

REACTION OF β, β -DIMETHYLDIVINYL KETONE WITH 2,5-DIMETHYL- AND 1,2,5-TRIMETHYL-4-PIPERIDONES

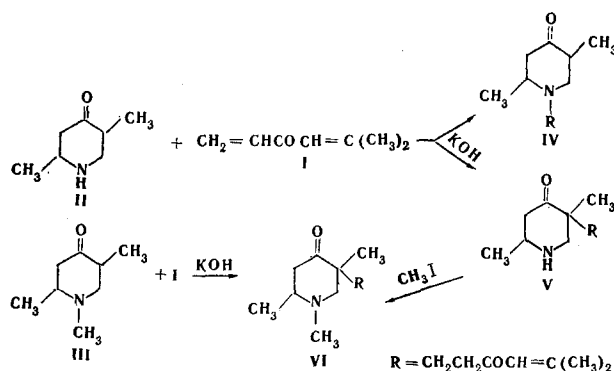
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1-(3-Oxo-5-methyl-4-hexen-1-yl)-2,5-dimethyl-4-piperidone, 5-(3-oxo-5-methyl-4-hexen-1-yl)-2,5-dimethyl-4-piperidone, and 5-(3-oxo-5-methyl-4-hexen-1-yl)-1,2,5-trimethyl-4-piperidone were synthesized. In the absence of a catalyst β, β -dimethyldiviny ketone adds to 2,5-dimethyl-4-piperidone at the 1-position, while in the presence of alkali it adds at the 5-position.

Continuing our systematic investigations of the reaction of α, β -unsaturated compounds with heterocyclic ketones [1], we have studied the reaction of β, β -dimethyldiviny ketone (I) with 2,5-dimethyl- and 1,2,5-trimethyl-4-piperidones (II and III). Owing to the presence of several labile hydrogen atoms in piperidone II, ketone I can react with it at the 1-, 5-, and 3-positions.

In the absence of a catalyst, ketone I reacts with piperidone II to form 1-(3-oxo-5-methyl-4-hexen-1-yl)-2,5-dimethyl-4-piperidone (IV).



When this reaction is carried out in the presence of potassium hydroxide (catalyst) at room temperature, β, β -dimethyldiviny ketone reacts at the methine group (5-position) rather than at the methylene group (3-position) since in the interaction of α, β -unsaturated compounds with ketones the reaction initially proceeds at the methine group, then at the methylene group, and finally at the methyl group [2, 3]. The imino group is not involved under these conditions. The presence of a labile hydrogen atom attached to the nitrogen of piperidone V is demonstrated by methylation of the latter with methyl iodide and conversion to piperidone VI, which is also obtained by alternative synthesis from 1,2,5-trimethyl-4-piperidone (III) and ketone I.

EXPERIMENTAL

1-(3-Oxo-5-methyl-4-hexen-1-yl)-2,5-dimethyl-4-piperidone (IV). β, β -Dimethyldiviny ketone (n_D^{20} 1.4793) [11 g (0.1 mole)] was added to 12.7 g (0.1 mole) of 2,5-dimethyl-4-piperidone (n_D^{20} 1.4660), and the mixture was warmed. To complete the reaction the mixture was heated at 100° for 4 h. Distillation yielded

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15 g (60%) of 4-piperidone IV with bp 140° (2 mm), n_D^{20} 1.4950, and d_4^{20} 1.0069. Found %: C 70.7, 70.8; H 10.1, 10.2; N 5.9, 5.9; MR_D 68.58. $C_{14}H_{23}NO_2$. Calculated %: C 70.8; H 9.7; N 5.9; MR_D 68.14.

5-(3-Oxo-5-methyl-4-hexen-1-yl)-2,5-dimethyl-4-piperidone (V). β,β -Dimethyldivinyl ketone [11 g (0.1 mole)] was added dropwise in the course of 15 min with stirring to a mixture of 25.4 g (0.2 mole) of 2,5-dimethyl-4-piperidone and 0.25 g of powdered potassium hydroxide. The mixture was stirred at room temperature for 4 h. The alkali was neutralized with the calculated amount of hydrochloric acid (sp. gr. 1.19), the resulting precipitate was filtered, and the mixture was distilled to give 14 g (59%) of piperidone V with bp 160° (2 mm), n_D^{20} 1.5040, and d_4^{20} 1.0209. Found %: C 70.6, 70.5; H 10.1, 10.1; N 5.7, 5.6; MR_D 68.31. $C_{14}H_{23}NO_2$. Calculated %: C 70.8; H 9.7; N 5.9; MR_D 67.81.

5-(3-Oxo-5-methyl-4-hexen-1-yl)-1,2,5-trimethyl-4-piperidone (VI). A. A total of 12 g (48%) of piperidone VI with bp 145° (2 mm), n_D^{20} 1.4950, and d_4^{20} 0.9953 was obtained under the conditions of the previous experiment from 28.2 g (0.2 mole) of 1,2,5-trimethyl-4-piperidone and 11 g of β,β -dimethyldivinyl ketone in the presence of 0.25 g of powdered potassium hydroxide. Found %: C 71.1, 71.3; H 9.7, 9.9; N 5.3, 5.6; MR_D 73.24. $C_{15}H_{25}NO_2$. Calculated %: C 71.7; H 9.9; N 5.6; MR_D 73.76.

B. A solution of 4 g (0.029 mole) of methyl iodide in 50 ml of acetone was added with stirring to a mixture of 7 g (0.029 mole) of piperidone V and 10 g of anhydrous powdered potassium carbonate in 100 ml of dry acetone. The mixture was heated with stirring at 65-70° for 4 h. The next day, the resulting precipitate was filtered, the acetone was removed from the filtrate by distillation, and the residue was vacuum distilled to give 5 g (69%) of piperidone VI with bp 145-146° (2 mm) and n_D^{20} 1.4950.

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