Tetrahedron Vol. 45, No. 3, pp. 877 to 888, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00
Pergamon Press plc

INTRAMOLECULAR REARRANGEMENT OF BENZYL BENZOATE OVER OXIDE CATALYSTS. FORMATION OF DIPHENYLMETHANE AND ANTHRONE

K. GANESAN and **C.N. PILLAI***
Department of Chemistry
Indian Institute of Technology
Madras-600 036, INDIA.

(*Received in UK* 21 *November* 1988)

ABSTRACT: Benzyl benzoate undergoes a novel intramolecular rearrangement over alumina at around 350°C to form o-benzylbenzoic acid which either decarboxylates to diphenylmethane or undergoes cyclodehydration to anthrone. Under the reaction conditions, the anthrone formed undergoes hydrogenation followed by dehydration to anthracene. By carrying out the reactions over modified aluminas, it was demonstrated that better selectivity for intramolecular rearrangement was obtained on more acidic catalysts.

Reactions of benzyl alcohol over alumina at temperatures below 400°C yield mainly dibenzyl ether by intermolecular dehydration and toluene, benzaldehyde and water by disproportionation[1-3]. At higher temperatures, benzyl alcohol yields anthracene by an ortho alkylation reaction.[4] The present paper describes the reactions of benzyl benzoate over alumina at 250-500°C. Diphenylmethane was one of the major products obtained in addition to the expected hydrolysis products, namely benzoic acid and benzyl alcohol and the products arising form them (viz., dibenzyl ether, toluene, benzaldehyde, anthracene, benzene, water and carbon dioxide). The formation of diphenylmethane corresponds to an overall decarboxylation of the ester.

Hydrolysis of esters to the corresponding acids and alcohols over alumina is known.[5] The alcohol formed undergoes secondary reactions like dehydration to give ether and olefins and disproportionation to give the corresponding carbonyl compounds, hydrocarbons and water. The reaction of benzyl benzoate leading to the alkylation of the benzene ring by the benzyl group has not been reported so far. The formation of diphenylmethane from benzyl benzoate suggests such an alkylation which forms the subject of the present study.

Table 1 gives the results of the reactions of benzyl benzoate **(1)** over alumina at different temperatures (250-500°C). The product mixture consists of diphenylmethane **(2)**, anthrone **(3)**, anthracene **(4)**, benzoic acid **(5)**, benzyl alcohol **(6)**, toluene **(7)**, benzaldehyde **(8)**, dibenzyl ether **(9)**, benzene **(10)**, diphenylethane **(12)** and other minor products (see Chart I). The gaseous effluent consists mainly of carbon dioxide **(11)** for which quantitative determination was not done. The products toluene **(7)**, benzaldehyde **(8)**, dibenzyl ether **(9)** and diphenylethane **(12)** are known to be formed from

Table I: Reactions of benzyl benzoate over alumina at 250-500°C

Reagent = 2 ml benzyl benzoate **(1)** in 18 ml benzene; Catalyst = 5 g alumina; Flow rate = 22 ml/hr.

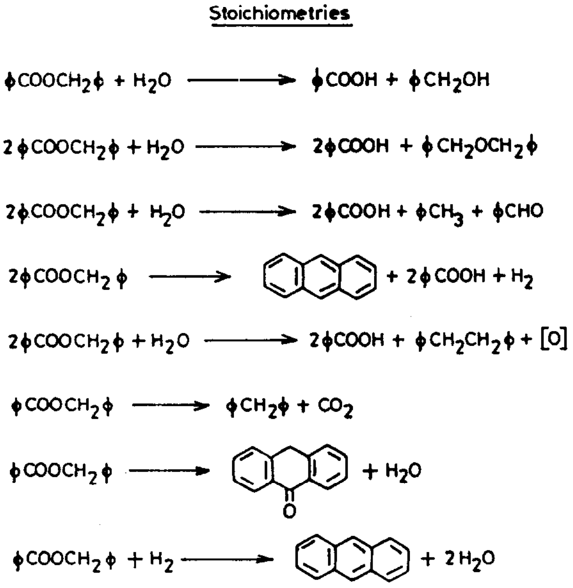
S.No	Temp. (°C)	Conversion (%)	[a]Product distribution (%)							
			Benzoic Acid	Benzyl Alcohol	Dibenzyl Ether	Benzaldehyde	Toluene	Diphenylmethane	Diphenylethane	Anthracene
1	250	35	30	6	7	3	3	3	2	-
2	300	54	41	4	12	5	5	9	3	-
3	325	67	44	3	9	6	6	15	4	6
4	345	85	47	2	8	8	7	19	3	19
5	395	96	41	-	-	11	11	31	3	28
6	450	100	40	-	-	10	9	27	2	35
7	485	100	38	-	-	10	9	24	2	37

[a] Percentage yields calculated on the basis of the stoichiometries listed in Scheme I.

benzyl alcohol over alumina[1-3]. Though benzyl alcohol can also give anthracene under these conditions over alumina[4], the amount of anthracene formed is more than that can be expected by this route alone.

It was possible to isolate anthrone **(3)** as one of the products when the reaction was carried out at low contact time. It was suspected to be formed from o-benzylbenzoic acid **(13)**, an intramolecularly rearranged product of **(1)**, by dehydrative cyclization. When the suspected intermediate **(13)** was subjected to the same experimental conditions, anthrone **(3)** was obtained in good yield. Effort to isolate the acid **(13)** was not successful.

The reactions of o-benzylbenzoic acid **(13)** over alumina gave diphenylmethane **(2)** and anthracene **(4)** in addition to anthrone **(3)** (Table II). Therefore, **13** was suspected to be the intermediate for the formation of diphenylmethane **(3)** also. Reaction of anthrone in benzene over alumina gave anthracene in fair yield. When the same reaction was carried out over alumina at 400°C using 2-propanol as the solvent, the conversion was 100% and anthracene was obtained in 95% yield (Table III). This suggests that the anthrone undergoes reduction by the alcohol to give dihydroanthranol which on dehydration gives anthracene (Scheme (V).



Scheme I

Table II Reactions of o-Benzylbenzoic acid over alumina

Reagent = 2.12 g o-Benzylbenzoic acid (**13**) in 20 ml benzene, Catalyst = 5 g alumina, Flow rate = 22 ml/hr

S.No.	Temp. (°C)	Conversion (%)	[a]Product distribution (%)		
			Anthrone	Anthracene	Diphenylmethane
1	350	100	34	27	20
2	400	100	27	35	25
3	450	100	8	42	31

[a] Mole % yields based on **13**.

Based on the above results, the mechanism in Scheme-II can be proposed for the formation of the intermediate acid (**13**) and Schemes III, IV and V for the formation of diphenylmethane (**2**), anthrone (**3**) and anthracene (**4**). An alternate route for anthrone involving an intramolecular acylation reaction to form o-benzoylbenzyl alcohol (**14**) which by dehydration gives anthrone (**3**) is shown in Scheme VI. The proposed intermediate **14** was not isolated but when **14** was subjected to the experimental conditions, anthrone

Table III Reactions of anthrone over alumina

Reagent = 0.971 g anthrone (**3**) in 20 ml solvent, Catalyst = 5 g alumina, Temp. = 400°C, Flow rate = 22 ml/hr.

S.No.	Solvent	Conversion (%)	[a]Product distribution (%)	
			Anthracene	Unaccounted
1	Benzene	80	45	[b]35
2	2-Propanol	100	95	5

[a] mole % yields based on **3**

[b] mainly coke formation

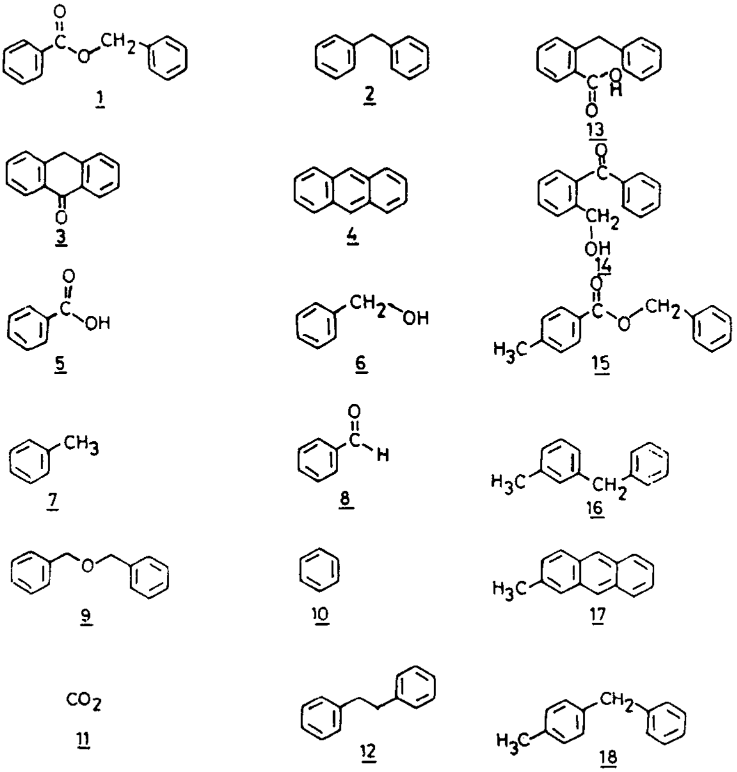
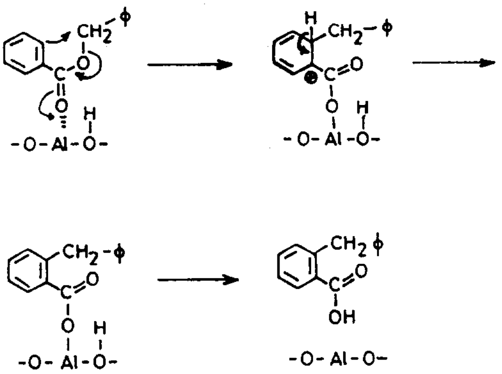


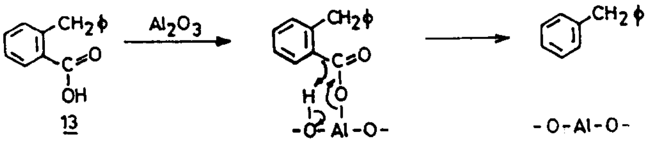
Chart I

was obtained in good yield in addition to various other minor products. A choice between the routes shown in Schemes IV and VI for the formation of anthrone could not be made on the basis of the present studies.

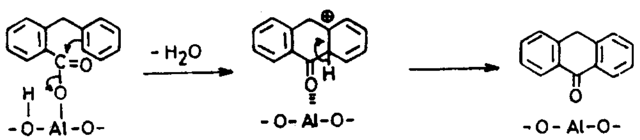


Scheme II

A direct decarboxylation reaction of benzyl benzoate to diphenylmethane is also conceivable. Its validity was checked by studying the reaction of a substituted benzyl benzoate. When benzyl 4-methylbenzoate **(15)** was passed over alumina at 400°C, 3-methyldiphenylmethane **(16)** was isolated in addition to 2-methylanthracene **(17)** (Scheme VII), in agreement with intramolecular rearrangement mechanism. 4-Methyldiphenylmethane **(18)** which could arise by the direct decarboxylation without rearrangement was not detected. In the above reaction, unsubstituted anthracene was also formed in 13% yield. The latter product clearly arises from the known bimolecular condensation of benzyl alcohol[4]. The formation of **13** is visualized as an intramolecular rearrangement without dissociation since mixtures of benzoic acid and benzyl alcohol yielded only trace amount of diphenylmethane.



Scheme III



Scheme IV

Reactions of benzyl benzoate were performed at different contact times over alumina catalyst at 350°C. The results are given in Table IV. At low contact time (high flow rate, S.No.1, Table IV), anthrone was detected. As the contact time increased, the amount of anthrone decreased showing that the anthrone formed in the reaction is converted into anthracene which is evident from the increase in anthracene formation with increase in contact time (Table IV). A separate reaction of benzoic acid and benzyl alcohol **(1:1)** over alumina at 400°C yielded small amounts of benzyl benzoate and diphenylmethane in addition to other products arising from the individual reactions of the acid and the alcohol. Decarboxylation of benzoic acid to benzene was also observed. Trace amount of benzophenone in the reaction product mixture suggests the decarboxylative dehydration of benzoic acid over alumina.

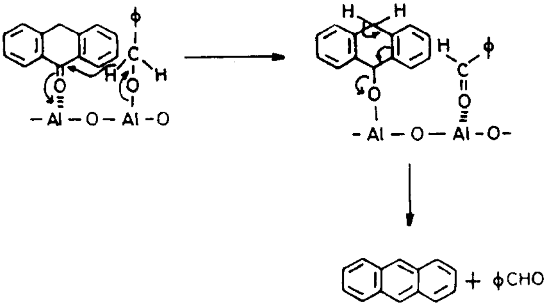
Table IV Reactions of benzyl benzoate over alumina at different flow rates

Reagents = 2 ml benzyl benzoate **(1)** in 18 ml benzene, Catalyst = 5 g alumina, Temperature = 350°C

S.No	Flow rate (ml/hr)	Conversion (%)	Benzoic Acid	Benzyl Alcohol	Dibenzyl Ether	Benzaldehyde	Toluene	Diphenylmethane	Diphenylethane	Anthracene	Anthrone
			[a]Product distribution (%)								
1	33	72	42	10	6	6	5	17	2	8	12
2	22	85	47	2	8	8	7	19	3	18	4
3	11	96	41	-	-	10	9	21	3	23	-

[a] Refer footnote to Table I.

The effect of temperature on the product distribution can be seen from Table I. Selectivities for the three major products, namely benzoic acid, diphenylmethane and anthracene are temperature dependant (Fig.1). The yield of benzoic acid **(5)** reached a maximum around 345°C and it decreased with further increase in temperature due to its decarboxylation at high temperatures. It was also observed that the amount of benzene **(10)** formed during the reactions of benzyl benzoate **(1)** over alumina increased with temperature. The formation of diphenylmethane **(2)** started even at 250°C and reached a maximum around 400°C. There was no further increase in the yield of diphenylmethane **(2)** with temperature which may be due to other competitive reactions leading to anthracene formation. The anthracene formation was noticed only at fairly high temperature (around 345°C). Anthracene **(4)** is formed via two routes. One is from benzyl alcohol **(6)**, one of the hydrolysis products, which requires high temperature[4] and the other route is from the intermediate, o-benzylbenzoic acid **(13)**.



Scheme V

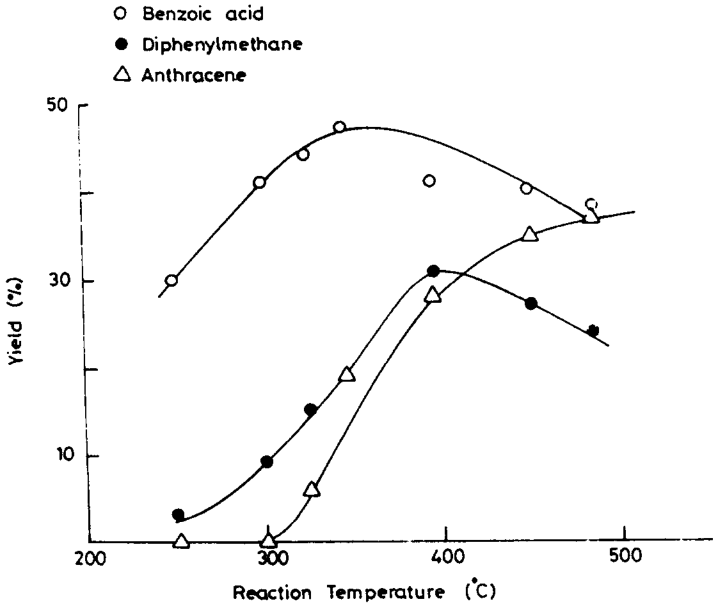


Figure 1

ROLE OF ACIDITY

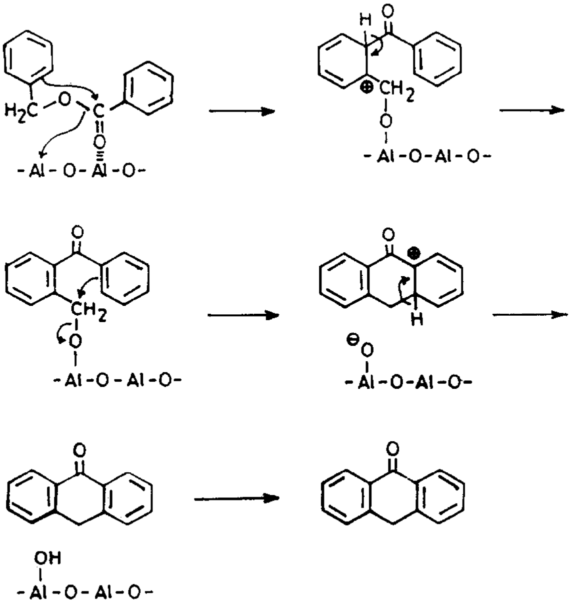
Reactions were carried out with fluorided alumina and sodium ion impregnated alumina catalysts to find the role of catalyst acidity on the selectivity for these reactions. The results are given in Table V. Over 1.5% Na^+/Al_2O_3 (the least acidic of the three catalysts studied), the selectivity was towards the hydrolysis reaction. When 4.75% F^-/Al_2O_3 (the most acidic of the three catalysts studied) was used, selectivity for both anthracene and diphenylmethane formation increased showing that the rearrangement is

Table V Reactions of benzyl benzoate over alumina and modified alumina catalysts

Reagent = 2 ml benzyl benzoate (1) in 18 ml benzene, Catalyst = 5 g, Temperature = 350°C Flow rate = 22 ml/hr.

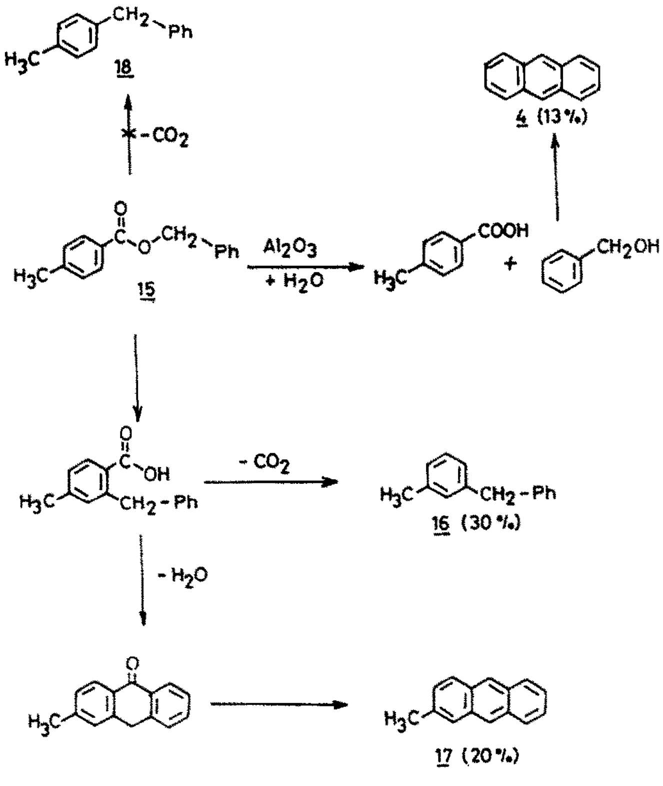
S.No	Catalyst	Conversion (%)	[a]Product distribution (%)							
			Benzoic Acid	Benzyl Alcohol	Dibenzyl Ether	Benzal-dehyde	Toluene	Diphenyl-methane	Diphenyl-ethane	Anthracene
1	1.5% Na^+/Al_2O_3	77	55	4	12	6	5	14	2	5
2	Al_2O_3	85	47	2	8	8	8	19	3	19
3	4.75% F^-/Al_2O_3	88	46	-	-	9	9	23	3	28

[a] Refer footnote to Table I.



Scheme VI

an acid catalysed reaction which is facilitated over the highly acidic catalyst. The benzyl alcohol (6) obtained from hydrolysis also leads to anthracene (4) formation selectively over fluorided alumina according to the earlier results from our laboratory[4].



Scheme VII

ALKYL ARYL ESTERS

Reactions were also carried out with methyl benzoate and ethyl benzoate over alumina at different experimental conditions. In all the cases, only the hydrolysis products and the products arising from them were observed. They failed to undergo the intramolecular alkylation reaction.

EXPERIMENTAL

Preparation of catalysts

Aluminium isopropoxide was hydrolysed by atmospheric moisture[6] and the solid formed was dried in an air oven at 100°C for 12 hrs and then calcined in a furnace at 600°C for 6 hrs. Sodium ion impregnated alumina catalyst was prepared by treating alumina with the required amount of aqueous sodium carbonate solution according to the procedure reported elsewhere.[7] Alumina was treated with known amount of aqueous HF solution to get fluorided alumina catalyst as reported in the literature.[8]

Characterization

X-ray diffraction studies were carried out to characterize the alumina (major phase η) and surface area was determined using BET method (216 ± 10 m^2/g for all the three catalysts). The sodium ion content was determined by flame photometry[9] and the fluoride ion content was estimated by a spectrophotometric method.[10] The acidity measurements were done by the titration of the solid catalyst suspended in dry benzene with n-butyl amine solution using Hammett indicators.[11] Five indicators, namely neutral red (pKa+6.8), methyl red (pKa+4.8), butter yellow (pKa+3.3), benzeneazodiphenylamine (pKa+1.5) and crystal violet (pKa+0.8) were used for the present investigation. The results are given in Table VI.

Table VI Strength and number of acid sites

S.No.	Catalyst	Acidity (m.mol, g^{-1}) at H_o					
		+ 0.8	+ 0.8 to + 1.5	+ 1.5 to + 3.3	+ 3.3 to + 4.8	+ 4.8 to + 6.8	Total
1.	1.5% Na^+/Al_2O_3	0.	0.018	0.037	0.275	0.180	0.510
2.	Al_2O_3	0.036	0.111	0.178	0.149	0.117	0.591
3.	4.75% F^-/Al_2O_3	0.053	0.398	0.198	0.105	0.065	0.819

From the results in Table VI, the total acidities of the catalysts were found to be in the order $F^-/Al_2O_3 > Al_2O_3 > Na^+/Al_2O_3$. When compared to alumina, fluoridation increased the total acidity and also created stronger acidic sites and the sodium ion impregnation brought down the total acidity and also the number of stronger acidic sites.

General experimental techniques

The reactions were carried out in a flow reactor.[12] A solution of 2 ml of benzyl benzoate in 18 ml of benzene was injected into the reactor containing 5 g of catalyst at the required flow rate using a syringe pump. The products were collected through a water cooled condenser and were analysed by gas chromatography using SE 30 (5% on chromosorb A, 60-80 mesh, acid-washed, white, 7 feet length and 1/8 inch diameter) column and Flame Ionization detector. Identifications and quantitative estimations were made by comparison of retention times and peak areas calibrated with the help of authentic samples. Structures were further confirmed by spectral (^1H NMR, IR and mass) data of pure compounds isolated from the reaction mixture by column chromatography.

In the case of benzyl 4-methylbenzoate, a solution of 2.26 g (0.01 mole) of the substrate in 20 ml of benzene was passed over 5 g of alumina at a flow rate of 22 ml/hr.

In an experiment, passing 4 ml of benzyl benzoate in 36 ml of benzene over 5g of alumina catalyst at 350°C at 33 ml/hr, the products were collected through a water cooled condenser and analysed by gas chromatography as described above. Further the mixture of products in benzene was washed with two 50 ml portions of 2N NaOH to extract anthrone, benzoic acid and o-benzylbenzoicacid. The organic layer was separated, washed with NaOH solution and water, dried over anhydrous sodium sulphate and the solvent benzene was evaporated. The gummy solid product obtained was chromatographed using silica gel and hexane. Both diphenylmethane (m.p. = 25°C) and anthracene (m.p. = 216°C) were obtained in the pure form and confirmed by spectral studies (^{1}H NMR and mass spectra) [Diphenylmethane, ^{1}H NMR, δ 7.2 (s,10H) and δ 3.8(s,2H); anthracene, ^{1}H NMR, δ 8.1(s,2H), δ7.6(m,4H) and δ7.0(m,4H)].

The alkali extract was neutralised with conc. HCl and extracted with CH_2Cl_2. It was boiled for a few minutes over a water bath. Then this solution was extracted with aqueous sodium bicarbonate solution, to remove the carboxylic acid components. The organic layer was separated, washed with aqueous $NaHCO_3$ solution and water and dried over anhydrous Na_2SO_4. Evaporation of CH_2Cl_2 gave anthrone as light yellow solid. It was recrystallised from methanol (m.p. = 154-155°C). The structure was confirmed by ^{1}H NMR [δ 8.2(m,2H), δ 7.2(m,6H) and δ 4.2(s,2H)], IR and mass spectra.

Benzyl 4-methylbenzoate was prepared by the reaction of 4-methylbenzoyl chloride and sodium benzyloxide. Other esters were purchased commercially (LR Grade) and used after purification.

Acknowledgement

KG thanks Council of Scientific and Industrial Research, New Delhi for the award of Senior Research Fellowship. The authors thank RSIC, IIT, Madras for the spectra.

References

1. Jayamani, M.; Pillai, C.N. J. Catal. **1983**, 82, 485-488.
2. Jayamani, M.; Murugesan, N.; Pillai, C.N. J. Catal. **1984**, 85, 527-529.
3. Ananthan, S.; Ganesan, K.; Pillai, C.N. Indian J. Chemistry **1987**, 26A, 512-513.
4. Ganesan, K.; Pillai, C.N. J. Catal. (Communicated).
5. Johns, W.F.; Jerina, D.M. J. Org. Chem. **1983**, 28, 2922-2924.

6. Jayamani, M.; Viswanathan, B.; Pillai, C.N. J. Catal. **1984**, 89, 560-563.

7. Ramana, D.V.; Pillai, C.N. Canadian J. Chemistry **1969**, 47, 3705-3707.

8. Scorkart, P.O.; Selim, S.A.; Daman, J.P.; Rouxhet, P.G. J. Colloid Interface Sci. **1979**, 70, 209-222.

9. Vogel, A.I. A Textbook of Quantitative Inorganic Analysis; 3rd Ed. Longman Green Co.: London, **1969**

10. Boltz, D.F.; Howel, J.A. Calorimetric Determination of Non-metals; 2nd Ed. John Wiley and Sons: New York, **1978**.

11. Benesi, H.A. J. Am. Chem. Soc. **1956**, 78, 5490-5494.

12. Jayamani, M.; Pillai, C.N. Synth. Commun. **1985**, 15, 535-542.