prepared by a seven-step synthesis from cyclohexanone and β-dimethylaminopropiophenone through the carbonyl-bridged intermediate, 2-phenylbicyclo[3.3.1]non-2-en-9-one (II). The phenylcycloöctadiene has been proved to contain an unbridged eight-membered ring by quantitative hydrogenation to phenylcycloöctane.

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[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

Catalytic Debenzylation. II. The Evaluation of the Relative Effect of Ring Substituents on the Stability of the N-Benzyl Linkage[1]

BY RICHARD BALTZLY AND PETER B. RUSSELL

In a previous study of catalytic debenzylation[2] it was shown that a variety of substituents in a benzyl group of a dibenzylamine hydrochloride tended to stabilize the carrier benzyl group against hydrogenolytic cleavage. For the most part these earlier competitive debenzylations involved comparison only of the substituted with an unsubstituted benzyl group and consequently the effect of the various groups relative to each other was largely undetermined. Insofar as comparisons could be made they were to the following effect (in order of decreasing stability): $(MeO)_2 \approx O\text{–}CH_2\text{–}O\text{–} > MeO \approx OH > H$; $p\text{-MeO} \approx m\text{-MeO} \approx o\text{-MeO}$; $NH_3^+ > NH_2 > H$; $Me > H$; $Cl > H$. The essential equivalence of the methoxyl group in the three different positions is taken to mean that the position of a substituent is not of much importance.

By means of the competitive debenzylations presented in Table I these previously disjointed relationships have been completed. The substituents that lend themselves to such a study fall into three classes: I, *p*-MeO, CH_3CONH, COOMe, and Cl; II, NH_3^+ and Me; III, NH_2. On the basis of earlier work,[2] class I may be extended by the addition of OH. The members of a given class stabilize the benzyl group to about the same extent. Thus, competitive debenzylations involving comparisons between the members of class I afforded a mixture of products varying from an equimolecular ratio to one of perhaps 4:1. A precise determination of the proportions in such a mixture would, in most cases, be a matter of great experimental difficulty and of doubtful value.

The order of stabilization of the three classes to each other and to the unsubstituted benzyl group (H) is: I > II > III > H. When members of class I are compared to the member (NH_2) in class III or to the unsubstituted benzyl group (H), the reaction is essentially unilateral; only the *p*-aminobenzyl group, or unsubstituted benzyl group, is removed by hydrogenolysis. With members of adjacent groups, some cleavage with removal of the more stabilized group occurs also. Thus, hydrogenolysis of the hydrochloride of 4-carbomethoxybenzyl-4-methylbenzylmethylamine (Reaction 7) takes place chiefly with removal of the 4-methylbenzyl group (as *p*-xylene) and formation of the hydrochloride of 4-carbomethoxybenzyl-methylamine (isolated in 70% yield), but some removal of the 4-carbomethoxybenzyl group occurs also, for *p*-toluic acid was isolated in 10% yield after hydrolysis of the products. In most other reductions that appeared to be unilateral, products present in such small amount would not be isolable and their complete absence cannot be assumed.

The results presented in Table I require some further explanation and discussion. The compounds listed as "Products Isolated" are not necessarily those produced in cleavage, but are sometimes modifications used for convenience in isolation. The instance of *p*-toluic acid has already been mentioned. Similarly, *p*-toluidine (Reductions 4, 5 and 10) was at times isolated as the hydrochloride, at others as *p*-acetotoluidide. In Reduction 3, *p*-acetotoluidide was an initial cleavage product. The vertical dotted lines crossing the formulas in Table I indicate the cleavages observed. In Reductions 4, 5, 6 and 8 cleavage was essentially unilateral. In Reductions 1, 1a, 2, 3 and 9, evidence was obtained that both possible cleavages occur to comparable extents. With reductions 7 and 10, both possible cleavages occurred and are indicated, with the letter P denoting the principal line of fission.

As arranged, Reductions 1–5 involve comparison of the methoxyl group with –Cl, –COOMe, $-NHCOCH_3$, $-NH_2$ and $-NH_3^+$, respectively. Reductions 6–9 show the results of comparison of the methyl group with –Cl, –COOMe, $-NH_2$ and $-NH_3^+$. Obviously, other combinations could have been added but the present group sufficed, in our opinion, for the purpose.

Reduction 1 was inconclusive. No hydrogen was absorbed at 25° and at 65° too much was taken. The *p*-methoxybenzylmethylamine hydrochloride isolated constituted a poor yield and we suspected that hydrogenolysis of chlorine had *preceded* debenzylation to a considerable extent. Since benzyl tertiary amines are more readily cleaved than their secondary analogs, it seemed likely that quaternization would afford a still more labile substance. This proved to be the

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[1] Presented before the Organic Division of the American Chemical Society, Atlantic City meeting, September 1949.

[2] Baltzly and Buck, THIS JOURNAL, 65, 1984 (1943).

TABLE I

RESULTS OF COMPETITIVE DEBENZYLATIONS

Reduction number	Substrate (dotted lines indicate cleavage)	Products isolated
1[b,e]	$\text{4-MeOC}_6\text{H}_4\text{—CH}_2 \vdots \underset{\text{HCl}}{\text{NMe}} \vdots \text{CH}_2\text{C}_6\text{H}_4\text{—Cl-4}'$	p-MeOC$_6$H$_4$—CH$_2$NHMe·HCl[k] Solution acid to congo
1a[a,c]	$\text{4-MeOC}_6\text{H}_4\text{—CH}_2\text{—} \vdots \underset{\text{Cl}^-}{^+\text{NMe}_2} \vdots \text{CH}_2\text{C}_6\text{H}_4\text{—Cl-4}'$	p-ClC$_6$H$_4$—CH$_2$NMe$_2$·HCl (50%)[l]
2[b,d]	$\text{4-MeOC}_6\text{H}_4\text{—CH}_2\text{—} \vdots \underset{\text{HCl}}{\text{NMe}} \vdots \text{—CH}_2\text{C}_6\text{H}_4\text{—COOMe-4}'$	p-MeC$_6$H$_4$—COOH (25–30%) p-MeOC$_6$H$_4$—CH$_2$NHMe·HCl (25–30%)[k] MeOOCC$_6$H$_4$—CH$_2$NHMe·HCl (II Z)
3[a,d]	$\text{4-MeOC}_6\text{H}_4\text{—CH}_2 \vdots \text{—}\underset{\text{Cl}^-}{^+\text{NMe}_2} \vdots \text{—CH}_2\text{C}_6\text{H}_4\text{—NHCOCH}_3\text{-4}'$	p-CH$_3$CONHC$_6$H$_4$—Me (40%) p-CH$_3$CONHC$_6$H$_4$—CH$_2$NMe·HCl (30%) (III Z)[m] p-MeOC$_6$H$_4$—CH$_2$NMe$_2$·HCl (10%)[n]
4[e,f]	$\text{4-MeOC}_6\text{H}_4\text{—CH}_2\underset{\text{HCl}}{\text{NMe}}\text{—} \vdots \text{—CH}_2\text{C}_6\text{H}_4\text{—NO}_2\text{-4}'$	p-CH$_3$CONHC$_6$H$_4$—CH$_3$ (70%) p-MeOC$_6$H$_4$—CH$_2$NHMe·HCl (90%)[k]
4a[b,g]	The same + 10 equivalents of HCl (no cleavage)	$\text{4-MeOC}_6\text{H}_4\text{—CH}_2\underset{\text{HCl}}{\text{NMe}}\text{CH}_2\text{C}_6\text{H}_4\text{—NH}_2\text{·HCl-4}'$(IVa)[m]
5[a,d]	$\text{4-MeOC}_6\text{H}_4\text{—CH}_2\underset{\text{Cl}^-}{^+\text{NMe}_2}\text{—} \vdots \text{—CH}_2\text{C}_6\text{H}_4\text{NH}_3{}^+\text{Cl}^-\text{-4}'$ (Excess HCl present)	p-CH$_3$CONHC$_6$H$_4$—Me (80%) p-MeOC$_6$H$_4$—CH$_2$NMe·HCl (90%)[m]
6[a,c]	$\text{4-MeC}_6\text{H}_4\text{—CH}_2\text{—} \vdots \text{—}\underset{\text{HCl}}{\text{NMe}}\text{CH}_2\text{C}_6\text{H}_4\text{—Cl-4}'$	p-ClC$_6$H$_4$—CH$_2$NHMe·HCl (85–90%)[k] + starting material (10–15%)
7[a,c]	$\text{4-MeC}_6\text{H}_4\text{—}\overset{\text{P}}{\text{CH}_2}\text{—} \vdots \text{—}\underset{\text{HCl}}{\text{NMe}} \vdots \text{CH}_2\text{C}_6\text{H}_4\text{—COOMe-4}'$	p-MeC$_6$H$_4$—COOH (10%) p-MeOOCC$_6$H$_4$—CH$_2$NHMe·HCl (70%) (II Z)[m]
8[a,h]	$\text{4-MeC}_6\text{H}_4\text{—CH}_2\underset{\text{HCl}}{\text{NMe}}\text{—} \vdots \text{—CH}_2\text{C}_6\text{H}_4\text{—NO}_2\text{-4}'$	p-MeC$_6$H$_4$—NH$_2$·HCl (95–100%) p-MeC$_6$H$_4$—CH$_2$NHMe·HCl (65–70%)[k,o]
9[b,i]	$\text{4-MeC}_6\text{H}_4\text{—CH}_2\text{—} \vdots \text{—}\underset{\text{HCl}}{\text{NMe}}\text{—} \vdots \text{—CH}_2\text{C}_6\text{H}_4\text{—NO}_2\text{-4}'$ + 20 equivalents of HCl	p-H$_2$NC$_6$H$_4$—CH$_2$NHMe·2HCl (15%)[k]
10[a,i]	$\text{4-O}_2\text{NC}_6\text{H}_4\text{—}\overset{\text{P}}{\text{CH}_2}\text{—} \vdots \underset{\text{HCl}}{\text{NMe}} \vdots \text{CH}_2\text{C}_6\text{H}_4\text{Cl-2}'$	p-C$_6$H$_5$—CH$_2$NHMe·HCl (20%) p-CH$_3$CONHC$_6$H$_4$—Me (60%)

[a] Reduction at 25°. [b] Reduction at 65°. [c] Sample, 20 mmoles; hydrogen absorption, 20 mmoles. [d] Sample, 10 mmoles; hydrogen absorption, 10 mmoles. [e] Sample, 20 mmoles; hydrogen absorption, 34 mmoles. [f] Sample, 20 mmoles; hydrogen absorption, 90 mmoles (80 mmoles calcd. for NO$_2$ → NH$_2$ + cleavage). [g] Sample, 20 mmoles; hydrogen absorption, 65 mmoles (60 mmoles calcd. for NO$_2$ → NH$_2$). [h] Sample, 20 mmoles; hydrogen absorption, 80 mmoles (80 mmoles calcd. for NO$_2$ → NH$_2$ + cleavage). [i] Sample, 5 mmoles; hydrogen absorption, 20 mmoles (20 mmoles calcd. for NO$_2$ → NH$_2$ + cleavage). [j] Sample, 10 mmoles; hydrogen absorption, 50 mmoles (40 mmoles calcd. for NO$_2$ → NH$_2$ + cleavage). [k] Baltzly and Buck (*loc. cit.*). [l] M. p. 212–213°; Thomson and Stevens, *J. Chem. Soc.*, 55 (1932), have reported the picrate, m. p., 125–126°. [m] New compound described in Table II. [n] Tiffeneau, *Bull. Soc. Chim.*, [4] 9, 825 (1911). [o] The m. p. is 176–177°, not 136–137° as previously reported (Baltzly and Buck, *loc. cit.*).

case and Reduction 1a proceeded smoothly at 25° with no dehalogenation. Of the possible products, *p*-chlorobenzyldimethylamine hydrochloride is relatively high-melting and insoluble, whereas the *p*-methoxy compound is isolated with difficulty when accompanied by similar substances. The 50% yield of the *p*-chloro amine salt is, of course, a minimum but is probably not far below the maximum. Isolation of the pure *p*-methoxy could not be expected from the mixture but we conclude that both substances were present in comparable amounts.

In Reduction 2, after saponification of the reaction mixture, one pair of complementary products, *p*-toluic acid (from methyl *p*-toluate) and *p*-methoxybenzylmethylamine (as the hydrochloride) were recovered cleanly and the quantities obtained (which were equivalent) must have been close to a maximum.

Reduction 3 afforded (after evaporation of methanol) a water-insoluble product, *p*-acetotoluidide, which presumably was recovered without appreciable loss. The amine salt produced by cleavage in the reverse direction, *p*-acetamidobenzyldimethylamine hydrochloride, was obtained pure without much loss, being relatively insoluble. Losses in the isolation of *p*-methoxybenzyldimethylamine hydrochloride, were, however, rather large. It seems clear that cleavage proceeded about equally in each direction.

In Reductions 4 and 4a, the nitro group undoubtedly was hydrogenated first. When the amino group so produced was free as such, cleavage was easy and unilateral. In the presence of excess acid (4a) debenzylation did not take place at 65° and the desired comparison had to be made through the quaternary salt (Reduction 5) which cleaved in the same direction as in Reduction 4.

Reductions 8 and 9 are analogous to 4 and 4a. Cleavage in 8 was unilateral. From 9 (which required heating) a mixture of amine salts was obtained. The known *p*-aminobenzylmethylamine dihydrochloride was isolated as a pure substance in only 15% yield. Had cleavage been unilateral, recovery of this substance would have been good. As it was, the mother liquors deposited only mixtures of salts and we take it that cleavage occurred to a comparable extent in both directions. Thus the substituent $-NH_3^+$ is comparable to the methyl group and is a distinctly stronger stabilizer than $-NH_2$. It is also clear that the change from NH_2 to NH_3^+ not only stabilizes the carrier benzyl group but the molecule as a whole.

The results of Reduction 10 are consistent with those of 1 and 1a, although somewhat inconclusive in themselves. Earlier work had shown that the position of substitution is not critical in its effect on debenzylation. The *ortho* chlorine is, however apparently more subject to hydrogenolysis than the *para* chlorine. The benzylmethylamine hydrochloride isolated from the mixture of amine salts is a rather low minimum recovery. Its presence can be explained only on the basis that dechlorination took place *after* cleavage, since in so far as it should occur before cleavage, toluene and *p*-aminobenzylmethylamine hydrochloride would be the only products. The *p*-acetotoluidide isolated (by acetylation of a weak-base fraction) also represents a minimum recovery. We are inclined to believe that the *o*-chlorobenzyl group is of a higher order of stability than the *p*-aminobenzyl group but have indicated cleavage in both directions.

The necessary dibenzylmethylamines and quaternary salts were prepared by conventional methods. Their properties are shown in Table II, the numbering (in Roman numerals) being coördinated with the Arabic figures identifying the reductions.

The findings of this and of the earlier paper on this subject show a consistency among themselves and clearly follow a definite pattern. This pattern is not, however, interpretable on the basis of current theories. Since these relate principally to the class of ionoid reactions of which catalytic reduction is almost certainly not a member, such an irrelevancy is not surprising.

We are aware that studies of this kind on the competitive debenzylation of variously substituted dibenzylmethylamines are open to objection on the ground that the observed results are due not to the weakening of the C–N bond but rather to its more favorable orientation on the catalyst brought about by the presence, nature and size of the substituent. Such an effect would not be expected to be constant but to be a property of the pair of substituents. We have attempted to eliminate this as an explanation of results by basing our conclusions on the comparison of a substituent with at least two other substituents of different kinds. The acetamido group, however, has been compared only with methoxyl.

Experimental

The technique of the reductions was that described by Baltzly and Buck.[2] Of the products isolated only IVa, IIz and IIIz are new: their properties are shown in Table II. Melting points are uncorrected.

Preparation of Tertiary Dibenzylmethylamines.—Compounds I, IV, VI, VIIa, VIII and X were prepared by a general procedure in which one mole of the appropriate benzyl chloride reacted with 2 moles of a benzylmethylamine in acetone. Compounds VI, VIIa and VIII resulted from the reaction of *p*-methylbenzylamine with *p*-chlorobenzyl chloride, *p*-cyanobenzyl chloride[3] and *p*-nitrobenzyl chloride, respectively. To prepare Compounds I and IV, *p*-chlorobenzyl chloride and *p*-nitrobenzyl chloride were treated with *p*-methoxybenzylmethylamine. From *o*-chlorobenzylmethylamine and *p*-nitrobenzyl chloride Compound X was obtained.

4-Methyl-4′-nitrodibenzylmethylamine Hydrochloride (VIII).—Fifteen grams of *p*-nitrobenzyl chloride in 100 cc. of acetone was added to a solution of 28.5 g. of *p*-methylbenzylmethylamine in 25 cc. of acetone. A heavy precipitate began to separate after five minutes. The mixture was allowed to stand sixteen hours and the precipitate (*p*-methylbenzylamine hydrochloride) was then collected (13 g.). The acetone was evaporated from the filtrate, 200 cc. of water was added and the basic oil was taken into ether. The ethereal solution was dried over sodium sulfate, the ether evaporated and the residual base was warmed one hour with 5 cc. of acetic anhydride. The excess anhydride was destroyed by addition of 10 cc. of methanol and further warming. The solution was then dissolved in 200 cc. of ether and the tertiary base was extracted with 3 *N* hydrochloric acid. The acid extracts were evaporated *in vacuo* and the residual hydrochloride crystallized from ethanol–ether mixtures (or similar solvent mixtures as shown in Table II).

The quaternary salt corresponding to I was prepared from *p*-methoxybenzyldimethylamine and *p*-chlorobenzyl chloride by refluxing for three hours in benzene. The chloride did not crystallize readily so the product was purified and analyzed as the picrate (Ib). For the reduction, the picrate was transformed to the chloride which melted at 152° (sealed tube) but was extremely hygroscopic.

4-Methyl-4′-carbomethoxydibenzylmethylamine Hydrochloride (VII).—Twelve grams of the corresponding nitrile (VIIa) was refluxed with 10 g. of sodium hydroxide in 100 cc. of 80% ethanol four hours. The solution was diluted with water, brought to *p*H 6-7 with acetic acid and evaporated to dryness *in vacuo*. The residual solid was refluxed five hours with 200 cc. of 10% (wt./wt.) methanolic hydrogen chloride. After removal of most of the solvent the solution was poured into water and basified with sodium carbonate. The oily ester was taken into

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(3) Mellinghoff, *Ber.*, **22**, 3207 (1889).

TABLE II

PROPERTIES OF COMPOUNDS REPORTED

Compound	Formula	M. p., °C.	Empirica formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
I	$4\text{-MeOC}_6\text{H}_4\text{CH}_2(4'\text{-Cl-C}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot\text{HCl}$	151.5–152	$C_{16}H_{19}Cl_2NO$	61.5	61.2	6.2	6.3
Ib	$4\text{-MeOC}_6\text{H}_4\text{CH}_2(4'\text{-Cl-C}_6\text{H}_4\text{CH}_2)\text{NMe}_2\text{-OC}_6\text{H}_2(\text{NO}_2)_3$	128–130^a	$C_{23}H_{23}ClN_4O_8$	53.3	53.6	4.5	4.5
II	$4\text{-MeOC}_6\text{H}_4\text{CH}_2(4'\text{-MeOOCC}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot\text{HCl}$	201–202	$C_{18}H_{22}ClNO_3$	64.5	64.5	6.6	6.4
IIIa	$4\text{-MeOC}_6\text{H}_4\text{CH}_2(4'\text{-CH}_3\text{CONHC}_6\text{H}_4\text{CH}_2)\text{NMe}_2\text{I}$	196–197^b	$C_{19}H_{25}IN_2O_2$	51.8	52.1	5.7	5.7
IIIb	$4\text{-MeOC}_6\text{H}_4\text{CH}_2(4'\text{-CH}_3\text{CONHC}_6\text{H}_4\text{CH}_2)\text{NMe}$	87^c	$C_{18}H_{22}N_2O_2$	72.5	72.7	7.4	7.2
IV	$4\text{-MeOC}_6\text{H}_4\text{CH}_2(4'\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot\text{HCl}$	148–149^{d,i}	$C_{16}H_{19}ClN_2O_3$	59.6	59.7	6.0	5.7
IVa	$4\text{-MeOC}_6\text{H}_4\text{CH}_2(4'\text{-H}_2\text{NC}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot 2\text{HCl}$	187–189 dec.	$C_{16}H_{22}Cl_2N_2O$	58.3	58.4	6.7	6.6
V	$4\text{-MeOC}_6\text{H}_4\text{CH}_2(4'\text{-H}_2\text{NC}_6\text{H}_4\text{CH}_2)\text{NMe}_2\text{Cl}\cdot\text{HCl}$	166–167 dec.	$C_{17}H_{24}Cl_2N_2O$	59.5	59.2	7.0	6.7
VI	$4\text{-MeC}_6\text{H}_4\text{CH}_2(4'\text{-ClC}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot\text{HCl}$	175.5–176	$C_{16}H_{19}Cl_2N$	65.1	65.1	6.5	6.3
VIIa	$4\text{-MeC}_6\text{H}_4\text{CH}_2(4'\text{-NCC}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot\text{HCl}$	199–200^e	$C_{17}H_{19}ClN_2$	71.2	71.3	6.6	6.6
VII	$4\text{-MeC}_6\text{H}_4\text{CH}_2(4'\text{-MeOOCC}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot\text{HCl}$	182^e	$C_{18}H_{22}ClNO_2$	67.7	68.0	6.9	6.7
VIII	$4\text{-MeC}_6\text{H}_4\text{CH}_2(4'\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot\text{HCl}$	160–161^f	$C_{16}H_{19}ClN_2O_2$	62.6	62.9	6.2	6.1
X	$2\text{-ClC}_6\text{H}_4\text{CH}_2(4'\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)\text{NMe}\cdot\text{HCl}$	173^d	$C_{15}H_{16}ClN_2O_2$	55.1	55.4	4.9	5.0
IIz	$4\text{-MeOOCC}_6\text{H}_4\text{CH}_2\text{NHMe}\cdot\text{HCl}$	215–215.5^h	$C_{10}H_{14}ClNO_2$	55.7	56.0	6.6	6.8
IIIz	$4\text{-CH}_3\text{CONHC}_6\text{H}_4\text{CH}_2\text{NMe}_2\cdot\text{HCl}$	228^i	$C_{11}H_{17}ClN_2O$	57.7	57.8	7.5	7.2

[a] Yellow prisms from ethanol. [b] Prisms from acetone or water. [c] Needles from hexane. [d] Needles from acetone–ether. [e] Needles from ethanol–ether. [f] Plates from ethanol–ethyl acetate–ether. [g] Flat needles from methanol–acetone–ether. [h] Yellow prisms from ethanol–ethyl acetate–ether. [i] B. p. (8 mm.) of base, 205–209°.

ether, washed with water, dried over potassium carbonate, and transformed to the hydrochloride by addition to methanolic hydrogen chloride solution.

Compound II was obtained similarly by hydrolysis and esterification of the corresponding nitrile (which was not analyzed though apparently homogeneous). The saponification of this nitrile was somewhat more difficult and required refluxing with 10% aqueous potassium hydroxide solution for fifteen hours.

Compound IVa was the product of the hydrogenation of IV in the presence of excess acid. It was successively transformed into IIIb, IIIa, the chloride corresponding to IIIa, and finally into V.

4-Methoxy-4'-acetamidodibenzylmethylamine (IIIb).—Eleven grams of 4-methoxy-4'-aminodibenzylmethylamine dihydrochloride (IVa) was dissolved in 100 cc. of water and neutralized with 2.8 g. of sodium bicarbonate. Twelve grams of acetic anhydride was added with stirring during one hour and the solution was then basified with sodium hydroxide solution. The oily base was taken into ether, dried and crystallized by addition of petroleum ether; yield, 9.6 g. When treated with methyl iodide in acetone, the corresponding methiodide IIIa was formed.

The methiodide was converted to the methochloride by the conventional treatment with silver chloride. On evaporation of the aqueous solution the chloride was obtained as a glass which crystallized on standing but was too deliquescent for characterization: it was used directly in Reduction 3.

4-Methoxy-4'-aminodibenzyldimethylammonium Chloride Hydrochloride (V).—The acetamido chloride not expended in Reduction 3, 8 g., was heated three hours on the steam-bath with 100 cc. of 6 *N* hydrochloric acid. The solution, which smelled strongly of acetic acid, was evaporated *in vacuo* and the residual glass was crystallized from ethanol-ether mixture.

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Summary

1. The effect of various substituents in stabilizing benzyl groups against hydrogenolytic cleavage has been studied by means of competitive debenzylations of appropriately substituted dibenzylmethylamines and dibenzyl quaternary salts.

2. Of the substituents examined, the methoxyl, hydroxyl, acetamido and carbomethoxy groups and chlorine form a class, approximately equivalent to each other, stabilizing the benzyl group most strongly. The amino group is the weakest stabilizer and the methyl and cationic amino groups (NH_3^+) are intermediate in stabilizing ability. As compared to hydrogen, all these substituents are stabilizers.

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