

# Aromatics Formation from Alumina-Catalyzed Reactions of Methanol with Aliphatic and Alicyclic Carbonyl Compounds

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Reactions of aliphatic and alicyclic carbonyl compounds with methanol over alumina and modified alumina (fluorided and Na<sup>+</sup>-doped) catalysts have been studied. At 250–260°C (low conversions) all carbonyl compounds, by a series of alkylation, dealkylation, condensation, and cleavage processes, lead to similar mixtures of simple ketones and products arising from them. At 350°C (100% conversion) hexamethylbenzene is formed in very good yield. In the absence of methanol, 3,5-dimethylphenol is the major product. Mechanistic studies have been carried out and the evidence for the reaction route carbonyl compounds → acetone → isophorone → 3,5-dimethylphenol → hexamethylbenzene is presented. Efficient and simple methods for the preparation of 3,5-dimethylphenol and HMB are also described. © 1989 Academic Press, Inc.

## INTRODUCTION

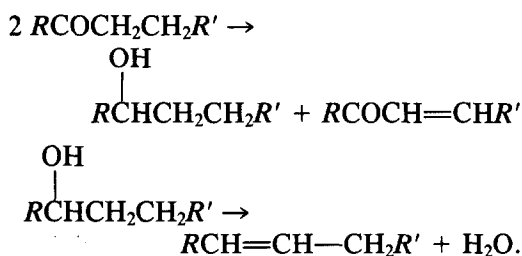
The aldol condensation reaction is one of the most important reactions of carbonyl compounds known to be catalyzed by solid oxide catalysts both in the vapor phase and in the liquid phase. Aldol condensation of formaldehyde with higher aldehydes and ketones has been reported to take place in the vapor phase over a catalyst composed of SiO<sub>2</sub> treated with CsOH, K<sub>2</sub>TiO<sub>3</sub>, or Rb with varying quantities of NaOH (1, 2). Aliphatic aldehydes and alicyclic ketones are known to give aldol condensation products in the vapor phase selectively over lithium phosphate while the Cannizzaro reaction is the competing reaction with aldehydes over Ca(OH)<sub>2</sub> (3). <sup>13</sup>C-NMR spectroscopy has been used to detect the short-lived intermediates and to distinguish the various reaction pathways in the series of aldol condensations of simple ketones like acetone, 2-butanone, and 3-pentanone over activated alumina (4, 5). Other techniques like IR spectroscopy (6), Raman spectroscopy (7), and pulse microreactor-GC (8) have also been used to study the

reactions of acetone over oxide catalysts. In the reaction sequence acetone → diacetone alcohol → mesityl oxide → phorone → isophorone, the last step is the irreversible formation of isophorone, which appears to be the net driving force (8). Mesitylene has also been detected in these studies. It has been suggested from the studies with butanone over alumina that aldol condensation is a base-catalyzed reaction (5). By comparing 11 kinds of aluminas prepared from various starting materials by different methods for the aldol condensation reactions of acetone at 0°C, Zhang and co-workers have concluded that aldol condensation requires an optimum arrangement of acidic and basic sites on the catalyst surface (9). Aldol condensation is the competing reaction observed during the liquid-phase condensation reactions of carbonyl compounds with simple aromatics such as phenol, thiophenol, and *m*-xylene over crystalline aluminosilicates (10). Acetophenone is known to give dypnone, an aldol condensation product with 98–99% selectivity over H-mordenite and HY-zeolite in liquid phase (10). Thoria is also known to catalyze aldol condensation reactions at room temperature (11). The kinetics and

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the effect of catalyst poisoning by benzoic acid and pyridine on the course of the aldol condensation of cyclohexanone in decalin at 210°C and retroaldolization over aluminium and iron oxides have been investigated in detail (12). Aldol condensation of aralkyl ketones in the liquid phase over basic alumina, with and without ultrasonic acceleration, has been used as a synthetic reaction (13, 14).

At higher temperatures over alumina, ketones having  $\alpha$  and  $\beta$  hydrogen atoms are known to undergo disproportionation (15–17):



Intramolecular dehydration of ketones to allenes, acetylenes, or dienes has also been reported over oxide catalysts (18–20). Thus by temperature-programmed desorption of aliphatic ketones from ZSM-5-type zeolites at temperatures up to 450°C, intramolecular dehydration has been shown to take place in addition to aldol condensation (19). The formation of hydrocarbons including aromatics from aliphatic ketones over zeolite catalysts at 300–350°C has been reported (20). Dehydration of dibenzyl ketone over alumina at 400°C yielded diphenylallene which further cyclized to phenylindene (21, 22).

These reactions are appreciably altered when mixtures of ketones and alcohols are made to react over oxide catalysts. Transfer hydrogenation becomes the major reaction (23, 24).

Alkylation of aromatics with alcohols is an important reaction catalyzed by zeolites (25, 26). Ortho alkylation of benzyl alcohol over oxide catalysts to give anthracene, an industrially important compound, has been observed in our laboratory (27). Reactions

of aryl alkyl ketones with methanol to yield  $\alpha$ -alkylation and dealkylation products over oxide catalysts have also been observed in our laboratory (28). Phenol is also known to react with methanol to yield anisole, cresols, polymethylphenols, and hexamethylbenzene (HMB) (29, 30). Reaction of acetone and methanol is one of the methods for the preparation of HMB (31). HMB is one of the products formed from methanol in the presence of a variety of acid catalysts (32) though over alumina itself its yield is very small (33). As an extension of our earlier studies, the reactions of aliphatic and alicyclic carbonyl compounds with alcohols, mainly methanol, over alumina have been carried out. Alumina catalysts, modified by fluoridation and by sodium ion impregnation, have been used to study the effect of acidity on reaction and selectivity.

## EXPERIMENTAL

### Reagents

Laboratory reagents acetone, methyl ethyl ketone, diethyl ketone, 2-pentanone, methyl isobutyl ketone, methyl *t*-butyl ketone, 2-octanone, propanal, *n*-butanal, *n*-heptanal, acetic acid, propionic acid, methyl acetate, ethyl acetate,  $\gamma$ -butyrolactone, acetylacetone, propargyl alcohol, allyl alcohol, mesitylene, mesityl oxide, isophorone, 3,5-dimethylphenol, benzene, and methanol were used after purification. 1-Octyne and 4-octyne purchased from Aldrich Chemicals Co., UK, were used without further purification. The ethanal used was prepared by depolymerizing pure dry paraldehyde.

### Catalyst Preparation

**Alumina, 1.** Aluminium isopropoxide has been used as the starting material for the preparation of pure alumina (34). Double-distilled aluminium isopropoxide (408 g) was placed in a wide porcelain dish so that the liquid formed a layer 1–2 cm in thickness and was exposed to the atmosphere for a few days. The container was covered

by a clean cloth to prevent contamination by dust from the atmosphere. As the slow hydrolysis by atmospheric moisture progressed, the crust formed on the surface was broken up periodically with a glass rod and the solid obtained was broken up and transferred to a silica crucible. This was dried in an air oven at 100°C for 12 h and then calcined in a furnace at 600°C for 6 h. The amount of alumina so obtained was 75 g.

*1.5% Na<sup>+</sup>/Al<sub>2</sub>O<sub>3</sub>, 2.* A solution of 0.195 g of anhydrous Na<sub>2</sub>CO<sub>3</sub> in 50 ml of water was added slowly with thorough stirring to 25 g of alumina, **1** and was further stirred for 15 min (23). It was then heated at 100°C for 12 h and calcined at 600°C for 6 h. The sodium ion content of the catalyst thus prepared was determined by flame photometry (35) and was found to be 1.5%.

*4.75% F<sup>-</sup>/Al<sub>2</sub>O<sub>3</sub>, 3.* Fluorided alumina catalyst was prepared by the impregnation method (36). A mixture of 12.5 ml of 40% HF solution and 12.5 ml of water was added dropwise to 25 g alumina-**1** in a polyethylene beaker and stirred thoroughly with a polyethylene rod. After complete addition and thorough mixing, the catalyst was placed in a quartz tube and heated at 600° for 6 h. The fluoride ion content, estimated by a spectrophotometric method (37), was found to be 4.75%.

### Characterization

X-ray diffraction studies were carried out to characterize alumina (major phase  $\eta$ ) and modified alumina catalysts. The surface area was determined by the BET method ( $216 \pm 10$  m<sup>2</sup>/g for all three catalysts). Acidities were determined by titration of the solid catalyst suspended in dry benzene with *n*-butyl amine solution using Hammett indicators (38). The results of acidity measurement (28, 46) showed that fluoridation increased the total acidity and also created strong acidic sites while sodium ion impregnation decreased the total acidity and also the number of stronger acidic sites.

### Catalytic Reactions

The reactions were carried out in a pyrex flow reactor consisting of a spiral preheater tube attached to the main reactor which is a pyrex tube of 2.5-cm diameter and 40-cm length kept in a cylindrical ceramic furnace mounted in a sloping manner. The required quantity of the catalyst was kept in the middle isothermal region of the reactor. Space above the catalyst was packed with pyrex glass beads which acted as a preheater zone. Provision was made to read the inside temperature of the catalyst zone using a thermocouple. The catalyst was activated at its activation temperature and the temperature was brought down to the reaction temperature in a stream of pure, dry nitrogen. The liquid was introduced at the top of the reactor by means of an infusion pump. The products were collected in a water-cooled receiver and analyzed. After each reaction, the catalyst was reactivated by passing CO<sub>2</sub>-free air at its activation temperature through the catalyst tube for 3 to 4 h (21).

### Product Analysis

Products were analyzed by GLC using FFAP (5% on Chromosorb A, 60–80 mesh, acid-washed, white, 210-cm length, 0.31-cm diam), SE 30 (5% on Chromosorb A, 60–80 mesh, acid-washed, white, 210-cm length, 0.31-cm diam), and Carbowax (10% on Chromosorb A, 60–80 mesh, acid-washed, white, 210-cm length, 0.31-cm diam) columns and a flame ionization detector. Identification and estimation of products were made by comparing retention times and peak areas calibrated with those of authentic samples. Retention time agreement on at least two of the above stationary phases was ensured for the identification of each component. Pure compounds were isolated wherever possible from the reaction mixture by distillation, column chromatography, or other methods and the structures were confirmed by spectral (<sup>1</sup>H-NMR, IR, and mass) data.

### 3,5-Dimethylphenol

Acetone (29 g, 0.5 mol) was passed over a bed of  $\text{Al}_2\text{O}_3$ , 2 (5 g) at a rate of 11 ml/h at 350°C. The products were collected through a water-cooled condenser. The products were extracted with three 50-ml portions of 2 N NaOH solution. It was neutralized with concd HCl, extracted with  $\text{CH}_2\text{Cl}_2$ , and dried over anhyd  $\text{Na}_2\text{SO}_4$ . Evaporation of  $\text{CH}_2\text{Cl}_2$  gave a solid residue (9.5 g). It was recrystallized from methanol to obtain white crystalline 3,5-dimethylphenol (mp = 65–66°C). Yield was 47% based on acetone. The structure was further confirmed by  $^1\text{H-NMR}$ , IR, and mass spectra.

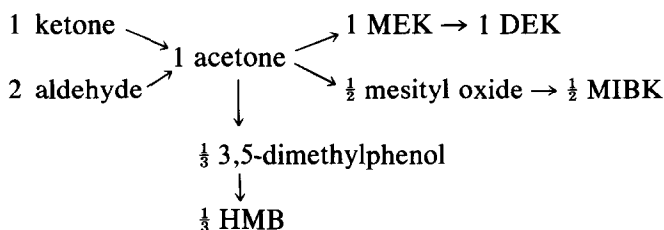
### Hexamethylbenzene

A mixture of acetone (29 g, 0.5 mol) and methanol (64 g, 2 mol) was passed over a bed of  $\text{Al}_2\text{O}_3$ , 1 (5 g) at a rate of 22 ml/h at 350°C. The products were collected in a water-cooled receiver. Solids had also condensed on the walls of the reactor and

condenser. They were dissolved in benzene, and combined with the condensate in the receiver and dried over anhyd  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent yielded solid product (25 g). Recrystallization of the product in methanol yielded pure, white, crystalline hexamethylbenzene (mp 166°C). Yield was 95% based on acetone. The structure was confirmed by  $^1\text{H-NMR}$  and mass spectra.

### RESULTS AND DISCUSSION

Reactions of carbonyl compounds with methanol have been carried out over  $\text{Al}_2\text{O}_3$ , 1 at 250–260 and 350°C and the results are given in Tables 1 and 2 respectively. Table 1 gives the mole percent yields of the major products in the reaction of several carbonyl compounds with methanol and Table 2 gives the mole percent yield of HMB. The mole percent yields are calculated based on the number of moles of the carbonyl compound used and assuming the following stoichiometries:



At the lower temperature, all the ketones and aldehydes studied gave similar mixtures consisting of acetone, methyl ethyl ketone (MEK), diethyl ketone (DEK), mesityl oxide, methyl isobutyl ketone (MIBK), mesitylene, 3,5-dimethylphenol, and HMB. In addition to the above products, small amounts of isophorone, other phenolic derivatives, and  $\alpha$ -alkylated products of carbonyl compounds and gaseous products consisting of alkenes, formaldehyde, methane, dimethyl ether, and other hydrocarbons were also formed. Quantitative deter-

mination of these compounds was not done.

At the higher temperature (350°C), regardless of the identity of the carbonyl compound used, the major product isolated in 80–90% yield was hexamethylbenzene. Small amounts of phenolic products and varying amounts of gaseous products consisting of formaldehyde, dimethyl ether, methane, and other hydrocarbons which were not analyzed quantitatively were also detected.

The product distribution in Table 1 sug-

TABLE I  
Reactions of Carbonyl Compounds and Methanol over Alumina at 250–260°C

Sample No.	Carbonyl compound <sup>a</sup>	Conversion (%)	Temp. (°C)	Yield (mol%) based on carbonyl compound <sup>b,c</sup>						Unreacted starting material <sup>d</sup>		
				Acetone	MEK	DEK	Mesitylene	Mesityl oxide	MIBK		3,5-dimethylphenol	HMB
1	Acetone	62	250	38	3	2	6	12	6	18	6	—
2	MEK	63	250	8	37	3	3	10	6	15	6	—
3	DEK	64	255	5	8	36	3	10	4	15	6	—
4	2-Pentanone	63	255	9	2	1	3	10	4	15	6	37
5	MIBK	66	260	9	2	1	3	8	34	15	6	34
6	MTBK	65	250	4	1	1	3	8	6	9	3	35
7	2-Octanone	60	250	9	3	1	3	10	4	15	6	40
8	Ethanal	74	250	5	2	1	3	10	4	15	6	26
9	Propanal	76	255	4	2	1	3	8	4	15	6	24
10	n-Butanal	75	250	4	2	1	3	6	6	12	3	25
11	n-Heptanal	78	255	3	2	1	3	8	4	15	6	22
12	Cyclohexanone	59	260	3	1	1	3	6	4	9	9	41
13	Cyclopentanone	56	255	2	1	1	3	6	4	9	6	44

Note. Reagents: (0.05 mol of carbonyl compound + 0.15 mol of methanol) in benzene = 20 ml. Catalyst: Al<sub>2</sub>O<sub>3</sub>, I (3 g). Flow rate: 22 ml/h.

<sup>a</sup> MEK: methyl ethyl ketone; DEK: diethyl ketone; MIBK: methyl isobutyl ketone; MTBK: methyl *t*-butyl ketone; HMB: hexamethylbenzene.

<sup>b</sup> Calculation based on the assumption that



<sup>c</sup> Isophrone, other phenolic products,  $\alpha$ -alkylated products of the carbonyl compounds, and gaseous products consisting of HCHO, CH<sub>4</sub>, CH<sub>3</sub>OCH<sub>3</sub>, and other hydrocarbons were also found. Alkene corresponding to the reductive dehydration of the ketone, e.g., cyclohexene from cyclohexanone, was present in all cases.

<sup>d</sup> In the case of acetone, MEK, and DEK, the values are given in the respective columns.

TABLE 2

Reactions of Carbonyl Compounds and Methanol over Alumina, 1  
at 350°C

Sample No.	Carbonyl compound	Conversion (%)	HMB yield (mol%) <sup>a,b</sup>
1	Acetone	100	90
2	MEK	100	87
3	DEK	100	87
4	2-Pentanone	100	90
5	MIBK	100	84
6	MTBK	100	84
7	2-Octanone	100	90
8	Ethanal	100	84
9	Propanal	100	84
10	<i>n</i> -Butanal	100	84
11	<i>n</i> -Heptanal	100	84
12	Cyclohexanone	100	78
13	Cyclopentanone	100	75

*Note.* Reagents: 0.068 mol of carbonyl compound + 0.359 mol of methanol. Catalyst: Al<sub>2</sub>O<sub>3</sub>, 1 (5 g). Flow rate: 22 ml/h.

<sup>a</sup> Calculation based on the assumptions that 3 ketone → 1 HMB and 6 aldehyde → 1 HMB.

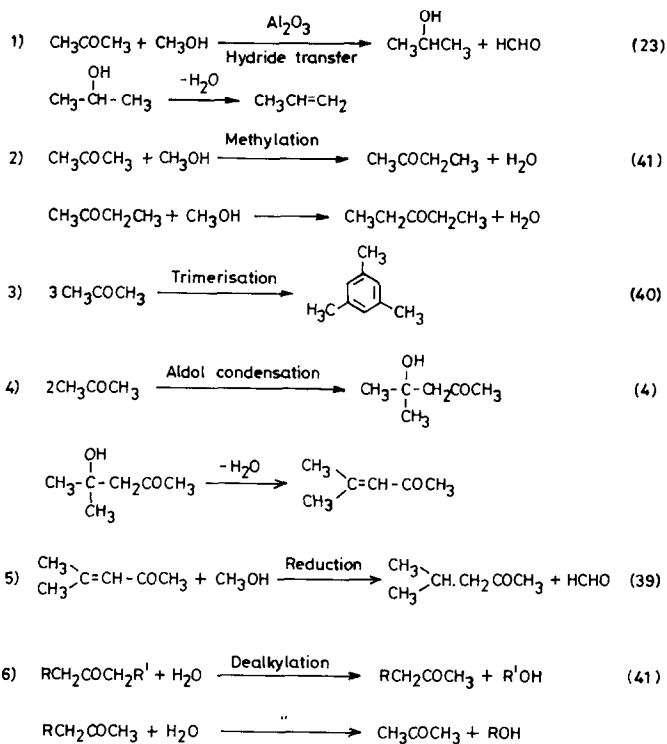
<sup>b</sup> Refer to footnotes under Table 1.

gests that all the carbonyl compounds, by a series of alkylation, dealkylation, condensation, and cleavage processes, lead to similar mixtures of simple ketones and products arising from them.

Probable routes for these processes, based on earlier reports in the literature, are shown in Scheme 1. Reaction 1, transfer hydrogenation followed by dehydration, is a well-established reaction of ketones with alcohols (23). Reaction 4, formation of mesityl oxide via diacetone alcohol from acetone is also well established (4). In an independent experiment passing mesityl oxide and methanol over alumina at 250°C, it was shown that MIBK is formed in up to 60% yield (Reaction 5). Trimerization of acetone to mesitylene, Reaction 3, has also been reported over alumina (40). Reactions 2 and 6, alkylation and dealkylation of ketones, have also been observed over alumina (41) but a detailed study has not been done. Methyl ethyl ketone (Reaction 2) could be isolated by fractional distillation

and confirmed by its <sup>1</sup>H-NMR spectrum. Methylation of acetophenone by methanol to form propiophenone and demethylation of propiophenone and isobutyrophenone have been reported elsewhere (28).

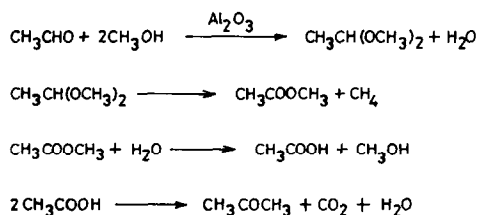
It is interesting to note that even aldehydes undergo reactions over alumina to give mixtures of simple ketones, predominantly acetone. Two probable routes for the formation of acetone from acetaldehyde are shown in Schemes 2 and 3. The first one, involving decomposition of dimethylacetal of acetaldehyde, is by analogy with the reported formation of alkyl benzoate by the decomposition of dialkylacetal of benzaldehyde over alumina (42) (Scheme 2). Acetals or ketals were not detected in the present study. However, methyl acetate and acetic acid, two of the proposed intermediates in Scheme 2, were detected in the reaction of acetaldehyde with methanol over alumina at 250°C. When methyl acetate and acetic acid were passed individually over alumina at 250°C, acetone and



SCHEME 1

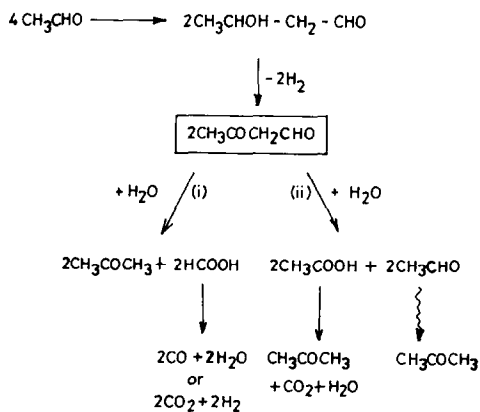
the products arising from acetone were observed. When methyl acetate or acetic acid were passed with methanol over alumina at 250°C, HMB was formed in 70% yield.

Scheme 3, involving aldol condensation, dehydrogenation, and 1,3-diketone cleavage, is formulated by analogy with a similar reaction reported for benzaldehyde and acetaldehyde over several oxide catalysts (43, 44). Cleavage of 1,3-diketone shown in Scheme 3 was verified by the observation



SCHEME 2

that acetylacetone gave mainly acetone when passed over alumina at 250°C. Acetylacetone reacted with methanol at 350°C to yield HMB in 65% yield. The detection of formic acid and acetic in the product mixture of the reaction of acetaldehyde and



SCHEME 3

methanol over alumina at 250°C is in agreement with the steps in Scheme 3.

Formation of HMB from all the carbonyl compounds studied suggests that some of the products in Table 1 are formed reversibly and one of these products should be the common intermediate for HMB. It has been suggested in an earlier paper (45) that dimethylacetylene is the common intermediate for HMB. The results of the present study strongly argue against the possibility. Although intramolecular dehydration of ketones to allenes, acetylenes, or dienes has been reported over oxide catalysts (18–20), in the present study alkynes could not be detected. Studies with alkynes showed that they are the precursors (by hydration) for carbonyl compounds rather than vice versa.

Mesitylene was recovered quantitatively when passed with methanol over alumina at different temperatures (250–350°C) showing that mesitylene is not the intermediate in the formation of HMB from acetone and methanol. By analogy with the trimerization of acetone to mesitylene, it was suspected that methyl ethyl ketone could form HMB by trimerization. However, in the absence of methanol, MEK over alumina under the same reaction conditions failed to yield any HMB, showing that MEK, which is formed from acetone by an  $\alpha$ -methylation, is not the source of HMB.

Isophorone, an aldol condensation product of acetone, was detected by TLC from the reaction of acetone and methanol over

alumina at 125°C. In the earlier studies of acetone over alumina reported in the literature (4, 8), isophorone is the final, irreversibly formed product. In the present study, acetone alone over alumina also yielded isophorone as one of the products. Isophorone was not detected in GLC analysis since under the condition isophorone decomposed over the column. It was possible to isolate an intermediate, 3,5-dimethylphenol, which can arise from isophorone. When isophorone alone was passed over alumina at 350°C, 3,5-dimethylphenol was formed in 90% yield, whereas with methanol, it yielded HMB as the major product in addition to a small amount of 3,5-dimethylphenol. It is also interesting to note that 3,5-dimethylphenol also yielded HMB in very good yield when passed over alumina with methanol at 350°C. The results of these studies are presented in Table 3.

Acetone is suspected to be the common intermediate for hexamethylbenzene. All the carbonyl compounds studied gave acetone as one of the products when passed alone and with methanol over alumina at 250°C. It appears that HMB is formed by the following route (all the intermediates in this route have been detected and each one was independently shown to lead to the subsequent products in the route):

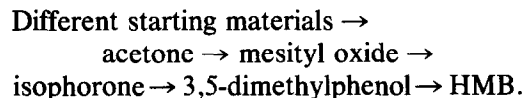
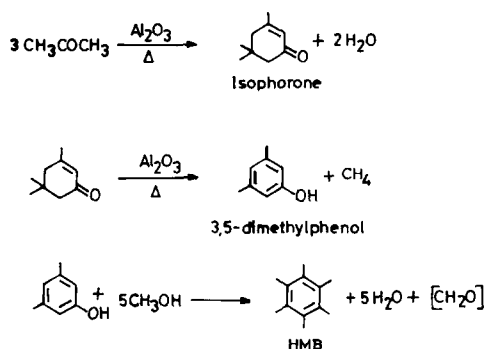


TABLE 3  
Reactions of Isophorone and 3,5-Dimethylphenol over Alumina at 350°C

Sample No.	Substrate	Solvent	Conversion (%)	Yield (mol%)	
				3,5-dimethylphenol	HMB
1	Isophorone	Benzene	100	90	0
2	Isophorone	Methanol	100	4	87
3	3,5-dimethylphenol	Methanol	100	0	92

Note. Reagents: 0.03 mol of substrate + 20 ml of solvent. Catalyst:  $\text{Al}_2\text{O}_3$ , 1 (5 g). Flow rate: 22 ml/h.





SCHEME 4

The details of this route are given in Scheme 4.

The possibility of methanol alone being the source of HMB was considered since, in the methanol to gasoline reactions over zeolites, HMB is one of the products. When methanol was passed over alumina and modified alumina catalysts at different temperatures (250°–450°C), gaseous products consisting of dimethyl ether, methane, formaldehyde, and other hydrocarbons and water were formed, but no HMB.

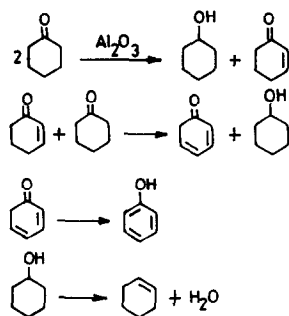
In the case of reactions of carbonyl compounds with methanol at the lower temperatures (250–260°C), the product mixture contained small amounts (≈5%) of unreacted methanol. But in the reaction product mixture at the higher temperature (350°C), methanol was not detected. The excess methanol was converted into formaldehyde, methane, and water with some dimethyl ether and other gaseous hydrocarbons. Formaldehyde gas passed over the catalyst at 250 and 350°C was essentially recovered unchanged, but coke formation was noticed during the experiment. The possibility of reactions between acetone and formaldehyde was considered. A mixture of acetone and formaldehyde was passed over alumina at various temperatures (250–350°C). Only the products arising from acetone under the experimental conditions were detected in the liquid product. HMB was not detected even in

trace amounts. The expected methyl vinyl ketone was not observed in the product mixture. The heavy coke formation over the catalyst in the reaction suggests that the methyl vinyl ketone, if formed, might have polymerized under the reaction conditions as in the reported coke formation due to the polymerization of phenyl vinyl ketone formed from the disproportionation of propiophenone over alumina catalyst (17).

#### Aliphatic Carbonyl Compounds

Aliphatic carbonyl compounds alone in the absence of methanol gave mainly condensation products, dealkylation products, and phenolic products over  $\text{Al}_2\text{O}_3$ , 1 at 200°C. Quantitative analysis of the above reaction mixtures was not carried out. Table 1 gives the results of the reactions of aliphatic carbonyl compounds with methanol at low temperatures (250–260°C) and Table 2 gives those at high temperature (350°C). In the case of methyl ethyl ketone, the phenolic product was mainly 3,5-dimethylphenol, but the  $^1\text{H-NMR}$  spectrum of the total phenolic fraction (alkali extract) showed the presence of ethyl group also. At high temperature (350°C), only HMB was obtained and no ethyl-substituted benzene derivative was obtained even from MEK and methanol. The absence of other alkylated benzene derivatives from the reactions of higher ketones over alumina suggests that either the higher ketones should undergo dealkylation to acetone, which in turn can give the expected and observed 3,5-dimethylphenol and HMB, or that the other alkylated phenolic derivatives, formed from the condensation products of higher ketones, might undergo further reactions with methanol to give HMB.

Hexamethylbenzene was obtained in 95% yield in the reaction of 4-ethylphenol and methanol over alumina at 350°C. The  $^1\text{H-NMR}$  spectrum of the nonphenolic products obtained from the above reaction showed signals for ethyl and aromatic protons. These results suggest that there may be an easy benzylic cleavage or a substi-



SCHEME 5

tution of ethyl group by methanol during alkylation. But the reaction of 4-ethylphenol alone in benzene over alumina at 350°C failed to yield the demethylated product, 4-methylphenol. The same is the case with ethylbenzene, which also failed to yield toluene over alumina under the reaction conditions. Therefore, substitution of ethyl group by methanol during methylation is the most probable route to the observed results. Thus it appears that due to the ready conversion of higher alkylbenzenes to methylbenzenes by displacement of alkyl groups by methyl group, higher ketones also give HMB even though in principle they can also give other alkylated derivatives.

#### Alicyclic Carbonyl Compounds

The reactions of alicyclic carbonyl compounds over alumina are also interesting.

The results of cyclohexanone and cyclopentanone with methanol over alumina at low temperatures (250–260°C) and at high temperature (350°C) are given in Tables 1 and 2, respectively. In the case of cyclohexanone, the phenolic fraction contained mainly unsubstituted phenol which can be formed as in Scheme 5 as reported in the literature (17). When cyclohexanone alone was passed over alumina at 250°C, mainly cyclohexene and phenol were obtained. Small amounts of acetone were also observed in the above reaction. HMB can arise from both phenol and acetone, the latter formed by the  $\alpha$ -cleavage, in the case of cyclohexanone. But in the case of cyclopentanone, acetone formed by  $\alpha$ -cleavage is likely to be the only source of HMB.

#### Acetone over Different Catalysts

In order to study the role of acidity in these reactions, the reaction of acetone was carried out over three different catalysts, namely, alumina, 1, sodium ion-doped alumina, 2, and fluorided alumina, 3, and the results are given in Table 4. Condensation to 3,5-dimethylphenol via isophorone is the major reaction on all three catalysts, the higher selectivity for the product being on the 1.5% Na<sup>+</sup>-doped alumina catalyst, 2 (the least acidic or most basic of the three catalysts studied). Apparently both acidic and basic sites catalyze the aldol condensation, leading to 3,5-

TABLE 4  
Reactions of Acetone over Different Catalysts at 300°C

Sample No.	Catalyst No.	Conversion (%)	Yield (mol%) <sup>a</sup>		
			Mesitylene	3,5-dimethylphenol	Others <sup>b</sup>
1	1	57	8	38	11
2	2	62	3	44	15
3	3	60	14	35	11

Note. Reagent: 20 ml acetone (neat). Catalyst: 5 g. Flow rate: 22 ml/h.

<sup>a</sup> Calculation based on the assumptions that 3 acetone  $\rightarrow$  1 mesitylene and 3 acetone  $\rightarrow$  1 3,5-dimethylphenol.

<sup>b</sup> Mainly other aldol condensation products.

TABLE 5  
Reactions of Acetone and Methanol over Different Catalysts at 300°C

Sample No.	Catalyst No.	Conversion (%)	Yield (mol%) <sup>a</sup>			
			Mesitylene	3,5-dimethylphenol	HMB	Others <sup>b</sup>
1	1	65	3	5	42	15
2	2	67	1	23	17	26
3	3	70	7	3	51	9

Note. Reagents: 0.068 mol of acetone + 0.18 mol of methanol. Catalyst: 3 g. Flow rate: 22 ml/h.

<sup>a</sup> Calculation based on the assumptions that 3 acetone → 1 mesitylene, 3 acetone → 1 3,5-dimethylphenol, and 3 acetone → 1 HMB.

<sup>b</sup> Mainly other aldol and alkylation products.

dimethylphenol, but the activity is slightly higher in the case of the basic catalyst. The earlier studies with butanone over alumina also suggest that basic sites catalyze aldol condensation (5) while Zhang and co-workers had concluded that an optimum arrangement of acidic and basic sites on the catalyst surface is required for aldol condensation (9).

#### Acetone and Methanol over Different Catalysts

The reactions of acetone and methanol were carried out over alumina and modified alumina catalysts to examine the selectivity of the catalysts toward the formation of HMB. The results are presented in Table 5. The best yield of HMB was obtained when the reaction was carried out over 4.75% F<sup>-</sup>/Al<sub>2</sub>O<sub>3</sub>, 3, even though, as seen from Table 4, the best catalyst for the formation of 3,5-dimethylphenol is the sodium ion-doped catalyst. It clearly shows that alkylation reaction is favored over the strongly acidic fluorided alumina catalyst.

#### Synthetic Utility

Synthesis of 3,5-dimethylphenol is very difficult by methylation of phenol by methanol since the -OH group is *o*- and *p*-directing. 3,5-Dimethylphenol is very useful in polymer synthesis. Reactions of acetone over sodium ion-doped alumina have been optimized to form a convenient method for

preparing 3,5-dimethylphenol. At present, HMB is used as a model compound to study the diffusion properties of heterogeneous catalysts. Conditions for the preparation of hexamethylbenzene from acetone and methanol have also been optimized (see Experimental).

#### CONCLUSIONS

Although there have been many studies of the reactions of acetone over oxide catalysts, a detailed mechanistic study of the reaction of acetone and methanol to yield HMB has not been done so far. In the present study, the sequence of reactions from acetone to hexamethylbenzene has been established. The observation in the present study that reactions of a variety of carbonyl compounds with methanol give similar product mixtures is a new finding. The following are the conclusions drawn from the present study:

1. Aliphatic aldehydes and ketones react with methanol over alumina at 250–260°C to give, regardless of the identity of the starting material, similar mixtures of lower ketones and their condensation products.
2. At a higher temperature (350°C) in the absence of methanol, the major final product from acetone is 3,5-dimethylphenol which arises from the aromatization of isophorone, a condensation product of acetone. When the reaction is done in the

presence of methanol at 350°C over alumina, the major final product from acetone and from the other carbonyl compounds studied is hexamethylbenzene which arises from the methylation of 3,5-dimethylphenol.

3. Sodium ion-doped alumina is the catalyst best suited for the condensation of acetone to prepare 3,5-dimethylphenol, whereas the more acidic undoped alumina or fluorided alumina catalyst is more suited for the alkylation leading to hexamethylbenzene.

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