

2. Ruthenocene is formed from Ru(III) chlorides and cyclopentadiene only in the presence of a reducing agent in the reaction medium.

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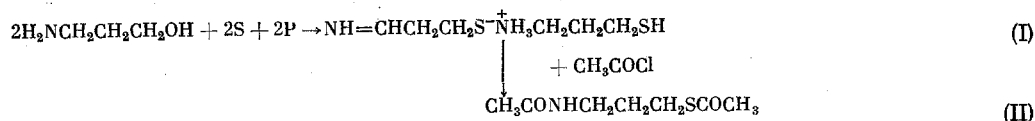
#### REACTION OF 3-AMINOPROPANOL WITH SULFUR AND RED PHOSPHORUS

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Elemental sulfur and red phosphorus when reacted with THF replace the oxygen in it by sulfur [1]. In the present paper, in order to expand this reaction to amino alcohols, we studied their reaction with 3-aminopropanol. The best yield of the desired product is obtained when 1 mole of the amino alcohol is reacted with 1 g-atom of sulfur and 1 g-atom of red phosphorus.

The reaction begins at 70°C and is accompanied by the marked evolution of heat, which raises the temperature of the reaction mixture up to 180°C. A dark tarry mass is formed here, from which the saltlike adduct (I) can be isolated in 46.6% yield by vacuum distillation.



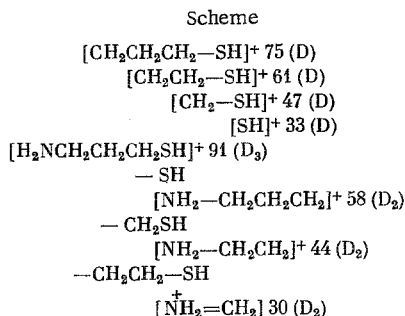
The treatment of (I) with 3 moles of  $\text{CH}_3\text{COCl}$  in the presence of 3 moles of triethylamine gives 3-(N-acetyl amino)propyl acetyl sulfide (II).

The structure of (I) and (II) agrees with the IR and mass spectra. The IR spectrum of (I) has the vibration bands ( $\text{cm}^{-1}$ ): 3360 ( $\nu\text{NH}$ ), 2300–2800 ( $\nu\text{NH}_3$ ), 1570 ( $\delta_{\text{as}}\text{NH}$ ), 1320 ( $\delta_{\text{s}}\text{NH}_2$ ), 825 ( $\rho\text{NH}_2$ ). The IR spectrum of (II) has the bands ( $\nu$ ,  $\text{cm}^{-1}$ ): 3300 (NH), 1660 (C=O), 1550 [amide (II)], 1640 [amide (I)]. In the mass spectrum of adduct (I) the signals of the heaviest ions ( $m/e$  91 and 89) correspond to the molecular ions of 3-amino-propyl mercaptan and 3-iminopropyl mercaptan. This result indicates that adduct (I) decomposes into 3-amino-propyl mercaptan (Ia) and 3-iminopropyl mercaptan (Ib), either during transition into the gas phase or under the influence of electron impact. The odd value of the indicated  $m/e$  testifies to the fact that the (Ia) and (Ib) molecules each contain one nitrogen atom. The presence of the 93 peak in 4.5% amount relative to the 91 peak indicates that (Ia) contains a sulfur atom (the natural amount of the  $^{34}\text{S}$  isotope in sulfur is 4.5%). Further proof for the structure of adduct (I) was obtained from the mass spectrum of the deuterated analog. The deuteration was accomplished by mixing adduct (I) with  $\text{D}_2\text{O}$  at  $\sim 20^\circ\text{C}$  and subsequent rapid evacuation of the  $\text{D}_2\text{O}$ . The peak of the ions with  $m/e$  91 was shifted by 3 units toward larger masses, while the peak with  $m/e$  89 was shifted by 1 unit. Consequently, (Ia) contains  $\text{NH}_2$  and SH, while (Ib) contains the SH group. Evidently, the  $\text{HN}=\text{CH}$  grouping of compound (Ib) is incapable of rapidly exchanging the hydrogen atom with  $\text{D}_2\text{O}$ . On the basis of analyzing the mass spectra of the undeuterated and deuterated adduct (I) it was established that (Ia) and (Ib)

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under the employed mass-spectrometric conditions represent two different compounds. The intensity of the peak with  $m/e$  30, which is maximum in the spectrum, was taken as 100. The intensity of the other peaks (indicated in parentheses) has the following values: 93 (0.51); 92 (0.96); 91 (11); 90 (0.96); 89 (7.8); 76 (1.4); 75 (1.7); 74 (7.0); 63 (12); 61 (12); 60 (4.3); 59 (4.8); 58 (7.8); 57 (6.1); 56 (17); 47 (11); 46 (5.7); 45 (12); 44 (17); 43 (7.0); 42 (11); 41 (19); 40 (2.0); 39 (7.8); 35 (2.6); 34 (3.5); 33 (1.2); 31 (9.6); 30 (100); 29 (11.3); 27 (21.7). The peaks with  $m/e$  32 and 28 are not given. The greater intensity of the peak with  $m/e$  30 is understandable, since this is characteristic for amines [2].

Below is given a scheme for the dissociative ionization of (Ia) with an indication of the number of deuterium atoms in the deuterio analog. As can be seen from the scheme, many of the ions in the mass spectrum are formed from the molecular ions by simple bond cleavage. The collection of these ions confirms the postulated structure of (Ia). The decomposition of (Ib) under the influence of electron impact proceeds in a similar manner.



## EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument. The liquid (II) was placed between two KBr plates, while the crystalline adduct (I) was recorded as a Nujol mull. The layer thickness of the compounds was not controlled. The mass spectra were obtained on an MI-1305 mass spectrometer, which was equipped with a direct insertion system, and using electrons with an ionization energy of 50 eV.

Adduct of 3-Aminopropyl Mercaptan with 3-Iminopropyl Mercaptan (I). With stirring and heating to 40°C, to 12.6 g (0.17 mole) of freshly distilled 3-aminopropanol was added in small portions a well-mixed mixture of 5.4 g (0.17 g-atom) of powdered sulfur and 5.2 g (0.17 g-atom) of red phosphorus. Rapid self-heating is observed when the mixture is heated to 70°C and white fumes appear, while reflux appears and a white precipitate is formed on further heating to 180°C. After cooling, from the reaction flask was distilled 7 g (46.6%) of adduct (I), bp 150–155°C (0.2 mm), which crystallizes rapidly to a white, very hygroscopic compound with mp 110–112°C. Adduct (I) is soluble in water or alcohol, and is insoluble in benzene. On contact with metal objects it turns black, and deliquesces in the air. Found: C 39.56; H 8.67; N 15.18; S 34.82%.  $\text{C}_6\text{H}_{16}\text{N}_2\text{S}_2$ . Calculated: C 40.03; H 8.90; N 15.55; S 35.55%.

3-(N-Acetylamino)propyl Acetyl Sulfide (II). With stirring and cooling of the flask in an ice-salt mixture, to a mixture of 15 g (0.09 mole) of a suspension of adduct (I) in 300 ml of abs. benzene and 25.5 g (0.07 mole) of triethylamine was added dropwise 19.8 g (0.27 mole) of  $\text{CH}_3\text{COCl}$  at such a rate that the temperature of the reaction mixture did not exceed 5°C. Here the mixture first assumes a pink, and then a red color. The amount of precipitate in the flask increases [deposition of  $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HCl}$ ]. Then the reaction mixture was stirred for 4 days at ~20°C. The sticky yellowish precipitate (42 g) was filtered and washed three times with hot benzene. The benzene was distilled from the filtrate, while the residue (19 g) was vacuum-distilled twice to give 14 g (93.3%) of (II), bp 104–105°C (0.004 mm);  $d_4^{20}$  1.1084;  $n_D^{20}$  1.5030. Found: C 47.02; H 7.35; N 7.77; S 18.15%; MR 49.96.  $\text{C}_7\text{H}_{13}\text{O}_2\text{NS}$ . Calculated: C 47.49; H 7.49; N 7.91; S 18.08%; MR 47.21. In addition, we isolated 4 g of a product with a broad boiling range.

## CONCLUSIONS

The reaction of 3-aminopropanol with sulfur and red phosphorus gave the 1:1 adduct of 3-aminopropyl mercaptan with 3-iminopropyl mercaptan, and its mass spectrum was discussed.

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