

Department of Pharmaceutical Chemistry, Pharmacy College
University of Kentucky

Benzotriazole Ring Cleavage and Rearrangement to 1-(2-Benzothiazolyl)benzotriazole

Ronald E. Orth and Soekení Soedigdo

While attempting the synthesis of several 1,1'-thiocarbonyldi-*N*-heteroaromatic compounds (1), the interaction of thiophosgene with benzotriazole was noted to result in an atypical product with an empirical formula of $C_{13}H_8N_4S$ (I), based on the microanalysis (2) and osmometric molecular weight determination (3), instead of the expected $C_{13}H_8N_6S$ (II). The sodium azide-iodine spot test for $\equiv C=S$ and $\equiv C-SH$, positive for the aforementioned thiocarbonyl products (liberation of nitrogen), gave a negative result for I (4).

Assignment of *ca.* 1530 cm^{-1} and *ca.* 708 cm^{-1} peaks, characteristic of two dome-shaped benzothiazole infrared absorption bands, was useful in making the determination of structure (5). I and II exhibited strong absorption in the $770\text{--}735\text{ cm}^{-1}$ region, indicative of 1,2- or 1,2,3-substitution of the benzene ring (6). Both showed no strong absorption in the $860\text{--}782\text{ cm}^{-1}$ region, suggesting that 1,2,4-benzene ring substitution was not the case. An absorption peak at 1618 cm^{-1} , attributed to benzotriazole, was present in I (7). The infrared spectra eliminated 5- or 6- substitution of benzothiazole as alternatives.

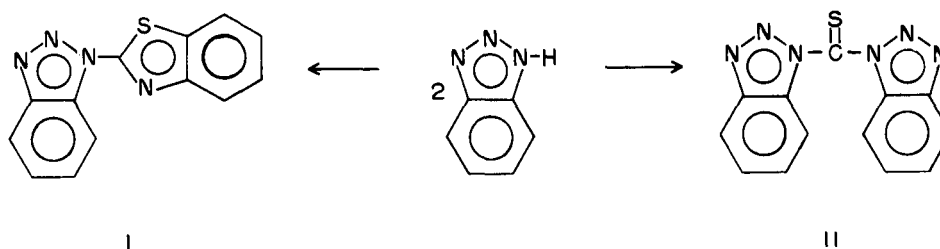
I absorbed in the ultraviolet region to give maxima comparable to those assigned to 1-alkyl- and 1-arylbenzotriazoles (8,9). Dal Monte Casoni, *et al.*, reported that the 1-methyl absorption peaks were attributed to excitations of the triazole chain and the B_{2u} transition of the benzene ring. Close structural similarity between benzotriazole and 1-methylbenzotriazole existed. The domination of the molecule state of benzotriazole by the asymmetric tautomeric $NH\cdot N:N$ group was shown (10). The same investigators stated that the $292\text{ m}\mu$, and $236\text{ m}\mu$ maxima

of 1-phenylbenzotriazole correspond to B_{2u} , triazole chain, and E_{2g} (or B_{1u}) vibrations, respectively. *p*-Nitro-substitution in the 1-phenyl- group shifted the $292\text{ m}\mu$ peak to $317\text{ m}\mu$ through the chromophore $p-O_2NC_6H_4N-$ (10). The data suggested that 1-substitution in the benzotriazoles accounted for the two shorter λ maxima and that an overlapping of the two aromatic π systems accounted for the large peak $>290\text{ m}\mu$. Since the proposed 1-(2-benzothiazolyl)- derivative exhibited maxima at slightly longer wave lengths in the three regions of mutual absorption than the 1-phenyl- compound, the results demonstrated that less energy was required to activate the more localized *N*-heteroaromatic π electrons than was the case with the electrons of the more resonance stabilized 1-phenylbenzotriazole. The reported λ maxima for benzothiazole were 216 , 252 , and $294\text{ m}\mu$ (11).

1-Substituted Benzotriazoles

Substituent	Maxima ($m\mu$)		
1-H-	260	274	-
1-Methyl-	250-260	270-280	-
1-(2-benzothiazolyl)- (a)	243	268	321
1-Phenyl-	236	261-268	292

(a) Acetonitrile solvent.



Nmr studies, using R. F. 60 mc. with a TMS internal reference standard, substantiated the infra-red and ultraviolet spectral studies. Peaks were found in the typically aromatic *H* region of 490-435 c.p.s. A doublet at 514 c.p.s. (δ 8.57) was assigned to the 7-*H* of the benzotriazole portion of the molecule. This proton exhibited *ortho* coupling and a paramagnetic shift of a magnitude indicative of an interaction with one of the heteroatoms of the thiazole ring (12). The electronegativity of *N* is 3.0 and 2.5 for *S* (13). The apparent preferred conformation was that shown by I, a planar molecule.

Preliminary studies, using gas chromatography, showed volatilization without fragmentation at 275°.

The formation of I appeared to involve an Elderfield Type E \rightarrow B general ring closure mechanism (-C-S- + -NC₆H₅) (14). II was easily prepared in good yield by modifying the conditions used to prepare I, and only one substituted-benzothiazole was found in the reaction mixture. A II to I rearrangement was suspected in the attempted synthesis of II from benzotriazole, rather than its sodium salt.

EXPERIMENTAL

1,1'-Thiocarbonyldibenzotriazole. Sodium Salt Method.

Six grams of benzotriazole (0.05 mole) was suspended in 70 ml. of benzene dried over sodium. To this suspension, 2.4 g. of sodium hydride (50% suspended in oil) was added in portions. A vigorous reaction took place with evolution of hydrogen leaving a curdy precipitate. The reaction mixture was refluxed for 1 hour. To this hot mixture, 2.9 g. of thiophosgene (0.025 mole) was added dropwise. The precipitate turned to a fine white-yellow powder, the mixture stirred at room temperature for 1 hour, then filtered through a Buchner funnel. No crystals separated when the dark yellow filtrate was evaporated, and cooled in an ice bath. The solid residue left on the funnel was extracted with hot acetone, from which yellow crystals were obtained, m.p. 176-178°.

Anal. Calcd. for C₁₃H₉N₃S: C, 55.6; H, 2.86; N, 30.0; S, 11.4. Found: C, 54.4; H, 3.05; N, 30.4; S, 12.0 (2).

1-(2-Benzothiazolyl)benzotriazole.

Benzotriazole (practical) was purified by dissolving in ethanol, treating with charcoal, filtering, and precipitating by the addition of water. Benzotriazole (11.9 g., 0.1 mole) was dissolved in 150 ml. of 1,4-dioxane in a reaction vessel, fitted with reflux condenser, stirrer, and dropping funnel. Thiophosgene (3.9 ml., 0.05 mole) in 25 ml. of dioxane was added dropwise with cooling and stirring. A precipitate formed with each drop of thiophosgene in the exothermic reaction. Following the addition which required a period of 30 minutes, the reaction was allowed to stir for 12 hours at room temperature before heating under reflux for another hour. The precipitate was collected by filtration and recrystallized from ethanol to give crystals melting at 168-169°. Fine pale yellow needles melting at 174° were obtained following recrystallization from aqueous ethanol. The yield was 50%.

Anal. Calcd. for C₁₃H₉N₃S: C, 62.0; H, 3.17; N, 22.2; S, 12.7. Found: C, 61.7; H, 3.10; N, 22.4; S, 12.5 (2). Molecular Weight Determination: Calcd: 252. Found: 252.5 \pm 0.8 (3).

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