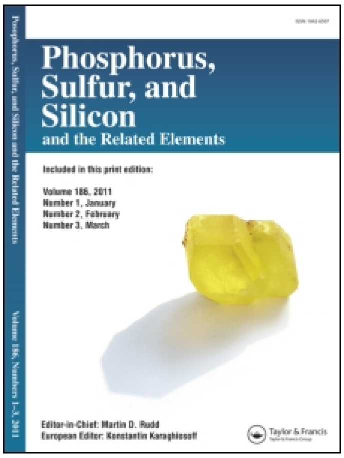

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1,1-BIS(PHENYLSULFONYL)-4-DIETHYLAMINO-1,3-BUTADIENE$_9$ A FULLY DELOCALIZED “PUSH-PULL” DIENE

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Communication

1,1-BIS(PHENYLSULFONYL)-4-DIETHYLAMINO-1,3-BUTADIENE, A FULLY DELOCALIZED "PUSH-PULL" DIENE

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The title compound is obtained from the reaction of phenyliodonium bis(phenylsulfonyl)methanide and diethylamine. Its structure and properties suggest that it is a fully delocalized system.

Key words: Phenyliodonium bis(phenylsulfonyl)methanide; 1,2-bis(phenylsulfonyl)-4-diethylamino-1,3-butadiene; push-pull butadiene.

Phenyliodonium bis(phenylsulfonyl)methanide, 1 is a reactive and versatile ylide. Most of its reactions involve a facile heterolytic C—I bond cleavage, furnishing formally bis(phenylsulfonyl)carbene. This may undergo loss of SO_2 with rearrangement[1] or typical C—H insertions,[2,3] transylidations[4] and cyclo-additions.[2,5] The carbanionic C of 1 is not nucleophilic and some reactions appearing formally to belong to this type follow probably electron transfer pathways.[6] In this communication a new unusual reaction of 1 is reported involving a series of transformations.

Simple stirring of 1 in dichloromethane with diethylamine leads to the isolation of a yellow compound to which the structure of 1,1-bis(phenylsulfonyl)-diethylamino-1,3-butadiene, 2, is assigned.

The structure of 2 was established by X-ray crystallography (Figure 1). It is worth noting that all three C—C bonds of the butadiene skeleton are virtually of equal length (1.375–1.378 Å) with a transoid configuration. Other features of interest in 2 are the short lengths of C_4—N and C_1—S bonds: the former (1.318 Å) is indicative of considerable double bond character, whereas the latter (1.745 Å) has an intermediate value between that of aromatic sulfones[7] (1.774 Å) and triphenylarsonium

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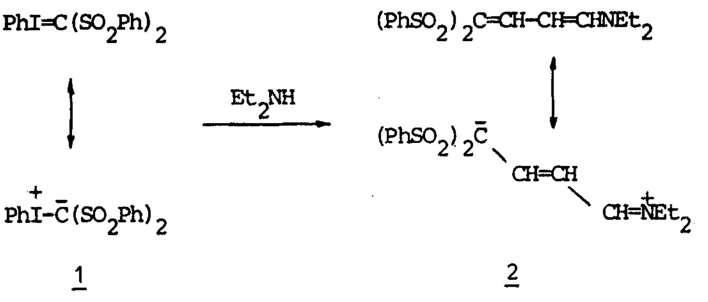

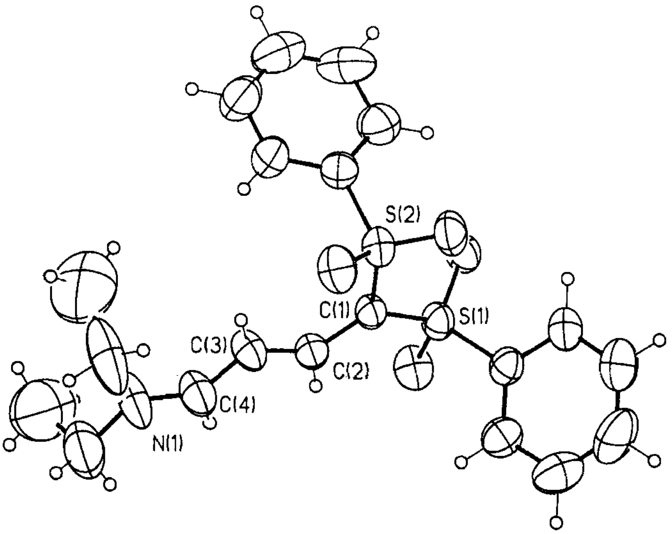

FIGURE 1 View of 2. Principal dimensions are: C(1)—S (mean) 1.746 (2); S—O (mean) 1.436 (3); S—C (phenyl) (mean) 1.774 (2); C(1)—C (2) 1.377 (5); C(2)—C(3) 1.378 (4); C(3)—C(4) 1.375 (6); C(4)—N(1) 1.318 (5) Å.

bis(phenylsulfonyl)methanide[8] (1.702 Å). These characteristics suggest that 2 may be best described as dipolar, belonging to the family of push-pull butadienes.[9]

In accordance with its structure, 2 is devoid of both enamine and Diels-Alder reactivity, e.g., it does not react with either acetyl chloride or such carbon dienophiles as tetracyanoethylene and dimethyl acetylenedicarboxylate. It reacted, however, with chlorosulfonyl isocyanate, 3,6-dipyridyl-1,2,4,5-tetrazine, 4-phenyl-1,2,4-triazoline-3,5-dione and singlet oxygen but in a complex way; in each case a mixture of no less than ten products was formed, so that these reactions were not further investigated. When treated with an excess of butyl lithium and then quenched in D_2O, both C_3 and C_4 hydrogen atoms of 1 were exchanged by deuterium.

The sequence of reactions leading to 2 is undoubtedly a very complex one. Catalysts such as Cu(acac)$_2$ and AIBN promoting, respectively, carbene and free radical generation do not favor its formation. Among other possibilities, a plausible pathway may involve the initial formation of a zwitterionic iodinane resulting from direct nucleophilic attack of diethylamine on positive iodine of 1, i.e., Et_2NH^+-

I(Ph)C$^-$(SO$_2$Ph)$_2$. This adduct can be transformed into 1,1-bis(phenylsulfonyl)-1-propene and then into its 3-isomer; reaction of the latter with more 1 would afford 1,1,4-tris(phenylsulfonyl)-1,3-butadiene which with diethylamine will eventually produce 2. It is noted that other secondary amines such as pyrrolidine and also N-methylpiperidine react with 1 with formation of products not yet identified.

EXPERIMENTAL

1,1-Bis(phenylsulfonyl)-4-diethylamino-1,3-butadiene (2). To a suspension of 1 (957 mg, 1.92 mmol) in dichloromethane (8 ml) diethylamine (400 μl, 3.84 mmol) is added and the mixture is stirred at room temperature for 4h, with light protection. Evaporation of the solvent followed by column chromatography (silica gel, hexane-CH_2Cl_2 7:3) gives 2 (257 mg; m.p. 174–176°C, from CH_2Cl_2-Et_2O); λ_{max} (MeOH) 367 nm (ε 69600); v_{max} (Nujol) 1610, 1545, 1310, 1140 cm^{-1}; δ_H ($CDCl_3$) 1.17 (t, 6H), 3.35 (m, 4H), 6.22 (t, 1H), 7.30 (t, 2H), 7.43–7.67 (m, 6H), 7.97–8.20 (m, 4H); m/z 405 (M$^+$, 2), 223 (7), 83 (100).

Anal. Calcd for $C_{20}H_{23}NO_4S_2$: C, 59.25; H, 5.67; N, 3.45.
Found: C, 59.14; H, 5.59; N, 3.54.
Crystal data: $C_{20}H_{23}NO_4S_2$, M = 405, yellow prisms 0.6 × 0.5 × 0.5 mm, monoclinic, space group C2/C, a = 25.639 (5), b = 11.097 (2), c = 15.461 (2) Å, β = 111.15 (2)^0, U = 4102 (1) Å,^{3} Z = 8, D_c = 1.31 g cm^{-3}, Mo-K radiation, λ = 0.71069 Å, μ (Mo-K$_a$) = 2.72 cm^{-1}, T = 291 K, F (000) = 1711.8, R = 0.0451 for 2142 unique observed [I > σ (I) > 3] reflections. Intensity data were collected on a Syntex P2$_1$ four circle diffractometer and the structure was solved by direct methods using SHELXTL.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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