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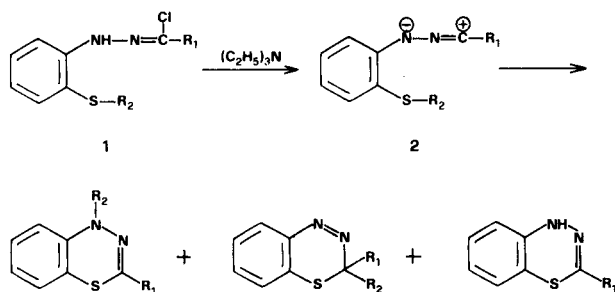
Received December 14, 1981

Functionalized 1-nitrohydrazones **5** react with sodium hydride in boiling benzene to afford different types of ring-closed products. The formation of the latter can be ascribed to competitive modes of evolution of first-formed nitrile imines.

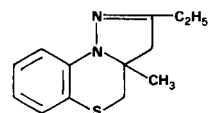
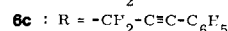
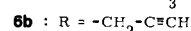
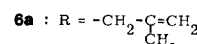
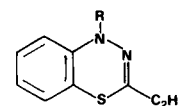
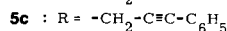
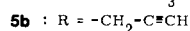
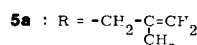
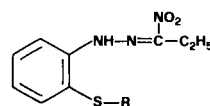
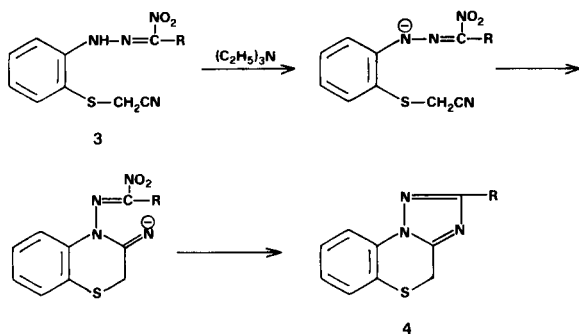
J. Heterocyclic Chem., **19**, 905 (1982).

Intramolecular reactions of functionalized nitrile imines are receiving attention as representing a versatile tool for the acquisition of heterocyclic systems (2-5). In this field, we reported (6) that the reaction of 1-chlorohydrazones **1** with triethylamine gives rise, *via* nitrile imines **2**, to 4,1,2-benzothiadiazine derivatives (see Scheme I). Later, we found (7) that 1-nitrohydrazones **3** react under the same conditions to afford exclusively the tricyclic compounds **4**, the formation of which was interpreted as occurring without the intermediacy of nitrile imines (see Scheme II). The present report deals with the base-promoted behaviour of the structurally related 1-nitrohydrazones **5a-c** which possess an unsaturated group other than $C\equiv N$.

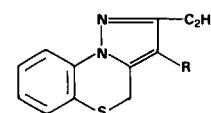
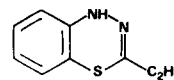
Scheme I



Scheme II



7

**8a** : R = F**8b** : R = C_6F_5 

9

Contrary to what previously had been observed in the case of **3**, compounds **5** were recovered unchanged after prolonged boiling in benzene (2-3 days) in the presence of a ten-fold excess of triethylamine. However, they disappeared within a few hours upon treatment with sodium hydride in boiling benzene. The chromatographic separation of the reaction mixtures gave the products indicated in the Table. The assigned structures are supported by elemental analyses, molecular weights, and spectral data; it is worthwhile to note that the uv spectra represent a useful tool for differentiating the various kinds of products.

These results are of interest since they demonstrate the following points: (i) the behaviour pattern illustrated in the Scheme II is peculiar to the 1-nitrohydrazones **3**, which possess a nitrile group able to undergo a nucleophilic attack by a neighbouring, negatively-charged nitrogen; (ii) as a consequence, the 1-nitrohydrazones **5** are not reactive towards weak bases, but can be forced to eliminate the

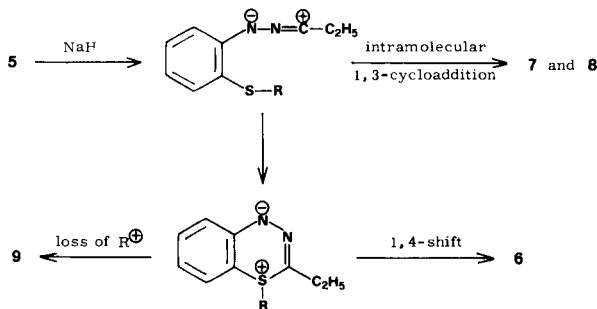
Table

Reaction of 1-Nitrohydrazones **5** with Sodium Hydride

Compound No.	Products	Yield %	Mp or Bp °C	UV, nm (ϵ) (ethanol)	NMR, δ (deuteriochloroform)	Analyses	
						Calcd.	Found
5a	6a	15	110-115/ 0.1 mm	309 (1100) 243 (8800)	1.24 (3H, t), 1.82 (3H, s), 2.50 (2H, q), 4.27 (2H, s), 4.8-5.1 (2H, m), 6.6-7.3 (4H, m)	C, 67.20 H, 6.94 N, 12.06	67.15 6.86 12.01
	7	36	76-77 (diisopropyl ether)		1.18 (3H, t), 1.31 (3H, s), 2.40 (2H, q), 2.82 (2H, s), 2.73, 3.00 (2H, AB type, J = 12 Hz), 6.6-7.2 (2H, m), 7.3-7.5 (1H, m)	C, 67.20 H, 6.94 N, 12.06	67.12 6.88 12.20
	9	8	125-130/ 0.5 mm	307 (950) 241 (6500)	1.22 (3H, t), 2.51 (2H, q), 6.6-6.8 (1H, m), 6.9-7.3 (3H, m), 7.4 (1H, broad s)	C, 60.66 H, 5.66 N, 15.72	60.81 5.73 15.62
5b	6b	6	180-185/ 0.5 mm	303 (2000) 241 (11400)	1.10 (3H, t), 2.18 (1H, t, J = 2.5 Hz), 2.43 (2H, q), 4.42 (2H, d, J = 2.5 Hz), 6.9-7.6 (4H, m)	C, 66.65 H, 5.59 N, 12.96	66.83 5.88 13.01
	8a	64	185-190/ 0.5 mm	304 sh (4600) 280 (7500) 255 (26100)	1.30 (3H, t), 2.74 (2H, q), 4.00 (2H, s), 5.98 (1H, s), 6.9-7.4 (3H, m), 7.8-8.0 (1H, m)	C, 66.65 H, 5.59 N, 12.96	66.55 5.47 12.87
	9	4					
5c	6c	40	165-170/ 0.2 mm	305 (2100) 241 (28200)	1.22 (3H, t), 2.58 (2H, q), 4.67 (2H, s), 6.9-7.7 (9H, m)	C, 73.94 H, 5.52 N, 9.58	73.81 5.68 9.52
	8b	7	39-41 (<i>n</i> -pentane)	305 sh (3400) 281 (5100) 254 (10100)	1.23 (3H, t), 2.78 (2H, q), 4.00 (2H, s), 7.1-7.7 (8H, m), 8.0-8.2 (1H, m)	C, 73.94 H, 5.52 N, 9.58	73.85 5.44 9.46
	9	24					

nitrite ion in the presence of sodium hydride, thus originating nitrile imine intermediates; (iii) the latter species (as illustrated in the Scheme III) evolve according to competitive, intramolecular pathways which substantially parallel those previously observed in the reaction of 1-chlorohydrazones **1** with triethylamine (**6**). The minor extent of the cycloaddition process in the case of **5c** is reasonably accounted for by steric factors due to the phenyl group adjacent to the dipolarophilic moiety.

Scheme III



EXPERIMENTAL

The nmr spectra were recorded on a Varian EM-390 instrument with TMS as an internal standard. The ir and uv spectra were taken on Perkin-

Elmer 377 and Cary 219 spectrophotometers, respectively. Melting points were determined on a Büchi apparatus and are uncorrected.

Compound **5a** was prepared as previously reported (7).

Preparation of 1-Nitrohydrazones **5b** and **5c**.

Sodium nitrite (10 mmoles) in water (15 ml) was added to a solution of 2-(2-propynylthio)aniline (**8**) (9 mmoles) in 1 *N* hydrochloric acid (27 ml) under stirring and ice-cooling. The resulting mixture was adjusted to pH 4 with sodium acetate and a solution of the sodium salt of 1-nitropropane (10 mmoles) in 90% ethanol (35 ml) was added under vigorous stirring at 0-5°. After 3 hours at room temperature, the aqueous layer was decanted off and the remaining paste was dissolved in dichloromethane. The organic solution was washed with water, dried over sodium sulphate and evaporated. Recrystallization of the residue from diisopropyl ether gave **5b** (55%), mp 94-95°; ir (Nujol): 3280 cm⁻¹; nmr (deuteriochloroform): δ 1.28 (3H, t), 2.20 (1H, t, J = 2.5 Hz), 2.89 (2H, q), 3.50 (2H, d, J = 2.5 Hz), 6.9-7.8 (4H, m), 13.0 (1H, broad s).

Anal. Calcd. for C₁₂H₁₃N₃O₂S: C, 54.73; H, 4.97; N, 15.96. Found: C, 54.94; H, 4.81; N, 15.79.

Following the same procedure, 2-(3-phenyl-2-propynylthio)aniline (**9**) was converted to **5c** (47%), mp 63-64°; ir (Nujol): 3250 cm⁻¹; nmr (deuteriochloroform): δ 1.17 (3H, t), 2.72 (2H, q), 3.70 (2H, s), 6.9-7.8 (9H, m), 13.1 (1H, broad s).

Anal. Calcd. for C₁₈H₁₇N₃O₂S: C, 63.69; H, 5.05; N, 12.38. Found: C, 63.65; H, 5.22; N, 12.21.

Reaction of 1-Nitrohydrazones **5a-c** with Sodium Hydride.

A solution of **5** (5 mmoles) in dry benzene (500 ml) was treated with sodium hydride (15 mmoles) and refluxed for 6 hours. The undissolved material was filtered off, the solution was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column

with light petroleum-diethyl ether (2:1) as eluent. The isolated products are indicated in the Table in order of elution. All of them exhibited correct molecular peaks in the mass spectra.

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