The Base-Promoted Rearrangements of α-Arylneopentylammonium Salts

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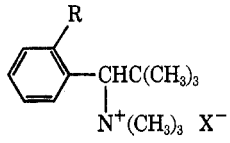
The base-promoted reactions of *N,N,N*-trimethyl-α-phenylneopentylammonium halides (**1a**) and *N,N,N*-trimethyl-α-*o*-tolylneopentylammonium iodide (**1b**) with numerous base–solvent systems lead to products of the Stevens **3**, ortho-Sommelet–Hauser **5**, and para-Sommelet–Hauser **6** rearrangements in addition to the demethylated tertiary amine **9**. The Stevens rearrangement is favored in nonpolar solvents and at increased temperatures, the solvent dependence being quite marked for **1a**. Increasing base concentration favors the ortho rearrangement at the expense of the Stevens and para products. The observation of nonbasic side products is considered. It is suggested that the ortho rearrangement may proceed by a mechanism different from the Stevens and para rearrangements.

As a continuation of our interest in the chemistry of quaternary ammonium salts,[1] we have investigated the base-promoted rearrangements of two series of compounds, *N,N,N*-trimethyl-α-phenylneopentylammonium iodide and chloride (**1a**) and *N,N,N*-trimethyl-α-*o*-tolylneopentylammonium iodide (**1b**). These molecules are the potential precursors for products of the Stevens[2] and Sommelet–Hauser[3] rearrangements with both pathways expected to occur. Scheme I illustrates the nitrogen ylides presumed to be involved and all of the potential products of these rearrangements.



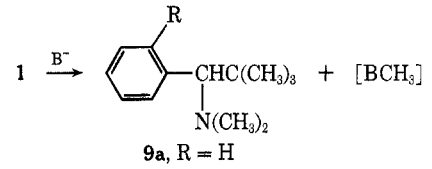
1a, R = H
b, R = CH_3

Both compounds are quite hindered sterically[4] and the influence of this on possible rearrangement pathways is of interest.[5] In addition, the effect of solvent and temperature on competing Stevens and Sommelet–Hauser (ortho) rearrangements is considered along with the total question of the reaction mechanism.

Results and Discussion

Quaternary ammonium salts **1** were allowed to react with various base–solvent systems in sealed tubes under nitrogen. A reaction (*n*-butyllithium–hexane) which was carefully degassed and sealed under vacuum gave identical results with the typical runs under nitrogen. Similarly, an air purge of the reaction tube did not appreciably affect the rearrangement products. Products were analyzed by gas chromatography and positive identification of each rearrangement product was accomplished through comparison with independently synthesized material. Tables I and II indicate representative results for the two systems.

α-Phenyl System.—The influence of solvent on the course of the rearrangements of **1a** is illustrated by the results listed in Table I. It is seen that the polar "aprotic" solvents ammonia (NH_3), dimethyl sulfoxide (DMSO), and hexamethylphosphortriamide (HMPT) favor the ortho rearrangement product **5a**, while the nonpolar solvent, hexane, leads predominately to the Stevens rearrangement product **3a**. If one compares only the relative yields of the rearrangement products (Table III), this trend is quite apparent. Although the low temperature may be a factor in the ammonia solvent,[6] a similar trend has been observed with the benzyltrimethylammonium salts.[7] Interestingly, DMSO appears to favor formation of the demethylated tertiary amine **9a**, presumably through a displacement reaction. This is consistent with the well-established enhancement of nucleophilic reactivity in DMSO.[8,9] Similarly, the predominant formation of **9a** with alkoxide in alcohol is consistent with the inability of the relatively weak basic species to form the requisite ylide. In the case of potassium *tert*-butoxide as base, *tert*-butyl methyl ether has been found as a product.



9a, R = H
b, R = CH_3

The Stevens rearrangement products **4** and **8** have not been detected in these reactions. The methyl-to-methyl carbanion migration required for the formation of **4** has been observed in only a few cases,[5,11] although methyl migration to a benzyl carbanion is often found.[7b,c] The absence of **8** is not surprising from a steric viewpoint. Formation of ylide **7** from **1** is sterically inhibited and **8** is considerably more crowded than the rearrangement products observed. We have found little or no analogous rearrangement product in the less crowded neopentylammonium system.[5]

(1) S. H. Pine, *Org. React.*, **18**, 403 (1970).
(2) T. S. Stevens, E. M. Creighton, A. B. Gordon, and M. McNicol, *J. Chem. Soc.*, 3139 (1928).
(3) (a) M. Sommelet, *C. R. Acad. Sci.*, **205**, 56 (1937); (b) S. W. Kantor and C. R. Hauser, *J. Amer. Chem. Soc.*, **73**, 4122 (1951); (c) S. H. Pine, *Tetrahedron Lett.*, 3393 (1967).
(4) H. C. Brown and W. H. Bonner, *J. Amer. Chem. Soc.*, **75**, 14 (1953).
(5) S. H. Pine, B. A. Catto, and F. G. Yamagishi, *J. Org. Chem.*, **35**, 3663 (1970).
(6) (a) H. E. Zimmerman in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 387; (b) C. R. Bumgardner, private communication.
(7) (a) K. P. Klein and C. R. Hauser, *J. Org. Chem.*, **31**, 4276 (1966); (b) K. P. Klein, D. N. Van Eenam, and C. R. Hauser, *ibid.*, **32**, 1155 (1967); (c) A. R. Lepley and R. H. Becker, *ibid.*, **30**, 3888 (1965).
(8) D. Martin, A. Weise, and H.-J. Niclas, *Angew. Chem., Int. Ed. Engl.*, **6**, 318 (1967).
(9) Control runs without base present provide only **9a** as product but in very low yield (<0.5%). Interestingly, the thermal decomposition of **1a** *at its melting point* leads principally to α-phenylneopentyl chloride or iodide.[10]
(10) S. H. Pine and E. M. Munemo, unpublished results.
(11) (a) H. Daniel and J. Paetsch, *Chem. Ber.*, **101**, 1445 (1968); (b) G. Wittig and D. Krauss, *Justus Liebigs Ann. Chem.*, **679**, 34 (1964); (c) W. K. Musker, *J. Org. Chem.*, **32**, 3189 (1967).

SCHEME I

POTENTIAL STEVENS AND SOMMELET-HAUSER REARRANGEMENT PATHWAYS FOR α-ARYLNEOPENTYLAMMONIUM SALTS

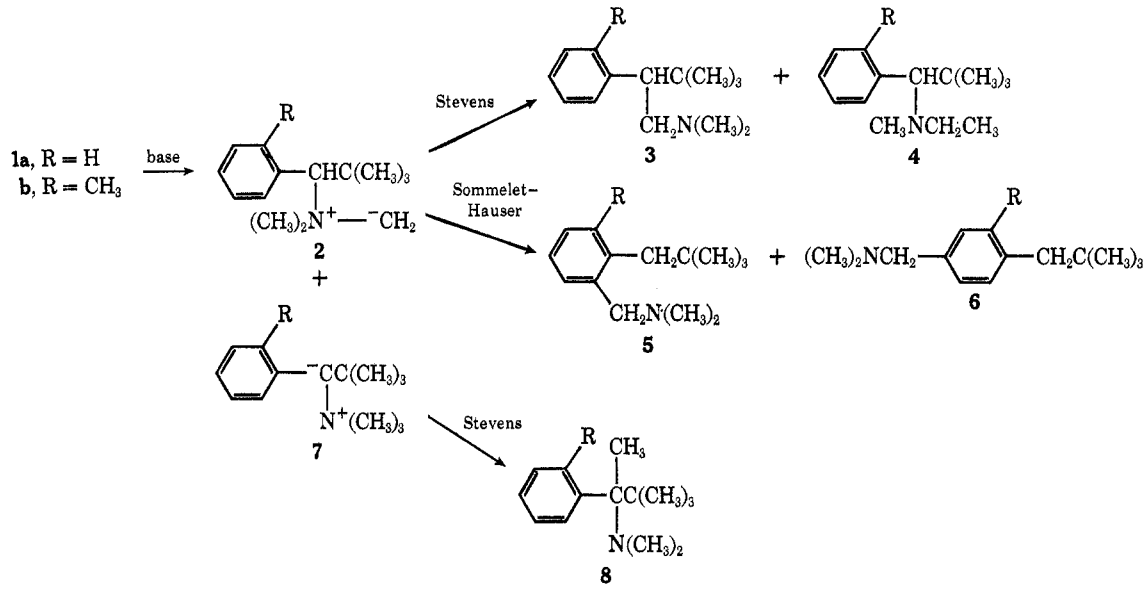


TABLE I

BASIC REACTION PRODUCTS FROM *N,N,N*-TRIMETHYL-α-PHENYLNEOPENTYLAMMONIUM CHLORIDE (1a)

Run	Solvent	Base[a]	T, °C	Time, hr	9a	5a	3a	6a	Yield,[b] %
1[c]	NH_3	$NaNH_2$	−33	6	6.0	81	12	0.8	75
2	DMSO	LiDMSO	51	47	49	31	18	1.2	
3	HMPT	$NaNH_2$	25	6	2.0	60	35	3.0	65
4	HMPT–hexane[d]	*n*-BuLi	25	6	1.5	63	32	3.5	
5	Hexane	*n*-BuLi	51	47	1.1	13	80	5.9	73
6	*tert*-BuOH	*tert*-BuOK	51	47	97	1.5	1.7	0.3	68
7	MeOH	MeOK	90	41	100				10

[a] Moles of base/mole of salt = 2, except run 7 (moles of base/mole of salt = 1.3). [b] Yield of total basic material assuming molecular weight of rearrangements products. [c] Iodide salt. No appreciable differences in products were observed over numerous runs in various systems with change of halide anion. [d] 85% HMPT–15% hexane.

TABLE II

BASIC REACTION PRODUCTS FROM *N,N,N*-TRIMETHYL-α-*o*-TOLYLNEOPENTYLAMMONIUM IODIDE (1b)

Run	Solvent	Base[a]	T, °C	Time, hr	9b	5b	3b	6b	Yield,[b] %
8	NH_3	$NaNH_2$	−33	6	1.4	32	63	3.7	70
9	DMSO	LiDMSO	80	46	74	2.0	20	4.5	32
10	DMSO–hexane[c]	LiDMSO	70	46	51	4.0	40	5.0	58
11	HMPT–hexane[d]	*n*-BuLi	71	48	5.1	31	60	3.6	79
12	Hexane	*n*-BuLi	83	43	7.5	6.6	73	13	54

[a] Moles of base/mole of salt = 2. [b] Yield of total basic material assuming molecular weight of rearrangements products. [c] 80% DMSO–20% hexane. [d] 75% HMPT–25% hexane.

TABLE III

RELATIVE YIELDS OF REARRANGEMENT PRODUCTS FROM *N,N,N*-TRIMETHYL-α-PHENYLNEOPENTYLAMMONIUM CHLORIDE (1a)

Run	Solvent	Base	5a	3a	6a
1	NH_3	$NaNH_2$	86	13	0.9
2	DMSO	LiDMSO	62	36	2.4
3	HMPT	$NaNH_2$	61	36	3.1
5	Hexane	*n*-BuLi	13	81	6.0

TABLE IV

INFLUENCE OF TEMPERATURE ON BASIC PRODUCT FORMATION FROM *N,N,N*-TRIMETHYL-α-PHENYLNEOPENTYLAMMONIUM IODIDE (1a)

Run[a]	T, °C	9a	5a	3a	6a	Yield,[b] %
13	−30	92	3.4	4.6	0.6	5
14	24	81	3.5	15	1.1	6
15	65	30	7.2	61	1.6	20

[a] All runs using *n*-BuLi in hexane with moles of base/mole of salt = 1; reaction time, 6 hr. [b] Yield of total basic materials.

The influence of temperature is illustrated (Table IV) by a series of reactions carried out under identical conditions in hexane, but at different temperatures. As the temperature is increased, rearrangements predominate over displacement. This result is similar to the increase in elimination reactions relative to displacement with increasing reaction temperature.[12] As has been noted in other systems, the Stevens rearrangement increases markedly with temperature.[6a]

(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 460.

α-Tolyl System.—The results shown in Table II indicate that the formation of tertiary amine **9b** is notably enhanced in the more hindered salt **1b**. Relief of strain through demethylation appears to be an important controlling factor.

In contrast to the α-phenyl salt **1a**, the rearrangements of **1b** all lead principally to the Stevens product **3b** (Table V). The decrease in Sommelet–Hauser re-

TABLE V

RELATIVE YIELDS OF REARRANGEMENT PRODUCTS FROM *N,N,N*-TRIMETHYL-α-*o*-TOLYLNEOPENTYLAMMONIUM IODIDE (**1b**)

Run	Solvent	Base	5b	3b	6b
8	NH_3	$NaNH_2$	32	64	3.7
9	DMSO	LiDMSO	7.6	76	17
11	HMPT–hexane	*n*-BuLi	33	63	3.8
12	Hexane	*n*-BuLi	7.1	79	14

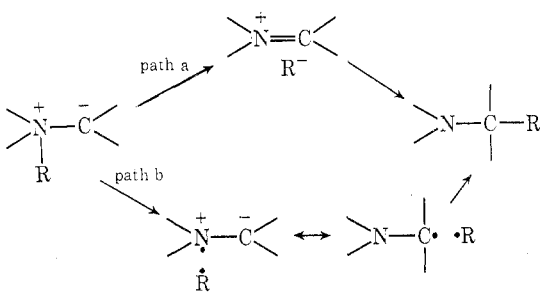
arrangement product **5b** cannot be accounted for by the statistical loss of one potential ortho rearrangement terminus. The data suggest that the increased crowding of the molecule inhibits the ortho rearrangement pathway, a result which may be related to the question of a concerted *vs.* a dissociation–recombination mechanism (see below).

Although the solvent effect trend of Sommelet–Hauser *vs.* Stevens rearrangements is in the same order as found for **1a**, the variation is much less. In addition, the novel para Sommelet–Hauser rearrangement product **6b** is quite significant in most of the base–solvent systems investigated.

Reaction Mechanism.—The question of the mechanism of base-promoted rearrangements of quaternary ammonium salts has been under active investigation in recent years.[1,13] The symmetry-forbidden[14] SNi pathway[15] has been discarded for the Stevens rearrangement in favor of a dissociation–recombination mechanism involving an ion pair (Scheme II, path a) or a radical pair (Scheme II, path b). The ortho Sommelet–Hauser re-

SCHEME II

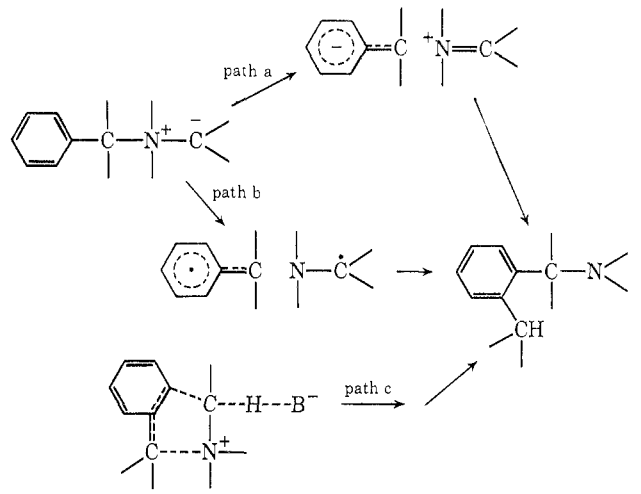
ION-PAIR AND RADICAL-PAIR PATHWAYS FOR STEVENS REARRANGEMENT



arrangement could also proceed *via* pathways involving an ion pair (Scheme III, path a) or radical pair (Scheme III, path b). In addition, the allylic nature of the rearrangement provides for a symmetry-allowed [2,3]-sig-

SCHEME III

ION-PAIR, RADICAL-PAIR, AND CONCERTED PATHWAYS FOR SOMMELET–HAUSER REARRANGEMENT



matropric rearrangement pathway (Scheme III, path c). The para rearrangement cannot be obtained by the concerted pathway.[3c]

Lepley[7c] had observed some base dependence in the ortho rearrangement and suggested that this supported the concerted pathway (Scheme III, path c), while the Stevens rearrangement might be better explained by a different mechanism. We have also observed such a base dependence in the rearrangements of **1a** using potassium *tert*-butoxide in cyclohexene (Table VI).

TABLE VI

INFLUENCE OF BASE CONCENTRATION ON PRODUCT FORMATION FROM *N,N,N*-TRIMETHYL-α-PHENYLNEOPENTYLAMMONIUM CHLORIDE (**1a**)

Run[a]	Mol of base/mol of salt	9a	5a	3a	6a
16	1.1	19	25	47	9
17	2.2	25	48	25	5

[a] Runs using *tert*-BuOK in cyclohexene at 87°.

When the base concentration is doubled, the ortho rearrangement product **5a** increases markedly at the apparent expense of the Stevens product **3a**. As expected, the displacement product **9a** also increases with base as does the *tert*-butyl methyl ether observed. Interestingly, the para rearrangement product **6a** decreases with increasing base concentration as does the Stevens product **3a**. This suggests that **3a** and **6a** may be formed through a common intermediate while the pathway to **5a** differs. Since it is unlikely that a concerted mechanism leads to the para product **6a**,[3c] a dissociation–recombination mechanism is favored. Very recently Baldwin, *et al.*,[16] have suggested that the Stevens rearrangement proceeds *via* a radical pathway (Scheme II, path b), while the ortho rearrangements involve the concerted mechanism (Scheme III, path c). They believe that this will account for the temperature dependence of the competing rearrangements.

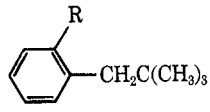
(13) (a) E. F. Jenny and J. Druey, *Angew. Chem., Int. Ed. Engl.*, **1**, 155 (1962); (b) A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 1237 (1969); (c) U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Lett.*, 3415 (1969).

(14) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 131.

(15) (a) C. R. Hauser and S. W. Kantor, *J. Amer. Chem. Soc.*, **73**, 1437 (1951); (b) J. H. Brewster and M. W. Kline, *ibid.*, **74**, 5179 (1952).

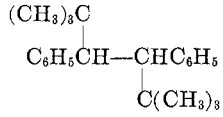
(16) J. E. Baldwin, J. E. Brown, and R. W. Cordell, *Chem. Commun.*, 31 (1970).

In the rearrangements of **1a** and **1b**, small amounts of the hydrocarbons **10** have been isolated. These products can be attributed to collapse of either the ion-pair



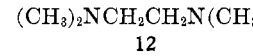
10a, R = H
b, R = CH_3

(Schemes II and III, path a)[3c] or the radical-pair (Schemes II and III, path b) intermediates with solvent. In the case of **1a**, another hydrocarbon has been identified as the dimer **11**.[17] This product suggests the pres-



11

ence of at least some radical intermediate. The other expected dimer from such a radical pathway, tetramethylethylenediamine **12**, has not been detected.[18]



12

In an attempt to favor formation of the dimer **11**, **1a** was allowed to react with sodium in ammonia. No evidence for **11** was found, **10a** being the only nonbasic product. Small amounts of rearrangement products obtained in this case are presumably due to the presence of some sodium amide.[19]

The dimer **11** has been shown not to come from a secondary reaction of **10a**, although it is apparently produced in low yield from α-phenylneopentyl chloride using *n*-butyllithium in hexane under typical reaction conditions.[20]

The marked solvent dependence in the rearrangements of **1a** seems inconsistent with a radical pathway. However, the direction of the effect (Stevens rearrangement favored in less polar solvents) is opposite to what might have been expected for an ionic mechanism.

It is clear that an answer to the mechanistic questions posed is not at hand. The data presented here do suggest that the Stevens and ortho Sommelet–Hauser reactions may proceed by different mechanistic pathways. The high stereospecificity[15b] found in related systems suggests that these rearrangements may proceed *via* a tight cage intermediate[21] whether it be ion pair or radical pair. We are continuing our studies in this area.

Structural Assignments.—All of the rearrangement products detected were independently synthesized for final structure proof. Scheme IV outlines the synthetic sequences. Although the syntheses outlined in B, C, and E are relatively straight forward, A, D, and F are worthy of comment.

(17) Estimated to be formed in 2–3% yield by nmr and gc.

(18) This dimer has been used in support of a radical intermediate in another Stevens rearrangement: G. F. Hennion and M. J. Shoemaker, *J. Amer. Chem. Soc.*, **92**, 1769 (1970).

(19) E. Grovenstein, Jr., and L. C. Rogers, *ibid.*, **86**, 854 (1964).

(20) Nmr and gc analysis suggest that **11** may be formed in less than 1% yield in this reaction. Although α-phenylneopentyl chloride is the thermal decomposition product from **1a**,[10] it is unlikely to be the source of **11** in the rearrangements.[9]

(21) J. P. Lorand, R. W. Grant, P. A. Samuel, E. O'Connell, and J. Zaro, *Tetrahedron Lett.*, 4087 (1969).

The syntheses of **3a** and **3b** (Scheme IVA) through the hydroboration sequence were accomplished using either chloramine or hydroxylamine-*O*-sulfonic acid with the chloramine reagent being better. In both cases, however, yields were poor. This contrasts to the report by Brown[22] that α-methylstyrene gives greater than 60% yield of amine. We established that the hydroboration step was not at fault by forming the alcohol in greater than 90% yield. Apparently steric considerations inhibit attack by the amine precursor.

In the synthesis of **5b** (Scheme IVD) the desired 1,2,3 isomer predominated (*ca.* 3:1) in the metalation step, a result similar to analogous work by Klein and Hauser.[23] This is surprising since the product is particularly hindered as indicated by the nmr spectrum. The benzyl hydrogen atoms are nonequivalent due to hindered rotation and give rise to an AB quartet. This quartet collapses to a singlet at elevated temperatures. The data are also consistent with our structural assignment based on infrared data. Chemical evidence for crowding within the molecule was shown by the difficulty in accomplishing reduction to **5b**.

In the synthesis of **6b** (Scheme IVF) assignment of the structure of the isomeric dibromoxylenes and bromobenzylamines was important. Initial assignments were made using infrared and nmr spectral data along with model compound comparisons. The concluding evidence was based on chemical reactivity data which also served as a means of obtaining the desired isomer. Hauser, *et al.*,[23,24] had shown that ortho metalation was predominant in dimethylbenzylamines. We thus predicted that the 2-bromo-5-methyl isomer would be more reactive. By metalating the isomer mixture with *n*-butyllithium, then rapidly quenching with water, this unwanted isomer could be protonated while the desired isomer remained essentially unchanged. Recovery of the pure 4-bromo-3-methyl isomer was then easily accomplished by distillation.

Experimental Section

Analytical Data.—Nmr spectra were obtained as solutions in carbon tetrachloride, D_2O, or deuteriochloroform using a Varian A-60 spectrometer. Chemical shifts are reported as downfield from internal TMS. Infrared spectra were obtained as solutions in carbon tetrachloride or chlorofyrm using a Perkin-Elmer Infracord or for the aromatic substitution patterns on a Beckman IR-12 spectrophotometer. Ultraviolet spectra were obtained using a Cary 14 spectrophotometer. Melting points were obtained using a Hoover apparatus and are uncorrected. Gas chromatographic analysis of the amines were obtained on an F & M Model 700 or 720 instrument using a Carbowax 20M column. Peak areas were measured using a Disc integrator. Products obtained in the rearrangements were identified by separation using gas chromatography and comparison of retention times, nuclear magnetic resonance, and infrared spectral data with samples independently synthesized.

Rearrangement Reactions.—The required quaternary ammonium salt and the appropriate base–solvent system were allowed to react in sealed tubes or in closed reaction vessels under nitrogen. An oil bath was used to control the temperature to ±3° except in the case of the liquid ammonia runs where solvent reflux was the temperature control. In all cases, the reactions were quenched with water, the basic and nonbasic materials separated by acid–base extraction, and the products analyzed by gas chromatography.

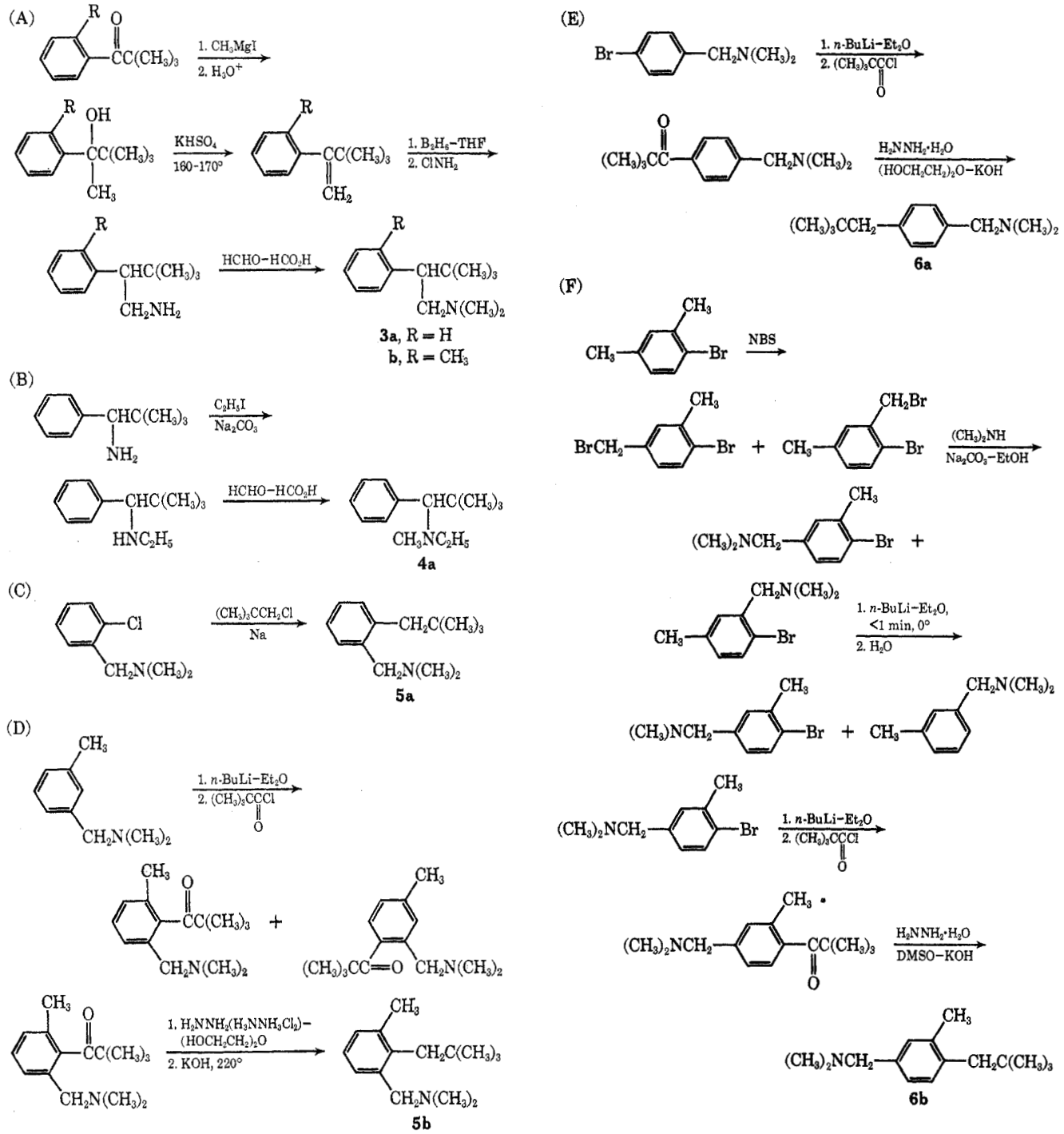
(22) H. C. Brown, W. R. Heydkamp, E. Beur, and W. S. Murphy, *J. Amer. Chem. Soc.*, **86**, 3565 (1965).

(23) K. P. Klein and C. R. Hauser, *J. Org. Chem.*, **32**, 1479 (1967).

(24) F. N. Jones, R. L. Vaulx, and C. R. Hauser, *ibid.*, **28**, 3461 (1963).

SCHEME IV

SEQUENCES FOR INDEPENDENT SYNTHESES OF REARRANGEMENT PRODUCTS



Reagents.—All solvents were dried and distilled. *n*-Butyllithium was obtained commercially as a solution in hexane. In some cases, the hexane was removed *in vacuo* under nitrogen and the appropriate dry solvent carefully added, usually at low temperatures. Potassium *tert*-butoxide was obtained commercially and sublimed before use. Sodium amide was prepared as needed as was lithium dimsyl.

***N,N,N*-Trimethyl-α-phenylneopentylammonium Iodide (1a).**—α-Phenylneopentylamine was prepared by the method of Brodhog and Hauser[25] in 94% yield: nmr (CCl_4) δ 0.84 (s, 9, $C(CH_3)_3$), 1.49 (s, 2, NH_2), 3.57 (s, 1, CH), 7.13 (s, 5, C_6H_5); uv max (95% ethanol) 258 mμ (ε 246); the benzenesulfonamide, mp 152.8–153.2°. *N,N*-Dimethyl-α-phenylneopentylamine was prepared using formic acid–formaldehyde in 55% yield:[26] nmr (CCl_4) δ 1.00 (s, 9, $C(CH_3)_3$), 2.18 (s, 6, $N(CH_3)_2$), 3.06 (s, 1, CH), 7.17 (s, 5, C_6H_5); $n^{25}D$ 1.5000; ir shows no NH absorption.

Anal. Calcd $C_{13}H_{21}N$: C, 81.61; H, 11.06. Found: C, 81.78; H, 11.11.

To 3.5 g (0.05 mol) of tertiary amine in 30 ml of anhydrous acetone was added 14 ml of methyl iodide. After the mixture was stirred for 32 hr in the dark, evaporation of the solvent gave 5.6 g (92%) of white solid, mp 162–163°. Recrystallization from absolute ethanol gave mp 164.2–164.8° dec; nmr ($CDCl_3$) δ 1.35 (s, 9, $C(CH_3)_3$), 3.53 (s, 9, $N(CH_3)_3$), 5.44 (s, 1, CH), 7.2–8.0 (m, 5, C_6H_5).

Anal. Calcd for $C_{14}H_{24}NI$: C, 50.46; H, 7.26; I, 38.08; N, 4.20. Found: C, 50.50; H, 7.27; I, 38.10; N, 4.38.

***N,N,N*-Trimethyl-α-phenylneopentylammonium Chloride (1a).**—To 0.5 g (0.0015 mol) of *N,N,N*-trimethyl-α-phenylneopentylammonium iodide in 9 ml of water was added 1.0 g (0.01 mol) of silver chloride. After the mixture was stirred for 13 hr

(25) A. Brodhog and C. R. Hauser, *J. Amer. Chem. Soc.*, **77**, 3024 (1955).
(26) S. H. Pine, *J. Chem. Educ.*, **45**, 118 (1968).

at 25°, the resulting precipitate was separated and washed with water, and the total filtrates were evaporated under reduced pressure to give 0.4 g (100%) of a white solid. Recrystallization from ethanol–ethyl acetate (1:5) gave a white solid: mp 198° dec; nmr ($CDCl_3$) δ 1.31 (s, 9, $C(CH_3)_3$), 3.54 (s, 9, $N(CH_3)_3$), 5.42 (s, 1, CH), 7.2–7.9 (m, 5, C_6H_5).

Anal. Calcd for $C_{14}H_{24}NCl$: C, 69.54; H, 10.00. Found: C, 69.56; H, 10.09.

N,N,N-Trimethyl-α-o-tolylneopentylammonium Iodide (1b).—2-Methylphenylmagnesium bromide, prepared from 50 g (0.26 mol) of 2-bromotoluene, in 125 ml of anhydrous ether was added over 1 hr to a solution of 31.8 g (0.26 mol) of pivalyl chloride in 100 ml of anhydrous ether. After an additional 1.5-hr reflux, the mixture was let stand overnight. Addition of dilute sulfuric acid, separation of the organic layer, further washing with a sodium bicarbonate solution, drying with anhydrous magnesium sulfate, and evaporation of the solvent gave 42.2 g of yellow oil. Distillation gave 31.2 g (68%) of *tert*-butyl-*o*-tolyl ketone: bp 94–95° (4 mm); nmr (CCl_4) δ 1.20 (s, 9, $C(CH_3)_3$), 2.16 (s, 3, CH_3), 7.10 (s, 4, C_6H_4); ir 1700 cm^{-1} (s).

To a 500-ml flask equipped with dropping funnel, stirrer, and reflux condenser was added 15.0 g (0.085 mol) of *tert*-butyl-*o*-tolyl ketone, 54 ml of 99% formamide, 33 ml of 88% formic acid, and 6.0 g of magnesium chloride hexahydrate. The mixture was refluxed for 30 hr and then the formic acid–water azeotrope was allowed to distil. An additional 45 ml of 99% formamide and 36 ml of 98% formic acid were added and refluxed 24 hr. The mixture was cooled and added to ice, and the resulting solid was collected by filtration. The crude product was refluxed for 24 hr with 200 ml of 7 *N* methanolic sodium hydroxide. Water (500 ml) was added and the solution extracted with four 100-ml portions of pentane. The pentane was washed with a saturated sodium chloride solution and dried over anhydrous magnesium sulfate, and the product was recovered by distillation to give 8.2 g (55%) of *o*-methyl-α-phenylneopentylamine: bp 91–92° (3 mm); nmr (CCl_4) δ 0.9 (s, 9, $C(CH_3)_3$), 1.1 (s, 2, NH_2), 1.3 (s, 3, CH_3), 4.0 (s, 1, CH), 7.2 (m, 4, C_6H_4); ir 3350 cm^{-1} (doublet).

N,N-dimethyl-α-*o*-tolylneopentylamine was prepared from the primary amine using formic acid–formaldehyde[26] over 2 hr to give an 84% yield: bp 88–89° (1 mm); nmr (CCl_4) δ 1.00 (s, 9, $C(CH_3)_3$), 2.23 (s, 6, $N(CH_3)_2$), 2.33 (s, 3, CH_3), 3.56 (s, 1, CH), 7.2 (m, 4, C_6H_4); ir shows no NH adsorption.

Anal. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.97; H, 11.53; N, 6.56.

To 3.0 g (0.015 mol) of *N,N*-dimethyl-α-*o*-tolylneopentylamine in 16 ml of anhydrous acetone was added 12 ml of methyl iodide. After the mixture was stirred for 24 hr, the solvent was evaporated to give 5.0 g (97%) of *N,N,N*-trimethyl-α-*o*-tolylneopentylammonium iodide as a white solid. Recrystallization from absolute ethanol–ether gave a white solid: mp 184° dec; nmr ($CDCl_3$) δ 1.31 (s, 9, $C(CH_3)_3$), 2.58 (s, 3, CH_3), 3.52 (s, 9, $N(CH_3)_3$), 4.85 (s, 1, CH), 7.3 (m, 4, C_6H_4).

Anal. Calcd for $C_{15}H_{26}NI$: C, 51.87; H, 7.55; N, 4.03. Found: C, 51.84; H, 7.63; N, 3.84.

3,3-N,N-Tetramethyl-2-phenyl-1-aminobutane (3a).—3,3-Dimethyl-2-phenyl-2-butanol was prepared from methylmagnesium iodide and *tert*-butyl phenyl ketone in 91% yield: bp 91–93° (4.5 mm) [lit.[27] 128° (20 mm)]; ir (CCl_4) 3450 cm^{-1}; nmr (CCl_4) δ 0.81 (s, 9, $C(CH_3)_3$), 1.45 (s, 3, CH_3COH), 1.50 (s, 1, COH), 7.2 (m, 5, C_6H_5).

The alcohol (1.53 g, 0.0086 mol) and 0.3 g of $KHSO_4$ were heated under nitrogen for 1 hr at 160–170°. The product was dissolved in ether and dried, and the solvent was removed to give 1.27 g (92%) of 3,3-dimethyl-2-phenyl-1-butene: bp 54–55° (4 mm) [lit.[27] 75° (10 mm)]; ir (CCl_4) 1620 and 905 cm^{-1}; nmr (CCl_4) δ 1.14 (s, 9, $C(CH_3)_3$), 4.75 (d, 1, J = 1.4 Hz, $C{=}CH_a$), 5.16 (d, 1, J = 1.4 Hz, $C{=}CH_b$), 7.21 (m, 5, C_6H_5).

To 2 g (0.013 mol) of the olefin in 25 ml of dry THF was added 0.013 mol of a 1 *M* solution of diborane–THF. Immediate effervescence occurred as the diborane solution was added. It was left stirring for 52 hr (24 hr would be sufficient). To the pale white solution was added 3 ml of water (considerable effervescence occurs) and 10 ml of 3 *N* NaOH solution to destroy the residual borane. Chloramine solution[28] (0.013 mol) was slowly added. The mixture was left stirring for 18 hr. It was made acid with 3 *N* HCl and extracted with ether. The ether was washed further with 3 *N* HCl solution, the washings being added to the total aqueous layer. The aqueous layer was made basic with 50% sodium hydroxide, and the basic material was extracted with pentane and dried. Evaporation of the solvent gave 0.63 g (28.5%) of 3,3-dimethyl-2-phenyl-1-aminobutane as a light yellow oil. The oil readily solidifies by CO_2 uptake if left standing in the air: nmr (CCl_4) δ 0.87 (s, 8.75, $C(CH_3)_3$), 1.15–1.53 (s, broad, 2, CH_2NH_2), 2.36 (m, 1, $CHCH_2$), 2.70–3.2 (s, broad, 2, CH_2NH_2), 7.20 (s, 5, C_6H_5).

To 0.1 g (0.0005 mol) of the primary amine was added 10 ml of 88% formic acid and 7.5 ml of 36% formaldehyde solution.[26] The stirred solution was heated to 90° and maintained at that temperature for 3 hr. The solution was cooled, 10 ml of 3 *N* HCl was added, and it was extracted with pentane. The aqueous phase was made basic with 50% sodium hydroxide and extracted with pentane, and the pentane was dried and evaporated to give 0.06 g (53%) of *N,N*-3,3-tetramethyl-2-phenyl-1-aminobutane: nmr (CCl_4) δ 0.87 (s, 9, $C(CH_3)_3$), 2.20 (s, 6, $N(CH_3)_2$), 2.5–2.6 (m, 3, $CHCH_2N$), 7.11 (s, 5, C_6H_5); uv max (absolute EtOH) 259 mμ (ε 230); ir shows monosubstitution pattern 1700–2000 cm^{-1}.[29]

Anal. Calcd for $C_{14}H_{23}N$: 81.88; H, 11.29; N, 6.82. Found: C, 82.03; H, 10.79; N, 7.19.

3,3-N,N-Tetramethyl-2-o-tolyl-1-aminobutane (3b).—3,3-Dimethyl-2-*o*-tolyl-2-butanol was prepared from methylmagnesium iodide and *tert*-butyl-*o*-tolyl ketone in 83% yield: bp 112–113° (5.5 mm); ir (CCl_4) 3650 cm^{-1}; nmr (CCl_4) δ 0.90 (s, 9, $C(CH_3)_3$), 1.44 (s, 1, COH), 1.57 (s, 3, CH_3COH), 2.55 (s, 3, *o*-$CH_3C_6H_4$), 7.1 (m, 4, C_6H_4).

The alcohol (10 g, 0.052 mol) and 1.5 g of $KHSO_4$ were heated at 165–170° for 2 hr. The product was dissolved in ether, dried, and recovered by distillation to give 7.5 g (83%) of 3,3-dimethyl-2-*o*-tolyl-1-butene: bp 83–84° (6 mm); ir (CCl_4) 1620 and 909 cm^{-1}; nmr (CCl_4) δ 1.10 (s, 9, $C(CH_3)_3$), 2.22 (s, 3, *o*-$CH_3C_6H_4$), 4.73 (d, 1, J = 1.5 Hz, $C{=}CH_a$), 5.26 (d, 1, J = 1.5 Hz, $C{=}CH_b$), 7.03 (m, 4, C_6H_4).

To 3.2 g (0.018 mol) of the alkene in 25 ml of dry THF was added 21 ml (0.021 mol) of a 1 *M* diborane solution. It was left stirring for 24 hr. To the solution was added 3 ml of water and 10 ml of 3 *N* sodium hydroxide. Chloramine solution[28] (0.04 mol) was slowly added. The milky white solution turned reddish purple. It was left stirring for 24 hr, made acidic with 3 *N* HCl, and extracted with ether. The aqueous acid solution was made basic with 50% sodium hydroxide and extracted with pentane. The pentane was washed with saturated sodium chloride solution, dried, and evaporated to give 0.53 g (15.4%) of 3,3-dimethyl-2-*o*-tolyl-1-aminobutane as a yellow viscous oil which readily solidifies by CO_2 uptake in the air: nmr (CCl_4) δ 0.91 (s, 9, $C(CH_3)_3$), 2.31 (s, 3, *o*-$CH_3C_6H_4$), 2.70–3.0 (s–broad, 3 $CHCH_2N$), 7.05 (s, 4, C_6H_4).

To 0.30 g (0.002 mol) of the primary amine was added 12 ml of 88% formic acid and 9 ml of 36% formaldehyde,[26] and the mixture was stirred at 90° for 22 hr. It was cooled, 10 ml of 3 *N* HCl was added, and the mixture was extracted with pentane. The aqueous solution was made basic with 50% sodium hydroxide and extracted with pentane. Drying and evaporation yielded 0.27 g (78.5%) of 3,3-*N,N*-tetramethyl-2-*o*-tolyl-1-aminobutane as a pale yellow oil: nmr (CCl_4) δ 0.81 (s, 9, $C(CH_3)_3$), 1.97 (s, 6, $N(CH_3)_2$), 2.29 (s, 3, *o*-$CH_3C_6H_4$), 2.4–2.98 (m, 3, $CHCH_2N$), 7.0 (s, 4, C_6H_4); the methiodide, mp 290–292°.

Anal. Calcd for $C_{16}H_{28}NI$: C, 53.19; H, 7.81; N, 3.88. Found: C, 53.09; H, 7.82; N, 3.63.

N-Ethyl-N-methyl-α-phenylneopentylamine (4a).—To 1.1 g (0.007 mol) of α-phenylneopentylamine in 15 ml of absolute ethanol was added 1.0 g (0.007 mol) of ethyl iodide and 0.7 g of sodium carbonate, and the mixture was stirred for 6 hr at 40°. Filtration and then evaporation of the solvent gave 0.9 g (70%) of the *N*-ethylamine: nmr (CCl_4) δ 0.88 (s, $C(CH_3)_3$) and 1.00 (t, CH_2CH_3, J = 7 Hz) (total area 13, NH presumed to be present), 2.35 (q, 2, NCH_2, J = 7 Hz), 3.28 (s, 1, CH), 7.19 (s, 5, C_6H_5).

N-ethyl-*N*-methyl-α-phenylneopentylamine was prepared from the *N*-ethylamine using formic acid–formaldehyde at 80° for 17 hr to give a 74% yield: bp *ca.* 237°; nmr (CCl_4) δ 1.0 (s, $C(CH_3)_3$) and 1.0 (t, CH_2CH_3) (total area 12), 2.19 (s, NCH_3)

(27) B. B. Corson, H. E. Tiefenthal, G. R. Atwood, W. J. Heintzelman, and W. L. Reilly, *J. Org. Chem.*, **21**, 584 (1956).

(28) G. H. Coleman and H. L. Johnson, *Inorg. Syn.*, **1**, 59 (1939).

(29) J. R. Dyer, "Applications of Absorption Spectroscopy to Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 52.

and 2.30 (m, NCH_2) (total area 5), 3.21 (s, 1, CH), 7.18 (s, 5, C_6H_5); the methofluoroborate salt, mp 141.5–143.5° (acetone–ether).

Anal. Calcd for $C_{15}H_{26}NBF_4$: C, 58.65; H, 8.53; N, 4.56. Found: C, 58.60; H, 8.46; N, 4.41.

***N,N*-Dimethyl-2-neopentylbenzylamine (5a).**—2-Chloro-*N,N*-dimethylbenzylamine was prepared by the reaction of 2-chlorobenzylamine with formic acid–formaldehyde[26] in 79% yield: nmr (CCl_4) δ 2.25 (s, 6, $N(CH_3)_2$), 3.55 (s, 2, CH_2), 7.1–7.6 (m, 4, C_6H_4).

To a 50-ml flask equipped with a reflux condenser and a rapid stirrer was placed 2.1 g (0.02 mol) of neopentyl chloride, 3.4 g (0.02 mol) of 2-chloro-*N,N*-dimethylbenzylamine, and 1.0 g (0.042 g-atom) of sodium metal. After rapid stirring for 55 hr, 2 ml of methanol was added to destroy excess sodium metal, then 15 ml of water was added, and the mixture was extracted with petroleum ether (bp 30–60°). The petroleum ether was extracted with 3 *N* hydrochloric acid and then the basic materials were regenerated with dilute sodium hydroxide. Extraction with petroleum ether, drying with anhydrous magnesium sulfate, and evaporation of the solvent gave 1.35 g of dark oil. A crude distillation gave 0.5 g of colorless liquid boiling below 150° (1 mm). Preparative gas chromatography provided a pure sample of *N,N*-dimethyl-2-neopentylbenzylamine: nmr (CCl_4) δ 0.9 (s, 9, $C(CH_3)_3$), 2.15 (s, 6, $N(CH_3)_2$), 2.65 (s, 2, CH_2), 3.4 (s, 2, NCH_2), 7.0–7.4 (m, 4, C_6H_4); uv max (absolute EtOH) mμ (ε 252); ir shows ortho substitution pattern 1600–2000 cm^{-1}.[29]

Anal. Calcd for $C_{14}H_{23}N$: C, 81.88; H, 11.29; N, 6.82. Found: C, 82.16; H, 11.24; N, 6.72.

3-*N,N*-Trimethyl-2-neopentylbenzylamine (5b).—To 6.7 g (0.045 mol) of 3-*N,N*-trimethylbenzylamine (prepared from 3-methylbenzylamine using formic acid–formaldehyde[26]) in a 125-ml flask was added 31 ml of 1.7 *N* *n*-butyllithium (0.045 mol) in hexane. The flask was filled with anhydrous ether and left overnight. This solution of metalated benzylamine was then added dropwise to a solution of 8.2 g (0.07 mol) of pivalyl chloride in 30 ml of anhydrous ether. The resulting white slurry was refluxed for 3 hr and then allowed to stand overnight, 30 ml of 3 *N* HCl was added, and the nonbasic material was extracted with ether. The basic products were regenerated using 50% NaOH, extracted with ether, and dried, and the solvent was removed to give 8.1 g of liquid, shown to consist of 21% starting material and 79% of the isomeric 3-*N,N*-trimethyl-2-pivalylbenzylamine (A) and 5-*N,N*-trimethyl-2-pivalylbenzylamine (B) with A/B ≈ 3:1. The isomers were separated by chromatography on silica gel with 4–10% ether in pentane. The 1,2,4-substituted isomer B eluted first: ir shows a typical 1,2,4-aromatic substitution pattern 1600–2000 cm^{-1};[29] nmr (CCl_4) δ 1.19 (s, 9, $C(CH_3)_3$), 2.10 (s, 6, $N(CH_3)_2$), 2.30 (s, 3, CH_3), 3.25 (s, 2, CH_2), 7.0 (m, 3, C_6H_3); the methiodide, mp 202° dec (absolute ethanol).

Anal. Calcd for $C_{16}H_{26}NOI$: C, 51.21; H, 6.98; N, 3.73. Found: C, 51.37; H, 7.17; N, 3.60.

The desired 1,2,3-substituted isomer A eluted next: ir shows a typical 1,2,3-aromatic substitution pattern 1600–2000 cm^{-1};[29] nmr (CCl_4) δ 1.19 (s, 9, $C(CH_3)_3$), 2.12 (s, 6, $N(CH_3)_2$), 2.20 (s, 3, CH_3), 3.22 (AB m, 2, CH_2), 6.9–7.3 (m, 3, C_6H_3); the methiodide, mp 190° dec (acetone–ether).

Anal. Calcd for $C_{16}H_{26}NOI$: C, 51.21; H, 6.98; N, 3.73. Found: C, 51.09; H, 7.03; N, 3.60.

The 1,2,3-substituted isomer A was reduced using a modified Wolff–Kishner reaction. To 0.55 g of ketone in 33 g of diethylene glycol was added 8 g of hydrazine dihydrochloride and then 35 g of 97% hydrazine. The reaction was refluxed for 72 hr and then cooled, 10 g of KOH was added, and the temperature was raised to 220° as the hydrazine distilled. (Unreacted starting material, 0.31 g, was recovered from this distillate.) The mixture was refluxed for 3 hr, 10 ml of water added, and the product recovered by extraction with pentane. Evaporation of the solvent gave 0.1 g of oil which was further purified by preparative gas chromatography to give pure 3-*N,N*-trimethyl-2-neopentylbenzylamine: nmr (CCl_4) δ 0.94 (s, 9, $C(CH_3)_3$, 2.13 (s, 6, $N(CH_3)_2$), 2.32 (s, 3, CH_3), 2.80 (s, 2, CH_2), 3.40, (s, 2, NCH_2), 7.01 (m, 3, C_6H_3); the methiodide, mp 190° dec (ether–dichloromethane).

Anal. Calcd for $C_{15}H_{28}NI$: C, 53.19; H, 7.81; N, 3.88. Found: C, 53.08; H, 8.19; N, 3.78.

***N,N*-Dimethyl-4-neopentylbenzylamine (6a).**—Into a 50-ml flask equipped with a reflux condenser, dropping funnel, and magnetic stirrer was placed 4.0 g (0.016 mol) of 4-bromo-*N,N*-dimethylbenzylamine and 15 ml of anhydrous ether. Then 15 ml of 1.7 *N* *n*-butyllithium in hexane (0.026 mol) was added over 10 min with cooling, and the mixture was allowed to stir at room temperature for 3 hr (all under nitrogen). The resulting cloudy solution was transferred to a dropping funnel and then added to a solution of 3.5 g (0.03 mol) of pivalyl chloride in 25 ml of anhydrous ether over 30 min. It was refluxed for 3 hr and then left overnight at room temperature. To the resulting white slurry was added 25 ml of 3 *N* HCl, the nonbasic organic phase removed, and the basic material regenerated with 50% sodium hydroxide. Extraction with petroleum ether (bp 30–60°), drying over magnesium sulfate, and distillation gave 1.6 g (50%) of *N,N*-dimethyl-4-pivalylbenzylamine: bp 142–155° (1.5 mm); nmr (CCl_4) δ 1.32 (s, 9, $C(CH_3)_3$), 2.20 (s, 6, $N(CH_3)_2$), 3.39 (s, 2, CH_2), 7.48 (m, AA′, BB′, 4, C_6H_4); ir 1685 cm^{-1}; the methiodide, mp 195.0–195.5°.

Anal. Calcd for $C_{14}H_{21}NO$: C, 49.87; H, 6.70; N, 3.88. Found: C, 50.10; H, 6.73; N, 3.85.

To a 35-ml flask equipped with a reflux condenser and Dean–Stark water separator was placed 1.0 g (0.005 mol) of the ketone, 15 ml of diethylene glycol, 1.0 g of potassium hydroxide, and 2 ml of 85% hydrazine hydrate. It was heated and the water was removed until the pot temperature reached 205°; then reflux was continued at this temperature for an additional 4 hr. The resulting colorless solution was cooled, and 50 ml of water was added and extracted with pentane. Drying over anhydrous magnesium sulfate and evaporation of the solvent gave 0.8 g (87%) of *N,N*-dimethyl-4-neopentylbenzylamine: bp *ca.* 70° (4 mm); nmr (CCl_4) δ 0.9 (s, 9, $C(CH_3)_3$), 2.2 (s, 6, $N(CH_3)_2$), 2.5 (s, 2, CH_2), 3.4 (s, 2, NCH_2), 7.0–7.4 (m, AA′, BB′, 4, C_6H_4); uv max (absolute EtOH) 256 mμ (ε 437); ir shows typical para substitution pattern 1600–2000 cm^{-1}.[29]

Anal. Calcd for $C_{14}H_{23}N$: C, 81.88; H, 11.29; N, 6.82. Found: C, 82.03; H, 11.23; N, 7.19.

3-*N,N*-Trimethyl-4-neopentylbenzylamine (6b).—To a 100-ml flask equipped with a reflux condenser and magnetic stirrer was placed 24.0 g (0.135 mol) of *N*-bromosuccinimide, 19.0 g (0.1 mol) of 4-bromo-*m*-xylene, 50 ml of carbon tetrachloride, and a trace of benzoyl peroxide. The temperature was slowly raised to *ca.* 82° where reaction initiated. After 15 min, a 5% solution of sodium sulfite was added, and the organic layer was separated and dried over anhydrous magnesium sulfate. Distillation gave 14.2 g of a mixture of 4-bromo-3-methylbenzyl bromide and 2-bromo-5-methylbenzyl bromide. Preparative gas chromatography provided pure samples of each isomer. 2-Bromo-5-methylbenzyl bromide had the following spectral properties: nmr (CCl_4) δ 2.25 (s, 3, CH_3), 4.46 (s, 2, CH_2), 7.0 (m, 3, C_6H_3). 4-Bromo-3-methylbenzyl bromide gave the following: nmr (CCl_4) δ 2.33 (s, 3, CH_3), 4.29 (s, 2, CH_2), 7.0 (m, 3, C_6H_3).

To a 100-ml flask equipped with a stirrer, dropping funnel, and Dry Ice condenser was added 60 ml of absolute ethanol, 3.5 g of anhydrous sodium carbonate, and 13.5 g (0.05 mol) of the mixed benzyl bromides (above). The mixture was cooled to 0°, then 6.0 g (0.1 mol) of dimethylamine was added rapidly, and the mixture was stirred for 1 hr. The precipitate was removed by filtration, and the filtrate evaporated. The residue was dissolved in dilute hydrochloric acid and washed with ether, and the basic products were regenerated with dilute sodium hydroxide. Extraction with ether, drying over anhydrous magnesium sulfate, and evaporation gave 6.0 g (54%) of a mixture of 4-bromo-3-*N,N*-trimethylbenzylamine and 2-bromo-5-*N,N*-trimethylbenzylamine. Preparative gas chromatography provided pure samples of each isomer. 2-Bromo-5-*N,N*-trimethylbenzylamine had the following spectral properties: nmr (CCl_4) δ 2.25 (s, 6, $N(CH_3)_2$), 2.29 (s, 3, CH_3), 3.44 (s, 2, CH_2), 7.25 (m, 3, C_6H_3). 4-Bromo-3-*N,N*-trimethylbenzylamine gave the following: nmr (CCl_4) δ 2.13 (s, 6, $N(CH_3)_2$), 2.32 (s, 3, CH_3), 3.28 (s, 2, CH_2), 7.25 (m, 3, C_6H_3). The structural assignments are based on analogy with the nmr spectra of similar systems and the following chemical reactivity difference.

The isomers were separated by the following reactivity difference. The mixed amines (3.5 g, 0.015 mol) were placed in a flask containing 60 ml of anhydrous ether and a magnetic stirrer. The solution was cooled in an ice bath, 15 ml of 1.6 *N* (0.024 mol) *n*-butyllithium in hexane was rapidly added (30 sec), and then a few drops followed by 10 ml of water were rapidly added (60 sec). Separation of the organic layer, drying over anhydrous magnesium sulfate, and evaporation of the solvent gave 3.3 g of product containing unreacted 4-bromo-3-*N,N*-trimethyl-

benzylamine and 3-*N*,*N*-trimethylbenzylamine. Purification was accomplished by distillation using a micro spinning-band column to give 4-bromo-3-*N*,*N*-trimethylbenzylamine: bp 105–115° (1.5 mm); the methiodide, mp 223–224° dec (absolute ethanol).

Anal. Calcd for $C_{11}H_{17}NBrI$: C, 35.90; H, 4.63; N, 3.78. Found: C, 35.90; H, 4.78; N, 3.47.

To 0.54 g (0.0024 mol) of 4-bromo-3-*N*,*N*-trimethylbenzylamine in 10 ml of anhydrous ether was added 2.0 ml of 1.6 *N* (0.0032 mol) *n*-butyllithium in hexane. After standing for 30 min (under nitrogen), the slurry was added to a solution of 0.4 g (0.0033 mol) of pivalyl chloride. It was stirred for 1.5 hr, and then 5 ml of water was added followed by 1 ml of concentrated hydrochloric acid. The ether phase was separated, the aqueous phase made basic, and the basic material extracted with ether. The ether was dried over anhydrous magnesium sulfate, and the solvent evaporated to give 0.43 g of yellow liquid, shown to be principally 4-pivalyl-3-*N*,*N*-trimethylbenzylamine by gas chromatography. A pure sample of 4-pivalyl-3-*N*,*N*-trimethylbenzylamine was obtained by preparative gas chromatography: nmr (CCl_4) δ 1.2 (s, 9, $C(CH_3)_3$), 2.18 (s, 6, $N(CH_3)_2$), 3.33 (s, 2, CH_2), 7.0 (m, 3, C_6H_3); ir 1700 cm^{-1}; the methiodide, mp 218° dec (absolute methanol–ether).

Anal. Calcd for $C_{16}H_{26}NOI$: C, 51.21; H, 6.98; N, 3.73. Found: C, 51.31; H, 7.09; N, 3.52.

To 0.4 g of 4-pivalyl-3-*N*,*N*-trimethylbenzylamine in 6 ml of dimethyl sulfoxide was added 1 ml of 85% hydrazine hydrate and 0.5 g of potassium hydroxide. It was heated at 165° for 45 hr, 10 ml of water added, the mixture extracted with 3 *N* hydrochloric acid, and then the basic material regenerated with dilute sodium hydroxide. Extraction with pentane, drying over anhydrous magnesium sulfate, and evaporation of the solvent gave 0.18 g of yellow liquid. Gas chromatography showed *ca.* 65% starting material. Preparative gas chromatography provided a sample of 3-*N*,*N*-trimethyl-4-neopentylbenzene: ir shows 1,2,4-aromatic substitution pattern 1700–2000 cm^{-1};[29] nmr (CCl_4) δ 0.92 (s, 9, $(CH_3)_3$), 2.16 (s, 6, $N(CH_3)_2$), 2.30 (s, 3, CH_3), 2.50 (s, 2, CH_2), 3.28 (s, 2, NCH_2), 6.9–7.1 (m, 3, C_6H_3); the methiodide, mp 245° dec (absolute ethanol–ether).

Anal. Calcd for $C_{16}H_{28}NI$: C, 53.19; H, 7.81; N, 3.88. Found: C, 53.45; H, 7.95; N, 3.69.

Neopentylbenzene (**10a**) was prepared by the method of Berliner:[30] bp 176.5–178.0°; nmr (CCl_4) δ 0.90 (s, 9, $C(CH_3)_3$), 2.85 (s, 2, CH_2), 7.13 (s, 5, C_6H_5).

***o*-Methylneopentylbenzene** (**10b**).—*tert*-Butyl-*o*-tolyl ketone was reduced using 85% hydrazine hydrate and potassium hydroxide in dimethyl sulfoxide at 163° for 3 hr: bp 216–218°; nmr (CCl_4) δ 0.92 (s, 9, $C(CH_3)_3$), 2.25 (s, 3, CH_3), 2.51 (s, 2, CH_2), 7.00 (m, 4, C_6H_4).

(30) E. Berliner and F. Berliner, *J. Amer. Chem. Soc.*, **71**, 1195 (1949).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.69; H, 11.31.

3,4-Diphenyl-2,2,5,5-tetramethylhexane (**11**).—The dimer was collected from the nonbasic material of various rearrangement reactions. It was purified by crystallization from pentane at low temperature to give white needles: mp 180.0–181.0°; nmr (CCl_4) δ 0.53 (s, 9, $C(CH_3)_3$), 3.06 (s, 1, CH), 7.25 (m, 5, C_6H_5).

Anal. Calcd for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.68; H, 10.32.

Registry No.—**1a** (iodide), 27617-91-0; **1a** (chloride), 18631-79-3; **1b** (iodide), 27557-79-5; **3a**, 27561-24-6; **3b**, 27561-25-7; **4a**, 27561-26-8; **4a** metho BF_4 salt, 27557-80-8; **5a**, 27561-27-9; **5b**, 27561-28-0; **5b** methiodide, 27561-29-1; **6a**, 27561-30-4; **6b**, 27561-31-5; **6b** methiodide, 27561-22-4; **10a**, 1007-26-7; **10b**, 24785-42-0; **11**, 27561-34-8; *N*,*N*-dimethyl-α-phenylneopentylamine, 27561-35-9; *tert*-butyl-*o*-tolyl ketone, 2041-37-4; *o*-methyl-α-phenylneopentylamine, 27561-36-0; *N*,*N*-dimethyl-α-*o*-tolylneopentylamine, 27561-37-1; 3,3-dimethyl-2-phenyl-2-butanol, 21811-48-3; 3,3-dimethyl-2-phenyl-1-butene, 5676-29-9; 3,3-dimethyl-2-phenyl-1-aminobutane, 27561-40-6; 3,3-dimethyl-2-*o*-tolyl-2-butanol, 27561-41-7; 3,3-dimethyl-2-*o*-tolyl-1-butene, 27561-42-8; 3,3-dimethyl-2-*o*-tolyl-1-aminobutane, 27561-43-9; *N*-ethyl-α-phenylneopentylamine, 27561-44-0; 2-chloro-*N*,*N*-dimethylbenzylamine, 10175-31-2; amine A methiodide, 27561-46-2; amine B methiodide, 27561-47-3; *N*,*N*-dimethyl-4-pivalylbenzylamine, 27561-48-4; *N*,*N*-dimethyl-4-pivalylbenzylamine methiodide, 27561-49-5; 2-bromo-5-methylbenzyl bromide, 27561-50-8; 4-bromo-3-methylbenzyl bromide, 27561-51-9; 2-bromo-5-*N*,*N*-trimethylbenzylamine, 27561-52-0; 4-bromo-3-*N*,*N*-trimethylbenzylamine, 27561-53-1, methiodide, 27561-54-2; 5-pivalyl-3-*N*,*N*-trimethylbenzylamine, 27561-23-5.

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