

THE REACTION OF 1-PHENYLBUT-1-YN-3-ONE WITH FURAN ALDEHYDES

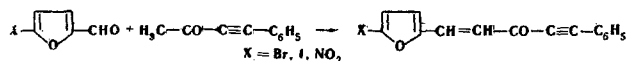
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The crotonic condensation of 5-bromo-, 5-iodo-, and 5-nitrofurfurals with 1-phenylbut-1-yn-3-one has been effected.

Continuing investigations in the field of highly unsaturated compounds of the furan series, we have attempted to synthesize vinylacetylenic furan ketones with a symmetrical arrangement of the unsaturated bonds relative to the carbonyl group. Up to the present time, there has been no information on this class of compounds in the literature. Of all the known methods, the most acceptable proved to be the crotonic condensation of an acetylenic methyl ketone with aldehydes in an acid or alkaline medium. As the methylene component we used 1-phenylbut-1-yn-3-one and as the carbonyl component bromo-, iodo-, and nitrofurfurals. In none of the cases did the reaction stop at the stage of the formation of the carbinol. The IR spectra of the compounds obtained showed the absence of a hydroxy group.



The bromo- and iodofurfurals reacted readily with the phenylbutynone in ethanolic solution in the presence of small amounts of 10-20% aqueous sodium hydroxide. Under these conditions nitrofurfural resinified completely. In this case, the reactions were carried out in glacial acetic acid solution with concentrated sulfuric acid as catalyst.

EXPERIMENTAL

a) Equimolar amounts of 1-phenylbut-1-yn-3-one and 5-bromo-furfural were dissolved with heating in a small amount of 70-80% ethanol. After cooling, a 10-20% aqueous solution of sodium hydroxide (in an amount of 0.5 ml per mM of the initial ketone) was added with stirring. The mixture was kept for 1 1/2 hr for the completion of the reaction. The crystals were filtered off with suction and washed with dilute hydrochloric acid and 50% ethanol. The yield of 5-(5'-bromo-2'-furyl)-1-phenylpent-4-en-1-yn-3-one was 69.2%, mp 119.5°-120° C (from 75% ethanol). Found, %: C 60.10; H 3.18; Br 26.41. Calculated for $\text{C}_{15}\text{H}_9\text{BrO}_2$, %: C 59.83; H 3.01; Br 26.53. IR spectrum: ν_{CO} 1617 (v.s.), $\nu_{\text{C}\equiv\text{C}}$ 2177 (w) and 2224 cm^{-1} (v.s.). 5-(5'-Iodo-2'-furyl)-1-phenylpent-4-en-1-yn-3-one was obtained similarly, yield 58.4%, mp 111-112° C (from ethanol). Found, %: C 52.01; H 2.76; I 36.31. Calculated for $\text{C}_{15}\text{H}_9\text{IO}_2$, %: C 51.77; H 2.61; I 36.46. IR spectrum: ν_{CO} 1609 (v.s.), $\nu_{\text{C}\equiv\text{C}}$ 2175 (m) and 2221 cm^{-1} (v.s.).

b) Concentrated sulfuric acid was added in drops to an equimolar mixture of 5-nitrofurfural and phenylbutynone in a small amount of glacial acetic acid and the mixture was left to stand at room temperature for 3 days. After this time, it had acquired a bright cherry-red coloration and the deposition of crystals had ceased. The yield of 5-(5'-nitro-2'-furyl)-1-phenylpent-4-en-1-yn-3-one was 40.7%, mp 202.5°-203.5° C (from ethanol). Found, %: C 67.11; H 3.54; N 5.43. Calculated for $\text{C}_{15}\text{H}_9\text{NO}_4$, %: C 67.42; H 3.39; N 5.24. IR spectrum: ν_{CO} 1606 (v.s.), $\nu_{\text{C}\equiv\text{C}}$ 2173 (m) and 2218 cm^{-1} (v.s.).

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6-(2-FURYL)IMIDAZOLO[2,1-b]THIAZOLE AND ITS DERIVATIVES

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Imidazol[2,1-b]thiazoles have been obtained by cyclizing thiazolium salts synthesized by the reaction of 2-aminothiazole and 2-amino-4-methylthiazole with 2-haloacetyl furans.

The reaction of 2-aminothiazole and 2-amino-4-methylthiazole with 2-haloacetyl furans in chloroform has given thiazolium salts (Table 1). If there is a 5-nitro-2-furyl or a 2-furyl group in position 4 of the thiazole ring, no thiazolium salts are formed. The

cyclization of the thiazolium salts has given imidazol[2,1-b]thiazoles (Table 2).

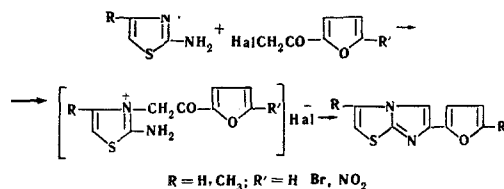


Table 1
Thiazolium Salts

Compound	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
2-Amino-4-methyl-3-(5-nitro-2-furacil)thiazolium bromide	253—255*	$C_{10}H_{10}BrN_3O_4S$	34.64	3.13	12.26	34.49	2.89	12.07	22.95
2-Amino-3-(2-furacil)-4-methylthiazolium bromide	174**	$C_{10}H_{11}BrN_2O_2S$	39.34	3.53	9.17	39.61	3.66	9.24	26.36
2-Amino-3-(5-nitro-2-furacil)-thiazolium bromide	208—210**	$C_9H_9BrN_3O_4S$	32.18	2.26	12.42	32.35	2.41	12.58	23.92
2-Amino-3-(5-bromo-2-furacil)-4-methylthiazolium chloride	223—225**	$C_{10}H_{10}BrClN_2O_2S$	35.30	2.69	8.14	35.57	2.99	8.30	34

*From a mixture of absolute ethanol and ether.

**From absolute ethanol.

Table 2

6-(2-Furyl)imidazolo[2,1-b]thiazole and Its Derivatives

Compound	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
3-Methyl-6-(5-nitro-2-furyl)imidazolo[2,1-b]-thiazole	214—215a	$C_{10}H_7N_3O_3S$	48.36	3.00	16.92	48.19	2.83	16.86	60
6-(2-Furyl)-3-methylimidazolo[2,1-b]thiazole	112—113a	$C_{10}H_8N_2OS$	58.58	3.79	13.64	58.80	3.95	13.72	66
6-(5-Nitro-2-furyl)-imidazolo[2,1-b]thiazole	220—221b	$C_9H_5N_3O_3S$	46.14	2.11	18.08	45.95	2.14	17.87	83
Its hydrobromide	240—242c	$C_9H_6N_3O_3S \cdot HBr$	34.00	2.14	13.55	34.19	1.91	13.29	74
6-(5-Bromo-2-furyl)-3-methylimidazolo[2,1-b]-thiazole	102—103a	$C_{10}H_7BrN_2OS$	42.44	2.84	10.15	42.40	2.49	9.90	42
Its hydrobromide	242—244c	$C_{10}H_7BrN_2OS \cdot HBr$	32.84	2.43	7.93	32.99	2.21	7.70	94
6-(2-Furyl)imidazolo[2,1-b]thiazole	96—98d	$C_9H_6N_2OS$	56.61	3.30	14.64	56.82	3.18	14.73	50

^aFrom ethanol. ^bFrom a mixture of benzene and heptane. ^cFrom absolute ethanol. ^dFrom aqueous ethanol.

2-Amino-3-(2-furacyl)thiazolium bromide [1, 2] and its 4-methyl derivative were cyclized by being boiled with an aqueous solution of sodium bicarbonate, while for the cyclization of the thiazolium salts containing bromine or a nitro group in position 5 of the furan ring it was sufficient to boil them with water or ethanol.

The action of hydrobromic acid in acetone on the imidazo[2, 1-b]thiazoles has given their hydrobromides.

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LUMINESCENCE OF SOME SULFUR-CONTAINING HETEROCYCLES AND THEIR SULFONES

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The luminescence spectra (of crystals and toluene solutions) and the absolute quantum yields of the fluorescence of thianaphtheno[3, 2-b]-thianaphthene, tetraphenylthiophene, 2-phenylthianaphthene, and their sulfones have been measured. The oxidation of the sulfur heterocycles to the corresponding sulfones leads to a marked decrease in the intensity of their luminescence.

Sulfur-containing heterocycles possess a smaller capacity for luminescence under irradiation with ultraviolet light than their oxygen and nitrogen analogs. This is clearly shown, in particular, with the 2, 5-diphenyl derivatives of thiophene, pyrrole, and furan [1].

A few years ago, it was reported [2] that toluene solutions of 2-phenylthianaphthene sulfone (II) luminesced more strongly than solutions of 2-phenylthianaphthene (I) itself.

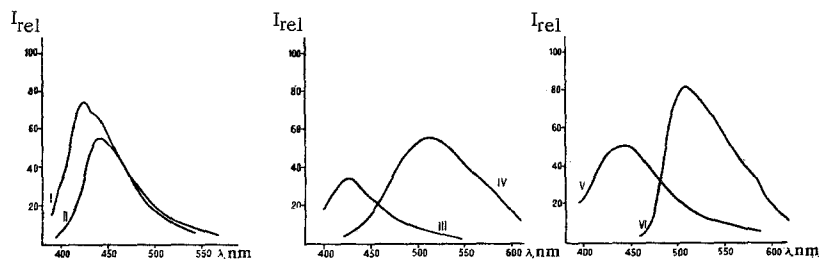
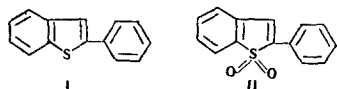
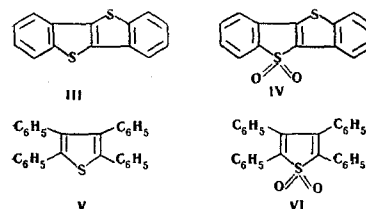


Fig. 1. Luminescence spectra of crystals of I-VI: I) 2-phenylthianaphthene; II) 2-phenylthianaphthene sulfone; III) thianaphtheno[3, 2-b]thianaphthene; IV) thianaphtheno[3, 2-b]thianaphthene monosulfone; V) tetraphenylthiophene; VI) tetraphenylthiophene sulfone.



It was interesting to ascertain whether this phenomenon was also observed for other sulfur-containing heterocycles and their sulfones.

For this purpose we have measured the luminescence spectra (of crystals and toluene solutions) and the absolute quantum yields (η_Q) of the photoluminescence of the sulfur heterocycles I, III, V, and their sulfones (II), (IV), and (VI).

Both in the crystalline state and in solutions, the sulfone IV luminesced in a longer-wave region and more strongly than the unoxidized heterocycle III (Figs. 1 and 2). Thus, for a solution of III in toluene, λ_{\max}