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THE DIRECTIVE INFLUENCE OF SUBSTITUENTS ON ANOMALOUS OZONOLYSIS
A HAMMETT TYPE RELATIONSHIP

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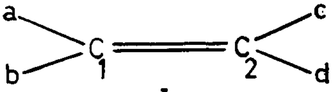
When 1,4-naphthoquinone was ozonised in chloroform[1] anomalous ozonolysis occurred to an extent of about 70%. Anomalous ozonolysis is, in this connection, a reaction where the principal ozonolysis products contain one carbon atom less than the starting material, i.e. reactions where a carbon atom originally located at the double bond is split off.

In unsymmetrical olefins of type I the question arises whether anomalous ozonolysis leads to predominant loss of carbon atom 1 or 2, i.e. the direction of anomalous ozonolysis.



I

In order to investigate this problem in some detail, different 2-substituted naphthoquinones have been ozonised. When carbon atom 2 and the substituent are eliminated from these substances, phenylglyoxal-o-carboxylic acid results.

All ozonolysis reactions were performed in chloroform at 0 - 3°C, followed by cold hydrolysis until the active oxygen had disappeared. Results are recorded in Table 1, where the different substituents and corresponding amounts (in per cent of theoretical) of phenylglyoxal-o-carboxylic acid are shown.

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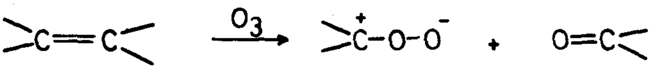
[1] Bernatek, E. Tetrahedron 4 (1958) 213.

Table 1

Substituent	Phenylglyoxal-o-carboxylic acid
-OH	90,4
-Cl	78,4
$-C_6H_5$	71,8
$-OCOCH_3$	71,3
$-N(CH_3)_2$	21,0
$-NHCOCH_3$	13,8
$-O^-$ (-OH + pyridine)	9,7
$-NH_2$	4,6
$-OCH_3$	3,9
$-CH_3$	2,5

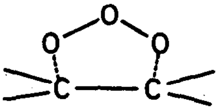
Discussion.

The currently accepted hypothesis for ozone cleavage of carbon - carbon double bonds was formulated by Criegee[2] in the following way:



The zwitterion can react in different ways, one of which is rearrangement where an oxygen atom is inserted between two carbon atoms, leadin to anomalous ozonolysis.

Bailey[3] has linked the question of direction of cleavage to the initial attack of ozone. It is felt, however, that the direction of anomalous ozonolysis will be determined in a primary and real intermediate, without regard to the mode of its formation. This intermedia is regarded as a simple cyclic adduct of the type II, where the tw carbon atoms may have retained their sp^2 hybridisation.



II

Such an entity may (in analogy to an epoxide[4-6]) have a fair degre

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[2] Criegee, R. Record Chem. Progress. (Kresge-Hooker Sci. Lib.) 18 (1957) 111.

[3] Bailey, P.S., Mainthia, S.B. and Abshire, C.J. J. Am. Chem. Soc. 82 (1960) 6136.

[4] Heilbron, J.M., Johnson, A.W., Jones, E.R.H. and Spinks, A. J. Chem. So 62 (1942) 727

[5] Campbell, T.W., Linden, S.L., Godshalk, S. and Young, W.G. J.Am. Chem. S 69 (1947) 881.

[6] Walsh, A.D. Trans. Farad. Soc. 45 (1949) 179

of electrical polarisability, and thus be influenced by the combined inductive and mesomeric effects of the substituents to bring about a preferred direction of cleavage.

The main problem is to find a rule, based on experimental results, which can predict whether a compound of the type I is split up by ozone in a way to form the zwitterion

1) in equal amounts at C_1 and C_2
2) in largest amount at C_1
3) in largest amount at C_2

On assumption that these three possibilities are caused by three corresponding substituent situations, these can be expressed through a function $f(C) = f(C_1) \div f(C_2)$ where $f(C_1)$ and $f(C_2)$ are the combined effects of substituents on C_1 and C_2 respectively. $f(C) = 0$ would correspond to case 1), $f(C_1) > f(C_2)$ to case 2), and $f(C_2) > f(C_1)$ to case 3).

The use of such a function will have a meaning only if it is possible to find a suitable measure for the effect of the substituents. Hammett's substituent constants σ may be suited as a measure, especially as they have shown a marked addivitivity[7].

The net influence of substituents at C_1 and C_2 is then $f(C_1) = f(\sum \sigma C_1)$ and $f(C_2) = f(\sum \sigma C_2)$.
For the molecule as a whole we define:

$$\Delta_1 = \left|\sum \sigma C_1\right| - \left|\sum \sigma C_2\right| \quad \text{when} \quad \left|\sum \sigma C_1\right| > \left|\sum \sigma C_2\right|$$
$$\Delta_2 = \left|\sum \sigma C_2\right| - \left|\sum \sigma C_1\right| \quad \text{when} \quad \left|\sum \sigma C_2\right| > \left|\sum \sigma C_1\right|$$

$\Delta_i = 0$ means electronic symmetry in the oxygen bridge of II, while $\Delta_i \neq 0$ means electronic unsymmetry, resulting in dominating zwitterion formation at C_i, whether this atom act as an electron donator or as an electron acceptor. This may only be understandable by assuming a dual mechanism: Electron donating groups will stabilise the ring system and the subsequent collapse goes in the direction where the zwitterion is maximally stabilised i.e. at the more negative carbon atom. Electron accepting groups, however, will further strain the unstable ring system causing an immediate breaking up governed by the strongest pull on electrons i.e. the zwitterion will in this case be formed at the more positive carbon atom. If one of the two

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[7] Jaffe', H.H. Chem. Revs. **53** (1953) 243.

carbon atoms of the ring intermediate is an electron donator and the other an electron acceptor of exactly corresponding strength, no unsymmetry will be imparted upon the oxygen bridge, as the polarisation caused by one bridge head will be compensated by the other.

Justification of the foregoing more or less formal deliberations can of course only be obtained by a satisfactory correlation with the experimental facts.

In Table 2 calculated Δ_i values are shown beside the corresponding experimental values given in per cent formation of zwitterion at C_i. The table shows that there exists a qualitative connection between calculated Δ_i values and the found direction of cleavage. Only the hydroxyl group forms an exception which is easily understandable on the assumption that there must exist a strong hydrogen bonding between this group and the neighbouring carbonyl of the quinone. (Calculation of Δ_i : Substituent constants are taken from Jaffe'[8] except the σ_p value for O^-, which is taken from Hine[9]. Only σ_p values are used. An unconjugated carbonyl is given the σ value 0,686 and the group $-OCOCH_3$ the value 0,418. Correction for a phenyl group out of plane is estimated to + 0,08).

Table 2

Substituent	Calculated Δ_i	% zwitterion at C_i
$-OH$	Δ_2 = 0.360	90,4 at C_1
$-Cl$	Δ_1 = 0,226	78,4 at C_1
$-C_6H_5$	Δ_1 = 0,01	71,8 at C_1
$-OCOCH_3$	Δ_1 = 0,4	71,3 at C_1
$-N(CH_3)_2$	Δ_2 = 0,60	79,0 at C_2
$-NHCOCH_3$	Δ_2 = 0,02	86,2 at C_2
$-O^-$	Δ_2 = 0,38	90,3 at C_2
$-NH_2$	Δ_2 = 0,66	95,4 at C_2
$-OCH_3$	Δ_2 = 0,27	96,1 at C_2
$-CH_3$	Δ_2 = 0,17	97,5 at C_2

In Table 2 no quantitative correlations are visible, which is not unexpected since σ_p values are used in the calculations instead of the in principle more correct σ_o values.

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[8] Jaffe', H.H. Chem. Revs. **53** (1953) 222.

[9] Hine, J. Physical Organic Chemistry. McGraw-Hill Book Company Inc. New York 1956.

By the aid of the Courtauld Atomic Models[10-12] it was attempted to correct for steric influences when calculating a new set of Δ_i values, considering the values associated with the conformations showing least strain and steric hindrance in general as the most reliable. In conformations where only one of the quinone carbonyls could be coplanar with the benzene ring, this carbonyl was given the benzoyl value 0,459 instead of our standard carbonyl value 0,686. The corrected Δ_i values indicated a probable quantitative relationship of a Hammett type:

$$\log \frac{x_i}{x_o} = \rho \Delta_i \qquad \text{where } x_o \text{ is a mole fraction} = 0{,}5$$

corresponding to symmetric cleavage, and x_i is a mole fraction in the interval 0,5 - 1,0 expressing the amount of zwitterion at C_i. In Table 3 are shown the corrected Δ_i values and ρ values calculated from these and the experimental x_i values by insertion in the modified Hammett equation. The mean value of ρ from all entries is 0,708, while that of the six "best" values is 0,693. This last value is used in calculating the "experimental" Δ_i and σ_o values given in the two last columns in Table 3. These new σ_o values differ more or less from the corresponding σ_p values in the literature. A closer inspection of the structural details of the compounds in question reveals, however, that these differences are of the expected signs and magnitudes.

The outlined hypothesis and the calculated ρ and σ_o values may be tested on ozonolysis reactions reported in the literature. Well suited for this purpose are the experiments of Bailey[3] on the ozonolysis of substituted 1,2-dibenzoylethylenes. By taking into account corresponding steric factors (making use of the Courtauld Atomic Models) as for the naphthoquinones, a satisfactory correlation between the calculated values and Bailey's experimental results is found, as will be seen from Table 4.

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[10] Hartley, G.S. and Robinson, C. Trans. Far. Soc. 48 (1952) 847

[11] Robinson, C. and Ambrose, E.J. Ibid. 854.

[12] Robinson, C. Discussion of the Faraday Soc. 16 (1954) 125.

Table 3

Substituent	Corrected Δ_i	ρ	Δ_i "exp."	σ_o "exp."
-OH	--	--	Δ_1 0,371	+ 0,144
-Cl	Δ_1. 0,226	0,8640	Δ_1 0,282	+ 0,282
$-C_6H_5$	Δ_1 0,236	0,6658	Δ_1 0,227	0,00
$-OCOCH_3$	Δ_1 0,191	0,8069	Δ_1 0,222	+ 0,449
$-N(CH_3)_2$	Δ_2 0,373	0,5340	Δ_2 0,287	÷ 0,514
$-NHCOCH_3$	Δ_2 0,242	0,9772	Δ_2 0,341	÷ 0,114
$-O^-$	Δ_2 0,372	0,6744	Δ_2 0,370	÷ 1,002
$-NH_2$	Δ_2 0,433	0,6479	Δ_2 0,405	÷ 0,632
$-OCH_3$	Δ_2 0,495	0,5732	Δ_2 0,409	÷ 0,182
$-CH_3$	Δ_2 0,397	0,7305	Δ_2 0,418	÷ 0,191

Table 4

Substance	Δ_i	Zwitterion formation at C_1 calculated	found
cis-1,2-Dibenzoyl-styrene	Δ_1 = 0,397	94% at C_1	91-97% at C_1
cis-1,2-Dibenzoyl-propene	Δ_1 = 0,191	60% at C_1	58% at C_1
cis-1,2-Dibenzoyl-1-methoxyethylene	Δ_2 = 0,354	88% at C_2	84% at C_2 88% at C_2 [13]
cis-1,2-Dibenzoyl-1-aminoethylene	Δ_2 = 0,381	92% at C_2	88-95% at C_2

A complete account of this work will appear in Det Norske Videnskaps-Akademi i Oslo, Avhandlinger.

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[13] Lutz, R.E., Wilder, F.N. and Parrish, C.I. J. Am. Soc. 56 (1934) 198