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ACCELERATION OF THE (4+2)-CYCLOREVERSION BY THE ALKOXIDE SUBSTITUENT [1]

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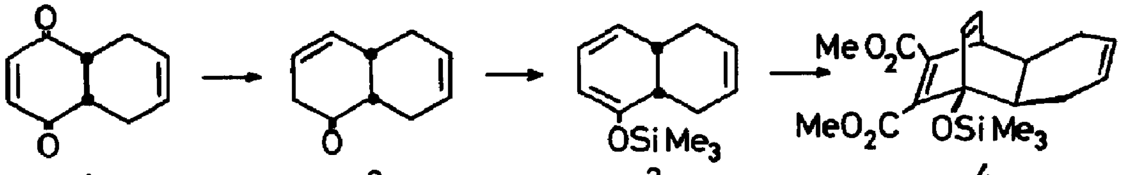
Summary: The (4+2)-cycloreversion of the Alder-Rickert type is powerfully accelerated by the 1-alkoxide substituent.

Cycloreversions attract interest in mechanistic as well as in synthetic aspect. As to the latter, the Alder-Rickert type [2] of the (4+2)-cycloreversion, forming dimethyl phthalate as the diene component, has proved a valuable olefin forming process inspite of its high reaction temperature. We have recen ly shown for some Diels-Alder adducts of 5-cyanocyclopentadiene that their cycloreversion is strongly accelerated by deprotonation [3]. The rate enhancemen for the anions was rationalized by the loss in basicity on formation of the cyanocyclopentadienide ion, which is already felt in the transition state of t concerted process.

The large difference in basicity between an alcoholate and a phenolate ion should afford the same effect when utilized in concerted cycloreversions and we here report on the rapid Alder-Rickert cleavage of an alkoxide to give a phenoxide ion.

The diene component 3 for the Diels-Alder synthesis of the model compound 4 is obtained by partial desoxygenation of the cycloadduct 1 of p-benzoquinone to butadiene via the monotosylhydrazone and the diazoketone [4]. The resulting unconjugated ketone 2 with lithium diisopropylamide in THF/hexane gives the conjugated dienolate which is trapped by chlorotrimethylsilane as the dienol silylether 3. Cycloaddition of dimethyl acetylenedicarboxylate (DAD) to 3 at room temperature produces the tricyclus **4** which undergoes Alder-Rickert cleavage to 3-trimethylsilyloxy-dimethyl-phthalate and cyclohexa-1,4-diene at 60° with a half-life ($t_{1/2}$) of 236 min.



1 **2** **3** **4**

Physical Data of **2**, **3**, **4** and **5**

2 δ^{CCl_4} 5.87 (2H,AB,$\Delta\nu$=19, J=9 Hz), 5.60 (2H,m), 2.82 (4H,m), 2.7 - 1.5 (4H, $\nu_{C=O}^{film}$ 1715 cm^{-1}; $\lambda_{max}^{cyclohexane}$ 276 (ε=265).

3 δ^{CCl_4} 5.67 (3H,m), 5.27 (1H,dd), 4.97 (1H,d), 2.7 (2H,m), 2.1 (4H,m), 0.2 (9H,s); $\nu_{C=C}^{film}$ 1645, 1575 cm^{-1}; $\lambda_{max}^{cyclohexane}$ 220 (sh, ε=5200), 276 (3000)

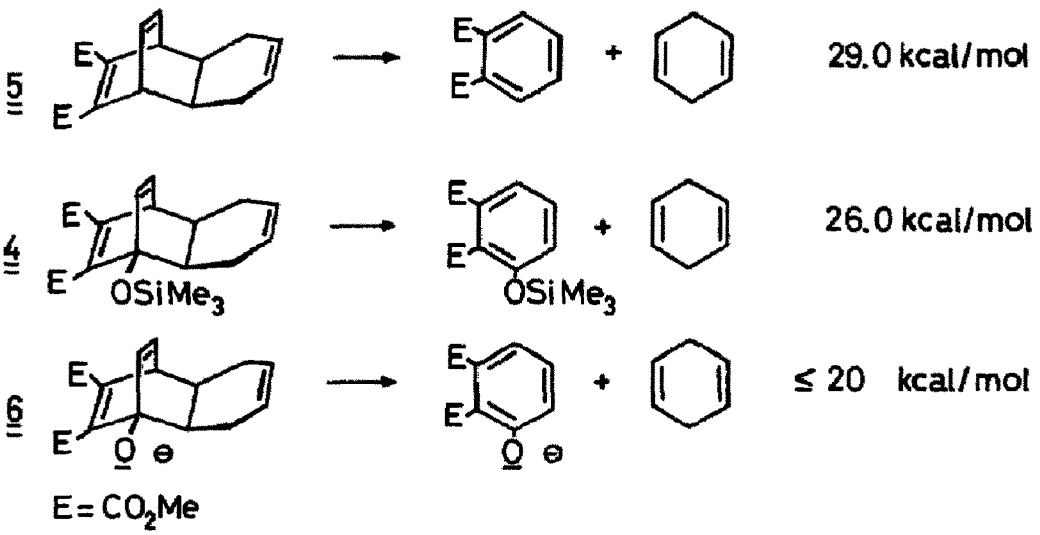
4 δ^{CCl_4} 6.42 (2H,m), 5.76 (2H,m), 3.7 (1H,m), 3.64 (3H,s), 3.61 (3H,s), 2.2 (4H,m), 1.7 (2H,m), 0.09 (9H,s).

5 δ^{CCl_4} 6.43 (2H,t), 5.7 (2H,m), 3.7 (2H,m), 3.72 (6H,s), 2.5 - 1.6 (6H,m).

The parent diester **5**, obtained from 1,4,9,10-tetrahydronaphthalene [5] and DAD, cycloreverts at 100°C with $t_{1/2}$ = 176 min, thus the trimethylsilyloxy substituent at the bridgehead increases the rate of cleavage of **4** ca. 150-fold [6]. When the alkoxide **6** is generated from **4** by treatment with tetra-n-butylammonium fluoride [7] in THF at room temperature the solution immediatel turns burgundy with the formation of the 2,3-dicarbomethoxy-phenolate ion anc cyclohexa-1,4-diene. The acceleration of the (4+2)-cycloreversion of **6** by the 1-alkoxide substituent amounts to the factor of 10^6 at least! We ascribe this dramatic rate increase to the loss in basicity of about 8 pK_b units in the transformation of an alcoholate to a phenolate ion. This stabilisation of th anion adds to the negative free enthalpy of reaction of the parent system $- 2.303 \cdot RT \cdot \Delta pK_b \approx - 11$ kcal/mol and as the transition state of even a highly exothermic (4+2)-cycloreversion is product-like [8], it participates appreciably in this free energy gain. Scheme 1 summarizes the free enthalpies of activation at room temperature for the (4+2)-cycloreversions of 4, 5 and 6.

Scheme 1

Free Enthalpy of Activation ($\Delta G^{\ddagger}$) for (4+2)-Cycloreversion



The rapid (4+2)-cycloreversion of alkoxide 6 complements the recently reported powerful acceleration of the [3,3]-[9] and [1,3]-sigmatropic rearrangement [10] in alkoxides. Although a weakening of the C-C bond adjacent to the oxy anionic group is indicated [11], a concerted process has been proved for the anionic oxy-Cope rearrangement [12]. To evaluate the thermodynamic advantage of the anionic process, one has to consider the basicity of the conjugate bases of the educt and product in the neutral case i. e., the basicity of an alcoholate and of an enolate at the oxygen atom [13]. As above, a loss in basicity is found ($\Delta pK_b \simeq 6$) suggesting itself as a powerful driving force in thi reaction.

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