C- and N-Acetylation of Phenylacetamide with Acetic Anhydride by Boron Trifluoride. Conversion of Phenylacetonitrile to Diacetyl Derivative of Phenylacetamide[1]

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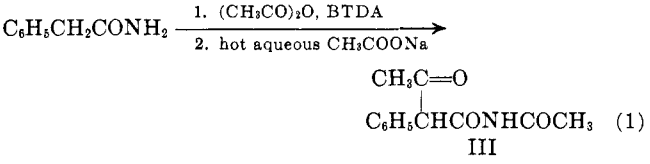
Acetylation at the α-carbon of phenylacetamide, accompanied by N-acetylation, was effected with excess acetic anhydride by means of boron trifluoride–diacetic acid complex to form N-acetyl-α-phenylacetoacetamide (III). α-Acetylphenylacetamide, which is an intermediate, was prepared by another method and converted through its boron difluoride complex to III. Phenylacetonitrile was converted to III with excess acetic anhydride and the reagent; this procedure is recommended for the synthesis of III. *p*-Chlorophenylacetonitrile was similarly converted to the diacetyl derivative of the corresponding amide. Attempts to effect acetylation of ethyl phenylacetate and phenylacetonitrile by means of boron trifluoride were unsatisfactory. A comparison with basic methods is made.

Benzoylation at the α-carbon of phenylacetamide has recently[2] been effected with methyl benzoate through dianion I which was prepared by means of 2 molecular equiv. of potassium amide in liquid ammonia; II was obtained in 50% yield.

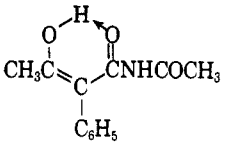
I II

Acetylation at the α-carbon of phenylacetamide, accompanied by N-acetylation, has now been accomplished with excess acetic anhydride and boron trifluoride; essentially pure III was obtained in 53% yield employing boron trifluoride–diacetic acid (BTDA) which is a liquid coordination complex (eq. 1).

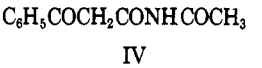


III (1)

Structure III was supported by analysis and absorption spectra. The infrared spectrum had bands at 3.1 and 5.85–6.1 μ (broad) for monosubstituted –NH[3] and the carbonyl system, respectively. The n.m.r. spectrum[4] showed aromatic absorption centered at 7.73 and singlets at 5.25 and 14.16 p.p.m. for the methinyl and enolic protons, respectively. In addition there were four singlets at 1.80, 2.14, 2.25, and 2.45 p.p.m. Two of these signals are considered to arise from the methyl protons of the C-acetyl and N-acetyl groups in III, and the two other signals, from the methyl protons of these two groups in enol form III′. Similar differences in the methyl signals of an acetyl group in the keto and enol forms have been reported recently for certain β-diketones and β-keto esters,[5] and now have been observed for the β-keto-imide IV,[6] the n.m.r. spectrum of which showed N-acetylmethyl singlets at 2.25 and 2.33 p.p.m.



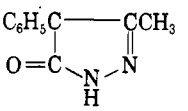
III



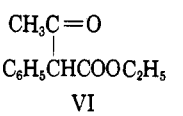
IV

Moreover, the ratio of keto form III to enol form III′ is indicated by the n.m.r. spectrum to be about 4:6 in deuteriochloroform. Thus the bands at 5.25 and 14.16 p.p.m. represented 0.4 and 0.6 protons, respectively, and the area ratio of the pair of methyl resonances at 1.80 and 2.45 p.p.m. to that of the pair at 2.14 and 2.25 p.p.m. was 4:6. Evidently the imide proton signal was obscured by the aromatic absorption, since the integrated area of the multiplet center at 7.73 p.p.m. was reduced by an area increment corresponding to one proton, after deuterium exchange. In addition the enolic proton band at 14.16 p.p.m. also disappeared from the spectrum.

Structure III was further supported by chemical evidence. Acid-catalyzed hydrolysis of III yielded phenylacetone, which presumably arose through decarboxylation of intermediate α-acetylphenylacetic acid. Treatment of III with hydrazine afforded pyrazolone V, which was independently synthesized for β-keto ester VI. The conversion of III to V was presumably accompanied by elimination of acetamide, a type of elimination reaction that has been reported recently.[6]

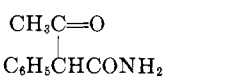


V



VI

The diacetylation of phenylacetamide (eq. 1, above) evidently involved C-acetylation followed by N-acetylation, since thin layer chromatography on the crude product (III) indicated the presence of VII not VIII.



VII

VIII

The N-acetylation of VII must have occurred more rapidly than the C-acetylation of phenylacetamide, since an attempt to prepare VII by employing only

(1) This investigation was supported in part by Public Health Service Research Grant No. CA 04455-05,06 from the National Cancer Institute.

(2) S. D. Work, D. R. Bryant, and C. R. Hauser, *J. Org. Chem.*, **29**, 722 (1964).

(3) See L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 206.

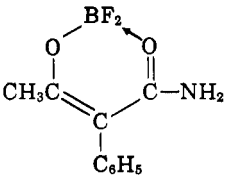
(4) Nuclear magnetic resonance spectra were obtained from deuteriochloroform solutions with tetramethylsilane as internal standard using a Varian A-60 spectrometer.

(5) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).

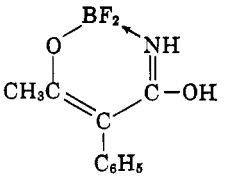
(6) See S. D. Work, D. R. Bryant, and C. R. Hauser, *ibid.*, **86**, 872 (1964).

molecular equivalents of the reactants afforded more of III than VII.

The mechanism for the C-acetylation of phenylacetamide is suggested to involve condensation of the acetyl carbonium ion (from the anhydride) with an enol-type complex (from the amide) to form the boron difluoride complex VII'[7] or VII''; this mechanism is similar to that proposed for the analogous acetylation of ketones.[8]



VII'



VII''

That the α-acetyl derivative VII arising from C-acetylation of phenylacetamide was produced as its boron difluoride complex was supported not only by the preparation of this complex from VII and BTDA reagent, but also by N-acetylation of the complex with acetic anhydride by means of this reagent to form III (eq. 2). Incidentally, this N-acetylation required only a catalytic amount of the reagent.

$$\text{VII} \xrightarrow{\text{BTDA}} \underset{\text{VII''}}{\overset{\text{VII'}}{\text{or}}} \xrightarrow[2.\ CH_3COONa]{1.\ (CH_3CO)_2O,\ BTDA} \text{III} \quad (2)$$

Although VII could not be prepared from phenylacetamide by the boron trifluoride method, it was synthesized by an earlier method involving acetylation of phenylacetonitrile by means of sodium amide,[9] followed by treatment of the resulting α-acetylphenylacetonitrile (IX) with boron trifluoride and aqueous acetic acid (eq. 3).[10]

$$C_6H_5CH_2CN \xrightarrow[2.\ CH_3COOC_6H_5]{1.\ NaNH_2} \underset{\text{IX}}{C_6H_5\overset{\displaystyle CH_3C{=}O}{\overset{|}{C}}HCN} \xrightarrow[2.\ CH_3COONa]{1.\ BF_3,\ CH_3COOH,\ H_2O} \text{VII} \quad (3)$$

Since the BTDA reagent has previously[11] been shown to convert phenylacetonitrile to phenylacetamide and has now been found to effect the diacetylation of this amide to form III (eq. 1), it seemed possible to accomplish the over-all reaction from the nitrile in a single experiment. This was realized to form essentially pure III in 56% yield; this procedure is recommended for the synthesis of III (eq. 4).

$$C_6H_5CH_2CN \xrightarrow[2.\ CH_3COONa]{1.\ (CH_3CO)_2O,\ BTDA} \text{III} \quad (4)$$

That this conversion of phenylacetonitrile to III involved the intermediate formations of phenylacetamide and its α-acetyl derivative VII, or boron difluoride complexes of them, was supported by detection of the free amides in the crude reaction product by thin layer chromatography. None of the possible α-acetyl derivatives of phenylacetonitrile (IX), which might have arisen through initial acetylation of the nitrile, was detected in the crude product. Moreover, no appreciable acetylation of phenylacetonitrile to form IX was observed in the absence of acetic acid under otherwise similar conditions (see next section). Nevertheless, had any of IX been formed when BTDA was employed, it would have been converted to III, as the latter reaction was realized (eq. 5).

$$\text{IX} \xrightarrow[2.\ CH_3COONa]{1.\ (CH_3CO)_2O,\ BTDA} \text{III} \quad (5)$$

It should be pointed out that the conversion of phenylacetonitrile to III (eq. 4) was accomplished in less time than that of phenylacetamide to this product (eq. 1) (see Experimental). This suggests that the reactive intermediate of phenylacetamide (presumably an enol-type complex) was produced more readily from phenylacetonitrile and BTDA than from phenylacetamide and this reagent.

Similarly *p*-chlorophenylacetonitrile was converted to the diacetyl derivative of the corresponding amide (X) with excess acetic anhydride and BTDA. The yield of IX was 25% but this yield could probably be improved.

$$p\text{-}ClC_6H_5\overset{\displaystyle CH_3C{=}O}{\overset{|}{C}}HCONHCOCH_3$$

X

In contrast to phenylacetamide, N-methylphenylacetamide and N,N-dimethylphenylacetamide failed to undergo acetylation with acetic anhydride under similar conditions. Most of the starting amides were recovered. Phenylacetanilide reacted under such conditions but no single pure product was isolated.

Attempts to Acetylate Ethyl Phenylacetate and Phenylacetonitrile by Boron Trifluoride. Comparison with Basic Methods.—Although various ketones having α-hydrogen have been acylated with aliphatic anhydrides by means of boron trifluoride,[8] there appears to be no example in the literature for such an acylation of an ester or nitrile. We have observed that even ethyl phenylacetate and phenylacetonitrile, which have relatively active α-hydrogens, fail to undergo appreciable acylation with acetic anhydride in the presence of this reagent under the usual conditions. In the reaction with the ester with which BTDA was used, the crude reaction product was indicated by vapor phase chromatography to contain not even a trace of the α-acetyl derivative; the original ester was largely recovered. In the reaction with the nitrile with which boron trifluoride in 1,2-dichloroethane was employed, the crude reaction product was indicated by vapor phase chromatography to contain a little (<10%) of the α-acetyl derivative IX but the method appears to be of little synthetic value.

In contrast to boron trifluoride, certain bases are known to effect satisfactorily the acetylations of esters and nitriles, including ethyl phenylacetate[12] and phenylacetonitrile,[3] with appropriate acetic esters.

(7) This structure appears to be supported by its N-acetylation (see eq. 2) and by its infrared spectrum which showed bands at 2.85 and 2.95 μ for the NH_2 group. However, structure VII'' or even other structures are possible.

(8) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 100 (1954).

(9) R. Levine and C. R. Hauser, *J. Am. Chem. Soc.*, **68**, 760 (1946).

(10) C. R. Hauser and C. J. Eby, *ibid.*, **79**, 725 (1957).

(11) C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, **20**, 1448 (1955).

(12) J. C. Shivers, M. L. Dillon, and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 119 (1947).

SCHEME I

$$C_6H_5COCH_3 \xrightarrow[\text{or } BF_3 \text{ method}]{\text{base-catalyzed method}} C_6H_5COCH_2COCH_3$$

$$C_6H_5CH_2COOC_2H_5 \xrightarrow[\textit{not } BF_3 \text{ method}]{\text{base-catalyzed method}} CH_3C{=}O \,|\, C_6H_5CHCOOC_2H_5$$

$$C_6H_5CH_2CN \xrightarrow[\textit{not } BF_3 \text{ method}]{\text{base-catalyzed method}} CH_3C{=}O \,|\, C_6H_5CHCN$$

A comparison of these acetylations as well as that of a ketone[13] by the two methods is summarized in Scheme I.

Experimental[14]

Diacetylation of Phenylacetamide to Form III.—To a stirred solution of 13.5 g. (0.10 mole) of phenylacetamide in 40.8 g. (0.40 mole) of acetic anhydride was added 52 g. (0.27 mole) of BTDA.[15] After 24 hr. the reaction mixture was added to a solution of 80 g. of sodium acetate trihydrate in 200 ml. of water. The resulting mixture was heated on the steam bath for 1 hr. and then cooled in an ice bath for several hours to precipitate 15.1 g. of crude N-acetyl-α-phenylacetoacetamide (III), m.p. 98–105°. One recrystallization from benzene–petroleum ether (b.p. 30–60°) afforded 11.8 g. (53%) of pure III as lustrous white plates, m.p. 118–119°. A sample of III produced a dark red enol test with ethanolic ferric chloride.

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.74; H, 5.89; N, 6.38.

The filtrate remaining on removal of precipitated III from the sodium acetate solution was partially neutralized with solid sodium bicarbonate and the mixture was extracted with ether–ethyl acetate (1:1). The combined organic extracts were washed thoroughly with saturated sodium bicarbonate solution, dried over sodium sulfate, and concentrated to yield 4.1 g. of light yellow solid. Examination of this material by thin layer chromatography revealed the presence of unreacted phenylacetamide, α-acetylphenylacetamide (VII), and some III.

When the above reaction was repeated with identical proportions of reactants and the reaction mixture was decomposed with hot aqueous sodium acetate after 4 hr., there was isolated 6.0 g. (27%) of III.

When the reaction was repeated employing 0.1 mole each of phenylacetamide, acetic anhydride, and BTDA only 2.4 g. (11%) of the diacetylated derivative III was obtained. A thin layer chromatogram of the crude product showed the presence of much stating material, α-acetylated derivative VII, and III.

In another experiment employing 0.1 mole of phenylacetamide, 0.4 mole of acetic anhydride, and a catalytic amount of BTDA (0.01 mole), no III could be isolated and 70% of the phenylacetamide was recovered.

The diacetylation of phenylacetamide was also effected by saturating a solution of 13.5 g. (0.1 mole) of phenylacetamide and 40.8 (0.40 mole) of acetic anhydride in 250 ml. of dry 1,2-dichloroethane with gaseous boron trifluoride at room temperature (copious white fumes evolved). The reaction solution was stirred for 12 hr. and then added to a solution of 80 g. of sodium acetate trihydrate in 200 ml. of water. The 1,2-dichloroethane was removed by distillation, and the residual aqueous solution was cooled overnight in an ice bath to afford, after recrystallization, 8.6 g. (39%) of III.

Hydrolysis of Diacetyl Derivative III.—A 5.50-g. (0.025-mole) sample of III was refluxed overnight with 50 ml. of 50% sulfuric acid. The acidic solution was cooled and extracted with ether. The ethereal solution was washed with sodium bicarbonate solution, dried over magnesium sulfate, and concentrated. The residual oil was distilled to afford 0.70 g. (25%) of phenylacetone, b.p. 62° (1.8 mm.), which was identified by comparison of its infrared spectrum with an authentic sample, and by mixture melting point of its *p*-nitrophenylhydrazone, m.p. 144–145°.

Reaction of III with Hydrazine to Form Pyrazolone V.—A 2.0-g. (0.009-mole) sample of III was dissolved in 30 ml. of 95% ethanol and 20 drops of 95% hydrazine was added. The mixture was refluxed for 2 hr., cooled, and poured into 50 ml. of water to precipitate 1.2 g. (76%) of 3-methyl-4-phenyl-5-pyrazolone (V), m.p. 210–212°, and 212–213° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.94; H, 5.88; N, 15.81.

The infrared spectrum of this product was identical with that of the pyrazolone (m.p. 212–213°) prepared from ethyl α-phenylacetoacetate[12] and excess hydrazone. A mixture melting point showed no depression.

Boron Difluoride Complex of α-Acetylphenylacetamide and Its N-Acetylation to Form III.—A mixture of 1.1 g. (0.006 mole) of α-acetylphenylacetamide (VII)[10] and 3.6 g. of BTDA was stirred at room temperature for 3 hr. The reaction mixture was cooled in an ice bath and diluted with ice–water to precipitate 1.25 g. (91%) of boron difluoride complex VII′ or VII″, m.p. 139–142°, and 140–141° after two recrystallizations from ether–petroleum ether (b.p. 30–60°). This boron difluoride complex was also prepared in 95% yield by saturation of a cooled solution of VII in 1,2-dichloroethane with gaseous boron trifluoride, followed by removal of the solvent under vacuum.

Anal. Calcd. for $C_{10}H_{10}BF_2NO_2$: C, 53.37; H, 4.43; N, 6.22. Found: C, 53.31; H, 4.14; N, 6.13.

A mixture of 1.1 g. (0.0049 mole) of the boron difluoride complex, 2.1 g. (0.02 mole) of acetic anhydride, and 1.9 g. (0.01 mole) of BTDA was stirred for 18 hr. The reaction mixture was decomposed with aqueous sodium acetate trihydrate (steam bath) to give 0.6 g. (56%) of III, m.p. 118–119°.

Reaction of 1.0 g. (0.004 mole) of the boron difluoride complex with 1.6 g. (0.016 mole) of acetic anhydride and 0.1 g. of BTDA (approximately 0.0005 mole) afforded, after hydrolysis and two recrystallizations from water, 0.2 g. (22%) of III.

Conversion of Phenylacetonitrile to Diacetylated Derivative III.—A solution of 11.7 g. (0.10 mole) of phenylacetonitrile in 40.8 g. (0.40 mole) of acetic anhydride was added, during 15 min., to 87.5 g. (0.46 mole) of BTDA, the temperature rising to 60°. The resulting red solution was stirred at room temperature for 4 hr., then decomposed with 80 g. of sodium acetate trihydrate in 300 ml. of water (steam bath, 1 hr.) The reaction mixture was cooled in an ice bath to precipitate 18.5 g. of crude III, m.p. 107–116°. Examination of a sample by thin layer chromatography showed, in addition to III, unreacted phenylacetonitrile, phenylacetamide, and α-acetylphenylacetamide VII. No α-acetylphenylacetonitrile (IX) or N-acetylphenylacetamide (VIII) was detected. Recrystallization of the crude product from benzene–petroleum ether (b.p. 30–60°) yielded 12.4 g. (56%) of III, m.p. 118–119°.

Conversion of α-Acetylphenylacetonitrile (IX) to III.—To a solution of 15.9 g. (0.10 mole) of α-acetylphenylacetonitrile[9] (IX) in 20.4 g. (0.20 mole) of acetic anhydride was added 87.5 g. (0.46 mole) of BTDA. After 24 hr. the reaction mixture was decomposed with hot aqueous sodium acetate trihydrate to afford 9.25 g. (42%) of III, m.p. 117–119°.

Conversion of *p*-Chlorophenylacetonitrile to Diacetylated Derivative of the Corresponding Amide.—A mixture of 15.1 g. (0.1 mole) of *p*-chlorophenylacetonitrile and 40.8 g. (0.4 mole) of acetic anhydride was added dropwise to 87.5 g. (0.46 mole) of BTDA. After stirring at room temperature for 5 hr., the reaction mixture was decomposed with hot aqueous sodium acetate trihydrate. The resulting semisolid was digested with 100 ml. of hot benzene, and the mixture was filtered. The insoluble solid (1.5 g.) evidently consisted of *p*-chlorophenylacetamide, m.p. 174–176° (lit.[19] 177–179°). The benzene filtrate was diluted with petroleum ether (b.p. 30–60°) to precipitate 6.7 g. of crude material which was recrystallized from aqueous ethanol to yield 6.5 g. (25%) of N-acetyl-α-*p*-chlorophenylacetoacetamide (X), m.p. 135.5–142.5°. Further recrystallization failed to give a

(13) See ref. 8, pp. 122 and 130.

(14) Melting points, taken on a Thomas–Hoover melting point apparatus in open capillary tubes, are corrected. Analyses were by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord using the potassium bromide pellet method for solids, and the neat liquid between sodium chloride plates for liquids. Thin layer chromatograms were run on silica gel G, developed with ethyl acetate–chloroform (1:9), and the spots were detected with iodine. Vapor phase chromatograms were obtained on an F and M Model 500 gas chromatograph using a 5-ft. apiezon column.

(15) This liquid coordination complex ($BF_3 \cdot 2CH_3COOH$), which contained 36% by weight of BF_3, was obtained from the Harshaw Chemical Co.

sharp-melting product.[16] A sample produced a wine-colored enol test with ethanolic ferric chloride. The infrared spectrum showed bands at 2.95 and 5.85–6.1 μ for the >NH and carbonyl groups, respectively. A thin layer chromatogram indicated a single component.

Anal. Calcd. for $C_{12}H_{12}ClNO_3$: C, 56.81; H, 4.77; Cl, 13.98; N, 5.52. Found: C, 57.01; H, 4.79; Cl, 14.08; N, 5.32.

Attempts to Acetylate Ethyl Phenylacetate and Phenylacetonitrile.—A mixture of 16.4 g. (0.1 mole) of ethyl phenylacetate, 40.8 g. (0.4 mole) of acetic anhydride, and 56.5 g. (0.3 mole) of BTDA was stirred at room temperature for 24 hr. The reaction mixture was decomposed with hot aqueous sodium acetate trihydrate. The resulting mixture was cooled, partially neutralized with solid sodium bicarbonate, and extracted with pentane. The organic extracts were washed with sodium bicarbonate solution, dried over sodium sulfate, and concentrated to afford 16.0 g. (97% recovery) of ethyl phenylacetate. The v.p.c. of the recovered ester showed no trace of the desired ethyl α-acetylphenylacetate.

A mixture of 11.7 g. (0.1 mole) of phenylacetonitrile and 40.8 g. (0.4 mole) of acetic anhydride in 150 ml. of 1,2-dichloroethane was cooled in an ice bath and saturated with gaseous boron trifluoride. After warming to room temperature and being stirred for 24 hr., the resulting orange solution was added to aqueous sodium acetate, and the 1,2-chloroethane was removed by distillation until the vapor temperature reached 90%. The residue was partially neutralized with solid sodium bicarbonate and extracted with ether. The ethereal extracts were washed with sodium bicarbonate solution, dried, and concentrated to afford 10.5 g. of an oil. A thin layer chromatogram of this oil indicated the presence of starting nitrile, traces of α-acetylphenylacetonitrile (IX), and α-acetylphenylacetamide (VII). A v.p.c. of this material indicated <10% of IX.

(16) The wide melting range may indicate a mixture of crystalline forms of X or the presence of a mixture of X and one or more enol forms.

Metalations of Certain β-Phenylethyl- and γ-Phenylpropyldimethylamines with *n*-Butyllithium[1]

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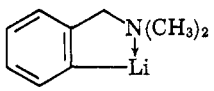
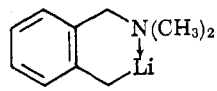
A study was made of metalation of amines of type $C_6H_5(CH_2)_nN(CH_3)_2$ (III) and $C_6H_5C(CH_3)_2CH_2N(CH_3)_2$ (V) with *n*-butyllithium, and of condensation of the resulting lithioamine with benzophenone. These reactions were realized with III (n = 3) and V but not with III (n = 2 or 4); with III (n = 2) dimethylamine was eliminated.

Benzyldimethylamine[2a] and 2-methylbenzyldimethylamine[2b] have recently been metalated with *n*-butyllithium in ether–hexane to form presumably I and II, in which lithium is coordinated with the unshared pair of electrons of nitrogen in five- and six-membered rings, respectively. The site of metalation was established by deuteration and by condensations with electrophilic compounds such as benzophenone.



I

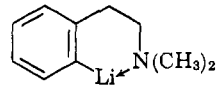


II

In view of these results it seemed possible that certain tertiary amines having the general formula III might undergo similar ring or side-chain metalation by *n*-butyllithium to form five- or six-atom coordination complexes. Thus, β-phenylethyldimethylamine (*III*, n = 2) might afford the six-atom coordination complex IV and, after addition of benzophenone, the corresponding condensation product. However, none of this product was isolated. Instead, hydrolysis of the reaction mixture afforded dimethylamine and neutral polymeric material. Apparently β-elimination of dimethylamine occurred (with or without prior metalation).

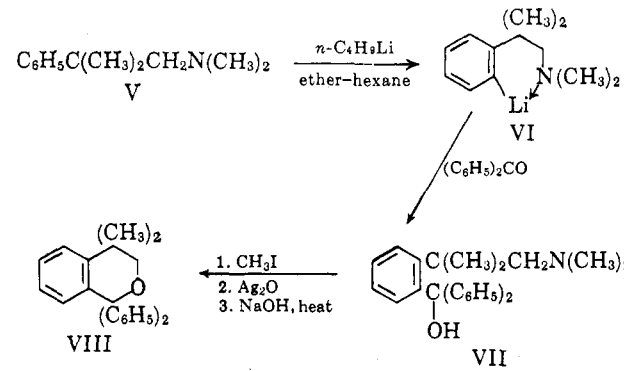
$C_6H_5(CH_2)_nN(CH_3)_2$

III



IV

SCHEME I



It then seemed plausible that the β-phenylethyl type of amine V, which has no β-hydrogens, might undergo metalation to form complex VI and subsequent condensation with benzophenone to afford VII (Scheme I). This was realized, VII being obtained in 17% yield. No appreciable side reaction occurred, and 73% of the starting amine V was recovered.

Structure VII was supported by analysis and absorption spectra. The infrared spectrum showed a band at 3497 cm.$^{-1}$ attributed to the hydroxyl group.[3] This peak was small and almost obliterated by the broad peaks around 3000 cm.$^{-1}$, which were due to the carbon–hydrogen absorption of the methyl groups. The spectrum of VII also showed peaks in the 770–730 and 710–690-cm.$^{-1}$ regions for five adjacent aromatic hydrogens.[4] The n.m.r. spectrum of VII in carbon tetrachloride exhibited no fine splitting either

(1) Supported by Army Research Office (Durham).

(2) (a) F. N. Jones, R. L. Vaulx, and C. R. Hauser, *J. Org. Chem.*, **28**, 3461 (1963); (b) R. L. Vaulx, F. N. Jones, and C. R. Hauser, *ibid.*, **29**, 1387 (1964).

(3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 96.

(4) See ref. 3, pp. 76–78.