Tetrahedron Vol. 42, No. 15, pp. 4325 to 4332, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
Pergamon Journals Ltd.

SYNTHESIS OF INDENES FROM PHENYLPROPANONES USING ALUMINA CATALYST

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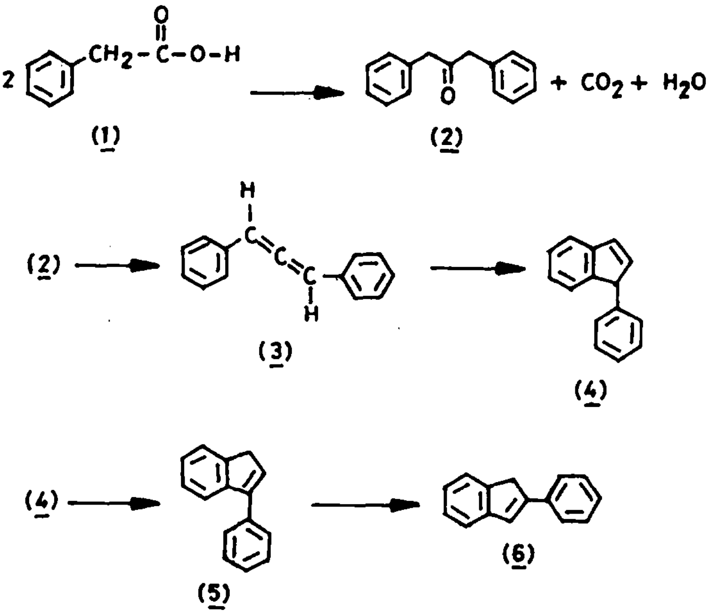
(*Received in UK* 2 *May* 1986)

Abstract: 1,3-Diphenylpropan-2-one undergoes dehydration over alumina at around 400°C to form 1,3-diphenylallene which cyclizes to 2-phenylindene. Since the parent ketone can be obtained under the reaction conditions from phenylacetic acid, the present reaction forms a one step syntheses of 2-phenylindene from phenylacetic acid. 3- and 4-methylphenylacetic acids also give the corresponding indenes. 1,3-Diphenylpropan-1-ones also give phenylindenes, presumably by a direct cyclodehydration reaction.

The conversion of 1,3-diphenylpropan-2-one (2) or its precursor, phenylacetic acid (1) to 1H,2-phenylindene (6) over alumina at 420°C was recently reported[1] from this laboratory. The present communication describes the extension of this reaction to substituted phenylacetic acids and to 1,3-diphenylpropan-1-ones (7).

Scheme I



In the preliminary communication it was proposed that the cyclization of (2) took place via 1,3-diphenylallene (3). This was confirmed by the isolation of the allene (3) from the reaction mixture and by the ready cyclization of (3) to (6) under the reaction conditions.

The initial product of the acid-catalyzed cyclization[2] of diphenylallene is expected to be 1H,1-phenylindene (4). This product was not detected in any of the experiments. The final product (6) could arise from (4) by a sequence of symmetry allowed 1,5-hydrogen and phenyl shift or from the initial carbocation by 1,2-phenyl shift. However, in the present study there is evidence to show that (6) is also formed from (4) via the intermediate (5), as shown in Scheme I. The product distribution in table 1 supports the intermediacy of (5), formed from (4)by two 1,5-hydrogen shifts. The intermediate (5) was prepared[3] independently from 1-indanone by Grignard reaction with phenylmagnesium bromide followed by dehydration. It readily isomerized to (6) when passed over alumina at 400°C, but did not undergo any change when passed over glass beads in the absence of the catalyst at that temperature. Hence the isomerization is believed to be an acid-catalyzed phenyl shift. 3-Phenylindene (5) has been reported[4] to give an isomer of melting point 167°C when distilled through a porcelain tube. The isomer was not characterized at that time, but was later[5] identified as (6). Porcelain is known to exhibit catalytic activity similar to that of alumina.

TABLE 1. Reaction of Dibenzyl Ketone [a]

Sl.No.	Temp. (°C)	Total conversion (%)[b]	Products, yield %[c]		
			(3)	(6)	(5)
1	350	30	20	0	5
2	380	45	15	20	2
3	420	80	5	60	0

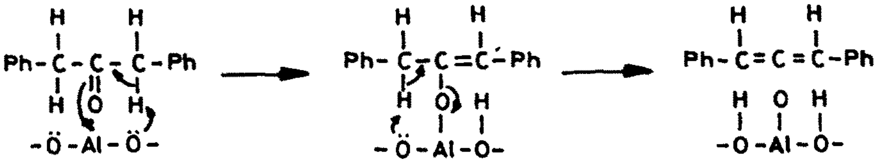
a - Passed neat over 1g of alumina at 6 ml/hr ; no carrier gas

b - Based on dibenzyl ketone recovered,

c - Based on GC analysis

The formation of diphenylallene by the dehydration of the ketone is expected to involve the cooperative action of the exposed oxide ions (basic sites) and aluminum ions (acidic sites) of the alumina surface as shown in Scheme II.

Scheme II



The α-hydrogen of ketones and other carbonyl compounds are readily exchanged for deuterium when contacted with alumina which has been pretreated with D_2O [6]. This observation is in support of the enolization step shown in Scheme II. While enolisation is facile for all ketones, the further decomposition to form allene is observed only for dibenzyl ketone and its derivatives. 1-Phenylpropan-2-one and 1-phenylbutan-2-one did not yield indenes under the experimental conditions. While the former was recovered unchanged, the latter underwent disproportionation as shown below:

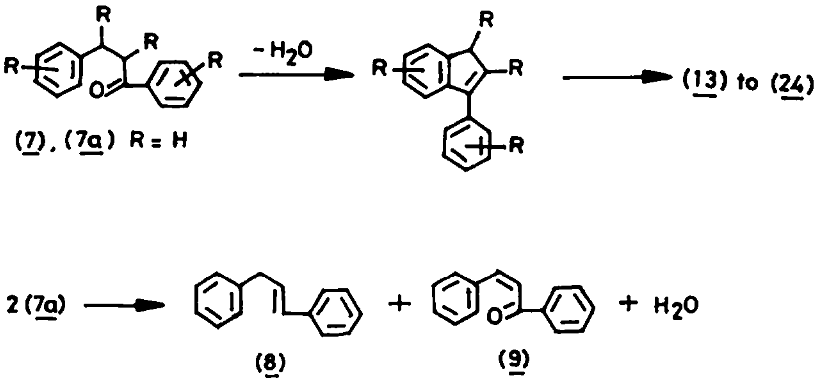
$$2PhCH_2COCH_2CH_3 \longrightarrow PhCH_2COCH{=}CH_2 + PhCH{=}CHCH_2CH_3 + H_2O$$

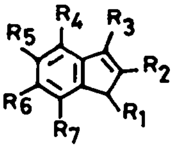
This is a reaction characteristic of ketones containing both α and β hydrogens[7].

4-Methyl and 3-methylphenylacetic acids gave the corresponding substituted indenes (23) and (24) when passed over alumina at 420° (Table 2). In these products the position of the methyl group on the indene ring could not be established.

It was felt that 1,3-diphenylpropan-1-ones (dihydrochalcones) (7) should be better precursors for phenylindenes since they can undergo direct cyclodehydration (Scheme III). It was found that (7a) did undergo cyclodehydration, but in poorer yield than (2) because of the facile disproportionation reaction (vide supra) to yield (8) and (9). Nevertheless, since the dihydrochalcones are readily prepared from the corresponding chalcones, their cyclodehydration

Scheme III





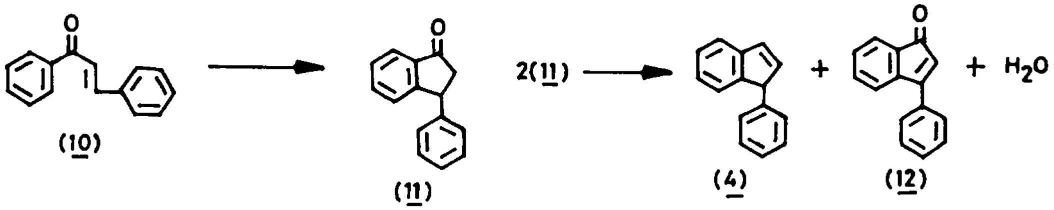
	R1	R2	R3	R4	R5	R6	R7
(13)	H	Me	Ph	H	H	H	H
(14)	H	Et	Ph	H	H	H	H
(15)	Ph	Me	Ph	H	H	H	H
(16)	H	Ph	Ph	H	H	H	H
(17)	Ph	H	Ph	H	H	H	H
(18)	Ph	Ph	H	H	H	H	H
(19)	H	H	Ph	H	Me	H	H
(20a)	H	Ph	H	H	H	Me	H
(20b)	H	Ph	H	H	Me	H	H
(21)	H	H	4'-MeC$_6$H$_4$	H	H	H	H
(22)	H	4'-MeC$_6$H$_4$	H	H	H	H	H
(23a)	H	4'-MeC$_6$H$_4$	H	H	Me	H	H
(23b)	H	4'-MeC$_6$H$_4$	H	H	H	Me	H
(24a)	H	3'-MeC$_6$H$_4$	H	H	H	H	Me
(24b)	H	3'-MeC$_6$H$_4$	H	Me	H	H	H
(24c)	H	3'-MeC$_6$H$_4$	H	H	Me	H	H
(24d)	H	3'-MeC$_6$H$_4$	H	H	H	Me	H

is a convenient method for the preparation of several substituted indenes as seen from Table 2. Even though yields are poor and the product mixture contains the disproportionation products, the indenes are readily isolated by column chromatography. With the various substituted dihydrochalcones listed in Table 2 products were generally as expected. In the case of 1,3,3-triphenylpropan-1-one (Ser.No.6) the initially formed 1,3-diphenyl-1H-indene (17) had undergone isomerization to (16) and (18) (cf. isomerization of (5) to (6)). Similarly the observed products under serial nos.7 and 8 are also products of phenyl migration. ((19) —> (20) in ser.No.7 and (21) —> (22) in ser.no.8)). The structures (20) and (22) are in agreement with the absence in their NMR spectra of signals for the C_2 proton which should appear around δ 6, by analogy with the spectrum of (5).

The derivatives of 1,3-diphenylpropan-1-one with a methoxy group on either of the rings failed to give identifiable products. It is a general observation that methoxyaryl substrates readily decompose over alumina at high temperatures to give phenols which carbonize and deactivate the catalyst.

1,3-Diphenylprop-1-en-3-one (chalcone) itself (10) underwent reaction (Scheme IV) over alumina to give a complex mixture of products from which (5) and (6) could be isolated in low yield. The expected reaction of (10) is the cyclization to the indanone (11), which was not detected. It could have undergone disproportionation[7] to (4) and (12). The latter, being an α,β-unsaturated ketone could have further reacted to give intractable products. The instability of α,β-unsaturated ketones over alumina has been reported[7]. In fact the bulk of the starting material (10) also seems to have undergone a similar fate.

Scheme IV



The catalyst used for these studies was an alumina prepared by the controlled hydrolysis of aluminium isopropoxide by atmospheric moisture[8]. Catalysts prepared by other methods gave poorer yields.

Experimental

Alumina catalyst was prepared by the controlled hydrolysis of aluminium isopropoxide by the moisture present in the atmosphere as reported elsewhere[8]. The catalytic flow reactor and the general experimental techniques have been described in the preliminary communication[1]. All the reactions were carried out at atmospheric pressure without carrier gas. Products were analysed by gas chromatography using an SE-30 (5% on 60-80 mesh chromosorb-G acid-washed, white, 1/8" dia, 6' length) column and FI-detector. Identification and quantitative estimations were made by comparison of retention times and peak areas calibrated with the help of authentic samples. Further the structures were confirmed by analysing and comparing spectral data of pure compounds isolated from the reaction mixture with those of authentic ones.

1,3-Diphenylpropan-2-one was prepared[15] by heating phenylacetic acid with iron powder. 1,3-Diphenylpropan-3-one was prepared[16] by the condensation of benzaldehyde with acetophenone.

1,3-Diphenylallene was prepared[17,18] by the modification of a general procedure for allenes by the dehydration of α,β-unsaturated alcohols. Instead of the dehydration of the alcohol, the substituted allyl alcohol was converted to the acetate and pyrolyzed.

TABLE 2. Formation of Phenylindenes from various Substrates[a]

Sl. No.	Substrate	Product[b]	Yield[c] (%)	Physical state b.p./m.p. (Reported value)°C	NMR signals, δ ($CDCl_3$)
1	1,3-Diphenylpropan-1-one	(5)	6	Liq.113-116°/0.4 mm (116/0.43[3])	3.2(d,2H), 6.15(t,1H), 6.8-7.3(m,9H)
		(6)	20	Solid, 164° (165° [9])	3.7(s,2H), 6.9-7.5(m,10H)
2	1,3-Diphenyl-2-methylpropan-1-one	(13)	15	Liq.150-3°/1 mm (153°/1 mm[10])	1.9(s,3H), 3.1(s,2H), 6.6-6.9 (m,9H)
3	1,3-Diphenyl-2-ethylpropan-1-one	(14)	15	Liq.150-6°/0.8 mm (156°/0.8 mm[11])	1.0(t,3H), 2.3(q,2H), 3.2(s,2H), 6.6-7.0(m,9H)
4	2-Methyl-1,3,3-triphenylpropan-1-one	(15)	18	Solid, 109° (109-110.5° [11,12])	1.9(s,3H), 4.2(s,1H), 6.5-7.1(m,14H)
5	1,2,3-Triphenylpropan-1-one	(16)	20	Solid 108-109° (108.5-9.5° [13])	3.65(s,2H), 6.7-6.9(m,14H)
6[d]	1,3,3-Triphenylpropan-1-one	(16)	10	-do-	-do-
		(18)	20	Solid, 176° (177-178° [13])	4.6(s,1H), 6.6-7.1(m,15H)
7	1-Methyl-3-(4'-methylphenyl)propan-1-one	(20)[e]	24	Solid, 179°	2.3(s,3H), 3.6(s,2H), 6.8-7.3(m,9H)

contd..

TABLE 2 (Continued)

8	1-(4'-methylphenyl)-3-phenylpropan-1-one	(22)	30	Solid, 180° (181-83° [14])	2.2(s,3H),3.4(s,2H), 6.6-7.3(m,9H)
9	1,3-Diphenylpropen-3-one	(5)	8	-	-
		(6)	10	-	-
10	4-Methylphenylacetic acid	(23)[f]	50	184°	2.3(s,6H), 3.5(s,2H), 6.6-7.2(m,8H)[h]
11	3-Methylphenylacetic acid	(24)[g]	36	126-127°	2.2(s,6H), 3.6(s,2H), 6.7-7.2(m,8H)[h]

a - 0.1 mole of reactant in 20 ml benzene was passed over 5g of alumina at 20 ml/h, 420°C.

b - In addition to the products listed, disproportionation products of the ketone were identified. Thus, from 1,3-dephenylpropan-1-one (ser.No.1) (8) (cis and trans) and (10) were isolated in 22 and 10%

c - Yield: isolated by column chromatography.

d - trans-Stilbene was identified as a product in these reactions.

e - Structure is either (20a) or (20b). Hitherto unreported. Calcd. for $C_{16}H_{14}$:C 93.7, H 6.3, found C,93.3, H,6.5.

f - Structure is either (23a) or (23b). Hitherto unreported. Calcd. for $C_{17}H_{16}$: C, 94.40, H, 5.60, found C, 94.29; H, 5.14.

g - Structure is one of (24a) or (24d). Hitherto unreported. Calcd. for $C_{17}H_{16}$: C, 94.40, H, 5.60, found C, 94.29; H, 5.19.

h - Addition of the shift reagent $Pr(fod)_3$ resulted in the singlet at 2.2/2.3 splitting into a doublet of equal intensity.

1,3-Diphenyl-3-hydroxypropene, 30g (b.p. 130°C/8 mm) was prepared by the sodium borohydride reduction of 41.6g 1,3-diphenylpropen-3-one. The former compound was acetylated in the presence of dry HCl gas to get 3-acetoxy-1,3-diphenylpropene. A benzene solution of this ester (25g) was pyrolysed by passing through pyrex glass beads kept at 490°-510°C at the rate of 39 ml/h. After the usual work up, the residue (20g) was chromatographed over 100g of silica gel. About 10g of a hydrocarbon fraction was eluted first with hexane. GC analysis, showed the presence of three compounds. This fraction was carefully rechromatographed over 80g silica gel. About 5g of 1,3-diphenylallene was eluted in the first few cuts. On cooling it solidified to a solid, m.p.48°C (lit.[19] m.p. 49-51°C. NMR: $CDCl_3$-TMS δ 3.25 (d,2H), 6.9 (m,10H).

3-Methylphenylacetic acid: m-Xylene was brominated by N-bromosuccinimide and the resulting 3-methylbenzyl bromide was converted into 3-methylbenzyl cyanide by standard procedure and was hydrolysed to 3-methylphenylacetic acid, m.p. 62°C (lit.[20], m.p.62°C).

4-Methylphenylacetic acid: 4-Methylacetophenone was prepared by the acetylation of toluene and was converted to 4-methylphenylacetic acid by the Willgerodt-Kindler reaction[21], m.p. 92°C (lit.[20], 94°C).

1,3-Diphenylpropan-1-one: 1,3-Diphenylpropen-3-one was prepared by the condensation of acetophenone with benzaldehyde using sodium hydroxide. This was hydrogenated using Raney Nickel in absolute alcohol to 1,3-diphenylpropan-1-one m.p. 72.5°C (lit.[22], 73°C).

1-Phenyl-3-(4'-methylphenyl)propan-1-one m.p.97°C (lit.[23], 96°C), 1-Phenyl-3-(4'-methoxyphenyl)propan-1-one m.p.65°C (lit.[24], 64°C), 1-(4'-methylphenyl)-3-phenylpropan-1-one m.p.69-70°C (lit.[25], 69°C) and 1-(4-methoxyphenyl)3-phenylpropan-1-one m.p.99°C (lit.[24] , 37°C) were prepared by condensing appropriately substituted acetophenones with suitably substituted benzaldehyde and then hydrogenating the unsaturated compounds.

1,3-Diphenyl-2-methylpropan-1-one: 1,3-Diphenyl-2-methylpropen-3-one was prepared by the condensation of propiophenone with benzaldehyde in the presence of dry HCl[26] and was hydrogenated using Raney nickel to 1,3-diphenyl-2-methylpropan-1-one liquid b.p. 148°C/6 mm (lit[27], 148-150°C/6 mm).

1,3-Diphenyl-2-ethylpropan-1-one was prepared by a similar procedure liquid b.p. 170°C/60 mm (lit[28], 183-184°C/13 mm).

2-Methyl-1,3,3-triphenylpropan-1-one m.p.104°C (lit[29], 105°C) and 1,3,3-triphenylpropan-1-one (m.p. 96°C, lit.[29], 96°C) were prepared by the Michael addition of phenylmagnesium bromide to 1,3-diphenyl-2-methylpropen-3-one and 1,3-diphenylpropen-3-one. 1,2,3-Triphenylpropan-1-one, m.p. 120°C (lit.[30], 120°C) was prepared by the benzylation of desoxybenzoin.

General procedure for the reaction on alumina: A solution of 0.025 mole of the substrate in 20 ml of benzene was passed over 5g of alumina at 420°C at a flow rate of 20 ml/hr. The products were collected in a water cooled receiver. The solvent was evaporated and the residue obtained was chromatographed over silica gel using hexane as eluent. Yields and other physical data of the indenes are given in Table 2.

Details of the reaction of 1,3-diphenylpropan-1-one alone are given below.

Reaction of 1,3-diphenylpropan-1-one: A solution of 5.2g (0.025 mole) of 1,3-diphenylpropan-1-one was passed over 5g of alumina at 420°C at a flow rate of 20 ml/hr. Products were collected in a water-cooled receiver. GC analysis of the crude product showed the presence of 1,3-diphenylpropene (cis and trans mixture) 35%, 3-phenylindene (10%), 2-phenylindene (30%) and chalcone (20%). The residue on chromatography over silica gel using hexane as eluent gave initially 1.8g of a liquid consisting of 1,3-diphenylpropenes and 3-phenylindene followed by 1g of 2-phenylindene as a colorless solid (m.p. 164°C, lit.[8], 165°C), 0.2g of a red gummy solid and 0.8g of 1,3-dephenylpropen-3-one.

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