liquid NH_3, and 40 mmoles of EtBr. After the usual workup and vacuum-distillation we isolated 0.3 g (70%) of ethyl phenyl sulfide, which in its constants and GLC retention time was identical with an authentic standard.

CONCLUSIONS

Three methods were developed for the synthesis of cyclopropyl organyl sulfides, which are based on the reaction of cyclopropyl halides with either thiols or alkali metal thiolates in a superbasic medium, the reaction of cyclopropyllithium with diorganyl disulfides, and the reaction of cyclopropyl alkyl sulfides with lithium in liquid ammonia and subsequent reaction with organic bromo derivatives. In contrast, the cleavage of cyclopropyl aryl sulfides leads to the formation of lithium arylthiolates.

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DESULFURIZATION OF TETRAHYDROTHIOPHENE BY TRIIRON DODECACARBONYL

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The reaction of such cyclic sulfides as tetrahydrothiophene (I) [1], 1,3-diethiacyclohexane (II) [2], 1,3-dithia-5-cycloheptene (III) [3], and thiacyclobutene (IV) [4] with iron carbonyls is described in the literature. When thiophene and its derivatives and benzothiophene are desulfurized using iron carbonyls it is characteristic for ferroles and thiaferroles to be formed, for example, $C_4H_4Fe_2(CO)_6$ [5] in the case of thiophene and $CH_3C_4H_3 \cdot SFe_2(CO)_6$ [6] in the case of 2-methylthiophene. The thiaferroles are apparently intermediate compounds in the formation of the ferroles. The possibility of the thiaferrole complexes existing is directly related to the presence of the stabilizing tricarbonylironthiacyclohexadiene ring system, which is π bonded with the $Fe(CO)_3$ group.

In the discussed cyclic sulfides (I)-(IV) the absence of stabilizing double bonds makes the formation of the thiaferrole complex improbable. For (IV) only the thiaacrolein iron carbonyl complex could be isolated [4]. Compound (III), which has two potentially possible fragments for coordination with a metal, a double bond and S atoms, also goes not give the thiaferrole complex. The reaction is accompanied by reductive decyclization [3]. The reaction of $Fe_2(CO)_9$ (V) with (II) in THF in a CO atmosphere leads to the formation of a mononuclear derivative (cyclo-1,3-$C_4H_8S_2$)$Fe(CO)_4$ (VI) [2], and in an N_2 atmosphere to a binuclear derivative (cyclo-1,3-$C_4H_8S_2$)$Fe_2(CO)_7$, which was not characterized [2].

The first attempt to obtain an iron carbonyl complex form (I) by treatment with $Fe(CO)_5$ and UV light did not lead to the isolation of the chemically pure product $C_4H_8Fe(CO)_4$ [7]. The presence of the $Fe(CO)_4$ group was confirmed by the exchange reaction with PPh_3. The reaction of (I) with (V) leads to the formation of an unusual complex $(C_4H_8S)_2Fe_3(CO)_8$ (VII) [1]. The (VII) structure can be regarded as being derived from triiron dodecacarbonyl (VIII),

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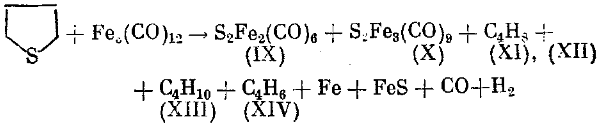
if in it two terminal CO groups on different Fe atoms are replaced by two molecules of (I), which in the given case serves as a neutral four-electron-donor bridge ligand.

Additional data are given in the present paper on the reaction of (VIII) with (I). The preliminary results were reported in [8]. It was found that the reaction of (VIII) with an equimolar amount of (I) is accompanied by the desulfurization of (I) to give dithiodiiron hexacarbonyl (IX), dithiotriiron nonacarbonyl (X), FeS, and Fe. The gas phase consists of a mixture of hydrocarbons, CO, and H_2. Based on the chromato-mass spectrometry data, the hydrocarbon portion consists of the following compounds: 1-butene (XI) (70%), 2-butene (XXII) (14%), butane (XIII) (14%), and traces of butadiene (XIV). Conversion of (I) (GLC): 27% (C_6H_6, 4 h, 60°); 40% ($C_6H_5CH_3$, 2 h, 100°): 70% ($C_{10}H_{22}$, 1 h, 160°). The reaction temperature is the decisive factor, since the nature of the solvent has no effect on the yield of the products.



The formed FeS is the decomposition product of (IX) and (X). Based on the data in [9], the incipient decomposition temperature is 45° for (IX), and 110° for (X). The generation of Fe metal occurs both via the decomposition of (X) and the partial decomposition of (VIII), and consequently the amount of formed hydrocarbons does not correspond to the amount of liberated carbonyl-containing sulfur clusters, because of either their partial or complete decomposition, and only the amount of formed FeS is determined when the reaction is run to the complete disappearance of (IX) and (X).

Based on the TLC data, complex (VII) is not formed. In addition, the thermal decomposition of (VII), obtained as described in [1], does not lead to (IX), (X), and FeS. In other words, the desulfurization of (I) does not proceed via the step of forming (VII). Special experiments also confirmed the fact that the Fe, formed by the decomposition of (X) and (VIII), lacks a desulfurizing effect under the studied conditions.

It is possible that the initial coordination proceeds without the ring cleavage of (I) and the first intermediate of the discussed reaction is the iron tetracarbonyl complex $(C_4H_8S)Fe(CO)_4$. Then Fe is inserted into the C—S bond and the formed six-membered heterocycle decomposes with the liberation of the hydrocarbon portion.

The discussed scheme is in agreement with the scheme for the reductive decyclization of organosulfur compounds by (V), which was proposed for (III) and then extended to other organic polysulfides [3]. The liberation of olefinic, dienic, and saturated hydrocarbons, and also H_2, indicates that the reaction is accompanied by dehydrogenation, hydrogenation, and isomerization, which is characteristic for iron carbonyl compounds. It is important to mention that dialkyl and diaryl sulfides react with iron carbonyls to give $(RS)_2Fe_2(CO)_6$ complexes, which on thermal decomposition do not form (IX) and (X) [10].

As a result, the formation of (IX) and (X) in the studied reaction shows for the first time that the desulfurization of (I) proceeds via the step of generating sulfur carbonyl clusters and indicates the theoretical differences in the reaction of iron carbonyls with cyclic and noncyclic sulfides.

It is known that tetrahydrothiophene and its derivatives constitute the main portion of the sulfides in petroleum and petroleum products. Sulfide sulfur is removed with the greatest difficulty from fuels. The obtained data clearly illustrate the high desulfurizing capacity of (VIII) toward the more stable organosulfur compounds of the (I) type, which was used to desulfurize petroleum and petroleum products [11].

EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD instrument using dimethylsulfolane deposited on diatomite, 45°C, and a 16 × 0.25 mm glass column. The chromato-mass spectrometry was run on a Varian-44S instrument in the temperature gradient 55-100° at a rate of 8 deg/min, on a glass column (25 × 0.25 mm, FFAP), and using helium as the carrier gas and an ionization energy of 70 eV.

Reaction of Tetrahydrothiophene (I) with Triiron Dodecacarbonyl (VIII) (general method). To a solution of (I) in 50-100 ml of dry solvent (C_6H_6, $C_6H_5CH_3$ or $C_{10}H_{22}$) was added in an argon stream an equimolar amount of (VIII) and the mixture was stirred and heated (at 60, 100, and 160° respectively) until (VIII) disappeared in the reaction mixture (based on the TLC data, 4, 2, and 1 h). The liberated gaseous products were collected an analyzed by chromato-mass spectrometry. The reaction mixture was filtered, and the precipitate was washed with hexane, dried to constant weight, and decomposed with 25% H_2SO_4 solution. The liberated H_2S was trapped in satd. $CdCl_2$ solution. The filtrate was evaporated in vacuo, and the residue, a reddish-orange oil, was chromatographed on a silica gel column, using hexane as the eluant. Two fractions were isolated: (IX), mp 44-46° (pentane), cf. [10]; (X) mp 114°(pentane) cf. [10]. Yield of (IX) and (X) (solvent, ratio of (IX) and (X)): 9% (C_6H_6, 1:1), 6% ($C_6H_5CH_3$, 1:1).

CONCLUSIONS

The desulfurization of tetrahydrothiophene using triiron dodecacarbonyl was run for the first time. The desulfurization proceeds via the step of forming sulfur carbonyl clusters.

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