

Reaction of Benzaldehyde with Other Carbonyl Compounds over Thoria and Mixed Oxides of Thoria: Development of an Effective Catalyst and a Process for the Conversion of Benzaldehyde to Phenyl Alkyl Ketones

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Aldol condensation of benzaldehyde with a variety of carbonyl compounds yielded phenyl alkyl ketones in addition to the expected condensation products over thorium oxide catalyst at 400°C. The β -hydroxyketone formed underwent both dehydration to yield α,β -unsaturated carbonyl compound and dehydrogenation to yield 1,3-diketone. The 1,3-diketone cleaved into the phenyl alkyl ketone and an acid. Mixed oxide catalysts of thorium oxide with zinc oxide or magnesium oxide were tested for improving the yield of phenyl alkyl ketones. A mixture 80% magnesium oxide-20% thorium oxide was found to be an effective catalyst.

INTRODUCTION

Vapor-phase aldol condensation reactions in the presence of solid catalysts are well known (1-5). In the present study the reaction between benzaldehyde and a variety of carbonyl compounds and alcohols over thoria to yield phenyl alkyl ketones in addition to the expected condensation products is reported. The reactions were shown to involve aldol condensation, dehydrogenation, dehydration, and retro-aldol condensation steps. Mixed oxide catalysts were developed, which showed better activity for the overall reaction.

EXPERIMENTAL

Catalysts

The thoria catalyst was prepared by the precipitation method from thorium nitrate as reported by Brey *et al.* (6). The precipitation was carried out by the addition of 25% ammonia to a 0.3 M solution of thorium nitrate. The precipitated hydroxide

was filtered, washed, and dried in an air oven for about 12 h at 120°C. Then it was heated at 600°C for 6 h.

The thoria-zinc oxide catalysts with different compositions were prepared by coprecipitation from the solution of calculated amounts of the nitrates, by careful addition of 25% ammonia solution. The precipitated hydroxides were allowed to settle for about 3 h, filtered, washed, and dried in an air oven for about 12 h at 120°C and then heated at 600°C for 6 h.

The thoria-magnesia catalysts were prepared in a similar manner.

Procedure and Analyses

The reactions were carried out in a flow-type reactor. The reactants were introduced into the reactor at the required flow rate using a syringe pump. The products were analyzed by gas chromatography using an SE-30 column. In almost all the reactions, the products were separated by column chromatography and their structures confirmed by comparing the ir and NMR spectra with those of authentic samples.

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TABLE I

Aldol Condensation of Benzaldehyde and Related Reactions over Thoria^a

Sample No.	Reactants (mol) (made up to 10 ml in benzene)	Percentage conversion ^b	Product distribution	
			Product	Weight % ^c
1	Benzaldehyde (0.01) + acetic acid (0.01)	33	Benzaldehyde	34
			Acetophenone	7(14 mol%) ^d
			Benzalacetone (I)	5
			Styrene	2
			Acetone	30
			Unaccounted	22
2	Benzaldehyde (0.01) + acetone (0.01)	32	Benzaldehyde	34
			Acetophenone	8(15 mol%) ^d
			Benzalacetone (I)	6
			Styrene	1
			Acetone	34
			Unaccounted	17
3	Benzalacetone (0.01) (I)	No acetophenone formation		
4	Benzalacetone (0.01) + Water (0.01) (I)			
5	Benzoylacetone (0.0025) (V)	78	No acetophenone formation	
			Benzoylacetone (V)	15
			Acetophenone	33(48 mol%) ^d
			Benzaldehyde	15
			Acetone	27
			Styrene	Traces
6	α -Methylbenzoylacetone (0.0025) (VI)	64	Unaccounted	10
			α -Methylbenzoylacetone (VI)	23
			Propiophenone	27(41 mol%) ^d
			Acetophenone	5(8 mol%) ^d
			Benzaldehyde	5
			Acetone	12
			2-Butanone	12
			Unaccounted	16
			Acetylacetone	40
7	Acetylacetone (neat)	60	Acetone	56
			Acetaldehyde	Traces
			Unaccounted	4
			4-Hydroxy-2-heptanone (VII)	15
			Acetone	30
			Butyraldehyde	15
8	4-Hydroxy-2-heptanone (0.014) (VII)	77	2-Pentanone (X)	10
			4-Heptanone (XI)	5
			Hept-3-en-2-one (VIII)	15
			Unaccounted	10
			Benzaldehyde	35
			2-Butanone	35
			Acetophenone	4(7 mol%) ^d
			Propiophenone	4(7 mol%) ^d
9	Benzaldehyde (0.01) + 2-butanone (0.01)	30	1-Phenyl-1-penten-3-one	4
			3-Methyl-4-phenyl-3-buten-2-one	1
			Acetone	2
			3-Pentanone	2
			Unaccounted	13

TABLE 1—Continued

Sample No.	Reactants (mol) (made up to 10 ml in benzene)	Percentage conversion ^b	Product distribution	
			Product	Weight % ^c
10 ^e	Benzoylacetone (0.0025) (V)	100	Acetophenone	65(98 mol%) ^d
			Acetone	32
			Unaccounted	3
11 ^f	Benzoylacetone (0.0025) (V)	100	Acetophenone	64(97 mol%) ^d
			Acetone	32
			Unaccounted	4

^a Temp. 400°C, flow rate: 15.0 ml/h, thoria 5 g, no carrier gas.

^b Based on the benzaldehyde taken for samples No. 1, 2, and 9, based on the reactants taken for No. 5 to 8, 10, and 11.

^c Actual weight percentage of the components present in the product mixture excluding solvent.

^d Mole% yield in terms of the benzaldehyde taken for No. 1, 2 and 9, in terms of the reactants taken for No. 5, 6, 10, and 11.

^e Passed over 5 g ZnO.

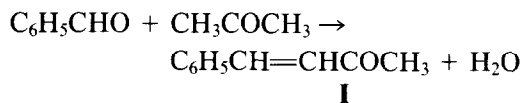
^f Passed over 5 g MgO.

For sample No. 2 (Table 1), a mixture of 1.06 g (0.01 mol) of benzaldehyde and 0.58 g (0.01 mol) of acetone was made up to 10 ml in benzene and the solution was passed over thoria at 400°C at the rate 15 ml/h. Products were collected in a water-cooled receiver. Gas chromatograph analysis of the crude reaction products showed the presence of acetone (34%), benzaldehyde (34%), acetophenone (8%), benzalacetone (6%), and styrene (1%)—all by weight. Benzene and acetone were distilled off and the crude residue (1.0 g) was chromatographed over 40 g silica gel (60–120 mesh) using mixtures of benzene and hexane as eluant. With 75% hexane–25% benzene mixture about 0.60 g (32%) of pure benzaldehyde, with 50% hexane–50% benzene mixture about 0.12 g (6%) of pure acetophenone, and with pure benzene about 0.10 g (5%) of pure benzalacetone were eluted.

RESULTS AND DISCUSSION

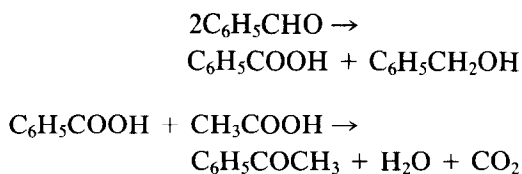
The results of the crossed aldol condensation of benzaldehyde with acetone and the related reactions over thoria at 400°C have been given in Table 1. It has been reported that, over alumina, the major reac-

tion between benzaldehyde and acetic acid is the formation of styrene (7). But on thoria (No. 1, Table 1) styrene formation is taking place to a minor extent. The major products are acetone, acetophenone, and benzalacetone (I). Thoria is an effective ketonization catalyst. Acetone arises by the ketonization of acetic acid, and benzalacetone (I) by the condensation of benzaldehyde with acetone.



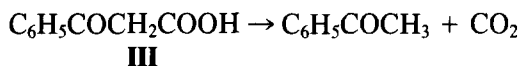
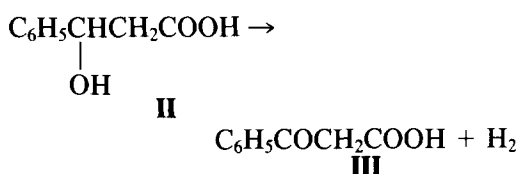
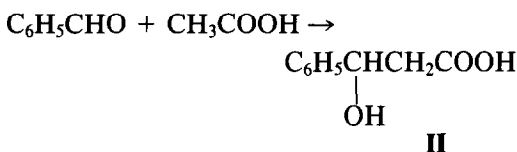
The formation of acetophenone in S. No. 1 (Table 1), can be visualized in three different ways:

(i) The first route envisages the Cannizzaro reaction of benzaldehyde over thoria, followed by the cross-reaction between the resultant benzoic acid and acetic acid.



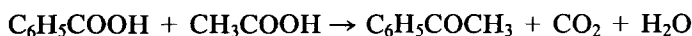
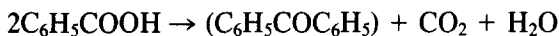
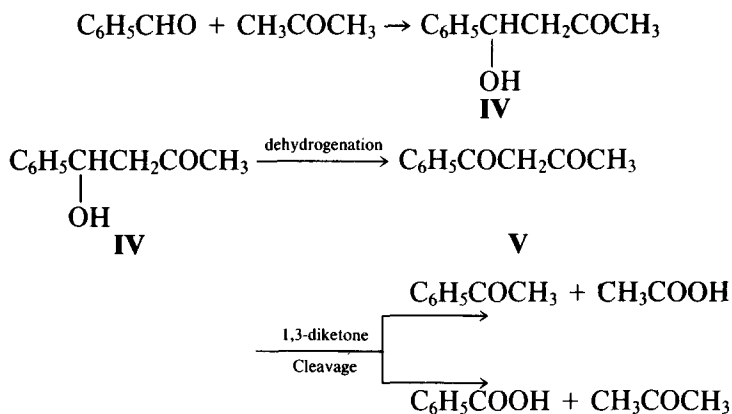
Since the formation of acetophenone took place to the extent of 14 mol% and not even traces of benzyl alcohol were detected, this route is ruled out. Moreover this scheme does not explain why a mixture of acetone and benzaldehyde should give rise to acetophenone (S. No. 2, Table 1).

(ii) The second route envisages the formation of the β -hydroxy acid (3-phenyl-3-hydroxy propanoic acid, **II**) from benzaldehyde and acetic acid, which may undergo dehydrogenation to give the β -keto acid (benzoylactic acid, **III**), and then decarboxylate to give acetophenone.



This route cannot explain S. No. 2 (Table 1), where there is no possibility of formation of carboxylic acid derivative (**II** or **III**) from benzaldehyde and acetone.

(iii) The third route involves the formation of acetophenone from the aldol condensation product (**IV**) of benzaldehyde and acetone. The condensation product (1-phenyl-1-hydroxy butan-3-one, **IV**) undergoes dehydrogenation to give the 1,3-diketone (benzoylacetone, **V**), which is cleaved to give acetophenone.

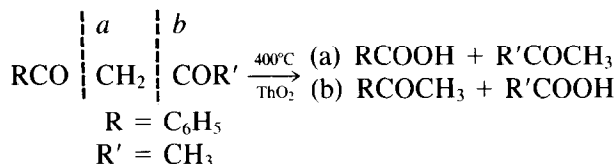


No benzophenone was detected in the product, because benzoic acid hardly ketonizes over thoria. The possibility of route (iii) was checked by independently passing vapors of benzoylacetone (**V**) over thoria catalyst under the same conditions (No. 5, Table 1) when acetophenone was formed as

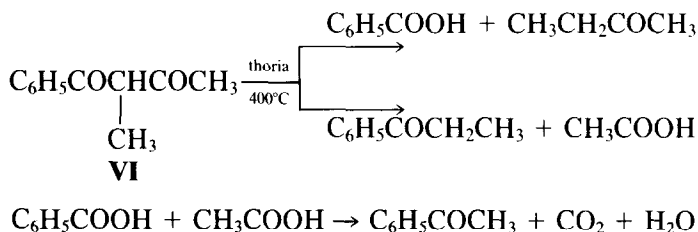
the major product. In order to verify the generality of 1,3-diketone cleavage over thoria, two other 1,3-diketones, namely, α -methyl benzoylacetone (**VI**) and acetylacetone (No. 6 and 7, Table 1) were passed over thoria. The expected cleavage products were formed. 1,3-Diketone cleavage

by alkali is well known in homogeneous conditions and, if R is an aryl and R' is an alkyl group, then cleavage affords almost

exclusively the alkyl aryl ketone by scission *b* (8).



But in the present study, over thoria, both types of scission took place as evidenced from the products of No. 6 (Table 1), where, α -methylbenzoylacetone (**VI**) gave propiophenone, 2-butanone, and acetophenone.

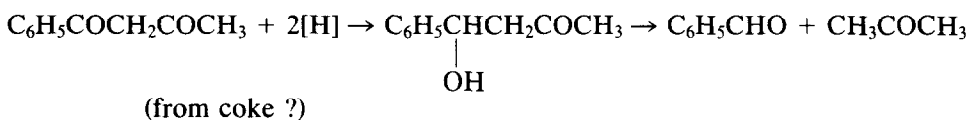


Acetophenone could not have arisen from benzalacetone (*I*), because benzalacetone alone or with equimolar amount of water (No. 3 and 4, Table 1) when passed over thoria, did not yield acetophenone.

In order to confirm the involvement of the β -hydroxyketone in the above proposed reaction mechanism, the β -hydroxyketone formed from butyraldehyde and acetone, namely, 4-hydroxy-2-heptanone (**VII**) was passed over thoria under the same conditions (No. 8, Table 1). The product mixture contained the expected products as per scheme I. (1) Hept-3-en-2-one (**VIII**) by the dehydration of the β -hydroxyketone (path a). (2) 2-Pentanone (**X**)-formed by the dehydrogenation of the β -hydroxyketone (path b) followed by cleavage of the 1,3-

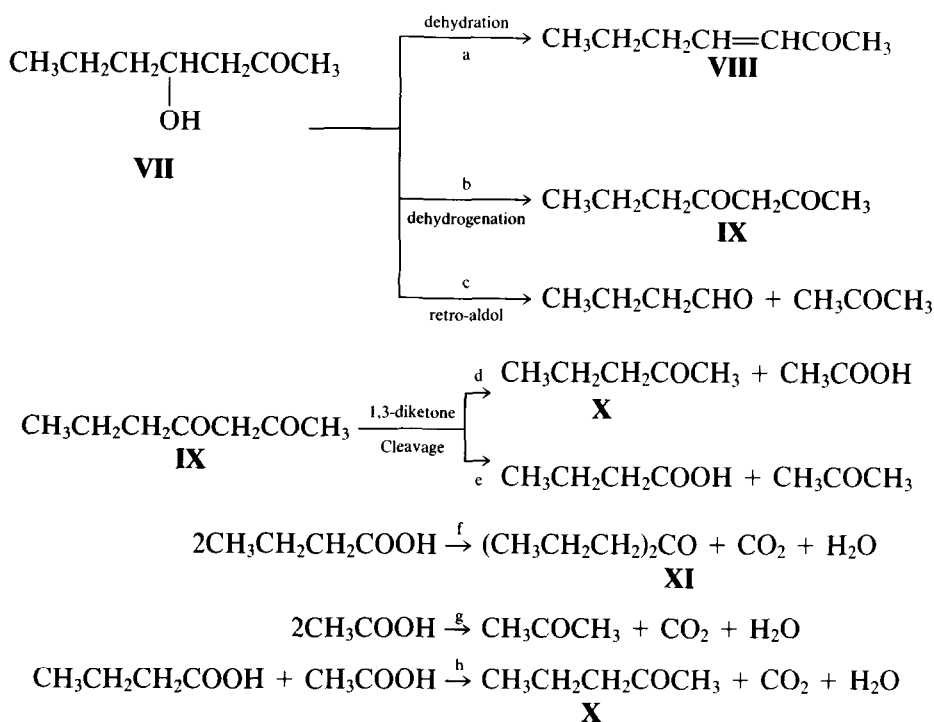
diketone (**IX**) (path d) and also by path h. (3) 4-Heptanone (**XI**) by the ketonization of butyric acid (path f), which was formed in the 1,3-diketone (**IX**) cleavage (path e). (4) Butyraldehyde, by the retro-aldol reaction (path c), and acetone by the reaction paths c, e, and g.

The formation of benzaldehyde in No. 5 and 6, and acetaldehyde in No. 7 (Table 1), is puzzling. Aldehyde can arise by a reductive cleavage of the 1,3-diketone. No obvious hydrogen donor is available in the reaction mixture. It is possible that hydrogen transfer took place from the coke to the 1,3-diketone, to form the β -hydroxyketone, which underwent retro-aldol reaction to give the aldehyde and ketone.



The cleavage of 1,3-diketone took place not only with thoria, but also nearly quanti-

tatively with zinc oxide and magnesium oxide (No. 10 and 11, Table 1). Generally, ba-



SCHEME I

sic catalysts seem to effect 1,3-diketone cleavage. This prompted us to design a new catalyst system which can give rise to good

yields of phenyl alkyl ketones. The basic nature of the catalyst effects the aldol condensation. In addition to being basic, the

TABLE 2
Acetophenone Formation over Different Catalysts^a

Sample No.	Catalyst ^b	% Conversion ^c	Yield of acetophenone ^d (mol%)
1	100% Thoria	35	16
2	80% Thoria-20% zinc oxide	38	18
3	50% Thoria-50% zinc oxide	40	22
4	20% Thoria-80% zinc oxide	65	50
5	100% Zinc oxide	No acetophenone formation	
6	80% Thoria-20% magnesia	45	18
7	50% Thoria-50% magnesia	85	60
8	20% Thoria-80% magnesia	90	70
9	10% Thoria-90% magnesia	35	10
10	100% Magnesia	No acetophenone formation	

^a Reaction between 0.01 *M* benzaldehyde and 0.01 *M* acetone—the reactants diluted to 10 ml in benzene.

^b Each catalyst 5 g, temp. 450°C, no carrier gas, flow rate 15.0 ml/h.

^c Conversion based on benzaldehyde taken.

^d In addition to acetophenone, products mentioned in No. 2 (Table 1), were also found.

TABLE 3
Reaction of Benzaldehyde and Aliphatic Ketones over Magnesia-Thoria^a

Sample No.	Aliphatic ketone	% Conversion ^b	Products yield ^c	
			Product	mol%
1	Acetone	90	Acetophenone	70
2	2-Butanone	90	Acetophenone	35
			Propiophenone	33
3	3-Pentanone	20	Propiophenone	5
4	4-Heptanone	10	Butyrophenone	1
5	3,3-Dimethyl-2-butanone	0	No phenyl alkyl ketone formation	

^a Catalyst 80% magnesia-20% thoria 5 g, Temp. 450°C, no carrier gas, 0.01 M of each reactant diluted to 10 ml in benzene, flow rate 15.0 ml/h.

^b Conversion based on the benzaldehyde taken.

^c In addition to phenyl alkyl ketone, α,β -unsaturated carbonyl compounds and styrene derivatives were found.

catalyst should also have dehydrogenation activity for giving a good yield of phenyl alkyl ketone. The presence of thoria is necessary because zinc oxide or magnesium oxide alone does not affect aldol condensation and dehydrogenation (No. 5 and 10, Table 2). Various combinations of thoria with zinc oxide or magnesium oxide were

tried and the yields of acetophenone in the reaction between benzaldehyde and acetone at 450°C are given in Table 2.

Since 80% magnesia-20% thoria was found to give good yield of acetophenone, reactions were carried out on this catalyst. Table 3 gives the results of the reaction of benzaldehyde with aliphatic ketones. As

TABLE 4
Reaction of Benzaldehyde with Alcohols over Magnesia-Thoria^a

Sample No.	Aliphatic alcohol	% Conversion ^a	Products yield ^b	
			Product	mol%
1	Ethanol	70	Acetophenone	25
			Benzyl alcohol	18
2	<i>n</i> -Propanol	64	Propiophenone	24
			Benzyl alcohol	17
3	Isopropanol	35	Acetophenone	13
			Benzyl alcohol	4
4	<i>n</i> -Butanol	40	Butyrophenone	20
			Benzyl alcohol	10
5	2-Butanol	25	Propiophenone	3
			Acetophenone	3
			Benzyl alcohol	10
6	Isobutanol	60	Isobutyrophenone	35
			Benzyl alcohol	10

^a As in Table 3.

^b In addition to phenyl alkyl ketone and benzyl alcohol, α,β -unsaturated carbonyl compounds and styrene derivatives were found.

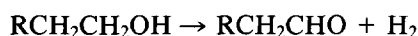
TABLE 5
Reaction of Benzaldehyde with Aliphatic Aldehydes over Magnesia-Thoria^a

Sample No.	Aliphatic aldehyde	% Conversion ^a	Products yield ^a	
			Products	Mol%
1	Acetaldehyde	60	Acetophenone	40
2	Propionaldehyde	50	Propiophenone	35
3	<i>n</i> -Butyraldehyde	50	Butyrophenone	30
4	Isobutyraldehyde	52	Isobutyrophenone	35

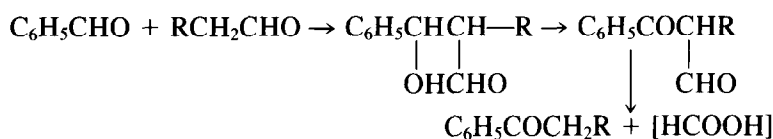
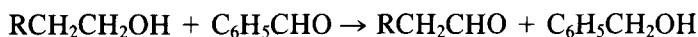
^a As in Table 3.

the size of the ketone increased, the yield of phenyl alkyl ketone decreased, probably because of steric reasons.

Table 4 gives the results of the reaction of benzaldehyde with alcohols. The alcohol is



or



When benzaldehyde was reacted directly with aliphatic aldehydes, rather than with the alcohols (Table 5), good yield of phenyl alkyl ketone was obtained.

The catalyst 80% magnesia–20% thoria

dehydrogenated to aldehyde or ketone directly, or by hydride transfer to benzaldehyde and then reacts with benzaldehyde (cf. Ref. (9)).

was also effective for ketonization of acids. So, the reaction between benzaldehyde and aliphatic acids (precursors of aliphatic ketones) also gave the phenyl alkyl ketones. The results are given in Table 6.

TABLE 6
Reaction of Benzaldehyde with Aliphatic Acids over magnesia-thoria^a

Sample No.	Aliphatic acid ^b	% Conversion ^a	Products yield ^a	
			Product	mol%
1	Acetic acid	80	Acetophenone	60
2	Propionic acid	30	Propiophenone	12
3	<i>n</i> -Butyric acid	20	Butyrophenone	5
4	Isobutyric acid	10	Isobutyrophenone	1

^a As in Table 3.

^b In all the reactions, the corresponding dialkyl ketone was also observed.

CONCLUSION

Thoria, because of its basic nature, is effective for aldol condensation and cleavage of the 1,3-diketone formed by the dehydrogenation of the β -hydroxyketone. Magnesia or zinc oxide, even though they alone do not effect the aldol condensation, when mixed with thoria, enhance the aldol condensation and further cleavage of the 1,3-diketone. The enhancement in the yield of phenyl alkyl ketone is due to the enhancement of the base strength of thoria and also due to the enhanced dehydrogenation and 1,3-diketone-cleavage activity of the mixed oxide as a whole.

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