Summer 6-28-1951

Derivatives of M-Xylene

Henry J. Muller

MULLER — DERIVATIVES OF m-XYLENE

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By

Henry J. Muller

A Thesis

In partial fulfillment of the

Requirements for the Degree of

Master of Science in Chemistry

The University of New Mexico
1951

This thesis, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

E. H. Castetter
DEAN

6/28/51
DATE

DERIVATIVES OF M-XYLENE

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ACKNOWLEDGMENTS

For suggesting the original problem and for encouragement given, the writer is indebted to Dr. J. L. Riebsomer.

The sample of m-xylene was obtained from Pan American Refining Corporation, Texas City, Texas, while the N-(2-aminoisobutyl)-isopropylamine was given by Commercial Solvents Corporation, Terre Haute, Indiana.

Mr. Jules Adelfang furnished the sample of pure m-toluic acid.

The carbon and hydrogen analyses on p. 31 were done by Eli Lilly and Company, Indianapolis, Indiana.

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CHAPTER I

INTRODUCTION

Since m-xylene of 95-98% purity has recently become available from petroleum, this is an appropriate time to prepare and examine its derivatives. Isophthalic and m-toluic acids can be prepared from the hydrocarbon. The purpose of this work was to prepare imidazolines from these acids.

As the information on many of the compounds discussed in the review of the literature was found to be extensive, representative preparative reactions are mentioned rather than a complete survey of the references available. Particularly in the case of the 2-imidazolines, the writer has made no attempt to cover the literature in a comprehensive manner since Pachter,[1] Ferm,[2] and Shapira,[3] have gone into it quite thoroughly.

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[1] I. Pachter, Unpublished Master's Thesis, University of New Mexico, Albuquerque, 1949.

[2] R. Ferm, Unpublished Doctor's Thesis, ibid., 1950.

[3] J. Shapira, Unpublished Master's Thesis, ibid., 1950.

CHAPTER I

INTRODUCTION

Since n-xylene and [illegible] have recently become available from petroleum, this is an appropriate time to prepare and examine the derivatives. Isophthalic and terephthalic acids can be prepared from the hydrocarbons. The purpose of this work was to prepare hydroxylated [illegible] acids.

As the information on many of the compounds discussed in the review of the literature was found to be extensive, representative preparative reactions are described rather than a complete survey of the field been available. Particularly in the case of the 3-hydroxylates, the writer has made no attempt to cover the literature in a comprehensive manner since Fischer,[1] Fern,[2] and Shapiro,[3] have done into it quite thoroughly.

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[1] I. Fischer, Unpublished Master's Thesis, University of New Mexico, Albuquerque, 1952.

[2] R. Fern, Unpublished Doctor's Thesis, ibid., 1950.

[3] L. Shapiro, Unpublished Master's Thesis, ibid., 1950.

CHAPTER II

REVIEW OF THE LITERATURE

Part 1

Cahours[1] discovered xylene in 1850 in crude wood alcohol; however, this xylene was later shown to be a mixture of o-, m-, and p-isomers rather than a pure compound.[2] Five years later Church showed that xylene was present in coal tar,[3] and since then it has become one of the main sources of this hydrocarbon. The separation of a mixture of xylenes to give pure m-xylene is discussed on pp. 4-6.

A. m-Xylene.

Probably the first synthesis of m-xylene was by Fittig and Velguth[4] in 1868. They found that upon heating a mixture of lime and 3,5-dimethylbenzoic acid, pure

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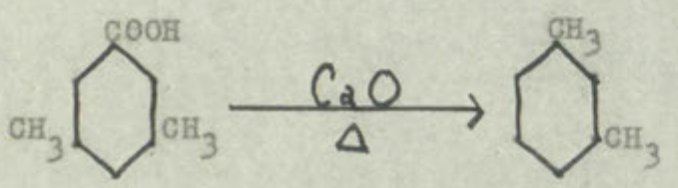
[1] Compt. rend. l'acad. agr. France, 30, 319; Ann., 74, 168 comment 1; 76, 286; Jahresbericht über die Fortschritte der Chemie, 1850, 492: cited by Beilstein, 5, 360 (1922).

[2] R. Fittig, Ann., 153, 265 (1870).

[3] J. prakt. Chem., [1] 65, 383; Jahresbericht über die Fortschritte der Chemie, 1855, 634: cited by Beilstein, 5, 360 (1922).

[4] R. Fittig and J. Velguth, Ann., 148, 2 (1868).

m-xylene resulted.



Later, Fittig and Bieber[5] oxidized 1,3,5-trimethylbenzene with dilute nitric acid to 2,4-dimethylbenzoic acid, and by the same reaction with lime were able to convert this to m-xylene. Since this synthesis by Fittig and co-workers, m-xylene has been obtained by many other methods. Not all of these methods have resulted in yields[6] to be worthy of discussing.

Anhydrous aluminum chloride has been used to bring about the rearrangement of aromatic hydrocarbons to form m-xylene. When o- or p-xylene is heated with this chloride at 100° for six hours while passing in hydrogen chloride gas, the aromatic hydrocarbon rearranged to give m-xylene.[7] Aluminum chloride has been used in the Friedel-Crafts synthesis of m-xylene from toluene and methyl chloride[8] or dimethyl sulfate.[9] With aluminum chloride, 1,3,4-trimethyl-

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[5] R. Fittig and P. Bieber, Ann., 156, 231-2 (1870).

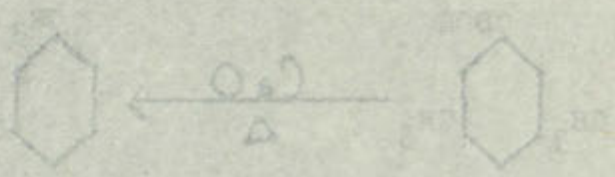
[6] E. Wroblewsky, Ann., 192, 200 (1878).

[7] R. Heise and A. Töhl, Ann., 270, 168, 171 (1892).

[8] E. Ador and A. Rilliet, Ber., 11, 1627, 1630 (1878).

[9] A. Shamshurin, Trudy Uzbek. Gosudarst. Univ., Sbornik Rabot Khim., 15, 26-32 (1939), cited by C.A., 35, 3981-82 (1941).

m-xylene results.



Later, Fields and Sleppy[5] reported 1,3,5-trimethylbenzene with dilute nitric acid to 3,5-dimethylbenzoic acid, and by the same reagent on this, they were able to convert this to m-xylene. Since this product is by Fields and co-workers, m-xylene has been obtained by many other methods. For all of these methods have resulted in yields too unsatisfactory dimensions.

Ambrosone already is suitable for use in the study about the rearrangement of aromatic hydrocarbons, m-xylene. Even o- or p-xylene in contact with this chloride at 100°C for six hours yields results in hydrogen chloride gas, the aromatic hydrocarbon rearrangement to give m-xylene. Aluminum chloride has been used in the industrial synthesis of m-xylene from toluene and methyl chloride or dimethyl sulfate.[6] With aluminum chloride, 1,3-dimethyl-

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5. H. Fields and J. Sleppy, J. Am. Chem. Soc., 80, 4-7 (1958).

6. E. Bradlow, Chem. Rev., 54, 67-112 (1954).

7. D. Nelles and J. Tuttle, J. Org. Chem., 22, 1-6 (1957).

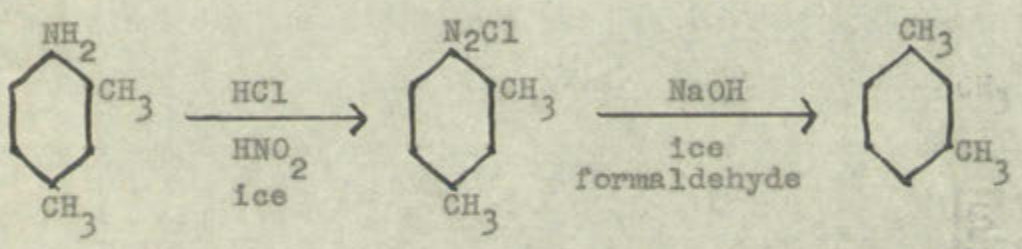
8. J. Ahrens and J. Tuttle, J. Org. Chem., 31, 1027-1030 (1966).

9. Shanmuganathan, Bull. Chem. Soc. Japan, 34, 1-4 (1961).

Rabot K. Ia., Ig, 20-21 (1950); Zhur. Obshchei Khim., 21, 1-4 (1951).

benzene splits off methyl chloride to give m-xylene along with other products such as toluene.[10]

Auwers[11] has prepared m-xylene by diazotization of 2,4-dimethylaniline and subsequent reduction. By using formaldehyde as the reducing agent, the yield was 80%.[13]



This hydrocarbon also has been prepared in 53% yield by adding an ether solution of methyl lithium to a solution of m-difluorobenzene.[13]

Various methods have been used for the separation of the xylene fraction of petroleum into the three isomers. Since this paper is concerned with m-xylene, the separation of the o- and p-xylenes is not discussed, although they are usually separated at the same time and by similar methods. In general, after fractional distillation has brought about a partial separation of the o-, m-, and p-isomers, the methods have involved one or a combination of the following

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[11] K. Auwers, Ann., 419, 108 (1919).

[12] R. Brewster and J. Poje, J. Am. Chem. Soc., 61, 2419 (1939).

[13] G. Wittig and W. Merkle, Ber., 75, 1500 (1942).

benzene splits off methyl chloride to give m-xylene along with other products such as toluene.[10]

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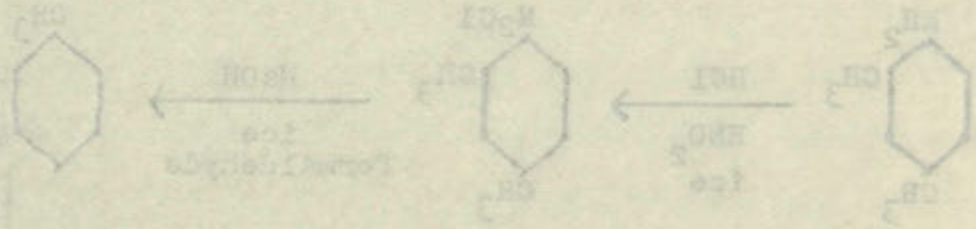

This hydrocarbon also has been prepared in 32% yield by adding an ether solution of methyl iodide to a solution of m-difluorobenzene.[13]

Various methods have been used for the separation of the xylene fraction of petroleum into the three isomers. Since this paper is concerned with m-xylene, the separation of the o- and p-xylenes is not discussed, although they are usually separated at the same time and by similar methods. In general, after fractional distillation has brought about a partial separation of the o-, m-, and p-isomers, the methods have involved one or a combination of the following

---

[11] M. Amore, Ann., 129, 106 (1919).

[12] R. Brunsum and J. Tong, J. Am. Chem. Soc., 52, 2419 (1929).

[13] G. Wittig and F. Bergin, Ber., 67, 1506 (1934).

processes.

1) The m-xylene-rich fraction, cooled to a low temperature, deposits crystalline m-xylene which can be removed by filtration.[14]

2) Treatment of the xylene mixture with sulfuric acid preferentially forms m-xylene-sulfonic acid which can be purified by recrystallization. Treatment of the crude sulfonic acid directly with super-heated steam gives a slightly less pure m-xylene than is obtained from the pure acid.[15,16,17,18]

3) Successful separation has also been accomplished by adding mercuric acetate to the m-xylene fraction and heating to 140-160°. The acetoxymercuro-m-xylene is separated from p-xylene, which does not react with mercuric acetate, and hydrolyzed with dilute hydrochloric acid to m-xylene.[19]

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[14] H. Spannagel and E. Tschunkur, Ger. 567,331 (1927), cited by C.A., 27, 1366 (1933).

[15] A. Nakatsuchi, J. Soc. Chem. Ind., Japan 32, Suppl. binding, 333-5 (1929), cited by C.A., 24, 4768 (1930).

[16] P. Lepers, U.S. 1,311,848, cited by C.A., 13, 2537 (1919).

[17] T. Patterson, A. McMillan, R. Somerville, J. Chem. Soc., 125, 2488-89 (1924).

[18] L. Beach and C. Morrell, U.S. 2,519,336 (1950), cited by C.A., 45, 649 (1951).

[19] L. Beach and J. Stewart, U.S. 2,506,289 (1950), Cited by C.A., 44, 6434 (1950).

procedure.

1) The m-xylene-rich fraction, cooled to a low temperature, deposits crystalline m-xylene which can be removed by filtration.[14]

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3) Successful separation has also been accomplished by adding mercuric acetate to the m-xylene fraction and heating to 140-150°. The mercuracetate-m-xylene is separated from p-xylene, which does not react with mercuric acetate, and hydrolyzed with dilute hydrochloric acid to m-xylene.[19]

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[14] H. Spencer and R. Fosbinder, Ind. Eng. Chem., 27, 1327 (1935), cited by C.A., 29, 3636 (1935).

[15] A. Ferrarsoni, J. Soc. Chem. Ind., Japan 32, Suppl. binding, 313-5 (1929), cited by C.A., 24, 4108 (1930).

[16] Z. Lupera, U.S. 1,911,865, cited by C.A., 28, 2577 (1934).

[17] T. Fahlgren, A. Wallin, H. Cassarille, J. Am. Chem. Soc., 72, 2488-89 (1950).

[18] L. Beach and G. Gerrish, U.S. 2,497,194 (1950), cited by C.A., 45, 6140 (1951).

[19] L. Beach and G. Stewart, U.S. 2,497,229 (1950), cited by C.A., 45, 6141 (1950).

4) The formation of an azeotrope with some added component such as methyl alcohol has also been used to separate the isomers.[20]

Several commercial methods isomerize a mixture of the three xylenes by using liquid hydrogen fluoride and boron trifluoride or liquid hydrogen fluoride alone. By making this a continuous process and recycling the recovered o- and p-xylenes, good yields of m-xylene may be obtained.[21,22]

B. Isophthalic acid.

For many years it had been known that oxidation of m-xylene with potassium dichromate in an acid solution gave isophthalic acid.[23,24] A better method for oxidation of m-xylene was developed in 1903. When m-xylene and water were heated at 95° for seventeen to ninteen hours, and potassium permanganate was slowly added to this mixture, a 95% yield of isophthalic acid was obtained.[25] By using violent agitation, the time was reduced to three to four

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[21] J. Kemp, U.S. 2,527,824 (1950), cited by C.A., 45, 2503 (1951).

[22] A. Lien and D. McCaulay, U.S. 2,528,892 (1950), cited by C.A., 45, 2977 (1951).

[23] R. Fittig and J. Velguth, Ann., 148, 11 (1868).

[24] R. Fittig and P. Bieber, Ann., 156, 235 (1870).

[25] F. Ullmann and J. Uzbachian, Ber., 36, 1798 (1903).

4) The formation of an azeotrope with zero alcohol component such as methyl alcohol has also been used to measure the isomers.[20]

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B. Isophthalic acid.

For many years it had been known that oxidation of m-xylene with potassium dichromate in an acid solution gave isophthalic acid.[23,24] A better method for oxidation of m-xylene was developed in 1953. When m-xylene and air were heated at 95° for seventeen hours in a solution of potassium permanganate and acetic acid, a 95% yield of isophthalic acid was obtained. By using cobalt catalyst, the time was reduced to [illegible]

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[21] J. Berg, U.S. 2,927,143 (1960); also [illegible] 52, 2903 (1958).

[22] J. Lien and G. Donnahay, U.S. 2,944,[illegible] (1960); cited by C.A., 52, 2917 (1958).

[23] A. Fridel and J. Crafts, Ann., 133, [illegible] (1865).

[24] R. Fittig and F. Ebert, Ann., 152, 257 (1870).

[25] G. Ullmann and [illegible] Dissertation, Bot., [illegible] 1,[illegible] (1901).

hours without changing the yield of acid.[26]

Isophthalic acid has also been obtained from m-xylene in 2-3% yield by electrochemical oxidation.[27]

The oxidation of m-toluic acid[28] and of certain aromatic hydrocarbons substituted in the 1,3- positions on the benzene ring leads to isophthalic acid.[29,30,31]

Baeyer and Villiger obtained isophthalic acid by first brominating m-xylene, then treating the α,α'-dibromo-m-xylene with an alcoholic solution of potassium acetate. Oxidation of the resulting m-xylene diacetate with alkaline potassium permanganate gave good yields of isophthalic acid which was purified by means of the barium salt.[32] In a similar manner, oxidation of α,α'-diethoxy-m-xylene by means of a cold chromic acid mixture, gave a quantitative yield of isophthalic acid.[33]

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[26] R. Fusco, and others, Gazz. chim. ital., 78, 511-16 (1948), cited by C.A., 43, 2190 (1949).

[27] F. Fichter and J. Meyer, Helv. Chim. Acta, 8, 74-83 (1925), cited by C.A., 19, 1251 (1925).

[28] W. Weith and A. Landolt, Ber., 8, 721 (1875).

[29] R. Fittig and H. Liepmann, Ann., 200, 11 (1880).

[30] W. Kelbe, Ann., 210, 19 (1881).

[31] O. Aschan, Ann., 387, 34-36 (1912).

[32] A. Baeyer and V. Villiger, Ann., 276, 257-58 (1893).

[33] J. Kipping, Ber., 21, 46-47 (1888).

bours without changing the yield of acid.[26]

Isophthalic acid was also obtained from 5-xylene in 2-3% yield by electrochemical oxidation.[27]

The oxidation of m-tolunitrile[28] and 2-methyl-m-xylene hydrocarbon, modified in the 2-position, the benzene ring lends to isophthalic acid.[29,30]

Bayer and Villiger obtained isophthalic acid by first oxidating m-xylene, then treating the m-xylene with an alcoholic solution of [illegible]. Oxidation of the resulting m-xylene dissolved with potassium permanganate gave good yields of isophthalic acid which was purified by recrystallization in a similar manner, oxidation of [illegible] in a solution of a cold concentrated acid mixture, gave a quantitative yield of isophthalic acid.[31]

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[26] R. Pinnow, and others, Ber., 51B, 1841-46 (1918).

[27] F. Fichter and G. Perret, Helv. Chim. Acta, 2, 711-83 (1925), cited by C.A., 19, 1291 (1925).

[28] W. Wahl and A. Lamotte, Ann., 5, 321 (1930).

[29] R. Fittig and W. Ebbinghaus, Ann., 216, 11 (1883).

[30] H. Kolbe, Ann., 210, 15 (1881).

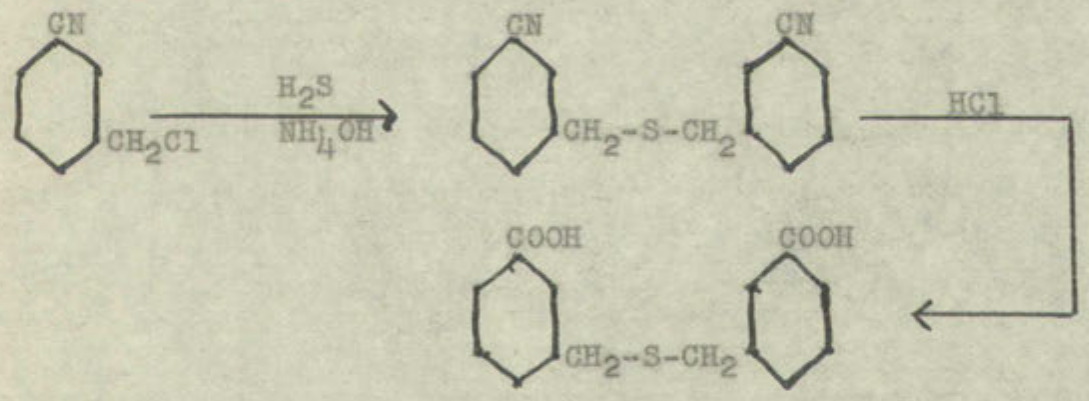
[31] O. Aschan, Ann., 3[illegible], 34-39 (1910).

[32] A. Bayer and V. Villiger, Ber., 33, [illegible] (1899).

[33] J. Higgins, Ber., 21, 4-6 (1888).

When a mixture of sodium formate and the potassium salt of m-sulfobenzoic acid was heated, Meyer[34] obtained isophthalic acid; however, the yield was only 18%.[35] The same product resulted when potassium m-bromobenzoate[36,37] or even potassium benzoate[38] was substituted for the potassium m-sulfobenzoate.

Bis-(3-carboxybenzyl) sulfide, prepared according to the equations below, has been oxidized almost quantitatively with nitric acid at 150° to isophthalic acid.[39]



Benzene undergoes a metallation reaction when treated with amylsodium to give a product, which upon the addition

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[34] V. Meyer, Ber., 3, 114-15 (1870).

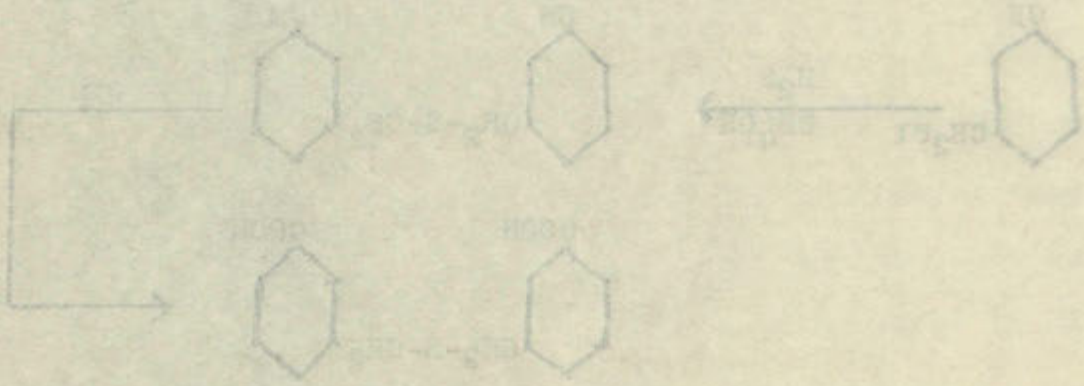
[35] V. Meyer, Ann., 156, 277 (1870).

[36] E. Ador and V. Meyer, Ber., 4, 260 (1871).

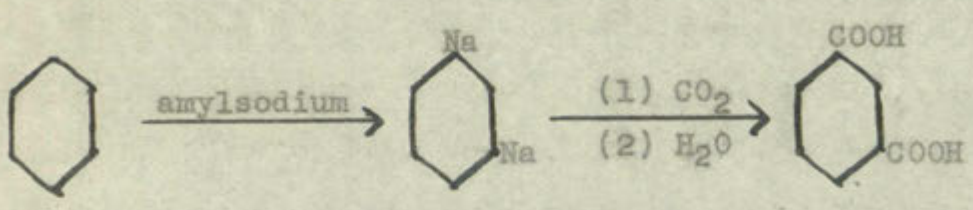
[37] E. Ador and V. Meyer, Ann., 159, 16 (1871).

[38] V. Richter, Ber., 6, 877 (1873).

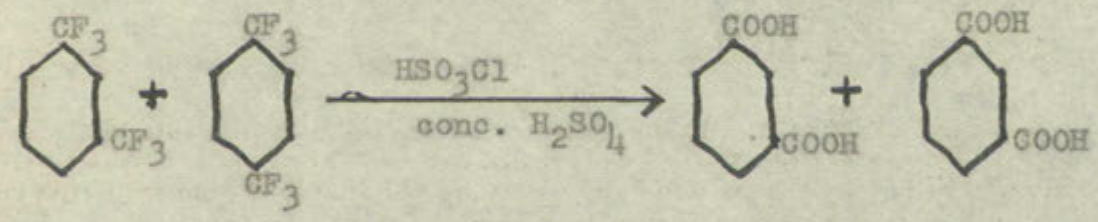
[39] F. Ehrlich, Ber., 34, 3373 (1901).



of carbon dioxide, gives a 51% yield of isophthalic acid.[40]



A commercially available mixture of 40% p- and 60% m-di-trifluoromethyl-benzene has been hydrolyzed to the terephthalic and isophthalic acids as indicated in the equation:



The mixture of acids was then separated by means of the barium salts. The barium salt of isophthalic acid is soluble in water, whereas that of terephthalic acid is not. The yields of acids were 55.5% and 39% respectively.[41]

C. Dimethyl isophthalate.

In the past, dimethyl isophthalate has been made from

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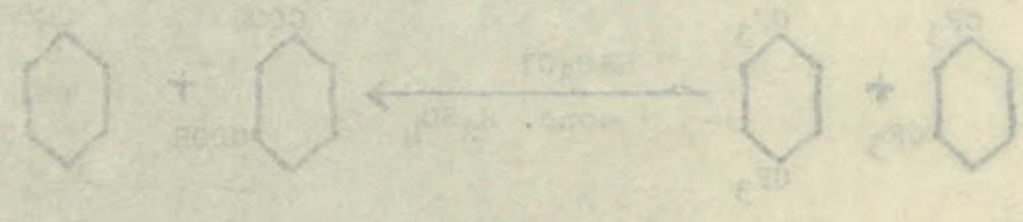
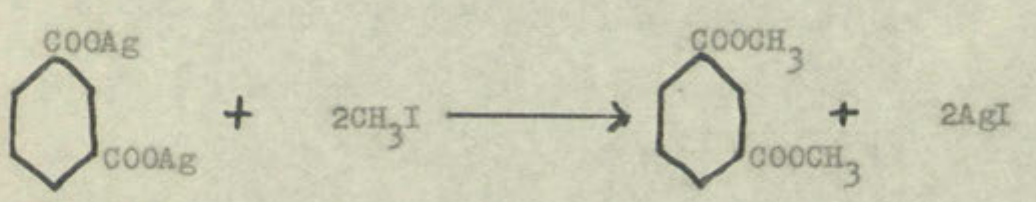
[40] A. Morton, E. Little, Jr., W. Strong, Jr., J. Am. Chem. Soc., 65, 1345 (1943).

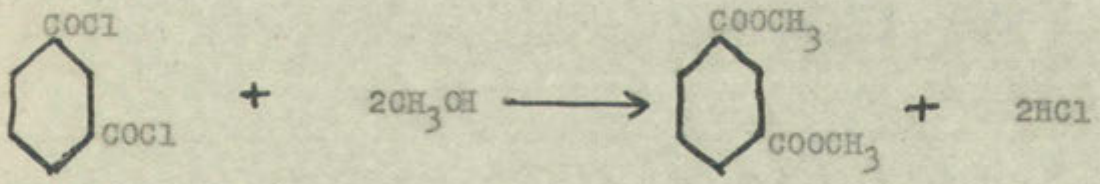
[41] P. Scheurer and Le Fave, J. Am. Chem. Soc., 72, 3308 (1950).



the reaction of the silver salt of isophthalic acid with methyl iodide.[42,43,44] Melting points of 65°[44] and 64-65°[43] were reported in the literature for the ester prepared in this manner.



Aschan[45] prepared the ester by the action of isophthaloyl chloride on methanol and reported the same melting point as Weith and Landolt;[43] however, melting points of 66-67°[46] and 67-68°[47] were reported in the literature for other preparations of dimethyl isophthalate by this same method.



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[42] E. Ador and V. Meyer, Ann., 159, 18 (1871).

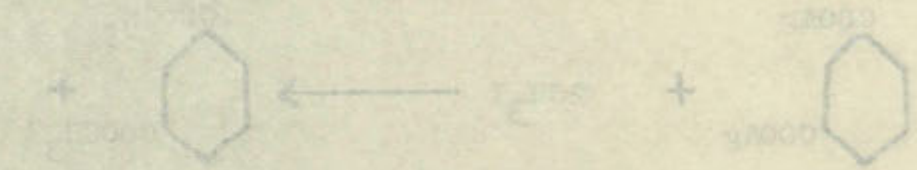
[43] W. Weith and A. Landolt, Ber., 8, 722 (1875).

[44] W. Kelbe, Ann., 210, 21 (1881).

[45] O. Aschan, Ann., 387, 34-36 (1912).

[46] O. Stark and O. Garben, Ber., 46, 663 (1913).

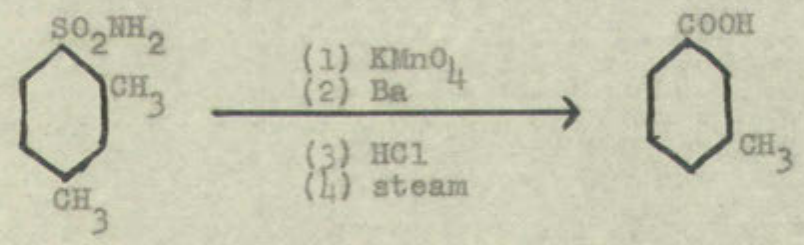
[47] A. Baeyer, Ber., 31, 1404 (1898).



D. m-Toluic acid.

Ahrens, the first to prepare m-toluic acid, did so by the oxidation of bromoxylene (b.p. 200-208°) in a potassium dichromate-dilute sulfuric acid solution. From this reaction, bromotoluic acid (m.p. 205-206°) was obtained and this, upon reduction with sodium amalgam, gave the desired acid.[48] This compound has been prepared in a similar manner by Boettinger and Ramsay.[49]

The oxidation of various compounds has given m-toluic acid. For example:[50]



m-Xylene is oxidized to m-toluic acid by refluxing with dilute nitric acid,[51] by heating with nitric acid in a closed tube at 130-150° for one to two days,[52] and even

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[48] W. Ahrens, Zeitschrift für Chemie, 1869, 106, cited by C. Boettinger and W. Ramsay, Ann., 168, 253 (1874).

[49] C. Boettinger and W. Ramsay, Ann., 168, 257-58 (1874).

[50] O. Jacobsen, Ber., 14, 2349 (1881).

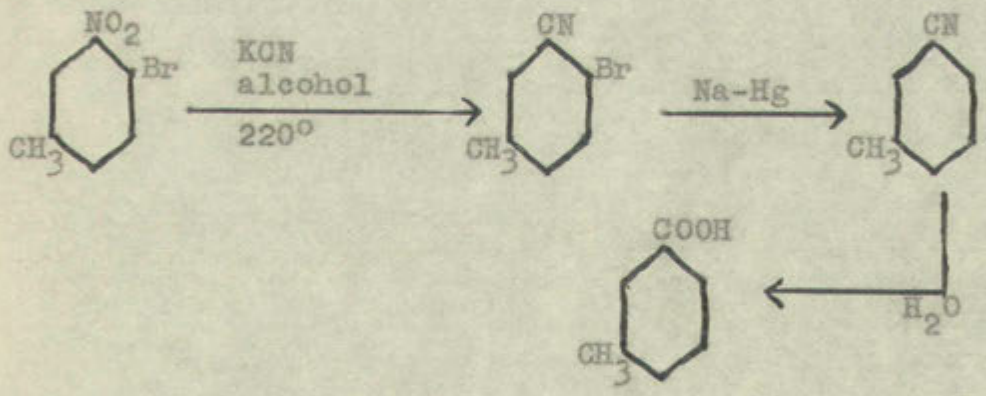
[51] Reuter, Ber., 17, 2028, cited by Beilstein, 9, 475 (1926).

[52] A. Brückner, Ber., 9, 406 (1876).

by exposing a flask containing water and m-xylene in the presence of air to light for a period of seven months.[53]

An interesting method for producing the acid in 20% yield was devised by Emerson, Lucas, and Heimsch.[54] Oxygen was passed through a tube containing n-butyric acid as a solvent, m-xylene, and a catalyst consisting of cobalt hydrate or acetate, lead acetate, and manganese acetate. The temperature was maintained at 140-145°.

The acid has been obtained from 4-bromo-3-nitrotoluene as indicated in the following equations:[55]



Another method, diazotization of m-toluidine, followed by a Sandmeyer reaction to form the cyanide which

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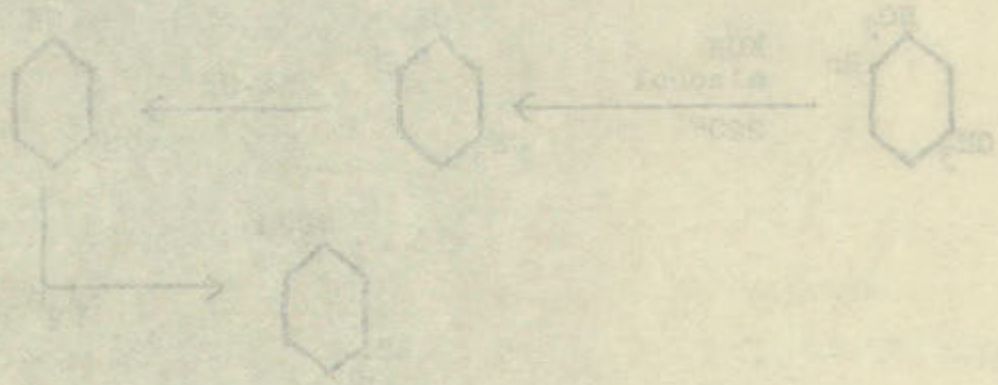
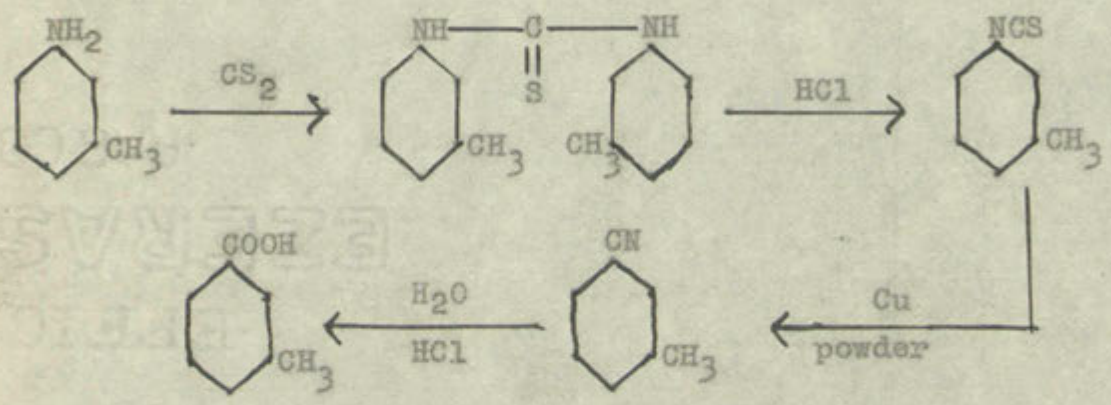
[53] G. Ciamician and P. Silber, Ber., 45, 40-41 (1912).

[54] W. Emerson, V. Lucas, and R. Heimsch, J. Am. Chem. Soc., 71, 1743 (1949).

[55] V. Richter, Ber., 5, 424-25 (1872).



upon hydrolysis gave m-toluic acid.[56,57] It has also been prepared from m-toluidine according to the equations indicated:[58]



Morton and co-workers devised a method for preparing m-toluic acid from 3-chlorotoluene.[59] The reaction was reported as rather dangerous without use of the proper equipment. Metallic sodium was added to a benzene solution of 3-chlorotoluene. This was followed by treatment with carbon dioxide under thirty-pounds pressure. The yield was 58%.[60] When the pressure was increased to four hundred pounds

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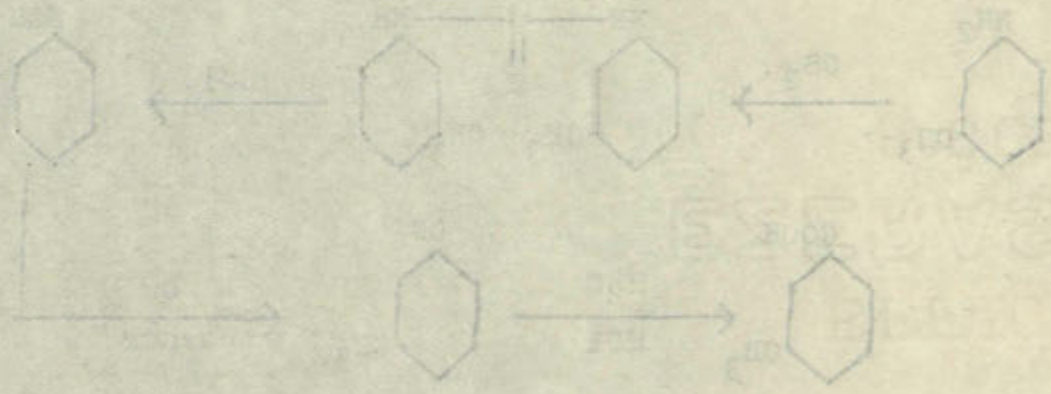
[56] K. Buchka and F. Schachtebeck, Ber., 22, 841-42 (1889).

[57] A. Tomisek, and others, J. Am. Chem. Soc., 68, 1588 (1946).

[58] W. Weith and A. Landolt, Ber., 8, 718-20 (1875).

[59] A. Morton, W. LeFevre, and I. Hechenbleikner, J. Am. Chem. Soc., 58, 755 (1936).

[60] A. Morton and J. Stevens, J. Am. Chem. Soc., 53, 4031-2 (1931).



at a temperature of 120°, the yield rose to 78%, but at pressures of five, six, ani seven hundred pounds, and at substantially the same temperature as before, the yields dropped to 22%, 0%, and slight per cent respectively.[59] From this it would appear that the pressure has a crucial influence on the amount of m-toluic acid to be obtained.[61]

Part 2

A. Imidazolines.

As mentioned in the introduction, the literature on imidazolines has already been extensively covered by Pachter,[62] Ferm,[63] and Shapira.[64] The following discussion will, therefore, be limited in scope.

Imidazolines substituted in the 2- position have been prepared by heating together a 1,2-diamine with an organic acid or its anhydride, acid halide, or ester in the

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[61] In a similar type of reaction, but without using pressure, Gilman reported a 65.4% yield. H. Gilman, W. Langham, and F. Moore, J. Am. Chem. Soc., 62, 2330 (1940).

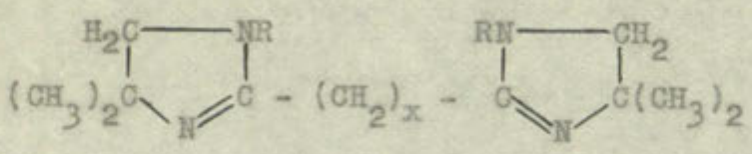
[62] I. Pachter, Unpublished Master's Thesis, University of New Mexico, Albuquerque, 1949.

[63] R. Ferm, Unpublished Doctor's Thesis, ibid., 1950.

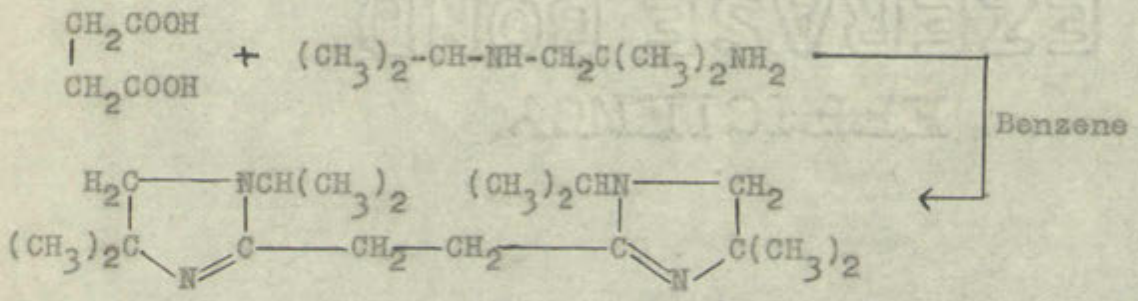
[64] J. Shapira, Unpublished Master's Thesis, ibid., 1950.

presence of some dehydrating agent.[65,66,67,68,69]

Bis-imidazolines of the following general structure



have been prepared by Riebsomer[70] by the reaction of a 1,2-diamine on an acid. For example:



These products were high-boiling liquids or solids.

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[65] H. Chitwood and E. Reid, J. Am. Chem. Soc., 57, 2424 (1935).

[66] A. Hill and S. Aspinall, J. Am. Chem. Soc., 61, 822 (1939).

[67] J. King and F. McMillan, J. Am. Chem. Soc., 68, 1774 (1946).

[68] L. Kyrides, and others, J. Org. Chem., 12, 577 (1947).

[69] J. Riebsomer, J. Am. Chem. Soc., 70, 1629 (1948).

[70] J. Riebsomer, J. Org. Chem., 15, 243 (1950).

CHAPTER III

DISCUSSION OF EXPERIMENTAL WORK

Part 1

A. m-Xylene and isophthalic acid.

The primary concern in the first section of the experimental work was to obtain pure isophthalic acid. Although satisfactory methods for preparing isophthalic acid from m-xylene by potassium permanganate oxidation had already been devised,[1,2] the present investigation attempted, without too much success, to simplify the procedure.

Previous workers[1,2] added potassium permanganate slowly to a neutral m-xylene-water solution; however, in this investigation the oxidizing agent was added all at once to a sodium hydroxide solution containing m-xylene. By this latter method a yield of isophthalic acid of 65-70% was realized. An insignificant amount of acid was recovered from the filtrate by evaporation.

When a burner was used for heating the permanganate solution serious bumping was experienced, however, this difficulty was finally overcome by injecting steam through

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[1] F. Ullmann and J. Uzbachian, Ber., 36, 1798 (1903).

[2] R. Fusco, and others, Gazz. chim. ital., 78, 511-16 (1948), cited by C.A., 43, 2190 (1949).

a glass tube reaching almost to the bottom of the reaction vessel.

In the opinion of the writer, the insolubility of m-xylene in the sodium hydroxide-potassium permanganate solution was the most important single factor determining the yield of isophthalic acid by the method outlined.

Isophthalic acid is reported in the literature to have the following melting points: 300°,[3] 347-348°,[4] 345-347°,[5] 330°, 312-314°,[6] 348°.[7] In view of these inconsistencies, it was not thought safe to accept the melting point of the acid as a criterion of purity.

Since the dimethyl ester of isophthalic acid has a sharp melting point, 67-68°,[8] it was decided to make the ester by the E. Fischer method and in this manner purify the acid. The yield of crude ester was 73.8% while that of the pure ester amounted to 36.7%, m.p. 68-70°. As mentioned

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[3] R. Shriner and R. Fuson, The Systematic Identification of Organic Compounds, p. 184.

[4] N. Lange, editor, Handbook of Chemistry, p. 453.

[5] I. Heilbron and H. Bunbury, editors, Dictionary of Organic Compounds, Vol. 2, p. 446.

[6] C. Hodgman, editor, Handbook of Chemistry and Physics, p. 849.

[7] S. McElvain, The Characterization of Organic Compounds, p. 446.

[8] A. Baeyer, Ber., 31, 1404 (1898).

on p. 26, the yield could be raised by repeated distillation and recrystallization of the material melting below 68-70°. The pure dimethyl isophthalate was saponified with sodium hydroxide and the resulting solution acidified with sulfuric acid to give what was assumed to be pure isophthalic acid. From this acid a bis-imidazoline was later prepared. (See page 19.)

Part 2

A. 1-Isopropyl-4,4-dimethyl-2-(3-tolyl)-2-imidazoline and 1,3-bis-(1-isopropyl-4,4-dimethyl-2-imidazolinyl-2)-benzene.

A mixture of m-toluic acid and N-(2-aminoisobutyl)-isopropylamine, when heated under a long helix-packed column with toluene present to remove the water formed in the reaction, gave the expected 1-isopropyl-4,4-dimethyl-2-(3-tolyl)-2-imidazoline. This latter product was obtained by treating the reaction mixture with base to remove unreacted m-toluic acid and to destroy any of the molecular complex reported by Riebsomer.[9] After extracting the imidazoline with ether, it was distilled at reduced pressure. Both a methiodide and a picrate were made of this compound.

To the isophthalic acid obtained from the dimethyl

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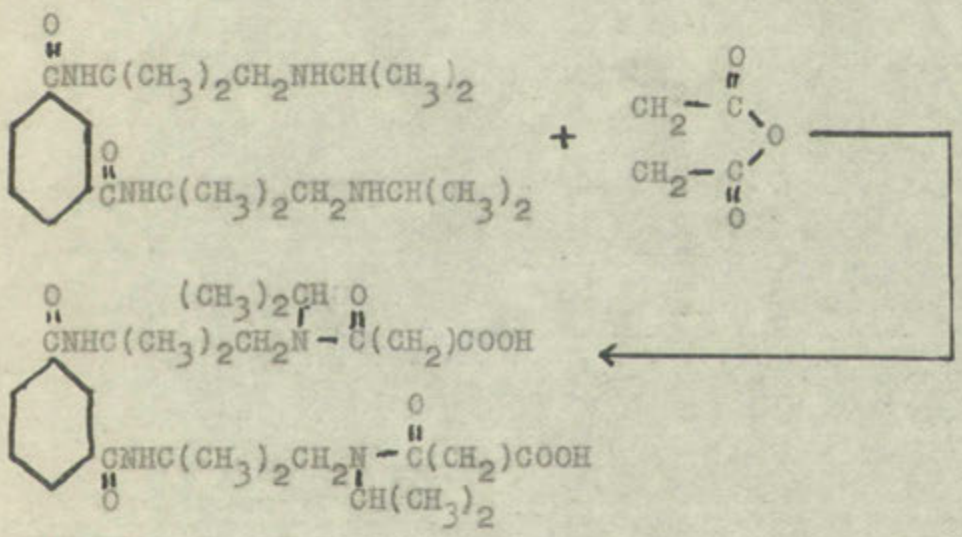
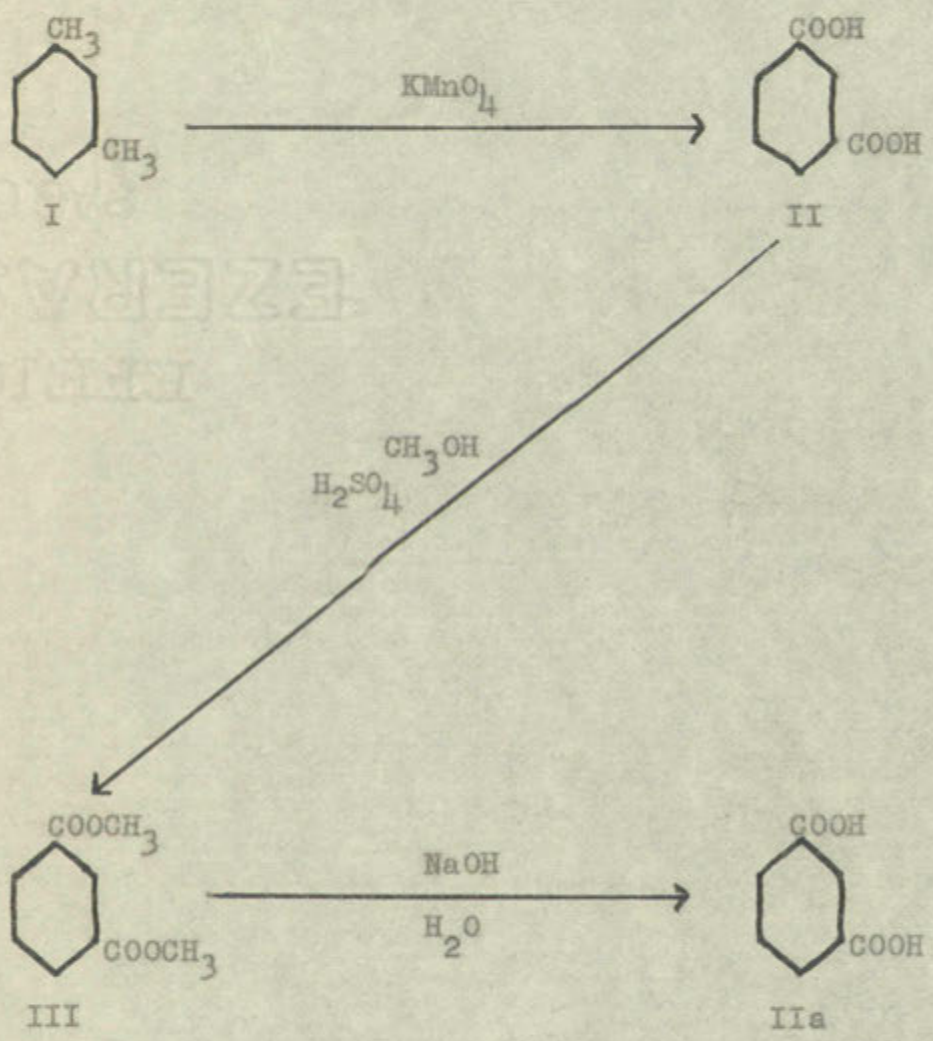
[9] J. Riebsomer, J. Am. Chem. Soc., 70, 1630 (1948).

ester was added the above 1,2-diamine and the mixture was then heated under the column as mentioned for the 1-isopropyl-4,4-dimethyl-2-(3-tolyl)-2-imidazoline. Before adding sodium hydroxide to this reaction mixture, succinic anhydride was introduced to react with any amides that might have been present. For example:

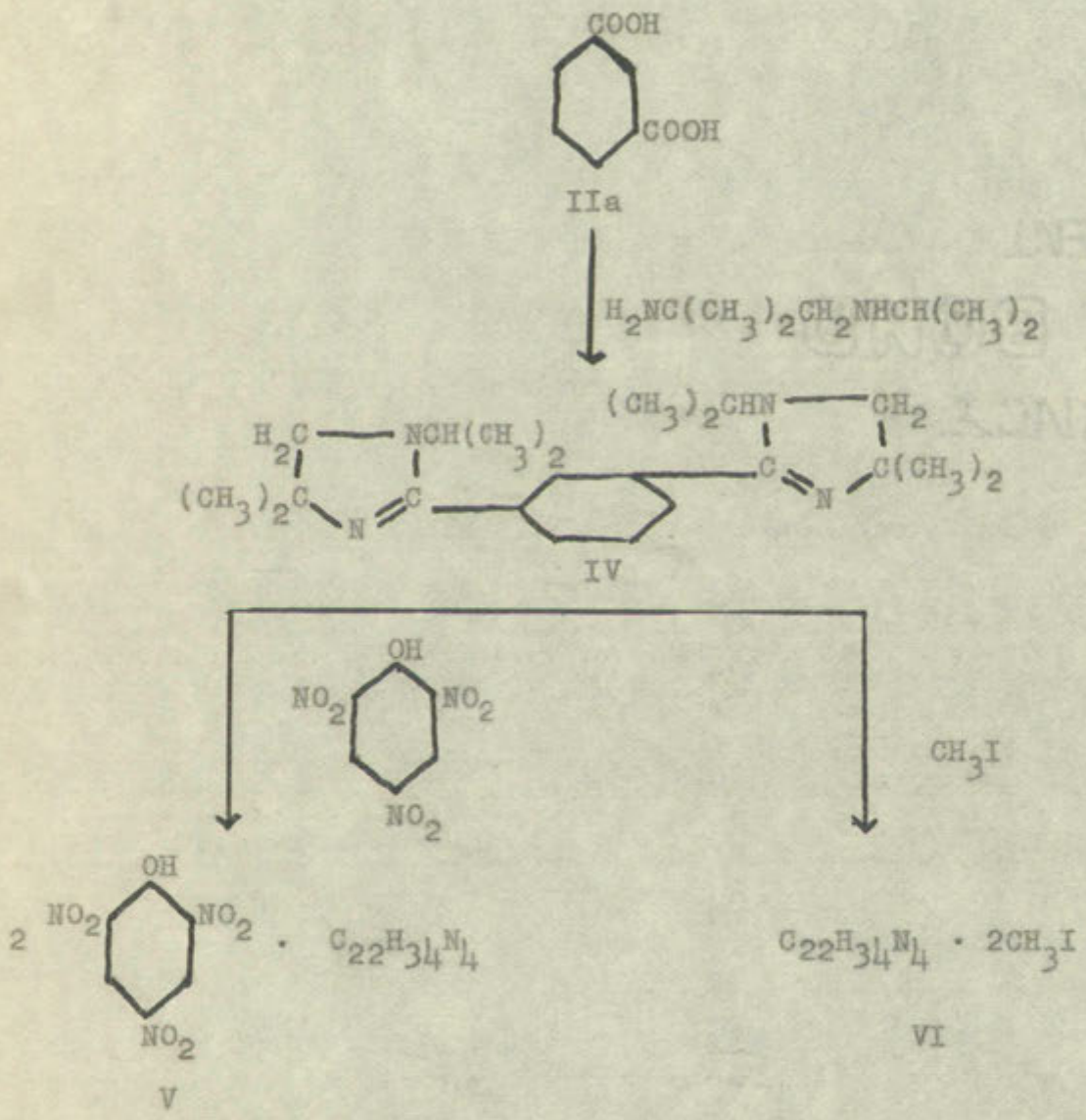


This mixture was then treated with an alkaline solution and the bis-imidazoline extracted with ether. When the succinic anhydride treatment was eliminated, the bis-imidazoline distilled over a range; but, a comparatively sharp fraction was obtained after the anhydride treatment.

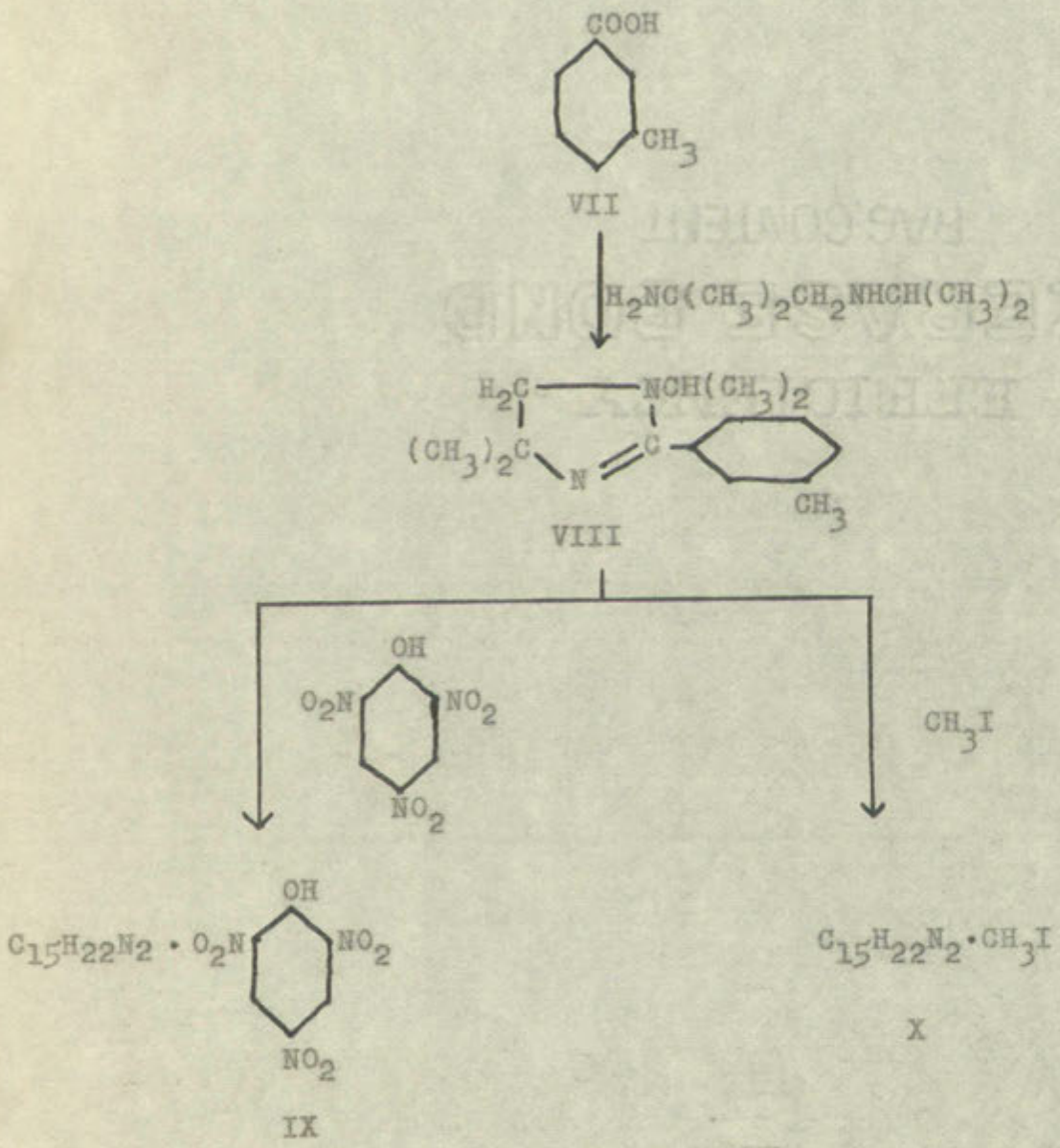
REACTIONS CARRIED OUT IN PART 1



REACTIONS CARRIED OUT IN PART 2



REACTIONS CARRIED OUT IN PART 2 (continued)



CHAPTER IV

EXPERIMENTAL WORK*

Part 1

The experimental procedure recorded below represents the most efficient method of preparation that was devised to secure isophthalic acid from m-xylene. Various modifications in experimental conditions were tried in order to increase the yield of isophthalic acid obtainable from the xylene.

A. Preparation of isophthalic acid II.

In a 5-l. round-bottomed flask were placed 50.0 g. (0.472 mole) of m-xylene,[1] 76.8 g. (1.92 moles) of dissolved sodium hydroxide, 151.7 g. (0.960 mole) of U.S.P. grade potassium permanganate, and 2-2.5 l. of water. Three 5-l. flasks were prepared in the above manner. Each was fitted with a rubber stopper, a water-cooled condenser, and a glass tube which reached to within an inch or two of the bottom of the vessel. Steam was then passed into the three flasks simultaneously through the glass tubes, and at the same time the flasks were gently heated with bunsen burners. The

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* All melting points are uncorrected.

[1] Pan American Refining Corp., Texas City, Texas

burners were turned off as soon as the mixtures were refluxing.. After the solutions had refluxed two and one-half hours, 25.0 g. (0.236 mole) of m-xylene were added to each through the condenser. At the end of four hours of further refluxing, a saturated solution of sodium bisulfite was slowly added to each flask through the condenser until all excess potassium permanganate had been destroyed. The steam was then stopped and the solution allowed to cool, after which the excess m-xylene was recovered.

The solutions were filtered through a large Büchner funnel into a 12-l. flask to free them of manganese dioxide. Concentrated sulfuric acid was slowly added to the filtrates until all of the white, flocculent isophthalic acid precipitated. The sulfuric acid dissolved the slight amount of manganese dioxide which was in the filtrate. When cold, the acid solutions were filtered by suction. The combined residues of isophthalic acid were washed free of inorganic salts and sulfuric acid by transferring them to a 1-l. beaker, adding 700-800 ml. of water, stirring, and filtering. This washing was repeated twice.

After warming in the air overnight, a total of 80.3 g. (66.0% yield based on potassium permanganate) of crude isophthalic acid were obtained.

B. Preparation of dimethyl isophthalate III.

To 121.3 g. (0.730 mole) of isophthalic acid (II) in a 1-l. round-bottomed flask were added 600 ml. of methanol. A reflux condenser was attached to the flask through which 70.0 ml. of concentrated sulfuric acid were slowly and carefully poured into the methanol solution and the mixture refluxed for one and one-half hours.

Upon cooling, the reaction mixture was poured into 3 l. of cold water. To the resulting solution, which contained a white precipitate, were added 400 ml. of benzene. The water-benzene solution was filtered free of the white precipitate. The filtered residue was washed with 100 ml. of benzene and the latter were added to the original 400 ml. to give a total of 500 ml. of benzene solution.

The precipitate was dissolved in 15% sodium hydroxide and this basic solution extracted with 100 ml. of benzene. This 100-ml. benzene layer was washed twice with 25-ml. portions of water and then combined with the washed 600-ml. benzene layer mentioned below.

The 500-ml. layer of benzene was separated from the water solution in a separatory funnel and the 3 liters of water extracted a second time with 100 ml. of benzene. The two benzene-ester layers were combined to give 600 ml. of benzene-ester solution. This 600-ml. layer was washed twice with 50 ml. of 15% sodium hydroxide solution and then washed

twice with 100-ml. portions of water.

Upon acidifying the combined sodium hydroxide solutions, 12.4 g. of air-dried crude isophthalic acid were recovered.

Without drying, the benzene-ester solution was distilled free of benzene and water at 630 mm. pressure, the last traces of benzene and water being removed with a water pump. A forerun amounting to 10.6 g. came over at 50-161° (26-27 mm.), followed by the main fraction, amounting to 104.6 g. (73.8% yield) of crude dimethyl isophthalate which distilled over at 161-169° (26-27 mm.). The main fraction had a melting point of 62-68°.

Recrystallization of the main fraction from petroleum ether gave 91.5 g. of crystals, m.p. 65-68°. A second recrystallization from petroleum ether of the 91.5 g. of product gave 51.9 g. (36.7% yield) of pure dimethyl isophthalate, m.p. 68-70°. (Lit. 67-68°).[2] The yield could, without doubt, be raised considerably by distillation and recrystallization of the subsequent crops which were 1-2° low in melting point.

C. Saponification of dimethyl isophthalate (III) to pure isophthalic acid (IIa).

To 29.1 g. (0.150 mole) of pure dimethyl isophthalate,

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[2] A. Baeyer, Ber., 31, 1404 (1898).

m.p. 68-70°, in a 1-l. round-bottomed flask were added 185 ml. of a 12% sodium hydroxide solution. A reflux condenser was attached to the flask and the contents heated for two hours. Upon cooling, the mixture was carefully acidified with concentrated sulfuric acid. During the addition of the acid it was necessary to dilute the mixture with 300 ml. of distilled water, since the quantity of isophthalic acid became so large that the reaction mixture virtually turned solid.

The isophthalic acid mixture was cooled, filtered by suction, and washed once by transferring the acid to a beaker, adding water, and filtering. After drying in the oven for two hours at 100-110°, 24.7 g. (99.2% yield) of pure isophthalic acid (IIa) was obtained.

Part 2

The technique employed by Riebsomer[3] for preparing imidazolines was used in the following work. In essence, this method consisted of using a long, helix-packed column equipped with a decanter still-head. Excess benzene (or toluene), poured into the decanter still-head, formed an azeotrope with the water coming from the reaction mixture. The water separated from the benzene in the decanter still-

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[3] J. Riebsomer, J. Am. Chem. Soc., 70, 1629 (1948).

head while the benzene returned to the column and reaction vessel.

A. Preparation of 1,3-bis-(1-isopropyl-4,4-dimethyl-2-imidazolinyl-2)-benzene.

To 24.7 g. (0.149 mole) of pure isophthalic acid in a 500-ml. round-bottomed flask were added 58.1 g. (0.447 mole) of N-(2-aminoisobutyl)-isopropyl-amine.[4] After the flask containing the above mixture was placed under the column, the temperature was raised from 55° to 106° during a one-half-hour period. At the end of this time 80 ml. of toluene were added at the decanter still-head, and the temperature was then increased to 113° to be maintained between 113-125° for eleven and one-fourth hours.

The second day the temperature was quickly raised to 110° and kept between 110-170° for seven hours. The next day the temperature was increased from 25° to 195° over a five-hour heating period after which it fluctuated between 180-205° for five hours and then held between 240-260° for three hours. Finally, the temperature was raised and kept between 270-280° for one-half hour. In sharp contrast to previous unrecorded experiments which resulted in questionable data, this reaction mixture showed little sign

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[4] Commercial Solvents Corporation, Terre Haute, Indiana.

of decomposition. A total of 12.4 ml. of water were obtained. Theoretically, approximately 11 ml. of water should have been formed.

In order to remove any amides which might be present in the reaction mixture, 60.0 g. (0.600 mole) of succinic anhydride were added to the cooled reaction flask. After removing the toluene-diamine mixture from the decanter still-head, the succinic anhydride mixture was heated under the column between 120-130° for one hour. The black-colored reaction mixture was cooled and treated with 440 ml. of 10% sodium hydroxide in small portions. In order to prevent possible rupture of the imidazoline ring, the basic solution was cooled from time to time. The tar-like product present on the bottom of the flask slowly dissolved in the sodium hydroxide and this cold solution was extracted with 200 ml. of diethyl ether. The ether-toluene layer was washed with 80 ml. of 10% sodium hydroxide, separated from the base, and dried overnight with solid potassium hydroxide.

The dried solution was filtered into a distillation flask and most of the ether and toluene distilled off at 630 mm. This was followed by application of the water pump to remove the last traces of solvent. Distillation in a 25-ml. Claisen flask of the remaining liquid at 2 mm. pressure gave 5.7 g. of a light-yellow colored forerun, b.p. 70-192°, and 25.3 g. (47.7% yield of crude material)

of a viscous orange-yellow colored main fraction, b.p. 192-205°. Redistillation of the 25.3 g. of main fraction at 2 mm. pressure gave 6.4 g. of a forerun, b.p. 160-194°, and 12.5 g. of a viscous light-yellow colored main fraction, b.p. 194-200°.

Analysis of the 12.5-g. fraction, b.p. 194-200°. Calculated, $C_{22}H_{34}N_4$: N, 15.81%. Found: N, 14.93%.

The 12.5-g. fraction, b.p. 194-200°, redistilled at 2 mm. pressure, gave a 3.5-g. fraction, b.p. 194-198°, plus a middle cut amounting to 4.0 g. (7.6% yield of pure material), b.p. 195-197°.

Analysis of middle cut. Calculated, $C_{22}H_{34}N_4$: N, 15.81%. Found: N, 15.16%.

B. Preparation of 1,3-bis-(1-isopropyl-4,4-dimethyl-2-imidazolinyl-2)-benzene, methiodide (VI).

To 1.0 g. (0.0016 mole) of the middle cut, b.p. 195-197°, in a 50-ml. Erlenmeyer flask was added sufficient methyl iodide to cover it. This mixture was gently warmed. When most of the methyl iodide had reacted, the above treatment was repeated. Freshly prepared absolute diethyl ether was added to the product and decanted in order to remove excess methyl iodide and unreacted (IV). The quaternary methiodide salt was dissolved in absolute ethanol. After standing overnight, a solid product was caked on the

bottom of the flask.

This cake was broken up, filtered, and washed with absolute ethanol. The solid, m.p. 329-330° decomp., was redissolved in dry ethanol to which a small amount of absolute diethyl ether was added. The recrystallized salt had the same melting point as before.

Analysis. Calculated, $C_{24}H_{40}N_4I_2$: N, 8.78%. Found: N, 8.51%.

C. Preparation of 1,3-bis-(1-isopropyl-4,4-dimethyl-2-imidazolinyl-2)-benzene, dipicrate (V).

To a 1.0-g. (0.0029-mole) sample of the middle cut, b.p. 195-197°, (IV) dissolved in 100-150 ml. of warm absolute ethanol, were added 1.4 g. (0.0061 mole) of picric acid dissolved in 75 ml. of warm absolute ethanol. Crystals, m.p. 231-233°, formed at once when the picric acid was added to the shaken (IV) solution. Three recrystallizations of these crystals from ethanol gave constant melting material, m.p. 237-239°.

Analysis.[5] Calculated, $C_{34}H_{40}N_{10}O_{14}$: C, 50.24%; H, 4.96%; N, 17.24%. Found: C, 50.26%; H, 5.11%; N, 16.72%.

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[5] The carbon and hydrogen analyses were performed by Eli Lilly and Company, Indianapolis, Indiana.

D. Preparation of 1-isopropyl-4,4-dimethyl-2-(3-tolyl)-2-imidazoline (VIII).

To 25.0 g. (0.184 mole) of m-toluic acid, m.p. 109-110°,[6] in a 500-ml. reaction vessel were added 23.0 g. (0.184 mole) of N-(2-aminoisobutyl)-isopropylamine. The reaction flask was placed under the column and 100 ml. of toluene were added at the decanter still-head. The reaction temperature was slowly raised from 41° to 195° over six and three-fourths hours, then kept between 170-210° for a like period. However, since there was no noticeable evidence of any more water coming over when the temperature was raised to 232°, the heat was turned off.

A total of 6.4 ml. of water were caught in the decanter still-head. Theoretically, approximately 6.6 ml. of water should have been obtained.

After the reaction mixture cooled, 150 ml. of 10% sodium hydroxide and 100 ml. of diethyl ether were poured into the reaction flask. The ether-toluene layer was separated from the sodium hydroxide in a separatory funnel. The separated ether-toluene solution was washed with 75 ml. of 10% sodium hydroxide, filtered, and dried with solid potassium hydroxide.

The dried solution was filtered into a 125-ml. Claisen

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[6] Prepared by Jules Adelfang in 31% yield by the procedure in Organic Syntheses, 27, 84 for the o-isomer. The crude m-toluic acid was purified by distillation of the ethyl ester followed by saponification.

flask. The ether and toluene were distilled off at 629 mm. pressure, and then the last traces removed under reduced pressure. A fraction boiling from 38° to 120° (35 mm.), which was probably mostly N-(2-aminoisobutyl)-isopropylamine, was removed first. Then two fractions were distilled over at 3 mm. pressure: a small, colorless forerun, b.p. 80-120°, and 23.6 g. of a light-yellow main fraction, b.p. 123-134°.

The 23.6-g. fraction, b.p. 123-134°, was transferred to a 50-ml. Claisen flask and redistilled at 2-2.5 mm. This gave a fraction weighing 14.0 g., b.p. 123-128°, and also a middle cut of 7.0 g., b.p. 124-126°. The yield of these two combined fractions amounted to 21.0 g. (49.7% yield). Since the middle cut darkened upon standing in a desiccator for seven days before analysis, it was redistilled at 2-2.5 mm. A fraction, b.p. 118-125°, amounting to 2.6 g. and a middle cut, b.p. 122-124°, were obtained.

Analysis of middle cut of 3.1-g. fraction, b.p. 122-124° (2-2.5 mm.). Calculated, $C_{15}H_{22}N_2$: N, 12.16%; neutral equivalent, 230. Found: N, 11.81%; neutral equivalent, 229.

E. Preparation of 1-isopropyl-4,4-dimethyl-2-(3-tolyl)-2-imidazoline, methiodide (X).

To 1.0 g. (0.0043 mole) of the 14.0-g. fraction, b.p. 123-128°, in a 50-ml. Erlenmeyer flask, 1.3 g.

(0.0093 mole) of methyl iodide were added. A violent reaction took place at once with the formation of a solid. Five drops more of methyl iodide were added from a dropper, followed by the addition of 10 ml. of benzene. This mixture was allowed to set overnight after loosening the solid from the bottom of the Erlenmeyer. A. previous test on a small quantity of the methiodide quaternary salt had indicated that it was not hygroscopic.

After filtering the salt free of benzene, the product was recrystallized to a constant melting point, m.p. 189-191°, from an ethanol-ether solution.

Analysis. Calculated, $C_{16}H_{25}N_2I$: N, 7.53%. Found: N, 7.49%.

F. Preparation of 1-isopropyl-4,4-dimethyl-2-(3-tolyl)-2-imidazoline, picrate (IX).

Sufficient picric acid was dissolved in 10 ml. of absolute ethanol to make a saturated solution of picric acid. This solution was poured into 10 ml. of absolute ethanol containing 1.0 g. (0.0043 mole) of the 14.0-g. fraction, b.p. 123-128°, and the mixture warmed for a few minutes. All attempts to induce crystal formation were unsuccessful; hence, about 10 ml. of ethanol were evaporated off. The crystals which formed were recrystallized from absolute ethanol to a constant melting point, m.p.

130-132°.

Analysis. Calculated, $C_{21}H_{25}N_5O_7$: N, 15.24%. Found: N, 14.78%.

CHAPTER V

SUMMARY AND CONCLUSIONS

Isophthalic acid was made by oxidation of m-xylene with alkaline potassium permanganate. The acid from this reaction was then converted by the E. Fischer method to the dimethyl ester which was purified by recrystallization and then saponified with sodium hydroxide in order to obtain pure isophthalic acid. This pure acid and N-(2-aminoisobutyl)-isopropylamine were used to prepare 1,3-bis-(1-isopropyl-4,4-dimethyl-2-imidazolinyl-2)-benzene. The yield was 48% of crude imidazoline.

A second imidazoline was produced in 49% yield by the reaction of N-(2-aminoisobutyl)-isopropyl-amine and m-toluic acid.

Picrates and methiodides were prepared from both imidazolines.

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