INDOLE DERIVATIVES

VI*. THE ALKYLATION OF β-OXO SULFOXIDES WITH GRAMINE

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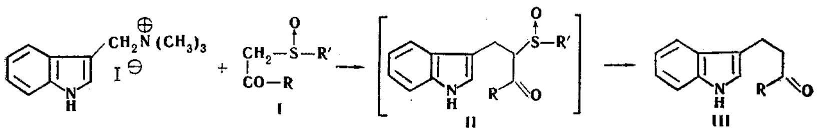
The reaction of gramine methiodide with the sodium or potassium derivatives of β-oxo sulfoxides leads to the formation of skatyl-substituted sulfoxides. When the latter are cleaved with amalgamated aluminum, skatyl-substituted ketones are obtained.

In recent years, because of their ready availability, high reactivity, and mild conditions of working up, β-oxo sulfoxides have been used to an ever-increasing extent in organic synthesis. We have shown that the reactions of gramine methiodide with sodium or potassium derivatives of β-oxo sulfoxides Ia and b in dimethyl sulfoxide form the skatyl sulfoxides II. These are amorphous substances which cannot be purified and were subjected in the crude state to reductive cleavage by the action of amalgamated aluminum to give the ketones IIIa, b, identical with samples synthesized by other methods [2, 3].



II a $R=C_6H_5$, $R'=CH_3$; b $R=CH_3$, $R'=CH_2C_6H_5$

The reaction with the oxo sulfoxides can be carried out under the action of sodium hydride or potassium tert-butoxide. The replacement of the dimethyl sulfoxide by other solvents (dimethylformamide, ethanol, hexamethylphosphoramide) led to a decrease in the yield. The main reaction is accompanied by the dealkylation of the quaternary salt with the formation of gramine, which was isolated in one experiment with a yield of 26 %.

EXPERIMENTAL

Skatylacetophenone (IIIa). 0.65 g (3.6 mmoles) of methylsulfinylacetophenone was added to 0.086 g (3.6 mmoles) of sodium hydride in 15 ml of anhydrous dimethyl sulfoxide, and the mixture was stirred until a clear solution had been formed. Then 1.14 g (3.6 mmoles) of gramine methiodide was added in several portions and stirring was continued at room temperature for another 1 hr 30 min. The suspension obtained was poured into water and extracted with ether, and the extract was washed with dilute acetic acid (gramine can be isolated by making this extract alkaline), sodium bicarbonate solution, and water. The residue after the evaporation of the ether (0.55 g) was dissolved in 33 ml of a mixture of tetrahydrofuran and water (9 : 1) and stirred with 0.47 g of amalgamated aluminum foil at 0°C for 20 min. The solid substances were filtered off, the tetrahydrofuran was distilled off in vacuum, and the residue was treated with water and extracted with ether. The ethereal extract was dried and evaporated to small volume. This gave 0.31 g of skatylacetophenone with mp 125-126°C [2]. A sample for analysis was chromatographed on alumina (elution with benzene) and crystallized from benzene. Found, %: C 82.19; H 6.05; N 5.36. Calculated for $C_{13}H_{15}NO$, %: 81.90; H 6.06; N 5.62.

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*For Communication V, see [4].

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Skatylacetone (IIIb). This was obtained in a similar manner to IIIa from gramine methiodide and benzylsulfinylacetone with subsequent reduction at 18-20°C for 40-60 min. mp 92-94°C. The product gave no depression of the melting point with a sample obtained as described by Merchant and Salgar [3].

LITERATURE CITED

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