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# 8-AMINO-*p*-CYMENE FROM *p*-CYMENE-TRICHLORAMINE–ALUMINUM CHLORIDE-t-BUTYL HALIDE

## SYNTHETIC AND THEORETICAL ASPECTS[1]

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**Abstract**—*p*-Cymene was aminated on the isopropyl side-chain with trichloramine aluminum chloride-t-butyl halide. At optimum conditions (*p*-cymene : trichloramine : aluminum chloride : t-butyl bromide = 1·0:1·0:0·2:0·3; 0–10°), 8-amino-*p*-cymene was obtained in 80% yield. Changes in temperature resulted in slightly lower yields. A 10-fold molar excess of *p*-cymene was required for best results. The indicated activity was found for various catalysts, aluminum chloride > aluminum bromide ≫ titanium tetrachloride. The efficiency of the t-alkyl halide additive was in the order, t-butyl bromide > t-butyl chloride. Isopropyl bromide was ineffective. The yield of 8-amino-*p*-cymene passed through a maximum with rising concentration of the t-alkyl halide. Concerning the mechanistic aspects, a hydride transfer is postulated in which the carbonium ion generated from the t-alkyl halide abstracts α-isopropyl hydrogen. The resulting *p*-methyl-α,α-dimethylbenzyl cation then reacts with a nitrogen-containing nucleophile to form the amine eventually. In the process isobutane was produced from the t-butyl halide.

IN A related study,[3] investigation of the *p*-cymene–trichloramine–aluminum chloride system showed that a mixture of bases was formed, including nuclear types and 8-amino-*p*-cymene [2-amino-2(4-methylphenyl) propane or *p*-methyl-α,α-dimethylbenzylamine]. Since the side-chain amine belongs to a class of t-carbinamines which can be obtained only by multistep procedures according to prior techniques, we were eager to pursue this intriguing lead. The present report[4] is concerned with development of the method into a useful synthetic procedure and with an appraisal of the theoretical aspects.

### RESULTS AND DISCUSSION

Under the appropriate conditions, 8-amino-*p*-cymene can be formed in high yield from *p*-cymene–trichloramine–aluminum chloride. Since addition of a t-alkyl halide was found to exert a profound favorable influence, the four component system was used as a basis for the investigation of reaction variables.

Optimum conditions for production of the side-chain amine (80% yield) comprised use of the reactants, *p*-cymene, trichloramine, aluminum chloride, and t-butyl bromide (1/0·1/0·2/0·3 molar ratio) in ethylene dichloride at 0–10° (Table 1). Slightly lower yields of the desired base were observed at −25 to −35° and at 25 to 35° (Table 2). Yield decreased when the molar ratio of *p*-cymene to trichloramine was less

[1] Paper VIII, Chemistry of N-Halamines.

[2] From the Ph.D. Thesis (1966) of R. J. Hopper.

[3] P. Kovacic and R. J. Hopper, *Tetrahedron* **23**, 3965 (1967).

[4] For a preliminary account see P. Kovacic, R. J. Hopper, S. S. Chaudhary, J. A. Levisky and V. A. Liepkalns, *Chem. Comm.* **8**, 232 (1966).

TABLE 1. EFFECT OF t-BUTYL BROMIDE[a]

| t-$C_4H_9Br$, moles | Yield, % Total | Basic product[b] Product Distribution, mole % 8-APC | 8-APC | 2-APC | 3-APC | 5-AMC | Toluidine meta | para | Residue, wt. % |
|---|---|---|---|---|---|---|---|---|---|
| 0[c] | 36 | 12 | 33 | 16 | 19 | 23 | 6 | 3 | 13 |
| 0·15[d] | 41 | 35 | 83 | 5 | 7 | 4 | 1 | 0 | 10 |
| 0·3[e] | 53 | 52 | 98 | — | — | –2– | — | — | 4 |
| 0·3[e,f] | 70 | 68 | 97 | | – | | – | – | – |
| 0·3[d] | 76 | 74 | 97 | — | — | —3 | — | — | 10 |
| 0·3[f] | 81 | 80 | 98 | — | — | 2 | — | — | 7 |
| 0·3[f,g] | 81 | 80 | 98 | — | — | —2 | — | — | 7 |
| 0·45[f] | 77 | 76 | 98 | — | — | -2- | — | — | 9 |

[a] $NCl_3$, 0·1 mole in ca. 160 ml of ethylene dichloride; $AlCl_3$, 0·2 mole; *p*-cymene, 1 mole; 0–10°; $NCl_3$ add'n time, 45 min; total reaction time, 90 min.

[b] APC = amino-*p*-cymene, AMC = amino-*m*-cymene.

[c] General procedure A.

[d] General procedure B1.

[e] 3 × scale.

[f] General procedure B2.

[g] $NCl_3$ in 136 ml of methylene chloride.

TABLE 2. EFFECT OF TEMPERATURE VARIATION WITH ADDED t-BUTYL BROMIDE[a]

| Temp, °C | Yield, % Total | Basic product[b] Product Distribution, mole % 8-APC | 8-APC | Other | Residue, wt. % |
|---|---|---|---|---|---|
| −30 ± 5 | 71 | 70 | 99 | 1 | 8 |
| 0–10 | 77 | 76 | 98 | 2 | 9 |
| 25–35 | 75 | 68 | 90 | 10 | 15 |

[a] $NCl_3$, 0·1 mole in ca. 160 ml of ethylene dichloride; $AlCl_3$, 0·2 mole; *p*-cymene, 1 mole; t-$C_4H_9Br$, 0·45 mole; $NCl_3$ add'n time, 45 min; total reaction time, 90 min; general procedure B2.

[b] 8-APC = 8-amino-*p*-cymene.

than 10:1 (Table 3). Variation in the catalyst (Table 4) showed aluminum chloride to be the most effective, followed by aluminum bromide. Titanium tetrachloride demonstrated only weak activity. Antimony pentachloride was found unsuitable because of an immediate reaction with *p*-cymene characterized by evolution of hydrogen chloride. This metal halide is known to function as an avid chlorinating agent for aromatic compounds.[5] Amination did not proceed with sulfuric acid or in

[5] P. Kovacic and A. K. Sparks, *J. Am. Chem. Soc.* **82**, 5740 (1960)

the absence of a catalyst. Of several alkyl halides (t-butyl bromide, t-butyl chloride and isopropyl bromide), t-butyl bromide proved to be the additive of choice (Tables 1, 5 and 6). We selected the 0·3 or 0·45 molar level after examining the effect of alteration in the concentration of the preferred alkyl halide. The t-butyl halides caused a dramatic increase in both the yield of crude basic product and the relative amount of 8-amino-*p*-cymene. Methylene chloride also functioned satisfactorily as the solvent (Table 1).

TABLE 3. EFFECT OF VARIATION IN *p*-CYMENE CONCENTRATION[a]

| *p*-Cymene, moles | Basic Product[b] Yield, % Total | 8-APC | 8-APC, mole % | Residue, wt. % |
|---|---|---|---|---|
| 0·5 | 59 | 56 | 95 | 12 |
| 0·7 | 66 | 63 | 96 | 10 |
| 1·0 | 81 | 80 | 98 | 7 |
| 1·5 | 80 | 79 | 98 | 10 |

[a] $NCl_3$, 0·1 mole in ca. 160 ml of ethylene dichloride; $AlCl_3$, 0·2 mole; t-$C_4H_9Br$, 0·3 mole; 0–10°; $NCl_3$ add'n time, 45 min; total reaction time, 90 min; general procedure B2.

[b] 8-APC = 8-amino-*p*-cymene.

TABLE 4. EFFECT OF VARIATION IN CATALYST[a]

| Catalyst | t-$C_4H_9X$, X | Basic product[b] Yield, % Total | 8-APC, | 8-APC, mole, % | Residue, % |
|---|---|---|---|---|---|
| none[c] | Cl | 0[d] | 0 | 0 | 0 |
| $H_2SO_4$[c,e] | none | 0 | 0 | 0 | trace |
| $AlCl_3$ | Br | 81 | 80 | 98 | 7 |
| $AlBr_3$ | Br | 53 | 52 | 98 | 8 |
| $TiCl_4$ | Br | 11 | 11 | 96 | 10 |

[a] $NCl_3$, 0·1 mole in ca. 160 ml of ethylene dichloride; catalyst, 0·2 mole; *p*-cymene, 1 mole; t-$C_4H_9Cl$, 0·2 mole; t-$C_4H_9Br$, 0·3 mole; 0–10°, $NCl_3$ add'n time, 45 min; total reaction time, 90 min; general procedure B2.

[b] 8-APC = 8-amino-*p*-cymene.

[c] General procedure A.

[d] 5% loss in active chlorine (iodometric titration) during 90 min.

[e] $NCl_3$ in 215 ml of *o*-$C_6H_4Cl_2$.

A problem was presented by formation during reaction of large quantities of hydrogen halide derived from the halamine and alkyl halide precursors. The acid caused a decrease in yield of 8-amino-*p*-cymene, particularly when t-butyl bromide

was incorporated into the reaction mixture. Presumably the adverse effect arises from the decomposing action of hydrogen halide upon trichloramine.[6] Fortunately, the difficulty could be largely circumvented by addition of trichloramine below the surface and efficient purging of the deleterious gas (resulting in yield enhancement from 53 to 76%). Increasing the reaction scale produced a decrease in yield from 80 to 70%, probably a reflection of less efficient removal of hydrogen bromide.

TABLE 5. EFFECT OF t-BUTYL CHLORIDE[a]

| | | | Basic product[b] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Product distribution, mole % | | | | | | |
| t-$C_4H_9Cl$, mole | Yield, % Total | 8-APC | 8-APC | 2-APC | 3-APC | 5-AMC | Toluidine meta | Toluidine para | Residue, wt % |
| 0 | 36 | 12 | 33 | 16 | 19 | 23 | 6 | 3 | 13 |
| 0·05 | 41 | 26 | 63 | 8 | 10 | 15 | 3 | 1 | 3 |
| 0·1 | 51 | 40 | 79 | 5 | 6 | 7 | 2 | 1 | 11 |
| 0·15 | 66 | 57 | 87 | 3 | 3 | 7 | 1 | 1 | 5 |
| 0·2[c] | 66 | 61 | 92 | 3 | 3 | 0 | 2 | | 13 |
| 0·2 | 62 | 56 | 91 | 5 | | 0 | 4 | | 13 |
| 0·2 | 70 | 67 | 96 | 2 | | 0 | 2 | | 16 |
| 0·3 | 54 | 51 | 94 | 1 | | 0 | 5 | | 11 |
| 0·5 | 52 | 49 | 95 | 1 | | 0 | 4 | | 2 |

[a] $NCl_3$, 0·1 mole in ca. 160 ml of ethylene dichloride; $AlCl_3$, 0·2 mole; *p*-cymene, 1 mole; 0–10°; $NCl_3$ add'n time, 45 min; total reaction time, 90 min; general procedure A.

[b] APC = amino-*p*-cymene, AMC = amino-*m*-cymene.

[c] Total reaction time, 6 hr; apparatus flushed with $N_2$ during reaction.

TABLE 6. EFFECT OF ISOPROPYL BROMIDE[a]

| | | | Basic product[b] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Product distribution, mole % | | | | | | |
| Yield, % Total | 8-APC | 8-APC | 2-APC | 3-APC | 5-AMC | Toluidine meta | Toluidine para | | Residue, wt. % |
| 19 | 6 | 33 | 10 | 11 | 37 | | 5 | | 15 |

[a] $NCl_3$, 0·1 mole in ca. 145 ml of ethylene dichloride; $AlCl_3$, 0·2 mole; *p*-cymene, 1 mole; isopropyl bromide, 0·2 mole; 0–10°, $NCl_3$ add'n time, 45 min; total reaction time, 90 min, general procedure B2.

[b] APC = amino-*p*-cymene, AMC = amino-*m*-cymene.

By products included 2- and 3-amino-*p*-cymenes, 5-amino-*m*-cymene, and *m*- and *p*-toluidines. The origin of these amines is treated elsewhere.[3]

With this experimental background, let us now consider the theoretical aspects. Side-chain amination is believed to entail the indicated sequence: formation of the t-butyl cation from t-butyl halide–aluminum chloride, subsequent abstraction of hydride from *p*-cymene, followed by attachment of a nitrogen-containing nucleophile

[6] W. A. Noyes, *J. Am. Chem. Soc.* **42**, 2173 (1920).

to the *p*-methyl-α,α-dimethylbenzyl cation. Since the actual nucleophile which participates is unknown, $NCl_2^-$ is used for simplicity.[7,8]

$$Me_3CX + AlCl_3 \rightleftarrows Me_3C^+AlCl_3X^- \quad (1)$$

$$p\text{-}MeC_6H_4CHMe_2 + Me_3C^+ \rightleftarrows p\text{-}MeC_6H_4\overset{+}{C}Me_2 + Me_3CH \quad (2)$$

I

$$I \xrightarrow{NCl_2^-} p\text{-}MeC_6H_4C(NCl_2)Me_2 \quad (3)$$

II

$$II \xrightarrow[Cl^+]{H^+} p\text{-}MeC_6H_4C(NH_2)Me_2 \quad (4)$$

The reaction scheme is in keeping with a number of the experimental observations: necessity of a catalyst, favorable influence of t-alkyl halides, and ability of the amination to proceed at quite low temperatures. The greater efficiency of t-butyl bromide *vs.* the chloride is very likely due to the more facile generation of the carbonium ion from the bromide. One may offer as evidence the finding that the rate of solvolysis of t-butyl bromide is 39 times that of the chloride in 80% ethanol at 25°.[9a] Also, the yield of 8-amino-*p*-cymene passed through a maximum with increasing quantities of the alkyl halide additive (Tables 1 and 5). Apparently, the t-butyl cation competes to some extent for the N-containing nucleophile as indicated by isolation of t-butylamine (10% yield) from a system containing large amounts of t-butyl chloride (Table 5, entry 9). However, with a low concentration of t-butyl chloride (Table 5, entry 2), no t-butylamine was detected. Recent work in our laboratory demonstrates the ability of trichloramine to convert t-alkyl halides to the corresponding amines under Friedel–Crafts conditions.[8] This type of interference may serve to explain the decrease in yield occasioned by the use of isopropyl bromide. Further compelling evidence for the hydride transfer is in hand. Isobutane, formed in greater than the theoretical molar yield of amine, was found to be a product arising from one of the amination reaction mixtures containing t-butyl chloride.

Several additional aspects associated with the involvement of t-alkyl halide merit consideration. For one thing, the situation is sterically unfavorable for consumption of alkyl halide via catalyzed alkylation of the aromatic nucleus (cf., i-PrBr). Thus, by analogy, *p*-xylene is quite obdurate to nuclear attack by a t-carbonium ion.[10] There are interesting ramifications associated with the equilibrium portrayed in Eq. 2. The equilibrium position would logically be related to stability of the carbonium ions. As a comparative measure of the energy levels, relative rates of solvolysis may be cited. In 90% aqueous acetone at 25°, *p*-tolyldimethylcarbinyl chloride solvolyzes 26 times as fast as phenyldimethylcarbinyl chloride,[11] which in turn undergoes $S_N1$ reaction 620 times faster than t-butyl chloride.[9b] Because of these factors and the evolution of isobutane, the equilibrium should therefore be displaced in favor of the t-benzylic carbonium ion.

[7] P. Kovacic, J. A. Levisky and C. T. Goralski, *J. Am. Chem. Soc.* **88**, 100 (1966).

[8] P. Kovacic and M. K. Lowery, *Chem. Comm.* 651 (1966).

[9] A. Streitwieser, Jr., *Solvolytic Displacement Reactions* [a] p. 82; [b] p. 44. McGraw-Hill, New York, N.Y. (1962).

[10] B. S. Friedman, F. L. Morritz, C. J. Morrisey and R. Koncos, *J. Am. Chem. Soc.* **80**, 5867 (1958); M. J. Schlatter, U.S. Patent 2,801,271 (1957); *Chem. Abstr.* **51**, 18,580 (1957).

[11] L. M. Stock and H. C. Brown in *Advances in Physical Organic Chemistry* (Edited by V. Gold) Vol. 1; p. 86. Academic Press, New York, N.Y. (1963).

The role of carbonium ions as hydride transfer agents, originally proposed by Bartlett, *et al.*[12] has become well established by a host of examples.[13] In their work, the process was observed to occur at a very fast rate.[12] Several literature citations will be made which are closely akin to the present situation.[14] Indane derivatives are formed from two moles of alkylcumene (including *p*-cymene) by exposure to hydrogen fluoride or sulfuric acid in the presence of an olefin. As part of the postulated reaction sequence, the authors suggested hydride abstraction from the side chain by a carbonium ion derived from olefin protonation. When a t-butyl cation, generated from the corresponding olefin or alcohol by hydrogen fluoride or sulfuric acid, reacted with *p*-cymene, 1,1,3,3,5-pentamethylindan was obtained along with isobutane. A mechanism involving reaction of the *p*-cymyl carbonium ion with isobutene was proposed. These data also serve to illustrate the resistance of *p*-cymene to t-butylation.[15]

A large excess of *p*-cymene is necessary because, (a) nuclear chlorination, an important side reaction, theoretically requires three moles of hydrocarbon per mole of trichloramine, and (b) the aromatic substrate acts as a diluent to decrease interaction of the t-butyl cation with the halamine.

In summation of the principal theoretical considerations, the proposed reaction scheme for side-chain amination is consistent with the mass of experimental evidence. Alternative mechanisms, e.g. a free radical pathway, would constitute only remote possibilities. No neutral products indicative of radical precursors were encountered.

Next, we wish to treat the aspect of synthetic utility. The production of 8-amino-*p*-cymene in 80% yield by this novel one-step procedure is by far the most efficient route yet developed. Alternate syntheses for this type of t-carbinamine are characterized by poor availability of starting materials, multistep procedures, and lower yields. In our preparation of the amine by adaptation of a literature route, a 4-step sequence was required.[16-18] The overall yield was only 5–6%, which admittedly might have been enhanced somewhat if optimum conditions were developed. Cope *et al.*[19] have prepared cumylamine from benzyl cyanide in 46% overall yield (3 steps). While this technique could no doubt also be applied to *para*-substituted cumenes, additional steps would be required to obtain the appropriate benzyl cyanide forerunner. Another classical route involves the Ritter reaction with *p*-methyl-α-methylstyrene-acetonitrile-sulfuric acid.[20] According to this method the acetamide derivative of the t-alkyl amine was produced in 39% yield. Hindered amides of this type undergo basic hydrolysis with extreme reluctance.[20] In an acidic environment they decompose to ammonia and olefinic product.[20]

[12] P. D. Bartlett, F. E. Condon and A. Schneider, *J. Am. Chem. Soc.* **66**, 1531 (1944).
[13] N. C. Deno, H. J. Peterson and G. S. Saines, *Chem. Rev.* **60**, 7 (1960).
[14] V. N. Ipatieff, H. Pines and R. C. Olberg, *J. Am. Chem. Soc.* **70**, 2123 (1948); H. Pines, D. R. Strehlau and V. N. Ipatieff, *J. Am. Chem. Soc.* **72**, 1563, 5521 (1950); H. Pines, A. Weizmann and V. N. Ipatieff, *J. Am. Chem. Soc.* **70**, 3859 (1948).
[15] L. R. C. Barclay in *Friedel-Crafts and Related Reactions* (Edited by G. A. Olah) Vol. II; p. 955. Interscience, New York, N.Y. (1964).
[16] F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, *J. Am. Chem. Soc.* **75**, 2705 (1953).
[17] N. Kornblum and H. J. Taylor, *J. Org. Chem.* **28**, 1424 (1963).
[18] N. Kornblum, W. D. Gurowitz, H. O. Larson and D. E. Hardies, *J. Am. Chem. Soc.* **82**, 3099 (1960).
[19] A. C. Cope, T. T. Foster and P. H. Towle, *J. Am. Chem. Soc.* **71**, 3929 (1949).
[20] J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.* **70**, 4045 (1948).

Interesting parallels can be drawn between our method and the Ritter reaction.[20, 21] Both processes involve, (1) a nitrogen-containing nucleophile, (2) preference for attachment to the carbonium ion rather than abstraction of a proton. (3) effectiveness in a highly acidic system, and (4) formation of an amine end-product.

The scope and mechanistic aspects are under further investigation.

## EXPERIMENTAL[22]

*Materials.* The alkyl halides were Eastman white label reagent grade. Other materials are described elsewhere.[3]

*Analytical procedures.* The preceding paper should be consulted[3] for these procedures and the yield basis.

*Trichloramine solution.* A published procedure[23] (method B) was used with ethylene dichloride as solvent. Caution: exercise the necessary precautions when working with N-halamines.

*8-Amino-p-cymene from p-cymene trichloramine aluminum chloride–alkyl halide —General procedure*

A. A previous procedure served as the basis.[3] The alkyl halide was introduced, following the $AlCl_3$, as rapidly as possible within the desired temp range. Little change in appearance of the mixture occurred with isopropyl bromide. In the case of the t-butyl halides, the contents became very dark red and evolved copious amounts of hydrogen halide during reaction.

B. With alkyl bromide additive the following modifications of the general procedure were employed.

1. The apparatus was equipped with a gas inlet and outlet, and a fairly rapid stream of dry $N_2$ was swept across the surface throughout the reaction. The dropping funnel was equipped with an extension for introduction of trichloramine below the surface of the reaction mixture

2. The reaction was carried out as in B1 except that during work-up no attempt was made to cool the aqueous acidic layer during treatment with 50% NaOH aq. The resulting hot mixture was stirred for 1 hr before cooling and extracting with ether.[3]

Studies on variation in the amount of aromatic were performed according to general procedure B2. In the cases where less than 1 mole (157 ml) of *p*-cymene was used, enough ethylene dichloride was added to bring the volume to 157 ml. With variations in the catalyst, general procedure B2 was followed except that $AlCl_3$ was replaced by another catalyst. Aluminum bromide was weighed and added in a dry $N_2$ atm.

An analytical sample of 8-amino-*p*-cymene was obtained by combining the products from several reactions carried out in the absence[3] of alkyl halide and fractionating through a 50-plate spinning band column, b.p. 76–77° 5·2 mm, 83·85° 5·8 mm, 213·215° 745 mm, $n_D^{20}$ 1·5160, $n_D^{25}$ 1·5135. (Found: C, 80·52; H, 10·26; N, 9·32. Calc. for $C_{10}H_{15}N$: C, 80·46; H, 10·15; N, 9·39%.)

The acetamide derivative, prepared from $Ac_2O$, melted at 157·158° subl., lit.[20] m.p. 137–138°.[24] (Found: C, 75·37; H, 8·91; N, 7·38. Calc. for $C_{12}H_{17}ON$: C, 75·34; H, 8·98; N, 7·32%.)

The IR spectrum[25] of the amine pointed to *para*-substitution (strong band at 815, weak band at 721 $cm^{-1}$) and a primary aliphatic amine group (doublet at 3200·3400, bands at 1575 and 1111 $cm^{-1}$, and broad absorbance at 930·760 $cm^{-1}$). The NMR spectrum (TMS internal reference) showed resonance (τ) attributable to amine H (8·76), isopropyl β-H (8·68), methyl H (7·80), and aromatic H (2·5·3·2). The relative intensities were, aromatic H:methyl H:(isopropyl β-H + amine H) = 4:3:8. The absence of the characteristic doublet septet pattern clearly indicates substitution at the α-carbon of the isopropyl group. In addition the amine proton resonance appears in the region expected for aliphatic types.

The product was identical (GLPC retention time, IR and NMR spectra) to authentic 8-amino-*p*-cymene prepared by an alternate route

[21] J. J. Ritter and J. Kalish, *J. Am. Chem. Soc.* **70**, 4048 (1948).

[22] Elemental analyses were performed by Galbraith Laboratories, Nashville, Tenn. M.ps and b.ps are uncorrected.

[23] P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky and R. M. Lange, *J. Am. Chem. Soc.* **87**, 1262 (1965).

[24] We found that this compound sublimed slowly at about 140°, which may explain the low m.p. reported by the previous investigators.

[25] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* pp. 78, 249, 253 and 256. Wiley, New York, N.Y. (1962).

*t-Butylamine.* The work-up procedure of a mixture involving 0·5 mole of t-butyl chloride (Table 5, entry 9) was modified in order to isolate the low-boiling, water-soluble products. 50% NaOH aq was added to the aqueous acid soln in an apparatus consisting of a 2-l., 3-necked flask equipped with a stirrer, simple distillation head, and dropping funnel. The basic solution was distilled to 100°, the distillate treated with conc HCl, and evaporated to dryness leaving a white solid residue. With the exception of several extraneous bands indicative of aromatic amine salt, the IR spectrum of the solid was essentially identical to that of t-butylamine hydrochloride. The free amine was reformed by treatment of the hydrochloride with caustic soln followed by ether extraction to remove selectively any water-insoluble amines from water-soluble t-butylamine. GLPC analysis (procedure E in Table 4 of Ref. 3) of the concentrated ether extract showed a peak having the same retention time as t-butylamine. The aqueous layer was acidified, heated, made basic, and distilled through a 1-ft helices-packed column. About 0·8 g (0·011 mole) of t-butylamine, b.p. 44–48°, lit.[26] b.p. 46°, was collected. The IR spectrum was identical to that of authentic t-butylamine.

When only 0·05 mole of t-butyl chloride was used (Table 5, entry 2) there was no evidence for t-butylamine based on a similar analytical procedure.

*Isobutane.* General procedure B1 was followed for *p*-cymene (Table 5, entry 5) except that a train of traps and drying tubes was connected to the gas outlet. The gases were passed through a cold trap at 0° and bubbled through water in a suction flask equipped with a burette and magnetic stirrer where evolved hydrogen halide was titrated with standard NaOH (phenolphthalein indicator). The gases from the suction flask were passed through a cold trap at 0°, a $CaCl_2$ drying tube, and a cold trap immersed in dry ice-acetone. Titration indicated approximately 0·06 mole of evolved HCl. The liquid in the dry ice-acetone trap was vaporized at 0° into a weighed and calibrated trap also in dry ice-acetone yielding 6·9 g (10·1 ml, 0·12 mole) of isobutane, b.p. −11 to −10°, lit[26] b.p. −11·7°. The IR spectrum, taken in a gas cell was identical to that of authentic isobutane, except for a small band due to ethylene dichloride. GLPC analysis (procedure F in Table 5 of Ref. 3) showed the product to be essentially pure isobutane. The retention time was identical to that of the authentic material. A trace amount of a lower boiling component was also present.

*Authentic 8-amino-p-cymene*

A. *4,4'-Dimethyldiphenyliodonium iodide.* The material was prepared from toluene by a 3 × scale of the published procedure.[16]

B. *4,4'-Dimethyldiphenyliodonium tosylate.* The moist iodide salt from the preceding section (theoretically, 0·28 mole) was converted to the corresponding tosylate by a modification of the procedure of Kornblum and Taylor.[17] Following suspension of the iodide in 420 ml MeOH with vigorous mechanical stirring, $Ag_2O$ (32·5 g) and *p*-toluenesulfonic acid monohydrate (47·6 g) were added. After being stirred overnight, the mixture was filtered and freed of MeOH under vacuum at room temp. The residue was dissolved in 200 ml $CHCl_3$ and washed with 5% NaOH aq until the washings remained basic. A fine black ppt formed which could not be entirely removed by filtration. The organic layer was washed twice with water, dried over $Na_2SO_4$, and freed of $CHCl_3$ with a vacuum evaporator, leaving a yellow–orange syrup.

This residue was dissolved in acetonitrile and evaporated in vacuum. The soln became quite cold during the evaporation, eventually crystallizing with difficulty into a solid mass which was mulled with a few ml of acetonitrile and filtered. The filtrate was recovered and subjected twice more to the crystallization procedure. Combination of the solids gave 23·8 g (0·05 mole, 18% based on toluene) of cream-colored powder, m.p. 153–160° dec. A small amount was recrystallized four times from acetonitrile, grey-white crystals, m.p. 170–177° dec. (Found: C, 52·00; H, 4·79; S, 6·56. Calc. for $C_{21}H_{21}O_3SI$: C, 52·30; H, 4·41; S, 6·67%.)

C. *8-Nitro-p-cymene.* A modification of a published procedure[17] was employed with the Na-salt of 2-nitropropane (2·5 g, 0·0245 mole) and the crude tosylate (12 g, ca. 0·025 mole). The crude product was obtained as a yellow liquid (6·5 g).

D. *8-Amino-p-cymene.* Reduction of the crude 8-nitro-*p*-cymene was performed by a method similar to that used for α-phenylnitroethane.[18] The nitro body was treated with acid-washed iron filings in AcOH for 3 hr at steam bath temp. Work-up provided the crude amine which was purified by distillation through an unpacked 3 in. column, b.p. 75–78° 5·2 mm, $n_D^{20}$ 1·5159.

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[26] R. C. Weast, ed., *Tables for Identification of Organic Compounds* 2nd Edition (Edited by R. C. Weast). The Chemical Rubber Co., Cleveland, Ohio (1964).