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

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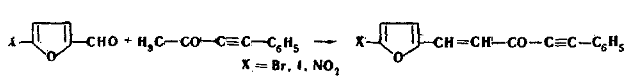
The crotonic condensation of 5-bromo-, 5-iodo-, and 5-nitrofurfurals with 1-phenylbut-1-yn-3-one has been effected.

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-bromofurfural 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 $C_{15}H_9BrO_2$, %: C 59.83; H 3.01; Br 26.53. IR spectrum: ν_{CO} 1617 (v.s), $\nu_{C\equiv C}$ 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 $C_{15}H_9IO_2$, %: C 51.77; H 2.61; I 36.46. IR spectrum: ν_{CO} 1609 (v.s), $\nu_{C\equiv C}$ 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 $C_{15}H_9NO_4$, %: C 67.42; H 3.39; N 5.24. IR spectrum: ν_{CO} 1606 (v.s), $\nu_{C\equiv C}$ 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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Imidazolo[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-haloacetylfurans.

The reaction of 2-aminothiazole and 2-amino-4-methylthiazole with 2-haloacetylfurans 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 imidazolo[2, 1-b]thiazoles (Table 2).