1,2-MIGRATION OF METHYL GROUP IN REACTION OF tert-BUTYLETHYLENE WITH PHENYLSULFENYL FLUOBORATE

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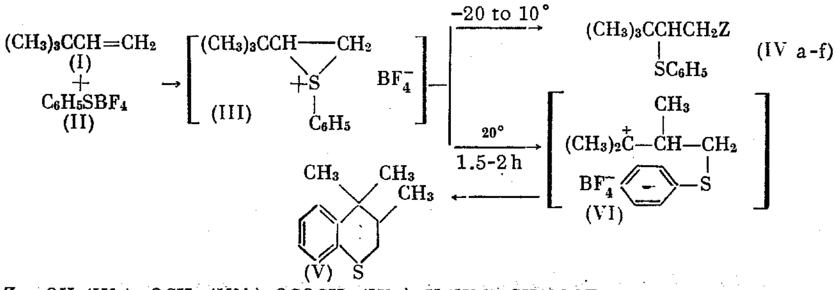
It is known that the reaction of 3,3-dimethyl-1-butene (I) with various covalent sulfur-containing electrophilic reagents always proceeds without rearrangement [1]. We discovered that the use of reagents of the cationoid type makes it possible to direct this reaction toward the formation of products with a rearranged skeleton. Thus, the reaction of (I) with $C_6H_5SBF_4$ (II) at −20°C in CH_2Cl_2—CH_3NO_2 solution leads to the formation of a colored solution of a complex with the hypothetical structure (III), which when treated with various nucleophilic reagents at −20 to −10°C gives 1,2-addition products with a rearranged structure of general formula (IV) (yield 60-90%, see [2] for the formation of analogous products when (II) is reacted with cyclohexene). However, if the solution of complex (III), obtained at −20°C, is kept at 20°C for 1.5-2 h, then the main reaction product, independent of the nature of the nucleophilic reagent Z, used to treat the mixture, becomes 3,4,4-trimethylthiochroman in 78% yield. These results can be explained if it is assumed that the reaction of (I) with (II) gives the episulfonium complex (III), which undergoes rearrangement when the temperature is raised to yield the intermediate (VI), which is capable of subsequently alkylating the phenyl ring. The composition and structure of products (IVa-f) and (V) were proved by the elemental analysis, IR, NMR, and mass spectral data.



Z = OH (IVa), OCH_3 (IVb), $OCOCH_3$ (IVc) H (IVd) $CH(COOEt)_2$ (IVe), $N(C_2H_5)_2$ (IVf)

LITERATURE CITED

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