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REACTION OF BENZO[b]THIOPHENE 1,1-DIOXIDE WITH IODINE AZIDE AND BROMINE AZIDE: X-RAY STRUCTURE ANALYSES OF THE ADDUCTS

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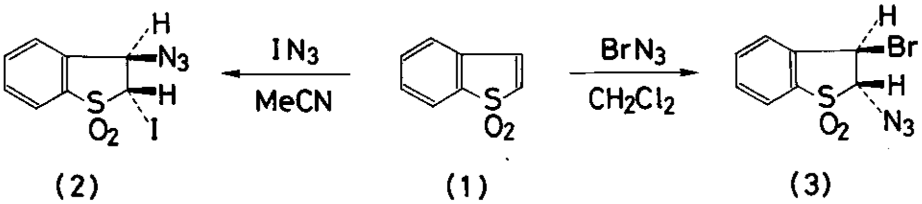
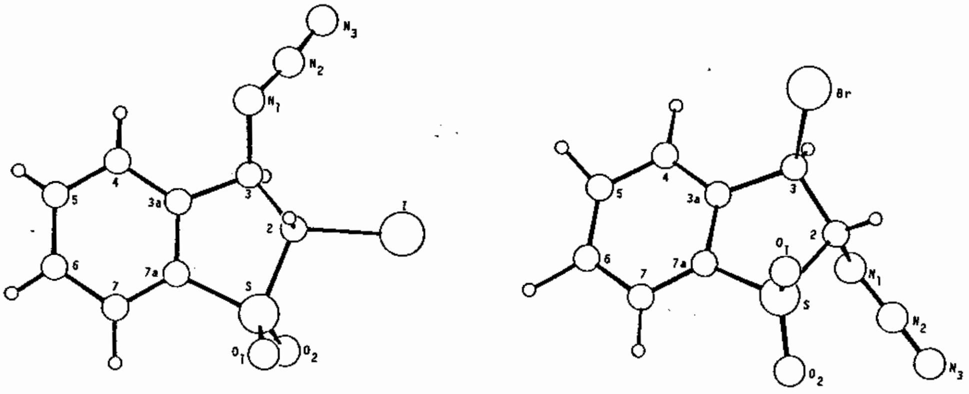
Abstract —— Benzo[b]thiophene 1,1-dioxide reacts with iodine azide and bromine azide to give trans-3-azido-2-iodo- and trans-2-azido-3-bromo-2,3-dihydrobenzo[b]thiophene 1,1-dioxides, respectively, whose structures were determined by X-ray structure analyses.

In a continuation of our studies on the reaction of iodine azide with the five-membered heterocyclic compounds such as indoles[1-3] and benzo[b]furan,[1] we have examined the behavior of benzo[b]thiophene and its 1,1-dioxide towards iodine azide and bromine azide.

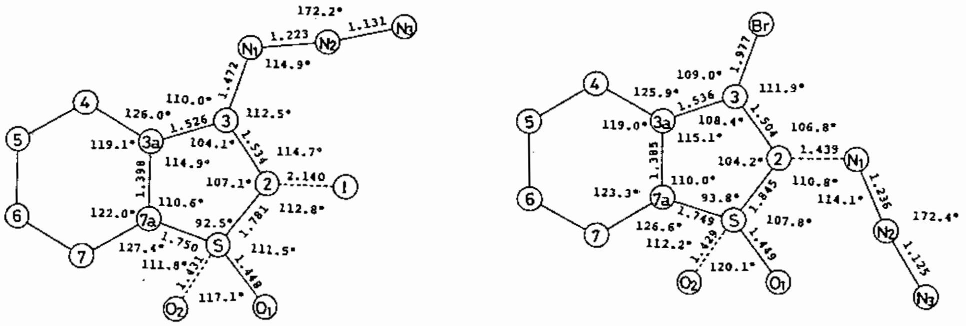
Benzo[b]thiophene 1,1-dioxide (1) was found to react smoothly with iodine azide (2 mol equiv) in dry acetonitrile[4] and bromine azide (1 mol equiv) in methylene chloride[5] at room temperature to give single 1:1 adducts (2)[6] (70%), m.p. 167-169°C, and (3)[6] (94%), m.p. 141-142°C, respectively. The structures of (2) and (3) were determined by the X-ray structure analyses.





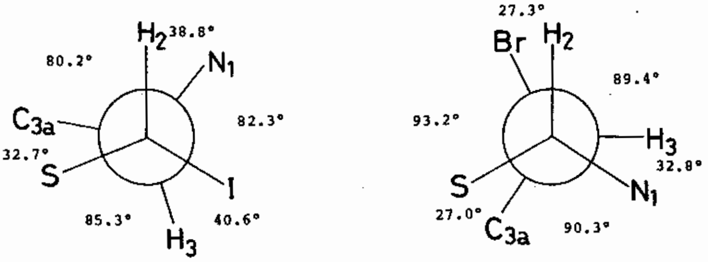
(2) (3)

Fig. 1. Perspective views of the molecules of (2) and (3).



(2) (3)

Fig. 2. Molecular dimension of compounds (2) and (3).

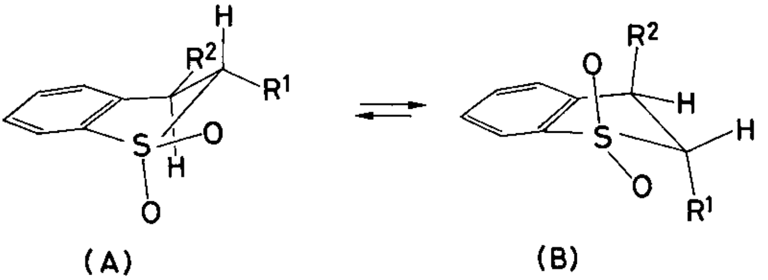


(2) (3)

Fig. 3. Dihedral angles in compounds (2) and (3).

Compound (2), $C_8H_6IN_3O_2S$, gave a triclinic crystal from methanol, space group $P\bar{1}$, a=7.659(3), b=8.058(3), c=9.806(3) Å; α=97.91(3), β=102.41(3), γ=111.45(3)°; μ (M_oK_α)=32.1 cm^{-1}; D_x=2.08 gcm^{-3}; Z=2. Compound (3), $C_8H_6BrN_3O_2S$, gave a monoclinic crystal from methanol, space group $P2_1/c$, a=8.605(5), b=16.256(7), c=7.258 (4), β=101.00(4)°; $\mu(M_oK_\alpha)$=45.5 cm^{-1}; D_x=1.92 gcm^{-3}; Z=4. The structures of both the compounds were solved by the heavy-atom method and refined by least squares to R=0.044 and 0.064, respectively. The molecular structures of (2) and (3) are illustrated in Figure 1; some of pertinent bond lengths and bond angles are provided in Figure 2. The five-membered rings of both the molecules have an envelope form in which C-2 atom lies out of the plane [0.508 Å for (2) and 0.406 Å for (3)] of the four other atoms (S, C_3, C_{3a}, and C_{7a}); in compound (2) the bulky 2-iodo and 3-azido groups are equatorial (conformer A), while in (3) both 2-azido and 3-bromo groups are axial (conformer B). The dihedral angles between H_2-C_2-C_3-H_3 were 161.7° for (2) and 89.4° for (3) as shown in Figure 3.

It is interesting to note that (2) and (3) have the same large coupling constant ($J_{2,3}$) of 7 Hz.[7] This suggests that in solution both (2) and (3) exist as conformer A.[8]



The formation of (2) is easily rationalized by a similar mechanism to that proposed for the reaction of open-chain vinyl sulfones with iodine azide,[9] which involves an iodonium ion intermediate. The reaction of (1) with bromine azide, however, may proceed by a radical mechanism[5] which would involve initial attack of $N_3\cdot$ radical on the double bond followed by attack of Br· at the benzylic position.

In contrast to the case of (1) treatment of benzo[b]thiophene with iodine azide in acetonitrile[4] above -10°C led to an explosion. When the reaction was carried out at -75°C, an oily mixture of azide-containing products was obtained but we discontinued further investigation because of poor reproducibility of the reaction and danger of explosion.

REFERENCES AND NOTES

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6. Compound (**2**): ν_{max} ($CHCl_3$) 2110 (N_3), 1320, 1145 (SO_2) cm^{-1}; δ ($DMSO-d_6$) 5.61 (1H, d, *J*=7 Hz), 5.83 (1H, d, *J*=7 Hz), and 7.55-8.1 (4H, m). Compound (**3**): ν_{max} ($CHCl_3$) 2110 (N_3), 1330, 1170 (SO_2); δ ($CDCl_3$) 4.98 (1H, d, *J*=7 Hz), 5.26 (1H, d, *J*=7 Hz), and 7.6-7.9 (4H, m).
7. Recently it has been shown that *cis*- and *trans*-2,3-dichloro-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxides have $J_{2,3}$=5.5 and 7 Hz, respectively. [P. Geneste, J. L. Olive, and S. N. Ung, *J. Heterocyclic Chem.*, 1977, **14**, 449].
8. The preferred conformation of these compounds may be determined by delicate balance of several factors: *e.g.*, a 1,3-diaxial repulsion between S-O and R^2 substituent (conformer B), an unfavorable interaction between peri-hydrogen (H-4) and equatorial R^2 substituent (conformer A), and dipole-dipole and/or steric repulsion between S-O and R^1 substituent (conformers A and B).
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