GF plates (1000 and 250 μm) were used for TLC with $CHCl_3$/CH_3CN/benzene (10:1:1) (I) or CCl_4/$CHCl_3$ (10:1) (II) as the developing solvent.

Aniline and *N*-methylaniline were vacuum distilled before use and stored under N_2. Phenylformamide was recrystallized twice in petroleum ether (bp 35–60 °C) and dried in vacuo. 4-Aminodiphenylamine was recrystallized once in CCl_4 and then again in petroleum ether (bp 35–60 °C). The crystals were dried in vacuo and stored in a desiccator, protected from light.

4-Nitrosodiphenylamine was purified by column chromatography on silica gel (70–230 mesh) using CH_2Cl_2/CH_3CN (10:1) as the eluting solvent. The crystals that formed upon evaporation were dried in vacuo and stored desiccated. All other compounds were used without further purification.

General Reaction Conditions. Solutions of 18-crown-6-ether (0.15 M) in Me_2SO were made and stored over 4-Å molecular sieves before use. Freshly crushed potassium superoxide was added to an aliquot of the Me_2SO solution, the mixture was shaken for 15 min, and the superoxide concentration was determined as described.[30] The superoxide solutions used in these experiments ranged between 0.08 and 0.12 M superoxide by assay. A typical experiment had 50 μL of amine (0.54 mmol of aniline, 0.47 mmol of *N*-methylaniline) added to 1 mL of the superoxide solution, which contained from 0.08 to 0.12 mmol of superoxide. The reaction was allowed to proceed for 24 h and then was quenched by the addition of the 0.2 mL of H_2O. For preparative work, the reaction was scaled up so that 0.5 mL of amine (5.4 mmol of aniline, 4.7 mmol of *N*-methylaniline) was added to 5 mL of superoxide solution. Reactions of amines with HOOH in Me_2SO were carried out by adding the amine and 0.5 mL of 30% HOOH to 0.5 mL of Me_2SO. This resulted in amine and HOOH concentrations of 0.18 and 4.4 M, respectively. Reaction times were 24 h.

Anaerobic reactions were carried out in sealed 100-mL flasks. Argon was dried and rendered oxygen-free by passage through a gas purifier (Matheson No. 6406). Reaction solutions were purged by bubbling with argon both prior to addition of aniline and during the reaction. All anaerobic and corresponding control reactions were quenched after 24 h by the addition of 0.5 mL of 0.2 N HCl.

Column chromatography was carried out using glass columns (30 × 1.9 cm). When silica was used, the elution solvent was CH_2Cl_2/CH_3CN (10:1). Depending on the starting material various color-containing fractions were isolated and then subjected to TLC. Solvent system I was used except in the aniline case where solvent system II was used on the first color-containing fraction eluted from the column. Standard graphs of peak area vs. weight were constructed for each compound via GC analysis. The product recoveries were calculated and were used in determining product yields.

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Registry No. I, 17082-12-1; II, 101-75-7; III, 836-30-6; IV, 156-10-5; V, 103-70-8; VI, 101-54-2; $PhNH_2$, 62-53-3; PhNHMe, 100-61-8; KO_2, 12030-88-5; HOOH, 7722-84-1.

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Notes

Crystal Structure of 3-(N^{α}-Tritylmethionyl)benzotriazole 1-Oxide, a Synthon in Peptide Synthesis

Kleomenis Barlos, Dionysios Papaioannou, and Stavros Voliotis*

Department of Chemistry, University of Patras, Patras, Greece

Roland Prewo and Jost H. Bieri

Organisch-Chemisches Institut, Universität Zürich, CH-8057 Zürich, Switzerland

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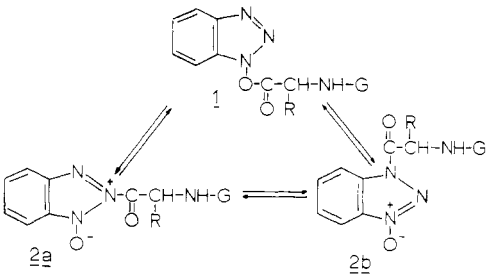
1-Hydroxybenzotriazole (HOBt) is widely used in peptide synthesis as an additive to DCC, because it is an effective racemization suppressant,[1] and sometimes as a catalyst.[2] The recognized intermediate implicated is the benzotriazolyl ester 1 with an IR carbonyl absorption band at around 1820 cm^{-1}. In solution ester 1 exists in equilibrium with an amide form which exhibits an IR carbonyl absorption at around 1740 cm^{-1}. Isolated crystalline compounds are in either one form or the other.[1,3a] Two amide forms **2a** and **2b** (Scheme I) have been postulated[1] with

Scheme I



2a preferred and associated with the 1740-cm^{-1} absorbance.[3] Horiki,[4] based on kinetic investigations, concluded in favor of **2b** whereas Davies et al.[5] used **2a** to accommodate seemingly anomalous results with *N*-methylamino acids.

Nevertheless it was not unambiguously known whether the amide with the carbonyl absorption band at 1740 cm^{-1} had structure **2a** or **2b**. Clarification of the issue would allow a better understanding of the mechanism of the racemization-suppressing and, sometimes, -promoting effect of HOBt. We thus decided to undertake an X-ray

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(5) Davies, J. S.; Mohammed, A. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2982.

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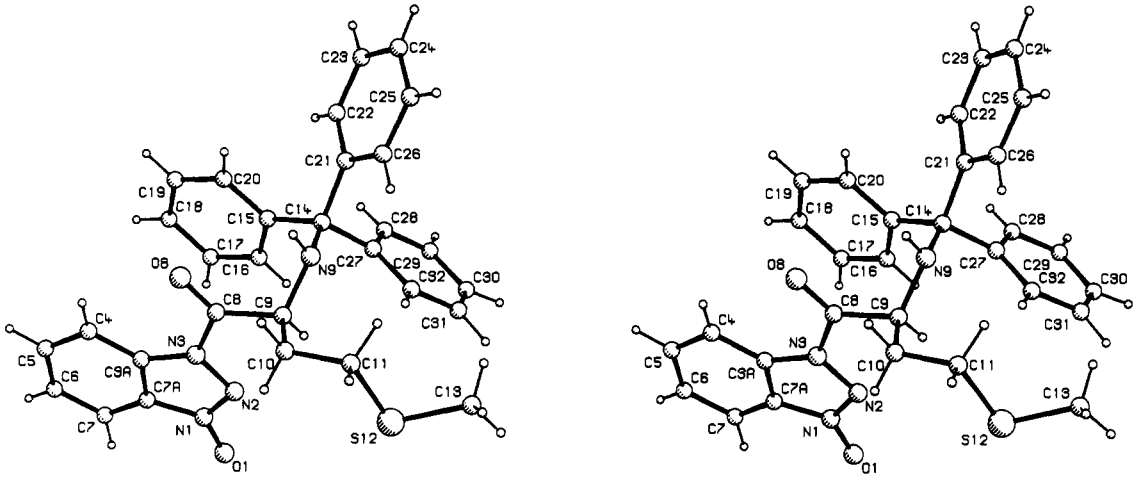

Figure 1. Stereoscopic view of the molecule with atomic numbering.

Table I. Bond Lengths (angstroms) and Bond Angles (degrees) with Standard Deviations in Parentheses

N(1)–O(1)	1.267 (2)	N(3)–C(3a)	1.393 (3)
N(1)–N(2)	1.311 (2)	N(3)–C(8)	1.412 (2)
N(1)–C(7a)	1.411 (3)	C(3a)–C(7a)	1.384 (3)
N(2)–N(3)	1.385 (2)		
O(1)–N(1)–N(2)	122.6 (2)	N(2)–N(3)–C(8)	120.4 (2)
O(1)–N(1)–C(7a)	124.9 (2)	N(3)–C(3a)–C(7a)	105.4 (2)
N(1)–N(2)–N(3)	105.0 (1)	N(3)–C(3a)–C(4)	133.6 (2)
N(1)–C(7a)–C(3a)	105.8 (2)	C(3a)–N(3)–C(8)	127.8 (2)
N(1)–C(7a)–C(7)	130.2 (2)	C(3a)–C(7a)–C(7)	123.9 (2)
N(2)–N(1)–C(7a)	112.5 (2)	C(4)–C(3a)–C(7a)	121.0 (2)
N(2)–N(3)–C(3a)	111.2 (1)		

crystallographic investigation on the well crystalline *N*-(N^{α}-tritylmethionyl)benzotriazole 1-oxide, exhibiting an IR carbonyl band at 1730 cm^{-1}.

The stereoscopic drawing of the examined compound as it is revealed by the crystallographic analysis is shown in Figure 1. Bond lengths and bond angles for the triazole ring are presented in Table I. The present X-ray analysis conclusively demonstrates that the methionyl moiety is attached at N3. Thus, the benzotriazolyl derivatives of N^{α}-protected amino acids in the amide form, with IR carbonyl absorbance in the region 1730–1750 cm^{-1}, must have the structure **2b** and not the structure **2a**. Moreover, although construction **2b** excludes the proximity of the basic oxygen atom (O1) on the benzotriazole ring, and the H atom (H9) of the chiral C atom, it places H9 very close to the second basic atom (N2) of the same ring. Indeed, the distance H9···N2 is ca. 2.38 Å, almost close enough to be considered a C–H–N hydrogen bond, if the CHN angle were straighter.

We therefore conclude that the extent of racemization through intramolecular direct hydrogen abstraction must depend not only on purely electronic considerations but also on steric factors which impose the possible proximity of the H atom (H9) of the chiral C atom and the central N atom (N2) of the benzotriazole ring.

X-ray Diffraction Analysis

Colorless crystals of 3-(N^{α}-tritylmethionyl)benzotriazole 1-oxide, $C_{30}H_{28}N_4O_2S$, were grown from acetone after recrystallization from diethyl ether/petroleum ether (60–80 °C). Crystals grown from acetone also showed the usual IR carbonyl absorption band at 1730 cm^{-1}. The space group is $P2_12_12_1$, a = 8.7008 (5) Å, b = 14.3777 (15) Å, c = 20.846 (3) Å, Z = 4, at ca. 130 K. Within (sin θ/λ = 0.74, 4838 unique reflections were measured on a Nicolet-R3 diffractometer with cooling device LT-1. The structure was solved by the heavy atom method and refined by a blocked-cascade least-squares refinement (ca. 100 variables per block). The H atoms were refined with individual isotropic temperature factors after their location in a difference Fourier map while the other atoms were varied anisotropically. The 446 variables converged at R = 0.064 by using all unique reflections.

Registry No. 3-(N^{α}-tritylmethionyl)benzotriazole 1-oxide, 93984-96-4; N^{α}-tritylmethionine benzotriazolyl ester, 93984-97-5.

Supplementary Material Available: Details of data collection and structure refinement, tables of atomic parameters and thermal vibration parameters, and complete tables of bond lengths and bond angles (7 pages). Ordering information is given on any current masthead page.

Selective Decarbethoxylation of Ethyl 1,4-Dimethyl-3-(ethoxycarbonyl)-1*H*-pyrrole-2-acetate in 85% Phosphoric Acid

M. Žinić,* J. Kuftinec, H. Hofman, and F. Kajfež

Podravka Research and Development, Department for Chemical Synthesis and Pharmacology, 41000 Zagreb, Radnička c. 224, Yugoslavia

Z. Meić

"Rudjer Bošković" Institute, POB 1016, 41000 Zagreb, Yugoslavia

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Decarboxylation of pyrrolecarboxylic acids is an important step in the synthesis of substituted pyrroles, giving intermediates for electrophilic substitution at vacated sites on the pyrrole ring.[1] Heating of some ethyl pyrrolecarboxylates or acyl pyrroles in 85% phosphoric acid results in decarbethoxylation or cleavage of acyl groups from the starting pyrrole molecule.[2,3] It was assumed that both decarbethoxylation and acyl cleavage proceed by the same mechanism involving a protonated pyrrole (Scheme I).[3]

However, the competitive route of hydrolysis and subsequent decarboxylation of the pyrrolecarboxylic acid may also be operative. This pathway was actually demonstrated by treating **1** (Chart I and II) in a mixture of 96% sulfuric acid, ethanol, and water.[4] In this medium intermediate

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