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SYNTHESIS OF 13-PHENYL-9,15-DITHIA-2-AZATRICYCLO-[9.3.1.0^{3,8}]PENTADECA-1(14),3,5,7-TETRAENE*

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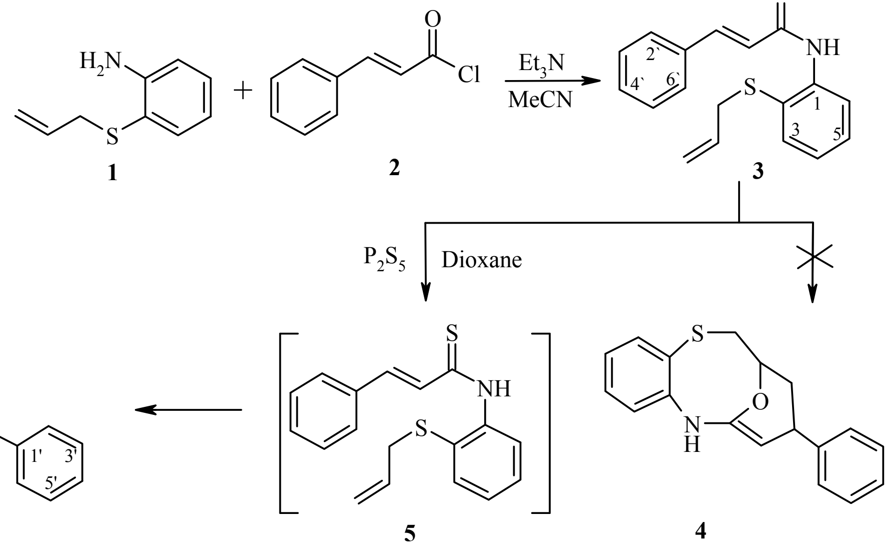
Domino reaction methodology has found increasing use in recent times for organic synthesis [1, 2]. In particular, domino reactions in which an initially formed heterodiene fragment takes part in subsequent cycloaddition reactions [1-4] are of particular interest.

In this work we have studied the potential formation of a novel heterocyclic system *via* an intramolecular hetero Diels-Alder type reaction of the initially formed product from the *N*-acylation of the 2-(2-propen-1-ylsulfanyl)aniline (**1**).



Reaction of the amine **1** with cinnamoyl chloride (**2**) gave compound **3** which has a C=C–C=O heterodiene system [5]. It was found that an intramolecular hetero Diels-Alder reaction to give compound **4** does not occur, even upon refluxing in toluene and with Lewis acid catalysts. It is known that α,β-unsaturated

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*Dedicated to the memory of Academician M. O. Lozinskii.

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thiocarbonyl fragments serving as dienes are convenient "building blocks" for the preparation of sulfur-containing six-membered heterocycles [3, 4]. Hence, it was of interest to prepare the thioamide analog of compound **3** and to study its possible participation in a cycloaddition reaction.

By carrying out a thionylation of compound **3** with P_2S_5 in dioxane, we prepared the 13-phenyl-9,15-dithia-2-azatricyclo[9.3.1.0^{3,8}]pentadeca-1(14),3,5,7-tetraene (**6**) which is a novel heterocyclic system containing thiopyran and dithiazocine rings. Formation of compound **6** evidently occurs *via* an intramolecular cycloaddition reaction of the intermediately formed compound **5**.

Hence, the scheme, we proposed for the conversion of the phenylpropeneamide **3** to the tricyclic compound **6,** makes an intramolecular thia type Diels-Alder reaction an attractive route to the synthesis of 3,4-dihydro-2*H*-thiopyrans condensed to eight-membered rings.

^{1}H NMR spectra were recorded on a Varian Mercury 400 MHz instrument for DMSO-d_6 solutions with TMS as internal standard. Mass spectra were obtained on an Agilent 1100 LC/MSD chromato-mass spectrometer with a Zorbax SB-C18 1.8 μ column using atmospheric pressure chemical ionization (APCI).

(2*E*)-3-Phenyl-*N*-[2-(2-propen-1-ylsulfanyl)phenyl]-2-propeneamide (3). Cinnamoyl chloride (**2**) (0.83 g, 5 mmol) was added with vigorous stirring to a solution of 2-(2-propen-1-ylsulfanyl)aniline (**1**) (0.82 g, 5 mmol) and Et_3N (0.7 ml, 5 mmol) in MeCN (5 ml). The product was heated to reflux, cooled to room temperature, and stirred to the formation of a precipitate. The precipitate was filtered off and purified by recrystallization from methanol. Yield 1.35 g (92%); mp 93-94ºC (mp 99-100ºC (EtOAc–hexane) [5]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.59 (2H, d, *J* = 6.8, CH_2); 5.03 (1H, d, *J* = 10.0) and 5.11 (1H, d, *J* = 16.9, $=CH_2$); 5.78-5.88 (1H, m, CH=); 7.10 (1H, d, *J* = 15.5, CH=); 7.18 (1H, t, *J* = 7.2, H-4); 7.25-7.29 (1H, m, H-5); 7.40-7.50 (4H, m, H-6 + H-3',4',5'); 7.60 (1H, d, *J* = 15.7, CH=); 7.67 (2H, d, *J* = 7.1, H-2',6'); 7.76 (1H, d, *J* = 7.5, H-3); 9.50 (1H, s, NH). Mass spectrum, *m/z*: 296 $[M+H]^+$. Found, %: C 73.01; H 5.99; N 4.58. $C_{18}H_{17}NOS$. Calculated, %: C 73.19; H 5.80; N 4.74.

13-Phenyl-9,15-dithia-2-azatricyclo[9.3.1.0^{3,8}]pentadeca-1(14),3,5,7-tetraene (6). Compound **3** (1.47 g, 5 mmol) was dissolved with heating in dry dioxane (10 ml) and P_2S_5 (0.6 g, 2.6 mmol) was added. The reaction mixture was refluxed for 72 h, cooled to room temperature, filtered through alumina, and the filtrate was poured into a beaker with ice. The precipitate formed was filtered off, washed with water, and recrystallized from aqueous ethanol. If the product formed a viscous liquid it was extracted with hot hexane and the extract was evaporated at room temperature. Yield 0.88 g (57%); mp 88-89ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.49 (2H, d, $^3J_{13,3a}$ = 7.0, H-13a,b); 5.04-4.98 (2H, m, H-2a,2b); 5.78-5.89 (1H, m, H-3); 7.05 (1H, d, $^3J_{14,15}$ = 15.6, H-14); 7.10 (1H, dd, *J* = 7.6 and *J* = 1.0, H-12); 7.24-7.29 (2H, m, H-10,11); 7.36-7.45 (3H, m, H-3',4',5'); 7.57 (1H, d, $^3J_{15,14}$ = 15.6, H-15); 7.62 (2H, d, *J* = 7.0, H-2',6'); 7.97 (1H, d, *J* = 8.0, H-9); 9.24 (1H, s, NH). Mass spectrum, *m/z*: 312 $[M+H]^+$. Found, %: C 69.20; H 5.58; N 4.37. $C_{18}H_{17}NS_2$. Calculated, %: C 69.41; H 5.50; N 4.50.

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