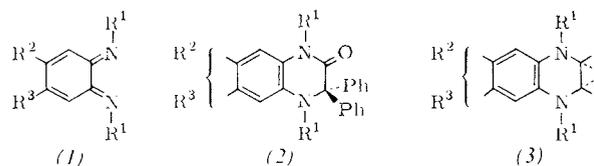


## Cycloaddition Reactions of *o*-Quinonoid Compounds<sup>[\*\*]</sup>

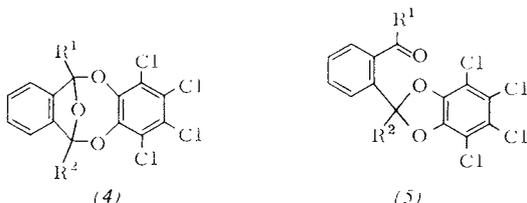
By Willy Friedrichsen<sup>[\*]</sup>

*o*-Benzoquinone diimides [(1), R<sup>1</sup> = benzoyl, benzenesulfonyl; R<sup>2</sup> = R<sup>3</sup> = H; R<sup>2</sup> = R<sup>3</sup> = CH<sub>3</sub>; R<sup>2</sup> = H, R<sup>3</sup> = Cl] react with diphenylketene and with olefins, like certain *o*-quinones<sup>[1]</sup>, to form 2-oxo-1,2,3,4-tetrahydroquinoxalines (2) or 1,2,3,4-tetrahydroquinoxalines (3)<sup>[2]</sup>. Unsymmetrical *o*-benzoquinone diimides [(1), R<sup>1</sup> = benzoyl, benzenesulfonyl; R<sup>2</sup> = H, R<sup>3</sup> = Cl] form both regioisomers (2) in the former case; the structures of the isomers were determined by partial synthesis.



Kinetic studies (activation parameters, solvent dependence of the rate constants, competition experiments) agree with the assumption that the reactions leading to (2) and (3) are Diels-Alder reactions with inverse electronic requirements.

1,3-Diarylisobenzofurans react with *o*-quinones thermally to form 6,11-epoxydibenzo[*b,f*][1,4]dioxocins (4) and/or dioxoles (5)<sup>[3]</sup> (formulated for the reaction with tetrachloro-*o*-benzoquinone). Investigations on the mechanism [reaction of 1-(tetramethylphenyl)-3-phenylisobenzofuran to form (5a) (R<sup>1</sup> = tetramethylphenyl, R<sup>2</sup> = phenyl)<sup>[4]</sup> and (5b)



(R<sup>1</sup> = phenyl, R<sup>2</sup> = tetramethylphenyl), (activation parameters, by measurement of the temperature dependence of the rate constants and of the product distribution)] show that the reaction is entropy-controlled and proceeds *via* an isopolar transition state.

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[1] Review: G. Pfundt and G. O. Schenck in J. Hamer: 1,4-Cycloaddition Reactions. Academic Press, New York 1967, Chap. 11.

[2] According to this, at least some of the results obtained by R. Adams *et al.* (review: R. Adams and W. Reifschneider, Bull. Soc. Chim. Fr. 1958, 23) must be corrected.

[3] See also: W. M. Horspool, J. M. Tedder, and Z. U. Din. J. Chem. Soc. C 1969, 1964.

[4] (5a) was synthesized by an independent route.

## Steric Effects in the Mass Spectra of Monocyclic and Bicyclic Diols and Their Derivatives

By Hans-Friedrich Grützmacher<sup>[\*]</sup>

The differences in the mass spectra of stereoisomeric compounds are partly due to elimination reactions of the molecular

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ions, which must proceed *via* a transition state with a specific steric arrangement. Since the steric conditions for the transition state can be easily checked with the aid of molecular models, a mass-spectrometric identification of stereoisomers is possible in this way without the use of reference spectra.

It is known that a stereospecific 1,4-elimination of H<sub>2</sub>O occurs in the molecular ions of cyclohexanol. Investigation of the mass spectra of stereoisomers of the cyclopentane diols, cyclohexane diols, and cycloheptane diols, and their dimethyl ethers also show stereochemical control for the elimination of HOR (R = H, CH<sub>3</sub>) and CH<sub>2</sub>O from the molecular ions if the substituents occupy the 1,3 or 1,4 positions. In the *trans* compounds the elimination of HOR dominates the fragmentation, whereas the elimination of CH<sub>2</sub>O is characteristic of the *cis* compounds. The stereochemical control of the fragmentations also persists in *C*-methylated derivatives of 1,3-cyclohexane diol, with the exception of the 2-methyl and 2,2-dimethyl derivatives, in which fast ring cleavage of the molecular ions occurs.

Surprisingly, however, the expected steric effects cannot be detected in the mass spectra of the positional isomers and stereoisomers of the bicyclo[2.2.1]heptane diols and their dimethyl ethers. On the other hand, the expected effects are again observed in the mass spectra of decalindiol and of corresponding dimethyl ethers, so that mass-spectrometric identification of the stereoisomers is possible in this series of compounds. It is interesting to note that stereochemical control of the elimination reactions is also found for the 1,5-dimethoxydecalins if the methoxy groups can come close together in any conformation of the molecular ions.

## Constitution of the Polymers and the Coordination Compounds of Formaldehyde Oxime<sup>[\*\*]</sup>

By Kai Arne Jensen<sup>[\*]</sup>

Evidence obtained from chemical properties and infrared spectra shows that "triformoxime" or "trimeric formaldehyde oxime" is actually a chain polymer. The known acetyl and benzoyl derivatives of formaldehyde oxime are, however, derivatives of a cyclic trimer, 1,3,5-trihydroxyhexahydro-1,3,5-triazine. Similarly, the known hydrochloride, (H<sub>2</sub>CNOH)<sub>3</sub>HCl, and also other salts, contain the cyclic trimer, but on neutralization they depolymerize to formaldehyde oxime. The cyclic trimer could, however, be prepared by a special method. It is readily soluble in water but is rapidly transformed into the water-insoluble polymer. In aqueous solution it is partially depolymerized to formaldehyde oxime.

Analysis of the <sup>1</sup>H-NMR spectra of solutions of (H<sub>2</sub>CNOH)<sub>3</sub>HCl in deuterium oxide has shown that, in aqueous solution, an equilibrium exists between monomeric and trimeric formaldehyde oxime and, at higher pH values, is shifted completely towards the monomeric form.

The hydrochloride, (H<sub>2</sub>CNOH)<sub>3</sub>HCl, forms very intensely colored coordination compounds with nickel, iron, and manganese salts. There has been some doubt whether these complexes are derived from monomeric or trimeric formaldehyde oxime. According to above mentioned studies the ligand must be the anion of monomeric formaldehyde oxime. This is substantiated by a detailed infrared spectroscopic investigation of the complexes, as well as by other physical methods. In

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