[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Alkylation of Diphenylmethane with Alkyl Halides by Sodium Amide. Substitution *versus* β-Elimination. Relative Acidities of Diphenylmethane and Ammonia

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Diphenylmethane was metalated by sodium amide in liquid ammonia and ether, and the resulting sodium diphenylmethide was alkylated with alkyl halides to produce excellent yields of hydrocarbons having the benzhydryl group. The method is superior to other methods of synthesis of such hydrocarbons. Sodium diphenylmethide shows a strong affinity for the carbon nucleus producing largely the alkylation product even with β-phenylethyl chloride which has been shown to undergo predominantly β-elimination with other strong bases. Potassium diphenylmethide yields some styrene with this halide. Sodium diphenylmethide was unaffected by *t*-butyl chloride. Evidence is presented that diphenylmethane is a stronger acid than ammonia in liquid ammonia.

Reactions of diphenylmethane involving one of its active methylene hydrogens have generally been effected through the intermediate formation of an ether suspension of potassium diphenylmethide. This red intermediate has been prepared by adding the hydrocarbon to potassium amide in liquid ammonia, and then replacing the ammonia with ether.[2] For example, the resulting suspension has been carbonated to form diphenylacetic acid in 91% yield (equation 1).[3,4]

$$(C_6H_5)_2CH_2 \xrightarrow[\text{liq. } NH_3]{KNH_2} (C_6H_5)_2CHK \xrightarrow[\substack{2,\ CO_2 \\ 3,\ \text{acid}}]{1,\ \text{ether}} (C_6H_5)_2CHCOOH \quad (1)$$

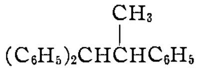
Although ether is a suitable medium for many reactions of carbanions, liquid ammonia is sometimes an even better medium. Thus certain alkylations of sodio- or potassiophenylacetonitrile have been realized in better yields in a mixture of liquid ammonia and ether than in ether alone.[5]

In the present investigation alkylations and aralkylations of sodium diphenylmethide with alkyl and aralkyl halides were effected in a mixture of liquid ammonia[6] and ether to form hydrocarbons having the benzhydryl group. The reaction may be illustrated with benzyl chloride which formed hydrocarbon I in 99% yield (equation 1).

$$(C_6H_5)_2CH_2 \xrightarrow[\text{liq. } NH_3]{NaNH_2} (C_6H_5)_2CHNa \xrightarrow[\text{ether}]{C_6H_5CH_2Cl} \underset{\text{I}}{(C_6H_5)_2CHCH_2C_6H_5} \quad (2)$$

Similarly, benzhydryl and α- and β-phenylethyl chlorides gave hydrocarbons II, III and IV in yields of 96, 97 and 88%, respectively. The last two yields were based on slightly impure products which are low melting solids.

$$\underset{\text{II}}{(C_6H_5)_2CHCH(C_6H_5)_2}$$



$$(C_6H_5)_2CH\overset{\overset{\displaystyle CH_3}{|}}{C}HC_6H_5$$

III

$$\underset{\text{IV}}{(C_6H_5)_2CHCH_2CH_2C_6H_5}$$

The purely aliphatic halides, isopropyl chloride, and 2-ethylbutyl and *n*-octyl bromides, produced hydrocarbons V, VI and VII in yields of 86, 94 and 99%, respectively.

$$\underset{\text{V}}{(C_6H_5)_2CHCH(CH_3)_2} \qquad \underset{\text{VI}}{(C_6H_5)_2CHCH_2CH(C_2H_5)_2}$$

$$\underset{\text{VII}}{(C_6H_5)_2CH(CH_2)_7CH_3}$$

These results are summarized in Table I. This method is convenient to carry out. The diphenylmethane is added to an equivalent of sodium amide in liquid ammonia, followed by an equivalent of the halide in ether. The metalation of the hydrocarbon occurs immediately, and the alkylation of the resulting sodium diphenylmethide takes place rapidly (see Experimental).

TABLE I

ALKYLATIONS OF SODIUM DIPHENYLMETHIDE WITH HALIDES TO FORM HYDROCARBONS

Halide	Hydrocarbon	Yield, %
Benzyl chloride	I	99
Benzhydryl chloride	II	96
α-Phenylethyl chloride	III	97
β-Phenylethyl chloride	IV	88
Isopropyl chloride	V	86
2-Ethylbutyl bromide	VI	94
n-Octyl bromide	VII	99

This procedure is more convenient than the related earlier method involving the preparation of sodium diphenylmethide from benzhydryl methyl ether and sodium in ethyl ether (equation 3).[7,8]

$$(C_6H_5)_2CHOCH_3 \xrightarrow[\text{ether}]{Na} (C_6H_5)_2CHNa \xrightarrow{RX} (C_6H_5)_2CHR \quad (3)$$

Not only is diphenylmethane more readily available than benzhydryl methyl ether, but the con-

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[1] Carbide and Carbon Chemicals Co. Fellow, 1955–1956.

[2] In contrast to potassium diphenylmethide, sodium diphenylmethide, prepared from diphenylmethane and sodium amide in liquid ammonia, reverts to the hydrocarbon and sodium amide on replacing the ammonia with ether; see ref. 3, and C. R. Hauser, D. S. Hoffenberg, W. H. Puterbaugh and F. C. Frostick, Jr., *J. Org. Chem.*, **20**, 1531 (1955).

[3] R. S. Yost and C. R. Hauser, THIS JOURNAL, **69**, 2325 (1947).

[4] Other reactions of potassium diphenylmethide in ether include acylations with acid chlorides (S. W. Kantor and C. R. Hauser, *ibid.*, **72**, 3290 (1950)), silicoalkylation with trimethylchlorosilane (C. R. Hauser and C. R. Hance, *ibid.*, **23**, 5846 (1951)), and nitrosation with butyl nitrite (ref. in note 2).

[5] C. R. Hauser and W. R. Brasen, *ibid.*, **78**, 494 (1956).

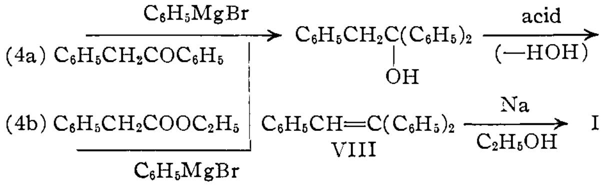
[6] The carbethoxylations of sodium and potassium diphenylmethides with ethyl carbonate to form ethyl diphenylacetate have been effected in this medium in yields of 38 and 45%, respectively; ref. 3. Also the additions of sodium diphenylmethide to benzophenone and certain aldehydes have been realized in this medium; these results will be published soon. However, such reactions as acylations with acid chlorides or carbonation with Dry Ice appear not to be feasible in liquid ammonia.

[7] W. Schlenk and E. Bergmann, *Ann.*, **479**, 72 (1930).

[8] E. Bergmann, *J. Chem. Soc.*, 412 (1936).

version of the hydrocarbon to the sodio derivative can be accomplished in much less time than that of the ether. In fact the ether was shaken with finely divided sodium for two days.[8] Moreover, the yields of hydrocarbons III and IV were 97 and 88%, respectively, by our method, and only 42 and 65%, respectively, by the earlier method.[8] However, the earlier method has been reported to produce hydrocarbon V in quantitative yield.[7]

The present method also appears preferable to known indirect methods, the most widely employed of which involves the synthesis of the corresponding olefin, and its reduction or hydrogenation. The olefins have generally been obtained by the dehydration of carbinols which usually have been synthesized by appropriate Grignard reactions. For example, olefin VIII, which was reduced to form hydrocarbon I, was synthesized by the action of phenylmagnesium bromide on the appropriate ketone[9] or ester[10] (equations 4a and 4b). No yields were reported.



$$\text{(4a)}\ C_6H_5CH_2COC_6H_5 \xrightarrow{C_6H_5MgBr} C_6H_5CH_2C(OH)(C_6H_5)_2 \xrightarrow[(-HOH)]{\text{acid}} \underset{\text{VIII}}{C_6H_5CH{=}C(C_6H_5)_2} \xrightarrow[C_2H_5OH]{Na} \text{I}$$

$$\text{(4b)}\ C_6H_5CH_2COOC_2H_5 \xrightarrow{C_6H_5MgBr} \underset{\text{VIII}}{C_6H_5CH{=}C(C_6H_5)_2}$$

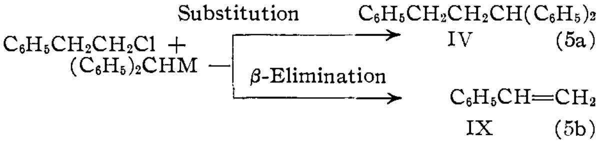
Similarly hydrocarbons III[10] and V[11] have been synthesized through the corresponding olefins and carbinols which were obtained from Grignard reactions. The yield for the former hydrocarbon was not given but that for the latter was reported to be good.

Hydrocarbon II has been prepared in this Laboratory by the reduction of tetraphenylethylene which was synthesized through the selfalkylation of benzhydryl chloride by means of sodium amide in liquid ammonia.[12] The over-all yield was good, but the present alkylation method is more convenient.[13]

Substitution *versus* β-Elimination.—It is rather remarkable that even β-phenylethyl and isopropyl chlorides and 2-ethylbutyl bromide underwent predominantly the substitution type of reaction with sodium diphenylmethide to form alkylation products (Table I), since such halides generally exhibit largely β-elimination with strong bases to yield the corresponding olefins.[14] For example, β-phenylethyl bromide is converted by ethanolic sodium ethoxide at 25° to styrene in almost quantitative yields (93–96%).[15] Although the low temperature (−33°) at which the reactions with sodium diphenylmethide were carried out should favor substitution,[16] the more strongly basic nature of this reagent compared to sodium ethoxide might be expected to more than compensate for the influence of temperature and to produce appreciable β-elimination. Apparently sodium diphenylmethide shows less tendency to attack the β-hydrogen of an alkyl halide than would be anticipated from its basic strength.[17]

The lack of appreciable tendency for sodium diphenylmethide to effect β-elimination was further demonstrated by its failure to react with *t*-butyl chloride which generally undergoes this type of reaction with bases.[18] Thus, in contrast to the halides listed in Table I, this halide failed to react with sodium diphenylmethide in liquid ammonia and ether, the red color of this reagent remaining even after four hours in the presence of two equivalents of the halide. That no appreciable amount of the sodium diphenylmethide had reacted was shown by the addition of benzhydryl chloride which produced the corresponding hydrocarbon II in 94% yield. Not only did the *t*-butyl chloride fail to react with the sodium diphenylmethide but apparently no appreciable amount of it underwent ammonolysis with the ammonia since much of the tertiary halide was recovered.

Since the potassium amide in liquid ammonia is known to effect relatively more β-elimination than sodium amide with certain halides,[19] it seemed likely that potassium diphenylmethide would effect relatively more β-elimination than sodium diphenylmethide under similar conditions. In agreement with expectation, potassium diphenylmethide converted β-phenylethyl chloride to styrene in 18% yield, although even the potassium reagent underwent mainly (70%) alkylation to form hydrocarbon IV. The influence of the metallic cation of the two courses of reaction may be illustrated by equations 5a and 5b.



$$C_6H_5CH_2CH_2Cl + (C_6H_5)_2CHM \xrightarrow{\text{Substitution}} \underset{\text{IV}}{C_6H_5CH_2CH_2CH(C_6H_5)_2} \quad \text{(5a)}$$

$$C_6H_5CH_2CH_2Cl + (C_6H_5)_2CHM \xrightarrow{\beta\text{-Elimination}} \underset{\text{IX}}{C_6H_5CH{=}CH_2} \quad \text{(5b)}$$

M = Na; yields 88% of IV, trace of IX
M = K; yields 70% of IV, 18% of IX

Relative Acidities of Diphenylmethane and Ammonia.—The fact that the yield of the alkylation product of sodium diphenylmethide with benzyl chloride or certain other halides was essen-

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[9] A. Klages and S. Heilmann, *Ber.*, **37**, 1455 (1904).

[10] W. Schlenk and E. Bergmann, *Ann.*, **463**, 44 (1928).

[11] P. Sabatier and M. Murat, *Ann. chim. phys.*, [9] **4**, 294 (1915).

[12] See C. R. Hauser, W. R. Brasen, P. S. Skell and A. E. Brodhag, THIS JOURNAL, **78**, 1653 (1956). The analogous reaction with benzyl chloride is represented by equation 7.

[13] Hydrocarbon II is generally formed as by-product in the conversion of benzhydryl halides to Grignard reagents, but this coupling reaction appears not to have been employed as a preparative method. Hydrocarbon II has also been obtained in connection with a study of active hydrogen compounds, such as ethanol, on the di-sodium derivative of tetraphenylethylene which was synthesized from diphenyldichloromethane and copper bronze; W. Schlenk and E. Bergmann, *Ann.*, **463**, 44 (1928).

[14] See especially, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 437.

[15] E. D. Hughes, C. K. Ingold, S. Masterman and B. J. MacNulty, *J. Chem. Soc.*, 899 (1940).

[16] See Ingold, ref. 14, p. 460.

[17] This tendency for sodium diphenylmethide to react at the α-carbon atom rather than at the β-hydrogen of the halides, together with the high rate at which these substitutions occur (see Experimental), suggests the mutual activation of both components through coordination of the sodium with the halogen leading to a low energy transition state.

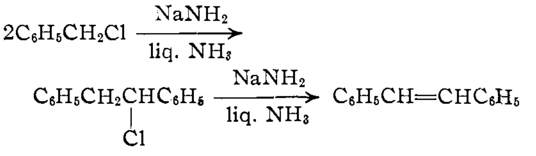
[18] J. U. Nef, *Ann.*, **309**, 136 (1899).

[19] For example, 2-ethylbutyl bromide has been reported to undergo β-elimination to the extents of 75 and 45% with potassium amide and sodium amide, respectively; see R. N. Shreve and L. W. Rothenburger, *Ind. Eng. Chem.*, **29**, 1361 (1937).

tially quantitative indicates that the equilibrium of the acid–base reaction between equivalents of diphenylmethane and amide ion in a mixture of liquid ammonia and ether is far on the side of the diphenylmethide ion (equation 6). Otherwise

$$(C_6H_5)_2CH_2 + \overline{N}H_2 \underset{\longleftarrow}{\xrightarrow{\text{liq. }NH_3}} \underset{\text{(red)}}{(C_6H_5)_2\overline{C}H} + NH_3 \quad (6)$$

the amide ion present in the equilibrium mixture might be expected to react with the halide. For example, benzyl chloride is rapidly converted by the amide ion in liquid ammonia to stilbene (equation 7).[12] This reaction is accompanied by the production of violet color.[12]



$$2C_6H_5CH_2Cl \xrightarrow[\text{liq. }NH_3]{NaNH_2} C_6H_5CH_2\underset{\displaystyle\overset{|}{Cl}}{C}HC_6H_5 \xrightarrow[\text{liq. }NH_3]{NaNH_2} C_6H_5CH{=}CHC_6H_5 \quad (7)$$

The possibility that an appreciable concentration of amide ion is present at equilibrium but that the diphenylmethide ion reacts more rapidly with the halide than the amide ion was eliminated by a competitive experiment. Thus, the addition of an equivalent of benzyl chloride to a mixture of one equivalent each of sodium diphenylmethide and sodium amide gave only a 35% yield of the alkylation product, hydrocarbon I. The main product was stilbene (62%), the violet color associated with its formation being observed (equation 7).

These results lead to the conclusion that diphenylmethane is a considerably stronger acid than ammonia.[20] This conclusion might appear to be at variance with reported pK values for diphenylmethane and ammonia which are 35[21] and 33,[22] respectively. On the basis of these values the hydrocarbon would be expected to be ionized by an equivalent of the amide ion to the extent of only about 10%. However, these values should probably not be compared since the value for diphenylmethane was determined in ether at room temperature,[21] and that for ammonia, in liquid ammonia at −55°.[22] On the basis of an early observation of Wooster[23] that diphenylmethane produces deep red solutions with sodium and potassium amides in liquid ammonia, Morton[24] concluded that the pK value for this hydrocarbon may be considerably lower than the reported value of 35.

Finally it should be mentioned that, in contrast to diphenylmethane, di-*p*-methoxyphenylmethane (X) is evidently a weaker acid than ammonia (equation 8). Thus, although the addition of compound X to an equivalent of sodium amide in liquid ammonia produced a red color, only about one-twentieth of an equivalent of benzyl chloride was required to change this color to the purple color associated with stilbene formation. On adding an equivalent of the halide, an 89% yield of stilbene was obtained, and 94% of X was recovered.

$$\underset{\text{X}}{(p\text{-}CH_3OC_6H_4)_2CH_2} + NaNH_2 \overset{\text{liq. }NH_3}{\underset{\longleftarrow}{\longrightarrow}} (p\text{-}CH_3OC_6H_4)_2CHNa + NH_3 \quad (8)$$

Experimental[25]

Alkylations and Aralkylations of Diphenylmethane (Table I).—To a stirred suspension of 0.1 mole of sodium amide in 200 ml. of anhydrous liquid ammonia[8] was added 16.8 g. (0.1 mole) of diphenylmethane in 100 ml. of dry ether. The red color of sodium diphenylmethide appeared immediately. After 10 minutes, 0.1 mole of the halide in 100 ml. of dry ether was added rapidly. Benzyl chloride, benzhydryl and α-phenylethyl chlorides decolorized the red solution as soon as all the halide solution was added. The other halides listed in Table I required a few minutes to discharge the red color. When no color remained the liquid ammonia was removed on the steam-bath to produce a suspension of salt in ether. An additional 100 ml. of ether was added and the mixture cooled. Water (100 ml.) was added to dissolve insoluble salts and the ether layer was separated. The aqueous layer was extracted twice with 50 ml. of ether and the combined ether layers were dried over anhydrous magnesium sulfate. After filtering, the solvent was removed. The residue was distilled or recrystallized from appropriate solvents as described below.

1,1,2-Triphenylethane (I) crystallized when the last traces of ether were removed under suction. The crude solid was taken up in warm ethanol and water was added to the cloud point. On cooling, 15.4 g. (99%) of the hydrocarbon was obtained which melted at 55–56°, reported m.p. 54°[9] and 56°.[7]

1,1,2,2-Tetraphenylethane (II) precipitated from the ether in the reaction mixture. The solid was filtered from the ether and water layers. The ether layer was then separated and the ether removed to obtain more solid. The combined crude solids were dissolved in excess hot benzene and the benzene solution was filtered. The clear filtrate was heated to remove excess solvent and ethanol was added from time to time. When white solid began to separate, the hot solution was allowed to cool. The yield of pure hydrocarbon was 32 g. (96%), melting at 214–215°. A mixed melting point with an authentic sample[26] (m.p. 214–215°) showed no depression.

1,1,2-Triphenylpropane (III) was taken up in hot ethanol (75 ml.) and filtered. Water was added until the solution was cloudy, and a few drops of ethanol were then added to clarify the solution. On standing, white cubic crystals separated. A total of 26 g. (97%) of the compound was obtained from the original crystallization and from the mother liquor. The crude solid melted at 68–71°. Two crystallizations from aqueous ethanol gave pure material, m.p. 73–75°, reported[10] m.p. 73–75°.

1,1,3-Triphenylethane (IV) was obtained from the residue remaining after attempted isolation of styrene by distillation in the presence of a few crystals of hydroquinone. Only a few drops of distillate were obtained at 50 mm. which decolorized bromine in carbon tetrachloride, but no styrene dibromide was obtained. The viscous residue was taken up in 50 ml. of ethanol and filtered. Cooling gave 24 g. (88%) of IV melting at 41–45°. Two recrystallizations from ethanol gave pure IV, m.p. 47°, reported[8] m.p. 47°.

1,1-Diphenyl-2-methylpropane (V) distilled at 126–127° at 5 mm. to produce 18 g. (86%) of V (reported b.p. 158–159° at 19 mm.[7] and 285–286° at 760 mm.[11]), $n^{25}\mathrm{D}$ 1.5551, reported[11] $n^{16}\mathrm{D}$ 1.560.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.35; H, 8.43.

1,1-Diphenyl-2-ethylpentane (VI) was distilled to give 23.7 g. (94%) of the product, b.p. 157–158° at 5 mm., $n^{25}\mathrm{D}$ 1.5415.

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(20) These results evidently are not due merely to physical factors. Indeed, essentially complete metalation of diphenylmethane occurs in spite of the fact that sodium amide is partly in suspension while sodium diphenylmethide dissolves in the medium, and also in spite of the mass action effect of the solvent, ammonia.

(21) W. K. McEwen, THIS JOURNAL, **58**, 1124 (1936).

(22) W. C. Fernelius and G. B. Bowman, *Chem. Revs.*, **26**, 5 (1940).

(23) C. B. Wooster and N. W. Mitchell, THIS JOURNAL, **52**, 688 (1930).

(24) A. A. Morton, *Chem. Revs.*, **26**, 5 (1940).

(25) Melting points were taken on a Fisher–Johns melting point apparatus. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(26) This sample was prepared by the catalytic hydrogenation of tetraphenylethylene.

Anal. Calcd. for $C_{19}H_{24}$: C, 90.41; H, 9.58. Found: C, 90.38; H, 9.85.

1,1-Diphenylnonane (VII) distilled at 173–174° at 0.75 mm. to produce 37 g. (99%) of VII, n^{25}_{D} 1.5310.

Anal. Calcd. for $C_{21}H_{28}$: C, 89.93; H, 10.07. Found: C, 90.08; H, 10.15.

Attempted Alkylation with *t*-Butyl Chloride.—To a stirred solution of 0.1 mole of sodium diphenylmethide in 250 ml. of liquid ammonia and 100 ml. of ether was added 9.3 g. (0.1 mole) of freshly distilled *t*-butyl chloride in 100 ml. of ether. A Dry Ice–acetone reflux condenser was fitted to the flask. After two hours the red color of sodium diphenylmethide remained. An additional 0.1 mole of *t*-butyl chloride in 100 ml. of ether was added and ammonia was refluxed an additional two hours. Finally 0.1 mole of benzhydryl chloride in 100 ml. of ether was added, the red color being discharged. The reaction mixture was worked up as described above for hydrocarbon II. The ether solution was distilled after solid 1,1,2,2-tetraphenylethane was filtered off. Ether and *t*-butyl chloride were difficult to separate, but 12.5 g. of *t*-butyl chloride was recovered. The residue after distillation was solid 1,1,2,2-tetraphenylethane. The combined solids were recrystallized from benzene and ethanol to give 31.5 g. (94%) of the hydrocarbon, m.p. and mixed m.p. 214–215°.

Reaction of Potassium Diphenylmethide with β-Phenylethyl Chloride.—To a stirred solution of 0.1 mole of potassium amide[3] in 200 ml. of anhydrous liquid ammonia was added 16.8 g. (0.1 mole) of diphenylmethane in 100 ml. of anhydrous ether. To the resulting deep red solution was added after 10 minutes 14.05 g. (0.1 mole) of β-phenylethyl chloride in 100 ml. of anhydrous ether. The red solution turned gray after 7 minutes. The ammonia was removed on the steam-bath, and water and ether were added. The ethereal layer was dried and, after adding a few crystals of hydroquinone, the solvent was removed. The residue was distilled at 50 mm. to give 1.9 g. (18%) of styrene, b.p. 70–71°; styrene dibromide, m.p. and mixed m.p. 72–73°, reported[27] m.p. 72–73°. The residue remaining after removing styrene yielded 3.85 g. of recovered diphenylmethane, b.p. 105° at 5 mm. The residue was taken up in 30–60° petroleum ether, filtered and methanol was added. There was obtained 18 g. (70%) of 1,1,3-triphenylpropane, m.p. 47°, on cooling in a Dry Ice–acetone-bath.

Competitive Experiment of Sodium Diphenylmethide and Sodium Amide with Benzyl Chloride.—To 0.11 mole of sodium amide in 200 ml. of anhydrous liquid ammonia was added with stirring 9.24 g. (0.055 mole) of diphenylmethane in 100 ml. of dry ether. After 10 min. 6.96 g. (0.055 mole) of benzyl chloride in 50 ml. of dry ether was added rapidly. The red color of sodium diphenylmethide remained until ammonia was removed on the steam-bath. The red color faded to become purple when only ether remained. After cooling the reaction mixture, 100 ml. of water was added. The purple color was discharged and the ether layer was separated. The aqueous layer was extracted with two 50-ml. portions of ether and the combined ether layers were dried and filtered. Ether was removed from the filtrate and the residue was dissolved in 75 ml. of ethanol. A few drops of water clouded the solution which was clarified by adding a small amount of ethanol. On standing overnight in a refrigerator white crystals of stilbene separated. The solid was recrystallized from ethanol to give 2.5 g. (62%) of stilbene, m.p. 123–125°, reported[28] 125°. A mixed m.p. with an authentic sample (m.p. 124–125°) showed no depression. The mother liquor was treated with more water and cooled in a Dry Ice–acetone-bath. Crude 1,1,2-triphenylethane (I) crystallized to give 5 g. (35%) of the product, m.p. 51–56°. It was recrystallized from ethanol, m.p. 55–56°, reported m.p. 56°[7] and 54°.[9]

Attempted Benzylation of Sodium Di-*p*-methoxyphenylmethide.—To a stirred suspension of 0.05 mole of sodium amide in 250 ml. of anhydrous liquid ammonia was added with stirring 11.4 g. (0.05 mole) of di-*p*-methoxyphenylmethane in 100 ml. of ether. A red color developed and after 15 minutes 6.33 g. (0.05 mole) of benzyl chloride in 50 ml. of ether was added. The red color was discharged when only a small fraction of the halide solution was added. A purple color was produced when the remaining halide was added. After 15 minutes solid ammonium chloride (4 g.) was added and ammonia was removed on the steam-bath. More ether (100 ml.) was added and then 100 ml. of water. The ether layer was separated and the aqueous layer was extracted with two 50-ml. portions of ether. The ether solvent was removed to give an oil which was taken up in ethanol. Stilbene (4.0 g., 89%) was obtained by alternately adding water and cooling in a Dry Ice–acetone-bath. The pure product melted at 124° after crystallization from methanol and chloroform. A mixed melting point with an authentic sample (m.p. 124–125°) showed no depression. Water was added to the remaining solution to precipitate unchanged di-*p*-methoxyphenylmethane (10.7 g., 94%).

DURHAM, NORTH CAROLINA

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[27] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. IV, p. 380.

[28] I. Heilbron, ref. 27, p. 374.

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Reactions of Amines. II. Degradation via Tertiary Amine Oxides[1]

BY HENRY E. BAUMGARTEN, FRANK A. BOWER[2] AND TED T. OKAMOTO[3]

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Degradative sequences (see chart) for amines derived from acids related to the naphthenic acids are described that include as an important step the pyrolysis of a *t*-amine N-oxide. Evidence is offered indicating that in the pyrolysis of *t*-amine N-oxides the direction of elimination may follow the Hofmann rule.

One of the most attractive procedures for the degradation of naphthenic acids in structural studies is the conversion of the acids into the amines of one less carbon atom by the Schmidt reaction.[4,5] The utility of this procedure is lessened somewhat, however, by the apparent unavailability of entirely satisfactory, unambiguous processes for the further degradation of the resultant amines. Of the reactions previously used, the Hofmann degradation[4] to the olefin is reasonably unambiguous but, as carried out by von Braun,[6] requires an undue amount of manipulation with a resultant relatively low yield of olefin (20-35%). The reaction of naphthenylamines with nitrous acid[7] to give olefins and alcohols has been shown to lead to extensive rearrangements of the Demjanov type, and the amine phosphate degradation to the olefin has been found also to proceed with considerable

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[1] Paper I, THIS JOURNAL, **76**, 4561 (1954).

[2] Standard Oil Co. (of Indiana) Fellow, 1951–1953.

[3] Standard Oil Co. (of Indiana) Fellow, 1953–1955.

[4] J. von Braun, *Ann.*, **490**, 100 (1931).

[5] H. L. Lochte and E. R. Littmann, "Petroleum Acids and Bases," Chemical Publishing Co., Inc., New York, N. Y., 1955, p. 100.

[6] Reference 5, pp. 103, 149.

[7] B. Shive, J. Horeczy, G. Wash and H. L. Lochte, THIS JOURNAL, **64**, 385 (1942).