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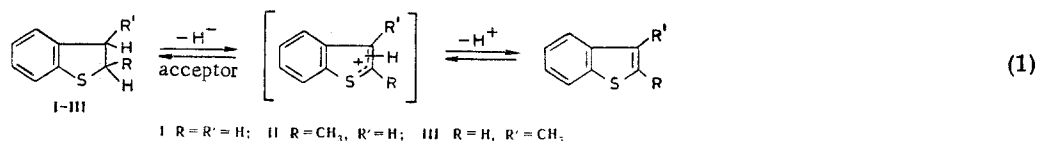
HYDRIDE SHIFT REACTIONS WITH THE PARTICIPATION OF TWO-RING SULFIDES

L. M. Kedik, A. A. Freger,
and E. A. Viktorova

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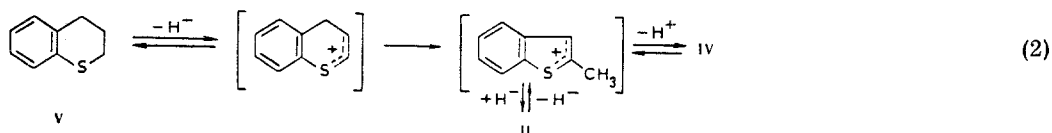
2,3-Dihydrobenzothiophenes are dehydrogenated to the corresponding benzothiophenes on reaction with the hydride-ion acceptors triphenylmethyl tetrafluoroborate and chloranil. Thiochroman reacts with chloranil to give 2-methyl-2,3-dihydrobenzothiophene and 2-methylbenzothiophene and reacts with triphenylmethyl tetrafluoroborate to give a thiochromenylium salt.

The dehydrogenation and isomerization reactions of two-ring sulfides in the presence of catalysts based on aluminum oxide apparently proceed through a step involving detachment of a hydride ion under the influence of the aprotic centers of the catalysts [1, 2], and dehydrogenation takes place without hydrogen evolution into the gas phase. In this connection, we investigated the dehydrogenation of 2,3-dihydrobenzothiophene (I), 2-methyl-2,3-dihydrobenzothiophene (II), and 3-methyl-2,3-dihydrobenzothiophene (III) on reaction with triphenylmethyl tetrafluoroborate and chloranil (tetrachloro-1,4-benzoquinone). The reaction gives high yields of the corresponding benzothiophene in aprotic solvents with high polarities (Table 1). At 80° in acetonitrile the dehydrogenation of II gives the product in yields up to 93%, whereas the yield at 20° after 1 h was only 29%. The character of the effect of the solvents and the absence of reaction products with doubled molecular weights make it possible to suppose that the reaction proceeds via an ionic scheme:



As compared with triphenylmethyl tetrafluoroborate, the use of chloranil requires an increase in the temperature and reaction time. Thus the yield of 2-methylbenzothiophene (IV) did not exceed 32% in the dehydrogenation of II in o-xylene at 100° for 15 h. The relative rates of dehydrogenation for I, II, and III, which were found to be, respectively, 1.5:2.4:1, were calculated on the basis of the dependence of the yields of the reaction products on the time.

Under the influence of chloranil, thiochroman (V) undergoes isomerization to give small amounts of II (2%) and its dehydrogenation product IV (3%):



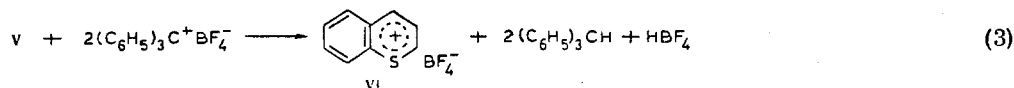
M. V. Lomonosov Moscow State University. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 3, pp. 328-330, March, 1976. Original article submitted January 3, 1975.

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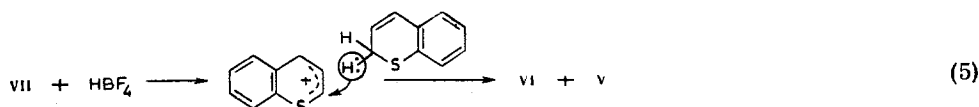
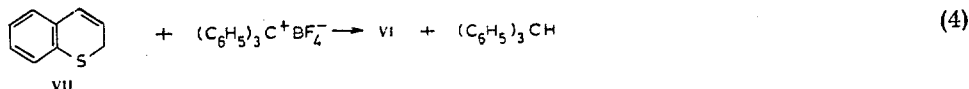
TABLE 1. Results of Experiments with 2-Methyl-2,3-dihydrobenzothiophene (with triphenylmethyl tetrafluoroborate as the acceptor and a sulfide-acceptor ratio of 1:1 at 80° C for 2 h)

Solvent	ϵ at 25°	Yield, %	
		2-methylbenzothiophene	triphenylmethane
Acetonitrile	37.5	93	98
Tetrachloroethane	8.1	88	99
Dichloroethane	10.4	88	90
o-Xylene	2.5	30	34

The reaction of thiochroman with triphenylmethyl tetrafluoroborate proceeds in a different manner: in this case a stable thiochromenylium salt with the BF_4^- anion, the yield of which reaches 91%, is formed

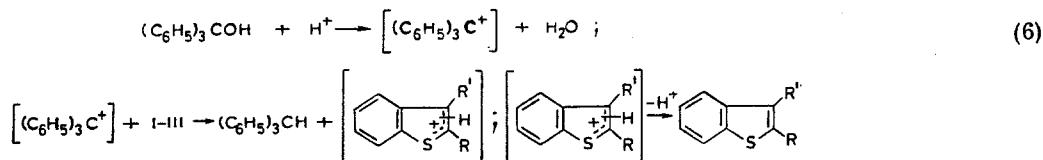


A similar salt was also obtained by the action of triphenylmethyl tetrafluoroborate and tetrafluoroboric acid on Δ^3 -thiochromene (VII):



Similarly constructed salts with a ClO_4^- anion were previously obtained by acidic disproportionation of Δ^3 -thiochromenes [3]. In our case, in the reaction of V with triphenylmethyl tetrafluoroborate, intermediate VII is evidently formed in the initial step of the reaction and then reacts in accordance with Eqs. (4) and (5). However, the contribution of reaction (5) to the conversion of V is small, inasmuch as VII reacts with triphenylmethyl tetrafluoroborate practically completely in 30 min (in acetonitrile at 40°), whereas under the same conditions the reaction with tetrafluoroboric acid proceeds only to a slight degree.

In order to evaluate the relative hydride lability of the hydrogen in 2,3-dihydrobenzothiophenes we also used the ionic reduction of triphenylcarbinol:



Trifluoroacetic acid was used as the proton donor.

On the basis of the above results, the 2,3-dihydrobenzothiophenes can be arranged in the following order with respect to decreasing hydride lability of the hydrogen in the heteroring: II > I > III.

Small amounts of II, IV, and 3-methylbenzothiophene were detected in the transformation products when thiochroman was used as the hydride-ion donor in this reaction; stable thiochromenylium salts are not formed under these conditions.

EXPERIMENTAL

The starting compounds were synthesized by known methods. The purity of all of the sulfides was 98-100% according to gas-liquid chromatography (GLC). The liquid products were analyzed by GLC by the method in [4]; the column temperature was 230°. The UV spectra of ethanol solutions of the compounds (10^{-2} mole/liter) were recorded with an SF-4A spectrophotometer. The PMR spectra of CCl_4 solutions of the compounds were recorded with a Varian T-60 spectrometer. The experiments with triphenylmethyl tetrafluoroborate were carried out by the method described in [5] and those with chloranil were carried out in accordance with the method in [6].

In the experiments on the reaction of V and VII with $\text{Ph}_3\text{C}^+\text{BF}_4^-$, at the end of the reaction the mixture was cooled and extracted with petroleum ether (bp 60–80°). The extract was then washed several times with water and dried with calcium chloride. The solvent was removed by distillation, and the residue was vacuum fractionated and analyzed. A thiochromenylium salt was isolated from the solid residue by chromatography on a loose layer of aluminum oxide (elution with hexane and development by UV irradiation).

Reaction of VII with HBF_4 . A 1-g sample of VII was added dropwise to a mixture of 5 g of HBF_4 and 0.2 g of $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ after which the mixture was heated with stirring at 40° for 3 h. It was then cooled and poured into ice water, and the liquid products were extracted with petroleum ether (bp 60–80°). The extract was washed with 5% sodium carbonate solution and water and dried with magnesium sulfate. The solvent was removed, and the residue was vacuum fractionated. The solid products were extracted with diethyl ether, and the extract was dried with sodium sulfate. The ether was removed, and the thiochromenylium salt was obtained as dark-cherry-red crystals with mp 110–112°. UV spectrum, λ_{max} (log ϵ): 338–340 (2.5) and 258–260 nm (3.1). The PMR spectrum contained only the signals of aromatic protons at 7.0–7.1 ppm.

Ionic Reduction of Triphenylcarbinol. The reduction was carried out in acetonitrile at 60–80° for 0.5–6 h at a sulfide–triphenylcarbinol–trifluoroacetic acid ratio of 3:1:3. The solid reaction products were analyzed by the method in [4].

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