Side-Chain Amination of Aryldialkylmethines with Trichloramine–Aluminum Chloride–*t*-Butyl Bromide[1]

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Various aryldialkylmethines were aminated on the alkyl side chain to form *t*-benzylamines in the system trichloramine–aluminum chloride–*t*-butyl bromide. *p*-Alkyl- and *p*-halocumenes gave the corresponding *para*-substituted cumylamines in yields of 61–80% based on trichloramine. With *p*-cyclohexyltoluene, 1-(*p*-tolyl)cyclohexylamine was produced. Amination of 3-(*p*-tolyl)pentane took place with rearrangement forming 2-(*p*-tolyl)-2-pentylamine, the same product as was obtained from 2-(*p*-tolyl)pentane. More highly alkylated benzenes produced poor results attributable to unfavorable steric influences, isomerization, and disproportionation. It was demonstrated in some cases that amination followed a single pathway even when isomeric mixtures comprised the starting material. Relative rate studies provided evidence for involvement of intermediate *t*-benzyl cations. The reaction possesses synthetic utility. Dealkylation of certain *p*-alkyl-*t*-benzylamines was effected smoothly.

In prior investigations we have shown that the combination of trichloramine and aluminum chloride is capable of aminating various types of organic compounds. The orientation of the entering group and varied nature of the organic substrates are of particular interest. For example, alkylbenzenes were found to be *meta* directing;[4] *t*-alkanes yielded *t*-carbinamines;[5] and *t*-alkyl halides were transformed into *t*-alkylamines.[6] Recently, the conversion of *p*-cymene into 8-amino-*p*-cymene was reported to proceed smoothly on exposure to trichloramine–aluminum chloride–*t*-butyl bromide.[7]

The purpose of the present study was to investigate the scope and theoretical aspects of the amination reaction with aryldialkylmethines as substrates. Our principal attention was devoted to the mechanistic features in relation to substituent effects and relative rates, as well as the synthetic utility.

Results

Since only a few of the requisite aryldialkylmethines are commercially available, literature procedures were generally followed for their preparation. Several of the hydrocarbons, namely, *p*-*t*-butylcumene, isopropylmesitylene, and 5-isopropyl-*m*-xylene, were readily obtained by Friedel–Crafts alkylation. However, in many instances this method proved unsuitable because of the formation of isomeric mixtures which were difficult to separate into the component parts. Multistep procedures were then employed, involving addition of a Grignard reagent to the appropriate ketone, dehydration of the resulting alcohol, and finally reduction of the olefin. Several miscellaneous procedures are also described.

The aminations were carried out by adding a solution of trichloramine to a mixture of the methine, aluminum chloride, and *t*-butyl bromide at 0–10°. Those experiments which met with success are summarized in Table I. The basic products were characterized by elemental analyses, ir and nmr (Table II) spectra, and amide derivatives (Table III). The *p*-alkylcumenes responded nicely producing the corresponding cumylamines in yields of 61–80% based on trichloramine. Similar findings were realized with the *p*-halocumenes. We observed essentially the same outcome (high yields of the *para*-substituted product) even when 20% of the *o*-bromo or *o*-chloro isomer was present in the aromatic starting material. Also, it was necessary to operate near room temperature with *p*-chloro- and *p*-fluorocumene to achieve optimum results. Of the two routes possible with 2-chloro-1,4-diisopropylbenzene, the one leading to 3-chloro-4-isopropylcumylamine was followed almost exclusively. In contrast, *p*-isopropylanisole resisted amination, and a number of other cumene derivatives (4-chloro-4′-isopropylbiphenyl, isopropylxylenes, 2,5-diisopropyl-*p*-xylene, 1,3,5-triisopropylbenzene, and isopropylmesitylene) gave low yields of basic material containing two to nine components.

Methine side chains, other than isopropyl, are also capable of undergoing amination. For example, 1-(*p*-tolyl)cyclohexylamine was formed in 57% yield from *p*-cyclohexyltoluene. A more complex picture with interesting ramifications emerged from our investigations with the 2- and 3-(*p*-tolyl)pentanes. In the case of the 2 isomer, reaction apparently proceeded in a straightforward manner to provide 2-amino-2-(*p*-tolyl)pentane. Quite unexpectedly, the same amine was formed as the major product from the 3 isomer.

p-Ethyltoluene gave a gross mixture of basic products in low yield.

Cumylamine, and presumably its *meta* derivatives, cannot be synthesized directly according to the general procedure since the aromatic substrate preferentially undergoes disproportionation and nuclear amination,[8] with the side chain being less susceptible to attack. Thus, cumene gave rise to a complex mixture including *m*-cumidine, cumylamine, and *p*-isopropylcumylamine.

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TABLE I

AMINATION OF ARYLDIALKYLMETHINES WITH TRICHLORAMINE–ALUMINUM CHLORIDE–*t*-BUTYL BROMIDE[a]

Substrate	Amine product	Yield, %	Bp, °C (mm)	Formula	Calcd, %				Found, %			
					C	H	N	X[b]	C	H	N	X[b]
p-Cymene	8-Amino-*p*-cymene[c]	80	76–77 (5.2)									
p-Ethylcumene	*p*-Ethylcumylamine	62[d]	100–108 (7.7)	$C_{11}H_{17}N$	80.94	10.47	8.58		80.73	10.65	8.41	
p-Diisopropylbenzene	*p*-Isopropylcumylamine	61	95–97 (4.5)	$C_{12}H_{19}N$	81.30	10.80	7.90		81.35	10.80	7.80	
p-*t*-Butylcumene[e]	*p*-*t*-Butylcumylamine	66	78–79.5[f]	$C_{13}H_{21}N$	81.61	11.07	7.32		81.78	11.02	7.43	
p-Fluorocumene[e]	*p*-Fluorocumylamine	72[g]	77–80 (7.3–7.5)	$C_9H_{12}FN$	70.55	7.90	9.14	12.40	70.46	7.92	9.20	12.43
p-Chlorocumene	*p*-Chlorocumylamine	69[g]	91 (4)	$C_9H_{12}ClN$	63.71	7.13	8.26	20.90	63.81	7.31	8.13	20.75
p-Bromocumene[e,h]	*p*-Bromocumylamine	74	122–124 (8.3)	$C_9H_{12}BrN$	50.47	5.61	6.54	37.38	50.45	5.75	6.60	37.20
2-Chloro-4-isopropylcumylamine	3-Chloro-4-isopropylcumylamine	40[i]	133–137 (8.3–8.5)	$C_{12}H_{18}ClN$	68.06	8.56	6.61	16.74	68.34	8.50	6.57	16.72
p-Cyclohexyltoluene	1-(*p*-Tolyl)cyclohexylamine	57[j]	125–127 (1.5–1.7)	$C_{13}H_{19}N$	82.48	10.12	7.40		82.35	10.20	7.23	
3-(*p*-Tolyl)pentane	2-(*p*-Tolyl)-2-pentylamine	52[k]	108–115 (6.8–7.5)									
2-(*p*-Tolyl)pentane	2-(*p*-Tolyl)-2-pentylamine	28[l]	107–109 (7.1–7.5)	$C_{12}H_{19}N$	81.30	10.80	7.90		81.27	10.76	7.81	

[a] See the general procedure. [b] X = halogen. [c] See ref 7. [d] About 88% pure; also contains *p*-isopropylcumylamine (8%), cumylamine (1%), and unidentified material (3%). [e] Aromatic: *t*-BuBr:$AlCl_3$:NCl_3 = 10:2:2:1 molar ratio. [f] Melting point. [g] Modified general procedure; see Experimental Section. [h] Contains about 20% *ortho* isomer. [i] Contains about 6% 2-chloro-4-isopropylcumylamine. [j] Contains about 4% unidentified material. [k] About 84% pure. The remainder consists of four unidentified materials. [l] We were unable to detect the presence of 3-(*p*-tolyl)-3-pentylamine. [m] Contains 3% unidentified component.

However, these types can conveniently be brought to hand since certain of the substituted *t*-benzylamines serve as suitable precursors. For example, on exposure to aluminum chloride–hydrogen chloride, *p*-isopropyl- and *p*-*t*-butylcumylamine were converted into cumylamine in good yield by dealkylation in the presence of toluene. In an analogous manner, *m*-chlorocumylamine was formed almost quantitatively from 3-chloro-4-isopropylcumylamine.

Several attempts were made to reduce the amount of aromatic substrate without adversely affecting yield. Since some of the aromatic reactant is being consumed through nuclear chlorination, part of the excess *p*-cymene was replaced by several candidates, namely *p*-xylene and mesitylene, which hopefully would suffer halogenation and, at the same time, participate to little or no extent in amination.[8] The experiments did not prove fruitful.

In the initial studies[9] evidence was obtained for the presence of N-chlorinated 8-amino-*p*-cymene under certain conditions in the amination of *p*-cymene. Subsequent work-up resulted in conversion into *ar*-chloro-8-amino-*p*-cymene of unknown orientation. We have now characterized the product as the 2 isomer. Identification was based upon reductive deamination of the *ar*-chloro-8-amino-*p*-cymene to a mixture of 2-chloro-*p*-cymene and, presumably, 3-chloro-4-methyl-α-methylstyrene. The results point to an intermolecular pathway for the nuclear halogenation.[10]

Discussion

The mechanistic scheme[7] for rationalization of side-chain amination is illustrated with *p*-cymene (eq 1 and 2). Alkyl groups *para* to the methine functionality

$$Cl_3N + AlCl_3 \rightleftharpoons Cl^{\delta+}(Cl_2NAlCl_3)^{\delta-} \quad (1)$$

(2)

would be expected to afford resonance stabilization[11] of the intermediate *t*-benzylic cation. Halogen atoms, although capable of effecting delocalization,[12] also possess an unfavorable inductive influence which apparently accounts for the increased temperatures required for optimum results with the more electronegative members.

In a number of cases (4-isopropyl-*m*-xylene, 2-isopropyl-*p*-xylene, 2,5-diisopropyl-*p*-xylene, isopropylmesitylene, and *o*-chlorocumene) the decreased susceptibility to amination can be interpreted by steric inhibition[11,12] of resonance including the participation of less favorable *o*-quinoid structures. This hypothesis nicely accounts for the preferential formation of 3-chloro-4-isopropylcumylamine from 2-chloro-*p*-diisopropylbenzene. The importance of resonance stabilization of the carbonium ion is further pointed up by the poor results obtained when the *para* position is un-

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(10) L. O. Brown and F. G. Soper, *J. Chem. Soc.*, 3576 (1953).
(11) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Amer. Chem. Soc.*, **79**, 1897 (1957).
(12) H. C. Brown, Y. Okamoto, and G. Ham, *ibid.*, **79**, 1906 (1957).

TABLE II

PROTON MAGNETIC RESONANCE DATA[a,b]

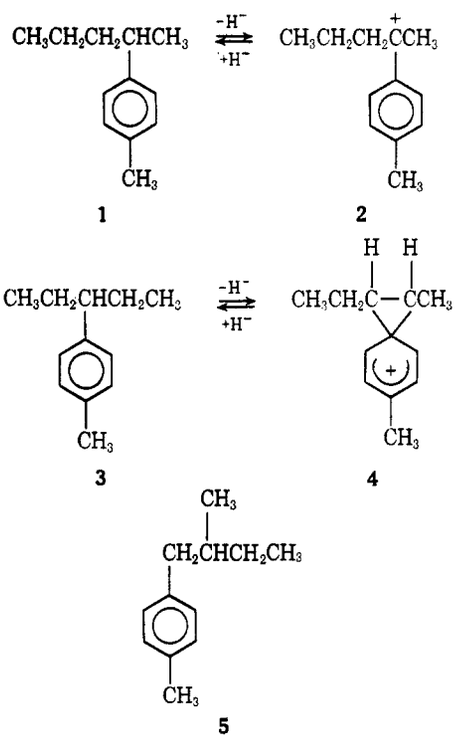
Compound	Registry no.	Chemical shifts, δ (ppm) ArH	ArCH	RCH	NCCH	NH	Rel intensities
p-Ethylcumylamine	17797-07-8	6.61 (dd)	2.29 (q)	1.01 (t)	1.17 (s)		3.9:2:11[c]
p-Isopropylcumylamine	17797-08-9	7.28 (dd)	2.82 (h)	1.17 (d)	1.33 (s)	1.36 (s)	4:0.9:14[c]
p-*t*-Butylcumylamine	17797-09-0	7.05 (d)		1.15 (s)	1.26 (s)		3.9:9:7.9[d]
p-Fluorocumylamine	17797-10-3	6.42–7.25 (c)			0.98 (s)	1.08 (s)	1:2[d]
p-Chlorocumylamine	17797-11-4	7.02 (dd)			1.04 (s)	1.17 (s)	1:1.9[d]
p-Bromocumylamine	17797-12-5	7.32 (bs)			1.32 (bs)		1:2[d]
3-Chloro-4-isopropylcumylamine	17797-13-6	6.81–7.32 (c)	3.11 (h)	0.92 (d)	1.02 (s)		3.5:0.9:14[c]
1-(*p*-Tolyl)cyclohexylamine	17797-15-8	6.94 (dd)	2.00 (s)	1.33 (c)		0.89 (s)	3.9:2.7:10[e]:1.8
2-(*p*-Tolyl)-2-pentylamine	17797-14-7	6.93 (dd)	1.93 (s)			*f*	
m-Chlorocumylamine	17790-50-0	6.77–7.39 (c)			1.01 (s)		1.1:2[d]

[a] Tetramethylsilane as external reference. [b] s, singlet; d, doublet; t, triplet; q, quartet; h, heptet; dd, two doublets; c, complex; b, broad. [c] RCH, NCCH, NH combined. [d] NCCH, NH combined. [e] RCH, NCCH combined. [f] A complex pattern from 0.56 to 1.48 with overlapping singlets at 1.06 (3H) (CH_3C) and 0.91 (2H) (NH_2). The remainder of the pattern, assigned to the *n*-propyl group, is similar to that obtained from 2-hydroxy-2-(*p*-tolyl)pentane (see the Experimental Section). The spectrum is consistent with that predicted for 2-(*p*-tolyl)-2-pentylamine. If the amino group is attached at some other position, the peak at 1.06 would be a doublet. If an isopropyl group, instead of *n*-propyl, were present, a doublet at about 0.9 and a heptet near 2.0 would be expected.

substituted (no steric inhibition of resonance since *ortho* positions are open) (cumene, 5-isopropyl-*m*-xylene, and 1,3,5-triisopropylbenzene). Lack of amination in the case of *p*-isopropylanisole is apparently due to inactivation of the catalyst by coordination with the ether oxygen.

Data resulting from variation in the nature of the side chain proved to be informative. The satisfactory response from *p*-cyclohexyltoluene is in accord with prior studies with related systems. Thus, solvolysis at a tertiary position which is part of the cyclohexane structure proceeds at about the same rate as for the acyclic analog.[13] Previous investigations[14] on isomerization of the analogous pentylbenzenes serve as a useful basis for discussion of our findings with the *p*-tolylpentanes. 2-Phenylpentane (A), 3-phenylpentane (B), and 1-phenyl-2-methylbutane (C) exist in mobile equilibrium in contact with aluminum chloride at 80°. After 24 hr, the composition was 50% A, 35% C, and 15% B, with C being much more stable toward rearrangement. A and B were interconverted rapidly, whereas production of C from either of these isomers was slower. The mechanistic features, which apparently include a phenonium ion intermediate, have been treated in some detail by Roberts and Fonken.[14]

With 2-(*p*-tolyl)pentane (**1**) abstraction of hydride to form the *t*-benzyl cation (**2**) would be followed by combination with the nitrogenous nucleophile. The rather low yield (28%) can be rationalized by steric interfence involving the β-alkyl group. In the case of the 3 isomer (**3**), we believe that abstraction of the tertiary hydrogen, which is hindered by two substituents β to the reaction center, is less likely than removal of a secondary hydrogen with formation of **4**, since steric blocking is diminished through anchimeric assistance by the aryl group.[14] Subsequently, **4** is converted into **2**. The better yield (52%) of 2-(*p*-tolyl)-2-aminopentane from 3-(*p*-tolyl)pentane indicates that **2** is more readily obtained from **3** than from **1**. Support for these conclusions is derived from an examination of the neutral products. In the amination of **1** no other isomers were detected in the neutral fraction, whereas with **3** the isomers, **3**, **1**, and **5**, were present in the ratio 81:17:2. The presence of rearranged products points to the formation of carbonium ion intermediates which would be susceptible to capture by an appropriate nucleophile. Control experiments, in which trichloramine was omitted, also demonstrated that **3** is more prone to rearrange than **1**. Starting with **3** we obtained **3**, **1**, and **5** in the ratio 58:40:2; under the same conditions **1** is altered only to a slight extent, **1**:**3** = 95:5. These findings are in accord with earlier observations with related systems.[14]



The unsatisfactory behavior of *p*-ethyltoluene, in contrast to *p*-cymene, probably reflects the greater difficulty in forming a *sec*-benzylic carbonium ion on hydride abstraction.

Additional evidence for participation of positively charged intermediates in the amination sequence was

(13) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., New York, N. Y., 1962, p 96.

(14) R. M. Roberts and G. J. Fonken in "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1963, pp 839–843.

TABLE III
AMIDE DERIVATIVES OF *t*-BENZYLAMINES

Compound	Registry no.	Derivative	Mp, °C	Formula	Calcd, %				Found, %			
					C	H	N	X[a]	C	H	N	X[a]
p-Ethylcumylamine	17790-51-1	Benzamide	155–156	$C_{18}H_{21}NO$	80.85	7.92	5.24		80.81	7.94	5.41	
p-Isopropylcumylamine	17790-52-2	Benzamide	162–164	$C_{19}H_{23}NO$	81.10	8.24	5.00		81.08	8.20	5.15	
p-*t*-Butylcumylamine	17790-53-3	Benzamide	199–201	$C_{20}H_{25}NO$	81.31	8.53	4.74		81.05	8.52	4.80	
p-Fluorocumylamine	17790-54-4	Acetamide	132.5–133.5	$C_{11}H_{14}FNO$	67.67	7.21	7.17	9.74	67.52	6.99	7.20	9.91
p-Chlorocumylamine	17790-55-5	Acetamide	173–174	$C_{11}H_{14}ClNO$	62.41	6.67	6.62	16.76	62.18	6.49	6.60	16.56
p-Bromocumylamine	17818-09-6	Acetamide	175.5–176	$C_{11}H_{14}BrNO$	51.60	5.47	5.47	31.21	51.63	5.57	5.60	31.07
3-Chloro-4-isopropylcumylamine	17790-56-6	Benzamide	178–179.5	$C_{19}H_{22}ClNO$	72.25	7.02	4.43	11.22	72.21	7.01	4.59	11.01
1-(*p*-Tolyl)cyclohexylamine	17790-57-7	Benzamide	151–152.5	$C_{20}H_{23}NO$	81.87	7.90	4.77		81.91	7.85	4.60	
2-(*p*-Tolyl)-2-pentylamine	17790-58-8	Benzamide	193–194	$C_{19}H_{23}NO$	81.10	8.24	5.00		80.93	8.27	4.96	
m-Chlorocumylamine	17790-59-9	Benzamide	192.5–194	$C_{16}H_{16}ClNO$	70.19	5.89	5.11	12.94	70.04	5.97	5.07	13.06

[a] X = halogen.

TABLE IV
RELATIVE RATES OF SIDE-CHAIN AMINATION

AH = *p*-YC_6H_4-$CH(CH_3)_2$	BH = *p*-ZC_6H_4-$CH(CH_3)_2$	Molar ratio	$[ANH_2]$:$[BNH_2]$	$k_{AH}:k_{BH}$
CH_3	Cl	1:8	0.766	6.13
Cl	$CH(CH_3)_2$	8:1	1.54	0.385[a]
CH_3	$CH(CH_3)_2$	1:2	0.395	1.58[a]
CH_3	$CH(CH_3)_2$	1:1	0.845	1.69[a]
CH_3	$CH(CH_3)_2$	1:1	0.620	1.24[a]
CH_3	$CH(CH_3)_2$	2:1	1.34	1.34[a–c]

[a] Per isopropyl group in the case of *p*-diisopropylbenzene. [b] $k_{CH_3}:k_{CH(CH_3)_2}$ = 1.46 (av); average deviation, 12%. [c] $k_{CH_3}:k_{CH(CH_3)_2}$ = 2.36, calculated from $(k_{CH_3}:k_{Cl}) \times (k_{Cl}:k_{CH(CH_3)_2})$.

provided by a study of relative rates (Table IV). The fairly large average deviation (12%) in the data can be explained in part by the limited occurrence of disproportionation reactions under the Lewis acid conditions. Our findings with *p*-$ZC_6H_4CH(CH_3)_2$, CH_3:$CH(CH_3)_2$:Cl = 1.46–2.36:1:0.38, fall in the same order as for solvolysis[11,12] of *para*-substituted cumyl chlorides in aqueous acetone at 0°, CH_3:$CH(CH_3)_2$:Cl = 1.48:1:0.012. Lack of precise agreement is not surprising since the media differ quite appreciably. In comparison, decomposition of *para*-substituted azocumenes, which exhibits the characteristic earmarks[15] of free-radical transformations, provided the indicated order,[16] Cl:CH_3:$CH(CH_3)_2$ = 2.72:1.46:1.

Finally, a summary of the synthetic aspects is appropriate. When the aromatic substrate is readily available by halogenation or Friedel–Crafts alkylation, *e.g.*, *p*-isopropyl-, *p*-*t*-butyl-, and *p*-halocumenes, the present technique comprises the most convenient route to the corresponding *t*-benzylamine. An additional advantage, as demonstrated with the halocumenes, is that the starting material need not be isomerically pure. Conceivably, the Ritter reaction might be the method of choice in certain cases from the standpoint of over-all yield based on the aromatic substrate. For example, Christol and coworkers[17] prepared α-methyl-α-isopropylbenzylamine in 60% yield from the requisite *t*-benzyl alcohol. However, α,α-dimethyl- and α,α-diethylbenzylamine were produced in low yield (5–10%) by the prior procedure. Conversion of alkylamines into various derivatives *via* the diazonium salt is discussed in review articles.[18]

Experimental Section[19]

Materials.—Most reagents were high purity commercial materials which were used as received. Purchased *p*-chlorocumene (Eastman, practical) and *p*-bromocumene (Columbia, practical) contained about 20% *ortho* isomer. Other required substrates, prepared as described, were checked for purity by glpc, and for the expected substitution pattern in the ir spectrum. 1,2-Dichloroethane was distilled from calcium hydride.

Analytical Procedures.—Infrared spectra of the starting materials and products were obtained with a Beckman 1R-5A or 1R-8 spectrophotometer on neat samples, or dilute solutions in

(15) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Amer. Chem. Soc.*, **90**, 354 (1968).

(16) P. Kovacic, R. R. Flynn, J. F. Gormish, A. H. Kappelman, and J. R. Shelton, unpublished data.

(17) H. Christol, A. Laurent, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 2319 (1961).

(18) R. J. Baumgarten, *J. Chem. Educ.*, **43**, 398 (1966); S. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1967).

(19) Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points and boiling points are uncorrected.

carbon disulfide or carbon tetrachloride. The amine products gave the expected pattern in the aromatic and amine regions. Nuclear magnetic resonance spectra (Table II) were obtained with a Varian A-60 instrument and on the same solutions as in the ir study. When necessary, samples were purified by glpc. Gas chromatographic work was carried out with a Matronic instrument on the indicated columns: (A) 8 ft by 0.25 in., Carbowax 20M (20%) on Chromosorb W (30–60 mesh) (5% KOH); (B) same as column A except 2 ft in length; (C) 6 ft by 0.25 in., Apiezon L (14%) on Chromosorb P (40–60 mesh) (5% NaOH); (D) 6 ft by 0.25 in., SF-96 (20%) on acid-washed Chromosorb P (30–60 mesh).

Preparation of Trichloramine Solutions.—A published procedure[20] (method B) was used with 1,2-dichloroethane as solvent. Analysis for positive halogen was performed by an iodometric method in acetic acid.[20] Caution: exercise the necessary precautions when working with N-halamines. Excess trichloramine can be destroyed by slow addition with stirring into a cold solution of sodium metabisulfite.

Amination with Trichloramine–Aluminum Chloride–*t*-Butyl Bromide.—A published procedure (B2)[7] was used except for *p*-fluoro- and *p*-chlorocumene, in which cases the temperature was increased to 25° after trichloramine addition was complete. The results are listed in Table I. Microanalyses were performed on samples collected by glpc.

Some of the substrates produced a mixture of bases in low yield [substrate (% crude yield, number of basic components)]: 4-isopropyl-*m*-xylene (32, 7); 5-isopropyl-*m*-xylene (18, 6); 2-isopropyl-*p*-xylene (20, 5); 2,5-diisopropyl-*p*-xylene (20, 4); isopropylmesitylene (24, 9); *p*-ethyltoluene (11, 10); 1,3,5-triisopropylbenzene (3, 3); *p*-isopropylanisole (0); 4-chloro-4′-isopropylbiphenyl (26, 2; crystallization of the crude product from heptane resulted in a 50% recovery of material, mp 152–185°, containing two components by glpc analysis); cumene[21] (39, 4; *p*-isopropylcumylamine, 66%; cumylamine, 14%; *m*-cumidine, 12%; unidentified, 8%).

The neutral layer from amination of *p*-cymene contained chlorination products in the ratio, *ar*-chloro-*p*-cymene/*p*-cymene = 0.41 (theory, 0.48). Analysis was carried out by comparison with an authentic mixture of *ar*-chloro-*p*-cymene (80% 2 isomer, 20% 3 isomer; glpc column D).

The experiments in which part of the excess *p*-cymene was replaced by *p*-xylene or mesitylene are described in Table V.

TABLE V

EFFECT OF AROMATIC ADDITIVES ON *p*-CYMENE AMINATION

p-Cymene, mol	Additive	Mol	8-Amino-*p*-cymene— Yield, %	Purity, %
0.5	*p*-Xylene	0.5	61	94[a]
0.3	*p*-Xylene	0.7	58	94[a]
0.2	*p*-Xylene	0.8	60	95[a]
0.1	*p*-Xylene	0.9	34	86[a]
0.5	Mesitylene	0.5	40	78[b]

[a] The remainder was mainly 2,5-dimethylaniline along with small amounts of unidentified material. [b] The remainder was unknown material.

Glpc determinations of the *p*-tolylpentanes were made with column C at 150°.

Competitive Aminations.—A mixture of the two substrates (0.2 mol total) in 100 ml of 1,2-dichloroethane was cooled to 0°, and aluminum chloride (5.32 g, 0.04 mol) was added in one portion followed immediately by *t*-butyl bromide (6.7 ml, 0.06 mol). At this point, the reaction mixture became homogeneous except for a very small amount of solid, presumably undissolved aluminum chloride. Then, while a nitrogen purge was maintained, trichloramine solution (40 ml, 0.02 mol) was added dropwise during 10 min at 0 to 5°. After an additional 5 min, the reaction mixture was poured over ice–hydrochloric acid and worked up. The amine products were analyzed by glpc (column A, 190°) with calibration by standard mixtures of pure materials (Table IV).

Examination of the neutral layer after reaction revealed the presence of about 3% disproportionation products (based on the aromatic substrate): cumene from *p*-diisopropylbenzene and toluene from *p*-cymene. No isomerization products were found.

Dealkylation of Alkylcumylamines.—Dry hydrogen chloride was bubbled through a mixture of *p*-isopropylcumylamine (4.9 g, 0.027 mol), toluene (58 ml) and anhydrous aluminum chloride (18.5 g, 0.138 mol) during 0.5 hr. After 25 hr of stirring at room temperature addition to ice–hydrochloric acid and subsequent work-up gave cumylamine (75% yield), bp 62–64° (5mm). The ir spectrum was identical with that of material prepared by a literature method.[22] The same procedure was used with *p*-t-butylcumylamine to give cumylamine (70% yield), and with 3-chloro-4-isopropylcumylamine to form *m*-chlorocumylamine (96% yield), bp 101–102° (7.5–7.8 mm). The ir spectrum showed characteristic absorption at 785 and 695 cm^{-1} in the *meta* region.

Anal. Calcd for $C_9H_{12}ClN$: C, 63.71; H, 7.13; N, 8.26; Cl, 20.89. Found: C, 63.56; H, 7.33; N, 8.38; Cl, 21.16.

Amide Derivatives.[23]—Benzamides were prepared by treating the amine in pyridine with benzoyl chloride. Acetamides were formed with acetic anhydride (Table III).

***p*-*t*-Butylcumene.**[24]—Cumene was alkylated with *t*-butyl alcohol and 85% sulfuric acid according to a literature procedure.[25]

Isopropylmesitylene.—To a cold (5–10°) mixture of isopropyl alcohol (47 ml, 0.615 mol) and mesitylene (416 ml, 3 mol) was added a cooled mixture of concentrated sulfuric acid (500 ml) and water (110 ml) during 3 hr. After being stirred at 24° for 19 hr, the mixture was worked up yielding 79 g (79%) of a fraction boiling at 82–84° (5.4–5.6 mm) [lit. bp 82.5–83.5° (5.5 mm),[26] 220° [27]]. The ir spectrum was identical with that of authentic material prepared by an alternate route.[27,28]

***p*-Ethylcumene.**—Attempts to prepare this compound by alkylation[29] gave a product which contained substantial amounts of other isomers. Better quality material was obtained by the indicated procedure. Cumene was acylated by an established technique[30] to give *p*-isopropylacetophenone from which *p*-ethylcumene was synthesized in 77% yield by a modified Wolff-Kishner reduction:[31] bp 194–196° (742 mm) [lit.[29] bp 193° (744 mm)].

Isopropyl-*p*-xylene.—To a mixture of *p*-xylene (375 ml) and isopropyl alcohol (50 ml) at 15° was added cold 85% sulfuric acid (250 ml) during 2 hr. After 20 hr at 23–25°, work-up provided a 56% yield of product, bp 196–199° (745 mm) [lit. bp 111.9–113.4° (60 mm),[26] 195–196° [27]].

5-Isopropyl-*m*-xylene.—This preparation is described by Nightingale and Carton.[32]

4-Isopropyl-*m*-xylene.—Since an attempt to prepare this material by a literature route[32] gave a mixture of products, an alternate multistep procedure was used. Acylation of *m*-xylene in the conventional manner[30] yielded 2,4-dimethylacetophenone,[33] bp 97–99° (8.5 mm) (88% yield). The ketone together with an equimolar amount of methylmagnesium iodide produced 2,4-dimethylcumyl alcohol. Dehydration was effected by the method of Hibbert.[34] A crystal of iodine was added to the crude alcohol and distillation at atmospheric pressure was continued until the calculated amount of water was collected. The residue was combined with the distillate; the organic phase was separated, washed with a dilute solution of sodium thiosulfate, and further worked up to give 2,4-dimethyl-α-methylstyrene, bp 71–75° (7.4–8 mm) (71% yield based on the ketone). Subsequently,

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(21) In the absence of *t*-butyl bromide, a 27% yield of *m*-cumidine (85% pure) was obtained in contrast to the 53% yield previously reported (see ref 8).

(22) A. C. Cope, T. T. Foster, and P. H. Towle, *ibid.*, **71**, 3929 (1949).

(23) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 226.

(24) We wish to thank Mr. J. T. Uchic for carrying out this preparation.

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(26) B. V. Ioffe and T. H. Yang, *Zh. Obshch. Khim.*, **33**, 2196 (1963).

(27) R. M. Roberts and D. Shiengthong, *J. Amer. Chem. Soc.*, **86**, 2851 (1964).

(28) We wish to thank Professor R. M. Roberts for kindly supplying the spectrum of isopropylmesitylene.

(29) C. E. Welsh and G. F. Hennion, *ibid.*, **63**, 2603 (1941).

(30) C. F. H. Allen in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 3.

(31) Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946).

(32) D. Nightingale and B. Carton, Jr., *ibid.*, **62**, 280 (1940).

(33) G. Marino and H. C. Brown, *ibid.*, **81**, 5929 (1959).

(34) H. Hibbert, *ibid.*, **37**, 1748 (1915).

it was found that addition of about 1 g of hydroquinone to the crude alcohol and washing the dehydrated product with dilute sodium hydroxide improved the yield somewhat, while decreasing the amount of high-boiling residue. The olefin (124 g) was hydrogenated on a Parr low-pressure apparatus with 10% palladium on charcoal (0.5 g) to yield 4-isopropyl-*m*-xylene, bp 72–75° (7–7.4 mm) (81% yield).

***p*-Cyclohexyltoluene.**—A modification of a published procedure was used[35] (dehydration was accomplished with iodine as described in the preceding section).

***p*-Chlorocumene.**—Synthesis from *p*-chloroacetophenone was accomplished by an adaptation of the method of Benkeser and coworkers[36] (dehydration was performed with iodine; see 4-isopropyl-*m*-xylene).

3-(*p*-Tolyl)pentane.—The sequence involved reaction of 3-pentanone with the Grignard reagent from *p*-bromotoluene, dehydration of the carbinol with iodine (see 4-isopropyl-*m*-xylene), and subsequent hydrogenation of the olefin. The product boiled at 83–85° (8.5 mm) (lit.[37] bp 205°).

2-(*p*-Tolyl)pentane.—The method was identical with that for 3-(*p*-tolyl)pentane, except that 2-pentanone was used. The intermediate alcohol was collected by glpc.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.92; H, 10.08.

Examination of the nmr spectrum revealed the indicated signals: Ar**H**, δ 6.9–7.35 (two doublets); ArC**H**, 2.29 (singlet); O**H**, 2.03 (broad singlet); C–C**H**, 1.43 (singlet superimposed on a complex pattern at 0.78–1.67). The end product was obtained in 60% over-all yield, bp 80–83° (7.5–7.8 mm) [lit.[38] bp 70.5–72° (4 mm)].

1-(*p*-Tolyl)-2-methylbutane.—The synthesis was accomplished from α-chloro-*p*-xylene and 2-butanone by means of a slightly modified published procedure.[39] Dehydration of the intermediate 1-(*p*-tolyl)-2-methyl-2-butanol with boric acid was incomplete after 17 hr at reflux. The olefin was isolated by distillation, bp 94–96° (7.5 mm) [lit.[39] bp 102–104° (13 mm)], and then hydrogenated with palladium catalyst to give the desired material, bp 90–91° (7.8 mm) [lit.[39] bp 92.5° (12.5 mm)].

This material was used for characterization (glpc retention time) of the corresponding substance present in the neutral layer from amination of 3-(*p*-tolyl)pentane.

2-Chloro-1,4-diisopropylbenzene.—Chlorine was passed into a solution of *p*-diisopropylbenzene in carbon tetrachloride at 10–15° in the presence of a small amount of powdered iron catalyst. The reaction was terminated when about 90% of the hydrocarbon was consumed (glpc analysis). Work-up, according to a published procedure[40] for bromination of triethylbenzene, afforded the desired compound in 51% yield, bp 100–104° (6.9 mm) [lit.[41] (impure material) bp 131–135° (35 mm)]. Our product contained about 5% impurity.

4-Chloro-4′-isopropylbiphenyl.—Methylmagnesium iodide was prepared from magnesium (8.75 g, 0.36 mol) and methyl iodide (22.42 ml, 0.36 mol) in 400 ml of anhydrous ether. Then a solution of 4-chloro-4′-acetylbiphenyl[42] (81 g, 0.351 mol) in 250 ml of warm benzene was added during 1 hr. After 0.5 hr at reflux, the mixture was poured over dilute hydrochloric acid with stirring. The solid which separated together with that obtained by evaporation of the organic liquid phase was recrystallized from 95% ethanol to give 70.3 g (81% yield) of the carbinol, mp 130–133° (not further purified).

The alcohol was dissolved in benzene, and gaseous hydrogen chloride was passed into the solution for 0.5 hr. After work-up and removal of the solvent, the crude product was dissolved in ligroin. Filtration and solvent evaporation gave the chloride, mp 98–100° dec (not further purified). A mixture of the chloride with excess pyridine was refluxed for 10 min. The hot solution was poured into water, and the resulting solid was collected by filtration. Purification, including repeated recrystallization from heptane, afforded 4-chloro-4′-isopropenylbiphenyl, mp 147–148°.

Anal. Calcd for $C_{15}H_{13}Cl$: 78.77; H, 5.73; Cl, 15.50. Found: C, 78.60; H, 5.75; Cl, 15.36.

Hydrogenation was accomplished on small portions of the olefin (10–15 g) in benzene (350 ml) with 10% palladium on charcoal (0.1 g). Work-up gave 4-chloro-4′-isopropylbiphenyl (88% yield from the chloride), mp 135–137° from ethanol.

Anal. Calcd for $C_{15}H_{15}Cl$: C, 78.08; H, 6.55; Cl, 15.36. Found: C, 77.85; H, 6.40; Cl, 15.36.

***p*-Isopropylanisole.**—Alkylation of *p*-isopropylphenol,[43] with methyl sulfate was carried out according to a literature procedure.[44]

N,N-Dichloro-8-amino-*p*-cymene.—To a stirred suspension of "HTH" (70% calcium hypochlorite, 6.21 g, 0.03 mol) in methylene chloride (30 ml) and water (20 ml) cooled to −5° was added over a period of 15 min a solution of 8-amino-*p*-cymene (4 g, 0.027 mol) in water (100 ml) and concentrated hydrochloric acid (33 ml, 0.04 mol). The mixture was stirred at −10° for 15 min; the organic layer was separated, washed three times with water, and then dried. Iodometric titration indicated a 50% yield. No N–H band[45] was present in the ir spectrum.

2-Chloro-8-amino-*p*-cymene. Preparation.—A published procedure was followed.[9]

Reductive Deamination.—The method[46] of Nickon and Hill yielded a mixture. One component (20%) was 2-chloro-*p*-cymene which was identified by glpc comparison with authentic material[9] prepared by iodine-catalyzed chlorination of *p*-cymene. The major product (80%), apparently 3-chloro-4-methyl-α-methylstyrene, gave a positive test with bromine.

Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.11; H, 6.60; Cl, 21.29. Found: C, 72.01; H, 6.40; Cl, 21.42.

The nmr spectrum possessed the indicated characteristics: Ar**H**, δ 6.53–6.81 (multiplet); C=C**H**, 4.48 and 4.76 (singlets); ArC**H**, 1.92 (singlet); C=C—C**H**, 1.66 (singlet).

Registry No.—Trichloramine, 10025-85-1; aluminum chloride, 7446-70-0; *t*-butyl bromide, 507-19-7; 4-chloro-4′-isopropenylbiphenyl, 17790-60-2; 4-chloro-4′-isopropylbiphenyl, 17790-61-3; 3-chloro-4-methyl-α-methylstyrene, 17790-62-4.

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