The synthetic carbamoyl diester **4** has been found to be a suitable intermediate for further selective functionalization of the pyrimidine moiety of BLM. The compound **4** was selectively hydrolyzed to afford the carbamoyl acid ester **7** [syrup, *m/e* 474 ($M^+ + 1$) (FD), $R_f$ 0.39 with BuOH–AcOH–$H_2O$, 4:1:1] in 93% yield by treatment with 0.1 N NaOH at 0 °C for 1 h. The hydrolyzed ethyl ester was clearly assigned to the one attached to the pyrimidine ring by UV shift (from 272 nm for **4** to 265 nm for **7**) and $^1H$ NMR data [only the lower signals for $CO_2Et$ at δ 4.48 (q) and 1.42 (t) disappeared, and the signals for the side-chain ester at δ 4.15 (q) and 1.20 (t) remained in **7**]. Next, the acid ester **7** was subjected to amination with $NH_3$ at 40 °C for 6 days, and the resulting product was treated with dry EtOH, depositing a crystalline material, [mp 223–225 °C dec; $[\alpha]^{28}_D$ −32.8° (*c* 0.75, $H_2O$)] chromatographically homogeneous in fair yield.[18] Fortunately, it was found to be *tert*-butoxycarbonylpyrimidoblamic acid (**8**) with the desired $S(C_\beta)$,*S* configuration by identification with the sample,[19] $[\alpha]^{28}_D$ −32.3° (*c* 0.75, $H_2O$), derived from pyrimidobleonic acid (**6a**) [mixed mp, IR, $^1H$ NMR, mass spectroscopy (FD), TLC, and high-pressure LC on chelation compound with $Cu^{2+}$ and ORD]. These results are the first evidence for the partial structure of the pyrimidine moiety of BLM by direct comparison of the synthetic materials with the degradation products derived from BLM. Furthermore, **7** was treated with L-histidine methyl ester (2 equiv) in the presence of *N,N'*-carbonyldiimidazole (2 equiv) in DMF at 25 °C for 4 h. After workup and preparative chromatography (silica gel), pyrimidoblamylhistidine equivalent **9** was obtained in 40% yield [syrup, *m/e* 625 ($M^+ + 1$) (FD);[20] silica gel plates, $R_f$ 0.32 with $CHCl_3$–EtOH, 4:1].

The research results described here provide a basis for further synthetic and transformational investigations relating to BLM and access to potentially useful analogues and open a route for a relay synthesis to BLM by using pyrimidobleonic acid and pyrimidoblamic acid available from natural BLM.

**Acknowledgment.** We thank Dr. H. Naganawa for obtaining spectroscopic data and Dr. Y. Muraoka for his advice of the chelation chemistry. This work was financially supported in part by grants-in-aid for Special Project Research from the Ministry of Education, Science and Culture of Japan.

(18) The deposited material was pure enough for further reactions but was obtained in only 10% yield, and the rest, including the epimer with *R,S* configuration and some of **8**, remained in the ethanol solution, but this step was found to be best for separation of the epimers.

(19) The acid **6a** derived from BLM was successively subjected to esterification (MeOH–HCl), selective hydrolysis of the methyl ester of the ring with $CuCO_3 \cdot Cu(OH)_2$, protection of the primary amine with Boc–S, and amination, affording **8**, namely *tert*-butoxycarbonylpyrimidoblamic acid.

(20) Compound **9** was negative for the ninhydrin test, showing absence of a primary amine, and the $^1H$ NMR spectra were well characterized and showed signals δ at δ 9.09 (d) for the amide (–CONH–) newly formed, 5.98 (d) for *tert*-butoxycarbonyl amide, and 6.12 (s) and 7.08 (s) for $CONH_2$.

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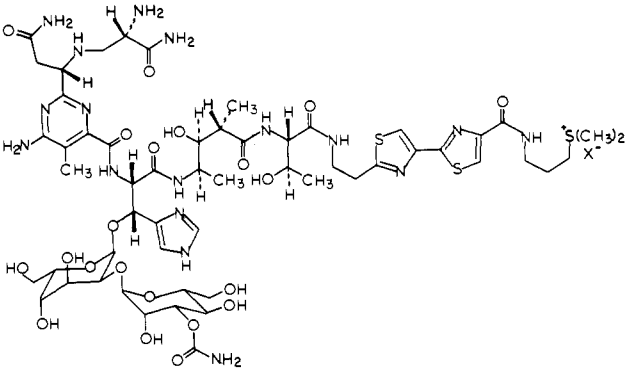
*Received April 28, 1980*

## Synthesis of the Pyrimidine Moieties of Bleomycin and Epibleomycin

*Sir:*

The bleomycins are a family of glycopeptide-derived antibiotics with remarkable biochemical and biological properties.[1] At present, the bleomycins are of considerable interest because of their utility in the treatment of certain malignancies[2] and the identification of new bleomycins with properties that may enhance their effectiveness in the clinic.[3] A workable synthesis of bleomycin would be of obvious importance, in the sense that it would permit definition of the structural features requisite to the expression of anticancer activity. Previous studies have focused on the synthesis of tetrapeptide S[4] and its components,[5] and on the elaboration of L-*erythro*-β-hydroxyhistidine[6] and the carbohydrates[5d,7] present in the antibiotic. The preparation of the pyrimidine moiety of bleomycin has not been reported, although the chemistry of this portion of the molecule has been studied.[8] Described herein is the synthesis of the pyrimidine moieties of bleomycin (**1**) and epibleomycin.[9]



**1**

Ethyl 3-(6-carboethoxy-4-oxo-5-methylpyrimidin-2-yl)acrylate (**2**)[8b] was hydrogenated over 1% palladium-on-charcoal (2:1 EtOH–EtOAc, 12 h), affording pyrimidinylpropionate **3a** as a white solid (99%), mp 124–125 °C. Successive treatments of **3a** with $POCl_3$ (100 °C, 30 min) and $NaN_3$ (DMF, 25 °C, 12 h) gave azide **3b** as colorless needles in 83% overall yield from **3a**: mp 60–61 °C; IR (neat) 1725 (br), 1620 $cm^{-1}$; NMR [$CDCl_3$, $(CH_3)_4Si$] δ 1.26 (3 H, t, *J* = 7.0 Hz), 1.48 (3 H, t, *J* = 7.0 Hz), 2.93 (3 H, s), 3.13 (2 H, t, *J* = 6.0 Hz), 3.81 (2 H, t, *J* = 6.0 Hz), 4.16 (2 H, q, *J* = 7.0 Hz), 4.50 (2 H, q, *J* = 7.0 Hz); mass spectrum, *m/e* 279 ($M^+$). The absence of an azide stretching band in the infrared reflected the equilibrium between azide **3b** and tetrazole **3b'**.[11,12]

(1) (a) Umezawa, H. *Biomedicine* **1973**, *18*, 459. (b) Umezawa, H. In "Bleomycin: Current Status and New Developments"; Carter, S. K.; Crooke, S. T.; Umezawa, H., Eds.; Academic Press: New York, 1978; p 15 ff. (c) Hecht, S. M. In "Bleomycin: Chemical, Biochemical and Biological Aspects"; Hecht, S. M., Ed.; Springer-Verlag: New York, 1979; p 1 ff.

(2) (a) Umezawa, H. *Prog. Biochem. Pharmacol.* **1976**, *11*, 18. (b) Ichikawa, T. *Ibid.* **1976**, *11*, 143. (c) Carter, S. K.; Blum, R. H. *Ibid.* **1976**, *11*, 158. (d) Bonadonna, G.; Tancini, G.; Bajetta, E. *Ibid.* **1976**, *11*, 172. (e) Depierre, A. *Ibid.* **1976**, *11*, 195. (f) Rygard, J.; Hansen, H. S. *Ibid.* **1976**, *11*, 205. (g) Rathert, P.; Lutzeyer, W. *Ibid.* **1976**, *11*, 223.

(3) (a) Tanaka, W. *J. Antibiot. (Tokyo)* **1977**, *30*, S-41. (b) Matsuda, A.; Yoshioka, O.; Ebihara, K.; Ekimoto, H.; Yamashita, T.; Umezawa, H. In "Bleomycin: Current Status and New Developments"; Carter, S. K.; Crooke, S. T.; Umezawa, H., Eds.; Academic Press: New York, 1978; p 299 ff.

(4) Levin, M. D.; Subrahamanian, K.; Katz, H.; Smith, M. B.; Burlett, D. J.; Hecht, S. M. *J. Am. Chem. Soc.* **1979**, *102*, 1452.

(5) (a) Cheng, K. Y. Z.; Cheng, C. C. *J. Heterocycl. Chem.* **1970**, *7*, 1439. (b) McGowan, D. A.; Jordis, U.; Minster, D. K.; Hecht, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 8078. (c) Yoshioka, T.; Hara, T.; Takita, T.; Umezawa, H. *J. Antibiot. (Tokyo)* **1974**, *27*, 356. (d) Hecht, S. M.; Burlett, D. J.; Mushika, Y.; Kuroda, Y.; Levin, M. D., ref 1c, p 48 ff.

(6) (a) Takita, T.; Yoshioka, T.; Muraoka, Y.; Maeda, K.; Umezawa, H. *J. Antibiot. (Tokyo)* **1971**, *24*, 795. (b) Hecht, S. M.; Rupprecht, K. M.; Jacobs, P. M. *J. Am. Chem. Soc.* **1979**, *101*, 3982.

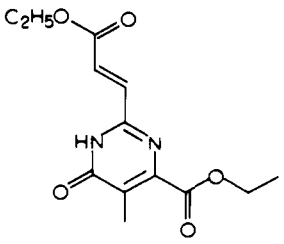
(7) (a) Omoto, S.; Takita, T.; Maeda, K.; Umezawa, S. *Carbohydr. Res.* **1973**, *30*, 239. (b) Minster, D. K.; Hecht, S. M. *J. Org. Chem.* **1978**, *43*, 3987.

(8) (a) Muraoka, Y.; Takita, T.; Maeda, K.; Umezawa, H. *J. Antibiot. (Tokyo)* **1970**, 252. (b) Yoshioka, T.; Muraoka, Y.; Takita, T.; Maeda, K.; Umezawa, H. *Ibid.* **1972**, *25*, 625. (c) Umezawa, Y.; Morishima, H.; Yoshioka, T.; Otsuka, M.; Ohno, M., ref 1c, p 63 ff.

(9) Kunishima, M.; Fujii, T.; Nakayama, Y.; Takita, T.; Umezawa, H. *J. Antibiot. (Tokyo)* **1976**, *29*, 853.

(10) Satisfactory spectral and analytical data were obtained for the new compounds reported.

0002-7863/80/1502-6631$01.00/0 



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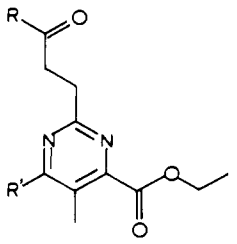
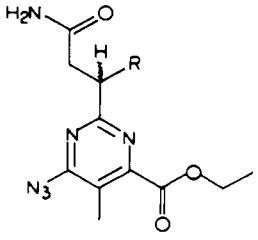
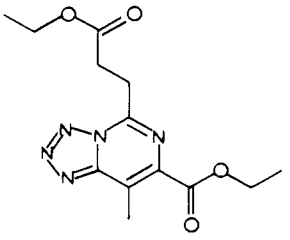
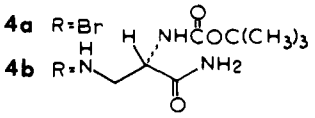


3a R = $OC_2H_5$, R' = OH
3b R = $OC_2H_5$, R' = $N_3$
3c R = $NH_2$, R' = $N_3$





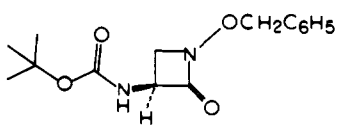
3b'



4a R = Br
4b R = N(H)CH(NHCOC(CH3)3)CH2CONH2

Although ammonolysis of **3b** (⇌**3b'**) afforded primarily the C-6 carboxamide, conversion to **3c** was achieved conveniently via initial treatment with THF–2 N HCl (3:2, 5 days, 25 °C). This procedure effected selective hydrolysis of the propionate ester, presumably by participation of a ring nitrogen atom.[13] After extractive workup, the carboxylic acid was obtained as colorless crystals from ether (mp 144 °C, 90% yield). Treatment with $SOCl_2$ ($CH_2Cl_2$, 25 °C, 1 h) and then ammonia (0 °C, 10 min) afforded the desired amide **3c**, which was isolated by extractive workup and crystallized from ethyl acetate–ether (49% yield, colorless crystals), mp 149 °C. Functionalization of the propionate moiety was achieved by bromination of **3c** (1.1 equiv of $Br_2$, dioxane, 75 °C, 15 min), which afforded monobromide **4a**[12] in 67% yield after crystallization from ethyl acetate, mp 145 °C; NMR [$CDCl_3$, $Me_2SO$-$d_6$, $(CH_3)_4Si$] $\delta$ 1.44 (3 H, t), 2.94 (3 H, s), 3.1–3.9 (2 H, m), 4.46 (2 H, q), 6.13 (1 H, t), 7.2 (1 H, m). Although not employed in the present scheme for the elaboration of **7** and **8**, it is of interest that the monobromide derived from **3b**, when treated with $NaN_3$ (DMF, 25 °C, 18 h), gave ethyl 2-amino-3-(4-azido-6-carboethoxy-5-methylpyrimidin-2-yl)acrylate, a compound of potential synthetic utility.[14]

(2*S*)-3-Amino-2-[*tert*-(butoxycarbonyl)amino]propionamide (**6b**) was obtained in good yield by treatment of *N*-benzyloxy-2-azetidinone **5**[15] with methanolic ammonia (0 °C, 30 min). After chromatography on silica gel (elution with 2:1 benzene–ethyl acetate), **6a** crystallized from benzene–hexane as colorless plates



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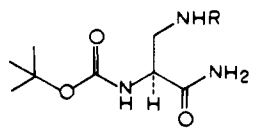
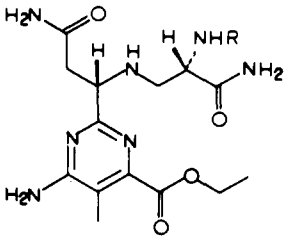


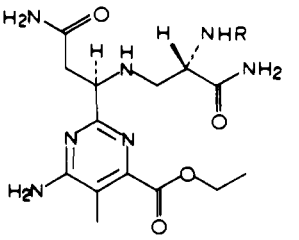
6a R = $OCH_2C_6H_5$
6b R = H

(97% yield), mp 93–94 °C. Hydrogenolysis over 10% palladium-on-charcoal (1 atmosphere of $H_2$, $CH_3OH$, 50–60 °C, 1 h) effected conversion into **6b**, which was isolated as a viscous oil (95% yield) that crystallized on standing; mp 95–97 °C, $[\alpha]^{25}_D$ +4.6° (*c* 1.0, $CH_3OH$).[16] Compound **6b** was stored conveniently as its crystalline hydrochloride salt; mp 179–180 °C, $[\alpha]^{25}_D$ −20.8° (*c* 1.2, $H_2O$); hydrolysis (3 N HCl, 100 °C, 2 h) afforded (2*S*)-2,3-diaminopropionic acid hydrochloride in 87% yield, having the same physical properties [mp 245–246 °C, $[\alpha]^{25}_D$ +26.3° (*c* 1.5, 1 N HCl] as an authentic sample.[17] This novel use of an optically active $\beta$-lactam for the elaboration of a multiply functionalized chiral molecule should be more generally applicable, especially where the desired product must be blocked selectively.

When stirred at 25 °C in ethanol in the presence of 2 equiv of $NaHCO_3$, **4a** and **6b** underwent reaction within 12 h, affording an equimolar mixture of isomeric azidopyrimidines **4b** in 67% yield. The isomers were separable by preparative TLC on silica gel (development twice with 7.5% $CH_3OH$ in $CHCl_3$) or by fractional crystallization from chloroform–ether, giving compounds (silica gel TLC, 7% $CH_3OH$ in $CHCl_3$) of $R_f$ 0.36 (mp 114–115 °C dec) and $R_f$ 0.31 (mp 133–135 °C dec). Separate reduction of these two compounds ($CH_3OH$, 10% palladium-on-charcoal, 1 atmosphere of $H_2$, 6 h) afforded compounds **7** [R = C(O)OC-



7



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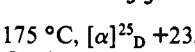


R = C(O)OC(CH3)3, H

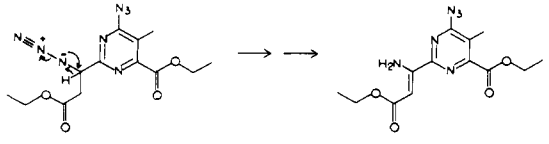
$(CH_3)_3$, 96% yield, mp 175 °C, $[\alpha]^{25}_D$ +23.7° (*c* 0.95, $CH_3OH$)] and **8** [R = C(O)OC$(CH_3)_3$, 80% yield, mp 87–89 °C, $[\alpha]^{25}_D$ +2.5° (*c* 0.8, $CH_3OH$)],[18] respectively, which were isolated by preparative TLC on silica gel (development with 85:15 $CHCl_3$–$CH_3OH$). Verification of the *S,S* configuration of **7** (R = H) was accomplished after N deblocking (1:1 2 N HCl–THF, 1 h) by degradation to a compound of known configuration.[19] The C-6 ester moieties in **7** and **8** were shown to undergo facile sa-

(11) See, e.g.: Temple, C., Jr.; McKee, R. L.; Montgomery, J. A. *J. Org. Chem.* **1965**, *30*, 829.

(12) Compounds **3b**, **3c**, and **4b** existed almost exclusively as the tetrazoles; for **4a**, the ratio of azide to tetrazole was ~1:1.4. For **4a** (azide): $^1$H NMR [$CDCl_3$, $Me_2SO$-$d_6$, $(CH_3)_4Si$] $\delta$ 1.40 (3 H, t), 2.22 (3 H, s), 3.1–3.9 (2 H, m), 4.41 (2 H, q), 5.47 (1 H, t), 6.1 (1 H, m).

(13) (a) Kröger, M.; Seela, F.; Cramer, F. *Chem. Ber.* **1976**, *109*, 3615. (b) Kirby, A. J.; Mujahid, T. G. *Tetrahedron Lett.* **1978**, 4081.

(14) Presumably, this species arose by Schmidt rearrangement of the initially formed diazide, followed by tautomerization of the derived imine.



(15) Mattingly, P. G.; Miller, M. J. *J. Org. Chem.* **1980**, *45*, 410.

(16) After filtration of the catalyst, silica gel chromatography afforded benzyl alcohol (90% of theoretical, removed from the product more routinely by azeotropic distillation with $H_2O$) and **6b**: NMR [$CDCl_3$, $(CH_3)_4Si$] $\delta$ 1.48 (9 H, s), 1.60 (2 H, br s), 2.79 (1 H, dd, *J* = 8.4, 12.6 Hz), 3.18 (1 H, dd, *J* = 4.5, 12.6 Hz), 4.07 (1 H, m), 5.74 (2 H, br s), 7.20 (1 H, br s); IR (neat) 3300, 1660 cm$^{-1}$. The crystalline *N*-acetate ($[CH_3C(O)]_2O$, pyridine, 25 °C, 1 h) had mp 145–149 °C; mass spectrum (CI), *m/e* 246 ($M^+$).

(17) Obtained from Calbiochem-Behring Corp.

(18) NMR [**7**; 2:1 $CDCl_3$, $CD_3OD$, $(CH_3)_4Si$] $\delta$ 1.43 (12 H, s and t), 2.14 (3 H, s), 2.50–3.25 (4 H, m), 3.47–3.65 (1 H, m), 3.99–4.17 (1 H, m), 4.40 (2 H, q). NMR [**8**; 2:1 $CDCl_3$–$CD_3OD$, $(CH_3)_4Si$] $\delta$ 1.43 (12 H, s and t), 2.15 (3 H, s), 2.60–3.26 (4 H, m), 3.69 (1 H, dd, *J* = 4.5, 9.0 Hz), 4.11 (1 H, m), 4.42 (2 H, q).

(19) Preliminary degradative studies of **7** (R = H) and **8** (R = H) (ref 8a) and comparison of CD spectra with those of bleomycin and epibleomycin (ref 9) provided a basis for assignment of absolute configurations. The CD spectra of **7** and **8** (R = H) were of opposite sign in the region of 240 nm and could be correlated directly with the spectra of bleomycin and epibleomycin. Compounds **7** and **8** were also compared with bleomycin $A_2$ by $^1$H NMR (360 MHz, $D_2O$) at three different pH values; cf.: Oppenheimer, N. J.; Rodriguez, L. O.; Hecht, S. M. *Biochemistry* **1979**, *18*, 3439.

ponification, affording the respective carboxylates.

The preparation of the pyrimidine moiety of bleomycin serves to verify the revised structure proposed[20] for this portion of the antibiotic. The syntheses of each of the components of bleomycin have now been described, suggesting the feasibility of a total synthesis of the antibiotic, as well as structurally related species of utility in defining its mechanism of action.

**Acknowledgment.** We thank Professor David G. Lynn for a helpful discussion during the course of this work and Mark Levin for assistance with the assignment of absolute configurations. This investigation was supported by research Grant CA-27603 from the National Cancer Institute, National Institutes of Health, Department of Health, Education and Welfare.

(20) Takita, T.; Muraoka, Y.; Nakatani, T.; Fujii, A.; Umezawa, Y.; Naganawa, H.; Umezawa, H. *J. Antibiot. (Tokyo)* **1978**, *31*, 801.

(21) National Cancer Institute Postdoctoral Trainee, 1978-1979; National Cancer Institute Postdoctoral Fellow, 1979-1980.

(22) Alfred P. Sloan Fellow, 1975-1979; NIH Research Career Development Awardee, 1975-1980.

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*Received May 28, 1980*

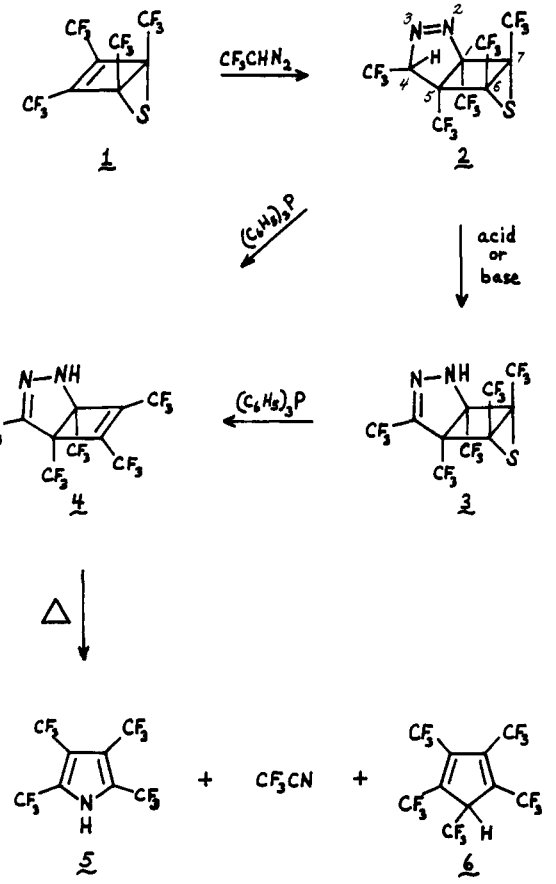
## 5*H*-Perfluoropentamethylcyclopentadiene, an Extraordinary Carbon Acid

*Sir:*

We report the synthesis of the title compound, a carbon acid which exceeds nitric acid in strength despite its lack of conjugating substituents.

2,2,2-Trifluorodiazoethane was added at room temperature to perfluorotetramethyl Dewar thiophene (**1**)[1] to yield azothiirane **2** (75%),[2] mp 53.5-54.5 °C (Scheme I). **2** had the following spectral data: IR ($CCl_4$) 3019 (C-H) $cm^{-1}$; mass spectrum (MS), *m/e* 466 (parent), 69 (base, $CF_3$); UV (cyclohexane) $\lambda_{max}$ 330 ($\epsilon$ 233), 270 (135), 235 nm (1230); $^{19}F$ NMR[3,4] ($CDCl_3$) $\delta$ 56.92 (A, $C_6$), 60.08 (B, $C_5$), 60.16 (C, $C_7$), 64.37 (D, $C_4$), 67.64 (E, $C_1$); $J_{AB} \simeq 3.0$, $J_{AC} \simeq 4.7$, $J_{BD} \simeq 16.4$, $J_{BE} \simeq 6.1$, $J_{CE} \simeq 2.7$, $J_{DH} = 7.0$, $J_{DE} \simeq 1.2$, $J_{AH} = 1$ Hz. From a set of four stereoisomeric possibilities, only configuration **2** was formed. Both candidates having a syn framework are inconsistent with the NMR data, and the $C_4$ epimer of **2** can be ruled out on the basis that nonbonded repulsions between the $C_4$ and $C_7$ trifluoromethyl groups would be severe. Though subtler, the origin of the preference for anti stereochemistry[5] is also presumed to be steric.

Scheme I




Surprisingly, attempts to contract the pyrazoline ring of **2** by elimination of nitrogen led to complex mixtures when carried out photochemically, and to an acyclic product[7] when performed thermally.[8] Desulfurization of **2** with triphenylphosphine was essentially instantaneous. The remarkable facility of this process is apparent from the following list of other reagents, each of which effected desulfurization at room temperature: phosphorus trichloride, zinc dust, sodium iodide, sodium benzenesulfinate, pyridine, acetone, and benzophenone. No matter how mild the conditions chosen for the reaction, however, a second transformation invariably accompanied the loss of sulfur, namely, prototropic rearrangement to the hydrazone tautomer **4**: mp 45-47 °C; IR (vapor) 3450 (N-H), 1704 (C=C), 1593 (C=N) $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ 242 ($\epsilon$ 2500), $\lambda_{sh}$ 263 nm; MS, *m/e* 434 (parent), 69 (base); $^{19}F$ NMR ($CDCl_3$) $\delta$ 62.48 (A, $C_7$), 62.93 (B, $C_6$), 63.65 (C, $C_4$), 67.02 (D, $C_5$), 72.38 (E, $C_1$); $J_{AB} \simeq 6$, $J_{AE} \simeq 3.2$, $J_{BC} \simeq 6$, $J_{BD} \simeq 4$-5, $J_{CD} \simeq 7$, $J_{DE} \simeq 10.8$ Hz.[2]

Gentle treatment with acid or base (even acetic acid or pyridine) brought about tautomerization of **2** without desulfurization, giving **3**, which was transformed in turn into **4** by triphenylphosphine. **3** had the following spectral properties: IR (neat) 3463 and 3395 (N-H), 1607 (C=N) $cm^{-1}$; MS, *m/e* 466 (parent), 69 (base); $^{19}F$ NMR ($CDCl_3$) $\delta$ 59.07 (A, $C_7$), 60.77 (B, $C_4$), 62.50 (C, $C_5$), 63.47 (D, $C_6$), 71.80 (E, $C_1$); $J_{AD} \simeq 5.5$, $J_{AE} \simeq 2.8$, $J_{BC} \simeq 8$,

(1) (a) Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y.; Mochizuki, H. *Chem. Pharm. Bull.* **1975**, *23*, 2773. (b) Wiebe, H. A.; Braslavsky, S.; Heicklen, J. *Can. J. Chem.* **1972**, *50*, 2721.

(2) Satisfactory analytical data (±0.3%) were obtained.

(3) All $^{19}F$ NMR chemical shifts are reported in ppm upfield from internal Freon 11 ($CFCl_3$).

(4) NMR spectra were analyzed with the help of spin-decoupling and spectral simulation techniques. $^{19}F$ NMR assignments and deductions regarding structure or configuration based on $^{19}F$ NMR depended upon a powerful generalization which we have tested on many compounds without finding an exception. This rule states that a F-F coupling constant greater than ~1 Hz between nongeminal $CF_3$ groups indicates the existence of van der Waals overlap of the coupled atoms, and that the larger the observed coupling the greater is the overlap.

(5) Anti stereochemistry has also been found in the Diels-Alder addition of **1** to furans: Kikutani, N.; Iitaka, Y.; Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1478. Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y. *Tetrahedron Lett.* **1974**, 2841. See also ref 1a. In other cycloadditions of **1**, anti stereochemistry has been assumed: Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y.; Ando, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2355. Also see ref 6.

(6) Kobayashi, Y.; Ando, A.; Kumadaki, I. *J. Chem. Soc., Chem. Commun.* **1978**, 509. Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Ando, A. *J. Am. Chem. Soc.* **1977**, *99*, 7350.

(7) Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.*, following paper in this issue.

(8) In contrast, adducts of **1** with azides (triazoline analogues of **2**) smoothly ring contract upon UV irradiation (ref 6).

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