis of Compound 5a. A benzene solution of 0.329 g (1 mmol) of compound **5a** in 25 mL of anhydrous benzene was heated at 85 °C under nitrogen for 3 days. After removal of the solvent, the solid material was purified by crystallization from 30 mL of hexane-benzene. This procedure afforded 0.27 g (82%) of the pure compound **6**: mp 162–163 °C dec; mass spectrum (CI), m/e (relative intensity) 330 ($M + 1$, 5), 275 (7), 274 (40), 218 (5), 207 (12), 181 (12), 180 (100), 166 (10), 124 (8); ¹³C NMR (CDCl_3) δ 163.3, 155.2, 140.6, 116.3, 114.6, 104.6, 61.8, 57.4, 51.7, 34.9, 30.3, 29.0, 26.7.

Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}_2$: C, 69.30; H, 8.21. Found: C, 69.36; H, 8.45.

Thermolysis of Compound 6. A solution of 0.329 g (1 mmol) of compound **6** in 20 mL of *o*-dichlorobenzene was heated at 145 °C for 50 min. The solvent was removed in vacuo, and the reaction residue was chromatographed on silica gel. It gave 0.260 g (95%) of the product **7**. Recrystallization in hexane afforded the analytical sample: mp 123–124 °C; mass spectrum (CI), m/e (relative intensity) 275 (17), 274 ($M + 1$, 100), 218 (12); ¹³C NMR (CDCl_3) δ 163.2, 154.2, 152.3, 117.5, 114.4, 104.6, 56.7, 36.0, 29.8, 29.3.

Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_2$: C, 65.93; H, 6.96. Found: C, 65.70; H, 7.20.

Reaction of Chlorocyanoketene with *tert*-Butyl Isocyanide. A solution of 0.57 g (3 mmol) of 4-azido-3-chloro-5-methoxy-2(5*H*)-furanone and 0.75 g (9 mmol) of *tert*-butyl isocyanide in 10 mL of anhydrous benzene was well stirred under nitrogen at 60 °C for 1 day. After removal of the volatile components in vacuo, the reaction residue was chromatographed on

silica gel. It gave 0.52 g (49%) of the product 9. Recrystallization in hexane furnished the pure sample with the following: mp 119–120 °C; mass spectrum (CI), m/e (relative intensity) 351 (M + 1, 10), 295 (17), 268 (34), 241 (52), 239 (100), 212 (36), 198 (15), 196 (11), 185 (74), 171 (22), 156 (14), 140 (20), 84 (23).

Anal. Calcd for $C_{18}H_{27}ClN_4O$: C, 61.63; H, 7.70. Found: C,

61.79; H, 8.03.

Acknowledgment. The authors are grateful to the Public Health Service (Grant No. AI 15651) for financial support of this work.

Ring Opening of Aziridines by Different Fluorinating Reagents: Three Synthetic Routes to α,β -Fluoro Amines with Different Stereochemical Pathways

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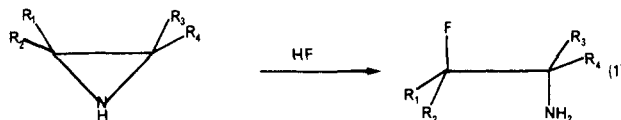
Received May 5, 1981

The syntheses of α,β -fluoro amines from the reaction of secondary aziridines with either Olah's reagent (HF, pyridine) or anhydrous hydrogen fluoride and of N-activated aziridines with partially neutralized Olah's reagent (NR_3-nHF) are reported. The stereochemistry of these reactions is highly dependent on the structure of the starting compound and on the fluorinating agent. From the same aziridine it is thus possible to synthesize selectively each diastereoisomeric fluoro amine by proper choice of fluorination conditions.

Fluorine compounds are widely used as drugs in pharmacology and chemotherapy.¹⁻⁴ However, a convenient synthetic route to α,β -fluoro amines, particularly those with a primary amine function, does not exist. These compounds exhibit biological activity on the central nervous system.⁵ A new synthetic route to fluoro amines has recently been reported by Kollonitsch and co-workers.⁶ This method, however, needs special handling of sulfur tetrafluoride, a very toxic reagent. More frequently used fluorinating reagents are fluoroalkylamines,⁷ metallic and nonmetallic fluorides,⁸ and trifluoromethyl hypofluorite.⁹ Fluorodesulfurization¹⁰ and diazotization¹¹ reactions have also been carried out in this connection. Finally, the possible replacement of the chlorine atom by an amine function in α,β -chlorofluoro compounds should be mentioned.¹²

The fact that the hydrogen fluoride addition to epoxides is a very clean and good method for preparing α,β -fluoro alcohols¹³ led us to investigate the same type of reaction

sequence (eq 1) with secondary aziridines. This reaction



has been performed in the mytomycine series.¹⁴ Numerous synthetic methods leading to secondary aziridines have been developed during the past 15 years, and these compounds in monocyclic, steroid, and acyclic series are now easily available.

Prompted by a recent paper of Wade¹⁵ concerning the synthesis of fluoro amines via aziridine ring opening by HF-pyridine (Olah's reagent), which appeared while this work was in progress, we present results obtained in our laboratory. In preliminary notes¹⁶ we have reported the synthesis of α,β -fluoro amines by ring-opening of secondary or N-activated aziridines with anhydrous hydrogen fluoride, Olah's reagent, or modified Olah's reagent. We present here a comparative study of the fluorinating ability of these three reagents toward aziridines. The stereoselectivity of the reaction appears to be very different in each case, and the synthetic advantages of each reagent are discussed.

Results

Two fluorinating agents were previously used with secondary aziridines ($R = H$), i.e., anhydrous hydrogen fluoride and Olah's reagent.¹⁶ Fluoro amines are generally obtained in fair yields (Table I). However, in some cases we could not get satisfactory results (i.e., 10aT and 10aC,

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