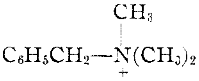
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Rearrangements of Benzyltrimethylammonium Ion and Related Quaternary Ammonium Ions by Sodium Amide Involving Migration into the Ring[1,2,3]

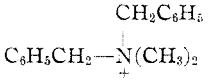
BY SIMON W. KANTOR[4] AND CHARLES R. HAUSER

Benzyltrimethylammonium ion and certain related quaternary ammonium ions were found to undergo with sodium amide in liquid ammonia rearrangements into the benzene ring instead of the 1,2-shift of an alkyl group realized earlier with other bases. Benzyltrimethylammonium iodide was rearranged to 2-methylbenzyldimethylamine practically quantitatively. The methiodide of this tertiary amine was further rearranged into the ring and the process repeated three times to form the completely substituted product, 2,3,4,5,6-pentamethylbenzyldimethylamine. These further rearrangements into the ring were accompanied by side reactions resulting in the formation of dimeric and trimeric olefins and amines along with smaller amounts of monomeric saturated hydrocarbons. With 2,4,6-trimethylbenzyltrimethylammonium iodide, the hydrocarbon, isodurene, was the principal product. Benzyltri-*n*-propyl- and benzyltri-*n*-butylammonium ions were found to undergo only β-elimination. The rearrangements into the ring are accounted for by an aromatic "nucleophilic" mechanism in which the benzene ring serves as an electron acceptor. The other reactions also are accounted for by reasonable mechanisms. These results extend the types of reaction exhibited by quaternary ammonium ions with bases. A summary of these types of reaction is given. The successive rearrangements into the ring furnish a better method for preparing certain vicinal methyl derivatives than that involving "abnormal" reactions of benzylmagnesium chloride and its derivatives with formaldehyde.

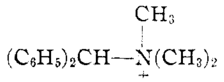
Quaternary ammonium ions I, II and III have previously been shown to exhibit with certain basic reagents the Stevens rearrangement involving the 1,2-shift of a methyl or benzyl group to form tertiary amines IV, V and VI, respectively. The bases that have been used to effect this rearrangement include lithium phenyl (with the bromides of I and III),[5] fused sodium methoxide or sodium amide (with the chloride of II),[6] and hydroxide ion (with III).[7]


$C_6H_5CH_2-\overset{CH_3}{\underset{+}{N}}(CH_3)_2$

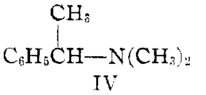
I


$C_6H_5CH_2-\overset{CH_2C_6H_5}{\underset{+}{N}}(CH_3)_2$

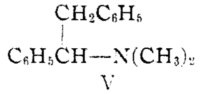
II


$(C_6H_5)_2CH-\overset{CH_3}{\underset{+}{N}}(CH_3)_2$

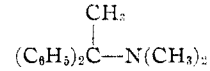
III


$C_6H_5\overset{CH_3}{CH}-N(CH_3)_2$

IV


$C_6H_5\overset{CH_2C_6H_5}{CH}-N(CH_3)_2$

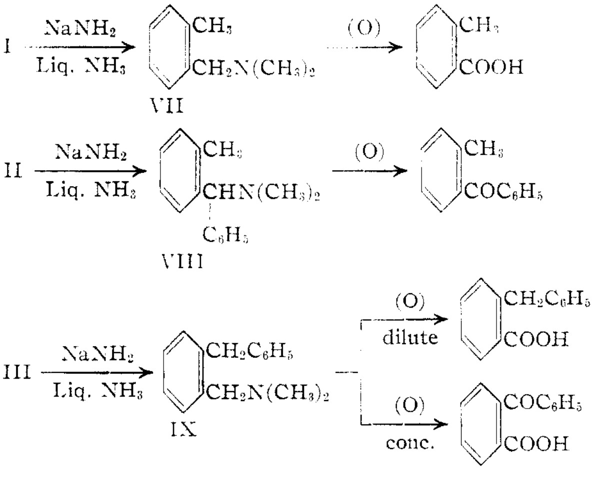
V


$(C_6H_5)_2\overset{CH_3}{C}-N(CH_3)_2$

VI

Quaternary ammonium ion III has also previously been reported to exhibit, under certain conditions, another type of rearrangement involving migration into the benzene ring to form tertiary amine (IX, below). Sommelet[8] realized this rearrangement by allowing an aqueous solution of the hydroxide of III to evaporate in a vacuum desiccator over phosphorus pentoxide in sunlight.[9] Wittig and co-workers[5] confirmed this rearrangement under these unusual conditions. These workers further reported that, with lithium phenyl, the bromide of III formed not only VI (by the 1,2-shift) but also a product which, on subsequent treatment with a mixture of sodium and potassium, gave tertiary amine IX and diphenylmethane. Apparently, IX was an intermediate which was alkylated by quaternary ammonium ion III.

We have found that, with sodium amide in liquid ammonia, the iodide of I, the chloride of II, and the iodide of III undergo exclusively migrations into the ring to form tertiary amines VII, VIII and IX, respectively. The structures of these products were determined as represented below, by permanganate oxidations which produced known carboxylic acids or 2-methylbenzophenone. This ketone was identified by its 2,4-dinitrophenylhydrazone and by reduction to 2-methylbenzohydrol which was found identical with the carbinol prepared from *o*-tolylmagnesium bromide and benzaldehyde.



The structure of the tertiary amine from the rearrangement of I was confirmed as VII by its synthesis from the hexamethylenetetramine salt of *o*-xylyl bromide,[10] and that of the tertiary amine from the rearrangement of II was confirmed as

---

[1] Paper II on Isomerizations of Carbanions; paper I, THIS JOURNAL, **73**, 1437 (1951).

[2] This work was carried out under Contract N7 onr-455 with the Office of Naval Research.

[3] Presented at the Conference on Reaction Mechanisms in Organic Chemistry, Northwestern University, Evanston, Ill., August, 1950; also presented in part at the Atlantic City Meeting of the American Chemical Society, September, 1949.

[4] Post-doctorate Research Associate, 1949-1951.

[5] Wittig, Mangold and Felletschin, *Ann.*, **560**, 116 (1948).

[6] Thomson and Stevens, *J. Chem. Soc.*, 1932 (1932).

[7] Hughes and Ingold, *ibid.*, 69 (1933).

[8] Sommelet, *Compt. rend.*, **205**, 56 (1937).

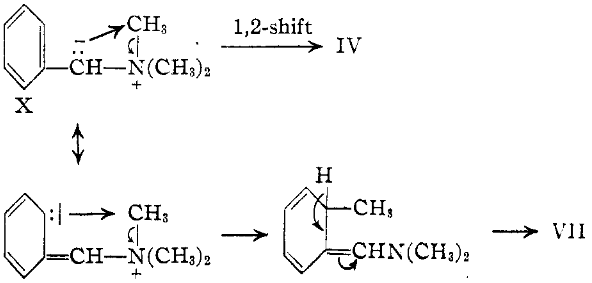
[9] The mechanism of this rearrangement under these conditions has not been determined. An attempt by us to effect the analogous rearrangement of the hydroxide of I to tertiary amine VII under Sommelet's conditions failed, the hydroxide being recovered.

[10] Thomson and Stevens (*J. Chem. Soc.*, 66 (1932)) performed this reaction but they did not isolate tertiary amine VII and the melting point of their picrate was 37° higher than that obtained by us.

VIII by its synthesis from *o*-methylbenzohydryl chloride and dimethylamine. The properties of the tertiary amine from the rearrangement of III agreed with those reported by Sommelet[8] and by Wittig.[5]

The exclusive rearrangement into the ring with sodium amide in liquid ammonia is rather remarkable, especially since the chloride of II has been shown to undergo only the 1,2-shift with fused sodium amide at 140–150°.[6] The rearrangement of I to VII was realized in yields of 94–97% with only slightly more than a molecular equivalent of sodium amide but the rearrangement of II to VIII, and presumably also that of III to IX, appeared to require a larger excess of the reagent for maximum yields.[11] Thus, VIII was obtained from II in reproducible yields of 85% with 1.4 equivalents of sodium amide, and in 95% yield with two equivalents of the base.

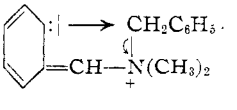
The mechanism of these migrations into the aromatic ring undoubtedly consists first, in the ionization of an α-hydrogen of the quaternary ammonium ion by the amide ion, followed by the isomerization of the resulting intermediate carbanion (dipolar ion). Since the Stevens 1,2-shift has been shown to involve an intramolecular three-atom ring displacement within an intermediate carbanion such as X,[12] the migrations into the aromatic ring might be expected to involve a similar five-atom ring displacement within another resonance form of the same carbanion in which the ortho position of the benzene ring would serve as the electron donor. Indeed, the rearrangement of I to VII might be accounted for by this aromatic "electrophilic" mechanism involving resonance structure XI, which is a resonance form of carbanion X.

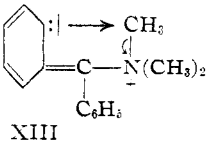


X

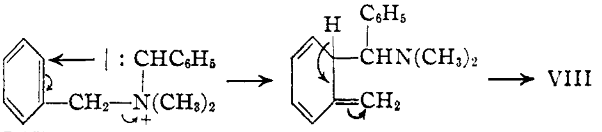
XI

However, the rearrangements of II to VIII and of III to IX cannot be explained by this type of mechanism which would involve resonance structures XII and XIII, respectively. Contrary to the facts, structure XII would lead to the formation of tertiary amine IX and structure XIII, to tertiary amine VIII.


XII

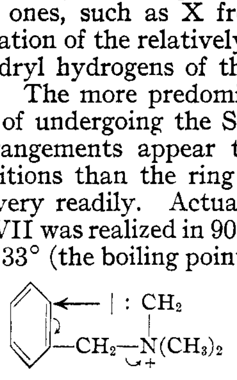

XIII

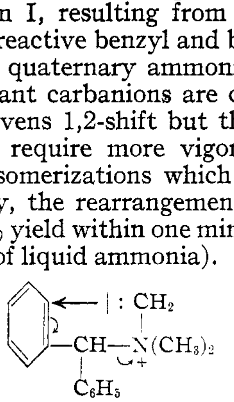
On the other hand, all three rearrangements may be accounted for by an aromatic "nucleophilic" mechanism in which the benzene ring serves as an electron acceptor in a five-atom ring displacement. In the rearrangement of II to VIII, this mechanism would involve carbanion XIV which would be formed as the intermediate by the ionization of the relatively reactive benzyl hydrogen of quaternary ammonium ion II.



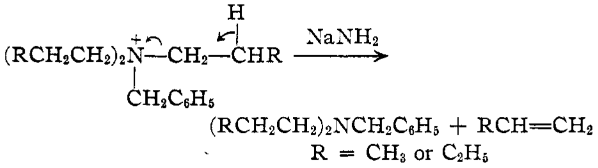
XIV

In the rearrangements of I to VII and of III to IX, this mechanism would involve carbanions XV and XVI, respectively. These carbanions would presumably be in equilibrium with more predominant ones, such as X from I, resulting from the ionization of the relatively reactive benzyl and benzohydryl hydrogens of the quaternary ammonium ions. The more predominant carbanions are capable of undergoing the Stevens 1,2-shift but these rearrangements appear to require more vigorous conditions than the ring isomerizations which occur very readily. Actually, the rearrangement of I to VII was realized in 90% yield within one minute at −33° (the boiling point of liquid ammonia).


XV


XVI

In contrast to quaternary ammonium ions I, II and III, the bromides of benzyltri-*n*-propylammonium and benzyltri-*n*-butylammonium ions which have β-hydrogens, were found to undergo with sodium amide in liquid ammonia only β-elimination to form benzyldialkyl amines and presumably the corresponding olefin.



$$(RCH_2CH_2)_2\overset{+}{\underset{CH_2C_6H_5}{N}}-CH_2-\overset{H}{C}HR \xrightarrow{NaNH_2} (RCH_2CH_2)_2NCH_2C_6H_5 + RCH{=}CH_2$$

$R = CH_3$ or C_2H_5

Further Rearrangements into the Ring and Side Reactions.—Tertiary amine VII, obtained from the rearrangement of I, was methylated with methyl iodide and the resulting quaternary ammonium ion, XVII, further rearranged by sodium amide in liquid ammonia to form tertiary amine XVIII. Similarly, three more successive rearrangements into the ring, involving quaternary ammonium ions XIX, XXI and XIII (prepared by methylating the appropriate rearranged tertiary amines), were effected to form, finally, the completely substituted product, XXIV. The structures of the products were determined, as represented below, by oxidations to known carboxylic acids and, in the last case, by the Emde[13] reduction to the corresponding hydrocarbon, hexamethylbenzene. Tertiary amines XVIII and XX were also

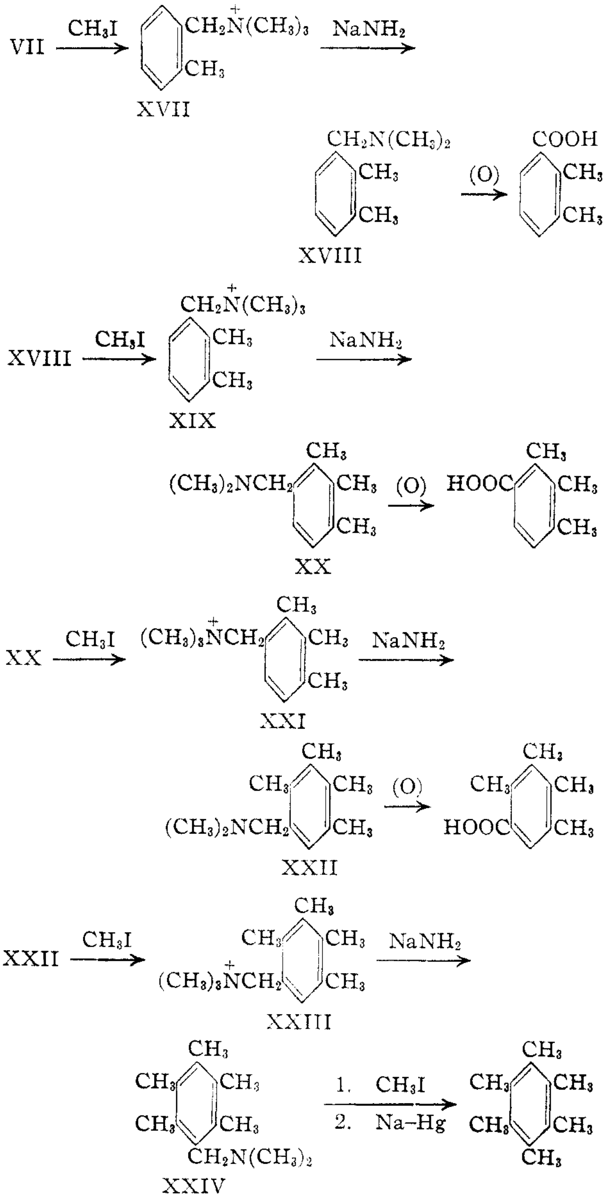
---

[11] The products of these two rearrangements are diphenylmethane derivatives which, like diphenylmethane and certain of its derivatives, were probably converted partly to their carbanions by the excess sodium amide. See Yost and Hauser, THIS JOURNAL, 69, 2325 (1947); Hauser, Flur and Kantor, *ibid.*, 71, 294 (1949).

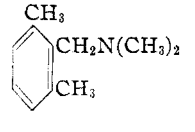
[12] Hauser and Kantor, *ibid.*, 73, 1437 (1951).

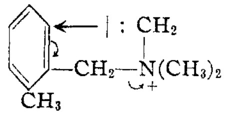
[13] Emde, *Ber.*, 42, 2590 (1909).

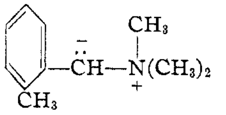
oxidized under more vigorous conditions to form 1,2,3-benzenetricarboxylic (hemimellitic) acid and 1,2,3,4-benzenetetracarboxylic (prehnitic) acid, respectively.



The structure of the product from the rearrangement of XVII was confirmed as XVIII by its synthesis from 2,3-dimethylbenzyl chloride and by the formation of 2,3-dimethylbenzyl alcohol from the decomposition of the hydroxide of quaternary ammonium ion XIX (prepared from the rearranged tertiary amine). These four successive rearrangements into the ring may be accounted for by the "nucleophilic" mechanism but not by the "electrophilic" mechanism. Indeed, they furnish striking support for the former mechanism since, had the "electrophilic" mechanism operated, quaternary ammonium ion XVII would have been rearranged to tertiary amine XXV which was not the product obtained; moreover, the methiodide of this amine could not have undergone further rearrangement into the ring. As with quaternary ion I, these rearrangements would involve presumably carbanions such as XXVI (from quaternary ion XVII) rather than the more predominant carbanions, such as XXVII, in which the "nucleophilic" mechanism could not operate.

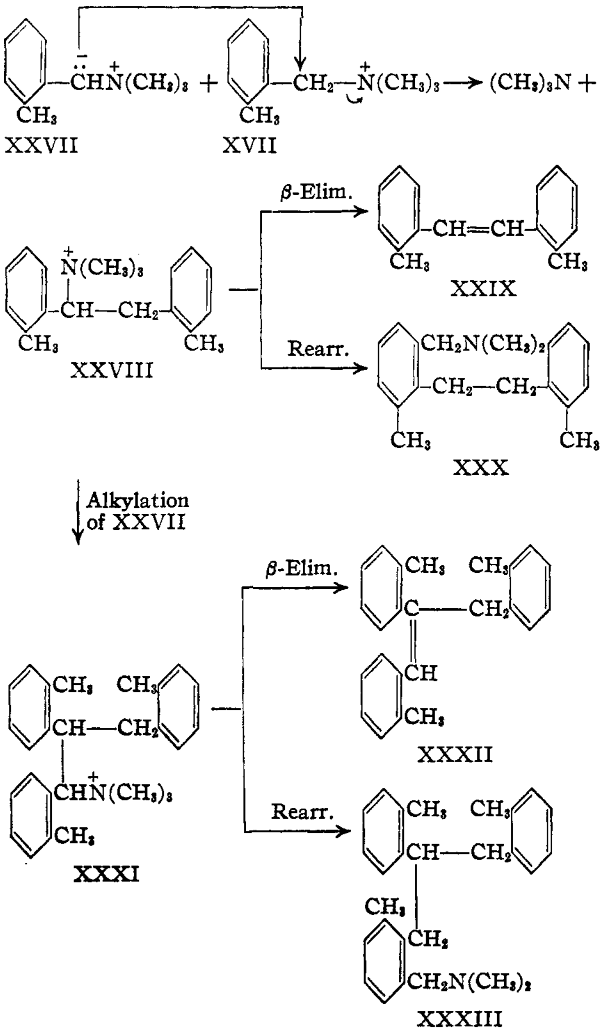

XXV


XXVI

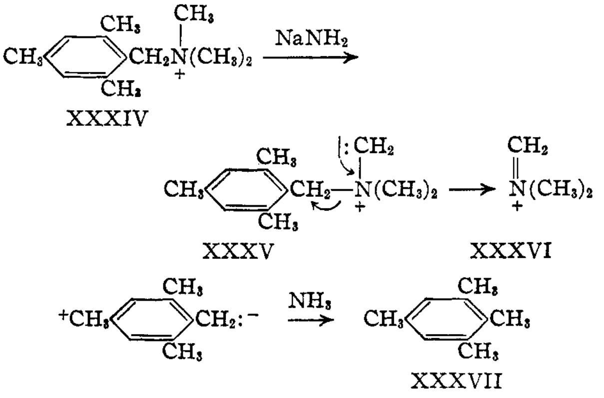

XXVII

These further rearrangements into the ring were realized in lower yields than the rearrangement of I and they were accompanied by side reactions. In order to minimize the side reactions, which evidently involved mainly dimerizations and trimerizations, the methiodides were added in small portions to the sodium amide in a relatively large volume of liquid ammonia. Under these conditions, the intramolecular rearrangements in the series were realized in the following yields: I → VII, 97%; XVII → XVIII, 64%; XIX → XX, 43%; XXI → XXII, 47%; XXIII → XXIV, 62%. The successive decrease in the yields of the first three rearrangements is understandable on the basis of the "nucleophilic" mechanism since both the inductive and hyperconjugation effects of the methyl groups would make the benzene ring a progressively poorer electron acceptor at the point of attack. Moreover, the increase in yield in the fourth and fifth rearrangements is not surprising since molecular models indicate that the hyperconjugation resonance of the methyl group, para to the point of attack, could be damped by the two adjacent methyl groups; consequently, the benzene ring may function as a relatively better electron acceptor in these cases than in the preceding ones. However, the relatively large yield of the fifth rearrangement, compared with that of the fourth, suggests that another factor might also be involved.

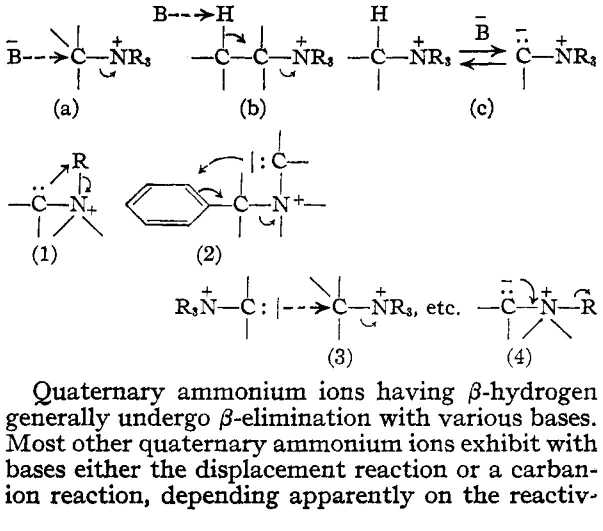
The dimerizations and trimerizations occurring as side reactions produced neutral and basic products. For example, from quaternary ammonium ion XVII there were obtained under the conditions that gave a 64% yield of tertiary amine XVIII, the dimeric olefin, 2,2′-dimethylstilbene XXIX, (6%), and products assumed to be the dimeric rearranged amine XXX, (7%), the trimeric olefin XXXII, (5%), and the trimeric rearranged amine XXXIII, (6%). Although the last three products were not completely identified, they analyzed for and had the properties expected of the structures given. The proportion of such dimers and trimers, relative to that of the tertiary amine XVIII, increased when the methiodide was added rapidly to a relatively concentrated reagent, a 22% yield of 2,2′-dimethylstilbene being obtained under these conditions. The formation of the dimers appears to involve the alkylation of carbanion XXVII (the predominant carbanion) by the quaternary ammonium ion XVII to form intermediate XXVIII (self-alkylation),[14] followed by β-elimination[15] or rearrangement. The formation of the trimers appears to involve the alkylation of carbanion XXVII by intermediate XXVIII followed by β-elimination or rearrangement. Since other similar alkylations might have occurred, mixtures of isomers may have been obtained. Moreover, carbanion XXVI might also have undergone similar reactions to form isomeric products. Analogous dimers and trimers, which evidently were higher homologs of the structures represented below, were obtained with XIX, XXI and XXIII (see Experimental).



Another type of side reaction product, the monomeric aromatic hydrocarbon corresponding to the quaternary ammonium ions, was isolated in very small yield in relatively large scale reactions. Thus *o*-xylene (0.6%) was obtained from XVII, hemimellitene (2%) from XIX, prehnitene (2.7%) from XXI and pentamethylbenzene (2.2%) from XXIII. Also, formaldehyde was detected on working up the reaction mixtures. With quaternary ammonium ion XXXIV which cannot rearrange and with which self-alkylation should be hindered, the corresponding hydrocarbon, isodurene (XXXVII), was obtained in 63% yield along with much formaldehyde. These products may be accounted for by a special type of β-elimination involving intermediate carbanion XXXV, the formaldehyde arising from XXXVI by subsequent hydrolysis.



Types of Reaction of Quaternary Ammonium Ions with Bases.—A quaternary ammonium ion may be attacked by a base ($\bar{B}$) at three positions, (a) at an α-carbon to effect the common displacement reaction, (b) at a β-hydrogen to effect the common β-elimination reaction, and (c) at an α-hydrogen to form a carbanion (dipolar ion). This carbanion may undergo four types of reaction, (1) the Stevens 1,2-shift of R (alkyl group), (2) migration into the aromatic ring, (3) alkylation by the quaternary ammonium ion followed by β-elimination or rearrangement, and (4) β-elimination of R (benzyl or substituted benzyl group). Although ionization of an α-hydrogen (c) has been quite well known, apparently only one type of reaction of the resulting carbanion, the Stevens 1,2-shift (1), has generally been recognized. Examples of types (2), (3) and (4) and their probable mechanisms have been presented above.



Quaternary ammonium ions having β-hydrogen generally undergo β-elimination with various bases. Most other quaternary ammonium ions exhibit with bases either the displacement reaction or a carbanion reaction, depending apparently on the reactiv-

---

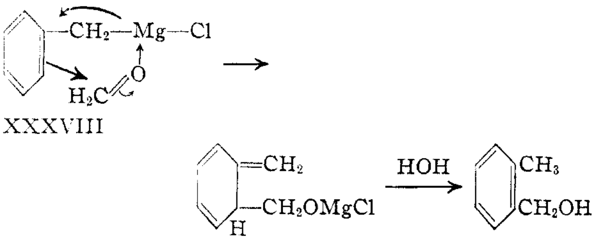
[14] Alkylations of carbanions, such as the carbanion of malonic ester, by quaternary ammonium ions involving the displacement of a tertiary amine have previously been observed. See Snyder, Smith and Stewart, THIS JOURNAL, **66**, 200 (1944).

[15] A similar type of reaction involving the conversion of 9-fluorenyltrimethylammonium bromide to bis-diphenylene-ethylene by lithium phenyl, has been reported by Wittig and Felletschin, *Ann.*, **555**, 133 (1943). This type of dimerization has been more common with halides such as benzyl chloride which is converted to stilbene by sodium amide, Kharasch, Nudenberg and Fields, THIS JOURNAL, **66**, 1276 (1944).

ity of the α-hydrogen and on the strength of the base. Thus, with hydroxide ion, tetramethylammonium and benzyltrimethylammonium ions undergo only the displacement reaction; benzohydryltrimethylammonium ion, which has a more reactive α-hydrogen, exhibits both the displacement reaction and the Stevens 1,2-shift; while phenacylbenzyldimethylammonium ion, which has a still more reactive α-hydrogen, undergoes largely the Stevens 1,2-shift.[16] With stronger basic reagents such as sodium amide and lithium phenyl, even tetramethylammonium and benzyltrimethylammonium ions exhibit carbanion reactions. The type of carbanion reaction depends not only on the structure of the carbanion but apparently also on the nature of the basic reagent and even on the conditions employed. Certain carbanions such as that from tetramethylammonium ion, $:\overset{-}{C}H_2\overset{+}{N}(CH_3)_3$, have been found sufficiently stable to be condensed with alkyl halides or ketones.[17]

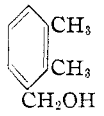
Methods for Introducing *o*-Methyl Groups into the Ring.—The successive rearrangements into the ring with the series starting with I furnishes a potentially useful method for introducing *o*-methyl groups into an aromatic ring.[18] The quaternary ammonium iodides were obtained practically quantitatively from the appropriate tertiary amines and methyl iodide, and their rearrangements to pure methyl substituted dimethylbenzylamines were realized in satisfactory yields. Such tertiary amines may be converted readily not only to their quaternary ammonium salts but also to other derivatives including mono- and polycarboxylic acids (by oxidation)[19] and vicinal methyl aromatic hydrocarbons (by reduction). For example, pure hemimellitene (1,2,3-trimethylbenzene) has been prepared from benzyldimethylamine through two successive rearrangements of the appropriate methiodides, followed by an Emde reduction, in an over-all yield of 55%.

Earlier workers have introduced *o*-methyl groups into the benzene ring by successive "abnormal" reactions of benzylmagnesium chloride and its *o*-methyl derivatives with formaldehyde (as trioxymethylene) to form alcohols XXXIX, XL and XLI.[20] In contrast to the rearrangements of quaternary ammonium ions, these "abnormal" Grignard reactions involve presumably an aromatic "electrophilic" mechanism within the coördination complex as indicated in XXXVIII.[21] Reichstein and coworkers[20] pointed out that the yields decreased markedly in the successive "abnormal" Grignard reactions, alcohols XXXIX, XL and XLI being obtained in yields of 55, 36 and 15%, respectively. Newman[22] showed that the product from the "abnormal" reaction with benzylmagnesium chloride was impure, the impurity presumably being the "normal" product, β-phenylethyl alcohol. By careful fractionation, he obtained pure alcohol XXXIX in 42% yield. Smith and Spillane[23] found that the "abnormal" product from *o*-methylmagnesium chloride also was contaminated with the "normal" product but they were able to isolate the carbinol XL, in yields of 41–48%. By effecting the two successive "abnormal" reactions followed by hydrogenation of the resulting carbinol XL, they obtained hemimellitene from benzyl chloride in an over-all yield of 26%, which is less than half that realized in our method starting with benzyldimethylamine. We have prepared alcohol XXXIX from *o*-toluic acid in 97% yield by reduction with lithium aluminum hydride, and have obtained alcohols XL and XLI by the Grignard method in yields of 50 and 20%, respectively. We believe that this Grignard method is less convenient and proceeds less smoothly than that involving the rearrangements of quaternary ammonium ions.

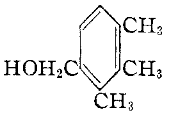


XXXVIII

XXXIX



XL



XLI

Experimental[24]

Benzyltrimethylammonium Iodide (I).—To a rapidly stirred solution of 270.4 g. (2 moles) of benzyldimethylamine (b.p. 177–178°) in 500 ml. of commercial absolute ethanol was added a few ml. of methyl iodide and the stirring continued until heat was generated. Then the remainder of the methyl iodide (total, 365 g., 2.5 moles) was added rapidly, care being taken that the reaction did not become too violent. The mixture was refluxed on the steam-bath for 0.5 hour, allowed to come to room temperature, and 1 liter of ether added. The precipitated salt was filtered off, washed with ether and air-dried. It melted at 178–179° (reported m.p. 179°)[25]; yield 99%. The melting point was not raised by recrystallization from commercial absolute ethanol.

Rearrangement of I to 2-Methylbenzyldimethylamine (VII).—A suspension of 2.5 moles of sodium amide in 1 liter of liquid ammonia was prepared[26] in a 2-l. three-necked flask equipped with a condenser and a mercury sealed stirrer. To the third neck of the flask was attached a 15 cm. (2.5 cm. bore) glass tube connected by a soft rubber tube to a 250 ml. erlenmeyer flask in which was placed part of the benzyltrimethylammonium iodide (total, 465 g., 1.68 moles). The iodide was added in portions to the stirred sodium

---

[16] Stevens, *J. Chem. Soc.*, 2107 (1930).

[17] Wittig and Wetterling, *Ann.*, **557**, 193 (1947).

[18] Application of this method to other aromatic carbocyclic systems and also to certain aromatic heterocyclic systems, which are better electron acceptors, is in progress in this Laboratory.

[19] Although these oxidations were carried out on a small scale, satisfactory yields of the corresponding mono carboxylic acids were obtained from tertiary amines VII and XVIII. However, the yield from tertiary amine XX was only fair and no pentamethylbenzoic acid was obtained from tertiary amine XXIV. Apparently the tendency to oxidize the methyl groups as well as the methlenedimethylamino group increased as the number of methyl groups on the ring increased.

[20] Reichstein, Cohen, Ruth and Meldahl, *Helv. Chim. Acta*, **19**, 412 (1936).

[21] See Johnson in Gilman's "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1880–1881.

[22] Newman, This Journal, **62**, 2295 (1940).

[23] Smith and Spillane, *ibid.*, **62**, 2639 (1940).

[24] Melting points and boiling points are uncorrected. Analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

[25] Emde, *Arch. Pharm.*, **247**, 353 (1909).

[26] Levine and Hauser, This Journal, **66**, 1770 (1944); Adams and Hauser, *ibid.*, **66**, 1220 (1944).

amide–ammonia mixture as rapidly as the reaction allowed (about 15–20 min.). The resulting light greenish-purple mixture was stirred for about 3 hours and the excess sodium amide was destroyed by adding very carefully 50 g. of ammonium chloride. The ammonia was allowed to evaporate and the residue was shaken with water and ether until it all dissolved. The ether layer was separated, washed with water, dried over sodium sulfate and the solvent distilled. The residue was distilled to give 2-methylbenzyldimethylamine (VII), b.p. 197–198° (80–80.2° at 14 mm.), in 96% yield.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39; neut. equiv., 149.2. Found: C, 80.21; H, 9.72; N, 9.32; neut. equiv., 153.

The picrate, recrystallized from 95% ethanol, melted at 112.5–113° (reported m.p. 148–150°).[10]

Anal. Calcd. for $C_{16}H_{18}N_4O_7$: C, 50.79; H, 4.79; N, 14.81. Found: C, 50.51; H, 4.80; N, 15.05.

The yield of the rearranged amine was essentially the same (94–97%) when the reaction was carried out on various scales (using as little as 0.05 mole of the methiodide) or when the ratio of sodium amide to salt was 2:1 or 1:1.

Oxidation of 0.5 g. of tertiary amine VII with potassium permanganate according to the directions in Shriner and Fuson[27] gave 0.3 g. of *o*-toluic acid, m.p. 103.5–104° after one recrystallization from water. The melting point was not depressed by admixture with an authentic sample of the acid.

Independent synthesis of tertiary amine VII was effected by an adaptation of the general method of Sommelet and Guioth.[28] A mixture of 9.76 g. (0.05 mole) of *o*-xylyl bromide and 7.01 g. (0.05 mole) of hexamethylenetetramine in 60 ml. of chloroform was refluxed 0.5 hour after the initial vigorous reaction had subsided. The resulting quaternary ammonia bromide (11.5 g., m.p. 179–182°, shrinking at 170°) was dissolved in 60 ml. of 50% formic acid. The solution was heated carefully until the evolution of carbon dioxide had subsided and then refluxed for an hour. After distilling off 30 ml. of liquid, the residue was neutralized with sodium carbonate. There was isolated 3.3 g. of 2-methylbenzyldimethylamine (VII), b.p. 195–196°; picrate, m.p. 112.5–113°. A mixed melting point with the picrate of the tertiary amine obtained from the rearrangement of I was the same.

Dibenzyldimethylammonium Chloride (II).—This salt was prepared by the method of Thomson and Stevens[6] who gave no details or yield. A solution of 40.6 g. (0.3 mole) of benzyldimethylamine and 38 g. (0.3 mole) of benzyl chloride (dried over phosphorus pentoxide and distilled, b.p. 79.5–79.7° at 23 mm.) in 200 ml. of anhydrous benzene was allowed to stand for 4 to 5 days. Ether (500 ml.) was added and the salt collected in two crops; yield 97%. The pure salt, m.p. 94–95° (reported m.p. 93–95°),[6] was obtained in 92% yield after one recrystallization from a mixture of absolute ethanol and ethyl acetate.

Rearrangement of II to 2-Methylbenzohydryldimethylamine (VIII).—This rearrangement was carried out with 26.2 g. (0.1 mole) of dibenzyldimethylammonium chloride (m.p. 94–95°) and 0.22 mole of sodium amide in 300 ml. of liquid ammonia essentially as described for I. The reaction mixture was light orange colored during the addition of the salt but became gray when all the salt had been added. The addition time was 15 minutes. Evaporation of the dried ether solution of the product gave an oil which solidified to 2-methylbenzohydryldimethylamine (VIII), m.p. 43–46°; yield 95%. Three recrystallizations from ethanol-water or petroleum ether (cooled to −78°) raised the melting point to 48–49°.

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.33; H, 8.62; N, 6.51.

The picrate, recrystallized from 95% ethanol, melted at 177–178°.

Anal. Calcd. for $C_{22}H_{22}N_4O_7$: C, 58.14; H, 4.88; N, 12.33. Found: C, 58.16; H, 4.70; N, 12.43.

Oxidation of 2 g. of the tertiary amine VIII was effected with 3 g. of potassium permanganate in 100 ml. of 0.5 *N* sodium hydroxide by stirring for 25 hours at room temperature. The mixture was acidified with 10% sulfuric acid and, after adding sufficient sodium bisulfite to dissolve the manganese dioxide, it was extracted twice with ether. The combined ether extract was washed with sodium carbonate solution followed by water, dried over sodium sulfate, and the solvent distilled. The residue was diluted with 5 ml. of methanol and divided into two portions. To one portion was added excess 2,4-dinitrophenylhydrazine reagent and, after standing 2 days, the derivative was collected; 0.3 g., m.p. 174–180°. Two recrystallizations from methanol raised the melting point to 184–189° which agrees with the reported value of 184–190° for the derivative of 2-methylbenzophenone.[29] To the other portion of the methanol solution of the residue was added 10 ml. of ethanol, 1 g. of potassium hydroxide flakes and 1 g. of powdered zinc. The mixture was stirred and heated on the steam-bath 0.5 hour, then cooled and filtered. The filtrate was diluted with 100 ml. of water, acidified with hydrochloric acid and scratched to obtain 2-methylbenzohydrol (0.2 g.) which, after three recrystallizations from petroleum ether (cooled to −78°) melted at 88.5–90°. A mixed melting point with an authentic sample of the carbinol (m.p. 90.5–91°, see below) was 89.5–91°.

Independent synthesis of tertiary amine (VIII) was effected in three steps. Reaction of *o*-tolylmagnesium bromide with benzaldehyde gave 2-methylbenzohydrol, m.p. 90.5–91°, in 82% yield.[30] Treatment of a cold benzene solution of the carbinol with dry hydrogen chloride gave 2-methylbenzohydryl chloride, m.p. 38.5–39.5°, in 92% yield.[31] Reaction of the chloride with dimethylamine by the method described below for benzohydryldimethylamine gave a 60% yield of 2-methylbenzohydryldimethylamine (VIII),[32] melting at 47–50° and, after one recrystallization from petroleum ether (cooled to −78°), at 48–49°. The identities of this product and its picrate with the tertiary amine and its picrate obtained from the rearrangement of II were established by mixed melting points.

Benzohydryltrimethylammonium Iodide (III.).—Benzohydryl chloride, b.p. 135–137° at 5 mm. (reported b.p. 158.5–159.5° at 12 mm.),[33] was obtained in yields of 93–95% from benzohydrol and gaseous hydrogen chloride.

Benzohydryldimethylamine was prepared by a simplification of the procedure of Stoelzel who employed benzohydryl bromide.[34] A solution of 55.1 g. (0.272 mole) of benzohydryl chloride and 50 g. (1.1 moles) of dimethylamine in 150 ml. of commercial absolute ethanol contained in a tightly stoppered flask, was allowed to stand at room temperature for 4.5 days. After removing most of the ethanol on the steam-bath, the mixture was cooled, made basic with sodium carbonate and stirred with ether and water. The ether layer, after washing with water, was thoroughly shaken with 200 ml. of 2 *N* hydrochloric acid precipitating the salt of the amine. The aqueous extract containing the solid salt was drawn off and the ether solution extracted again with acid. The combined acid extract was made basic with sodium hydroxide solution and after standing overnight, there was isolated benzohydryldimethylamine, m.p. 69–70° (reported m.p. 72–73°),[34] in 83% yield. This amine was used without purification.

The iodide[35] (III), m.p. 169–171° dec., was obtained in 98% yield from 47.4 g. (0.224 mole) of benzohydryldimethylamine and 64 g. (0.45 mole) of methyl iodide in 250 ml. of absolute ethanol as described for I. A sample, recrystallized four times from absolute ethanol, melted at 174–175° dec.

Anal. Calcd. for $C_{16}H_{20}NI$: C, 54.40; H, 5.71; N, 3.97. Found: C, 54.36; H, 5.71; N, 3.91.

---

[27] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 164.

[28] Sommelet and Guioth, *Compt. rend.*, **174**, 687 (1922);

[29] Newman and McCleary, THIS JOURNAL, **63**, 1540 (1941). The wide melting range is due to the presence of two isomers.

[30] Chichibabin, *J. Russ. Phys. Chem. Soc.*, **41**, 1116 (1909); *C. A.*, **4**, 1488 (1910).

[31] Norris and Blake, THIS JOURNAL, **50**, 1808 (1928).

[32] An attempt to prepare this amine by the Sommelet hexamethylenetetramine reaction was unsatisfactory due to the failure of the chloride to form a salt with hexamethylenetetramine.

[33] Ward, *J. Chem. Soc.*, 2288 (1927).

[34] Stoelzel, *Ber.*, **74B**, 985 (1941).

[35] Benzohydryltrimethylammonium chloride was prepared in 90% yield from benzohydryl chloride and trimethylamine essentially as described for the bromide by Hughes and Ingold (*J. Chem. Soc.*, 72 (1933)). However, this salt was somewhat hygroscopic and therefore not as suitable for the rearrangement as the iodide.

Rearrangement of III to 2-Benzylbenzyldimethylamine (IX).—This rearrangement was carried out with 35.3 g. (0.1 mole) of benzohydryltrimethylammonium iodide (m.p. 169–171°) and 0.21 mole of sodium amide in 300 ml. of liquid ammonia essentially as described for I. The addition period was 15 minutes and the resulting red mixture was stirred for 2.75 hours. There was obtained 2-benzylbenzyldimethylamine (IX), b.p. 189–191° at 33 mm. (reported b.p. 189–190° at 33 mm.),[8] in 88% yield. The methiodide, after three recrystallizations from absolute ethanol, melted at 214.5–215° (reported m.p. 213.5–214.5°,[5] and 224–225°[8]). The picrate, after three recrystallizations from 95% ethanol, melted at 151.5–152° (reported m.p. 156–156.5°).[5]

Anal. Calcd. for $C_{22}H_{22}N_4O_7$: N, 12.33. Found: N, 12.47.

Oxidation of 2 g. of tertiary amine IX with 4 g. of potassium permanganate in 350 ml. of 0.2 *N* sodium hydroxide (5 hours stirring at room temperature) gave 0.5 g. of *o*-benzylbenzoic acid, m.p. 112–115°. One recrystallization from ethanol–water raised the melting point to 116–117°, which was not depressed by admixture with an authentic sample of the acid (m.p. 116.5–117°).[36]

Oxidation of 2 g. of tertiary amine IX with 8 g. of potassium permanganate in 200 ml. of 0.5 *N* sodium hydroxide (10 hours stirring at room temperature) gave 1.4 g. of crude acid, m.p. 112–114°. Recrystallization from ethanol–water gave 0.8 g. of *o*-benzoylbenzoic acid hydrate, m.p. 93–95°. The hydrate was converted to the anhydrous acid, m.p. 126–127°; a mixed melting point with an authentic sample (m.p. 127–128°) was 126.5–127.5°.

Benzyltri-*n*-propyl- and Benzyltri-*n*-butylammonium Bromides.—These salts were prepared in yields of 87–89% by refluxing for 12 hours benzene solutions of equivalent amounts of benzyl bromide (b.p. 75–76° at 10 mm.) and tri-*n*-propylamine and tri-*n*-butylamine[37] (b.p. 155–157° and 212–215°, respectively). After recrystallization from a mixture of ethyl acetate and ethanol, benzyltri-*n*-propylammonium bromide melted at 187.5–188° and benzyltri-*n*-butylammonium bromide, at 174.5–175°.

Anal. Calcd. for $C_{16}H_{28}NBr$: N, 4.46. Found: N, 4.59. Calcd. for $C_{19}H_{34}NBr$: N, 3.93. Found: N, 3.86.

Benzyl chloride failed to form the quaternary salts with these amines in refluxing benzene or in the absence of solvent at temperatures as high as 170°.

β-Eliminations with Benzyltri-*n*-propyl- and Benzyltri-*n*-butylammonium Bromides.—The reaction of each of these salts (0.05 mole) with 0.1 mole of sodium amide in 250 ml. of liquid ammonia was carried out as described for the reaction of I. With benzyltri-*n*-propylammonium bromide, there was obtained a 92% yield of benzyldi-*n*-propylamine, b.p. 240–248° (reported b.p. 235–243°).[38] Calcd. neut. equiv., 191.3. Found: neut. equiv., 189, 194. The picrate melted at 121–122° (reported m.p. 121°).[38]

With benzyltri-*n*-butylammonium bromide, there was obtained an 85% yield of benzyldi-*n*-butylamine, b.p. 134–136° at 10 mm.

Anal. Calcd. for $C_{15}H_{25}N$: C, 82.12; H, 11.49. Found: C, 82.12; H, 11.59.

Oxidation of benzyldi-*n*-butylamine with potassium permanganate gave benzoic acid. The amine was not sufficiently basic to be titrated satisfactorily but it formed a picrate (with difficulty) which after 5 recrystallizations from 95% ethanol, melted partly at 75–76°, and completely at 90°.

Anal. Calcd. for $C_{21}H_{28}N_4O_7$: C, 56.24; H, 6.30; N, 12.49. Found: C, 56.35; H, 6.09; N, 12.43.

Since the picrate analyzed satisfactorily, its unusual behavior when heated appears to be due to decomposition into its components.

2-Methylbenzyltrimethylammonium Iodide (XVII).—This salt (m.p. 210–211.5°) was obtained in yields of 98–99% from 1.5 moles of methyl iodide and 1.0 mole of 2-methylbenzyldimethylamine (VII) in 350 ml. of absolute ethanol as described for I. A sample, recrystallized twice from absolute ethanol, melted at 211–211.5° dec.

Anal. Calcd. for $C_{11}H_{18}NI$: C, 45.37; H, 6.23; N, 4.81. Found: C, 45.47; H, 6.17; N, 5.01.

Rearrangement of XVII to 2,3-Dimethylbenzyldimethylamine (XVIII) and Side Reactions.—In a 5-l. three-necked flask equipped with a condenser, a mercury-sealed stirrer and an extension joint (diameter, *ca.* 2.5 cm.) 15 cm. longer than the original neck, was prepared 2.0 moles of sodium amide in about 3 l. of liquid ammonia. A large powder funnel was placed at the end of the extension joint and 480 g. (1.65 moles) of 2-methylbenzyltrimethylammonium iodide (XVII) (m.p. 210–211.5°) was introduced in small portions into the well-stirred reaction mixture over a period of 75 minutes. The resulting light purple mixture was stirred for about 2 hours and the excess sodium amide was destroyed by the careful addition of 50 g. of ammonium chloride. The ammonia was allowed to evaporate and the residue was shaken with water and ether. The ether layer was washed with water and extracted twice with 6 *N* hydrochloric acid solution (400-ml. and 200-ml. portions). The ether solution (containing the neutral products) was washed with water, dried over sodium sulfate and the solvent distilled. The residue was fractionated through a 15 cm. Vigreux column giving (1) 1.0 g., b.p. 143–145° atm.; (2) 14.0 g., b.p. 175–180° at 8 mm.; (3) 9.0 g., b.p. 235–240° at 5 mm. Fraction (1) was *o*-xylene (0.6%) (reported b.p. 144°)[39]; the 1,2-dimethylbenzene-4-sulfonamide, after one recrystallization from water, melted at 143–144° (reported m.p. 143.5–144°).[39] Fraction (2), which mostly solidified, was washed twice with methanol giving 10 g. (6%) of 2,2′-dimethylstilbene (XXIX), m.p. 81–82.5°. One recrystallization from methanol raised the melting point to 82.5–83°, in agreement with the reported value.[40] The picrate melted as reported[40] at 102–103°, after one recrystallization from ethanol. The dimeric olefin XXIX reduced neutral permanganate and decolorized bromine in carbon tetachloride or carbon disulfide, especially in sunlight. It was oxidized with 3 *N* nitric acid (18 hours refluxing) to give *o*-toluic acid, m.p. and mixed m.p. 103–104°. Fraction (3), b.p. 231–232° at 3 mm. (on redistillation), analyzed for the trimeric olefin XXXII (5%).

Anal. Calcd. for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.95.

The combined acid extract (containing the basic products) was cooled, made basic with cold 50% sodium hydroxide solution and thoroughly extracted with ether. The combined ether extract was washed with water, dried over sodium sulfate, and the solvent distilled. The residue was fractionated through a 15 cm. Vigreux column giving (1) 169.7 g., b.p. 99–101° at 14 mm., 225–226° atm.; (2) 14.8 g., b.p. 165–170° at 3 mm., 183–188° at 7 mm.; (3) 11.6 g., b.p. 223–225° at 3 mm., 245° at 7 mm. Fraction (1) was identified as 2,3-dimethylbenzyldimethylamine (XVIII); yield 63%. A redistilled sample boiled at 101–102° at 15 mm.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.47; N, 8.58; neut. equiv., 163.3. Found: C, 80.91; H, 10.10; N, 8.31; neut. equiv., 164.6, 164.3.

The picrate, recrystallized three times from 95% ethanol, melted at 124.5–125°.

Anal. Calcd. for $C_{17}H_{20}N_4O_7$: C, 52.04; H, 5.14; N, 14.28. Found: C, 51.63; H, 5.28; N, 14.20.

Fraction (2), b.p. 164–164.2° at 3 mm. (on redistillation), analyzed for the dimeric rearranged amine XXX (7%).

Anal. Calcd. for $C_{19}H_{25}N$: C, 85.34; H, 9.42; N, 5.24. Found: C, 85.23; H, 9.14; N, 5.48.

Fraction (3), b.p. 221–222° at 2.5 mm. (on redistillation), analyzed for the trimeric rearranged amine XXXIII (6%).

Anal. Calcd. for $C_{27}H_{33}N$: C, 87.28; H, 8.95; N, 3.77. Found: C, 87.59; H, 8.82; N, 3.50.

Similar results were obtained in several runs under the above conditions, the yields of 2,3-dimethylbenzyldimethylamine (XVIII) being 61–64%. However, when XVII (0.308 mole) was added rapidly (5 minutes) to sodium amide (0.616 mole) in 300 ml. of liquid ammonia and the mixture stirred for 2.5 hours, there was obtained only a 30% yield of rearranged amine XVIII and a 22% yield of 2,2′-di-

---

(36) Kindly supplied by Dr. C. K. Bradsher.

(37) We are indebted to Sharples Chemicals Inc., for samples of these amines.

(38) v. Braun and Schwarz, *Ber.*, **35**, 1281 (1902).

(39) Huntress and Mulliken, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524.

(40) Wislicenus and Wren, *Ber.*, **38**, 504 (1905).

methylstilbene, m.p. 82.5–83°. 2,2′-Dimethylstilbene was also isolated (without distillation) by stirring the residue of neutral products with methanol and filtering. The crude solid, m.p. 60–73°, was recrystallized twice from methanol to give the pure dimer.

Oxidation of 4.2 g. of tertiary amine XVIII was effected with 12.6 g. of potassium permanganate in 200 ml. of 0.5 *N* sodium hydroxide solution at room temperature (10 hours stirring). A portion (6.6 g.) of the permanganate was added at the start and the rest was added in three equal portions each time the purple color was discharged. After filtering, the solution was acidified to give 2.9 g. of 2,3-dimethylbenzoic (hemimellitic) acid, m.p. 138–142°. One recrystallization from ethanol–water raised the melting point to 142–143°, which was not depressed by admixture with an authentic sample of acid (see Grignard method).

Oxidation of 10 g. of tertiary amine XVIII was effected also with 80 g. of potassium permanganate in 500 ml. of 0.1 *N* sodium hydroxide solution (16 hours refluxing). After filtering, the solution was carefully acidified with dilute sulfuric acid to maximum precipitation giving 9.0 g. of monopotassium hemimellitate dihydrate (air-dried), m.p. 360° dec. This salt was converted in 75% yield (through the barium salt) to 1,2,3-benzenetricarboxylic (hemimellitic) acid dihydrate m.p. 188.5–189.5° (reported m. p. 190°).[41] Trimethyl hemimellitate, prepared in 57% yield from the silver salt of the acid and methyl iodide at 120°, melted at 99–100° (reported m.p. 100°).[41]

Decomposition of 2,3-dimethylbenzyltrimethylammonium hydroxide, prepared from 15.3 g. of the corresponding iodide (XIX, see below) and an equivalent of freshly precipitated silver oxide in boiling water solution, gave 0.3 g. of 2,3-dimethylbenzyl alcohol (XL), b.p. 123–130° at 13 mm. It solidified on cooling and scratching and melted at 63–64.5° after washing with 2 ml. of petroleum ether. This melting point was not depressed by admixture with a sample of the alcohol synthesized by the Grignard method.

Independent synthesis of tertiary amine XVIII, b.p. 101.5–102.5° at 15.5 mm., was effected in 42% over-all yield from 0.05 mole of 2,3-dimethylbenzyl chloride (see Grignard method) through the hexamethylenetetramine salt (obtained in 83% yield after 20 hours refluxing in chloroform, m.p. 189–192°) essentially as described for the synthesis of VII. The picrates of samples of the amine obtained from this reaction and from the rearrangement of XVII were shown to be identical by mixed melting points.

2,3-Dimethylbenzyltrimethylammonium Iodide (XIX).—This salt was obtained in yields of 98–99% from 1.5 moles of methyl iodide and 1.0 mole of 2,3-dimethylbenzyldimethylamine (XVIII) in 500 ml. of absolute ethanol. A sample, recrystallized twice from absolute ethanol, melted at 235–236° dec., with previous shrinking and darkening at 231°.[42]

Anal. Calcd. for $C_{12}H_{20}NI$: C, 47.22; H, 6.59; N, 4.59. Found: C, 47.32; H, 6.54; N, 4.28.

Rearrangement of XIX to 2,3,4-Trimethylbenzyldimethylamine (XX) and Side Reactions.—This reaction was carried out with 438.7 g. (1.438 moles) of 2,3-dimethylbenzyltrimethylammonium iodide (XIX) and 1.95 moles of sodium amide in 3 l. of liquid ammonia as described for XVII. The addition period was 1 hour.

Fractionation of the neutral products gave (1) 3.5 g., b.p. 63–64° at 15 mm.; (2) 14.0 g., b.p. 187–197° at 7 mm.; (3) 6.0 g., b.p. 197–227° at 7 mm.; (4) 7.0 g.; b.p. 240–255° at 2 mm. The residue (8 g.) which solidified to a glassy brittle solid was discarded. Fraction (1) was hemimellitene (2%) (reported b.p. 70° at 20 mm.)[43]; the trinitro derivative melted at 207.5–208° (reported m.p. 209°).[44] Fraction (2) was stirred with 40 ml. of cold methanol and the remaining solid (10.5 g., m.p. 78–82°) was fractionally recrystallized from methanol to give 5 g. of a product, m.p. 142.5–144.5°. More of this solid (1.9 g., m.p. 142.5–

ml. of petroleum ether. After one recrystallization from methanol, it melted at 144.5–145° and analyzed for 2,2′,-3,3′-tetramethylstilbene (a homolog of XXIX, probably the *trans* isomer); yield 4–7%.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.43; H, 8.51.

Fraction (4), b.p. 241–242° at 2 mm. (on redistillation), analyzed for a higher homolog of trimeric olefin XXXII; yield 4%.

Anal Calcd. for $C_{27}H_{30}$: C, 91.47; H, 8.53. Found: C, 91.67; H, 8.62.

Fractionation of the basic products gave (1) 106.5 g., b.p. 124–125° at 16 mm., 120–121° at 14 mm.; (2) 30.4 g., b.p. 203–210° at 6 mm., 180–195° at 2 mm. The residue (31 g.), a dark brown tar, was discarded. Fraction (1) was 2,3,4-trimethylbenzyldimethylamine (XX), 42% yield, redistilling at 120.6–120.8° at 14 mm.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.80; N, 7.90. Found: C, 81.40; H, 10.79; N, 7.90.

The picrate, recrystallized from 95% ethanol, melted at 152–153°.

Anal. Calcd. for $C_{18}H_{22}N_4O_7$: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.73; H, 5.38; N, 14.14.

Fraction (2), on redistillation boiled at 204–205° at 7 mm. and analyzed for a higher homolog of dimeric rearranged amine XXX; yield 14%.

Anal. Calcd. for $C_{21}H_{29}N$: C, 85.36; H, 9.89; N, 4.74. Found: C, 85.37; H, 9.64; N, 4.88.

Similar results were obtained in several runs under the above conditions, the yields of 2,3,4-trimethylbenzyldimethylamine (XX) being 42–43%. However, rapid addition (2 minutes) of 0.2 mole of the methiodide XIX to 0.22 mole of sodium amide in 250 ml. of liquid ammonia (2.25 hours stirring) gave only a 32% yield of rearranged amine XX along with hemimellitene (2%), the dimeric rearranged amine (14%), and the other neutral products (25%).

Oxidation of 4.2 g. of tertiary amine XX with 12.6 g. (total) of potassium permanganate as described for tertiary amine XVIII (at room temperature) gave 1.6 g. of crude acid, m.p. 154–195°, which after recrystallizations from ethanol, ethanol–water, and ligroin (b.p. 90–120°) gave 2,3,4-trimethylbenzoic (prehnitylic) acid (0.2 g.), m.p. 166–166.5°. A mixed melting point with an authentic sample of this acid (m.p. 166–167°, see under Grignard method) was the same.

Oxidation of 10 g. of tertiary amine XX with 100 g. of potassium permanganate was effected as described for XVIII (at refluxing temperature). Since no acid precipitated on acidifying the filtrate with hydrochloric acid, a solution of barium chloride was added; maximum precipitation of the barium salt of the organic acid was realized in slightly acidic medium. A suspension of the dried barium salt (12 g.) in a solution of 60 ml. of 3 *M* sulfuric acid was boiled 20 minutes and filtered hot. The filtrate was concentrated to give 1,2,3,4-benzenetetracarboxylic (prehnitic) acid (5.5 g., 39%) in two crops, m.p. 237–240° (reported m.p. 236–238°).[45] The tetramethyl ester, prepared from the silver salt of the acid and methyl iodide at 130° according to the directions used for hemimellitic acid, melted at 129.5–130° (reported m.p. 131–133°).[45]

2,3,4-Trimethylbenzyltrimethylammonium Iodide (XXI).—This salt was prepared in 97% yield from 0.98 mole of methyl iodide and 0.65 mole of 2,3,4-trimethylbenzyldimethylamine (XX) in 600 ml. of absolute ethanol. A sample, recrystallized 3 times from absolute ethanol, melted at 245–246° dec.[42]

Anal. Calcd. for $C_{13}H_{22}NI$: C, 48.91; H, 6.95; N, 4.39. Found: C, 49.17, 49.15; H, 6.92, 6.88; N, 3.89.

Rearrangement of XXI to 2,3,4,5-Tetramethylbenzyldi-

Fraction (1) was prehnitene (2.7%) (reported b.p. 82° at 10 mm.)[43]; the dinitro derivative melted at 175–176° (reported m.p. 176°).[46] Stirring fraction (2) with 10 ml. of petroleum ether and fraction (3) with 30 ml. of methanol gave 1.5 g. of solid, m.p. 139–144°, assumed to be the dimeric olefin (a higher homolog of XXIX); yield 1.7%.

Fractionation of the basic products gave (1) 56.2 g., b.p. 139–142° at 15.5 mm.; (2) 9.8 g., b.p. 195–210° at 2 mm. The residue (17 g.) of hard brittle material was discarded. Fraction (1) was 2,3,4,5-tetramethylbenzyldimethylamine (XXII), 47% yield, b.p. 140–140.5° at 16 mm. on redistillation.

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.61; H, 11.07. Found: C, 81.60; H, 11.01.

The picrate, recrystallized from 95% ethanol, melted at 147–147.5°.

Anal. Calcd. for $C_{19}H_{24}N_4O_7$: C, 54.28; H, 5.75; N, 13.33. Found: C, 54.37; H, 5.29; N, 13.53.

Fraction (2), on redistillation boiled at 195–197° at 2 mm. and analyzed for a higher homolog of dimeric rearranged amine XXX; yield, 10%.

Anal. Calcd. for $C_{23}H_{33}N$: C, 85.39; H, 10.29; N, 4.33. Found: C, 85.55, 85.73; H, 9.95, 10.18; N, 4.27, 4.35.

Oxidation of 2 g. of tertiary amine XXII was effected with 6.0 g. of potassium permanganate in 175 ml. of 0.45 *N* sodium hydroxide solution at room temperature (10 hours stirring). A portion (4 g.) of the permanganate was added at the start and the rest was added when the purple color was discharged. There was obtained 0.7 g. of crude acid which, after two recrystallizations from ethanol (cooled to -78°), gave 0.1 g. of 2,3,4,5-tetramethylbenzoic acid, m.p. 167–168.5°. This melting point was not depressed by admixture with an authentic sample of acid (m.p. 166.5–168°, prepared from pentamethylbenzene).[47]

2,3,4,5-Tetramethylbenzyltrimethylammonium Iodide (XXIII).—This salt was obtained in 94% yield from 0.404 mole of methyl iodide and 0.269 mole of 2,3,4,5-tetramethylbenzyldimethylamine (XXII) in 300 ml. of absolute ethanol. A sample, recrystallized twice from absolute ethanol, melted at 238–240° dec.[42]

Anal. Calcd. for $C_{14}H_{22}NI$: C, 50.45; H, 7.26; N, 4.20. Found: C, 50.35; H, 7.22; N, 4.32.

Rearrangement of XXIII to 2,3,4,5,6-Pentamethylbenzyldimethylamine (XXIV) and Side Reactions.—This reaction was carried out with 81.5 g. (0.244 mole) of 2,3,4,5-tetramethylbenzyltrimethylammonium iodide (XXIII) and 0.304 mole of sodium amide in 600 ml. of liquid ammonia (addition time, 15 minutes) as described for XVII.

Fractionation of the neutral products gave (1) 0.8 g., b.p. 103–104° at 13 mm.; (2) 1.0 g., b.p. 185–235° at 2 mm. The hard brittle residue (1.3 g.) was discarded. Fraction (1) solidified to pentamethylbenzene (2.2%) melting at 48–49° and at 52–53° after steam distillation and recrystallizing from methanol; a mixed melting point with authentic pentamethylbenzene (m.p. 54–55°) was 53–54°. Fraction (2) was stirred with 10 ml. of petroleum ether to give 0.2 g. of solid, m.p. 146–147°, assumed to be the dimeric olefin (a higher homolog of XXIX); yield 0.6%.

Fractionation of the basic products gave (1) 30.9 g., b.p. 157–161° at 15 mm.; (2) 3.5 g., b.p. 223–233° at 3 mm. The dark tarry residue (3.5 g.) was discarded. Fraction (1) solidified to 2,3,4,5,6-pentamethylbenzyldimethylamine (XXIV), 62% yield, m.p. 41–42° after one recrystallization from methanol (cooled to -78°).

Anal. Calcd. for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 82.02; H, 11.45; N, 6.95.

The picrate, recrystallized twice from 95% ethanol, melted at 198–199°.

Anal. Calcd. for $C_{20}H_{26}N_4O_7$: C, 55.29; H, 6.03; N, 12.90. Found: C, 55.55; H, 6.38; N, 12.66.

Fraction (2) appeared to be the dimeric rearranged amine (a higher homolog of XXX); yield 9%.

Methylation of tertiary amine XXIV (0.03 mole) with methyl iodide (0.1 mole) in 50 ml. of commercial absolute ethanol gave a 98% yield of 2,3,4,5,6-pentamethylbenzyltrimethylammonium iodide, m.p. 220–221° dec.,[42] after two recrystallizations from absolute ethanol.

Anal. Calcd. for $C_{15}H_{26}NI$: C, 51.87; H, 7.55; N, 4.03. Found: C, 52.00; H, 7.50; N, 3.95.

Reduction of 4.34 g. (0.0125 mole) of this iodide with 92 g. of 5% sodium amalgam in 125 ml. of hot water by the general method of Emde[13] gave 2 g. (99%) of hexamethylbenzene, melting at 155–160° and at 161.5–163.5° after one recrystallization from ethanol. After steam distillation and recrystallizing from ethanol, the hydrocarbon melted at 163.5–164.5° which was not depressed by admixture with an authentic sample (m.p. 164–165°).

2,4,6-Trimethylbenzyltrimethylammonium Iodide (XXXIV).—2,4,6-Trimethylbenzyldimethylamine, b.p. 112–113° at 13 mm., was prepared in 80% yield from 2,4,6-trimethylbenzyl chloride[48] through the hexamethylenetetramine salt by the Sommelet reaction[49] (see independent synthesis of VII).

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.80; N, 7.90. Found: C, 81.22; H, 10.55; N, 8.30.

The picrate melted at 149–150° (reported m.p. 144–145°).[49]

Anal. Calcd. for $C_{18}H_{22}N_4O_7$: N, 13.79. Found: N, 14.03.

The iodide (XXXIV) was obtained in 98% yield from 0.65 mole of methyl iodide and 0.325 mole of 2,4,6-trimethylbenzyldimethylamine in 350 ml. of absolute ethanol. A sample, recrystallized three times from absolute ethanol, melted at 196–197° dec.[42]

Anal. Calcd. for $C_{13}H_{22}NI$: C, 48.91; H, 6.95; N, 4.39. Found: C, 49.29; H, 6.87; N, 4.62.

Reaction of XXXIV with Sodium Amide. Isodurene (XXXVII).—This reaction was carried out with 31.93 g. (0.1 mole) of 2,4,6-trimethylbenzyltrimethylammonium iodide (XXXIV) and 0.21 mole of sodium amide in 350 ml. of liquid ammonia essentially as described for the rearrangement of XVII (addition time, 5 minutes; stirring time, 3 hours). Because of the presence of much formaldehyde the working up of the reaction mixture was tedious.

Fractionation of the neutral products gave 8.5 g. (63%) of isodurene (XXXVII), b.p. 81–82° at 14 mm. (reported b.p. 84.6–84.7° at 17 mm.),[50] $n^{25}\text{D}$ 1.5108 (reported $n^{20}\text{D}$ 1.5134).[51] The dinitro derivative, after two recrystallizations from ethanol, melted at 179.5–181° (reported m.p. 181°).[52]

Fractionation of the basic products failed to give any definite compounds; some high boiling material (1.0 g., b.p. 135–200° at 3 mm.) distilled with decomposition.

Reduction of 2,3-Dimethylbenzyltrimethylammonium Iodide (XIX) to Hemimellitene.[53]—The general procedure of Emde[13] for the reduction of salts to hydrocarbons was adapted to this case. To a stirred suspension of 100 g. (0.329 mole) of 2,3-dimethylbenzyltrimethylammonium iodide (XIX) in 2.5 l. of water heated on the steam-bath, was added gradually (45 minutes) 2800 g. of 5% sodium amalgam and the stirring continued until all the sodium had reacted (*ca.* 24 hours). The hemimellitene was steam distilled out of the reaction mixture, taken up in ether and isolated. It had the following constants: b.p. 174° (reported b.p. 172.2–172.4°),[23] $n^{25}\text{D}$ 1.5137 (reported $n^{20}\text{D}$ 1.5130)[23]; yield 90%. The over-all yield of pure hemimellitene from benzyldimethylamine was 55%.

Grignard-Formaldehyde Method. 2,3-Dimethylbenzyl Alcohol (XL) and 2,3,4-Trimethylbenzyl Alcohol (XLI).—2-Methylbenzyl alcohol, b.p. 109–110° at 14 mm. (reported b.p. 109° at 12 mm.)[22] was prepared in 97% yield by the reduction of 0.8 mole of *o*-toluic acid with 1.0 mole of lithium aluminum hydride employing the general directions of Nystrom and Brown[54] for ether-soluble acids. By passing hydrogen chloride gas in a petroleum ether solution of this alcohol, there was obtained in 89% yield 2-methylbenzyl chloride, b.p. 81–82° at 13 mm. (reported b.p. 84° at 14 mm.).[22]

---

(46) Smith and Hac, THIS JOURNAL, **56**, 477 (1934).

(47) Smith and Harris, *ibid.*, **57**, 1291 (1935).

(48) Vavon, Bolle and Calin, *Bull. soc. chim. France*, [5] **6**, 1025 (1939).

(49) Angyal, Morris, Rassack and Waterer (*J. Chem. Soc.*, 2704 (1949)) carried out this reaction without isolating the amine.

(50) Smith and MacDougall, THIS JOURNAL, **51**, 3004 (1929).

(51) Smith and Cass, *ibid.*, **54**, 1611 (1932).

(52) Smith and Moyle, *ibid.*, **55**, 1680 (1933).

(53) This experiment was performed by Mr. Wallace R. Brasen of this Laboratory.

(54) Nystrom and Brown, THIS JOURNAL, **69**, 2548 (1947).

2,3-Dimethylbenzyl alcohol (XL) was prepared from 2-methylbenzylmagnesium chloride (obtained from 96.5 g., 0.686 mole of 2-methylbenzyl chloride) and excess trioxymethylene according to the directions of Reichstein and coworkers.[20] This alcohol, b.p. 124–129° at 13 mm. (reported b.p. *ca.* 125° at 12 mm.,[20] 126–133° at 23 mm.[23]), solidified; yield 57%. Two washings with cold petroleum ether gave the pure alcohol, m.p. 63.5–64.5° (reported m.p. 64°,[20] 65–66.5°[23]); yield 50%. Also, there was obtained 3.5 g. (5%) of *o*-xylene, b.p. 40° at 23 mm., 3.8 g. (5%) of the dimer, 2,2'-dimethyldibenzyl, b.p. 190–200° at 16 mm. (reported b.p. 170–180° at 12 mm.),[20] and 11.7 g. of material, b.p. 235–255° at 16 mm. The dimer solidified and, after washing with methanol, melted at 60.5–63° (reported m.p. 65°).[20] Reichstein reported this dimer as the main side reaction product. The 11.7 g. of high boiling material appeared to consist mostly of a single product, possibly the formal derivative of 2,3-dimethylbenzyl alcohol.[23]

2,3-Dimethylbenzoic (hemimellitic) acid, m.p. 142–143° (reported m.p. 144°),[20] was prepared in 71% yield by oxidizing 4 g. of 2,3-dimethylbenzyl alcohol with potassium permanganate.

2,3-Dimethylbenzyl chloride, b.p. 102–103° at 12 mm. (reported b.p. 99° at 12 mm.),[20] was obtained in 89% yield by treating 2,3-dimethylbenzyl alcohol in petroleum ether with hydrogen chloride.

2,3,4-Trimethylbenzyl alcohol (XLI), b.p. 106–110° at 2 mm. (reported b.p. 110–150° at 1 mm.),[20] was obtained from 2,3-dimethylbenzylmagnesium chloride (prepared from 30 g., 0.194 mole, of 2,3-dimethylbenzyl chloride) and excess trioxymethylene as described by Reichstein. Our product (32%) which was obviously purer than that of Reichstein, solidified on cooling to −78° and scratching. Two washings with petroleum ether gave pure 2,3,4-trimethylbenzyl alcohol (XLI), m.p. 49–50° (reported m.p. 49–50°)[20]; yield 20%. Reichstein obtained the pure alcohol in 15% yield by tedious purification through the phthalic acid ester. In agreement with Reichstein, we obtained as side products, hemimellitene (37%) and 2,2',3,3'-tetramethyldibenzyl (17%).

2,3,4-Trimethylbenzoic (prehnitylic) acid, m.p. 166–167° (reported m.p. 166–168°),[20] was prepared in 73% yield by oxidizing 2.25 g. of 2,3,4-trimethylbenzyl alcohol with potassium permanganate.

DURHAM, N. C. RECEIVED APRIL 11, 1951

[COMMUNICATION NO. 1390 FROM THE KODAK RESEARCH LABORATORIES]

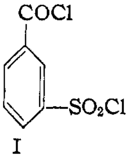
The Reaction of 3-Chlorosulfonylbenzoyl Chloride with Amines

BY C. R. BARR, I. F. SALMINEN AND A. WEISSBERGER

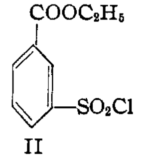
The selective reactivity of 3-chlorosulfonylbenzoyl chloride with amines is demonstrated with the following examples: aniline, *o*- and *p*-aminophenol, 1-aminoanthraquinone, 1-phenyl-3-*m*-aminobenzamido-5-pyrazolone and methylamine. This property is utilized to prepare, (1) mixed amides of the type (R)R'NCO—C_6H_4—$SO_2NR''(R''')$, and (2) pure compounds containing sulfonic acid groups.

Making use of the well-known difference in reactivity of carboxy acid chlorides and sulfonyl chlorides, *m*-chlorosulfonylbenzoyl chloride (I) can, under suitable conditions, react with two different amines in two stages.[1] The carboxyamide is formed in the first reaction, the sulfonamide in the second. Thus, amines containing active methylene or methine groups have been linked to amines which contain some other function needed in couplers used in color photography. Moreover, the chlorosulfonylcarboxyamides can often be readily purified by recrystallization, and their hydrolysis affords a method for the preparation of pure compounds containing sulfonic acid groups which is sometimes more convenient than the purification of the sulfonic acids or their salts. 3,5-Dichlorosulfonylbenzoyl chloride can be used like I where introduction of *two* sulfonic acid groups is desired.

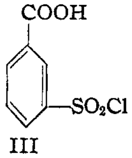
The marked difference in the reactivity of the functional groups of *m*-chlorosulfobenzoyl chloride is shown by the reactions with alcohol[2] and with water.[3] In the former, ethyl *m*-chlorosulfonylbenzoate (II) and in the latter, *m*-chlorosulfonylbenzoic acid (III) can be obtained in quantitative yields.



I

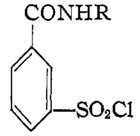


II



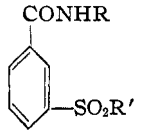
III

Suitable conditions for the formation of 3-chlorosulfonylbenzanilide (IVa) are the heating of slightly more than one mole of I with one mole of aniline in toluene, or the reaction at room temperature in toluene of one mole of I with two moles of aniline. Use of dioxane or ethyl acetate instead of toluene gave lower yields. Other conditions lead to the dianilide, Va,[4] for instance, the use of more than one mole of aniline at room temperature in the presence, or of more than two moles of aniline in the absence, of a tertiary amine or inorganic base, or prolonged heating of a reaction mixture containing I and two moles of aniline, or aniline hydrochloride. The m.p. of Va was found to be 13° higher than in the literature. The reaction of IVa with a second



IV

a R = C_6H_5
b R = $C_6H_4OH(2)$
c R = $C_6H_4OH(4)$
d R = anthraquinone(1)



V

a R = C_6H_5; R' = NHC_6H_5
b R = $C_6H_4OH(2)$; R' = NHC_6H_5
c R = $C_6H_4OH(2)$; R' = $N(CH_3)C_6H_5$
d R = $C_6H_4OH(2)$; R' = $NHC_6H_4OH(2)$
e R = C_6H_5; R' = OH

---

[1] A. Weissberger and I. F. Salminen, Eastman Kodak Company, U. S. Patent 2,484,477 (October 11, 1949).

[2] R. Wegscheider and M. Furcht, *Monatsh.*, **23**, 1093 (1902).

[3] S. Smiles and J. Stewart, *J. Chem. Soc.*, **119**, 1792 (1921).

[4] P. Ruggli and F. Grün, *Helv. Chim. Acta*, **24**, 197 (1941).