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SYNTHETIC AND POLAROGRAPHIC STUDIES IN THE 3-TROPINONE SERIES

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THE reactions of 3-tropinone and its sulphur analogue 8-thia-bicyclo-3,2,1)-octan-3-one represent a complete set of reactions enabling a demonstration of the mutual interrelation of β-amino and β-alkylmercapto ketones in which the reactive components are the corresponding methoiodides II and IV. These are cleavaged in alkaline solutions to yield a mixture of cycloheptadienones. For tropinone methoiodide this particular reaction was described by Meinwald and co-workers.[1] The possible routes of synthetic reactions (partially studied earlier by one of us[2]) can be depicted as shown on page 747 (only the synthetic routes are given, the actual mechanisms of the particular synthetic reaction being more complicated) This scheme clearly shows the relation of all the heterocyclic compounds involved (I-IV) to the mixture of cycloheptadienones (V). The exchange of heteroatoms can occur in all the synthetic reactions via the mixture of cycloheptadienones.

In the formation of V from methoiodides II and IV we were able, using the polarographic method, to prove the existence of 6-dimethylaminocyclohept-2-en-one (VI) and 6-methylmercaptane cyclohept-2-en-one (VII) as inter-

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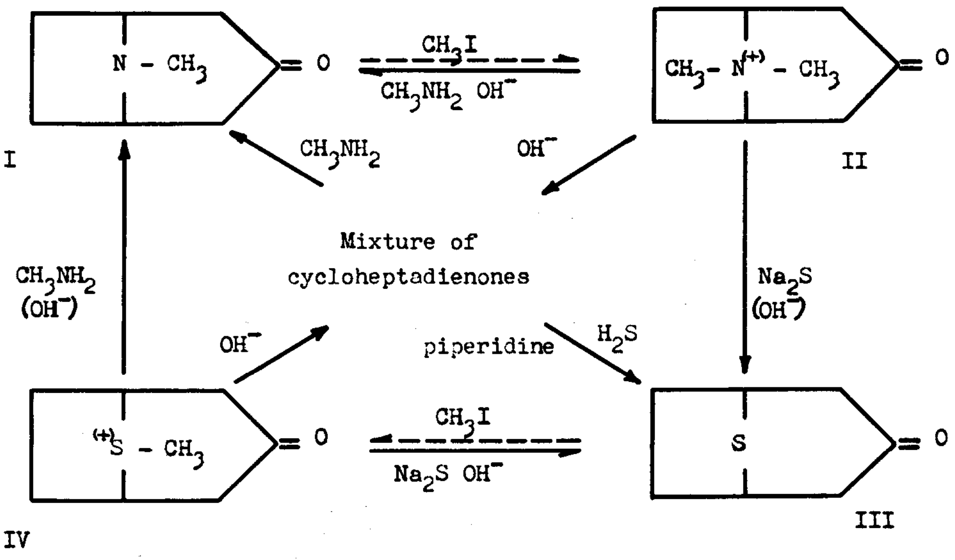
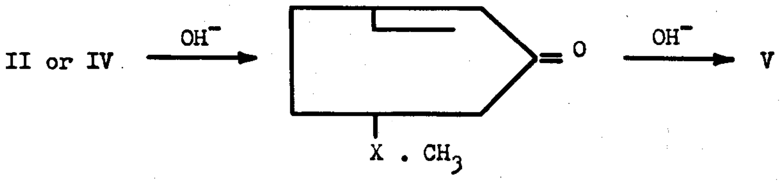
[1] J. Meinwald, S.L. Emerson, N.C. Yang and G. Büchi, J.Amer.Chem.Soc. 77, 4401 (1955).

[2] V. Horák, J. Závada and A. Pískala, Acta Chim.Acad.Sci.Hung. 21, 97 (1959).



mediates. Using polarography optimum reaction conditions were found enabling the isolation of VII.



VI X = NCH_3

VII X = S

Since both VII and its 2,4-dinitrophenylhydrazone and similarly its semicarbazone and thiosemicarbazone are unstable, VII was reduced by sodium borohydride in methanolic solution into corresponding alcohol. This alcohol is an oil distilling (16 mm Hg) at 160-170° (bath temperature), n_D^{20}= 1.5346. Its purity was proved by chromatography on thin alumina layer (Al_2O_3 bas.

deactivated with 10% H_2O, chloroform, $R_F = 0.5$). (Found: C, 60.90; H, 9.06; S, 19.94; H, 0.68 act. Calc. for $C_8H_{14}SO$ (158.26); C, 60.75; H, 8.92; S, 20.24; H, 0.63 act.)

On polarographic curves separate waves for II, V and VI (or IV, V and VII respectively) were found. Whereas the waves for methoiodides II and IV have shown a behaviour similar to that found for other β-aminoketones,[3] the waves for intermediates VI and VII resemble that for simple α, β-unsaturated ketones.[4] Cycloheptadienones V show polarographic curves similar to that of tropone.[5]

From polarographic measurements it was found that the formation of VI from II occurs at pH higher than about 10 whereas cycloheptadienones V are formed from VI at pH higher than about 11. The cycloheptadienones undergo in alkaline solutions above pH 12 a further reaction (isomerisation or dimerisation) resulting in the formation of a polarographically inactive compound (without conjugated system).

On the other hand with the sulphur analogue IV the formation of the intermediate VII occurs at pH above 4. The second elimination step resulting in the formation of V occurs again at pH above 10. Hence the intermediate IV is stable between pH 5 and 9 and under such conditions VII may be isolated by extracting the aqueous solution with ether.

The possibility of mutual interchange of β-aminoketones and β-alkylmercaptanes via the highly reactive onium **salts** in addition to substitutive demethylation of these compounds is demonstrated here on substances I-IV and seems to have a quite general validity.

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[3] P. Zuman and V. Horák, Advances in Polarography, Proc.IInd Int. Congr. Polarograph., Cambridge 1959 Part II, p. 804. Pergamon Press, London, (1960).

[4] R. Pasternak, Helv.Chim.Acta 31, 753 (1948).

[5] J. Bartek, T. Mukai, T. Nozoe and F. Šantavý, Coll.Czech.Chem.Comm. 19, 885 (1954).