$MgSO_4$. Evaporation of the eluant gave an amber oil (9.5 mg, 71%). Pure (±)-retronecine could be prepared by sublimation (100 °C (0.01 mm)) of the crude base in 70% yield, followed by recrystallization of the solid sublimate from acetone to give a crystalline white solid, mp 129–130 °C (lit.[11a] mp 130–131 °C). The NMR spectrum and TLC mobility of (±)-17 were identical with an authentic sample of racemic retronecine.[14]

Coupling of Retronecine and 19. Conversion to *d,l*-Indicine. Monoprotected retronecine 16 (*d,l*) (14.5 mg, 0.050 mmol), *d,l*-acetonide 19 (20.2 mg, 0.10 mmol), *N,N'*-dicyclohexylcarbodiimide (20.6 mg, 0.10 mmol), and (*N,N*-dimethylamino)pyridine (1.7 mg, 0.014 mmol) were stirred in dry toluene (0.9 mL) for 14 h according to the procedure used for unprotected retronecine.[13] (A white precipitate, dicyclohexylurea, appeared during this time.) The resulting suspension was filtered, and the filtrate was diluted with toluene to a volume of 5 mL and extracted with 5% aqueous HCl (3 × 4 mL). The combined acid extracts were allowed to stand overnight at ambient temperature, and then were brought to pH 11 with 28% aqueous NH_4OH. The resulting cloudy suspension was extracted with ether (10 mL), saturated with NaCl, and extracted additionally with ether (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated (aspirator) to give 20.6 mg of pale yellow glass consisting of a ca. 3:1 ratio of diastereomeric products together with DMAP. PTLC (silica gel, 20% methanol–chloroform) separated the coupling products (R_f 0.40) from DMAP (R_f 0.19) but failed to resolve the unequal mixture of diastereomers, giving 15.5 mg (71%) of the esters: IR (neat film, cm^{-1}) 1730 (s); partial 270 MHz NMR ($CDCl_3$, ppm) major diastereomer, 1.20 (methyl, d, J = 6.2 Hz), minor diastereomer, 1.18 (methyl, d, J = 6.2 Hz).

The unequal mixture of diastereomeric coupling products (10.4 mg, 0.024 mmol) was dissolved in dry THF (10 mL) and photolyzed (275-W sunlamp through Pyrex, cooling to maintain ≤28 °C) for 30 min, after which TLC (33% CH_3OH–CH_2Cl_2) showed total consumption of starting material (R_f 0.50) and appearance of a new high R_f spot (*o*-nitrobenzaldehyde derived products) and one at R_f 0.07 (deprotected product). Solvent was removed (aspirator) and the residue taken up in water (2 mL). The aqueous layer was washed with chloroform (2 × 1 mL) and evaporated to yield 5.0 mg of yellow oil (70%) which was identified as protonated indicine and its diastereomer. The material was dissolved in THF and stirred over excess solid, anhydrous K_2CO_3 for 15 min. Removal of solvent gave a mixture of the free bases: IR (KBr, cm^{-1}) 1725 (s); partial 270 MHz NMR ($CDCl_3$, ppm) minor (unnatural) diastereomer 1.21 (methyl, d, J = 5.5 Hz), 1.11, 0.83 (isopropyl, two d, J = 6.2 Hz), major diastereomer[15] (indicine) 1.17 (methyl, d, J = 6.5 Hz), 0.92, 0.91 (isopropyl, two d, J = 7.2 Hz).

Acknowledgment. This work was supported by the National Institutes of Health (CA 17918) and by an NSF predoctoral fellowship (FGW).

Registry No. 1, 76596-19-5; 2, 76596-20-8; 4, 96246-59-2; 8a, 96246-60-5; 13, 96246-61-6; 14, 96246-62-7; 15, 96246-63-8; 16, 96246-64-9; 17, 73466-19-0; 18 (isomer 1), 96246-65-0; 18 (isomer 2), 96346-14-4; 19, 96291-80-4; 20 (isomer 1), 96291-81-5; 20 (isomer 2), 96291-82-6; 2-pyrrolidinone, 616-45-5; (iodomethyl)trimethylsilane, 4206-67-1; *o*-nitrobenzyl bromide, 3958-60-9; methyl acrylate, 96-33-3; phenylselenenyl chloride, 5707-04-0.

(14) Kindly provided by Dr. A. R. Mattocks, Medical Research Council Laboratories, United Kingdom.

(15) Identical with spectra of natural indicine, a sample of which was kindly provided by the National Cancer Institute.

Rearrangement of Unsaturated (Acyloxy)benzotriazoles

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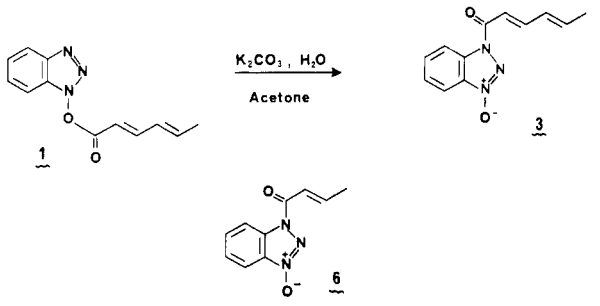
In an attempt to use hydroxybenzotriazole to synthesize *C*-acyl tetramic acid analogues of streptolydigin and tirandamycin, preformed 1-(crotonyloxy)benzotriazole rearranged to give β-methyl-3-benzotriazolepropionic acid 1-oxide (7) through the intermediate ketene. 1-(Crotonyloxy)benzotriazole (formed in situ) and 1-(sorbyloxy)benzotriazole (in situ or preformed) were found to rearrange to give the corresponding 3-acylbenzotriazole oxides (6 and 3). Structures of 3 and 7 were established by X-ray crystallography. The ^{15}N NMR spectra of the rearrangement products and related compounds are also discussed.

Hydroxybenzotriazole has been used widely as a coupling agent for forming peptide bonds[1] and as a phosphorylating agent[2] and, recently, has been successfully employed to effect C-acylation of a pyrrolidinedione to give malonomicin,[3] an acyl tetramic acid antibiotic. In our continuing studies of potential routes to the acyl pyrrolidinedione antibiotics tirandamycin and streptolydigin,[4] we attempted to acylate α-(1-methyl-2,4-dioxo-5-pyrrolidinyl)-*N*-methylacetamide, employing preformed 1-(sorbyloxy)benzotriazole (1, Scheme I) and 1-(crotonyloxy)benzotriazole (2, Scheme II) rather than in situ generated esters; however, unexpected rearrangements were observed instead.

Scheme I



Results and Discussion

During the preparation of 1-(sorbyloxy)benzotriazole (1) from the potassium salt of 1-hydroxybenzotriazole and sorbyl chloride in acetone, a small amount of rearrangement product 3 was obtained. This compound could also be obtained when the sorbyl ester 1 was stored for several weeks or, in large quantities, when the sorbyl ester was

(1) For a review, see: Munekata, E.; Sakakibara, S. *J. Synth. Org. Chem., Jpn.* **1973**, *31*, 853–858.
(2) van Boeckel, S. A. A.; van der Marel, G.; Wille, G.; van Boom, J. H. *Chem. Lett.* **1981**, 1725–1728.
(3) van der Baan, J. L.; Barnick, J. W. F. K.; Bickelhaupt, F. *Tetrahedron* **1978**, *34*, 223–231.
(4) Lee, V. J.; Branfman, A. R.; Herrin, T. R.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 4225–4236.

0022-3263/85/1950-2174$01.50/0

Table I. ^{1}H NMR Spectral Data ($CDCl_3$)

	chemical shift, δ (multiplicity, J (Hz))								
	1[a]	2[a]	3[b]	6[b]	7[c,d,g]	9[c,g]	sorbic acid[e]	crotonic acid[f]	benzotriazole[e]
C4			8.49 (d, 8.4)	8.47 (d, 8.6)	7.86 (d, 8.3)	7.65 (m)			8.01
C5	7.23–7.73 (m)	7.2–7.6 (m)	7.77 (t, 7.41)	7.79 (t, 7.4)	7.68 (t, 7.6)*	7.65 (m)*			7.44
C6			7.56 (t, 8.0)	7.60 (t, 8.0)	7.43 (t, 7.6)*	7.38 (m)*			7.44
C7	8.03 (dd, 9, 2)	8.08 (dd, 9, 2)	8.02 (d, 8.3)	8.01 (d, 8.4)	7.99 (d, 8.5)	7.94 (d, 8.6)			8.01
α	6.04 (d, 15)	6.18 (dq, 15, 1.5)	7.02 (d, 15.0)	7.12 (dq, 15.3, 1.6)	2.99 (dd, 7.2, 2.3)	2.90 (dd, 17.1, 4.9)	5.73 (d)	5.82 (dq)	
						3.17 (dd, 17.1, 9.0)			
β		7.2–7.6 (m)	7.64 (dd, 15.1, 10.2)	7.46 (dq, 15.3, 7.0)	5.29 (dq, 6.8, 2.3)	5.22 (m)	6.01–6.51 (m)	7.04 (m)	
γ	6.30–6.40 (m), 7.23–7.73		6.39–6.43 (m)						
δ							7.30 (m)		
CH_3	1.91 (d, 5)	2.08 (dd, 7.5, 1.5)	1.97 (d, 5)	2.09 (dd, 7.0, 1.6)	1.53 (d, 6.7)	1.64 (d, 6.8)	1.89 (d)	1.89 (dd)	
other						3.57 (OMe)			

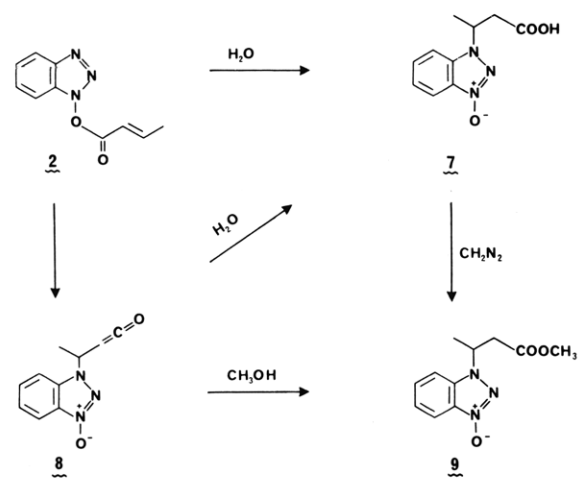
[a] 90-MHz spectra. [b] 360-MHz spectra. [c] 220-MHz spectra. [d] Me_2SO-d_6 solution. [e] "The Sadtler Handbook of Proton NMR Spectra"; Simmons, W. W., Ed.; Sadtler Research Laboratories, Inc.: Philadelphia, PA 19104. [f] "The Sadtler Guide to NMR Spectra"; Simmons, W. W., Zanger, M., Eds.; Sadtler Research Laboratories, Inc.: Philadelphia, PA 19104. [g] Signals marked with the same superscript (*) may be interchanged.

Table II. ^{13}C NMR Spectral Data ($CDCl_3$)

	chemical shifts, δ, and off-resonance multiplicity							
	3[d]	6[d]	7[a,d]	9[d]	ethyl sorbate[b]	crotonic acid[b]	benzotriazole[b]	hydrobenzotriazole[b]
C4	132.8 d*	132.8 d*	130.0 d*	130.3 d*			115.0	118.6
C5	115.9 d‡	115.5 d‡	112.0 d‡	110.6 d‡			125.9	124.8
C6	115.6 d‡	116.3 d‡	114.5 d‡	115.7 d‡			125.9	127.0
C7	126.7 d*	126.8 d*	124.2 d*	124.3 d*			115.0	109.9
C4A[c]	133.4 s		129.1 s†	126.9 s†			139.1	128.2
C7A[c]			133.4 s†	133.9 s†			139.1	142.5
α	144.0 d	120.5 d	39.7 t	40.2 t	138.6	122.6		
β	149.5 d	150.4 d	51.8 d	51.9 d	144.7	147.5		
γ	130.2 d				130.2			
δ	116.4 d				119.5			
CH_3	19.1 q	18.9 q	20.3 q	20.8 q	18.4	16.9		
C=O	162.1 s	161.3 s	171.2 s	170.6 s	166.9	172.5		
other				51.9 q (OMe)				

[a] Me_2SO-d_6 solution. [b] Bremster, W.; Ernst, L.; Franke, B. "Carbon-13 NMR Spectral Data"; Verlag-Chemie: Weinheim, West Germany, 1978. [c] One of the quaternary carbons of 3 and both the quaternary carbons of 6 were not observed even after 2 days of accumulation. [d] Signals marked with the same superscript (*, ‡, †) may be interchanged.

Scheme II



heated in refluxing acetone containing a catalytic amount of potassium carbonate and a few drops of water (Scheme I). Traces of base and moisture in the potassium salt of hydroxybenzotriazole used in the preparation of **1** apparently catalyze the formation of **3**, since the rearrangement of **1** to **3** does not take place in pure acetone. Similarly, purification of **3** was complicated by apparent equilibration between the product and the starting material during column chromatography. Structure assignment of **3** from ^{1}H and ^{13}C NMR data (Tables I and II) was difficult since structures like **4** or **5** (R = COCH=CHCH=$CHCH_3$) were also, in principle, possible. Structure **3** was established by X-ray analysis, as shown by the computer representation in Figure 1.

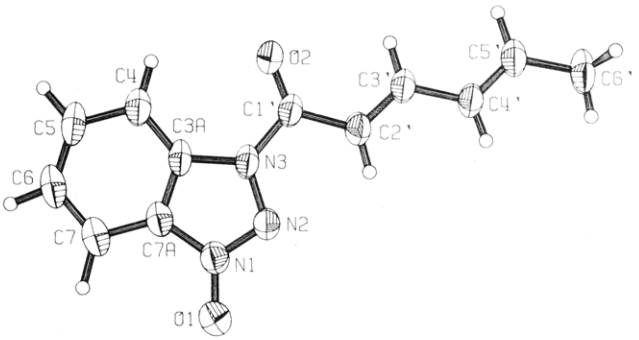
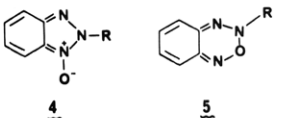


Figure 1. ORTEP drawing of 3-sorbylbenzotriazole 1-oxide (**3**) showing 35% electron density probability ellipsoids.



An *N*-acyl structure like **3** was noted originally by König and Geiger[5] from IR data as one of the possible structures

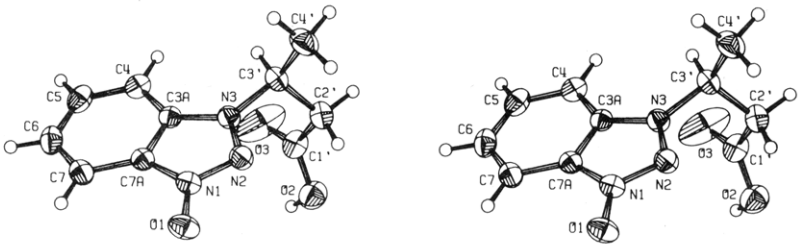


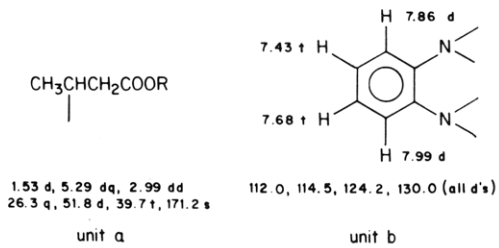
Figure 2. Stereoview of β-methyl-3-benzotriazolepropionic acid 1-oxide (**7**).

of acylhydroxybenzotriazoles (for amino acid coupling) in the crystal state. Later, McCarthy et al.[6] reported an X-ray study of 1-(benzoyloxy)benzotriazole and concluded that the compounds they studied exist in the solid state in the *O*-acyl form rather than in one of the *N*-acyl forms. Horiki,[7] however, used IR data to assign a structure similar to **3** to the rearrangement product in aqueous acetone from 1-(acyloxy)benzotriazoles. Although Horiki's conclusions concur with ours, it is not clear how IR data would differentiate between the two possible *N*-acyl structures **3** and **4**; we believe the present study provides the first conclusive proof of structure of an *N*-acylhydroxybenzotriazole.

In the similar reaction of crotonyl chloride with the potassium salt of hydroxybenzotriazole, 3-crotonylbenzotriazole 1-oxide (**6**) was isolated, albeit in low yields, in addition to the expected **2**. Its structure assignment is based on the similarity of its spectral data to those for **3** (Tables I and II).

When α-(1-methyl-2,4-dioxo-5-pyrrolidinyl)-*N*-methylacetamide and **2** were allowed to react in the presence of triethylamine in acetonitrile, the expected product, α-(1-methyl-3-crotonyl-2,4-dioxo-5-pyrrolidinyl)-*N*-methylacetamide, was not obtained. Instead, 1-(crotonyloxy)benzotriazole (**2**) rearranged (Scheme II), with addition of 1 mol of water, to β-methyl-3-benzotriazolepropionic acid 1-oxide (**7**). The same compound (**7**) was also obtained when a sample of solid **2** or a chloroform solution of **2** was allowed to stand for several weeks at room temperature. The rearrangement appears to involve the intermediate ketene **8** since **2** in methanol after several weeks gives the methyl ester **9**, which can also be obtained by treatment of the acid **7** with diazomethane.

The molecular formulas for **7** and **9** were obtained by high-resolution electron ionization mass spectrometry (HREIMS) and their ^1H and ^{13}C NMR spectra (Tables I and II) indicated the units a and b (^1H and ^{13}C values for **7**). The structure of **7** could not, however, be assigned on



the basis of spectral data alone, because the structural units could, in principle, be combined in several ways, e.g., into **4** or **5** [R = $CH(CH_3)CH_2COOH$], as well as into **7**. The structure **7** was assigned, therefore, by X-ray crystallography, with a stereoscopic presentation shown in Figure 2. A particular point of interest concerns the bond lengths in **3** and **7** (Table III). While most of the benzotriazole oxide bonds are of similar lengths in the two molecules (within 0.016 Å of each other), the exocyclic bonds from N3 and N1 are much shorter in **3** (0.065 and 0.053 Å, respectively), in keeping with a partial N3, C1′ double-bond character due to amide delocalization in **3**, with an accompanying electron shift from the oxide oxygen toward the triazole ring. The bonds joining these units (N3, C3A; C3A, C7A; C7A, N1) are also adjusted in the two molecules.

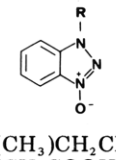
Table III. Selected Bond Lengths (Å) of 7 and 3

bond	7	3
O1–N1	1.315 (2)	1.262 (3)
N1–N2	1.315 (2)	1.302 (3)
N2–N3	1.341 (2)	1.371 (3)
N3–C3A	1.369 (2)	1.400 (3)
C3A–C4	1.400 (3)	1.384 (4)
C4–C5	1.373 (3)	1.384 (4)
C5–C6	1.417 (3)	1.395 (5)
C6–C7	1.358 (3)	1.370 (5)
C7–C7A	1.394 (3)	1.387 (4)
C7A–N1	1.369 (2)	1.409 (4)
C7A–C3A	1.392 (3)	1.367 (4)
N3–C3′	1.481 (3)	1.416 (3)[a]

[a] N3–C1′.

The reaction that forms **7** probably goes through a seven-membered cyclic transition state to give the ketene **8** (Scheme II), which is trapped by moisture. A molecular model of the starting material shows a perfect orientation of the N=N and C=C bonds for effective overlap.

Although the photolysis of several hydroxybenzotriazoles has been reported previously[8-13] to give mainly nitrosobenzene[13] and the pyrolysis of 1-(acetyloxy)benzotriazole has been observed[14] to give *o*-alkoxyphenyl isocyanates, a rearrangement of the present type (**2** → **7**) seems not to have been described. It is unclear why neither compound **10** nor **11**, analogues of **7**, was observed as a product of the



10, R = $CH(CH_3)CH_2CH{=}CHCOOH$
11, R = $CH(CH_2COOH)CH{=}CHCH_3$

rearrangement of 1-(sorbyloxy)benzotriazole.

(5) König, W.; Geiger, R. *Chem. Ber.* **1970**, *103*, 788–798.
(6) McCarthy, D. G.; Hegarty, A. F.; Hathaway, B. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 224–231.
(7) Horiki, K. *Tetrahedron Lett.* **1977**, 1897–1900, 1901–1904.
(8) Burgess, E. M.; Carithers, R.; McCullagh, L. *J. Am. Chem. Soc.* **1968**, *90*, 1923–1924.
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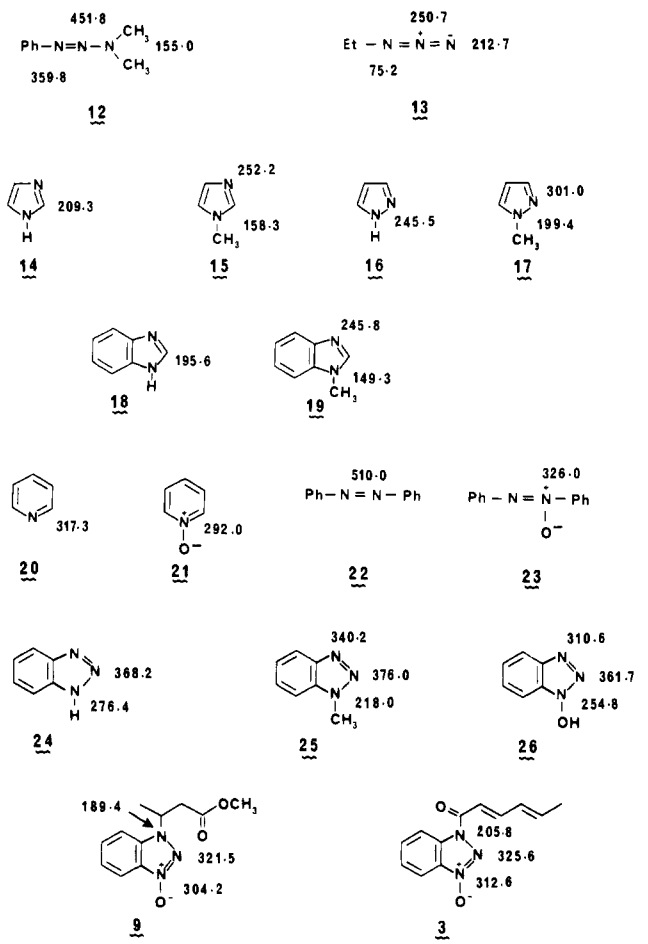
(12) Tsujimoto, K.; Ohashi, M.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 515–519.
(13) Serve, M. P. *J. Heterocycl. Chem.* **1974**, *11*, 245–246.
(14) Leonard, N. J.; Golankiewicz, K. *J. Org. Chem.* **1969**, *34*, 359–365.

Chart I



^{15}N NMR Spectra of Oxybenzotriazoles. Although their structures were ultimately determined by X-ray analysis, compounds **3** and **9** gave interesting ^{15}N NMR spectra which were assigned by using spectra obtained for benzotriazole and the following considerations from literature reports. (1) Signals for a nitrogen bonded to two other nitrogens occur at particularly low field,[15] as in compounds **12** and **13** (Chart I). (2) In heterocyclic systems such as imidazoles, pyrazoles, and benzimidazoles, signals for the "pyrrole"-type nitrogens occur at higher field than for the "pyridine"-type nitrogens in "locked" systems such as **15**, **17**, and **19**,[16] while in the corresponding unsubstituted compounds (**14**, **16**, and **18**) one peak is observed, due to proton exchange, at an approximately average value of the two shifts observed for the substituted compounds. (3) Removal of the lone pair of electrons on nitrogen (e.g., in *N*-oxides) shifts the signal for the nitrogen to higher field,[17] as illustrated by the spectra of **21** vs. **20** and **23** vs. **22**.

In the present study the ^{15}N NMR spectrum of benzotriazole **24** shows two peaks, a sharp, intense peak at 368.2 ppm which is assigned to N2 (according to (1) above) and a broad, less intense peak at 276.4 ppm assigned to N1 and N3, the line broadening being due to N–H coupling. Witanowski[18] reported only one peak in the ^{14}N NMR spectrum of benzotriazole, at 298.6 ppm.

The ^{15}N NMR spectrum of hydroxybenzotriazole showed three peaks—at 361.7 ppm assigned to N2, at 254.8 ppm assigned to the "pyrrole"-type nitrogen (N1), and at 310.6 ppm assigned to the "pyridine"-type nitrogen (consistent with (2) above). This agrees with Stefaniak's assignment[19] of the ^{14}N NMR spectrum of 1-methylbenzotriazole (**25**), though the chemical shifts differ quantitatively. The methyl group shifts the "pyridine"-type nitrogen to much lower field and the "pyrrole"-type nitrogen to much higher field than does the hydroxyl group.

The solubility of **7** in common solvents was too limited for ^{15}N NMR spectroscopy, but the spectrum of its methyl ester (**9**) showed three peaks. The signal at 321.5 ppm was assigned to N2, but the presence of both alkyl and *N*-oxide groups complicated the assignment of N1 and N3. Since *N*-oxides shift the nitrogen signals to higher fields, the peak at 304.2 ppm was assigned to N1 (a shift of ca. 36 ppm compared to 1-methylbenzotriazole) and the peak at 189.4 ppm was assigned to N3.

Assignment of the ^{15}N NMR spectrum of **3** was similar to that of **9**, with only minor shifts of the individual nitrogens relative to **9**.

Experimental Section

General Methods. Melting points, determined on a Kofler hot stage, are uncorrected. Infrared spectra (IR) were determined on a Beckman Model IR-12 spectrophotometer and ultraviolet spectra (UV) in ethanol on a Perkin-Elmer Lambda-3 spectrophotometer. ^{1}H NMR spectra were determined by L. Johnson on Varian EM 390 and Varian HR 220 spectrometers and by D. G. Vandervelde on a Nicolet NTC 360 spectrometer, and ^{13}C NMR spectra were obtained by D. L. Warrenfeltz on a Varian XL-100 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane as an internal standard. ^{15}N NMR spectra were determined by D. L. Warrenfeltz on the NSF-250 spectrometer at 25.352 MHz with nitromethane as external standard, with later conversion (conversion factor, 380.23 ppm) to liquid ammonia standard.[15] Compounds **3** and **9** were run with tris(acetylacetonate)chromium(III). In the absence of this relaxation agent no signal was observed. Low-resolution mass spectra were obtained on a Finnigan MAT CH5 mass spectrometer by Dr. R. M. Milberg and M. K. Cochran, and high-resolution spectra were recorded on a Finnigan MAT 731 mass spectrometer by J. C. Cook. Microanalyses were determined by J. Nemeth and associates.

1-(Sorbyloxy)benzotriazole (1). Compound **1** was prepared by a reported procedure.[14] Sorbyl chloride (3.77 g) was added to 5.0 g of the potassium salt of 1-hydroxybenzotriazole, prepared from the latter compound (Aldrich) and potassium hydroxide in ethanol in 50 mL of acetone, and the mixture was heated at reflux for 30 min and then poured over ice–water. The product (4.4 g, 67%) crystallized as pale yellow needles from chloroform–hexane: mp 85–86 °C; IR (KBr) 1795, 1740, 1640 cm^{-1}; UV λ_{max} (ϵ) 269 nm (34 400), 335 (2300), 346 (2300); ^{1}H NMR (see Table I).

Anal. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.88; H, 4.80; N, 18.34; M_r, 229. Found: C, 62.84; H, 4.87; N, 18.21; M_r, 229 (EIMS).

3-Sorbylbenzotriazole 1-Oxide (3). A mixture of **1** (3 g, 13.1 mmol), anhydrous potassium carbonate (0.5 g), and water (2 mL) in 300 mL of acetone was heated under reflux for 4 h and then filtered. The acetone was evaporated at reduced pressure, and the brown residue was triturated with hexane containing chloroform and then concentrated to give a pale yellow solid which was filtered hot. The solid was crystallized again from the same solvent to give pure **3** as a pale yellow powder (2 g, 67%). Slow recrystallization from acetone (300 mL, ca. 1 week) gave pale brown needles suitable for X-ray analysis:[20] mp 158–160 °C (powder); IR (KBr) 1710, 1640, 1610, 1495, 1465, 1430, 1370, 1350, 1250 cm^{-1}; UV λ_{max} (ϵ) 209 nm (13 600), 286 (15 100), 334 (12 200), 349 (12 500); ^{1}H NMR (see Table I); ^{13}C NMR (see Table II).[21]

(15) (a) Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley: New York, 1979; p 94. (b) Witanowski, M. *J. Am. Chem. Soc.* **1968**, *90*, 5683–5689. (c) Beck, W.; Becker, W.; Chew, K. F.; Derbyshire, W.; Logan, N.; Revitt, D. M.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1972**, 245–247.

(16) Reference 15a, pp 78, 84–85.

(17) Reference 15a, p 82.

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Anal. Calcd for $C_{12}H_{11}N_3O_2$: M_r, 229.0850. Found: C, 62.40; H, 4.81; N, 18.34; M_r, 229.0846 (HREIMS).

1-(Crotonyloxy)benzotriazole (2). Compound **2** was prepared in the same way as compound **1** above with 3.46 g of the potassium salt of 1-hydroxybenzotriazole and 2.08 g of crotonyl chloride in 50 mL of acetone. The solid was filtered (3.1 g) and recrystallized from petroleum ether (80 mL) and benzene (few drops). The first crop of pale yellow crystals (0.68 g) was found by ^1H NMR spectroscopy to be a mixture of cis and trans isomers. The mother liquor on refrigeration for 1 day gave white crystalline **2** (2.40 g, 59%): mp 70 °C; IR (KBr) 1795,[14] 1655 cm^{-1}; ^1H NMR (see Table I).

Anal. Calcd for $C_{10}H_9N_3O_2$: C, 59.11; H, 4.43; N, 20.68; M_r, 203.0694. Found: C, 58.42; H, 4.23; N, 20.80; M_r, 203.0706 (HREIMS).

3-Crotonylbenzotriazole 1-Oxide (6). A mixture of the potassium salt of hydroxybenzotriazole (1.8 g), crotonyl chloride (1.4 g), and acetone (40 mL) was heated at reflux for 1 h and poured into ice–water. The precipitate (1.5 g) was filtered and recrystallized from hexane–chloroform to give needles of **6** (0.125 g, 6%): mp 159–162 °C; IR (KBr) 1740, 1640 cm^{-1}; ^1H NMR (see Table I); ^{13}C NMR[21] (see Table II). Evaporation of the filtrate and recrystallization of the residue from petroleum ether–benzene gave the expected **2** as the major product.

Anal. Found: C, 58.83; H, 4.33; N, 20.67; M_r, 203.0696 (HREIMS).

β-Methyl-3-benzotriazolepropionic Acid 1-Oxide (7). A. From 2. A solution of **2** (0.2 g) in chloroform (50 mL) was allowed to stand for several weeks at room temperature and then was evaporated. The residue was washed several times with chloroform, and the off-white solid was crystallized from methanol (0.09 g, 41%):[20] mp 228 °C; IR (KBr) 1725, 1505, 1460, 1430, 1390 cm^{-1}; UV λ_{max} (ϵ) 322 nm (6300), 219 (19 500); ^1H NMR (see Table I); ^{13}C NMR (see Table II).

Anal. Calcd for $C_{10}H_{11}N_3O_3$: C, 54.29; H, 4.97; N, 19.00; M_r, 221.0800. Found: C, 54.08; H, 5.15; N, 18.88; M_r, 221.0813 (HREIMS).

B. From Attempted Reaction of 2 with α-(1-Methyl-2,4-dioxo-5-pyrrolidinyl)-*N*-methylacetamide. Triethylamine (0.175 g) was added dropwise to a solution of α-(1-methyl-2,4-dioxo-5-pyrrolidinyl)-*N*-methylacetamide (0.289 g, 1.57 mmol)[4] and **2** (0.305 g, 1.5 mmol) in 200 mL of acetonitrile, and the solution was stirred at room temperature for 4 days. The acetonitrile was evaporated at room temperature, and ethyl acetate was added to the residue. The solid formed was filtered (0.30 g, mp 155–165 °C) and then was recrystallized from methanol–ethyl acetate (1:20) to give crystals (0.24 g, 84%) of recovered (1-methyl-2,4-dioxo-5-pyrrolidinyl)-*N*-methylacetamide identified by ^1H NMR spectroscopy.[4] The insoluble residue was recrystallized from methanol and shown by spectral data to be identical with **7** from route A.

Methyl β-Methyl-3-benzotriazolepropionate 1-Oxide (9). A. From Reaction of 7 and Diazomethane. The acid **7** (0.10 g) was suspended in dry ether (35 mL) and treated with diazomethane in ether until the yellow color persisted. On concentration, colorless flakes separated, which were filtered and dried (0.07 g, 66%): mp 94–95 °C; IR (KBr) 1745, 1507, 1467, 1442, 1430, 1405, 1372 cm^{-1}; UV λ_{max} (ϵ) 332 nm (8600), 217.8 (28 200); ^1H NMR (See Table I); ^{13}C NMR (see Table II).

Anal. Calcd for $C_{11}H_{13}N_3O_3$: M_r, 235.0956. Found: M_r, 235.0944 (HREIMS).

B. From Rearrangement of 2 in Methanol. A solution of **2** (0.15 g) in methanol (50 mL) stood for 50 days at room temperature and then was concentrated. A white solid separated and was filtered; evaporation of the mother liquor left a pasty residue. Trituration of the paste with petroleum ether and evaporation of the petroleum ether gave an oily residue (15 mg), whose ^1H NMR spectrum was identical with that of the product obtained from A above.

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Registry No. **1**, 96228-04-5; *trans*-**2**, 96228-05-6; *cis*-**2**, 96228-10-3; **3**, 96228-06-7; **6**, 96228-07-8; **7**, 96228-08-9; **9**, 96228-09-0; **12**, 7227-91-0; **13**, 871-31-8; **14**, 288-32-4; **15**, 616-47-7; **16**, 288-13-1; **17**, 930-36-9; **18**, 51-17-2; **19**, 1632-83-3; **20**, 110-86-1; **21**, 694-59-7; **22**, 103-33-3; **23**, 495-48-7; **24**, 95-14-7; **25**, 13351-73-0; **26**, 2592-95-2; 1-hydroxybenzotriazole potassium salt, 62244-77-3; 1-methyl-2,4-dioxo-5-pyrrolidinyl-*N*-methylacetamide, 67513-26-2; sorbic acid, 110-44-1; sorboyl chloride, 2614-88-2; 1-hydroxybenzotriazole, 2592-95-2; crotonyl chloride, 10487-71-5; crotonic acid, 3724-65-0.

Supplementary Material Available: Details concerning the X-ray experiments as well as listings of structure factor amplitudes, positional and thermal parameters, and bond distances and angles for **3** and **7** (11 pages). Ordering information is given on any current masthead page.

(21) One of the quaternary aromatic carbons of **3** and both of the quaternary aromatic carbons of **6** were not observed even after 2 days of accumulation.