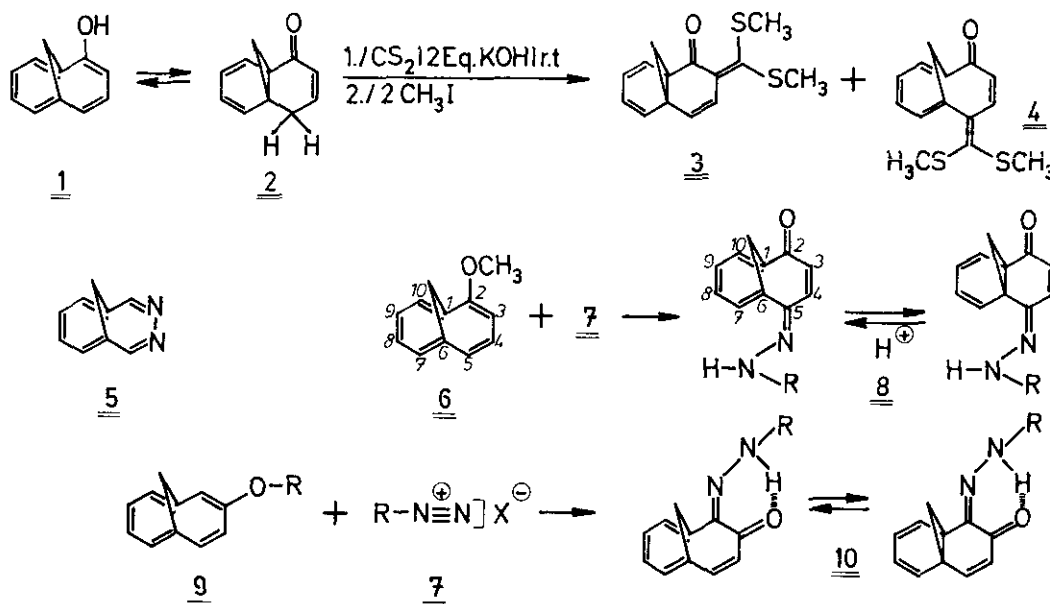


SYNTHESES OF A NEW CLASS OF DYES - COUPLING REACTIONS OF  
DIAZONIUMSALTS WITH BRIDGED ANNULENES - SYNTHESIS OF NEW BRIDGED  
HETEROCYCLES

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In continuation of our experiments in syntheses of new bridged molecular systems, bridged heterocyclic annulenes etc. we found that the valence-isomer-tautomer-mixtures 1 and 2 react with CS<sub>2</sub>, KOH and CH<sub>3</sub>I to the bridged acyl-ketene-dithioacetals 3 and 4. About syntheses and chemical properties of the new heterocyclic compound 5 will be reported and about the coupling-reactions of diazoniumsalts



with 2- and 3-alkoxy-substituted 1,6-Methano-[10]-annulenes 6 and 9 as iso- $\pi$ -electronic  $\alpha$ - and  $\beta$ -Naphtholederivatives - the aims are new classes of dyes. The reaction-products of 6 and 7 and 9 and 7 are the hydrazones 8 and 10 - corresponding azo-dyes are synthesized also. In all cases the question was of interest, whether the new molecular systems exist as cycloheptatriene- or nor-caradiene-valence-isomer-tautomers or as mixture of both.

The results of spectroscopic experiments and of X-ray-structure-analysis are discussed.