〔Added in proof〕 After this paper was submitted for publication, the communications of M. Barash and J. M. Osbond (Chem. & Ind. (London), **1958**, 490) and of A. Brossi, A. Cohen, J. M. Osbond, Pl. A. Plattner, O. Schnider, and J. C. Wickens (*ibid.*, **1958**, 491) became available in our Library. The former authors describe the synthesis of emetine and its stereoisomers, and the latter, stereochemistry of emetine.

UDC 542.941.7 : 547.554

118. **Shigehiko Sugasawa and Hisayuki Matsuo**: A Modified Emde Degradation. Reductive Cleavage of Quaternary Ammonium Salts by Raney Nickel.[†]

(*Faculty of Pharmaceutical Sciences, University of Tokyo*[*])

An important rôle of Emde degradation[1] in alkaloid chemistry and allied fields is well known. Thus the cleavage of C-N linkage of even those quaternary ammonium salts, which are resistant to Hofmann degradation, can in many cases be achieved by heating them with 5% sodium amalgam in aqueous solution, hence under a strong alkaline working condition. In order to avoid working in alkaline medium Emde[2] carried out the cleavage through catalytic hydrogenation in the presence of platinum oxide or palladium on barium sulfate. Emmert[3] used electrolytic reduction for the same purpose and zinc-copper couple in amyl alcohol was used by Kishi.[4] However, none of these modified methods is so widely used as the original Emde method.

It was in 1942 when Papa, *et al.*[5] introduced a combination of aqueous sodium hydroxide solution and Raney nickel alloy as a strong reduction agent for organic compounds. Thus by this means aryl ketones gave arylmethylenes, aliphatic carbonyl compounds yielded the corresponding alcohols, and isolated ethylenes and acetylenes were reduced to the saturated compounds. The efficacy of this combination can be attributed to the nascent hydrogen, which is activated over nickel catalyst formed.

We now applied the Papa type of reduction method to various quaternary ammonium salts with the expectation that the Emde type of cleavage would be possible under milder working conditions and in simpler manipulation than the conventional Emde method, and so far our preliminary experiments, which will be described in this paper, are concerned the cleavage was effected usually with better yield of the products and in shorter working time than the original method.

As open-chain model compounds phenethyl-(I), benzyl-(II), phenyl-(III), and 2-biphenyltrimethylammonium (IV) salts were chosen. The compound was mixed with aqueous sodium hydroxide solution (15~20%) and to the resultant alkaline solution of ammonium compound 1.5~2.5 times the required amount of 50% Raney nickel alloy was added in small portions with stirring and cooling to keep the temperature of the reaction mixture within 25° as was required for the preparation of Raney nickel W-2.[6] The evolution of trimethylamine, which was collected in hydrochloric acid and characterized, became evident as soon

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[*] Hongo, Tokyo （菅澤重彦，松尾寿之）.

[†] cf. S. Sugasawa, H. Matsuo: This Bulletin, **4**, 142(1956).

[1] H. Emde: Arch. Pharm., **667**, 332, 369, 391(1909); **249**, 108(1911); Ber., **42**, 2539(1909); Ann., **391**, 93(1912).

[2] H. Emde: Arch. Pharm., **274**, 173(1936).

[3] B. Emmert: Ber., **42**, 1507, 1997(1909); *ibid.*, **45**, 430(1912).

[4] N. Kishi: Yakugaku Zasshi, **48**, 141(1928).

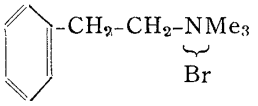
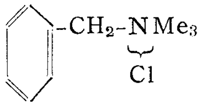
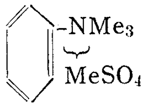
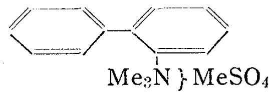
[5] D. Papa, E. Schwenk. B. Whitman: J. Org. Chem., **7**, 587(1942).

[6] R. Mozingo: Org. Syntheses, **21**, 15(1941).

as the first portion of the alloy was added. After all the alloy had been introduced the whole was stirred for some time (ca. one hour) at room temperature to ensure completion of the reaction. The des-N product, which separated oily, was collected, purified, and characterized appropriately. As can be seen from Table I the cleavage of these ammonium compounds proceeded smoothly and gave the corresponding des-N products in a fair to good yields, but the hydrocarbons, such as ethylbenzene, toluene, and benzene obtained from (I), (II), and (III), respectively, are so volatile that the true yields of the products may have been somewhat higher than are recorded in Table I.

The above-mentioned four compounds were also subjected to the conventional Emde method, which proceeded by treating the substrates with a large excess of 5% sodium amalgam in aqueous solution at boiling water-bath temperature for 8～48 hours, whereas the present method required only about 1.5～2 hours for completion at the reaction temperature of 10～25°. Remarkable facts are that Emde⁽⁷⁾ obtained styrene from (I), while we, as was expected, had ethylbenzene instead, and he⁽⁸⁾ recovered either dimethylaniline or metho-salt from (III), whereas benzene was produced in 70% yield without the recovery of dimethylaniline in our case. By the original Emde method, (IV) yielded biphenyl in 58% yield with simultaneous recovery of 11% of 2-dimethylaminobiphenyl, while the present method gave solely biphenyl in a yield of 79%.

TABLE I.

	Quaternary Salt	Product (yield, %) Raney Ni method		Conventional Emde degradation	
(I)		Ethylbenzene Me_3N	(85%) (87%)	Styrene	a)
(II)		Toluene Me_3N	(90%) (95%)	Toluene (81%)	b)
(III)		Benzene Me_3N	(70%) (64%)	Negative	c)
(IV)		Biphenyl Me_3N	(79%) (75%)	Biphenyl (58%) 2-Dimethylaminobiphenyl (11%)	d)

a) H. Emde: Apotheker Ztg., **27**, 18 (1912).
b) *Idem.*: Arch. Pharm., **247**, 380 (1909).
c) *Idem.*: *Ibid.*, **247**, 385 (1909).
d) This report.

This method was now applied to the degradation of cyclic bases and as such, phenanthridine and its 6-methyl derivative were chosen. 6-Methylphenanthridine⁽⁹⁾ was converted to the metho-salt (V) of 5,6-dimethyl-5,6-dihydrophenanthridine by the usual method and this was subjected to the modified Emde degradation, when a dihydromethine base was obtained as a colorless oil of b.p. 109～110° in a yield of 91.5%.⁽¹⁰⁾ The unity of this oil

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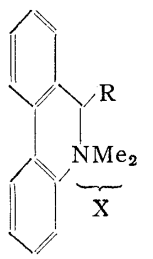
7) H. Emde: Apotheker Ztg., **27**, 18 (1912).
8) *Idem*: Arch. Pharm., **247**, 385 (1909).
9) G. M. Morgan, L. P. Walls: J. Chem. Soc., **1931**, 2450.
10) The yield of this same compound by the conventional Emde method was 82%.

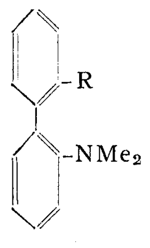
was proved by the fact that it gave a single picrate of m.p. 167∼168°(decomp.) and a methiodide of m.p. 181∼182°(decomp.), both in excellent yields. Of the two expressions (VI) and (VII), we are in favor of the former, because it is a fairly weak base, dissolving in 10% hydrochloric acid but not in 3% acetic acid, and it can be nitrosated to give a compound which responds to Liebermann's color test. When the metho-salt of (VI) was subjected to the modified method for the second time a smooth evolution of trimethylamine was recognized and an oil of b.p$_{17}$ 135∼136° was obtained in a yield of 71% as a des-N compound. Its structure of being 2-ethylbiphenyl was proved by the fact that it furnished 2-biphenylcarboxylic acid (IX) by oxidation, which was identified with an authentic sample prepared from fluorenone according to Graebe's method.[11] From the mother liquor of (IX) there was obtained a minute amount of a crystalline substance, soluble in sodium hydrogen carbonate but not identical with (IX), but this was not investigated further. The conventional Emde method yielded the same des-N compound from the metho-salt of (VI) in 42% yield with a simultaneous recovery of (VI) in 12% yield.

5,5-Dimethyl-5,6-dihydrophenanthridinium methylsulfate (XII) was prepared from phenanthridine[12] as usual. In the preparation of the intermediate, 5-methyl-5,6-dihydrophenanthridine (X) of m.p. 46∼48°, air must be rigorously excluded since this compound is so easily oxidized in the air, forming 5-methyl-6(5*H*)-phenanthridone (XI), as was already pointed out by Karrer, *et al.*,[13] and hence the base (X) must be immediately converted to the metho-salt. When the latter was dissolved in sodium hydroxide solution there appeared a faint violet coloration followed by separation of a reddish purple syrupy substance. However, on addition of the alloy, this disappeared with simultaneous discoloration and toward the end of the reaction there separated a colorless oily substance in a yield of 74%, to which we assigned the expression (XIII) by the same reason mentioned above. In this case, however, a substance of m.p. 106∼108° was also obtained in 10% yield, which did not dissolve in 10% hydrochloric acid but did so in 20% acid, and this was found to be N-methyl-6(5*H*)-phenanthridone (XI). The latter probably owed its formation to 5-methyl-5,6-dihydrophenanthridine (X), formed by strong sodium hydroxide solution from (XII) during the degradation process, which then suffered air oxidation during work up.[14] The yield of des-N compound from (XIII) by our method was 73%, the structure of which was proved to be 2-methylbiphenyl (XIV) by converting this to 2-biphenylcarboxylic acid through oxidation.

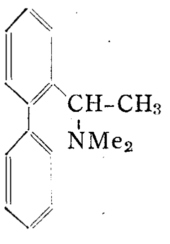
From the above-mentioned results the modified Emde method appears to work just as well as the original method under milder working conditions and with better yields of the products, and the scope of this procedure will be examined by some further experiments.



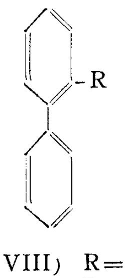
(V) R=Me
(XII) R=H



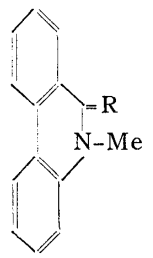
(VI) R=Et
(XIII) R=Me



(VII)



(VIII) R=Et
(IX) R=COOH
(XIV) R=Me



(X) R=H$_2$
(XI) R=O

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[11] C. Graebe, A. S. Rateanu: Ann., **279**, 260(1894).

[12] G. T. Morgan, L. P. Walls: J. Chem. Soc., **1932**, 2229.

[13] R. B. Brook, F. Blumer, H. J. V. Krishna, S. Schnell, P. Karrer: Helv. Chim. Acta, **39**. 667 (1956); P. Karrer, L. Szabo, H. J. V. Krishna, R. Schwyzer: *Ibid.*, **33**, 294(1950).

[14] If so, the reverse addition may give a better yield of the product with exclusion of the recovery of (XII).

The authors thank the members of the Central Analysis Room of this Faculty, and also Mrs. F. Hisamichi and Mr. T. Yoda of Tokyo Research Laboratory of Tanabe Seiyaku & Co. for microanalytical data.

Experimental

Degradation of Open-chain Quaternary Salts

Cleavage of Phenethyltrimethylammonium Bromide (**I**)—The quaternary bromide (I) (5.0 g.) in 50 cc. of water was mixed with 20 g. of 50% NaOH soln., and to the resultant turbid solution was now added powdered Raney Ni alloy[15] (1.5 g.) in small portions during 30 mins. under vigorous stirring and cooling to keep the temp. of the reaction mixture within 25°. The evolution of trimethylamine, which was collected as its hydrochloride in an ice-cooled 10% HCl, became evident as soon as the first portion of Raney Ni alloy was added. After being stirred for additional 1 hr. at room temp. to complete the reaction, the oily substance separated out was collected in ether. The ethereal layer was successively washed with 10% HCl, $NaHCO_3$, and water, dried over anhyd. Na_2SO_4, and distilled fractionally. Yield of ethylbenzene (b.p. 135～136°) was 1.86 g. or 85%. This substance did not decolorize $KMnO_4$-acetone or Br_2-AcOH soln. The HCl-solution and washings were combined and evaporated *in vacuo* to dryness to give 1.7 g. of crude trimethylamine hydrochloride (yield, 87%). Recrystallized from EtOH to colorless needles of m.p. 270～273° (decomp.). Picrate: Yellow prisms (from EtOH), m.p. 215～217°. No m.p. depression was observed on admixture with an authentic sample.

For characterization of ethylbenzene, 1.8 g. of the above-obtained sample was nitrated according to Menke's method[16] to give 1.5 g. of 1-nitro-4-ethylbenzene (b.p$_{28}$ 134～137°) in a yield of 70%. The latter was then reduced catalytically over Raney Ni and acetylated to yield 1.24 g. of white crystals (yield, 82%), which separated in colorless scales of m.p. 93～94° from EtOH. This was identified by mixed fusion with an authentic 1-acetamido-4-ethylbenzene.

Cleavage of Benzyltrimethylammonium Chloride (**II**)—5.0 g. of (II) was subjected to this modified degradation under the same working conditions as in the case of (I) and worked up as usual. Yield of toluene (b.p. 110～111°) was 2.2 g. or 90%. Trimethylamine was recovered as its hydrochloride, m.p. 270～273° (decomp.), which weighed 2.45 g. or 90%. The toluene was characterized as follows:

i) The specimen (1.0 g.) was nitrated according to Beilstein's method[17] to yield 2,4-dinitrotoluene, which formed light yellow needles of m.p. 69～70° from hydr. EtOH. Yield, 1.4 g. or 71%. No m.p. depression occurred on admixture with an authentic sample of m.p. 68～69°.

ii) Another 1-g. portion was oxidized with $KMnO_4$-pyridine to give 0.72 g. of benzoic acid as colorless needles (from hydr. EtOH), m.p. 120～121°. Identified with an authentic sample by mixed fusion.

Cleavage of Phenyltrimethylammonium Methylsulfate (**III**)—Degradation of the quaternary methylsulfate (III) (15 g.) with Raney Ni alloy (50 g.) in a medium of 210 g. of 17% NaOH soln. proceeded smoothly under the same conditions as in above cases. Yield of benzene (b.p. 76～79°) was 3.3 g. or 70% and trimethylamine was recovered as its hydrochloride, which weighed 3.7 g.; yield, 64%. Benzene thus obtained (1.5 g) was characterized as acetanilide (overall yield, 72%) and identified by melting point test.

Cleavage of 2-Biphenyltrimethylammonium Methylsulfate (IV)

Preparation of (**IV**): **2-Dimethylaminobiphenyl**—Prepared from 2-aminobiphenyl according to Popkin's method.[18] Colorless oil, b.p$_9$ 139～140°.

Picrate: Yellow prisms (from EtOH), m.p. 193° (decomp.). *Anal.* Calcd. for $C_{20}H_{18}O_7N_4$: C, 56.33; H, 4.26; N, 13.14. Found: C, 56.20; H, 4.29; N, 12.94.

2-Biphenyltrimethylammonium Methylsulfate (**IV**)—To the foregoing base (2.0 g.) in 10 cc. of xylene, 1.3 g. of freshly distilled Me_2SO_4 was added and the whole was refluxed in an oil bath for 1 hr. to form two layers. After cool, the supernatant xylene was decanted, the residual viscous syrup was dissolved in water, treated with decolorizing charcoal, and evaporated *in vacuo* to dryness to leave a vitreous substance (IV); yield, 3.0 g. or 93%.

Iodide: Colorless prisms (from EtOH), m.p. 184～185° (decomp.). *Anal.* Calcd. for $C_{15}H_{17}NI$: C, 53.25; H, 5.03; N, 4.14. Found: C, 52.86; H, 5.51; N, 4.19.

Cleavage of (**IV**)—i) With Raney Ni alloy: 5.1 g. of (IV) in 30 cc. of water was mixed with 50% NaOH (20 g.) and to the resultant turbid solution Raney Ni alloy (2.5 g.) was added as in the above case, but in this case the evolution of Me_3N was somewhat sluggish. Therefore, after addition of all the alloy, the whole was warmed at 40° for 1 hr. to complete the reaction and was worked up

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[15] Raney Ni alloy used was Ni-Al (50:50).

[16] J. B. Menke: Rec. trav. chim., **44**, 141, 269 (1925).

[17] F. Beilstein, A. Kuhlberg: Ann., **155**, 13 (1870).

[18] A. H. Popkin, G. M. Perretta, R. Selig: J. Am. Chem. Soc., **66**, 833 (1944).

as usual. White crystalline biphenyl was obtained as the des-N product, which formed colorless scales of m.p. 70° from EtOH. Yield, 1.9 g. or 79%. Biphenyl thus obtained was identified by mixed fusion with an authentic sample synthesized according to the method of Hey, *et al.*[19] Trimethylamine was recovered as its hydrochloride; yield, 1.14 g. (75%).

ii) With 5% Na-Hg (Conventional Emde degadation): To the quaternary methosulfate (IV) (6.5 g.) in 50 cc. of water, 150 g. of 5% Na-Hg was added in small portions under stirring and heating on a boiling water bath. After 16 hrs.' heating, an oily substance that separated out was extracted with benzene and worked up as usual. The des-N compound, biphenyl, was obtained in a yield of 1.8 g. (58%). Recrystallized from hydr. EtOH to form colorless scales of m.p. 69~70°. The mixed melting point with an authentic biphenyl did not show any depression.

Besides Me_3N, a colorless basic oil of $b.p_{20}$ 150~156° was obtained, which weighed 0.43 g (11%). This gave a picrate of m.p. 192~193° (decomp.), forming yellow prisms from EtOH, whose analytical values and m.p. agreed well with those of the picrate of 2-dimethylaminobiphenyl. *Anal.* Calcd. for $C_{20}H_{18}O_7N_4$: C, 56.33; H, 4.26; N, 13.14. Found: C, 56.18; H, 4.29; N, 12.98.

Degradation of Cyclic Bases

Cleavage of 5,5,6-Trimethyl-5,6-dihydrophenanthridinium Chloride (V). Preparation of (V).

5,6-Dimethylphenanthridinium Methylsulfate—6-Methylphenanthridine[9] (9.0 g.) in 50 cc. of xylene was mixed with freshly purified Me_2SO_4 (5.9 g.) and the whole was refluxed for 30 mins., separating crystalline methylsulfate, which was purified from dehyd. MeOH, forming colorless needles of m.p. 236~238° (decomp.). Yield, 14.4 g. or 97%. *Anal.* Calcd. for $C_{16}H_{17}O_4NS$: C, 60.18; H, 5.37; N, 4.39. Found: C, 60.26; H, 5.05; N, 4.15.

5,6-Dimethyl-5,6-dihydrophenanthridine—The above-mentioned methylsulfate (14 g.) in 50% hydr. EtOH (100 cc.), acidified with 5 cc. of 10% HCl, was subjected to catalytic hydrogenation over Adams' Pt, absorbing about 1 molar portion of H_2 (1020 cc.) smoothly. The free base was isolated as usual, yielding 9.0 g. of an oil, which soon solidified. Yield, 98%. This crude base melted at 64~66° and was directly used in the next stage.

5,5,6-Trimethyl-5,6-dihydrophenanthridinium Iodide—i) The afore-mentioned base (1.0 g.) in 10 cc. of MeOH was heated with 10 g. of MeI in a sealed tube in a steam bath for 30 mins. After cool, the solvent was evaporated *in vacuo*, furnishing white crystals, which were purified from water, forming colorless scales of m.p. 137~138° (decomp.) in a yield of 1.62 g. or 96%. *Anal.* Calcd. for $C_{16}H_{17}NI$: C, 54.71; H, 5.17; N, 3.99. Found: C, 54.38; H, 5.29; N, 4.27.

ii) The foregoing base (7.0 g.) and Me_2SO_4 (5.0 g.) in 50 cc. of xylene were refluxed for 30 mins., separating a viscous syrup, which was collected in water. To this aqueous solution was added the excess of KI, precipitating white crystalline iodide, which was recrystallized from water, furnishing colorless scales of m.p. 137~138° (decomp.). Yield, 10.2 g. or 85%.

5,5,6-Trimethyl-5,6-dihydrophenanthridinium Chloride (V)—The foregoing iodide (10.0 g.) in 100 cc. of EtOH and AgCl, freshly prepared from 15 g. of $AgNO_3$, were thoroughly mixed and refluxed on a steam bath under stirring for 3 hrs. The precipitate was filtered off while hot and washed several times with hot EtOH. The filtrate and washings were combined and evaporated to leave 7.1 g. of light yellow syrup. Yield, 96%.

The First Cleavage of (V): 2-Ethyl-2′-dimethylaminobiphenyl (VI)—i) With Raney Ni alloy: To a mixture of 3.1 g. of the above-mentioned chloride (V) and 50 g. of 20% NaOH, 3.0 g. of powdered Raney Ni alloy was added in small portions under stirring and cooling to maintain the reaction temp. below 25.° After addition of all the alloy the whole was stirred at room temp. for ca. 2 hrs. to complete the reaction. The separated oily upper layer was extracted with ether and the ethereal solution was washed with satd. NaCl soln., dried over anhyd. Na_2SO_4, and evaporated. The oily residue distilled at 109~111°/1 mm.Hg, forming a colorless oil (VI) in a yield of 2.35 g. or 91.5%. This was soluble in 10% HCl but not in 3% AcOH and did not decolorize $KMnO_4$-acetone soln. The nitroso compound of (VI) gave a positive Liebermann color-test.

Picrate: Yellow prisms, m.p. 167~168° (decomp.) (from hydr. EtOH). *Anal.* Calcd. for $C_{22}H_{22}O_7N_4$: C, 58.14; H, 4.88; N, 12.33. Found: C, 58.00; H, 4.66; N, 12.01.

Methiodide: Colorless needless, m.p. 181~182° (decomp.) (from H_2O). *Anal.* Calcd. for $C_{17}H_{22}NI$: C, 55.59; H, 6.04; N, 3.91. Found: C, 55.62; H, 5.94; N, 3.63.

ii) With 5% Na-Hg (Conventional Emde degradation): The afore-mentioned quaternary chloride (V) (2.55 g.) in 50 cc. of water and 5% Na-Hg (22 g.) were heated for 8 hrs. on a boiling water bath. After cool, the oil that separated was collected in benzene and worked up as usual, furnishing a colorless oil of $b.p_{1.5}$ 113~115°, which behaved similarly as (VI) mentioned above. Yield, 1.8 g. or 82%.

Picrate: Yellow prisms, m.p. 167~168° (decomp.) (from hydr. EtOH).

Methiodide: Colorless needles, m.p. 181~182° (decomp.) (from H_2O). These derivatives were

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[19] D. H. Hey, W. S. M. Grieve: J. Chem. Soc., **1934**, 1798.

identified with those of (VI) obtained by the method described in i).

The Second Cleavage of (VI): 2-Ethylbiphenyl (VIII)—The foregoing (VI) (2.0 g.) was treated with Me_2SO_4 in boiling xylene to form the methyl methosulfate, which was a colorless viscous syrup, but gave the same crystalline methiodide as mentioned above. Yield, 2.5 g. or 82%. The quaternary salt thus obtained was subjected to the second degradation.

i) With Raney Ni alloy: The degradation of the foregoing methylsulfate (2.0 g.) with 1.0 g. of alloy in the presence of 20% NaOH (50 g.) proceeded under the same conditions as in the above cases with smooth evolution of Me_3N, which was characterized as its hydrochloride (m.p. 274∼276° (decomp.)), weighing 0.3 g. (55%). The reaction mixture was extracted with ether, which was washed, dried, and evaporated. The oily residue distilled at 135∼136°/17 mm. Hg forming a colorless oil (VIII) in a yield of 0.73 g. or 0.71%. (VIII) thus obtained gave a negative N-test and did not decolorize $KMnO_4$-acetone solution.

ii) With 5% Na-Hg (Conventional Emde degradation): The above-mentioned quaternary salt (1.6 g.) was subjected to the original Emde degradation with 5% Na-Hg (12 g.) and worked up as usual, furnishing 0.35 g. of (VIII) of b.p$_{10}$ 126∼130° (42%) with recovery of the starting base (VI) (0.12 g. or 12%), which was characterized as its picrate of m.p. 165∼167° (decomp.).

2-Biphenylcarboxylic Acid (IX)—With the purpose of proving the structure of (VIII), this (0.5 g.) was oxidized with $KMnO_4$-pyridine to form white crystalline acid. Recrystallization from hydr. EtOH furnished (IX) as colorless leaflets of m.p. 111∼112°, which was identified with an authentic 2-biphenylcarboxylic acid[11] by mixed fusion. Yield, 0.14 g. or 31%. *Anal.* Calcd. for $C_{13}H_{10}O_2$: C, 78.79; H, 5.05: Found: C, 78.45; H, 5.21.

From the mother liquor of (IX) there was obtained a minute amount of a crystalline substance, soluble in $NaHCO_3$ but not identical with (IX), but this was not investigated further.

Cleavage of 5,5-Dimethyl-5,6-dihydrophenanthridinium Methylsulfate (XII): Preparation of (XII):

5-Methyl-5,6-dihydrophenanthridine (X)—7.0 g. of phenanthridine methiodide[13] (m.p. 201∼202°) in 100 cc. of EtOH and AgCl, freshly prepared from $AgNO_3$ (15 g.), were mixed and refluxed on a steam bath under stirring for 2 hrs. The precipitate was filtered while hot and washed three times with 50-cc. portions of hot EtOH. The filtrate and washings were combined and concentrated to about 50 cc. The resultant solution was acidified with 10 cc. of 10% HCl and subjected to catalytic hydrogenation over Adams' Pt, absorbing about 1 molar portion of H_2 (510 cc.) smoothly. After filtering off the catalyst, the filtrate was diluted with 50 cc. of water and EtOH was distilled off *in vacuo*. The resultant acidic aq. solution was basified with 10% NaOH under effective cooling in an ice-salt bath and extracted with ether. The ethereal layer was dried over anhyd. K_2CO_3 and evaporated, leaving a light yellow oil (X) in a yield of 4.0 g. or 94%. All treatments were carried out in hydrogen atmosphere to exclude the air rigorously. (X) thus obtained was easily oxidized to 5-methylphenanthridone (XI)[13] and, therefore, subjected to the next step directly.

In nitrogen atmosphere, (X) soon solidified and was recrystallized from petr. ether, forming colorless needles of m.p. 46∼48°, which was identified by mixed fusion with an authentic sample of (X), synthesized according to the method of Karrer, *et al.*[13]

5,5-Dimethyl-5,6-dihydrophenanthridinium Methylsulfate (XII)—The foregoing dihydro base (X) (3.5 g.) and Me_2SO_4 (2.3 g.) in 50 cc. of benzene were refluxed for ca. 2 hrs. under the introduction of H_2, separating a viscous syrup, which was collected in 50 cc. of water. The aqueous layer was treated with decolorizing charcoal and evaporated *in vacuo* to dryness, leaving 5.2 g. of a light yellow viscous syrup (XII). Yield, 5.2 g. or 86.5%.

The First Cleavage of (XII): 2-Methyl-2′-dimethylaminobiphenyl (XIII)—Degradation of the above-mentioned methylsulfate (XII) (3.0 g.) with Raney Ni alloy (3.0 g.) in the medium of 20% NaOH (50 g.) proceeded under the same conditions as in above cases. In this case, however when the methylsulfate was dissolved in NaOH solution, there appeared a faint violet coloration followed by separation of a reddish purple syrupy substance, which disappeared with simultaneous discoloration on addition of the alloy. Toward the end of the reaction, there separated a colorless oil, which was extracted with benzene. The benzene layer was worked up as usual and 1.6 g. of an oil was obtained as a basic substance which was soluble in 10% HCl. The basic oil thus obtained distilled at 136∼137°/6 mm. Hg, forming a colorless oil (XIII) in a yield of 1.45 g. or 74%. This was soluble in 10% HCl but not in 3% AcOH. The nitroso compound of (XIII) gave a positive Libermann color-test.

Methiodide: Colorless needles, m.p. 179∼179.5° (from H_2O). *Anal.* Calcd. for $C_{16}H_{20}NI$: C, 54.39; H, 5.67; N, 3.96. Found: C, 54.30; H, 5.51; N, 3.71.

From the fraction insoluble in 10% HCl, 0.28 g. of a crystalline substance was obtained, which was insoluble in 10% HCl but soluble in 20% HCl. Recrystallized from hexane, it formed colorless needles (XI), m.p. 106∼108°, in a yield of 0.2 g. or 10%. This was identified by mixed melting point test with an authentic sample synthesized according to the method of Karrer, *et al.*[13]

The Second Cleavage of (XIII): 2-Methylbiphenyl (XIV)—The foregoing (XIII) (1.2 g.) was treated with Me_2SO_4 (0.8 g.) in boiling benzene to form the methyl methosulfate as a colorless viscous syrup which gave the same crystalline methiodide as mentioned above. Yield, 1.6 g. or 83%.

The quaternary salt thus obtained (1.08 g.) was subjected to the second degradation with 3.0 g. of Raney Ni alloy in the medium of 17% NaOH (60 g.). The reaction proceeded under the same conditions as in above cases, with a smooth evolution of Me_3N, which was recovered as its hydrochloride (m.p. 271~274° (decomp.)), weighing 0.15 g. (49%). The reaction mixture was extracted with ether, which was worked up as usual to furnish an oily des-N product. The oily substance distilled at 150~153°/33 mm. Hg, forming a colorless oil (XIV) in a yield of 0.38 g. or 69%. (XIV) thus obtained gave a negative N-test.

2-Biphenylcarboxylic Acid (IX)—For the characterization of (XIV), 0.35 g. of (XIV) obtained as above was oxidized with $KMnO_4$ according to the method of Jacobson[20] to form white crystals. Recrystallization from hydr. EtOH furnished colorless leaflets (IX) of m.p. 110~112° in a yield of 0.3 g. or 73%. This was identified with an authentic specimen[11] by mixed fusion.

Summary

A modified Emde degradation, in which a combination of Raney nickel alloy and sodium hydroxide solution was used as the reduction agent in place of sodium amalgam in the original Emde reaction, was applied to four open-chain quaternary salts (I to IV) to give the corresponding des-N products and trimethylamine in a good yield as summarized in Table I. Degradation of cyclic bases, such as phenanthridine and its 6-methyl derivative, by this modified method also proceeded smoothly under the same conditions as above to form the corresponding des-N compounds (VIII and XIV) via dihydromethine bases (VI and XIII). So far as these experiments were concerned, the cleavage was effected usually with a better yield of the products and under milder working conditions than those of the original method.

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[20] P. Jacobson: Ber., **28**, 2552 (1895).