

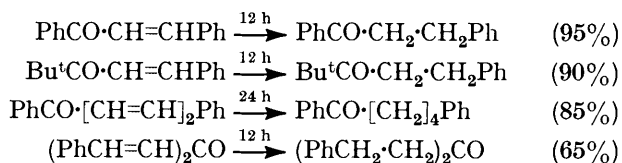
Aspects of Catalysis. Part IV.¹ Hydrogen Transfer from Propan-2-ol to $\alpha\beta$ -Unsaturated Ketones catalysed by a Soluble Hydrido-iridium Complex. Isolation of a Compound containing a Carbon-Iridium Bond and a Chelated Keto-group

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Double bonds in some $\alpha\beta$ -unsaturated ketones are reduced by propan-2-ol in the presence of soluble iridium-sulphoxide catalysts. Chalcone gives (2-benzoyl-1-phenylethyl-O)dichlorobis(dimethyl sulphoxide)iridium as a crystalline intermediate, which is converted into dihydrochalcone on treatment with acids.

HAVING found that hydrogen-transfer processes between alcohols and saturated ketones can be catalysed by soluble iridium complexes,¹ we turned our attention to the possibility of reducing groups other than carbonyl. An olefinic bond in conjugation with a carbonyl group may be more susceptible to reduction than an isolated C=C group, and chalcone was chosen for study. When this unsaturated ketone was heated in solution in slightly aqueous propan-2-ol containing small amounts of either the *cis*- or the *trans*-acid, $\text{H}[\text{Cl}_4\text{Ir}(\text{Me}_2\text{SO})_2]$, the C=C bond was reduced first. A good yield of dihydrochalcone was obtained, the carbonyl group not being readily reduced when attached to an aryl group; *cf.* the resistance of benzophenone to reduction.¹

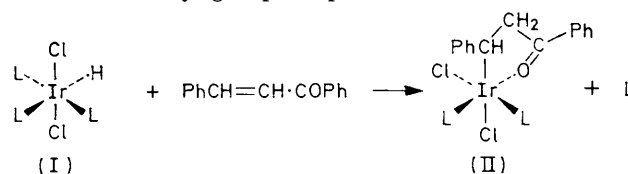
Compounds related to chalcone were also reduced by this method: the following equations summarise the results obtained when the unsaturated ketone and the *trans*-iridium-sulphoxide acid, in a *ca.* 6 : 1 weight ratio (16—20 : 1 mol ratio), were heated in propan-2-ol.



Hydridic species, *e.g.* $\text{IrHCl}_2(\text{Me}_2\text{SO})_3$, are formed when either of the acids $\text{H}[\text{IrCl}_4(\text{Me}_2\text{SO})_2]$ is heated in propan-2-

¹ Part III, Y. M. Y. Haddad, H. B. Henbest, J. Husbands, T. R. B. Mitchell, and J. Trocha-Grimshaw, preceding paper.

ol,² and reduction of chalcone is likely to involve reaction with a hydrido-iridium complex. Experiment showed that the hydride (I) reacted with chalcone in propan-2-ol (or benzene) at 73° during 4 h to give a 40—50% yield of a crystalline substance, shown from analytical and spectroscopic evidence and an X-ray study³ to have structure (II) in which a carbon-iridium bond and a chelated carbonyl group are present.



L = Me_2SO

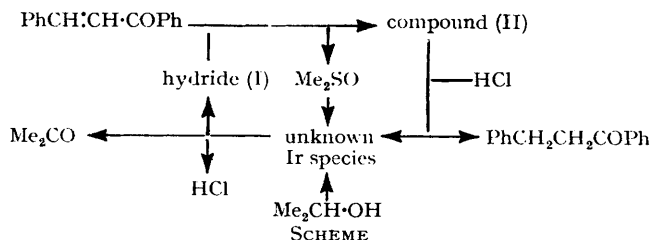
Treatment of the substance (II) with a dilute solution of hydrochloric acid in propan-2-ol gave dihydrochalcone in high yield. Compound (II) is therefore a likely intermediate in the catalytic cycle wherein chalcone is reduced by propan-2-ol with one of the iridium-sulphoxide acids as the source of catalyst (hydrogen chloride is formed from these complexes when they are heated in propan-2-ol). Dihydrochalcone was rapidly formed in high yield when chalcone was heated in propan-2-ol containing hydrochloric acid (2 mol per mol

² Part II, Y.M.Y. Haddad, H. B. Henbest, and J. Trocha-Grimshaw, *J.C.S. Perkin I*, 1974, 592.

³ M. McPartlin and R. Mason, *J. Chem. Soc. (A)*, 1970, 2205.

of ketone) and a catalytic amount of hydride (I). By this procedure 300–400 mol of chalcone were reduced per g atom of iridium (in solution).

The mechanism of the catalysis, based on the available evidence, can be depicted as in the Scheme.



Acetone was formed in good yield (based on the chalcone reduced). Hydrochloric acid was much more effective for promoting the reaction than the corresponding quantity of sulphuric acid. The order of effectiveness of solvents was propan-2-ol > ethanol > methanol, in accord with their hydrogen donor properties.

and 1 h later a cream precipitate began to separate. After another 0.5 h the mixture was cooled, and 0.5 h later (2-benzoyl-1-phenylethyl-O)dichlorobis(dimethyl sulphoxide)-iridium (II) (100 mg), m.p. 211–212°, was collected. Crystallisation from benzene-pentane did not change the m.p. (Found: C, 36.3; H, 4.0; Cl, 11.3; S, 10.2. $C_{19}H_{25}Cl_2IrO_3S_2$ requires C, 36.4; H, 4.1; Cl, 11.2; S, 10.2%); ν_{max} . 1580 cm^{-1} (C=O co-ordinated to Ir); τ 1.6–2.8 (10H, m), 6.08, 6.50, 6.62, and 7.96 (each 3H, s), and AMXm with τ_A 4.29 (1H, q), τ_M 5.31 (1H, q), τ_X 6.35 (1H, q), J_{AM} 10, J_{AX} 4, J_{MX} 22 Hz.

(b) Chalcone (50 mg) and the hydride (I) (50 mg) were added to benzene (15 ml) and the mixture was heated under nitrogen at 73° for 1 h; the hydride had then dissolved. It was then kept at 40° overnight to give a light brown solution and a pale yellow precipitate of the product (II) (20 mg), m.p. 211–212°, identical (i.r.) with the foregoing material.

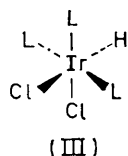
(c) Chalcone (50 mg) and the hydride (I) (50 mg) were heated in propan-2-ol (15 ml) containing dimethyl sulphoxide (8 mg) at 52° under nitrogen for 3 h. The solution became clear after 15 min. Cooling to room temperature afforded a yellow precipitate of unchanged hydride (30 mg).

TABLE I

Chalcone (mg)	Hydride (I) (mg)	Propan-2-ol (ml)	Water (ml)	Additive	Time of reflux (h)	Products	
						Chalcone (%)	Dihydrochalcone (%)
100	16	8	0.1		2	90	10
125	5	5	0.2		24	15	85
100	16	8			2	2	98
125	5	5		N-HCl (0.1 ml)	7	0	98*
100	16	15		N-HCl (0.2 ml)	144 †	63	37
208	12.5	10	0.2	N-HCl (0.1 ml) H ₂ SO ₄ (2 mol. equiv)	4	94	6

* 1,3-Diphenylpropanol (2%) also formed. † Mixture stirred at 20°.

A possible mechanism for the formation of compound (II) from the hydride (I) and chalcone is that a sulphoxide ligand dissociates before addition to the unsaturated ketone occurs. The formation of (II) was inhibited when dimethyl sulphoxide (1 mol. equiv.) was added to the initial reaction mixture. Compound (II)



was also formed by the reaction of the hydride (III) * with chalcone [the yield was similar to that from (I), an observation that could be in keeping with the formation of a common reactive (e.g. pentaco-ordinate) intermediate from both hydrides by loss of a sulphoxide group].

EXPERIMENTAL

Reactions of Chalcone with Hydrides.—(a) Chalcone (130 mg) and the hydride (I) (130 mg) were added to propan-2-ol (15 ml) and water (0.2 ml). The stirred mixture was heated under nitrogen at 73°. After 1 h the hydride had dissolved

* Hydride (IIa) in Part II.

(d) Chalcone (60 mg) and the hydride (III) (60 mg) were suspended in propan-2-ol (10 ml) and water (0.2 ml). The procedure (a) was followed, the hydride dissolving within 10 min. The reaction gave the product (II) (47 mg), m.p. 211–212°, identical (i.r. and n.m.r. spectra) with the product from the hydride (I).

Dihydrochalcone from Chalcone.—(a) **Compound (II) as catalyst (source).** (i) Compound (II) (18 mg) was suspended in propan-2-ol (5 ml) and N-hydrochloric acid (0.1 ml) was added. The mixture was heated under reflux for 3 h; most of the solid had then dissolved. G.l.c. showed that dihydrochalcone, but no chalcone, was present.

(ii) Compound (II) (16 mg) was added to a solution of chalcone (0.1 g) in propan-2-ol (5 ml) containing N-hydrochloric acid (0.1 ml) and the mixture was refluxed under nitrogen. The complex dissolved during 1 h. At this time 2% of dihydrochalcone had been formed, but after a further 2 h reduction was essentially complete.

(b) **Hydride (I) as catalyst (source).** A solution of chalcone (0.25 g) and the hydride (I) (10 mg) in propan-2-ol (10 ml) and N-hydrochloric acid (0.1 ml) was heated under reflux under nitrogen for 8.5 h. The product was chromatographed on deactivated alumina (30 g). Elution with light petroleum-benzene (1:1; 4 × 50 ml) yielded dihydrochalcone (0.239 g), m.p. 69.5–71° (after crystallisation, m.p. 71.5–72°).

The results in Table I show that the effectiveness of the

hydride as a catalyst is increased by the presence of hydrochloric acid but not sulphuric acid. The chalcone-dihydrochalcone mixture was analysed by g.l.c. (2 m Apiezon column at 250°).

(c) *trans*-Acid $\text{H}(\text{Me}_2\text{SO})_2[\text{IrCl}_4(\text{MeSO})_2]$ as catalyst (source). (i) Control experiment. Chalcone (100%) was recovered when a solution of this ketone (0.3 g) was heated under reflux for 48 h with or without the addition of 5*N*-hydrochloric acid (0.18 ml).

(ii) In propan-2-ol containing various amounts of water. Chalcone (0.3 g) in the solvent (5 ml; see Table 2) containing the *trans*-acid (50 mg) was heated under reflux. The organic products were isolated with dichloromethane and chromatographed over alumina (15 g). Elution with benzene-pentane (1 : 1) gave dihydrochalcone, m.p. 69–70°, followed by a liquid ether, ν_{max} 1090 cm^{-1} (probably $\text{PhCH}_2\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OPr}^1$).¹ Elution with ether-ethanol (9 : 1) gave 1,3-diphenylpropanol, ν_{max} 3490 cm^{-1} , characterised as its phenylurethane, m.p. 83° (Found: C, 79.75; H, 6.4; N, 4.2. Calc. for $\text{C}_{22}\text{H}_{21}\text{NO}_2$: C, 79.8; H, 6.75; N, 4.2%) (lit.,⁴ m.p. 83°). Separate experiments, starting with dihydrochalcone, showed that the alcohol $\text{PhCH}_2\cdot\text{CH}_2\text{CH}(\text{OH})\text{Ph}$ is formed from the dihydro-ketone under these conditions.

TABLE 2
Product yields (%)

Water (%)	Time (h)	Product yields (%)		
		$\text{PhCH}_2\cdot\text{CH}_2\cdot\text{COPh}$	Ether	$\text{PhCH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\text{Ph}$
2	12	98.5		1.5
2	24	79.5		20
1	24	64.5	Trace	31
0	24	24	ca. 20	49

(iii) Other alcohols. A solution of chalcone (0.1 g) and the *trans*-acid (16 mg) in methanol or ethanol (5 ml) and water (0.1 ml) was refluxed for 6 h. Dihydrochalcone (2% from methanol; 15% from ethanol) was formed, the remainder being unchanged chalcone.

(iv) Acid scavenger. A solution of chalcone (0.3 g) and the *trans*-acid (50 mg) in propan-2-ol (5 ml) containing water (0.1 ml) and 2,6-di-*t*-butylpyridine (29 mg) was heated under reflux under nitrogen for 6 h. Product analysis showed chalcone (83%) and dihydrochalcone (17%). In the absence of the amine the yield of dihydrochalcone was 98%.

(v) Formation of acetone. Chalcone (0.15 g) and the *trans*-acid (25 mg) were dissolved in propan-2-ol (2.5 ml) and water (0.1 ml). The mixture was sealed in a tube and kept at 82° for 22 h. The solvent was distilled off, and the residue was separated by chromatography into chalcone (67 mg, 45%) and dihydrochalcone (82 mg, 55%). The

distillate was treated with 2,4-dinitrophenylhydrazine reagent to give acetone 2,4-dinitrophenylhydrazone (91.4 mg; 97% based on dihydrochalcone formed).

(vi) Catalytic efficiency of the hydride (I). A solution of chalcone (2 g) and hydride (10 mg) in propan-2-ol (35 ml containing 1% water) and *N*-hydrochloric acid (0.05 ml) was refluxed under nitrogen for 8 days. The colour changed from light yellow to deep yellow. G.l.c. analysis showed dihydrochalcone (82%) and chalcone (18%). One mol of hydride therefore catalysed the reduction of 374 mol of chalcone.

Reduction of Other Unsaturated Ketones.—(a) *Dibenzylideneacetone*. A solution of the ketone (0.3 g) and the *trans*-iridium-sulphoxide acid (50 mg) in propan-2-ol (5 ml) and water (0.1 ml) was refluxed for 12 h. The product was isolated with dichloromethane and chromatographed over deactivated alumina (30 g). Elution with ether-light petroleum (1 : 1; 6 × 25 ml) gave 1,5-diphenylpentan-3-one (0.21 g, 65%) as an oil, ν_{max} 1700 cm^{-1} (CO). The 2,4-dinitrophenylhydrazine formed yellow needles, m.p. 114–115° (lit., 115°). Elution with ether-ethanol (9 : 1) gave 1,5-diphenylpentan-3-ol (89 mg, 29%), m.p. 40–41°, ν_{max} 3410 cm^{-1} (OH) (lit., m.p. 48°).

(b) *1,5-Diphenylpenta-2,4-dien-1-one*. A solution of the ketone (0.3 g) and the *trans*-iridium-sulphoxide acid (50 mg) in propan-2-ol (5 ml) and water (0.1 ml) was heated under reflux for 12 h. The product was isolated with dichloromethane and dried (MgSO_4). Evaporation gave a yellow oil (0.36 g) which was chromatographed on deactivated alumina (20 g). Elution with benzene-pentane (1 : 1; 8 × 25 ml) gave 1,5-diphenylpentan-1-one (0.172 g, 57%), ν_{max} 1700 cm^{-1} (CO). Elution with ether-ethanol (9 : 1; 5 × 25 ml) afforded 1,5-diphenylpentan-1-ol (0.125 g, 42%) as an oil, ν_{max} 3415 cm^{-1} (OH).

The experiment was repeated without water [ketone (0.3 g) and *trans*-acid (50 mg) in dried propan-2-ol (6 ml); reaction time 24 h]. Separation as before gave 1,5-diphenylpentan-1-one (0.26 g, 85%) as an oil, and 1,5-diphenylpentan-1-ol (0.035 g, 10%).

(c) *4,4-Dimethyl-1-phenylpent-1-en-3-one*. A solution of the ketone (0.3 g) and the *trans*-acid (60 mg) in propan-2-ol (5 ml) and water (0.1 ml) was heated under reflux for 12 h. Isolation with dichloromethane followed by chromatography over deactivated alumina (20 g) and elution with benzene-pentane (1 : 1) gave 2,2-dimethyl-5-phenylpentan-3-one (0.263 g, 90%), ν_{max} 1730 cm^{-1} (CO). The 2,4-dinitrophenylhydrazine formed orange needles, m.p. 170–172° (from ethanol).

J. T.-G. thanks Queen's University for financial assistance.

¹ S. Grindel, *Annalen*, 1924, **439**, 295.