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TRANSITION METAL PROMOTED ISOMERIZATION OF 3-OXAQUADRICYCLANES: PREPARATION OF A NEW OXEPINE DERIVATIVE.

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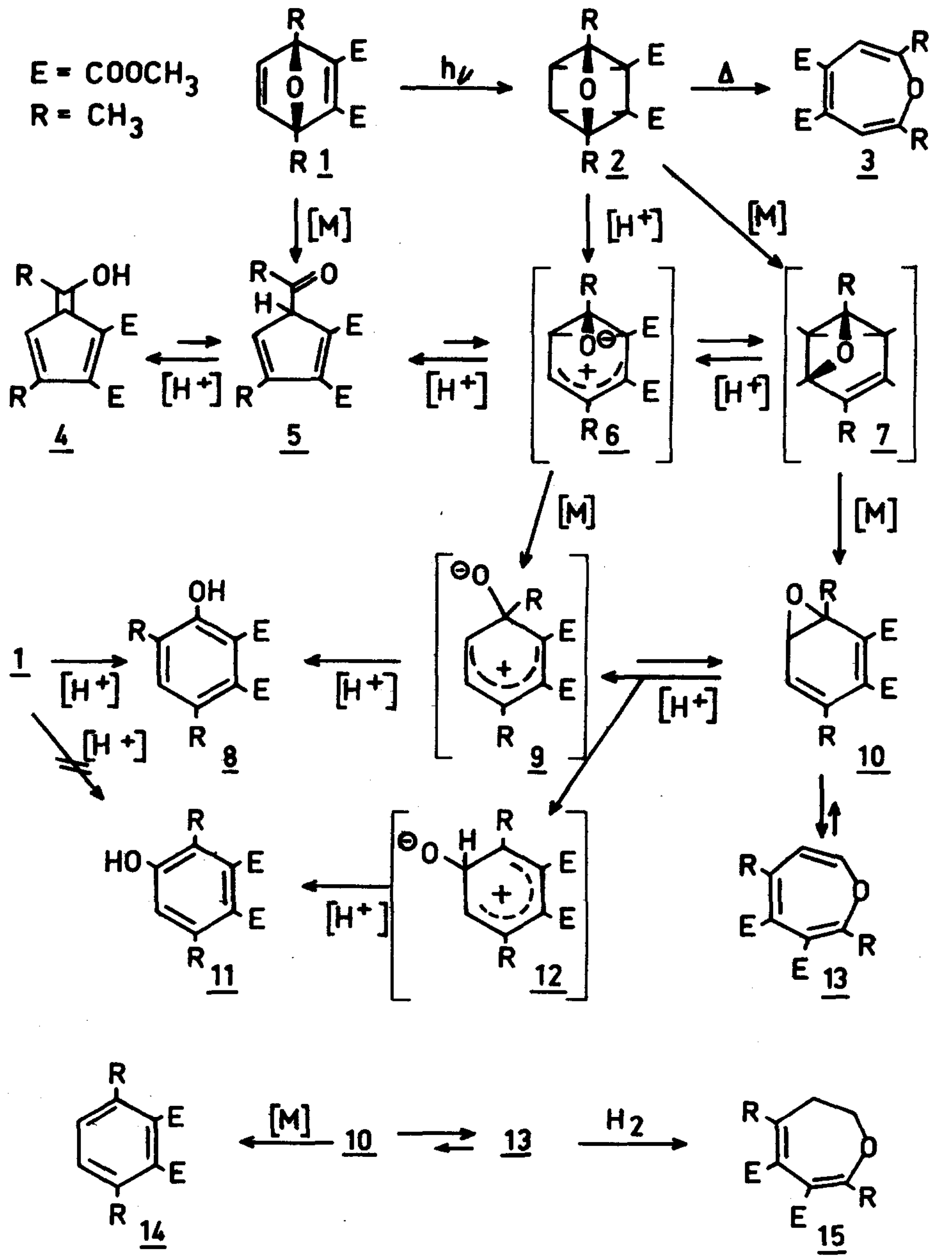
HOGEVEEN et al. found that Rh^I complexes isomerize oxaquadricyclanes and oxanorbornadienes into 6-hydroxyfulvenes [1]. We present results demonstrating that the outcome of those isomerizations depends upon the presence or absence of traces of protic solvent in the reaction mixture. Furthermore, we show that a new oxepine 13, different from that obtained thermally 3 [2], is formed in good yield by transition metal promoted isomerization of the oxaquadricyclane 2 (R = CH_3).

2 dissolved in C_6H_6 or $CDCl_3$ containing various amounts of $Pt(C_6H_5CN)_2Cl_2$ or $[Rh(CO)_2Cl]_2$ isomerizes to yield a mixture of oxepine 13, 6-hydroxyfulvene 4, hydroxyphtalate 8 and at least two non-identified compounds. The product ratio depends upon the relative amount of catalyst, its nature (Pt^{II}, Rh^I, ligands), the solvent and the temperature. For instance, when a 0.2 molar solution of 2 in pure $CDCl_3$ containing 15 mole % $[Rh(CO)_2Cl]_2$ is heated at 40° for 3 Hr., 60 - 70 % of 13, 10 - 15 % of 4 and 2 - 6 % of 8 are formed. The rate of isomerization of 2 and the ratio 13 vs. other products increase with the relative amount of Pt^{II} or Rh^I catalysts. When a trace of methanol is added to the reaction mixture, the 6-hydroxyfulvene is the main product formed (> 90 %).

The oxepine 13 is isolated by SiO_2-column chromatography from the reaction mixture (2 + $[Rh(CO)_2Cl]_2$) previously treated with charcoal and extracted with 5 % aq. KOH. The structure of 13 is suggested by its spectroscopic characteristics [3] and comparison with other oxepine derivatives [2]. The vicinity of one methyl group with one ring proton is indicated by the ^{1}H-nmr spectrum which shows a residual coupling between the protons of δ = 5.62 and 2.22 ppm. The UV and MS

Scheme 1.



spectra of 13 are consistent with a boat-shaped, monocyclic oxepine. 13 absorbs one mole of H_2 (Pd/C 10 %; AcOEt) and gives a 6,7-dihydrooxepine 15. The ^{1}H-nmr spectrum of 15 [3] demonstrates that the two ring hydrogens in 13 are α and β relative to the etheral oxygen. When a few drops of CF_3COOH are added to a chloroform solution of 13, a mixture of o-hydroxyphtalate 8 and m-hydroxyphtalate 11 (60:40) is obtained. 8 was found to be identical to the known hydroxyphtalate prepared by acidic isomerization of 1 (R = CH_3) [5]. 13 deoxygenates slowly at 40 - 60° and yields the phtalate 14 in presence of Rh^I complexes as observed for simpler oxepines [6].

The rearrangement 2 → 13 corresponds formally to a migration of the etheral oxygen without changing the relative positions of the six carbons of the original framework of 2. At least two mechanism limits (see scheme 1) are acceptable for the observed isomerizations. The route 2 → 6 → 5 → 4 implies an orbital symmetry allowed cyclopropyl-allyl cation rearrangement [7]. It is acid catalyzed and competes with the "forbidden" process 2 → 7 → 10, thus explaining the high yield of 6-hydroxyfulvene 4 when 2 [8] is treated with Pt^{II} or Rh^I catalysts in presence of protic solvents (known to generate acidic conditions [9]) or with H_2SO_4 [10], CuCl or $AgBF_4$ [11]. In an acid free medium, the oxygen of intermediate 6 is nucleophilic enough to yield the tricyclic ether intermediate 7 (that can also arise directly from 2). The metal catalyzed isomerization to benzeneoxide 10 gives the observed major product 13. The oxepine 13 could also arise via 6 → 9 → 10 where the "forbidden" isomerization 6 → 9 [12] would be metal catalyzed and the oxygen of intermediate 9 nucleophilic enough (in absence of H^+) to yield 10 → 13. 9 can also yield the observed o-hydroxyphtalate 8.

The tricyclic intermediate 7 is the internal Diels-Alder adduct of the C=O double-bond on the cyclopentadiene 5. Therefore, in presence of transition metals, 6-hydroxyfulvenes might yield oxepines of type 13 that can further react (via 10) and give, for instance, deoxygenated, stable aromatic compounds. This hypothesis finds some support with our observation that 4 (R = H, CH_3) yield phtalates 14 (R=H, CH_3) when treated with $[Rh(CO)_2Cl]_2$ for long reaction times at 40 - 60 °C.

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[3] Physical and spectroscopic characteristics of :
13 Mp. 53 - 54 ^{o}C; ^{1}H-nmr (CDCl$_3$) δ = 6.25 ppm (1;d;5.4 Hz); 5.62 (1;d;5.4); 3.61 (3;s); 3.60 (3;s); 2.33 (3;s); 2.22 (3;s); UV (isooctane) λ_{max} = 306 nm (ε = 1940); 285 (1900); 252 (sh, 4100); IR (CHCl$_3$) : 1730; 1640; 1630; 1590 cm^{-1}; MS (70 eV) : m/e$^+$ (% b.p.) 238 (35); 222 (1.5); 207 (43); 206 (100); microanalysis : 60.30 % C, 5.82 % H (calc. : 60.50 % C, 5.92 % H).
15 : oil; ^{1}H-nmr (CDCl$_3$) δ = 4.40 (2;m;5.0); 3.58 (3;s); 3.56 (3;s); 2.37 (2;m;5.0); 2.25 (3;s); 2.18 (3;s); UV (isooctane) λ_{max} = 237 (9200); 208 (16 000); IR (CHCl$_3$) : 1720; 1600 cm^{-1}; MS (70 eV) : 240 (27); 209 (47); 208 (100).

[4] 3,4-dimethoxycarbonyloxepine (2 - 4 %) has been isolated when 2 (R=H) was treated with Pt(C$_6$H$_5$CN)$_2$Cl$_2$ in CHCl$_3$; R. Roulet, R. Favez, M. Hardy and P. Vogel, unpublished results.

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