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REDUCTIVE CLEAVAGE OF STRAINED RING COMPOUNDS

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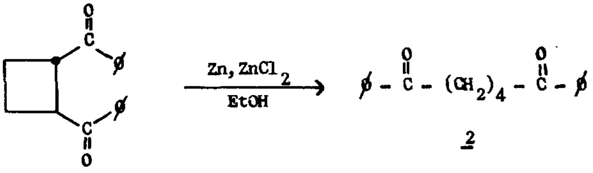
It was recently[1] reported that 1,2,3,4-tetracarbonylic cyclobutanes with cis-trans-cis and all-cis configurations suffer facile ring cleavage, leading to enedione compounds, when treated with zinc and zinc cations.

We now wish to report that 1,2-dicarbonylic cyclobutanes are selectively converted[2] to the corresponding dihydroketones when treated with zinc and zinc chloride in protic solvents. In aprotic solvents, e.g. benzene, no reductive cleavage is noticed.

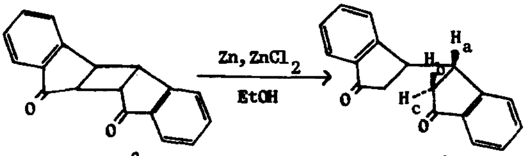
In a typical experiment trans-1,2-dibenzoyl cylcobutane[3] 1 was treated with excess zinc powder (BDH reagent) and zinc chloride in boiling ethanol for 10 minutes. Filtration and concentration of the colourless filtrate rendered 2 in 80% yield.



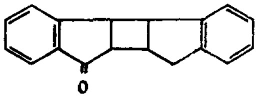
$\phi - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - \phi$

1 2

The general applicability of this reduction is clearly demonstrated by the practically quantitative conversion of 3[4] to 4.



3 4



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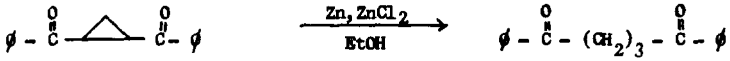
The structure of 4 is proved by its nmr spectrum (in CCl_4). The aromatic protons and the protons H_a are recorded at δ 7.25-7.85 and δ 4.1-4.3 as multiplets respectively. The protons H_b and H_c are centered at δ 2.4 and δ 1.9 respectively. A model study reveals that protons H_c should, in comparison to H_b, experience a stronger combined shielding effect by the carbonyl and phenyl groups of the nearby freely rotating indanone rest. Both pairs are recorded as double doublets and the coupling constants J_{ab} and J_{ac} are 3 and 7 Hz respectively. This corresponds[5] to the fact that the dehedral angles H_aCCH_b and H_aCCH_c are about 0° and 110° respectively.

It is rather interesting to note that both carbonyl groups in the cyclobutane compound are essential for reductive ring cleavage since 5[4] appeared to be totally inert towards zinc and zinc chloride in ethanol.

The influence of ring strain[6] on the cleavage reaction is illustrated by the quantitative rapid conversion of 6[7] to 7.



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$$\phi - \overset{O}{\overset{\|}{C}} - (CH_2)_3 - \overset{O}{\overset{\|}{C}} - \phi$$

Acknowledgement

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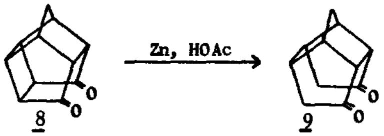
References

(1) J. Dekker, F.J.C. Martins, J.A. Kruger and A.J. Goosen, Tetrahedron Letters, 42, 3721 (1974).

(2) According to E. Wenkert and J.E. Yoder (J. Org. Chem., 35, 2985 (1970)) reductive cleavage of 8 to 9 is accomplished by treatment with zinc in acetic acid.



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(5) L.M. Jackman and S. Sternhell, "Nuclear magnetic resonance spectroscopy in Organic Chemistry", Pergamon Press (1969), p 281.

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