REACTIONS OF *NN*-DIPHENYLCARBAMOYL CHLORIDE

III.* AS AN ACYLATING AGENT IN THE FRIEDEL–CRAFTS REACTION

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[*Manuscript received September* 5, 1966]

Summary

The reaction of *NN*-diphenylcarbamoyl chloride with aromatic compounds under Friedel–Crafts conditions to give aromatic acid *NN*-diphenylamides has been studied. Chlorinated hydrocarbon solvents, especially ethylene dichloride, were the most useful reaction media. Acylation of naphthalene occurred predominantly at the 1-position. Mesitylene, durene, and pentamethylbenzene were readily acylated but not fluoro- or chloro-benzene. With the exception of the sterically hindered amides obtained from mesitylene, durene, and pentamethylbenzene, the resultant diphenylamides were readily hydrolysed by alkali to the parent aromatic acids.

INTRODUCTION

It has long been known[1,2] that *NN*-diphenylcarbamoyl‡ chloride can act as an acylating agent in the Friedel–Crafts reaction (as in equation (1)).

$$ArH + (C_6H_5)_2NCOCl \xrightarrow{\text{anhyd. } AlCl_3} ArCON(C_6H_5)_2 \qquad (1)$$

In view of the stability and commercial availability of this reagent, it seemed worthwhile to study the above reaction in more detail since it affords an excellent method of introducing a disubstituted amide residue (and eventually the carboxylic acid group by subsequent hydrolysis) into an aromatic nucleus.§ It was of particular interest to investigate the role of the solvent in this acylation since, except for the use of ethylene dichloride in the acylation of ferrocene,[4] the aromatic compound being acylated is normally used (in excess) as solvent.[1,2]

* Part II, *Aust. J. Chem.*, 1966, **19**, 165.

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‡ The prefix *NN*- will be omitted.

§ Except for the useful study of Weygand and Mitgau[3] on the corresponding reaction of the less stable *N*-methylphenylcarbamoyl chloride (the aromatic substrate being used, in excess, as solvent), no detailed investigation of the Friedel–Crafts reaction involving any other carbamoyl chloride has been reported.

[1] Lellmann, E., and Bonhoffer, O., *Ber. dt. chem. Ges.*, 1887, **20**, 2118.

[2] Morgan, G. T., and Coulson, E. A., *J. chem. Soc.*, 1931, 2326.

[3] Weygand, F., and Mitgau, R., *Ber. dt. chem. Ges.*, 1955, **88**, 301.

[4] Little, W. F., and Eisenthal, R., *J. Am. chem. Soc.*, 1960, **82**, 1577.

Results and Discussion

Diphenylcarbamoyl chloride (1 equiv.) reacted readily with a number of aromatic compounds (1 equiv. in each case) in ethylene dichloride with anhydrous aluminium chloride (1·1 equiv.) as catalyst. Except in the case of naphthalene (see below), a single diphenylamide ($ArCON(C_6H_5)_2$) was isolated, although in some cases thin-layer chromatography revealed other minor products. In each case acylation occurred at the same site (see Table 1) as that observed for Friedel–Crafts

Table 1

Friedel–Crafts acylations with *NN*-diphenylcarbamoyl chloride

Parent Compound	Yield (%) of Diphenylamide[a]	Parent Acid
m-Xylene	50[b]	2,4-dimethylbenzoic
p-Xylene	41[c,d]	2,5-dimethylbenzoic
Mesitylene	66[c]	mesitoic
Durene	63[c]	2,3,5,6-tetramethylbenzoic
Pentamethylbenzene	68[c]	pentamethylbenzoic
Anisole	61[b]	*p*-methoxybenzoic
Veratrole	65[b]	3,4-dimethoxybenzoic
m-Dimethoxybenzene	55[b]	2,4-dimethoxybenzoic
p-Dimethoxybenzene	54[b]	2,5-dimethoxybenzoic
Chlorobenzene	0	—
Fluorobenzene	0	—
Naphthalene	61[c]	1- and 2-naphthoic

[a] Acylation of 0·01 mole in ethylene dichloride with anhydrous aluminium chloride (0·011 mole) as catalyst (see acylation of veratrole).

[b] Isolation by crystallization of crude reaction product.

[c] Isolation by silica gel chromatography.

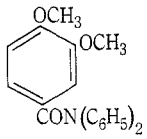
[d] Previous workers (see ref. 1) reported that *p*-xylene could not be acylated.

acetylation.[5] In addition, no unusual susceptibility to steric effects was uncovered, since *p*-xylene, mesitylene, durene, and pentamethylbenzene were readily acylated. The corresponding reaction with fluorobenzene and chlorobenzene failed, although in the latter case a small amount of an unknown chlorine-containing compound* was obtained which was different from the expected product, *p*-chlorobenzoic acid diphenylamide.

A study was made of the effect of solvent on the reaction with veratrole (see Table 2). Veratrole was chosen because the product, 3,4-dimethoxybenzoic acid

* In addition to a maximum at 1660 cm^{-1} ($ArCON(C_6H_5)_2$), the infrared spectrum of this product revealed a maximum at 1740 cm^{-1} (Ar_2NCOCl?). No information about its structure could be obtained from its p.m.r. spectrum (in carbon tetrachloride), which revealed a complex multiplet centred at δ 7·2 p.p.m.

[5] Gore, P. H., Ch. 31, "Friedel–Crafts and Related Reactions". Vol. III, Part 1. (Ed. G. A. Olah.) (Interscience: New York 1964.)



(I)

diphenylamide (I), could be separated by crystallization from diphenylamine (invariably formed (see below)) and unchanged diphenylcarbamoyl chloride. However, in order to ascertain the maximum yield in each experiment, the filtrate from this crystallization was chromatographed on silica gel and yielded a fraction consisting of 3,4-dimethoxybenzoic acid diphenylamide and two minor products, which were not investigated further.*

Nitrobenzene and nitromethane were unsatisfactory solvents for the acylation reaction with veratrole (but not necessarily with other aromatic compounds). The highest yield of pure product was obtained in ethylene dichloride with 1·5 equiv. of aluminium chloride (the greater excess of aluminium chloride may be responsible

TABLE 2

FRIEDEL–CRAFTS REACTION OF VERATROLE WITH DIPHENYLCARBAMOYL CHLORIDE

Expt.[a]	Solvent	Temp.	Yield (%)		M.P. of Product A[c]
			A[b]	B[b]	
1	Methylene chloride	41°	50	5	162–164°
2	Nitrobenzene	20	17	8	161–163
3[d]	Nitrobenzene	82[g]	—	—	—
4[d]	Nitromethane	82	—	—	—
5	*sym*-Tetrachloroethane	82	59	10	159–162
6	Ethylene dichloride	82	65	5	161–164
7[e]	Ethylene dichloride	82	74	15	162–164
8[f]	Ethylene dichloride	82	55	24	157–160

[a] Veratrole (0·010 mole), diphenylcarbamoyl chloride (0·010 mole), and anhydrous aluminium chloride (0·011 mole).

[b] A refers to product obtained by crystallization of the crude neutralpro duct; B refers to additional product (impure diphenylamide A) obtained by silica gel chromatography.

[c] Pure 3,4-dimethoxybenzoic acid diphenylamide has m.p. 163–164°.

[d] No crystalline product obtained from the dark oily neutral product.

[e] Anhydrous aluminium chloride (0·015 mole) used.

[f] Anhydrous aluminium chloride (0·020 mole) used.

[g] Actual internal reaction temperature.

for eliminating traces of water). However, 2 equiv. of aluminium chloride gave a less pure product in lower yield. Methylene dichloride and *sym*-tetrachloroethane were also useful solvents, the lower yield in the former probably being due to the lower temperature of the reaction.

The reaction of diphenylcarbamoyl chloride with naphthalene in ethylene dichloride gave a mixture of isomers (in 61% yield) which could not be separated by column chromatography on alumina or silica gel. The infrared spectra of the isomeric diphenylamides were not sufficiently different to permit quantitative

* Demethylated products are frequent by-products in the Friedel–Crafts acylation of aromatic ethers.[5]

analysis but an estimate of their relative proportions in the above mixture was obtained by hydrolysis with alkali in aqueous dimethyl sulphoxide to a mixture (obtained in 97% yield) of 1- and 2-naphthoic acids. Infrared analysis of the latter mixture indicated that the original diphenylamide mixture consisted of 77% 1-naphthoic and 23% 2-naphthoic acid diphenylamides. Reaction with alkali in aqueous ethanol caused hydrolysis of 2-naphthoic acid diphenylamide but not of the 1-isomer, presumably for steric reasons, and when this hydrolytic treatment was applied to the original mixture of isomers, 1-naphthoic acid diphenylamide and 2-naphthoic acid (from the alkali-soluble portion) were isolated (see Experimental, p. 581).

In general, hydrolysis of the diphenylamides to the parent carboxylic acids occurred readily with sodium hydroxide either in 85% aqueous ethanol or, where some difficulty was expected because of steric factors, in 85% aqueous dimethyl

TABLE 3

HYDROLYSIS OF AROMATIC ACID DIPHENYLAMIDES

Parent Acid	Yield (%)	
	Acid	Diphenylamine
p-Methoxybenzoic	88	97
2,4-Dimethoxybenzoic	90[c]	85
2,5-Dimethoxybenzoic[a,b]	54[c]	—[d]
3,4-Dimethoxybenzoic	74	89
2,5-Dimethylbenzoic[a]	77	80
p-Chlorobenzoic	95	93
1-Naphthoic[a,e]	87	88
2-Naphthoic	94	94

[a] Hydrolysis (3 hr on steam-bath) by sodium hydroxide in 85% aqueous dimethyl sulphoxide (otherwise 85% aqueous ethanol).

[b] 7 hr hydrolysis.

[c] Acidic product isolated by ether extraction.

[d] Mixture (optimum hydrolysis conditions not studied).

[e] Recovered in 94% yield after attempted hydrolysis in 85% aqueous ethanol for 1 hr.

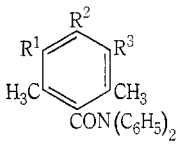
sulphoxide (see Table 3). However, 2,5-dimethoxybenzoic acid diphenylamide proved surprisingly difficult to hydrolyse, even in 85% aqueous dimethyl sulphoxide. The diphenylamides obtained from mesitylene, durene, and pentamethylbenzene could not be hydrolysed by alkali under a variety of conditions (see Experimental). This result was not unexpected, since hindered acid amides are hydrolysed with marked difficulty in the usual acidic or basic media.[6] Acidic hydrolyses* were not attempted in these difficult cases; firstly, because, in general, acidic hydrolysis of primary amides is much slower than alkaline hydrolysis,[7] and secondly, because of the known tendency of such sterically hindered acids (for example, pentamethyl-

* The earlier workers[1,2] used acidic hydrolyses for unhindered diphenylamides.

[6] Chang, F. C., and Wood, N. F., *Tetrahedron Lett.*, 1964, 2969, and references cited therein

[7] Meloche, I., and Laidler, K. J., *J. Am. chem. Soc.*, 1951, **73**, 1712.

benzoic acid[8]) to suffer decarboxylation under acidic conditions drastic enough to effect hydrolysis. Since the acylation conditions are mild, it is considered unlikely that methyl group migration occurred during the acylation of mesitylene and durene, and therefore the structures (II) and (III) respectively are given to the resultant diphenylamides. Their resistance to alkaline hydrolysis is a strong indication that the diphenylamide group is flanked by two methyl groups.



	R^1	R^2	R^3
(II)	H	CH_3	H
(III)	CH_3	H	CH_3

Clearly, diphenylcarbamoyl chloride is a useful reagent for the introduction of a disubstituted amide group into an aromatic nucleus. Its commercial availability and stability give it a marked advantage over other carbamoyl chlorides,* for

TABLE 4

AROMATIC ACID *NN*-DIPHENYLAMIDES

Parent Acid	M.P. of Diphenylamide	Solvent[a]	Molecular Formula	Found (%)			Calc. (%)		
				C	H	N	C	H	N
2,4-Dimethylbenzoic	140–142[b]	A							
2,5-Dimethylbenzoic	90– 92	A	$C_{21}H_{19}NO$	83·8	6·4	4·7	83·7	6·4	4·7
2,4,6-Trimethylbenzoic	105–106	B	$C_{22}H_{21}NO$	83·6	6·8	4·2	83·8	6·7	4·4
2,3,5,6-Tetramethylbenzoic	143–145	C	$C_{23}H_{23}NO$	83·6	6·9	4·2	83·9	7·0	4·3
Pentamethylbenzoic	190–191	C	$C_{24}H_{25}NO$	83·7	7·3	4·1	83·9	7·3	4·1
p-Methoxybenzoic	137–139[c]	C							
2,4-Dimethoxybenzoic	173–175	C	$C_{21}H_{19}NO_3$	75·5	5·9	4·3	75·7	5·7	4·2
2,5-Dimethoxybenzoic	118–120	A	$C_{21}H_{19}NO_3$	75·8	5·9	4·2	75·7	5·7	4·2
3,4-Dimethoxybenzoic	163–164	A	$C_{21}H_{19}NO_3$	75·4	5·8	4·4	75·7	5·7	4·2
p-Chlorobenzoic	142–143[c]	C							
1-Naphthoic	182–184	C	$C_{23}H_{17}NO$	85·1	5·2	4·3	85·4	5·3	4·3
2-Naphthoic	162–163	C	$C_{23}H_{17}NO$	85·1	5·3	4·3	85·4	5·3	4·3

[a] Recrystallization solvent: A, methylene chloride/hexane; B, pentane; C, aqueous ethanol.

[b] Lellmann and Bonhoffer[1] give 141–142°.

[c] Chapman, A. W., *J. chem. Soc.*, 1927, 1749, gives m.p. 139–140° (*p*-methoxybenzoic acid diphenylamide), and m.p. 138–138·5° (*p*-chlorobenzoic acid diphenylamide).

example, *N*-methylphenylcarbamoyl chloride ($C_6H_5(CH_3)NCOCl$).[3] An interesting example of the comparative stability of diphenylcarbamoyl chloride is the observation that it could be recovered practically unchanged from a Friedel–Crafts reaction in ethylene dichloride either with the aromatic substrate omitted or in presence of an unreactive aromatic compound (fluorobenzene), and it seems probable that its decomposition (to diphenylamine) occurs only when hydrogen chloride is being evolved (that is, when the diphenylamide is being formed). Although diphenylamine cannot be removed by washing with acid, it (and unchanged diphenylcarbamoyl chloride) can be readily removed by silica gel chromatography from the more strongly

* The preparation of carbamoyl chlorides involves the use of phosgene which, because of its high toxicity, is often not kept in the average laboratory.

[8] Jacobsen, O., *Ber. dt. chem. Ges.*, 1889, **22**, 1221.

adsorbed diphenylamide. However, for the purpose of preparing the corresponding aromatic acid, isolation of the diphenylamide would not, in general, be necessary, as alkaline hydrolysis of the crude reaction mixture followed by removal of the neutral by-products by extraction with a suitable solvent would furnish the acid (in alkali) directly.

The melting points and analytical figures of the diphenylamides prepared in this investigation are collected in Table 4.

Experimental

(*a*) *General*

Benzene and light petroleum (b.p. 60–70°) used for chromatography were distilled and kept over sodium wire. Reagent grade nitromethane, nitrobenzene, and *sym*-tetrachloroethane were dried over calcium chloride and distilled to constant boiling point. Methylene chloride and ethylene dichloride were distilled over anhydrous potassium carbonate. Column chromatography was carried out on Merck silica gel (0·2–0·5 mm), and thin-layer chromatography on Merck silica gel G (spots were detected by iodine vapour). All melting points are uncorrected. The elementary analyses were carried out by the Australian Microanalytical Service, Melbourne. All analytical samples were dried *in vacuo* over P_2O_5 at 60° for 4 hr. Spectra were measured on a Beckman DK2 recording spectrophotometer (ultraviolet) and on a Perkin–Elmer 137 instrument (infrared). A Beckman IR9 instrument was employed for the quantitative infrared analysis of the mixture of naphthoic acids. The proton magnetic resonance spectrum was obtained on a Varian A60 spectrometer (tetramethylsilane as internal standard).

Diphenylcarbamoyl chloride, m.p. 84–85°, was prepared by the method of Erdtmann and Huth.[9]

(*b*) *Friedel–Crafts Acylations with Diphenylcarbamoyl Chloride*

The reaction of diphenylcarbamoyl chloride with veratrole exemplifies the experimental procedure used where the diphenylamide was obtained directly by crystallization of the crude reaction product. The yields in such cases (see Table 1) could probably be raised by chromatography of the filtrate as described below. In some cases, however, silica gel chromatography was essential for the isolation of the diphenylamide.

(i) *Reaction with Veratrole*

Veratrole (b.p. 203–205°) was dried ($CaCl_2$) and fractionated. Veratrole (1·38 g; 0·01 mole) and diphenylcarbamoyl chloride (2·32 g; 0·01 mole) were dissolved in ethylene dichloride (20 ml) and anhydrous aluminium chloride (1·47 g; 0·011 mole) added. On warming (steam-bath), the mixture slowly became a dark red colour and hydrogen chloride was evolved. Evolution of hydrogen chloride appeared to cease after 3 hr and after 6 hr almost all the aluminium chloride had dissolved. The reaction mixture was cooled and poured onto a mixture of ice and concentrated hydrochloric acid (10 ml). The solvent (and some of the unchanged veratrole) was quickly removed by steam distillation. The supernatant liquor was cooled, decanted from the semi-solid reaction product, and extracted with ether (100 ml). The product was dissolved in benzene (50 ml) (warming) and the combined benzene/ether solution was washed successively with water (20 ml), 1M sodium bicarbonate solution* (2×20 ml), and finally with water (3×25 ml) before being dried over anhydrous sodium sulphate. Removal of the solvent left a semicrystalline residue which was crystallized from hexane/methylene chloride to give *3,4-dimethoxybenzoic acid diphenylamide* as colourless needles (2·17 g; 65% yield), m.p. 161–164°. The filtrate from this crystallization was evaporated to dryness and the oily residue chromatographed in benzene (15 ml) on silica gel (10 g). The column was eluted with light petroleum containing increasing

* In one experiment (Table 2, expt. 5), acidification of these alkaline washings gave 3,4-dimethoxybenzoic acid (0·102 g), m.p. and mixed m.p., 183–186°.

[9] Erdtmann, H., and Huth, P., *J. prakt. Chem.*, 1897, **56**, 7.

amounts of benzene, the fraction (0·56 g) containing diphenylamine and diphenylcarbamoyl chloride (both identified by thin-layer chromatography) being eluted with benzene/light petroleum (2 : 1). A solid fraction (0·18 g), eluted with chloroform, was examined by thin-layer chromatography using the solvent system hexane/ethyl acetate (2 : 1) and appeared (infrared spectrum) to consist mainly of the compound (m.p. 161–164°) (R_F value 0·32). Two other components (R_F values 0·22 and 0·10) were also present.

The effect of varying the solvent and the proportions of aluminum chloride and of different solvents on the yield of 3,4-dimethoxybenzoic acid diphenylamide is shown in Table 2.

(ii) *Reaction with Naphthalene*

A mixture of naphthalene (1·92 g; 0·015 mole), diphenylcarbamoyl chloride (3·42 g; 0·015 mole), and anhydrous aluminium chloride (2·20 g; 0·0165 mole) in ethylene dichloride (30 ml) was warmed on the steam-bath for 6 hr. The usual work-up was followed by chromatography on silica gel (40 g) as described above. The mixture of diphenylamides (2·96 g; 61% yield), which was eluted with benzene and benzene containing increasing amounts of chloroform, had m.p. 162–174°, and showed only one spot when examined by thin-layer chromatography with a variety of solvent systems. A portion of this solid (1·86 g) was recrystallized twice from hexane/methylene chloride and once from cyclohexane to give impure 1-naphthoic acid diphenylamide (0·85 g), m.p. 176–178° (see below).

A purer product was obtained in the following manner. The diphenylamide mixture (2·88 g) in ethanol (50 ml) was added to sodium hydroxide (1·5 g) in water (10 ml) and the mixture boiled under reflux for 90 min. More ethanol (30 ml) was added to dissolve solid material and the reaction was continued for a further 90 min. *1-Naphthoic acid diphenylamide* (1·38 g), m.p. 179–180°, crystallized out on cooling and was washed with a little 80% ethanol and then with water. The combined filtrates were poured onto ice and the oily product extracted with ether (extract A). The alkaline layer was acidified and extracted continuously with ether. The ether layer was washed several times with saturated salt solution and dried over anhydrous sodium sulphate. Removal of the solvent left a pinkish solid (0·37 g; m.p. 167–172°) whose infrared spectrum was identical with that of 2-naphthoic acid. Recrystallization of this solid from aqueous ethanol gave 2-naphthoic acid (0·22 g; 14% yield), m.p. and mixed m.p. 182–184°. Extract A yielded an oily solid which was chromatographed in benzene (10 ml) on a column of silica gel (20 g). Diphenylamine (0·40 g; 26% yield), m.p. 49–50°, was eluted with benzene/light petroleum (1 : 3). The solid (0·63 g) eluted with benzene/chloroform (1 : 3) had m.p. 165–175°. Recrystallization of this solid from hexane/methylene chloride gave a further quantity (0·29 g) of 1-naphthoic acid diphenylamide, m.p. 179–181°, making a total yield of 1·67 g or 58% based on the weight of the original mixture.

A more accurate estimate of the relative proportions of the naphthoic acid diphenylamides in the mixture was obtained by hydrolysis to a mixture of 1- and 2-naphthoic acids which was estimated by quantitative infrared spectral analysis (see below) to contain 77% 1-naphthoic acid. The mixture (455 mg) in 85% aqueous dimethyl sulphoxide (10 ml) was warmed on the steam-bath with sodium hydroxide (0·5 g) for 4 hr. Diphenylamine (193 mg; 81% yield) and the mixture of naphthoic acids (237 mg; 97% yield) were isolated as described in the previous section. The infrared quantitative analysis (0·5% KBr disks) of this mixture (237 mg) depended on the following characteristic infrared maxima: 810 and 1152 cm^{-1} (1-naphthoic acid), 836 (isolated hydrogen?), and 1137 cm^{-1} (2-naphthoic acid). The ratios (absorbance at 836/absorbance at 810 cm^{-1}) and (absorbance at 1137/absorbance at 1152 cm^{-1}) for the mixture were compared with the same ratios for a series of standard mixtures.

(iii) *Reaction with Chlorobenzene*

As for naphthalene but with chlorobenzene (1·78 g; 0·015 mole). Elution with benzene/light petroleum (3 : 2) gave a mixture (3·01 g; m.p. 73–77°) of diphenylamine and diphenylcarbamoyl chloride. Elution with chloroform (300 ml) gave a gummy solid (0·14 g) which was crystallized from hexane/methylene chloride to give a compound of unknown structure (0·08 g), m.p. 183–186° (Found: C, 72·4; H, 4·7; Cl, 9·2; N, 5·15%).

(iv) *Reaction with Fluorobenzene*

As for veratrole (0·01 molar scale) but with fluorobenzene (0·96 g; 0·01 mole). Diphenylcarbamoyl chloride (2·25 g; 97% yield), m.p. and mixed m.p. 80–82°, was recovered. Thin-layer chromatography revealed the presence of diphenylamine.

(v) *Reaction without Aromatic Substrate*

A mixture of diphenylcarbamoyl chloride (1·16 g; 5 mmole) and anhydrous aluminium chloride (0·61 g; 5 mmole) in ethylene dichloride (10 ml) was boiled under reflux for 6 hr. The usual work-up gave back diphenylcarbamoyl chloride (1·03 g), m.p. and mixed m.p. 80–81°. Thin-layer chromatography revealed the presence of diphenylamine.

(c) *General Preparation of Aromatic Acid Diphenylamides*

The aromatic acid (0·02 mole) was converted (4 hr on steam-bath) into its acid chloride by means of excess thionyl chloride in benzene (15 ml) containing pyridine (3 drops). Removal of the solvent gave the crude acid chloride which was converted without further purification into its diphenylamide by reaction (1 hr on steam-bath) with diphenylamine (0·02 mole) in benzene (20 ml). The solvent was removed and the crude product was recrystallized from aqueous ethanol. The following acids were converted into their diphenylamides (% yield in brackets): 1-naphthoic (52), 2-naphthoic (44), *p*-chlorobenzoic (54), and *p*-methoxybenzoic (64).

(d) *General Hydrolysis of Diphenylamides*

Hydrolysis with sodium hydroxide in 85% aqueous ethanol or 85% aqueous dimethyl sulphoxide was usually effective (see Table 3). The hydrolysis mixture was poured onto ice and kept at 0° overnight. Diphenylamine was filtered off and the alkaline filtrate acidified to give the parent aromatic acid which was isolated either by filtration or by ether extraction. The acidic products were identical, m.p. and mixed m.p., with authentic samples. The following attempts to hydrolyse the diphenylamides obtained from the acylation of mesitylene, durene, and pentamethylbenzene were unsuccessful (diphenylamide recovered unchanged): warming for 72 hr on the steam-bath with sodium hydroxide in (*a*) 85% aqueous ethanol, (*b*) 85% aqueous dimethyl sulphoxide, and (*c*) 90% aqueous hexamethylphosphoramide.

Acknowledgments

The author wishes to thank Mr D. E. Rivett for carrying out several preliminary experiments, Mr W. Lankhorst for technical assistance, and Mr J. L. Little, Division of Applied Chemistry, CSIRO, for recording the proton magnetic resonance spectrum.