Base-promoted Reaction of a Hydrazonyl Chloride with 1-Phenylsulphonylpropyne

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Treatment of methyl 2-chloro-2-phenylhydrazonoacetate (**1**) with 1-phenylsulphonylpropyne (**3**) in the presence of triethylamine gives pyrazole derivatives due to cycloadditions of a nitrile imine intermediate with **3** and with its rearranged product phenylsulphonylallene (**4**).

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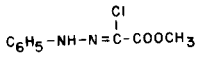
1,3-Cycloadditions of nitrile imines to acetylenes represent a well known route to pyrazoles. Aiming to the synthesis of the unreported derivative **5** for biological testing, we thought to obtain it upon treatment of the hydrazonyl chloride **1** with 1-phenylsulphonylpropyne **3** in the presence of triethylamine, according to the most common procedure for generating *in situ* nitrile imines [2]. In reality, a complex reaction course was observed due to the concomitant isomerization of **3** to phenylsulphonylallene **4**



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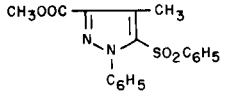
When equimolecular amounts of **1** and **3** were heated in boiling benzene in the presence of some excess of triethylamine, the resulting product was a mixture of several components which were isolated in the pure state after repeated chromatographic separations. The following compounds were obtained: **7** (14%), **8** (10%), **5** (7%), **9** (21%) and **10** (9%) [3]. The isolation of these products suggested the opportunity of control experiments, which actually demonstrated that: (i) triethylamine promotes the reversible isomerization of **3** to **4**, the latter being rather unstable under prolonged heating; (ii) compound **4** reacts with **1** in the presence of triethylamine to give a mixture of the same products as those obtained from **3**.

A plausible accomodation of the above findings is summarised in the Scheme. That compound **4** may add nucleophilic species to the central carbon is a documented matter [4]. On the other hand, the obtainment of **5** as the sole cycloaddition product between **2** and **3**, with esclusion of the regioisomer **6**, is not fully surprising in the light of



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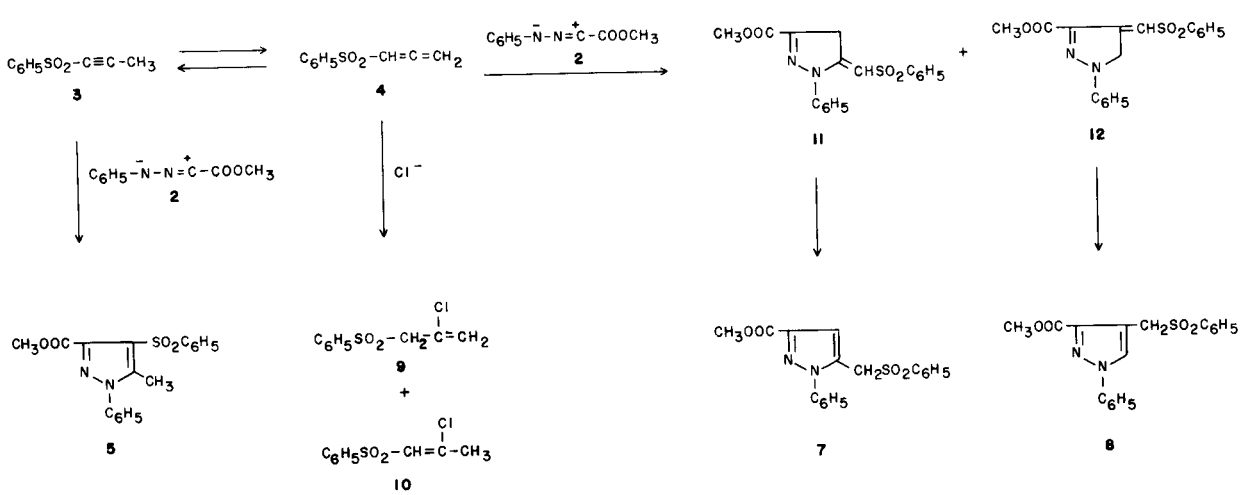
previous findings concerning the dipolarophilic reactivity of acetylenes bearing an electron-withdrawing substituent [5,6]. Finally, the product distribution observed in the reaction of **2** with **4** is particularly worthy of attention in view of the paucity of data dealing with 1,3-cycloadditions of nitrile imines to allenes [7].

It remains to be added that compound **5** can be alternatively prepared in substantial yield upon treatment of **1** with phenylsulphonylacetone in the presence of sodium methoxide.

SCHEME



EXPERIMENTAL

Melting points were determined on a Büchi apparatus and are uncorrected. The nmr spectra were recorded on a Varian EM-390 instrument with TMS as an internal standard. Ir spectra were taken on a Perkin-Elmer 377 spectrophotometer.

Preparations of compounds **1** [8], **3** [4] and **4** [4] are available in the literature.

Reaction of Hydrazonyl Chloride **1** with 1-Phenylsulphonylpropyne **3**.

A solution of **1** (3.5 g) and **3** (3.0 g) in benzene (170 ml) was treated with triethylamine (2.5 g) and refluxed for 20 hours. The mixture was washed with aqueous hydrochloric acid and dried with sodium sulphate. The solvent was removed and the residue was chromatographed on a silica gel column (550 g) with diethyl ether-light petroleum (2:1) as eluent.

First fractions gave unchanged **1** (0.35 g) followed by 2-chloro-1-phenylsulphonylpropene **10** (0.33 g), bp 130-135° at 0.4 mm Hg; nmr (deuteriochloroform): δ 2.60 (3H, s), 6.55 (1H, s) and 7.4-8.1 (5H, m); ms: 216 (M^+). Subsequent fractions contained **9** [4] (0.76 g). Further elution gave 3-methoxycarbonyl-5-methyl-1-phenyl-4-phenylsulphonylpyrazole **5** (0.42 g), mp 141° (from diisopropyl ether-benzene); ir (Nujol): 1750 cm^{-1}; nmr (deuteriochloroform): δ 2.65 (3H, s), 3.90 (3H, s), 7.2-7.7 (8H, m), and 8.1-8.3 (2H, m); ms: 356 (M^+, 23), 77 (100).

Anal. Calcd. for $C_{18}H_{16}N_2O_4S$: C, 60.7; H, 4.5; N, 7.9. Found: C, 60.5; H, 4.4; N, 7.6.

Subsequent fractions provided 3-methoxycarbonyl-1-phenyl-4-(phenylsulphonyl)methylpyrazole **8** (0.60 g), mp 149° (from ethanol-diisopropyl ether); ir (Nujol): 1730 cm^{-1}; nmr (deuteriochloroform): δ 3.74 (3H, s), 4.80 (2H, s), 7.3-7.9 (10H, m) and 8.16 (1H, s); ms: 356 (M^+, 2), 215 (100).

Anal. Calcd. for $C_{18}H_{16}N_2O_4S$: C, 60.7; H, 4.5; N, 7.9. Found: C, 60.8; H, 4.5; N, 7.7.

The last eluted product was 3-methoxycarbonyl-1-phenyl-5-(phenylsulphonyl)methylpyrazole **7** (0.84 g), mp 144° (from benzene-diisopropyl ether); ir (Nujol): 1735 cm^{-1}; nmr (deuteriochloroform): δ 3.95 (3H, s), 4.42 (2H, s), 6.91 (1H, s) and 7.0-7.8 (10H, m); ms: 356 (M^+, 3), 215 (100).

Anal. Calcd. for $C_{18}H_{16}N_2O_4S$: C, 60.7; H, 4.5; N, 7.9. Found: C, 60.9; H, 4.6; N, 7.8.

Reaction of Hydrazonyl Chloride **1** with Phenylsulphonylacetone.

A solution of **1** (4.4 mmoles) and phenylsulphonylacetone [9] (4.4 mmoles) in methanol (35 ml) was treated with 0.22 *M* sodium methoxide in methanol (20 ml) and refluxed for 30 minutes. The solvent was removed under reduced pressure, and the residue was taken up with water and extracted with benzene. The organic solution was dried with sodium sulphate and evaporated. The remaining material was treated with diisopropyl ether and filtered to afford practically pure **5** (54%).

REFERENCES AND NOTES

[1] To whom correspondence should be addressed.

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[3] The yields refer to the starting moles of **3**. An amount of unchanged **1** was also recovered.

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