

SYNTHESIS OF CYCLIC SATURATED SULFONES BY THE CATALYTIC
REDUCTION OF UNSATURATED COMPOUNDS.

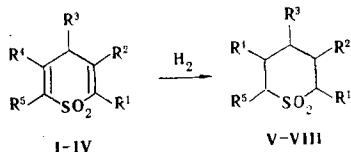
V. G. Kharchenko, A. M. Plotnikov,
and A. D. Shebalova

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The synthesis of sulfones of thiacyclohexanes, thiadecalins, and perhydrothioxanthenes by the catalytic hydrogenation of the corresponding α, β -unsaturated cyclic sulfones in the presence of palladium on carbon was developed. The effects of the temperature conditions, excess hydrogen pressure, the nature of the grouping in the 4 position of the heteroring, and the degree of shielding of the double bond on the process were established.

The synthesis of cyclic sulfones, which are potentially biologically active substances, is a difficult task in a preparative respect. The most widely used method for their preparation consists in oxidation of the corresponding cyclic sulfides, the synthesis of which in most cases is extremely complex and laborious [1]. Considering the accessibility of poly-substituted thiapyrans and their condensed analogs, as well as the ability of these sulfides to readily undergo oxidation to give the corresponding sulfones, we studied the possibility of the preparation of thiacyclohexanes, thiadecalins, and perhydrothioxanthenes from them by means of catalytic hydrogenation.

The catalytic hydrogenation of the sulfones was studied at 20-120°C and 5.07-10.13 MPa (50 and 100 atm) in various solvents (dioxane, isopropyl alcohol, and ethanol). On the basis of the literature data [2] on the reduction of sulfur-containing compounds and the high catalytic activity of metals of the platinum group in the hydrogenation of α, β -unsaturated cyclic sulfides [3], we used 10% palladium on carbon as the catalyst. The reduction of sulfones I-IV proceeds at low rates at 50°C and 5.07 MPa. Raising the temperature to 120°C leads to appreciable hydrogenolysis. Reduction of both double bonds occurs at 100°C and an initial hydrogen pressure of 5.07 MPa with ethanol as the solvent, and thiacyclohexane, thiodecalin, and perhydrothioxanthene sulfones (V-VIII) are formed in 66-80% yields (Table 1). The individuality of sulfones V-VIII was confirmed by gas-liquid chromatography (GLC) and thin-layer chromatography (TLC).



I*, V R¹=R⁵=Ph, R²=R⁴=CH₃, R³=H; II, VI R¹=R³=Ph, R⁴=R⁵=(CH₂)₄, R²=H; III, VII R¹=R²=(CH₂)₄, R⁴=R⁵=(CH₂)₄, R³=CH₃; IV, VIII R¹=R²=(CH₂)₄, R⁴=R⁵=(CH₂)₄, R³=Ph

*Compound I is the dihydro derivative.

The IR spectra of sulfones V-VIII at 1600-1700 cm^{-1} do not contain absorption bands of a C=C bond, whereas the S=O vibrations are retained at 1120-1150 and 1285-1350 cm^{-1} . Thus the sulfone group is not involved in the hydrogenation under the conditions that we selected.

The substituent in the 4 position of the heteroring has a definite effect on the rate of hydrogenation. In particular, when there is no substituent in this position (sulfone I), 100% hydrogenation takes place after 6 h (GLC), whereas when a phenyl substituent is present (sulfone IV), the degree of conversion after the same time was 90-95%, as compared with ~70% in the case of a methyl substituent (sulfone III). This is evidently associated with steric

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TABLE 1. Cyclic Saturated Sulfones

Com- ound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	S		C	H	S	
V	249-251	73,0	7,2	10,3	C ₁₉ H ₂₂ O ₂ S	72,9	7,0	10,2	80
VI	212-214	73,9	7,2	9,6	C ₂₁ H ₂₄ O ₂ S	74,1	7,1	9,4	75
VII	158-160	66,1	9,5	12,2	C ₁₄ H ₂₄ O ₂ S	65,6	9,4	12,5	78
VIII	172-172,5	70,8	7,9	10,4	C ₁₉ H ₂₆ O ₂ S	71,1	8,2	10,1	66

TABLE 2. Effect of the Degree of Shielding of the Double Bond on the Catalytic Hydrogenation of Sulfones

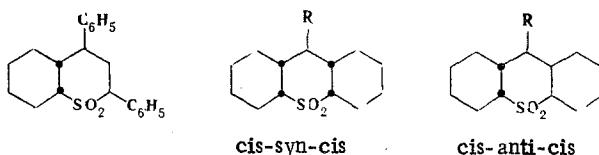
Starting compound	Degree of conversion after 2 h, %	Degree of conversion after 4 h, %	Degree of conversion after 6 h, %
II	52-55	76-78	100
IV	30-40	60-66	90-95

reasons, since the methyl group is a bulkier substituent [4]. The possibility that rotation of the phenyl group is retarded due to possible interaction with the sulfone group, a consequence of which may be better contact of sulfone IV with the catalyst surface as compared with sulfone III, also is not excluded.

One might have expected that the hydrogenation of sulfones I-IV would proceed more readily than the hydrogenation of sulfides with similar structures [3], since the poisoning effect of sulfur is not manifested as markedly as in sulfides as a consequence of participation of its free electron pairs in the formation of bonds with oxygen. In fact, in the hydrogenation of 9-phenyl-sym-octahydrothioxanthene and its sulfone IV under identical conditions we found that the degree of conversion of the sulfide is 60-62% (GLC), whereas the degree of conversion of sulfone IV is 90-95%. In addition, in the hydrogenation of sulfones the catalyst does not lose its activity and can be used repeatedly.

The rather severe conditions for the hydrogenation of sulfones I-IV are probably associated with the high degree of shielding of the double bonds, which is confirmed by an examination of Dreiding models of these compounds. To clear up this problem we compared the results of the catalytic hydrogenation of compounds with tri- and tetrasubstituted double bonds (sulfones II and IV) (Table 2). The rate of hydrogenation of the sulfone with a trisubstituted double bond (sulfone II) is appreciably higher than in the case of the sulfone with a tetrasubstituted double bond (sulfone IV), which indicates the substantial effect of the number of substituents attached to the double bond on the reactivity of the latter in I-IV.

The formation of the corresponding saturated sulfones in several stereoisomeric forms is possible in the catalytic hydrogenation of the α,β -unsaturated sulfones that we investigated. However, we isolated individual substances without impurities, and this constitutes evidence for the stereospecificity of the hydrogenation of I-IV under the investigated conditions. The explanation for this apparently must be sought in *cis* addition of hydrogen on palladium, which is in agreement with the literature data on the hydrogenation of similarly constructed sulfides and sulfones [3, 5-8] and makes it possible to assume that *cis* structures are formed in the hydrogenation of the sulfones:



The formation of any of the *trans* structures suggests electrophilic addition of hydrogen [4, p. 320], which is difficult to realize in the case of sulfones I-IV, since the double bond becomes less protophilic under the influence of the electron-acceptor SO₂ group, and this

decreases its tendency to add a proton and makes the corresponding carbonium ion less stable. The fact that the indicated sulfones, as we have established, do not undergo ionic hydrogenation ($\text{HSiEt}_3/\text{CF}_3\text{COOH}$, 10–15 h, 60–70°C) serves as a certain confirmation of this.

The melting points of sulfones V and VI are in agreement with the melting points for the sulfones obtained by oxidation of the saturated sulfides isolated from disproportionation reactions [9], which are processes that are modeled by ionic hydrogenation. We explain this by the fact that the resulting *cis* isomers are evidently the most energetically favorable compounds because of the absence of an appreciable interaction between the substituents and the heteroatom, which is confirmed by the construction of Dreiding models.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were recorded with a UR-20 spectrometer. The course of the reaction was monitored by means of thin-layer chromatography (TLC) on Silufol UV-254 plates in a benzene–ether system (1:1) and by means of gas–liquid chromatography (GLC) with a column ($h = 1000$ mm, $d = 3$ mm) packed with 4% Lucoprene G on Chromaton N-AW-HMDS. The 10% palladium on carbon was prepared by the method in [10].

Method for Catalytic Hydrogenation. A weighed sample (1 g) of the substance and ethanol in a 50-fold amount (by mass) were placed in a rotating autoclave, after which the catalyst [5–10% (based on the metal) of the mass of the starting substance] was introduced. Hydrogenation was carried out at 20–120°C at an initial hydrogen pressure of 5.07–10.13 MPa. The catalyst was separated after absorption of the calculated amount of hydrogen, which required 5–6 h. Colorless crystals were isolated by partial evaporation of the solution in air.

The characteristics of the hydrogenation products are presented in Table 1. Sulfones VII and VIII are isomers of the compounds that we previously described; this is confirmed by depression of the melting points when they are mixed.

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