II. Radicals produced by the abstraction of hydrogen atoms from olefinic substances. By the use of the nitroxide method, radicals have been trapped which are formed by the abstraction of a hydrogen atom in the reaction between the *N*-halogen imides and a variety of olefinic substances such as 2-propen-1-ol, 2-buten-1-ol, 2-propenenitrile, 6-methyl-5-hepten-2-one, 3-methyl-2-cyclopenten-2-ol-1-one, cyclopentene, cyclohexene, 1-methyl-1-cyclohexene, or *d*-limonene. With an excess of the olefinic compounds the nitroxide radicals formed from these substances were found to dominate over the species (IV) derived from the trapping of the succinimidyl radicals. In several cases the radicals could be identified by the secondary hfs of the corresponding nitroxide radicals.
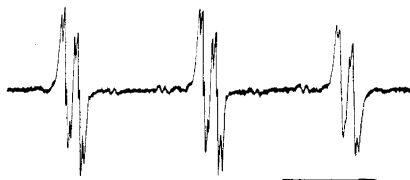

Fig. 2. ESR spectrum of the nitroxide radicals formed by the trapping of the radicals produced in the reaction between 2-propen-1-ol and *N*-chlorosuccinimide (NClS). Solvent: CH_2Cl_2. The reaction mixture was irradiated by UV light.

Fig. 2 shows the spectrum of the nitroxide radicals obtained with 2-propen-1-ol and NClS ($a^N = 14.9$ g). The secondary doublet splitting ($a^H = 1.43$ g) indicates the trapping of a radical with the structure $CH_2 = CH - \dot{C}H - OH$, though the structure $\dot{C}H = CH - CH_2 - OH$ is a possible alternative. However, the former structure is supported by the result obtained with 2-buten-1-ol and NClS, which also gave rise to a nitroxide radical with a doublet splitting ($a^N = 14.9$ g, $a^H = 1.43$ g) indicating the trapping of $CH_3 - CH = CH - \dot{C}H - OH$ radicals.

In other cases the structure of the trapped radical was uncertain, as no complete analysis of the secondary hfs was possible.

In view of the possible selective survival of certain nitroxide species, and the different ability of the *C*-nitroso compound (II) to trap different species of short-lived radicals,[4-7] it should be emphasized that

the nitroxide radicals actually observed do not necessarily represent the intermediate radicals of the main path of the reaction between *N*-halogen imides and the olefinic substances concerned.

1. Walling, C. *Free Radicals in Solution*, Wiley, New York 1957.
2. Horner, L. and Winkelmann, E. H. In Foerst, W. *Newer Methods of Preparative Organic Chemistry*, Academic, New York 1964, Vol. III.
3. Pryor, W. A. *Free Radicals*, McGraw, New York 1966.
4. Lagercrantz, C. and Forshult, S. *Nature* **218** (1968) 1247.
5. Lagercrantz, C. and Torssell, K. *Acta Chem. Scand.* **22** (1968) 1935.
6. Forshult, S., Lagercrantz, C. and Torssell, K. *Acta Chem. Scand.* **23** (1969) 522.
7. Lagercrantz, C. and Forshult, S. *Acta Chem. Scand. In press.*
8. Mackor, A., Wajer, Th. A. J. W. and de Boer, Th. J. *Tetrahedron* **24** (1968) 1623.

Relative Thermodynamic Stabilities of 4-Methylene-1,3-dioxane and the Isomeric 4-Methyl-1,3-dioxene-(4) and the Kinetics of Their Hydrolytic Cleavage

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In a recent study of five-membered cyclic vinyl ethers[1] it was found that the kinetic behavior depended greatly on the site of unsaturation; 4-alkylidene dioxolanes were cleaved in acid solutions

by a general acid-catalyzed mechanism involving a rate-limiting proton transfer to the double bond, whereas the isomeric compounds with the double bond located in the ring itself, 4-alkyl-1,3-dioxoles, displayed specific hydronium ion catalysis decomposing by the *A*-1 mechanism of acetal hydrolysis.

The present paper describes the preparation, equilibrium of isomerization and the kinetics of acid-catalyzed cleavages of the closely related six-membered cyclic vinyl ethers, 4-methylene-1,3-dioxane (I) and 4-methyl-1,3-dioxene (II). The primary aim
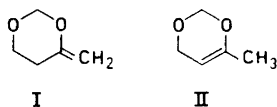
of the study was to obtain further information about the structural factors that determine the site and mode of cleavage of unsaturated cyclic acetals. In addition, as the relative stabilities of methylene-cyclohexane and the isomeric methyl-cyclohexene-(1) have been studied in detail,[2-4] it was of interest to compare the stabilities of the corresponding hetero-cycles, (I) and (II).

Syntheses. Compounds (I) and (II) were prepared by the following route:

$$CH_2=CHCH_2Cl + 2\ CH_2O \xrightarrow{H_2SO_4}$$
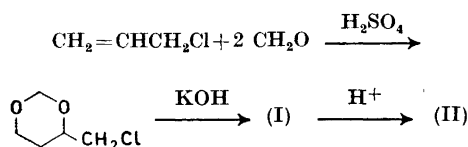
The first step, the preparation of 4-chloro-methyl-1,3-dioxane, was performed as described by Price and Krishnamutri.[5] The experimental procedures used in the subsequent steps leading to (I) and (II) were those employed in the synthesis of the corresponding five-membered unsaturated acetals.[6] The crude products were purified by repeated fractional distillation in a Todd precision fractionation assembly and the purities of the fractions collected were continuously followed by gas-liquid chromatography and by IR spectroscopy. Only fractions over 99 % pure were used in the equilibrium and rate studies. The following physical constants were recorded for these fractions: (I), b.p. 55.0°C/75 torr, d_4^{20}

1.0229, n_D^{20} 1.4453, $(R)_D$ 26.06 (calc. 25.82); (II), b.p. 108.5°C/748 torr, d_4^{20} 1.0244, n_D^{20} 1.4382, $(R)_D$ 25.66 (calc. 25.79).

Kinetic measurements. The hydrolytic decomposition reactions were followed by spectrophotometry from the disappearance of the absorption peak of the ethylenic linkage at $226-232$ mμ. The technique of the measurements has been described.[1,7]

Isomerization equilibrium. The equilibrium between (I) and (II), which was easily attained in the presence of an acid catalyst, was studied by the same experimental procedure as was used for the *endo-exo* isomeric derivatives of furan.[8]

The kinetic data for the acid-catalyzed cleavages of (I) and (II) are seen in Table 1. The following values, determined by Pihlaja[9] for the saturated analog of (I) and (II), 4-methyl-1,3-dioxane, may be cited for comparison: $k_{H_3O^+}$ 1.012×10^{-6} M^{-1}s^{-1}, E 27.7 kcal/mole, $\Delta S^{\ddagger}$ +4.6 E.U. (at 25°C).

Although (I) and (II) are acetals, like their saturated analog, the *A*-1 mechanism displayed by the latter compound seems to be excluded from their hydrolytic cleavages. First, the hydrolysis rates are faster by about six powers of ten, which is difficult to understand in terms of the *A*-1 mechanism. In fact, in the case of five-membered cyclic acetals similar unsaturation led to only minor changes in the rate of the *A*-1 reaction.[1] Second, the reactions of (I) and (II) exhibit general acid catalysis. Third, the solvent deuterium isotope effects measured for the lyonium ion-catalyzed hydrolyses of (I) and (II), $k_D/k_H = 0.39$ and 0.41, respectively, are of the magnitude observed for the hydrolysis of vinyl ethers.[1,6,7,10]

All these facts suggest that (I) and (II) are cleaved by rate-determining proton transfers to the unsaturated linkages. Also an inference that can be drawn from stereochemical arguments, *viz.*, that (I) should be cleaved more easily than (II), is in qualitative accord with the data. In the case of compound (I), the attainment of the transition state does not significantly alter the ring geometry; in the initial state the ring is in a chair form with the *exo* double bond at one of the flaps,[11] and in the transition state leading to the intermediate carbonium-oxonium ion the 4-carbon atom still maintains its sp^2 configuration. Thus, distortions within the ring are not necessary. On the contrary, compound (II) is initially in the half-chair

Table 1. Kinetic values for the acid-catalyzed cleavages of (I) and (II) in water solution.

	Catalyst	°C	k_{HA} M^{-1} s^{-1}	E kcal/mole	$\Delta S^{\ddagger}$ E.U.
(I)	H_3O^+	15	3.20		
»	»	25	6.53	11.8	-18.3
»	»	35	11.83		
»	CH_3COOH	25	0.0245 [a]		
»	D_3O^+ (in D_2O)	25	2.54		
(II)	H_3O^+	15	0.163		
»	»	25	0.442	17.8	$-$ 2.3
»	»	35	1.232		
»	HCOOH	25	0.0244 [a]		
»	D_3O^+ (in D_2O)	25	0.183		

[a] Buffer mixtures with constant ionic strength of 0.5 M. The value is based on four runs conducted at different concentrations of the undissociated acid.

form like the cyclohexene ring,[12] and the attainment of the transition state with the 4-carbon atom as the center of the nascent cation involves a distortion of the ring toward the chair geometry. These factors may also qualitatively account for the changes in the energies and entropies of activation when going from (I) to (II), although the magnitudes of these changes seem surprisingly large.

Another factor, apart from those associated with the transition states, which makes (II) less reactive than (I) is the initial state stability. The equilibrium constant measured for the isomerization reaction (I)⇌(II) at 25°C was (1.37 ± 0.16) $\times 10^2$, which corresponds to a value of -2.91 ± 0.07 kcal/mole for the standard free energy difference between (II) and (I). It can be seen that the latter difference does not significantly differ from the value -3.15 kcal/mole reported for the carbocyclic analogs of (I) and (II), methylenecyclohexane and methylcyclohexene-(1).[3] This, in turn, further confirms the previous conclusions about the "aromatic stabilization" of 1,3-dioxoles and its kinetic implications,[1] in view of the fact that such stabilization is not possible in the present case.

1. Salomaa, P., Kankaanperä, A. and Launosalo, T. *Acta Chem. Scand.* **21** (1967) 2479.
2. Cope, A. C., Ambros, D., Giganek, E., Howell, C. F. and Jacura, Z. *J. Am. Chem. Soc.* **82** (1960) 1750.
3. Herling, J., Shabtai, J. and Gil-Av, E. *J. Am. Chem. Soc.* **87** (1965) 4107.
4. Coppens, P., Gil-Av, E., Herling, J. and Shabtai, J. *J. Am. Chem. Soc.* **87** (1965) 4111.
5. Price, C. C. and Krishnamutri, J. V. *J. Am. Chem. Soc.* **72** (1950) 5335.
6. Kankaanperä, A., Launosalo, T. and Salomaa, P. *Acta Chem. Scand.* **20** (1966) 1790.
7. Salomaa, P., Kankaanperä, A. and Lajunen, M. *Acta Chem. Scand.* **20** (1966) 1790.
8. Kankaanperä, A., Taskinen, E. and Salomaa, P. *Acta Chem. Scand.* **21** (1967) 2487.
9. Pihlaja, K. *Ann. Acad. Turkuensis, Ser A* **I** (1967) No. 114.
10. Kresge, A. J. and Chiang, Y. *J. Chem. Soc.* **B 1967** 53, 58.
11. Gerig, J. T. *J. Am. Chem. Soc.* **90** (1968) 1065.
12. Eliel, E. L., Allinger, N. L., Angyal, S. J. and Morrison, G. A. *Conformational Analysis*, Wiley, New York 1965, Ch. 2.