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HOMOGENEOUS ISOAROMATIZATION OF ALICYCLIC DIENONES CATALYZED BY COMPLEXES OF THE PLATINUM GROUP

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The isoaromatization of alicyclic dienones by *heterogeneous* catalysts (e.g., Ni, Pd-C, PtO_2[1]), provides a rather useful method for the synthesis of monocyclic phenols. Polycyclic ketones, however, are often deoxygenated to give hydroxyl-free hydrocarbons[2].

We wish to report the isoaromatization of alicyclic ketones by *homogeneous* Ru, Rh and Ir catalysts, under conditions in which the oxygen atom is preserved. When, e.g., a solution of 102 mg (10^{-4} mole) $IrCl(CO)(PPh_3)_2$ (**1**) in 10g (3.65×10^{-2} mole) *trans, trans-2,6*-dibenzylidenecyclohexanone (**4**, R = C_6H_5; R' = R'' = H) is heated at 250°for 2 hr, the distilled reaction mixture [240°(15mm)] yields 7.6g (76%) pure *2,6*-dibenzylphenol (**7**, R = C_6H_5; R' = R'' = H).

The iridium catalyst can be substituted by $RhCl(PPh_3)_3$ (**2**), though the reaction rate decreases by a factor of 3. $RuCl_2(PPh_3)_3$ is almost inactive under these conditions.

When the reaction is carried out in some high boiling non-hydroxylic solvents (e.g., Ph_2O) the activities of **2** and **3** become similar to that of **1** (in the same solvent).

The results of some isoaromatization experiments using **1** in Ph_2O are summarized in Table I.

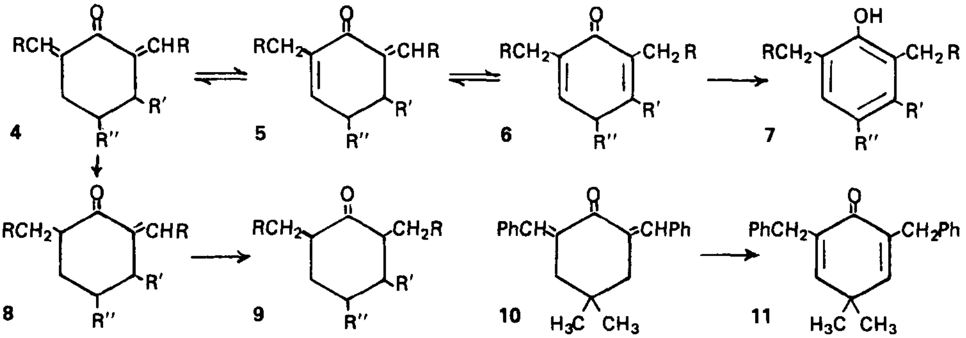

TABLE I. Isoaromatization of Alicyclic Dienones by $IrCl(CO)(PPh_3)_2$ (**1**)

(2×10^{-3} mole ketone, 10^{-5} mole **1**, 1 ml Ph_2O at 250°)

Exp.	Ketone	Phenol formed[a]	Reaction time, hr	Yield %[b]
1	Carvon	Carvacrol	1.5	97
2	*2*-Benzylidene-*1*-tetralone	*2*-benzyl-*1*-naphthol	0.5	95
3	**4**, R = C_6H_5; R′ = R″ = H	**7**, R = C_6H_5; R′ = R″ = H	1.75	100
4	**4**, R = *o*-ClC_6H_4; R′ = R″ = H	none	24	
5	**4**, R = *p*-ClC_6H_4; R′ = R″ = H	**7**, R = *p*-ClC_6H_4; R′ = R″ = H	3.5	98
6	**4**, R = *p*-$CH_3C_6H_4$; R′ = R″ = H	**7**, R = *p*-$CH_3C_6H_4$; R′ = R″ = H	0.5	97
7	**4**, R = C_6H_5; R′ = CH_3; R″ = H	**7**, R = C_6H_5; R′ = CH_3; R″ = H	2.5	87
8	**4**, R = *o*-$CH_3OC_6H_4$; R′ = R″ = H	**7**, R = *o*-$CH_3OC_6H_4$; R′ = R″ = H	15	52
9	**4**, R = *p*-$CH_3OC_6H_4$; R′ = R″ = H	**7**, R = *p*-$CH_3OC_6H_4$; R′ = R″ = H	0.25	98
10	**4**, R = C_6H_5; R′ = H; R″ = $C(CH_3)_3$	**7**, R = C_6H_5; R′ = H; R″ = $C(CH_3)_3$	2	92
11	**4**, R = *2*-furyl; R′ = R″ = H	**7**, R = *2*-furyl; R′ = R″ = H	2	98
12	**4**, α-$C_{10}H_7$; R′ = R″ = H	none	24	
13	**4**, β-$C_{10}H_7$; R′ = R″ = H	**7**, R = β-$C_{10}H_7$; R′ = R″ = H	15	95

[a] All known products were identified by comparison with authentic samples, IR, NMR and mass spectrometric measurements.

7, R = *p*-$CH_3OC_6H_4$; R′ = R″ = H. Calc. for $C_{22}H_{22}O_3$: C, 79.0; H, 6.6. Found: C, 78.8; H, 6.7. δ ($CDCl_3$) 3.69 (s 6H), 3.82 (s 4H), 6.70-7.15 (m 12H).

7, R = C_6H_5; R′ = H; R″ = $C(CH_3)_3$. Calc. for $C_{24}H_{26}O$: C, 87.2; H, 7.9. Found: C, 87.0; H, 7.7. δ ($CDCl_3$) 1.65 (s 9H), 3.83 (s 4H), 6.87-7.12 (m 13H).

7, R = *2*-furyl; R′ = R″ = H. Calc. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.5. Found: C, 75.5; H, 5.4. δ ($CDCl_3$) 3.82 (s 4H), 5.89-6.12 (m 6H), 7.00-7.13 (m 4H).

[b] Determined by G. L. C.

While ketones **4** are converted by catalytic amounts of **1**, **2** or **3** in *diphenyl ether* exclusively to phenols **7**, the application of OH-containing solvents leads to different catalyses by the various complexes. Only $RhCl(PPh_3)_3$ remains a selective isoaromatization catalyst in benzyl alcohol (as well as in other carbinols). $RuCl_2(PPh_3)_3$, which has already been shown to transfer-hydrogenate α,β-unsaturated ketones in carbinols[3], reduces **4** ($R = C_6H_5$; $R' = R'' = H$) stepwise to *2,6*-dibenzylcyclohexanone (*cis*- and *trans*- **9**, $R = C_6H_5$; $R' = R'' = H$) (88%, 5 hr in boiling $PhCH_2OH$; mp 122°[4]) *via* **8**, ($R = C_6H_5$; $R' = R'' = H$) [present in 17% in the reaction mixture after 60 min; mp 120°. Calc. for $C_{20}H_{20}O$: C, 87.0; H, 7.3. Found: C, 86.9; H, 7.3. $\nu_{C=O}$ 1680 cm^{-1}. λ max (EtOH) 290 mμ (ϵ 1.6 x 10^4). δ ($CDCl_3$) 2.2-3.0 (m 7H), 3.65 (s 2H), 7.24 (m 11H). MS 276 (M^+)] Likewise, **4** ($R = p\text{-}CH_3C_6H_4$, $R' = R'' = H$) is reduced in 80% yield to *2,6*-di-(*p*-methylbenzyl)cyclohexanone [mp 107°. Calc. for $C_{22}H_{26}O$: C, 86.3; H, 8.5. Found: C, 86.1; H, 8.4. $\nu_{C=O}$ 1700 cm^{-1}. MS 306 (M^+)], and **4** ($R = p\text{-}CH_3OC_6H_4$, $R' = R'' = H$) gives the saturated ketone [76%; mp 139°. Calc. for $C_{22}H_{26}O_3$: C, 78.1; H, 7.7. Found: C, 77.9; H, 7.6. $\nu_{C=O}$ 1700 cm^{-1}. MS 338 (M^+)].

Carvon is an exception. It isoaromatizes by **3** even in $PhCH_2OH$ or $(CH_2OH)_2$ to give carvacrol as the only product. This fact cannot be explained by the pre-existence of an endocyclic double bond in the starting ketone, as *2*-benzylidene-*1*-tetralone, e.g., is quantitatively reduced by **3** in boiling $PhCH_2OH$ (5 hr) to *2*-benzyl-*1*-tetralone [Calc. for $C_{17}H_{16}O$: C, 86.4; H, 6.8. Found: C, 86.4; H, 7.0. $\nu_{C=O}$ 1680 cm^{-1}. MS 236 (M^+)]

The iridium complex **1** catalyzes *both* isoaromatization and transfer-hydrogenation reaction in $PhCH_2OH$; *2,6*-dibenzylidenecyclohexanone, e.g., gives after 5 hr at 180° the phenol and the reduced ketone in the ratio 2:1.

The isoaromatization of ketones **4** has been shown to proceed *via* intermediates **5** and **6**. In exp. 3 (Table I) the formation and disappearance of **5** ($R = C_6H_5$, $R' = R'' = H$) can be followed. A maximum of 35% is present in the reaction mixture after 40 min. [δ ($CDCl_3$) 1.89-2.96 (m 4H), 3.66 (s 2H), 6.64 (m 1H), 7.24-7.61 (m 11H). λmax (EtOH) 290 (ϵ 6.8 x 10^3), as compared with 330 mμ (ϵ 3 x 10^4) for **4** and 280 mμ (ϵ 2 x 10^3) for **7**]. The dienone **6** ($R = C_6H_5$, $R' = R'' = H$) cannot be trapped, but *2,6*-dibenzylidene-*4,4*-dimethylcyclohexanone (**10**) that would not undergo the final step **6**→**7**, is transformed to *2,6*-dibenzylidene-*4,4*-dimethylcyclohexa-*2,5*-dienone (**11**).

The electronic nature of R in **4** exerts a marked influence on the reaction rate[5], which is in the order $p\text{-}CH_3OC_6H_4 > p\text{-}CH_3C_6H_4 > C_6H_5 > p\text{-}ClC_6H_4$. [The corresponding initial rates in the Ir (I)-catalyzed reactions are 6.7, 3.3, 1.1 and 0.72% min^{-1}].

Even more pronounced is the steric effect[6]. *3*-Methyl-*2,6*-dibenzylidenecyclohexanone (**4**, R = C_6H_5; R' = CH_3; R'' = H) is isoaromatized slower than **4** (R = C_6H_5; R' = R'' = H) (The initial rate in exp. 7 is 0.77% min^{-1}), and ketones with *ortho* substituted phenyl groups (exps. 4, 8, 12) react either very slowly or not at all.

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