tion bromonitromethane reacts like an aliphatic halide, according to the Friedel and Crafts synthesis, the group $—CH_2.NO_2$ enters the nucleus and hydrogen bromide is freed. The ease of decomposition of phenylnitromethane, especially in the presence of strong acid, explains the formation of the aldehyde and acid. In various runs the total percentages of this type of compound are 19–45%. The second type of reaction is shown in the formation of bromobenzene. In this case the bromonitromethane acts as a brominating agent, the bromine atom entering the aromatic nucleus. Bromobenzene is formed in yields of 12–30%. The products formed in the two types of reaction account for from 40 to 80% of the total bromonitromethane used.

3. Bromonitromethane reacts with bromobenzene, chlorobenzene and anisole in the same way to give two types of compounds. The group enters in the *para* position in each case, the yields accounting for approximately 40–85% of the material used.

4. The two types of reaction are interpreted on the assumption that bromonitromethane in this reaction exists as an equilibrium mixture of two electromeric forms: $\overset{+}{\mathrm{Br}}.\overset{-}{\mathrm{C}}\mathrm{H_2.NO_2} \leftrightarrows \overset{-}{\mathrm{Br}}.\overset{+}{\mathrm{C}}\mathrm{H_2.NO_2}$, one in which the bromine atom is negatively charged and therefore reacts as an alkyl halide in a Friedel and Crafts synthesis, and a second form in which the bromine atom is positively charged and therefore capable of brominating the aromatic nucleus.

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[Contribution from the Chemical Laboratory of the University of Illinois]

THE STRUCTURE OF DEHYDRO-ACETIC ACID

By C. F. Rassweiler[1] with Roger Adams

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Dehydro-acetic acid is easily formed by the action of dehydrating agents on aceto-acetic ester or by acetic anhydride on acetone dicarboxylic acid and is readily converted by various reagents into a large variety of compounds such as diacetyl-acetone, pyridines, dimethylpyrone, etc. It has proved to be a most useful substance in organic chemistry.

Its structure has been a subject of controversy since its discovery in 1866.[2] Omitting a discussion of the earlier proposed formulas which have been readily disproved,[3] a brief review of the two alternative formulas which will explain all of the reactions of this substance may be

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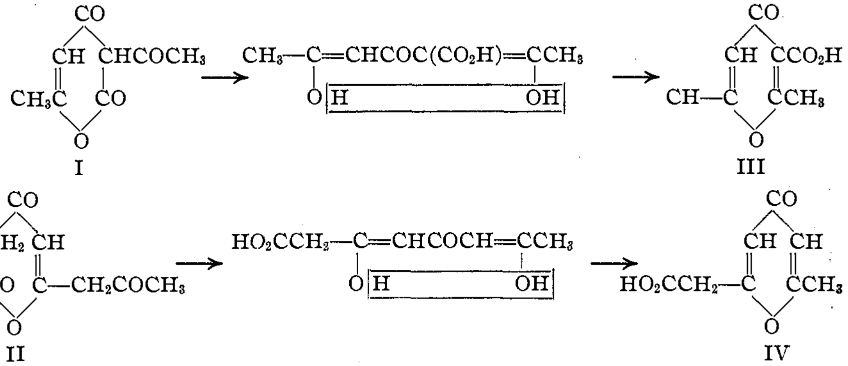
[1] This communication is an abstract of a portion of a thesis submitted by C. F. Rassweiler in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Geuther, *Chem. Zentr.*, **11**, 801 (1866); *Z. Chem.*, **2**, 8 (1866).

[3] (a) Feist, *Ann.*, **257**, 253 (1890). (b) Hale, This Journal, **33**, 1119 (1911).

given. Feist[3a] has proposed Formula I (or one of its tautomeric forms); Collie,[4] Formula II (or one of its tautomeric forms).



I III II IV

Numerous investigators[5] have presented evidence for one or the other of these two formulas but in no case has a direct proof of either formula been made. In general, the indications point toward the Feist formula as being the correct one, and this formula has been commonly accepted. The object of this investigation was to prove, without question, the constitution of dehydro-acetic acid.

One of the most important reactions of dehydro-acetic acid is its conversion by 85% sulfuric acid or by preparation of a dichloride and treatment with sulfuric acid, into an isomeric compound containing a carboxyl group[6] which, according to Feist's views, must have Formula III, and according to Collie's, Formula IV.

The simplest way of determining the structure of dehydro-acetic acid would be to determine the structure of this secondary product. Previous investigators have attempted this without success—in particular may be mentioned the attempted synthesis of this acid by a process which would leave no doubt as to its structure. Feist hydrolyzed dimethyl-γ-pyrone dicarboxylic ester, V, a compound whose formula was well established. It was impossible, however, to limit the reaction to one of the ester groups. In every case, both ester groups were saponified and carbon dioxide split out simultaneously with the formation of dimethyl γ-pyrone,[7] VI.

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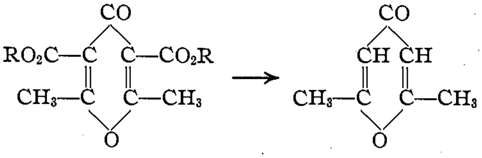
[4] (a) Collie, *J. Chem. Soc.*, **59**, 179 (1891). In the following papers, the known reactions of dehydro-acetic acid, and a detailed discussion of the two possible formulas for it, are given. Ref. 3 a. Ref. 4 a. (b) Feist, *Ber.*, **25**, 340 (1892). (c) Collie, *J. Chem. Soc.*, **59**, 617 (1891); (d) **63**, 122, 329 (1893); (e) **67**, 401 (1895); (f) **77**, 971 (1900); (g) **91**, 787 (1907). (h) v. Pechmann, *Ber.*, **24**, 4098 (1891); (i) *Ann.*, **273**, 186 (1893).

[5] Ref. 3 b. Dieckmann and Breest, *Ber.*, **37**, 3387 (1904). Stollé, *Ber.*, **38**, 3026 (1905). Bülow, *Ber.*, **41**, 4161 (1908). Benary, *Ber.*, **43**, 1070 (1910).

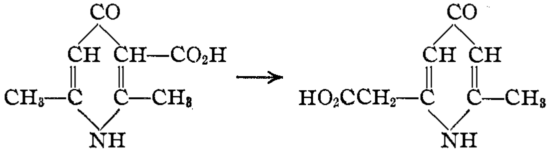
[6] (a) Ref. 3 a, p. 286. (b) Ref. 4 g.

[7] Ref. 3 a, p. 282.



V VI

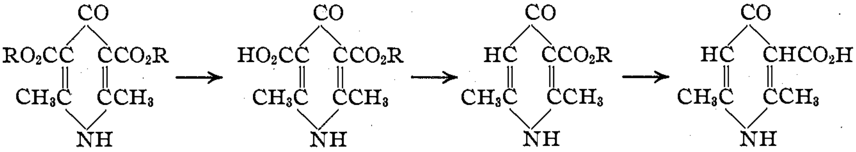
When the acid formed by the rearrangement of dehydro-acetic acid is treated with ammonia,[8] it is readily converted into a compound which contains an imine (=NH) group in place of the oxygen of the ring and may be represented by Formula VII or VIII, depending upon the constitution of the original acid.



VII VIII

A determination of the structure of this nitrogen compound would, therefore, give a simple proof for the structure of the oxygen acid from which it was derived and, therefore, of dehydro-acetic acid.

By the condensation of copper ethylaceto-acetate with phosgene and treatment of the product with ammonia,[9] there is produced a γ-lutidone dicarboxylic ester, IX, the formula of which is unquestioned. Whereas the corresponding pyrone compound cannot be partially saponified without complete decomposition to dimethyl-pyrone, the lutidone may be thus saponified; an ester acid, X, first obtained when heated, loses carbon dioxide with the formation of a monobasic acid ester, XI. This latter compound, by saponification, yielded a monobasic acid, VII. These last two substances proved to be identical, respectively, with the ethyl ester of the acid and the acid itself obtained from dehydro-acetic acid by rearrangement and treatment with ammonia. The ester melted at 163° and the free acid at 258°, and no depression of the melting point was obtained when the substance was mixed with the corresponding nitrogen compound from dehydro-acetic acid.



IX X XI VII

The Feist formula, I, for dehydro-acetic acid is thus definitely established.

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[8] Ref. 4 g. Ref. 4 f, p. 975. See also Ref. 4 e. Ref. 4 a, p. 172. Michaelis, *Ann.*, **366**, 340 (1909).

[9] Conrad and Guthzeit, *Ber.*, **19**, 19 (1886).

Experimental Part

3,5-Dicarbo-ethoxy-γ-lutidone (IX).—This compound was prepared according to the directions of Conrad and Guthzeit.[9] The copper salt of aceto-acetic ester was oven-dried at 120° but not recrystallized. It was found that in converting the copper salt to the pyrone, a slight excess of phosgene did not affect the yield and insured a white product. The yields were the same as those reported in the original article.

3-Carboxy-5-carbo-ethoxy-γ-lutidone (X).—A solution of 100 g. of 3,5-dicarbo-ethoxy-γ-lutidone in 2 equivalents of 4 *N* alcoholic potassium hydroxide was refluxed for 30 minutes or until the insoluble dipotassium salt began to separate. At this point the alcoholic solution was poured into an equal volume of ice water and 70 cc. of concd. hydrochloric acid (slightly more than two equivalents) was added. It was necessary to allow the solution to stand overnight before precipitation was complete. Concentration of the mother liquors in a vacuum yielded from 5–10% of additional material. The product from the saponification was a mixture of mono-acid mono-ester, diacid and unchanged diester. Saponification with aqueous alkali, or saponification with alcoholic alkali in the cold, gave the same mixture of products. One equivalent of alkali gave the enolic salt and no saponification. Barium hydroxide gave an insoluble enolic salt and no saponification.

The diacid and mono-acid mono-ester were extracted from the unchanged material with as small a volume as possible of 4 *N* sodium carbonate solution and the acids reprecipitated with slightly more than the equivalent quantity of concd. hydrochloric acid. The mono-acid mono-ester was extracted from the dried precipitate with cold chloroform. It was often impossible to filter this solution clear, and when the mono-acid mono-ester was crystallized from water and again extracted with chloroform, an additional half gram of diacid was usually separated. It was found advisable to recover the mono-acid mono-ester from the chloroform extract by crystallizing it from the concentrated solution. Attempts to evaporate the extract directly to dryness on a steam cone gave a sticky mass from which the chloroform evaporated very slowly. After filtering the solution, the precipitate was dried at 100°, for otherwise it held considerable chloroform which caused frothing when the material was dissolved in hot water. The mono-acid mono-ester, recrystallized from hot water, separated in white, flattened needles that melted at 181–184° (corr.) with decomposition. This melting point was not changed by repeated recrystallizations of the solid from water or chloroform. The mono-acid mono-ester was slightly soluble in cold water and soluble to the extent of about 16 parts in 100 of hot water.

Neutral equiv. Subs., 0.2000: 7.8 cc. of NaOH (0.1074 *N*). Calc. for $C_{11}H_{13}O_5N$: neut. equiv., 239. Found: 238.

About 80–90% of the material was recovered from the saponification, but the proportion of diester, diacid and mono-acid mono-ester varied. For example, in one run, 100 g. of diester gave 26.5 g. of unchanged material, 22.5 g. of diacid and 34 g. of mono-acid mono-ester. In another, 100 g. of diester gave 5 g. of unchanged material, 16.5 g. of diacid and 49 g. of mono-acid mono-ester.

The diacid, after recrystallization from hot water, melted at 275–277° with decomposition, and was found to be identical with the diacid prepared from 3,5-dicarbo-ethoxy-γ-lutidone according to the directions of Conrad and Guthzeit.[10] The melting point reported in the original article is 267°, but this variation is not hard to understand for the melting point, even of the same sample, varied widely depending on the speed with which the temperature was raised.

3-Carbo-ethoxy-γ-lutidone (XI).—Into a 50cc. Claisen distilling flask with a short,

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[10] Conrad and Guthzeit, *Ber.*, **20**, 155 (1887).

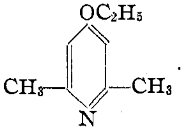
wide side-arm, was packed 30 g. of 3-carboxy-5-carbo-ethoxy-γ-lutidone. The flask was fitted for vacuum distillation, evacuated with a water pump and heated on a metal bath to 200°. When the material had all melted, the temperature was raised to 240° when the elimination of carbon dioxide proceeded rapidly but without excessive frothing. After the decomposition had subsided somewhat, and the vacuum had increased to about 30 mm., the temperature of the bath was raised slowly until distillation began. At 30 mm. the temperature of the bath was between 240° and 260° and the temperature of the distilling material was between 165° and 185°. When this temperature passed 200° the distillation was stopped. The distillate, which had begun to crystallize, was washed out of the receiver with hot ethyl acetate, concentrated and chilled to precipitate as much as possible of the solid material. Usually about 18 g. of distillate was collected, of which approximately half could be separated in the solid form and half represented liquid by-products. About 1 to 2 g. of γ-lutidone was secured from the residue in the distilling flask by extracting with hot water, heating with bone black and concentrating to a small volume.

The solid material secured from the distillation always contained some 3,5-dicarbo-ethoxy-γ-lutidone. This diester was not present as an impurity in the starting material, for the mono-acid mono-ester was purified by extraction with sodium bicarbonate solution, in which the diester is not soluble. Even after the mono-acid mono-ester had been reprecipitated several times from bicarbonate, alternating these purifications by recrystallizations from water, the quantity of diester isolated from the decomposition remained unchanged. It seems probable, therefore, that the diester was formed from the mono-acid mono-ester during the course of the decomposition.

The solid material from the distillation was dissolved in hot water and the solution concentrated to a small volume (about 10–15 cc.). This solution, seeded and allowed to stand overnight, deposited 1–1.5 g. of diester which was collected on a filter. The mother liquors were evaporated to dryness and the residue was recrystallized from absolute alcohol, absolute ethyl acetate or acetone. The crude material thus secured melted at 154–58°; yield, 7–8 g., or 30% of the calculated amount. The yield varied considerably, even under carefully controlled conditions, sometimes dropping as low as 10%. After several recrystallizations, the melting point was raised to 161–162° (corr.). The ester separated from ethyl acetate or acetone in white needles, easily soluble in water or 95% alcohol, only slightly soluble in absolute alcohol, ethyl acetate or acetone and insoluble in ether.

Anal. Subs., 0.2304: N_2, 14.5 cc. (19°, 741 mm.). Calc. for $C_{10}H_{13}O_3N$: N, 7.18. Found: 7.08.

Liquid By-products from Decarboxylation.—The liquid by-products produced during the preparation of 3-carbo-ethoxy-γ-lutidone represent 9 to 10 g. from 30 g. of mono-acid mono-ester. This liquid material was dissolved in a little ether and the ether solution extracted with water to remove any 3-carbo-ethoxy-γ-lutidone that had not crystallized. After drying the solution with anhydrous sodium sulfate and evaporating the ether, the liquid was distilled through an efficient fractionating column and shown to be a mixture of several compounds. The mixture had an amine-like odor and dissolved completely in hydrochloric acid, showing that it probably consisted of pyridine derivatives.

Ethoxy-lutidine,  .—By far the largest portion of the liquid by-products just mentioned boils constant at 107–108° (19 mm.), and on analysis proved to be ethoxy-lutidine; n_D^{25}, 1.5018; d^{25}, 0.9822. In order to identify this compound, the picrate[11] and metho-iodide[12] were prepared which melted, respectively, at 113–114° and 195–196°. These are in agreement with the melting points mentioned in the literature.

Anal. Subs., 0.2685, 0.2608, 0.2075: 22.5 cc. of N_2 (24.5°, 740.5 mm.); CO_2, 0.6725, 0.5470; H_2O, 0.2019, 0.1625 g. Calc. for $C_9H_{13}NO$: C, 71.5; H, 8.6, N, 9.27. Found: C, 70.25, 72.0; H, 8.6, 8.75; N, 9.2.

HYDROCHLORIDE.—

Anal. Subs., 0.2012, 0.1500: 10.53, 7.85 cc. of $AgNO_3$ (0.0996 *N*). Calc. for $C_9H_{13}NO.HCl$: Cl, 18.9. Found: 18.5, 18.5.

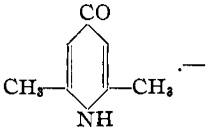
3-Carboxy-γ-lutidone (VII).—A solution of 3 g. of 3-carbo-ethoxy-γ-lutidone in an excess of 4 *N* alcoholic potassium hydroxide was refluxed for 1.5 hours. The solution was poured into an equal volume of ice water, filtered and the equivalent quantity of concd. hydrochloric acid added; yield, 2 g. of free acid. This was recrystallized from hot water in which it is much more soluble than the 3,5-dicarboxy-γ-lutidone. The 3-carboxy-γ-lutidone, dried at room temperature, contains one molecule of water of crystallization, as is shown by its neutral equivalent and the loss of weight when dried at 100°. Since the acid is only very slightly soluble in water or alcohol, the neutral equivalent is best secured by dissolving the acid in an excess of alkali and titrating back with standard acid.

Neutral equiv. Subs., 0.2000: 20 cc. of NaOH (0.1074 *N*); 10.3 cc. of HCl (0.103 *N*). Calc. for $C_8H_9O_3N.H_2O$: neutr. equiv., 185. Found: 184.

Detn. of H_2O. Subs., 0.3000 g.: loss in weight when oven-dried for two hours at 100°, 0.0300. Calc. for $C_8H_9O_3N.H_2O$: H_2O, 9.8. Found: 10.0.

The anhydrous material melted at 158–159° with decomposition. It was almost insoluble in cold water or alcohol, fairly soluble in hot water or alcohol and insoluble in ether, benzene or chloroform.

Neutral equiv. Subs. (dried for two hours at 100°), 0.2000: 20 cc. of NaOH (0.0989 *N*); 7.35 cc. of HCl (0.103 *N*). Calc. for $C_8H_9O_3N$: neutr. equiv., 167. Found: 164.

γ-Lutidone,  .—One g. of 3-carboxy-γ-lutidone was heated in a test-tube at 270° until the elimination of carbon dioxide had ceased (about ten minutes). The material was extracted with hot water, heated with bone black several times and concentrated to a small volume. On standing, 0.5 g. of γ-lutidone crystallized. After this had dried at 120° the melting point was 227.5–229° (corr.). It was compared with some γ-lutidone prepared from 3,5-dicarboxy-γ-lutidone according to the method of Conrad and Guthzeit.[10] The samples were identical in crystalline structure, ease of dehydration and melting point. No depression of the melting point was noted when the two samples were mixed.

Summary

The structure of dehydro-acetic acid has been definitely determined as

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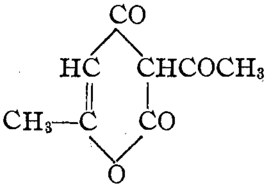
[11] Marckwald, *Ber.*, **27**, 1328 (1894).

[12] Conrad and Eckhardt, *Ber.*, **22**, 82 (1889).



. To accomplish this, 3-carboxy-γ-lutidone, the compound obtained by the rearrangement of dehydro-acetic acid with sulfuric acid and then by treatment with ammonia, was synthesized by a method which left no doubt as to its structure.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

CERTAIN REACTIONS OF THE ALKYL AND ARYL MERCURIC HYDROXIDES

BY I. A. KOTEN[1] WITH ROGER ADAMS

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Although alkyl mercuric hydroxides have been known since 1853,[2] the properties of these compounds have never been extensively studied. Early investigators report these substances as strong bases,[3] but recently Maynard and Howard[4] have shown them to be very weak bases. The aryl mercuric hydroxides[5] have also been prepared but a study of their properties has also been neglected. Beyond the reaction of the alkyl and aryl mercuric hydroxides with acids to give salts, very little is known concerning them. This research had as its purpose, a study of certain chemical reactions of both alkyl and aryl mercuric hydroxides. A comparison of their reactivity with that of mercuric oxide has been made.

The method most commonly used for the preparation of alkyl and aryl mercuric hydroxides has previously been by the action of silver oxide on alkyl or aryl mercuric halides. A much simpler procedure has been used in this research, namely, the reaction of sodium hydroxide in absolute alcohol upon an absolute alcoholic solution of an alkyl or aryl mercuric chloride.[6] The sodium chloride is filtered off and the hydroxides are ob-

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[1] This communication is an abstract of a thesis submitted by I. A. Koten in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Frankland, *Ann.*, **85**, 363 (1853). Cahours, *J. prakt. Chem.*, [2] **8**, 397 (1873). *Jahresber.* **1873**, 517; *Compt. rend.*, **76**, 1403 (1874). Eichler, *Ber.*, **12**, 1880 (1879). Seidel, *J. prakt. Chem.*, [2] **29**, 135 (1884). Tiffeneau, *Bull. sci. pharmacol.*, **28**, 65 (1921). Sneed and Maynard, THIS JOURNAL, **44**, 2946 (1922).

[3] Dünhaupt, *Ann.*, **92**, 381 (1854).

[4] Maynard and Howard, *J. Chem. Soc.*, **123**, 960 (1923).

[5] Otto, *J. prakt. Chem.*, [2] **1**, 183 (1870). Dimroth, *Ber.*, **35**, 2043 (1902). Reissert, *Ber.*, **40**, 4209 (1907). Fränkel, "Arzneimittel-Synthese" Julius Springer, **1921**, 5th ed., pp. 677–680.

[6] Mills and Adams, THIS JOURNAL, **45**, 1842 (1923).