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RING CONTRACTION REACTIONS IN CYCLOOCTATETRAENE OXIDE CATALYZED BY TRANSITION METALS

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Summary

The ring contraction of cyclooctatetraene oxide (COTEO) catalyzed by transition metal compounds is reported. The organic intermediates have been characterized and stabilization of the labile cycloheptatrienealdehyde in the presence of a copper salt is reported.

Introduction

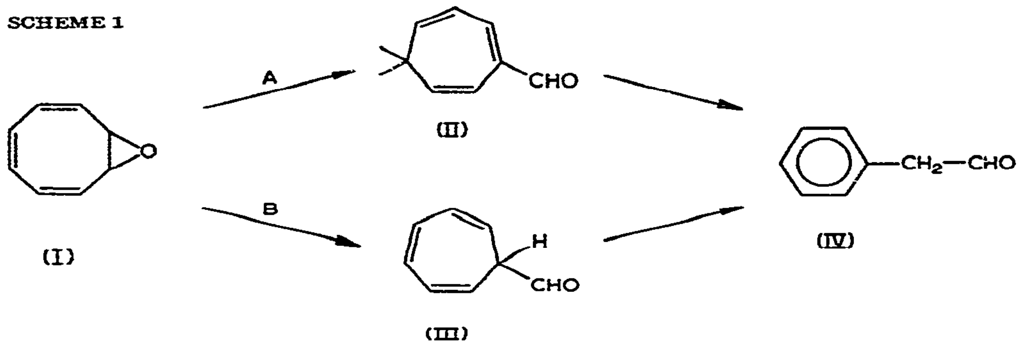
There is at present a great deal of interest in molecular rearrangements promoted by metal ions because some reactions lead to various products in the presence and absence of metal ions [1]. Evidence favoring a step-wise mechanism [2,3], rather than a concerted process has been reported for Rh^I-catalysed rearrangements of alicyclic compounds containing a strained ring, but kinetic evidence for a possible concerted mechanism has been proposed recently for the Ag^+-catalysed norbornadiene—quadricyclene conversion [4].

During our studies of metal insertions across carbon—carbon bonds in electronegatively-activated epoxides [5] we became interested in the reactivity of cyclooctatetraene oxide (COTEO), which has different reaction sites such as olefinic, carbon—carbon, and carbon—oxygen bonds. It rearranges thermally to phenylacetaldehyde [6] or through an acid- [7] or rhodium- [8] catalysed reaction. The ring contraction reaction of cyclooctatetraene oxide has been reported to proceed thermally [6] according to reaction path A in Scheme 1.

The reaction proceeds only at high temperature (≈ 400°) and gives phenylacetaldehyde IV as the final product. Path B has been proposed for the acid-catalysed rearrangement [7] where III could only be trapped as its hydrazone derivative. Rhodium complexes of the type $[Rh(CO)_2Cl]_2$ catalyze the rearrangement of cyclooctatetraene oxide [8] via formation of cycloheptatrienealdehyde III as a labile reaction intermediate, which slowly rearranges at 0° even in the absence of catalyst.

This paper deals with the rearrangement of cyclooctatetraene oxide to

SCHEME 1



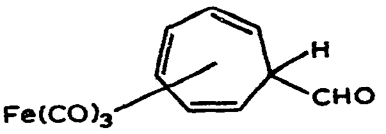
phenylacetaldehyde catalyzed by complexes of Cu^I, Pt^{II}, Pd^{II} and Ag^I. The synthesis of complexes of these metals which are believed, and in some cases have been proved, to be intermediates in these rearrangements, has also been undertaken. Under special conditions cycloheptatrienealdehyde, which is an unstable intermediate in the acid-catalyzed rearrangement, has been found to be particularly stable.

Results and discussion

Rearrangements I→III→IV were carried out in the presence of the following species as catalysts: CuCl, $[COTEO(CuCl)_3]$, $[M(CH_3CN)_2Cl_2]$, $[M(COTEO)Cl_2]$ (M = Pd, Pt), and $AgNO_3$.

Copper catalyst

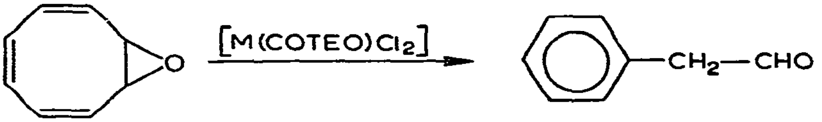
When cyclooctatetraene oxide was treated at room temperature with CuCl in $CDCl_3$, or in the absence of solvent, a white compound $[COTEO(CuCl)_3]$, was formed which probably had a polymeric structure and decomposed at room temperature to give phenylacetaldehyde and an unidentified aldehyde. If cyclooctatetraene oxide was kept at room temperature in contact with CuCl (20/1 molar ratio) or $[COTEO(CuCl)_3]$ in a sealed NMR tube, a slow reaction took place. The appearance of cycloheptatrienealdehyde in the solution could be followed using NMR. The ratio COTEO/cycloheptatrienealdehyde changed with time, but no phenylacetaldehyde was present after 10 days at room temperature when the ratio I/III reached a maximum value very close to 1 and a red precipitate was formed. On standing for a longer time at 40° some polymerisation occurred and the liquid became too viscous for NMR spectroscopy to be used. The red precipitate, which might be an organometallic complex of Cu^I, was very air-sensitive and attempts to isolate it in the pure state failed because of its high instability during work-up. It was insoluble in $CDCl_3$ and could not be detected in the NMR spectrum of the solution. This red complex may be responsible for the unexpected stability of cycloheptatrienealdehyde III which does not rearrange over many days in the presence of Cu^I. This stabilisation might be due either to a trapping of the non-formylic intermediate that has been proved to be involved in the III→ IV rearrangement [8], or an inhibition of this reaction in the presence of copper salt. Although V, an iron—cycloheptatrienealdehyde complex has been trapped stoichiometrically [9] we do not have any evidence for an analogous copper—cycloheptatrienealdehyde complex.



(V)

Platinum and palladium catalysts

On treating cyclooctatetraene oxide with $[Pd(CH_3CN)_2Cl_2]$ or $[Pt(CH_3CN)_2Cl_2]$ in the absence of solvent an explosive reaction occurred to give phenylacetaldehyde. This reaction was slowed down in the presence of $CDCl_3$ as solvent. After a few minutes the NMR spectrum showed three products to be present throughout the course of the reaction: cyclooctatetraene oxide, cycloheptatrienealdehyde, and phenylacetaldehyde. No stabilisation of III was observed in contrast to the copper system. Although the rearrangement reaction III→IV has also been proved to proceed in the absence of metal complexes it could well be possible that this step of the rearrangement becomes faster in the presence of platinum and palladium complexes. The reaction is acid-catalyzed and cyclooctatetraene oxide rearranges (albeit very slowly) in $CDCl_3$ because of traces of acid present in the solvent. The reaction is also catalyzed by $[M(COTEO)Cl_2]$ complexes (M = Pt or Pd) prepared separately (eqn. 1). Although the same products are obtained in these reactions (and also in the acid-catalyzed rearrangement), different mechanisms are probably operative. When palladium or platinum is used, an oxidative addition or a metal insertion reaction into the C—O bond probably occurs, but with Cu^I salts the reaction is much slower, probably because of the reluctance of Cu^I to undergo oxidative addition, and a different mechanism may again operate, such as coordination of cyclooctatetraene oxide to copper through the oxygen atom, similarly to the acid-catalyzed reaction.



(1)

Silver catalyst

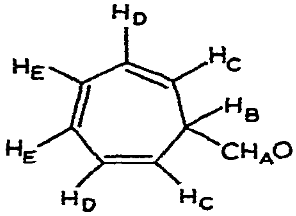
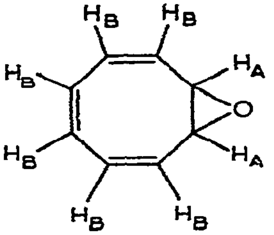
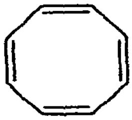
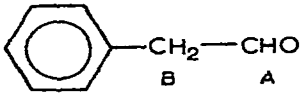
The reaction is also catalyzed by silver ion to give the same intermediate and final product, together with other products. It is well known that silver ion catalyzes the skeleton rearrangement of strained carbocycles [10] to give a variety of products, depending on the ring substituents. It is very possible that a similar type of reaction occurs in competition with the usual ring contraction to give different organic products.

Experimental

All materials were reagent grade. $CDCl_3$ was purified by distillation over KOH pellets. Cyclooctatetraene oxide was prepared by the usual method of Reppe et al. [11]; $[Pd(CH_3CN)_2Cl_2]$ and $[Pt(CH_3CN)_2Cl_2]$ were prepared according to Walton [12].

TABLE 1

NMR SPECTRA (δ ppm, $CDCl_3$ solution)

	H_A	H_B	H_C	H_D	H_E
	9.56	2.62	5.18	6.20	6.40
	3.23	5.80			
	5.60				
	9.58	3.41	≈ 7.2		

IR spectra were recorded on a Perkin—Elmer model 457 spectrophotometer, ^{1}H NMR spectra on a Varian HA 100 MHz spectrophotometer, using HMDS as internal standard. The chemical shifts and relative assignments are recorded in Table 1. All samples were evacuated on a vacuum line, flame sealed, and shaken at room temperature. Before recording NMR spectra, solid phases were centrifuged to the top of the NMR tube.

Preparative reactions

(1) [COTEO(CuCl)$_3$]. CuCl (0.5 g) was suspended in 95% ethanol and cyclooctatetraene oxide (1.5 ml) was added under nitrogen with vigorous stirring at room temperature. The green slurry slowly became greenish-white. After 12 h the off-white solid was filtered off, washed with petroleum ether, and dried; m.p. 95—97°, yield almost quantitative. (Found: C, 22.28; H, 1.79; Cl, 24.5.

$C_8H_8Cl_3Cu_3O$ calcd.: C, 23.03; H, 1.93; Cl, 24.49%.) IR (nujol): 842 cm^{-1} (oxirane).

The same compound was obtained using $CHCl_3$ as solvent.

(2) [(COTEO)AgNO$_3$]. $AgNO_3$ (0.3 g) was dissolved in 95% ethanol and cyclooctatetraene oxide (1.0 ml) was added under nitrogen with vigorous stirring at room temperature. A white solid was rapidly obtained. After 1.5 h this was filtered off, washed with ethanol and ether, and dried under nitrogen (in almost quantitative yield); m.p. 96—99°. (Found: C, 33.06; H, 2.97; N, 4.77. $C_8H_8AgNO_4$ calcd.: C, 33.13; H, 2.78; N, 4.83%.) IR (nujol): 837 cm^{-1} (oxirane).

(3) [Pd(COTEO)Cl$_2$]. Cyclooctatetraene oxide (2.0 ml) was added under nitrogen to a saturated solution of $[Pd(CH_3CN)_2Cl_2]$ (0.5 g) in benzene at 50°. After stirring the solution for 5 h at room temperature the yellow precipitate was filtered off and washed with petroleum ether. Recrystallization from methylene chloride/petroleum ether containing COTEO (1.0 ml), yielded the yellow product; m.p. 102—104° (dec.). (Found: C, 33.02; H, 2.68; Cl, 23.23. $C_8H_8Cl_2OPd$ calcd.: C, 32.30; H, 2.71; Cl, 23.83%.) IR (nujol): 858 cm^{-1} (oxirane).

(4) [Pt(COTEO)Cl$_2$]. This complex was prepared and recrystallized in a similar way to that described above; pale-yellow product; m.p. 175—180° (dec.). (Found: C, 25.20; H, 2.11; Cl, 18.07. $C_8H_8Cl_2OPt$ calcd.: C, 24.88; H, 2.09; Cl, 18.36%.) IR (nujol): 853 cm^{-1} (oxirane).

Catalytic reactions

(1) Copper. CuCl (0.1 mmol) or $[COTEO(CuCl)_3]$ (0.03 mmol) was suspended in $CDCl_3$ (0.5 ml) in an NMR tube, and cyclooctatetraene oxide (2.0 mmol) was added. Reaction was slow. After about 2 days the cyclooctatetraene oxide/cycloheptatrienealdehyde ratio was about 4/1, and 1/1 after 10 days, when an unidentified brownish-red solid was slowly precipitated. The isomerisation stopped and no phenylacetaldehyde was produced. The clear solution was transferred to another NMR tube, whereupon the usual rearrangement of cycloheptatrienealdehyde to phenylacetaldehyde began to take place. The brownish-red precipitate decomposed on exposure to air istantaneously to give a green product.

(2) Silver. $AgNO_3$ (0.05 mmol) was suspended in $CDCl_3$ (0.5 ml) and cyclooctatetraene oxide (3.0 mmol) was added. A slow reaction occurred and after about 20 days the cyclooctatetraene oxide/cycloheptatrienealdehyde/phenylacetaldehyde ratios were about 3/1/2; after 45 days these ratios were 1/1/8. However, during the whole of the reaction cycloheptatrienealdehyde never amounted to more than 15%.

(3) Palladium and platinum. $[M(CH_3CN)_2Cl_2]$ or $[M(COTEO)Cl_2]$ (M = Pd or Pt) (0.1 mmol) was suspended in $CDCl_3$ (0.5 ml) and cyclooctatetraene oxide (2.0 mmol) was added. After a few minutes appreciable amounts of both cycloheptatrienealdehyde and phenylacetaldehyde were present and the cycloheptatrienealdehyde concentration was nearly constant (15%) throughout the reaction. After 1.5 h the reaction was over and only phenylacetaldehyde was present.

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