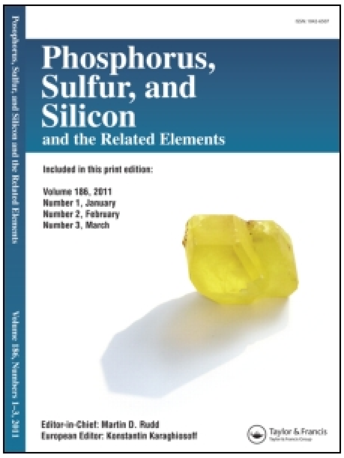

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The Reaction Between Phenyliodonium Bis(Phenylsulfonyl)Methanide and Pyrrolidine

Spyros Nikas[a]; Nestor Rodios[a]; Aris Terzis[b]; Anastassios Varvoglis[ac]
[a] Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki, Greece [b] Nuclear Research Center "Democritos" Aghia Paraskevi Attikis, Athens, Greece [c] Prof. A. Varvoglis, Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki, Greece

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Communication

THE REACTION BETWEEN PHENYLIODONIUM BIS(PHENYLSULFONYL)METHANIDE AND PYRROLIDINE

SPYROS NIKAS,[a] NESTOR RODIOS,[a] ARIS TERZIS[b] and ANASTASSIOS VARVOGLIS[a]*

[a]*Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki 540 06, Greece;* [b]*Nuclear Research Center "Democritos," Aghia Paraskevi Attikis, Athens, Greece*

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The main product from the title reaction is the enamine N-[2,2-bis(phenylsulfonyl)vinyl]-pyrrolidine, **4**. Tetrakis(phenylsulfonyl)propane, **3**, is a by-product, when dichloromethane is used; it is formed independently from this solvent and bis(phenylsulfonyl)methane in the presence of pyrrolidine.

Key words: Phenyliodonium bis(phenylsulfonyl)methanide, N-[2,2-bis(phenylsulfonyl)vinyl]-pyrrolidine, 1,1,3,3-tetrakis(phenylsulfonyl)propane, dichloromethane, pyrrolidine.

Some time ago an unusual reaction was reported[1] between the iodonium ylide **1** and diethylamine, leading to the formation of the dienamine 1,1-bis(phenylsulfonyl)-4-diethylamino-1,3-butadiene, i.e. $Et_2N—CH=CH—CH=C(SO_2Ph)_2$. In order to investigate further the behaviour of **1** towards amines, we have studied its reaction with pyrrolidine. With this amine a change in reactivity occurs and another unexpected enamine, **4**, is formed; in addition, when dichloromethane is used, the tetrasulfone **3** is also isolated.

Upon reaction of **1** with pyrrolidine in dichloromethane the following products were obtained: iodobenzene; bis(phenylsulfonyl)methane; N-(phenylsulfonyl)pyrrolidine, **2**; 1,1,3,3-tetrakis(phenylsulfonyl)propane, **3**; and N-[2,2-bis(phenylsulfonyl)vinyl]-pyrrolidine, **4** (Scheme I).

The structure of **3** was confirmed by X-ray crystallography (Figure 1). Its formation is due to an interaction of dichloromethane with bis(phenylsulfonyl)methane, which is always a by-product of the decomposition of **1**. Indeed, when pure bis(phenylsulfonyl)methane was allowed to react with dichloromethane in the presence of pyrrolidine, **3** was obtained in 80% yield. The mild conditions required for this double carbon—carbon bond formation are noteworthy, since dichloromethane does not usually serve as a good CH_2^{2+} synthon, especially with carbon nucleophiles. The mechanism of this substitution, after the initial formation of 1,1-bis(phenylsulfonyl)-2-chloroethane may involve either its reaction with more bis(phenylsulfonyl)methane or its convertion to 1,1-bis(phenylsulfonyl)ethylene,

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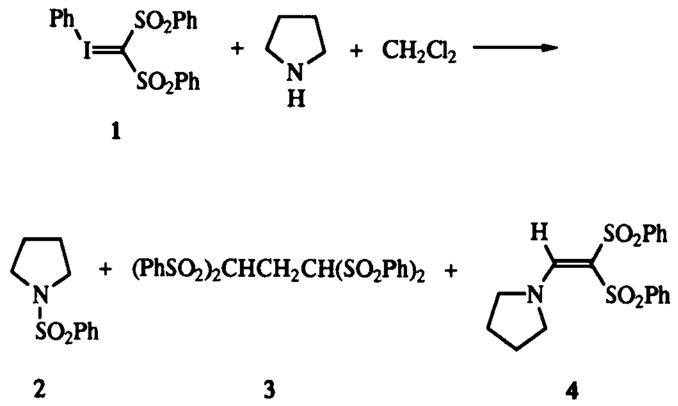
*Correspondence to: Prof. A. Varvoglis, Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki 540 06, Greece.



SCHEME I

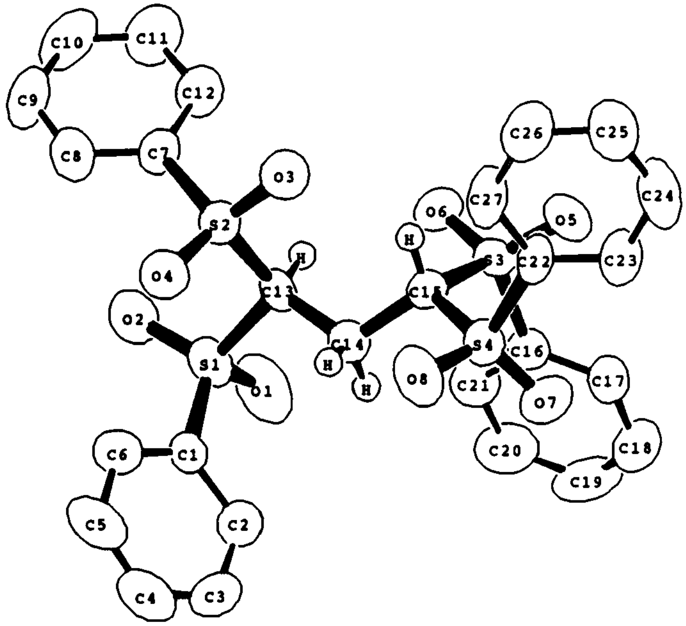


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FIGURE 1 ORTEP drawing of **3** with thermal ellipsoids at 50% probability.

which is known[2] to give with amines the tetrasulfone **3**. Actually, this compound was previously obtained also by several other methods, e.g. reaction of bis(phenylsulfonyl)methane with formaldehyde in basic environment[3] and from 1,1-bis(phenylsulfonyl)ethylene using no less than three different routes.[4]

A possible series of reactions leading to **4** involves the initial formation of an adduct, **5**, which is converted to **6**, with benzene elimination; this would react with the anion of bis(phenylsulfonyl)methane, probably through **7**, eliminating ben-

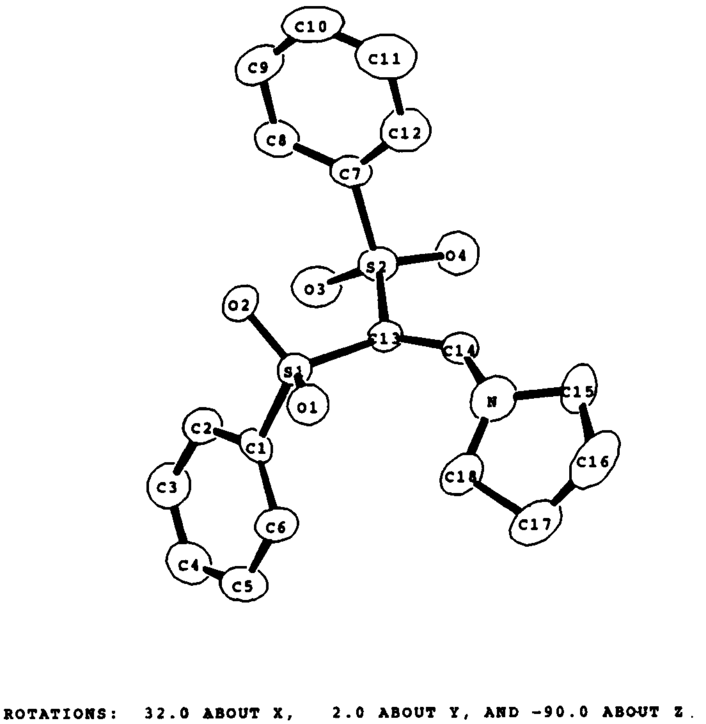
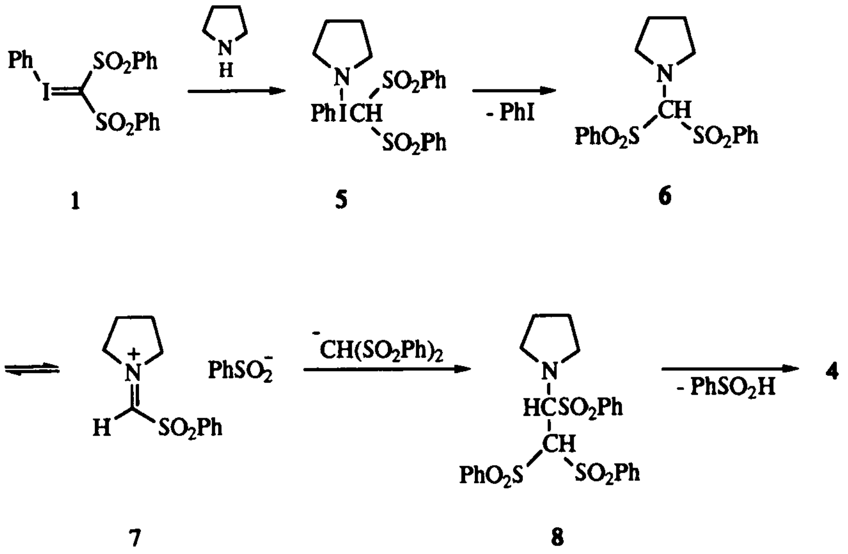


FIGURE 2 ORTEP drawing of **4** with thermal ellipsoids at 50% probability.



SCHEME II

zenesulfinic acid, to afford **8** and eventually **4** (Scheme II). An alternative pathway might involve the intermediacy of N-[tris(phenylsulfonyl)vinyl]-pyrrolidine, which with pyrrolidine should afford **4** and **2**.

EXPERIMENTAL

N-[2,2-bis(phenylsulfonyl)vinyl]-pyrrolidine (**4**). To a cold (−10°C) suspension of **1** (400 mg, 0.8 mmol) in dry chloroform (2 ml) a solution of pyrrolidine (200 mg, 0.8 mmol) in chloroform (1.3 ml) is added slowly, keeping temperature below −5°C. The reaction mixture is stirred at room temperature for 5 h, the solvent is evaporated and the residue subjected to column chromatography (silica gel, hexane-ethyl acetate). After iodobenzene, **2** and bis(phenylsulfonyl)methane, compound **4** is obtained (57 mg; 15% yield; m.p. 204–206°C, from chloroform-diethyl ether); ν_{max} (Nujol) 1618, 1315, 1291, 1140 cm^{-1}; δ_H ($CDCl_3$), (300 MHz): 1.89 (m, 4H), 3.47 (m as bs, 2H), 3.72 (m as bs, 2H), 7.46–7.58 (m, 6H), 7.93–7.97 (m as d, 2H), 8.14–8.17 (m as d, 2H), 8.19 (s, 1H); m/z 377 (M, 22), 236 (35), 235 (66), 170 (100).

1,1,3,3-Tetrakis(phenylsulfonyl)propane (**3**). To a solution of bis(phenylsulfonyl)methane (300 mg, 1 mmol) in dichloromethane (2 ml), cooled at −10°C, is added a solution of pyrrolidine (71 mg, 1 mmol) in dichloromethane (1 ml). The reaction mixture is allowed to stand at room temperature for 5 days and the residue, after evaporation of the solvent, is recrystallized from chloroform-diethyl ether (245 mg, 80%; m.p. 199–201°C, reported[4] m.p. 191–192°C); ν_{max} (Nujol) 1577, 1328, 1312 cm^{-1}; δ_H ($CDCl_3$) 2.98 (2H, t, J = 6.5 Hz), 5.64 (2H, t, J = 6.5 Hz), 7.36–7.80 (12H, m), 7.81–8.14 (8H, m); m/z 449 (1), 437 (1), 385 (12), 373 (15), 309 (55), 297 (50), 141 (55), 77 (100).

Crystal Data. a) $C_{18}H_{19}NO_4S_2$ (**4**), M = 377.47, orthorhombic, a = 20.794 (2), b = 9.2550 (8), c = 18.592 (1) A, V = 3577.87 A, λ = 0.7107 A, space group Pbca (No. 61), Z = 8, Dcalc = 1.402 Mg·m^{-3}, μ (Mo-Ka) = 3.10 cm^{-1}. b) $C_{27}H_{24}O_8S_4$ (**3**), M = 604.72, orthorhombic, a = 8.3033 (5), b = 15.687999), c = 21.062 (1) A, V = 2743.56 A, λ = 0.7107 A, space group $P2_12_12_1$ (No. 19), Z = 4, Dcalc = 1.494 Mg·m^{-3}, μ (Mo-Ka) = 3.80 cm^{-1}. Unit cell dimensions were determined by using the angular settings of 24 automatically centered reflections in the range $11 < 2\theta < 24$.

Data Collection and Processing. $P2_1$ Nicolet diffractometer, θ-2θ scan, scan range 2.5 + a_1a_2 separation, Zr-filtered Mo-radiation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no delay. Lorentz, polarization but no absorption corrections were applied using Crystal Logic software. For (**4**): scan speed 1.5 deg/min, 3779 reflections collected ($2\theta_{max}$ = 51 deg, +h, k.1), 3332 unique [merging R = 0.0077], giving 2449 with Fo > 2.0σ(Fo). For (**3**): scan speed 4.5 deg/min, 5810 reflections collected ($2\theta_{max}$ = 52 deg, +h, k.1), 5387 unique [merging R = 0.0330], giving 3604 with Fo > 4.0σ(Fo).

NOTE

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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