REACTION OF SULFOLENE WITH β-γ-δ-ε-OCTAFLUOROPENTANOL

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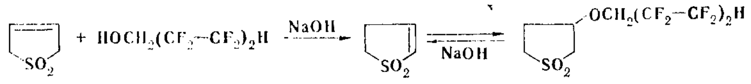
The reaction of 3-sulfolene with β-γ-δ-ε-octafluoropentanol in an alkaline medium at 90-100°C was studied. It is shown that the reaction proceeds through isomerization of 3-sulfolene to 2-sulfolene with subsequent addition of the fluorinated alcohol. The reversibility of the last step of the reaction was proved by gas—liquid chromatography.

It has been previously shown that 3-sulfolene readily adds alcohols in alkaline media to give alkoxysulfolanes [1-3]. In order to synthesize fluorine-containing derivatives of sulfolane we studied the reaction of 3-sulfolene with a fluorinated alcohol, viz., β-γ-δ-ε-octafluoropentanol. It is known that the introduction of halogen atoms in an alcohol molecule increases the acid properties of alcohols, in connection with which it seemed of interest to investigate the addition of this reagent to the double bond of sulfolene.

Our studies showed that β-γ-δ-ε-octafluoropentanol adds to 3-sulfolene when these compounds are heated in the presence of alkali metals or alkali. Thus β-γ-δ-ε-octafluoropentoxysulfolane is formed along with 2-sulfolene in the reaction of sulfolene with excess alcohol (2.5 moles per mole of sulfolene) in an alkaline medium at 90-100°C. The desired product was obtained in 25-27% yield in all of the experiments. We were unable to increase the yield by changing the conditions. In this connection, we assumed that the reaction proceeds via the following scheme:



I IV II III

The reversibility of the last step of the reaction was proved by the action of alcohol IV on III in an alkaline medium, in which case the reaction proceeds in the direction favoring the formation of 2-sulfolene until equilibrium is established. According to the results of analysis by gas—liquid chromatography (GLC), the ratio of 2-sulfolene and addition product III in the reaction mixture is 1:2.

To confirm the proposed reaction scheme we subjected the reaction of 3-sulfolene with alcohol IV to a study by differential thermal analysis (DTA). An exo effect at 80-105°C with a maximum at 95°C is clearly expressed on the thermogram. The thermographic curve then levels off, and a significant endo effect, which is evidently due to destruction of the products, commences only at 150°C. Analysis of a sample by thin-layer chromatography (TLC) confirmed the formation of addition product III in addition to a very small amount of starting I and isomerization product II. Interruption of the recording of the thermogram at the end of the exo peak (105°C) and subsequent analysis by TLC demonstrated the presence in the mixture of the same components, while stopping the thermographic reaction at the start of the exo effect (85°C) revealed the presence of starting I and intermediate II. The formation of addition product III evidently takes place immediately as I undergoes isomerization, which explains the presence of a broad but low exo peak. The subsequent leveling off of the curve can be explained by the fact that in addition to the addition of alcohol IV to isomer II, it is also split out from product III until equilibrium between III and II is established.

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The formation of isomer II as an intermediate is also in agreement with a study by Zimmermannova and Prochazka [2], in which the existence of intermediate 2-sulfolene is demonstrated in the case of alkaline catalysis in an alcoholic medium.

Thus the studies showed that when β-γ-δ-ε-octafluoropentanol is used, one can combine the synthesis of β-γ-δ-ε-octafluoropentoxysulfolane with a simple and convenient method for the preparation of 2-sulfolene.

It should be noted that β-γ-δ-ε-octafluoropentoxysulfolane was found to be a good intensifier for the dyeing of acetylcellulose fibers [4]. It readily decomposes via the scheme presented above in the washing of printed textile materials.

EXPERIMENTAL

The analysis of the mixtures of substances obtained was performed with a Khrom-4 gas—liquid chromatograph with a flame-ionization detector and a 250 × 0.3 cm column filled with 5% SE-30 silicone on Chromaton N-AW (0.200-0.250 mm); the temperature was 190°C, and the carrier gas was helium. The course of the reactions was monitored by TLC on Silufol in petroleum ether—ethyl acetate (1:1) and benzene—petroleum ether—ethyl acetate (0.3:1:1) systems. Thermographic analysis was carried out with a PDS-021 two-coordinate potentiometer with a Chromel—Alumel thermocouple under linear heating conditions at 3°/min. The samples were heated up from room temperature in a sealed Stepanov vessel.

The starting 3-sulfolene had mp 64-65°C. The β-γ-δ-ε-octafluoropentanol had bp 49-52°C (10 mm) and n_D^{20} 1.3180.

2-Sulfolene and β-γ-δ-ε-Octafluoropentoxysulfolane (III). A) A 0.06-mole sample of NaOH was added to 2.5 moles of IV, and the mixture was heated at 95-100°C for 2.5 h. It was then cooled and neutralized with concentrated HCl, and the precipitated NaCl was removed by filtration. The filtrate was distilled *in vacuo* to give II (37%), with mp 48-49°C (no melting-point depression was observed fof a mixture with a sample obtained by the method in [5]), and III (27%) with bp 140°C (0.08 mm), n_D^{20} 1.4035, and d_4^{20} 1.6191. Found: C 30.7; H 3.3; S 9.4%; MR_D 52.85. $C_9H_{10}F_8O_3S$. Calculated: C 30.86; H 2.88; S 9.16; MR_D 52.25. After isolation of desired product III, intermediate II and unchanged IV can be reused for the preparation of III.

B) A 0.045-mole sample of NaOH was dissolved with stirring in 0.25 mole of alcohol IV, and 0.1 mole of I was added. The composition of the reaction mixture did not change after heating at 90-100°C for 3 h, according to GLC data. The II:III ratio was 1:1.6.

Action of NaOH on III. A 0.045-mole sample of NaOH was dissolved by heating in 0.25 mole of IV, after which 0.085 mole of III was added. The composition of the reaction mixture did not change after heating at 90-100°C for 3 h. According to GLC, the II:III ratio was 1:2. Compounds II (47%) and III (37%) were isolated as a result of vacuum distillation.

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