[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, FACULTY OF SCIENCE, AND THE INSTITUTE FOR MEDICAL CHEMISTRY, UNIVERSITY OF ZAGREB]

ON THE REACTION OF 2,3-DICHLORO-1,4-DIOXANE WITH MERCAPTANS

M. PROŠTENIK AND K. BALENOVIĆ

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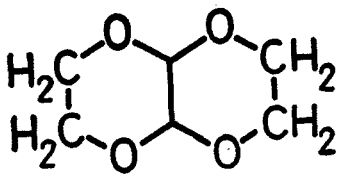
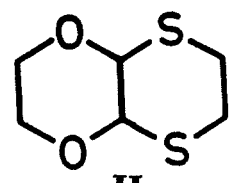
In the endeavor to prepare the analogous compound of naphthodioxane (I) (1) of the structure II, we have investigated the reaction of 2,3-dichloro-1,4-dioxane with 1,2-ethanedithiol.

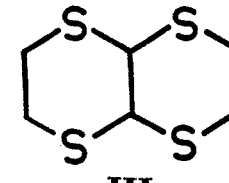
On heating these two components in anhydrous benzene, a reaction product was obtained which did not contain oxygen. The empirical formula of this compound is $C_6H_{10}S_4$, m.p. 135.5°, and it is identical with glyoxaldiethylenemercaptal (2). This fact does not, however, facilitate the choice between the structures III and IV, proposed for this compound.



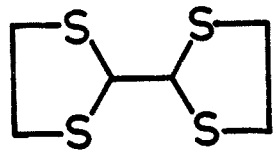
I



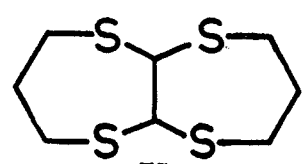
II



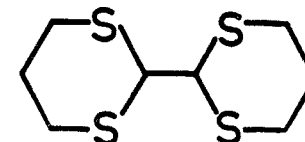
III



IV



V



VI

$(PhCH_2S)_2CH—CH(SCH_2Ph)_2$

VII

In the same manner an analogous compound was prepared from 2,3-dichloro-1,4-dioxane and 1,3-propanedithiol in anhydrous benzene, and it had the formula $C_{18}H_{14}S_4$. It can be regarded as the trimethylenemercaptal of glyoxal, with possible structures V or VI.

Further, a compound of the formula $C_{30}H_{30}S_4$ was prepared from 2,3-dichloro-1,4-dioxane and benzylmercaptan, which is the tetrabenzylmercaptal of glyoxal (VII).

It is known (3) that mild hydrolysis of 2,3-dichloro-1,4-dioxane readily yields glyoxal, therefore it is possible that during the reaction of 2,3-dichloro-1,4-dioxane with mercaptans, glyoxal is first formed, which then reacts normally further. The question of the structure of glyoxalethylenemercaptal thus remains unanswered.

Moreover, the assumption has recently been made (4) that the lower-melting

isomer of naphthodioxane should have the structure analogous to IV. In our case we have not been able to obtain two isomers of III, even by very careful fractional crystallization.

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EXPERIMENTAL

Reaction of 2,3-dichloro-1,4-dioxane with 1,2-ethanedithiol (III or IV). 2,3-Dichloro-1,4-dioxane (10.3 g., 0.066 mole) [prepared according to Boeseken, Tellegen, and Cohen Henriquez (5)], 1,2-ethanedithiol (12.4 g., 0.132 mole), and 12 ml. of anhydrous benzene were refluxed for 40 hours, *i.e.* till the evolution of hydrochloric acid ceased. The benzene was then evaporated at 30° under reduced pressure. Colorless platelets remained (18.3 g.), m.p. 131°. Recrystallized from ethanol, they had m.p. 135.5°. From the mother liquor a further amount was obtained. The substance was sublimed at 140°/0.1 mm. Mixture m.p. with glyoxal diethylenemercaptal prepared according to Fasbender (2) was unchanged.

Anal. Calc'd for $C_6H_{10}S_4$ (210.38): C, 34.25; H, 4.79; S, 60.91.
Found: C, 33.93, 34.26, 34.48; H, 4.83, 4.59, 4.85; S, 58.09.

Reaction of 2,3-dichloro-1,4-dioxane with 1,3-propanedithiol (V or VI). 2,3-Dichloro-1,4-dioxane (1.4 g., 0.0089 mole), 1,3-dimercaptopropane (2 g., 0.0185 mole), and 2 ml. of benzene were treated in the same manner as in the above preparation. Long, colorless needles were obtained; they were recrystallized from benzene and sublimed at 140°/0.1 mm; m.p. 140–141°.

Anal. Calc'd for $C_8H_{14}S_4$ (238.44): C, 40.29; H, 5.92.
Found: C, 40.55; H, 5.97.

Tetrabenzylmercaptal of glyoxal (VII). By proceeding in the same manner as described above, a reaction product was obtained from 1.24 g. (0.0079 mole) of 2,3-dichloro-1,4-dioxane and 3.9 g. (0.0315 mole) of benzylmercaptan in 6 ml. of benzene, which crystallized after standing for a few hours. From the viscous mixture 2.5 g. of crystals were obtained, which were recrystallized from ethanol. The large, colorless prisms, m.p. 67–68° were dried *in vacuo* at 20° for 6 hours.

Anal. Calc'd for $C_{30}H_{30}S_4$ (518.78): C, 69.45; H, 5.83.
Found: C, 69.61; H, 5.95.

SUMMARY

The reaction of 2,3-dichloro-1,4-dioxane with mercaptans yields glyoxal mercaptals. Mercaptals VI–VII are new.

Strosmajerovtrg 14,
Zagreb, Yugoslavia.

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