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A NOVEL NEW HETEROCYCLE FROM THE REACTION OF AZIDE ION WITH 2,3-DIPHENYLTHIIRENE 1,1-DIOXIDE

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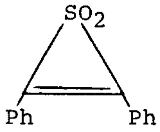
Previous studies of the reactions of 2,3-diphenylthiirene 1,1-dioxide (**1**) have shown that nucleophiles react with **1** either *via* attack at the sulfur center by harder nucleophiles, or at the vinyl carbon atom by softer nucleophiles.[1] We anticipated that azide ion would react with **1** either at sulfur or carbon to give an intermediate(s) which might undergo ring closures[2] to generate interesting heterocycles containing sulfur and one or more nitrogen atoms.

In acetonitrile, **1** reacts with lithium azide at room temperature to give the vinyl azides **2** and **3**, azirine **4**, triazole **5**, and a new compound, shown by a X-ray diffraction study to be the first reported member of a new class of heterocycles: 2,6-diphenyl-4-(E-1,2-diphenylvinyl)-1,3,4,5-thiatriazine 1,1-dioxide (**6**). Interestingly, this compound results from a reaction in which all three of the nitrogen atoms of azide ion are alkylated in the final product.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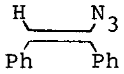
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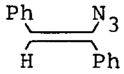
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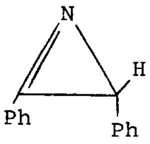
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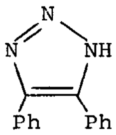
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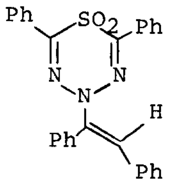
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In a typical experiment, lithium azide (255 mg, 5.20 mmoles) was allowed to react with **1** (250 mg, 1.03 mmoles) in 8 ml of acetonitrile at room temperature. After 20 hrs., the reaction mixture was filtered, and the solvent was removed *in vacuo*. Chromatography of the resulting yellow oil (preparative TLC, silica gel, 50:50 dichloromethane:petroleum ether) afforded fractions A (R_f = 1.0, 29 mg), B (R_f = 0.5, 51 mg), C (R_f = 0.4, 18 mg), and D (R_f = 0.0, 51 mg). Fraction A provided cis vinyl azide 2 and trans vinyl azide 3, which were thermally cyclized (refluxing hexane, 3 hrs) to azirine 4. These compounds were identified by comparison with authentic samples prepared independently.[3] Crystallization of fraction C from hexane gave additional 4; the total yield of this compound was 23 mg (11%). Crystallization of fraction B from dichloromethane-hexane afforded 47 mg (20%) of 6.[4] Further chromatography (preparative TLC, silica gel, 97:3 dichloromethane:methanol) of fraction D provided 17 mg (7%) of triazole 5, which was identified by comparison with an independently synthesized sample.[5]

Slow crystallization of 6 from isooctane gave crystals suitable for X-ray diffraction analysis. Data were collected on a Picker FACS-I diffractometer with graphite crystal monochromatized MoK radiation (λ = 0.71069 Å). The crystal data are: monoclinic, $P\ 2_1/n$; a = 8.580(2) Å, b = 11.174(3) Å, c = 24.592(7) Å, B = 95.04(2)°; Z = 4. Intensities were measured with the θ - 2θ scan method to a 2θ maximum of 50°. 2635 of the 4133 unique reflections were $3\sigma(I_o)$ above background. The structure was solved by direct methods and refined by the full-matrix least-squares technique. The calculations included anisotropic temperature factors for C,S,O, and N, and isotropic terms for H. The final $R(\Sigma|F_o - F_c|/\Sigma F_o)$ and weighted $R([\Sigma w(F_o - F_c)^2/\Sigma w\ F_o^2]^{1/2}$; $w = 1/\sigma\ (F_o)$ factors are 0.043 and 0.036. An ORTEP drawing is shown in Figure I.

Scheme 1 offers a rationalization for the products observed in this reaction. Presumably, the azirine 4 results from the thermal loss of nitrogen from the vinyl azides; the cis isomer 2 is particularly prone to undergoing this reaction.[3] Control experiments have shown that 2 and 3 do not isomerize under reaction conditions, but are converted to 4.[6]

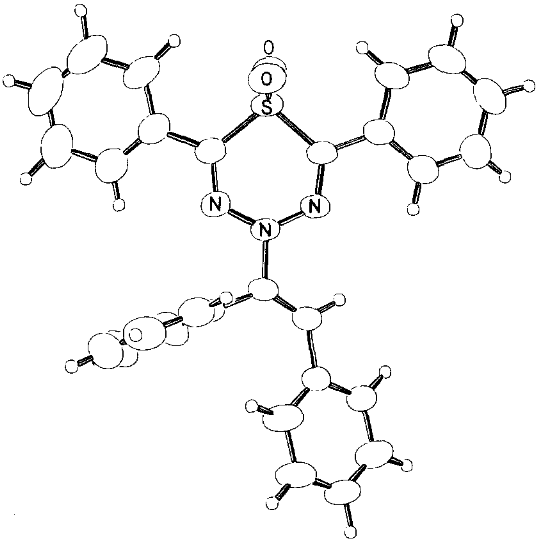
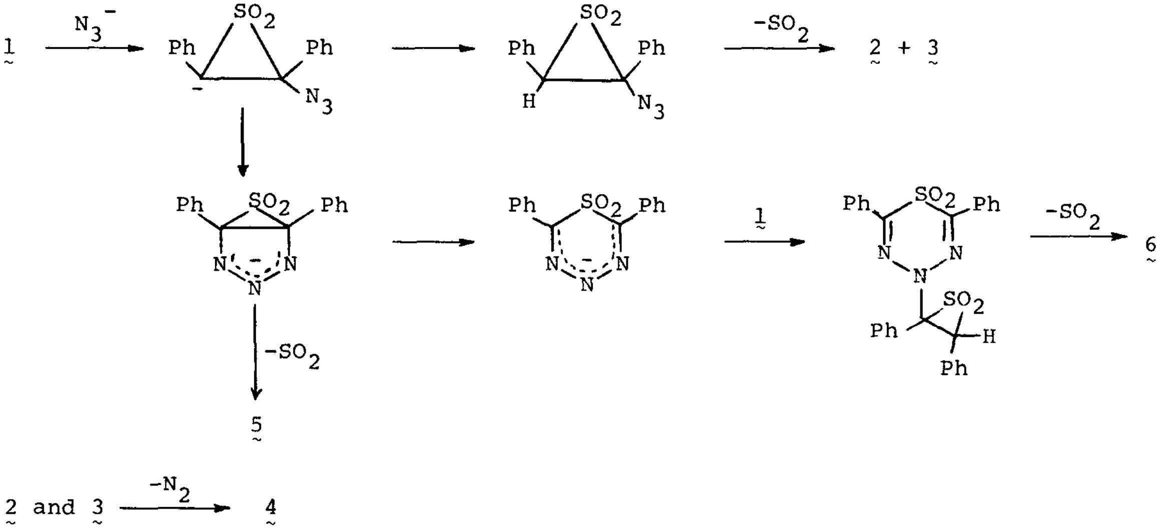


Figure I. ORTEP Drawing of 2,6-Diphenyl-4-(E-1,2-diphenylvinyl)-1,3,4,5-thiatriazine 1,1-Dioxide

Scheme 1



Acknowledgment. The crystallographic computations were supported through the facilities of the University of Maryland Computer Science Center.

References and Footnotes.

1) B. B. Jarvis, W. P. Tong, and H. L. Ammon, J. Org. Chem., **40**, 3189 (1975).
2) For example, vinyl azides possessing an acidic terminal proton undergo base promoted cyclizations to triazoles: G. Beck and D. Gunter, Chem. Ber., **106**, 2758 (1973) and references therein.
3) F. W. Fowler, A. Hassner, and L. A. Levy, J. Am. Chem. Soc., **89**, 2077 (1967)
4) 6: m.p. 181.5-182°; IR(KBr) 1305, 1290, and 1125 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 6.9-8.0 (m); UV (EtOH) λmax 230 (ε = 43,000), 275 (sh), 330 (ε = 44,000), and 375 (sh)nm. Anal. Calcd. for $C_{28}H_{21}N_3O_2S$: C, 72.57, H, 4.54, N, 9.07, S, 6.91. Found: C, 72.58, H, 4.55, N, 8.92, S, 6.89.
5) F. P. Woerner and H. Reimlinger, Chem. Ber., **103**, 1908 (1970).
6. After 2 hrs. at room temperature, the reaction of **2** → **4** is 55% complete. **3** proved to be more stable under reaction conditions; after 20 hrs it was only 25% converted to **4**.