Tetrahedron. Vol 27, pp. 581–591. Pergamon Press 1971. Printed in Great Britain

BENZYLATION OF BENZENE AND ALKYLBENZENES AT LOW TEMPERATURES

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(*Received in the UK* 3 *September* 1970; *Accepted for publication* 28 *September* 1970)

Abstract—Reactivity of benzene and certain alkylbenzenes (toluene, *p*-xylene, mesitylene) during benzylation with benzylchloride and some derivatives (α-chloroethylbenzene, benzhydrylchloride, chloromethylmesitylene) has been determined under non-isomerizing conditions, in the temperature range $-10°$ and $-120°$, in ethyl chloride solution with $AlCl_3$ as a catalyst.

Steric effects are found to play a major role in the reactivity when benzylchloride derivatives are used as benzylating agents.

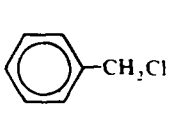
Isomer distribution in the benzylation of toluene has been investigated as a function of the temperature and of the benzylating agent.

Experimental data are related to the results obtained in the low temperature polymerisation of benzylchloride and α-chloroethylbenzene.

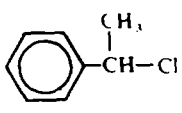
INTRODUCTION

INVESTIGATION of the mechanistic aspects of Friedel and Crafts reactions[1–3] has revealed that alkylation is a temperature-sensitive reaction.[4]

In order to further explore this concept and the isomer distribution of products the following arylating agents were used:



I



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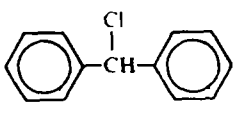

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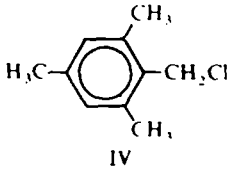


IV

with $AlCl_3$ as a catalyst and C_2H_5Cl as solvent.

RESULTS AND DISCUSSION

The benzylation reactions at low temperature in homogeneous ethylchloride solution develop a yellow or red colour and are complete in a few minutes. The yields are quantitative except for benzhydrylchloride and chloromethylmesitylene below $-70°$.

Under the experimental conditions used, all reactions went to completion without formation of by-products. A constant excess of aromatic hydrocarbon was used (mole ratio $ArH/ArCH_2Cl$ = 10–20) to avoid polysubstitution.

Alkylation of the hydrocarbons by the solvent was tested by gas-chromatography and spectroscopic analysis and found negligible in all cases, except for mesitylene below $-70°$.

Relative rates of benzylation were at first determined at T = -50. In Table 1

TABLE 1. RELATIVE RATES FOR THE BENZYLATION AT T = −50°. SYSTEM BENZYLCHLORIDE–ArH–C_2H_5Cl–$AlCl_3$

No.	Benzene	Toluene	*p*-Xylene	Mesitylene
1	1	4·20		
2	1	3·94		
3	1	3·90		
4	1	4·40		
5		(4·11)[a]	8·70	
6		(4·11)	9·10	
7		(4·11)		24·85
8		(4·11)		24·30
9		(4·11)		24·75
10			(8·90)[a]	25·00
11			(8·90)	23·85
12			(8·90)	24·75
Average deviation	1	4·11 ± 0·19	8·90 ± 0·20	24·58 ± 0·34
%	—	4·60	2·25	1·38

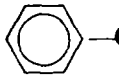
[a] Values in parentheses are referred to the relative reactivities used for the reference compounds.

are reported data concerning benzylchloride. The method of competitive relative rates was employed as described by Francis[5] using the Ingold[6] formula:

$$\frac{K_1}{K_2} = \frac{\log.\,[(C_1^0 - x_1/C_1^0)]}{\log.\,[(C_2^0 - x_2/C_2^0)]} \qquad (1)$$

where C_1^0 and C_2^0 are the initial concentrations of the hydrocarbons and x_1, x_2 are final concentrations of the products. This method can be safely applied in our case.

In changing the concentration ratio benzene–toluene from 1·7 to 3·6 the relative rate was found to remain almost unchanged if a first-order dependence on the aromatic substrate is accepted.[7] Other hydrocarbons examined show a similar behaviour.

Relative rate values in Table 1 reveal a low substrate selectivity; this points out that the electrophilic complex  is highly reactive and attacks the molecule in the fundamental state.

Benzylation rates in ethyl chloride are more substrate dependent with respect to those observed in nitromethane.[3]

The latter feature was also found in the Friedel-Crafts acetylation of these hydrocarbons,[8–10] and is related to the basicity of the solvent.

The relative reactivity of the systems benzene–toluene and toluene-*p*-xylene as functions of temperature remains almost unchanged as may be seen from data reported in Table 2.

For the system toluene–mesitylene (Table 3) it was not possible to determine the reactivity ratio below −70° because, contrary to that found for the other systems,

TABLE 2. RELATIVE RATES FOR THE BENZYLATION AS TEMPERATURE FUNCTION. SYSTEM BENZYLCHLORIDE–ArH–C_2H_5Cl–$AlCl_3$

No.	T°C	Benzene	Toluene	*p*-Xylene
1	0	1	3·89	
2	−21	1	4·02	8·77
3	−31	1	3·88	
4	−41	1	4·08	
5	−50	1	4·10	8·90
6	−80	1	3·72	8·63
7	−81	1	3·81	
8	−90	1	3·72	8·79
9	−98	1	3·77	
10	−99	1	4·13	
11	−110	1	4·08	8·76
12	−120	1	4·02	
Average deviation		1	3·94 ± 0·13	8·77 ± 0·07
%		—	3·30	0·84

TABLE 3. CONVERSION AS A FUNCTION OF TEMPERATURE AND CATALYST AMOUNT. SYSTEM TOLUENE–MESITYLENE–BENZYLCHLORIDE–C_2H_5Cl–$AlCl_3$

No.	T °C	$AlCl_3$ (mole)	Conversion* %
1	−50	0·0015	100
2	−50	0·0030	100
3	−50	0·0060	100
4	−55	0·0018	100
5	−70	0·0037	60
6	−80	0·0045	35
7	−80	0·0060	43
8	−91	0·0045	23
9	−100	0·0026	9
10	−100	0·0030	12
11	−100	0·0045	22
12	−100	0·0060	27
13	−110	0·0045	18
14	−110	0·0082	36
15	−121	0·0027	8
16	−121	0·0030	11
17	−130	0·0027	7·7
18	−130	0·0030	10
19	−130	0·0045	20
20	−130	0·0060	25

* Determined by VPC

the yield was not complete below that temperature being a function of the catalyst concentration. A certain amount of ethylmesitylene was also found.

The formation of a stable σ complex between $AlCl_3$–HCl-mesitylene and ethylchloride–$AlCl_3$–mesitylene below −70° is thought to occur in this case. In fact, σ complexes of mesitylene–HBF_4 and mesitylene–HBF_4–C_2H_5Cl have been found very stable.[11] The reaction goes to completion with the less basic hydrocarbons, benzene, toluene and *p*-xylene, because their basicity constants are extremely low compared to mesitylene.[11]

These facts may also explain why the polymerization of benzylchloride at −135° shows a yield that is a function of the catalyst amount.[12a,b] In fact, the disubstituted and trisubstituted aromatic rings, formed during the polymerization, trap the catalyst and do not allow the reaction to proceed further.

In Table 4 is reported the relative reactivity of α-chloroethylbenzene, benzhydrylchloride and chloromethylmesitylene with respect to benzylchloride as arylating agent.

Substituted benzylchlorides are more selective with respect to the parent compound. In fact, in the system benzene–toluene, the latter is benzylated almost exclusively as it is more activated toward electrophilic substitution. But as methyl substitution increases, steric effects play a major role and the arylating agents react preferentially with the less substituted hydrocarbon. In the systems toluene-*p*-xylene and toluene–mesitylene the benzylated hydrocarbon is almost exclusively toluene, and this is little influenced by the temperature.

The competition between steric effect and electrophilic activation is evidenced by the reactions of α-chloroethylbenzene with mixtures of toluene-*o*-xylene and toluene-*m*-xylene, respectively (Table 4). In the first case *o*-xylene is converted to an higher extent with respect to toluene because it is more activated toward substitution and the steric situation at the reaction center is comparable to that of toluene. In the second case, *m*-xylene is converted to a lesser extent with respect to toluene because the more activated positions are sterically hindered.

In contrast with benzylchloride and α-chloroethylbenzene which are converted completely even at −120°, benzhydrylchloride and chloromethylmesitylene undergo partial conversion below −70°.

This may suggest that a stable and non-reactive carbonium ion is formed below −70°, in the case of benzhydrylchloride. The benzhydryl carbonium ion is reported to be stable[13] and some of its salts have been isolated.[14]

In the case of chloromethylmesitylene the yield below −60° is a function of temperature and amount of catalyst (Table 5). This suggests the formation of a stable σ complex analogous to that assumed when mesitylene was used as hydrocarbon in the reaction with benzylchloride.

In Table 6 are reported the isomer distribution of products formed from toluene and various benzylating agents, under non-isomerizing conditions (kinetically controlled) as a function of the temperature.

There are no drastic changes in these distributions over the temperature range investigated, although *para* substitution requires lower temperatures.

A comparison of the isomer distribution found using benzylchloride with that obtained with its derivatives shows that the steric hindrance presented by the various benzylating agents controls the attack on the *ortho* positions of toluene, so that

TABLE 4. REACTIVITY OF BENZYLCHLORIDE AND ITS DERIVATIVES IN THE BENZYLATION OF AROMATICS IN C_2H_5Cl AND $AlCl_3$ AS A CATALYST. C_2H_5Cl = 200 ml; $AlCl_3$ = 0·0015 mole

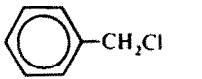
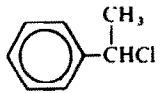
Benzylating Agent (mole)	ArH (mole)	T °C	Conversion[a] %	% of product formed[a] with					
				Benzene	Toluene	*p*-Xylene	Mesitylene	*o*-Xylene	*m*-Xylene
 0·0170	Benzene 0·22500 Toluene 0·14098	−50	100	29·0	71·0				
	Toluene 0·14098 *p*-Xylene 0·16221	−50	100		29·3	70·7			
	Toluene 0·23497 Mesitylene 0·07204	−50	100		36·6		63·4		
	p-Xylene 0·16221 Mesitylene 0·07204	−50	100			45·5	54·5		
 0·0110	Benzene 0·22500 Toluene 0·14098	−50	100	5·5	94·5				
	Toluene 0·14098 *p*-Xylene 0·16221	−50	95		87·0	13·0			
	p-Xylene 0·16221 Mesitylene 0·07204	−50	98			93·0	7·0		
	Toluene 0·23497 Mesitylene 0·07204	−50	100		⩾99·0		⩽1·0		
	Toluene 0·14098 *o*-Xylene 0·12400	−50	98		42·0			58·0	
	Toluene 0·14098 *m*-Xylene 0·12170	−50	100		97·0				3·0
	Benzene 0·22500 Toluene 0·14098	−12	100	5·3	94·7				
	Benzene 0·22500 Toluene 0·14098	−30	100	5·3	94·7				
	Benzene 0·22500 Toluene 0·14098	−95	100	5·5	94·5				
	Benzene 0·22500 Toluene 0·14098	−125	98	3·8	96·2				
	Toluene 0·23497	−10	100		98·2		1·8		

TABLE 4—*continued*

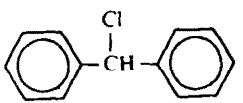
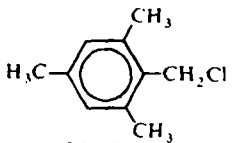
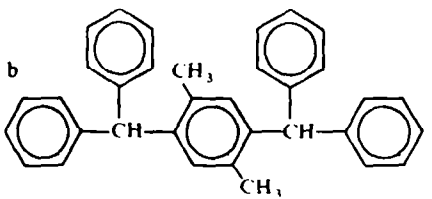
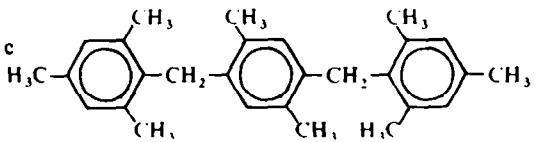
Benzylating Agent (mole)	ArH (mole)	T °C	Conversion[a] %	% of product formed[a] with Benzene	Toluene	*p*-Xylene	Mesitylene	*o*-Xylene	*m*-Xylene
	Mesitylene 0·07204 Toluene 0·23497	−30	100		≥99·0		≤1·0		
	Mesitylene 0·07204 Toluene 0·14098 *p*-Xylene 0·12170	−10	98		82·0	18·0			
 0·0010	Benzene 0·22500 Toluene 0·14098	−20	99	7·0	93·0				
	Benzene 0·22500 Toluene 0·14098	−41	99	6·0	94·0				
	Toluene 0·14098 *p*-Xylene 0·12170	−42	99		94·0	--[b]			
	Toluene 0·14098 Mesitylene 0·10800	−10	99		97·5		2·5		
	Toluene 0·14098 Mesitylene 0·10800	−50	99		97·5		2·5		
	p-Xylene 0·12170 Mesitylene 0·07204	−42	99			56[b]	2·5		
	p-Xylene 0·12170 Mesitylene 0·07204	−60	99			50[b]	2·5		
	Toluene 0·14098 Mesitylene 0·10800	−70	28		91·5		8·5		

TABLE 4—*continued*

Benzylating Agent (mole)	ArH (mole)	T °C	Conversion[a] %	% of product formed[a] with Benzene	Toluene	*p*-Xylene	Mesitylene	*o*-Xylene	*m*-Xylene
 0·01170	Benzene 0·22500 Toluene 0·14098	−50	100	5·0	95·0				
	Toluene 0·18798 Mesitylene 0·14408	−50	100		75·0		25·0		
	p-Xylene 0·12170 Mesitylene 0·07204	−50	100			5·7[c]	2·0		
	Toluene 0·18798 *p*-Xylene 0·12170	−50	100		77·0	—[c]			

[a] Determined by VPC.

b  is also formed.

c  is also formed.

substituted benzylchlorides yield almost exclusively the *para* derivative (Table 6).

The isomer distribution found for these systems provides a good explanation also for the structure and properties of the polymers prepared from the corresponding monomers at low temperature.[15a,b]

TABLE 5. CONVERSION AGAINST TEMPERATURE AND CATALYST AMOUNT IN THE BENZYLATION OF TOLUENE WITH CHLOROMETHYLMESITYLENE AND $AlCl_3$ IN C_2H_5Cl

No.	T °C	$AlCl_3$ (mole)	Conversion* %
1	−10	0·0015	100
2	−30	0·0015	100
3	−30	0·0030	100
4	−50	0·0015	100
5	−70	0·0037	75
6	−80	0·0037	50
7	−90	0·0022	21
8	−90	0·0037	35
9	−110	0·0022	14
10	−110	0·0037	25
11	−130	0·0022	12
12	−130	0·0037	21

* Determined by VPC

EXPERIMENTAL—

Materials. Benzene, alkylbenzenes, benzhydrylchloride and benzylchloride were commercial products of highest available purity; they were dried and further purified by distillation. α-Chloroethylbenzene and chloromethylmesitylene were prepared according to the literature.[16,17] Ethylchloride (≥99·7%) was purified by passage over BaO. $AlCl_3$ was sublimed before use and ethylchloride solns were obtained and titrated by the method of Kennedy and Thomas.[18]

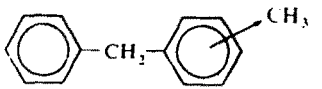
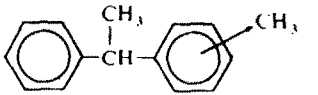
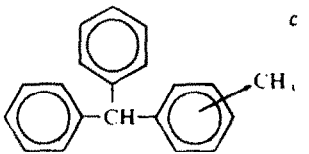
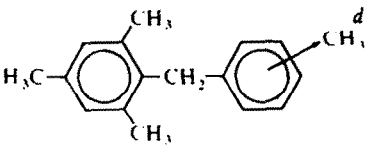
Tolylphenylmethane isomers (*o,m,p*) were synthesized in good yield (≥85%) starting from the corresponding α-chloroxylenes and benzene according to Friedel-Crafts reaction in nitroethane as solvent. The purity (≥99·6%) was checked by gas-chromatography and IR spectra. The physical constants were coincident with those reported[19] for the same compounds prepared by another method.

Polymethyldiphenylmethanes were obtained by Friedel-Crafts reactions in good yield. The purity was checked by gas-chromatography (≥99·6–99·8%). The physical constants agreed with those reported.

General procedure for competitive benzylation. All reactions were carried out with stirring at constant temp, under dry N_2. The $AlCl_3$ in ethylchloride soln was added dropwise, cooled at the same reaction temp. A deep red colour immediately developed which disappeared when cold acetone was introduced in the flask to terminate the reaction, generally after 15 min. The mixture was poured into 5% HCl–water soln, extracted with $CHCl_3$, dried (Na_2SO_4) and analysed by VPC. The extractions were quantitative and neither losses or formation of by-products were observed.

In order to establish if the experimental conditions used were isomerizing,[3] pure *ortho*-methyldiphenylmethane and mesitylphenylmethane were added to a twentyfold excess of benzene which was then benzylated under our standard conditions. No isomerization or disproportionation products were observed by VPC. Reasonable amounts of isomerization and disproportionation products were detected when the reaction was carried out without solvent, analogous to results obtained in similar systems.[10]

TABLE 6. ISOMER DISTRIBUTION AT DIFFERENT TEMPERATURES

No	T	*a*		*b*		*c*		*d*		
										
	°C	*para*[a] %	*ortho + meat*[a] %	*para*[a] %	*ortho + meta*[a] %	*para*[a] %	*ortho + meta*[a] %	*para*[a] %	*meta*[a] %	*ortho*[a] %
1	−1	52·22	47·78							
2	−10	52·87	47·13	90·0	10·0	90·0	10·0	86·33	1·0	12·67
3	−20	53·33	46·66							
4	−30	55·60	44·60	93·0	7·0			95·5	0·5	4·3
5	−40	56·47	43·53			90·0	10·0			
6	−50	56·80	43·20	95·0	5·0	92·8	7·2	99·0		1·0
7	−70	59·00	41·00			95·0	5·0	99·0		⩽1·0
8	−90	59·83	40·17	98·0	2·0			99·0		⩽1·0
9	−110	63·70	36·30	99·5		⩾99·5		99·0		⩽1·0
10	−130	66·40	33·60	⩾99·5		⩾99·5		⩾99·5		

[a] System Benzylchloride–Toluene–C_2H_5Cl–$AlCl_3$.
[b] System α-Chloroethylbenzene–Toluene–C_2H_5Cl–$AlCl_3$.
[c] System Benzhydrylchloride–Toluene–C_2H_5Cl–$AlCl_3$.
[d] System Chloromethylmesitylene–Toluene–C_2H_5Cl–$AlCl_3$.
[e] Determined by V.P.C.

The very low percentage of *meta* isomer formed in the benzylation of toluene with chloromethylmesitylene is a further proof that the conditions employed one non-isomerizing.

Analytical procedure. The VPC analyses were carried out using a C. Erba Fractovap C, with a 80 cm column packed with 25% of methylsilicone polymer SE 30 on Celite. The column temp was 210° for all determinations; He flowing at 61./h was used as carrier gas. Peaks were all symmetric providing a good quantitative determination. From the areas of individual peaks mole % figures were calculated for each product using a calibration curve obtained injecting authentic samples and recontrolled every time the determination was done.

The accuracy of gas-chromatographic analyses was checked with mixtures of known composition and was found to be within the limit of ±5% relative error. In the case of small amounts of *ortho* and *meta* isomers the relative error may be higher. However, even in these cases, the accuracy was found good and generally it was still possible to determine an amount of 0·5% of *ortho* and *meta* in 99·5% of *para* isomer, in the concentration used.

The tolylphenylmethane and 1-tolyl, 1 phenylethane isomers were determined by VPC using a 3·70 meters column (4 × 2) filled with 10% of Apiezon L grease on Cromosorb W, at T = 156° and He = 1·5 l./h. This column separated the *para* from the total of *ortho* and *meta* isomers. The same column was used at T = 186° and He = 1·5 l./h for separating the mesityl-tolyl-methane isomers and mesitylphenylmethane from 2,3,5-trimethyldiphenylmethane.

For the separation of diphenyl-tolyl-methane isomers a column (6 × 4) of 2·20 mt packed with methylsilicone polymer SE 30 on Celite was used. The column temp was 200 and He = 6 l./h. IR spectra were recorded on a Perkin-Elmer 237 Infrared spectrometer. Molecular weights were obtained by VPO using a Mechrolab 302.

Syntheses

1-*Phenyl*, 1-m-*tolylethane*. To a stirred suspension of benzene (1·7 mole) with H_2SO_4 (5 ml, d = 1·84) at T = 40 was added dropwise *m*-methylstyrene (0·083 mole). After 15 min the mixture was poured into water, neutralized with Na_2CO_3, the product extracted with $CHCl_3$ and distilled under vacuum; Kp_2 = 110°; yield 50%; n_D^{20} = 1·5665; ν_{meta} 770 cm^{-1}. (Found: C, 91·65; H, 8·31. $C_{15}H_{16}$ requires: C, 91·78; H, 8·22% molecular weight (dichloroethane 50°: Found 199; Calcd. for $C_{15}H_{16}$ 196·3.

1-*Phenyl*, 1-o-*tolylethane*. The same procedure reported for the *meta* isomer was used, starting, from *o*-methylstyrene; Kp_2 = 110°; yield 55%; n_D^{20} = 1·5715; ν_{ortho} = 760 cm^{-1}. (Found: C, 91·85; H, 8·15. $C_{15}H_{16}$ requires: C, 91·78; H, 8·22% molecular weight (dichloroethane 50°C): Found 194; Calcd. for $C_{15}H_{16}$ 196·3.

1-*Phenyl*, 1-p-*tolylethane*. This was synthesised in one of two ways: starting from benzene and *p*-methylstyrene according to the procedure reported (yield 40%); or, in good yield (85%) by reacting α-chloroethylbenzene (0·056 mole) with toluene (0·70 mole) in C_2H_5Cl (200 ml) at T = −125° with $AlCl_3$ as a catalyst (0·0015 mole); at this temp only the *para* derivative was formed (Table 6); Kp_2 = 115°; n_D^{20} = 1·5640; ν_{para} 820 cm^{-1}. (Found: C, 91·70; H, 8·20. $C_{15}H_{16}$ requires: C, 91·78; H, 8·22%; molecular weight (dichloroethane 50°): Found 198; Calcd. for $C_{15}H_{16}$ 196·3.

2,5-*Bis*(*diphenylcarbinyl*)-1,4-*dimethylbenzene*. To a stirred soln of benzhydrylchloride (0·11 mole) and *p*-xylene (0·80 mole) in nitroethane (100 ml) was added at T = 0° $AlCl_3$ (0·01 mole). During the reaction a white solid precipitated. After 1 hr the mixture was poured into 5% HCl–water and extracted by $CHCl_3$; the white product insoluble in $CHCl_3$, was removed by filtration and from the chloroform soln 1-diphenycarbinyl-2,5-dimethylbenzene was obtained and crystallized from EtOH, m.p. 90–91; yield 20%; reported m.p. 90·5–91·2.[20]

The crude white product insoluble in $CHCl_3$, (about 80%) was crystallized from xylene, m.p. 283–284°. (Found: C, 92·90; H, 6·94. $C_{34}H_{30}$ requires: C, 93·10; H, 6·90%, molecular weight (*o*-dichlorobenzene 130°): Found 432; Calcd. for $C_{34}H_{30}$ 438·5.

Mesityl-o-tolylmethane. To a stirred soln of mesitylene (0·58 mole) and *o*-methylbenzylchloride (0·078 mole) in nitroethane (100 ml) at T = 0° was added $SnCl_4$ (0·01 mole). After 30 min the mixture was poured into 5% HCl–water, extracted with $CHCl_3$ and the crude product distilled under vacuum, Kp_2 = 140°; yield 85%. The white crystalline product (from EtOH) has m.p. 55°. (Found: C, 90·88; H, 8·90. $C_{17}H_{20}$ requires: C, 91·01; H, 8·98%; molecular weight (dichloroethane 50°): Found 227; Calcd. for $C_{17}H_{20}$ 224·3.

Mesityl-p-xylylmethane. Reaction of chloromethylmesitylene with a large excess of *p*-xylene yielded only 2,5-bis(2,4,6-trimethylbenzyl)-1,4-dimethylbenzene identical (m.p., molecular weight and IR) with the product obtained by reaction 1,4-bis(chloromethyl)-2,5-dimethylbenzene with mesitylene.[21]

As a consequence the product required was prepared from 2,5-dimethylbenzylchloride (0·078 mole) and mesitylene (0·66 mole) in $C_2H_3NO_2$ (100 ml) at T = 0° with $SnCl_4$ as a catalyst (0·015 mole). The crude product, was distilled (Kp_2 = 145°) and crystallized (EtOH) m.p. 102–103°; yield 90%. (Found: C, 90·50; H, 9·27. $C_{18}H_{22}$ requires: C, 90·69; H, 9·30%); molecular weight (dichloroethane 50°): Found 240; Calcd. for $C_{18}H_{22}$ 238·36.

Acknowledgement—The author is indebted to Dr. Giorgio Montaudo for helpful discussion on this paper and for the revision of the manuscript.

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