the excess reagent was removed, and a precipitate (in 50-90% yield) with mp 85-90°C, which was identified as alcohol VI (ν_C=O 1620 cm⁻¹) was isolated.

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LITERATURE CITED


FORMATION OF SPIRO-SUBSTITUTED 1,3-DITHIOLANES AND THIIRANES IN THE REACTION OF 3-AMINOINDENE-1-ThIONES WITH ALIPHATIC DIAZO COMPOUNDS*

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3-Aminoindene-1-thiones react readily with diazomethane to give the corresponding 4,4',5,5'-dispiro-substituted 1,3-dithiolanes. The production of both 2,2-spiro-substituted thiiranes and products of desulfurization of the latter is possible in the reaction of 3-aminoindene-1-thiones with substituted diazomethanes. The thermolysis, hydrolysis, and salt-forming reactions of the compounds obtained were investigated.

The reactions of thiocarbonyl compounds with diazomethane have been investigated in greatest detail in the case of thioketones [2-9]: thiadiazoles [2, 3], dithiolanes [4-6], thiiranes [4, 7], and other sulfur compounds [8, 9] were obtained. It is assumed that the direction of the reaction does not depend on the reagent ratio but is determined by the specific structures of the thioketone and the diazo compound and the reaction conditions [4]. No data on the cycloaddition of diazomethanes to the C=S bond of thioamides are available, but individual representatives of thioamides are capable of methylation by diazomethane at the sulfur atom [10]. The reactions of vinylogs of thioamides with diazomethanes have not been studied.

3-Aminoindene-1-thiones (I) react with diazomethane in ether, benzene, or acetone at -60 to 20°C to give 4,4',5,5'-dispiroindene-substituted 1,3-dithiolanes (II) in high yields. The PMR (Table 1) and IR spectra (see the experimental section) confirm the structure of dithiolanes II. The protons of the -S=CH₂-S- group resonate in the form of a singlet, which indicates their equivalence and, consequently, the trans orientation of the indene rings. The described reactions of unsymmetrically substituted thiocarbonyl compounds with diazomethane lead to a mixture of dithiolanes with cis and trans orientations of the substituents [5, 8]. The stereoselectivity of the I→II transformation is evidently due to steric hindrance that develops in the case of cis orientation of the indene rings in the transition state. A complex multiplet is observed instead of the usual triplet signal for the protons of the -CH₂NCH₂- fragment of the piperidine ring in the PMR spectra of IIe,h. This is due to restrained

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rotation about the \( =C-N \) bond. The above-noted manifestations of the steric factors are confirmed by modeling of the II molecules and will be the subject of a separate communication.

Under the influence of light, solutions of dithiolanes II in aprotic solvents rapidly turn dark green but do not give ESR signals. When methanol or hexane is added, the green solutions are decolorized, and dithiolanes II crystallize without any changes. Under the prolonged action of light, solutions of dithiolanes II turn red because of the formation of a complex mixture of photolysis products.

When II are heated in solvents (at 80-110°C) or melted, the dithiolane ring is cleaved to give a mixture of substances from which starting enaminothiones I were isolated. Other probable thermolysis products [11] could not be identified.

In the reaction of hydrogen chloride with dithiolanes II the aminoindene fragments of the molecules are converted to indanimmonium fragments (see [12]) and unconjugated dihydrochlorides III, the neutralization of which leads to starting bases II, are formed. The IR spectra of salts III contain an intense \( \nu_{C=N} \) band (1645-1652 cm\(^{-1}\)) and \( \nu_{C=C} \) bands of aromatic rings (1595 and 1497 cm\(^{-1}\)). The \( \nu_{C=C} \) band of the five-membered indene ring (1530-1580 cm\(^{-1}\)) is absent.

The action of aqueous mineral acids on dithiolanes H causes hydrolysis of the amino groups and leads to dispiro[bis(indane)-1',4;1',5-(1,3-dithiolanes)] IV. The N-substituted (IIa) and N-phenyl-substituted (IIb, g) compounds undergo hydrolysis most readily; hydrolysis of N,N-disubstituted aminoindenedithiolane IIe gives primarily a mixture of dioxo compounds IV and aminooxo derivative V in a molar ratio of 1:4. This result has not as yet been explained unambiguously. The reaction of hydrogen chloride with V gives a hydrochloride salt, which, like salts III, has an indanimmonium structure (\( \nu_{C=N} 1653 \text{ cm}^{-1}, \nu_{C-O} 1725 \text{ cm}^{-1} \)). In contrast to dithiolanes II, dithiolanes IV and V are stable when they are heated up to their melting points (220-240°C). Bis(1-oxo-2-phenyl-3-indenyl) sulfide VI (see [13]) is present in the products of pyrolysis of dithiolane IVa.

The reaction of many thioketones with diazomethane differs from their reaction with substituted diazomethanes [4]. Aromatic thioketones react with diazomethane to give 1,3-dithiolanes but react with diphenyl-diazomethane to give thiiranes. The reaction with monophenyl-diazomethane often leads to a mixture of dithiolanes and thiiranes [4].