REACTION OF ETHYNYL KETONES WITH o-PHENYLENEDIAMINE

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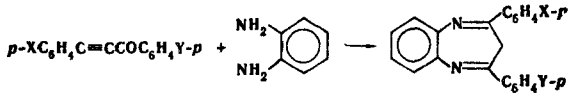
2,4-Diaryl-3H-benzo-1,5-diazepines were obtained by reaction of ethynyl ketones with o-phenylenediamine.

In a continuation of our study [1] of nucleophilic addition to activated acetylenes we investigated the reaction of o-phenylenediamine with some 1,3-diarylpropynones. It is known that α,β-unsaturated ketones react with aromatic diamines to give, depending on the structure of the ketones and the reaction conditions, both β-amino ketones and cyclic products – benzodiazepine and benzimidazole derivatives [2-4]. However, there is little information available on the reaction of ethynyl ketones with primary diamines and, in particular, o-phenylenediamine [5]. The reaction of ethynyl ketones with o-phenylenediamine was carried out by refluxing alcohol solutions of equimolar amounts of the components:



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a X = Y = H; b X = CH_3, Y = H; c X = Cl, Y = H; d X = Br, Y = H; e X = CH_3O, Y = H;
f X = H, Y = CH_3; g X = H, Y = Br

The structure of the reaction products (Table 1) was confirmed by alternative synthesis of 2,4-diphenylbenzo-1,5-diazepines from o-phenylenediamine and dibenzoylmethane [6].

The diazepines obtained from isomeric ketones Ib and If, and Id and Ig, proved to be identical. This and the absence of absorption in the region of vibrations of the NH group in the IR spectrum are evidence for the predominant existence of the synthesized diazepines in the symmetrical diimino form (II).

EXPERIMENTAL

2,4-Diaryl-3H-benzo-1,5-diazepines (IIa-e). (Table 1). An alcohol solution of equimolar amounts of ethynyl ketones Ia-g and o-phenylenediamine was refluxed on a water bath for 5-6 h. It was then cooled, and the solvent was removed in vacuo. The dark-red solid was recrystallized from aqueous ethanol to give colorless or light-yellow needles.

TABLE 1. 2,4-Diaryl-3H-benzo-1,5-diazepines (II)

Comp.	mp., °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	N	C	H	N	
IIa	139—140	$C_{21}H_{16}N_2$	85,3	5,4	9,6	85,1	5,4	9,5	86
IIb	160—161	$C_{22}H_{18}N_2$	85,2	5,9	9,0	85,2	5,8	9,0	79
IIc	149—150	$C_{21}H_{15}ClN_2$	75,9	5,0	8,7	76,3	4,5	8,4	81
IId	159—160	$C_{21}H_{15}BrN_2$	67,5	4,0	7,6	67,2	4,0	7,5	81
IIe	105—106	$C_{22}H_{18}N_2O$	80,7	6,0	8,8	81,0	5,5	8,6	85

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2,4-Diphenyl-3H-benzo-1,5-diazepines (IIa). A solution of 22.4 g (0.1 mole) of dibenzoylmethane, 10.8 g (0.1 mole) of o-phenylenediamine, and 10 g (0.058 mole) of p-toluenesulfonic acid in 100 ml of dry xylene was refluxed for 5 h. It was then cooled, and the precipitated 2-benzimidazole (4.85 g with mp 286-289°) was removed by filtration, and the filtrate was vacuum evaporated. The benzodiazepine (IIa) that precipitated on cooling was recrystallized from 90% methanol to give 11.5 g (39%) of a product with mp 139-140°. No melting-point depression was observed for a mixture of this product with the preparation obtained from phenylbenzoylacetylene (Ia). The UV and IR spectra also proved to be identical.

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