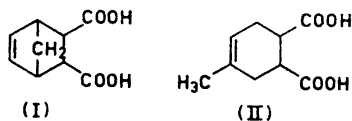


Ozonolysis of Cyclic Olefins in Formic Acid

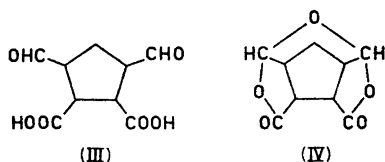
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As an extension of our investigations on the "solvolytic ozonolysis",^{1,2} a number of cyclic olefins have been ozonised in formic acid. The olefins in question are: *endo-cis*-3,6-*endo*-methylene- Δ^4 -tetrahydrophthalic acid (I), its anhydride, mono- and dimethyl ester as well as the corresponding dihydric alcohol; further, *cis*-4-methyl- Δ^4 -tetrahydrophthalic acid (II), its anhydride and dimethyl ester.



Alder³ ozonising (I) in aqueous solution did not obtain the expected product $C_6H_{10}O_6$ (III), but a compound $C_5H_8O_5$, which was named "O₅-Körper" and assigned the structure (IV).



The present work is concerned with the formation of peroxidic compounds, while the nature of other reaction products is left for later discussion.

The ozonolyses took place in concentrated formic acid at a temperature just above the freezing point of the mixture. After ozonation the content of active oxygen, of peracid, and of volatile peracid was determined. In Table I are summarised the analytical results.

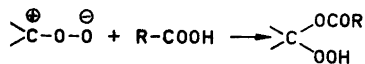
The total content of active oxygen was, with one exception, close to the theoretical amount, while the figures for peracid varied. It is seen that the monocyclic compounds gave more peracid than the corresponding bicyclic ones, and that the free acids gave the highest yields in each group. Greater variations were found in the amounts of volatile peracid, which in the present case consists of performic acid. Also here the monocyclic system gave the higher yields. Conspicuous are the low yields from I and its anhydride as compared to the total amount of peracid. Some performic acid is decomposed during distillation, but having discounted for this, the mentioned results are still exceptionally low. There is no reason why performic acid should be consumed to a larger extent by aldehydic reaction products from (I) and the anhydride than by products from the other olefins. The small yields of performic acid from the bicyclic compounds must therefore be regarded as real. Consequently the directly titrated peracid only for a certain percentage consists of performic acid; the rest is probably made up by a non-volatile peracid formed from the ozonised material, or it may even be a very reactive hydroperoxide. The residues after distillation of

Table I.

Substance	Total act. oxygen	Peracid	Volatile peracid
	Per cent of theoretical yield		
(I)	98.1	81.4	2.8
(I), anhydride	73.9	57.5	2.2
(I), monomethyl ester	98.3	59.6	12.8
(I), dimethyl ester	96.6	44.6	24.3
(I), corresponding alcohol	98.1	57.2	35.9
(II)	99.3	91.9	39.3
(II), anhydride	96.2	70.8	35.3
(II), dimethyl ester	98.2	63.8	40.8

performic acid contained active oxygen, some of which could be titrated as peracid.

The mode of peracid formation is not known in detail, but it seems reasonable that the reaction takes place at the zwitterion ⁴⁻⁸ stage. A carboxylic acid and a zwitterion can react in the following way:



This has been demonstrated in the ozonolysis of 9,10-octalin.⁴ Such hydroperoxides are very reactive and may in their action upon iodide approach the effect of a peracid. Further it is to be expected that they can split up into a carbonyl compound and a peracid, in our case performic acid.

In the bicyclic series the zwitterion is part of a cyclic system, the stereochemistry of which may be favourable for the formation of intramolecular peroxy compounds, e.g. peracetals. Such products are certainly reactive towards iodide, but may have little tendency towards forming performic acid.

The present investigation indicates that in the solvolytic ozonolysis, the steric conditions in the intermediates play an active part in determining the yield of volatile peracid.

Experimental. Ozonation technique. The ozonolyses were performed by passing an oxygen stream containing 3–4 vol. % ozone through the reaction mixture. The ozone output from the generator as well as unreacted ozone in the effluent gas was determined iodometrically. A gas-washing bottle with a fritted disc just above the gas inlet served as reaction vessel. When the ozonation was finished, the electric current was cut off and dissolved ozone removed with dry oxygen. In all experiments 0.500 g substance was dissolved to 50 ml in formic acid. A small amount of the solvent disappeared during the ozonation and the solution was therefore afterwards adjusted to exactly 50 ml.

Materials. Formic acid was Merck, analytical reagent (98–100%). *Endo-cis-3,6-endo-methylene-Δ⁴-tetrahydrophthalic anhydride* was prepared from maleic anhydride and cyclopentadiene as described by Diels and Alder;⁹ m.p. 162°C (Lit. 165°C). The free acid was made by recrystallising the anhydride from water; m.p. 175–177°C (Lit. 177–179°C). The monomethyl ester was prepared according

to Morgan *et al.*¹⁰ from the anhydride and anhydrous methanol; m.p. 76–78°C. (Lit. 78.5°). The dimethyl ester was prepared in the same way, but *p*-toluenesulphonic acid was added as a catalyst and the reaction time increased from 1.5 to 10 h; b.p. 129–130°C, 9 mm Hg. *Endo-cis-3,6-endo-methylene-Δ⁴-tetrahydrophthalyl alcohol* is not described in the literature. It was prepared by LiAlH₄-reduction of the anhydride in ether solution and purified by recrystallisation from petrol ether; m.p. 89–90°C; yield 70%. (Found: C 70.2; H 9.1. Calc. for C₉H₁₄O₂: C 70.1; H 9.1).

Cis-4-methyl-Δ⁴-tetrahydrophthalic anhydride was prepared from maleic anhydride and isoprene according to Diels and Alder,⁹ m.p. 62–63°C. (Lit. 63–64°C). The free acid was made from the anhydride by recrystallisation from water; m.p. 153–154°C. (Lit. 155°C). The dimethyl ester was prepared as for the bicyclic compound; b.p. 149–150°C, 12 mm Hg.

Analytical. Total active oxygen was determined by running aliquots of the reaction mixture into sodium iodide in glacial acetic acid under a carbon dioxide atmosphere. The mixture was kept in the dark for 45 min and the liberated iodine titrated with standard thiosulphate. Peracid was also determined iodometrically. The samples were run into aqueous potassium iodide to which some titanium reagent had been added in order to bind any hydrogen peroxide which might be present.¹¹ A peracid reacts rapidly and completely with aqueous iodide and can thus be distinguished from most other peroxidic compounds. Performic acid was distilled in an ordinary ground joint distillation apparatus fitted with a splash head, at 40°C and 15 mm Hg. The distillate was collected directly in aqueous potassium iodide and the liberated iodine titrated with standard thiosulphate.

The analytical results are summarised in Table 1 and all values are averages of at least four different experiments.

1. Bernatek, E. and Ledaal, T. *Tetrahedron Letters* **26** (1960) 30.
2. Bernatek, E. *Ozonolyses in the Naphthoquinone and Benzofuran Series. Thesis.* Oslo University Press 1960.
3. Alder, K. and Schneider, E. *Ann.* **524** (1936) 189.
4. Criegee, R. and Wenner, G. *Ann.* **564** (1949) 9.
5. Criegee, R. *Ann.* **583** (1953) 1.
6. Criegee, R., Blust, G. and Zinke, H. *Chem. Ber.* **87** (1954) 766.
7. Criegee, R., Kerechow, A. and Zinke, H. *Chem. Ber.* **88** (1955) 1878.

8. Criegee, R. *Record Chem. Progress (Kresge-Hooker Sci. Lib.)* **18** (1957) 111.
9. Diels, O. and Alder, K. *Ann.* **460** (1928) 111.
10. Morgan, M. S., Tipson, R. S., Lowry, A. and Baldwin, W. E. *J. Am. Chem. Soc.* **66** (1944) 404.
11. Ledaal, T. and Bernatek, E. *Anal. Chim. Acta* **28** (1963) 322.

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Bonds Connecting Group VI Donor Atoms and Halogen Atoms in Ethylene Derivatives

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Several crystal structures of addition compounds exhibiting bonds between group VI donor atoms and halogen atoms of organic molecules are known, but in-

formations are lacking for halogen derivatives of ethylene. One addition compound of this kind has been described, however; the 1:1 compound containing 1,4-dioxan and tetraiodoethylene.¹

We have prepared this compound and also some new compounds in which oxygen is replaced by other group VI atoms. For X-ray investigation we first chose the 1,4-diselenane-tetraiodoethylene compound. In crystals of this kind we expected the presence of endless chains of alternating acceptor and donor molecules, with a nearly linear arrangement donor atom, halogen, carbon. Further that the chain halogen atoms of the acceptor molecule might be *trans* situated. In this case both donor and acceptor molecule would be expected to occupy centrosymmetrical sites in the crystal. These expectations were actually confirmed for the compound investigated. The other moiety of iodine atoms are also linked to selenium atoms, however, but these iodine atoms belong to neighbour chains. The I...Se distances are equal (3.43 resp. 3.40 Å) and the C-I...Se arrangements both nearly linear. In the (1:1) diiodoacetylene compound where each selenium atom is linked to *one* iodine atom only, the distance is a little shorter (2.35 Å).² In this compound no indication of a

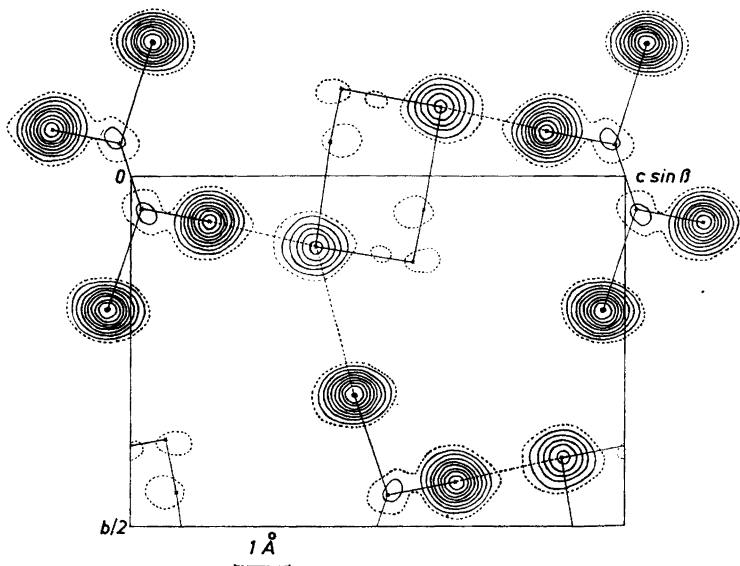


Fig. 1. Fourier projection along the *a* axis. Contour intervals of $10 \text{ e}/\text{\AA}^2$; the dotted contour corresponds to $5 \text{ e}/\text{\AA}^2$.