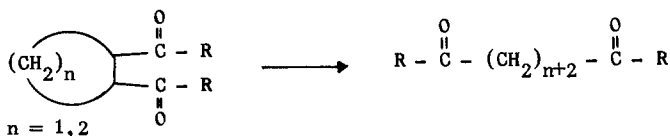


A NOVEL CLEAVAGE OF THE STRAINED CYCLOBUTANE RING

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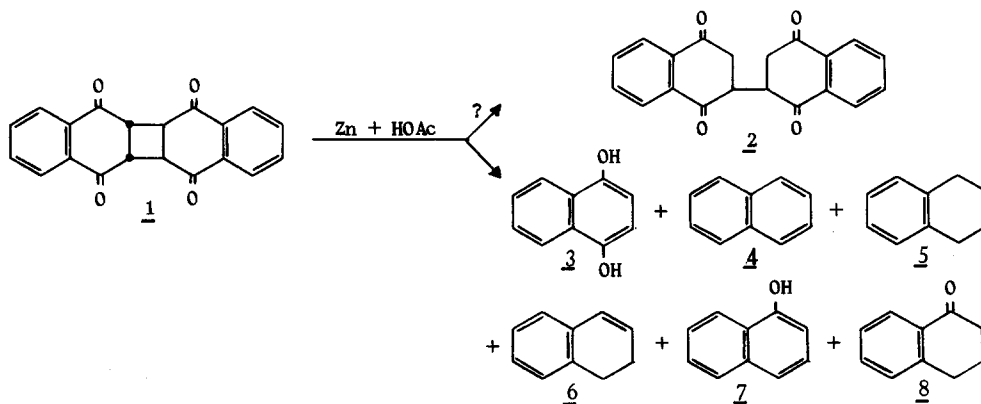
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Treatment of strained cyclopropane and cyclobutane compounds containing two vicinal carbonylic substituents with metals in appropriate solvents affords reductive cleavage of the α, β -bonds¹:-

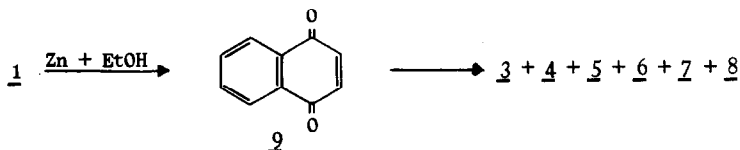


We now wish to report that 1,2,3,4-tetracarboxylic cyclobutanes with cis-trans-cis and all-cis configurations suffer facile ring cleavage, leading to enedione compounds which are prone to secondary reactions, depending on structure and reaction conditions. Further, this novel reaction² renders a handy tool for the rapid determination of the stereochemistry (and perhaps even the structure in some cases) of cyclobutane dimers of 1,4-quinones.

In our studies of the chemistry of the photodimers³ of 1,4-naphthoquinone and related compounds we investigated the reaction of the anti-configured 1 with zinc and acetic acid, hoping to obtain 2. The reaction mixture, which was analyzed gas chromatographically⁴, contained mainly hydroquinone 3 plus small amounts of 4, 5, 6, 7 and 8.



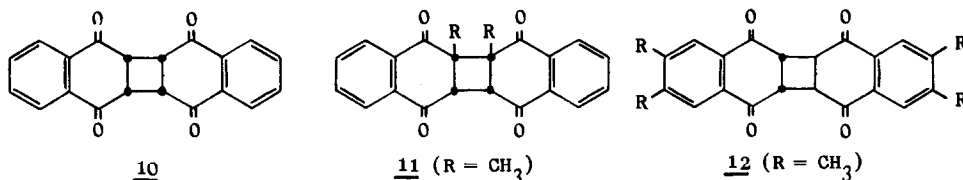
The reaction of 1 with zinc and ethanol proceeded much slower (in comparison to the reaction with zinc and acetic acid) and yielded 1,4-naphthoquinone (9), which on prolonged reaction periods rendered very slowly the secondary products 3, 4, 5, 6, 7 and 8



If 1 was treated with zinc in absolute benzene no reaction occurred. By addition of a small amount of ethanol to the reaction mixture, a very slow conversion of 1 to 9 ensued, indicating the necessity of a protic partner in the cleavage reaction. Since no "chemical reduction" participates in the conversion of 1 to 9, one might argue that the positive influence of the ethanol on the reaction is due to the slow formation of zinc cations in solution. This was confirmed by treating 1 with zinc and zinc chloride in absolute benzene, whereby a relative fast cleavage to 9 resulted.

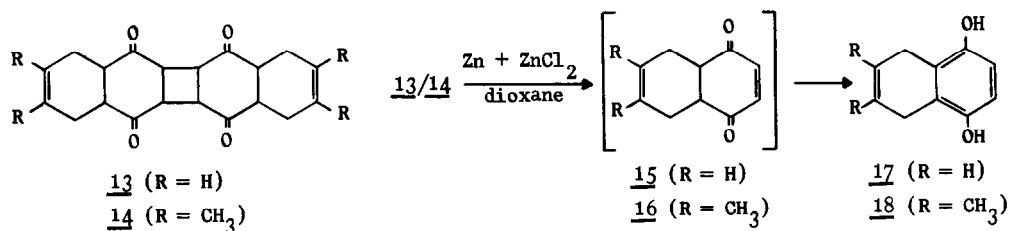
In order to gain information regarding the influence of the electron deficient character of the zinc cations, we treated 1 with zinc in (a) absolute ethanol, (b) ethanol containing zinc oxide, (c) ethanol containing zinc acetate and (d) ethanol containing zinc chloride. An increase in the reaction rate⁵ was observed in the mentioned order. Since no reaction occurred in the absence of zinc itself, we are forced at this stage to assume that a zinc-cyclobutane-zinc cation type of complex⁶ participates in the cleavage reaction. The polar character of this complex is emphasized by the fact that the conversion 1 → 9 is accelerated by improving the polarity of the medium⁷.

In order to determine the generality of this reaction we investigated the behavior of 10³, 11⁸ and 12⁹ towards zinc and zinc chloride in dioxane. In all cases cleavage to the corresponding monomeric quinone was observed.

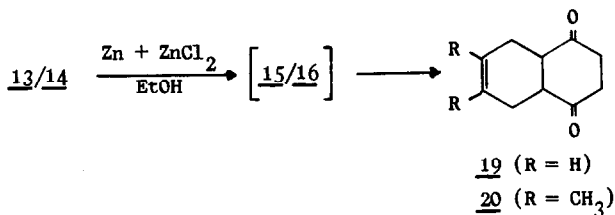


The relative rates of cleavage of 1, 10 and 11 differ markedly, the sequence being: $1 \ll 10 < 11$. This can be interpreted in terms of the higher internal strain³ of the syn-configured 10 and 11 compared to the anti-configured 1. The additional internal strain in 11, due to the two adjacent methyl groups, causes further enhancement. This clearly demonstrates that the cleavage reaction might be a useful tool to elucidate configuration by comparative studies. The observation that the rate of ring cleavage of the newly synthesized 12⁹ is of the same order as that of 1 therefore indicates that 12 has an anti configuration.

In order to determine whether the aromatic rings in 1, 10, 11 and 12 affect the course of the cleavage reaction, we extended our investigation to examine the behaviour of 13¹⁰ and 14¹¹, of which the stereochemistry is unknown. Despite the low solubility of 13 and 14 a relative fast reaction occurred on treatment with zinc and zinc chloride in 1,4-dioxane. The primarily formed 15 and 16 could, however, not be detected since enolization to 17 and 18 resulted rapidly.



The cleavage of the cyclobutane ring of 13 and 14 with zinc and zinc chloride in ethanol, in which the latter compounds are far less soluble compared to 10 and 11, proceeded at an even higher rate than the cleavage of 10 and 11 under identical conditions, rendering 19 and 20.



Although one is tempted to deduce that the relative fast reactions of 13 and 14 might be a strong evidence in favour of syn configurations, we feel that such a conclusion is somewhat risky, since we cannot (at least at this stage) visualize the influence of the electron clouds of the aromatic nuclei (in 1, 10, 11 and 12) and of the olefinic groups (in 13 and 14) on the ease of formation of the postulated zinc-cyclobutane-zinc chloride complex.

Acknowledgement

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References

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b. J. Dekker, J.A. Kruger, L. Fourie, G.L. Wenteler and F.J.C. Martins, unpublished results.
- (2) Clemmensen reduction of the p-benzoquinone dimer produces hydroquinone in high yield (U. von Gizycki, *Liebigs Ann. Chem.*, 753, 1 (1971)). This reaction probably proceeds via p-benzoquinone.
- (3) J. Dekker, P. Janse van Vuuren and D.P. Venter, *J. Org. Chem.*, 33, 464 (1968).
- (4) a. 3m x 3mm column, 5% Carbowax 20M on Chromosorb W-HP 80-100 mesh, 100-200° at 10°/min., F.I.D.
b. 5% Apiezon M on Chromosorb W-HP, *ibid.*
- (5) The slope of the curves, obtained by plotting the yield of cleavage products vs. reaction time, was taken as a measure of the reaction rate. The analysis was done gas chromatographically (see ref. 4b, isothermal at 200°).
- (6) We are presently involved in a kinetic study of the cleavage reaction in order to obtain more information regarding the postulated complex.
- (7) In switching from dioxane to 10% ethanolic dioxane a considerable increase in rate was observed.
- (8) H. Werbin and E.T. Strom, *J. Am. Chem. Soc.*, 90, 7296 (1968).
- (9) Exposure of 6,7-dimethyl-1,4-naphthoquinone in ethyl acetate to pyrex filtered sunlight yielded 12 (mp 260-265°, with decomposition). Compound 12 was characterized by its ms and ir spectra, micro analysis and conversion to 2,3,8,9-tetramethyl-5,6,11,12-tetra-acetoxydibenzo [b,h] biphenylene.
- (10) R.C. Cookson, E. Grundwell, R.R. Hill and J. Hudec, *J. Chem. Soc.*, 1964, 3062.
- (11) Pyrex filtered sunlight irradiation of 6,7-dimethyl-5,8,9,10-tetrahydro-1,4-naphthoquinone rendered 14 (mp 265-268°, with decomposition), which was characterized micro analytically and by its ir and ms spectra.