

Lawrence Berkeley National Laboratory

Recent Work

Title

I. The Synthesis of Toluene-1,3,5.-C14 and Oxalic Acid-C14 from Pyruvic Acid-C14 II. The Mechanisms of the Reactions

Permalink

<https://escholarship.org/uc/item/18x7p2v8>

Authors

Hughes, Dorothy
Reid, James C.

Publication Date

1948-09-15

UNIVERSITY OF
CALIFORNIA

*Radiation
Laboratory*

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

UCRL-180
C.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL 180

Chemistry-General

RESTRICTED

CLASSIFICATION CANCELLED BY AUTHORITY
OF THE SECRET ENGINEER
BY THE DECLASSIFICATION COMMITTEE

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

I. THE SYNTHESIS OF TOLUENE -1,3,5,-C¹⁴ AND OXALIC ACID-C¹⁴
FROM PYRUVIC ACID - C¹⁴

II. THE MECHANISMS OF THE REACTIONS

By

Dorothy M. Hughes and James C. Reid

September 15, 1948

Special Review of Declassified Reports

Authorized by USDOE JK Bratton

Unclassified TWX P182206Z May 79

REPORT PROPERLY DECLASSIFIED

CLASSIFICATION CANCELLED BY AUTHORITY
OF THE SECRET ENGINEER
BY THE DECLASSIFICATION COMMITTEE
CAUTION

This document contains information affecting the
National Defense of the United States.
Its transmission or the disclosure of its contents in
any manner to an unauthorized person is prohibited
and may result in severe criminal penalties under
applicable Federal Laws.

<u>J N Green</u>	<u>8/16/79</u>
Authorized Derivative Classifier	Date
<u>R O K Albert</u>	<u>8/17/79</u>
By	Date

Berkeley, California

~~RESTRICTED~~
CLASSIFICATION CANCELLED BY AUTHORITY
OF THE DIRECTOR GENERAL
BY THE DECLASSIFICATION COMMITTEE

STANDARD DISTRIBUTION: Series A

Argonne National Laboratory	1-8
Armed Forces Special Weapons Project	9
Atomic Energy Commission, Washington	10-11
Battelle Memorial Institute	12
Brookhaven National Laboratory	13-22
Carbide & Carbon Chemicals Corporation (K-25 Area)	23-26
Carbide & Carbon Chemicals Corporation (Y-12 Area)	27-30
Columbia University (Failla)	31
General Electric Company	32-35
Hanford Directed Operations	36-42
Iowa State College	43
Kellex Corporation	44-45
Los Alamos	46-48
Massachusetts Institute of Technology	49
Monsanto Chemical Company, Dayton	50-51
National Bureau of Standards	52-53
Naval Radiological Defense Laboratory	54
NEPA	55
New York Directed Operations	56-57
Oak Ridge National Laboratory	58-69
Patent Advisor, Washington	70
Technical Information Division, ORDO	71-85
UCLA Medical Research Laboratory (Warren)	86
University of California Radiation Laboratory	
Information Division	87-89
Chemistry Department	90
University of Rochester	91-92
Western Reserve University	93
Office of Chicago Directed Operations	94

DECLASSIFICATION PROCEDURE:

Declassification Officer	95-98
Publication Officer	99
Patent Department	100-101
Area Manager	102
E. O. Lawrence	103
Information Division	104

INFORMATION DIVISION
Radiation Laboratory
Univ. of California
Berkeley, California

- I. THE SYNTHESIS OF TOLUENE-1,3,5-C¹⁴ AND OXALIC ACID-C¹⁴
FROM PYRUVIC ACID- α -C¹⁴
- II. THE MECHANISMS OF THE REACTIONS

By

Dorothy M. Hughes and James C. Reid

Radiation Laboratory and Department of Chemistry
University of California, Berkeley*

September 15, 1948

ABSTRACT

1. A synthesis of toluene labeled with C¹⁴ in the 1, 3 and 5 positions of the ring is described. Labeled oxalic acid is obtained as a second product. The starting material is pyruvic acid- α -C¹⁴; the yields of toluene and of sodium oxalate are 62% and 84%, respectively.

2. Certain aspects of the mechanisms of the reactions involved have been checked by tracer technique, with results consistent with concepts expressed in the literature.

3. The decarboxylation of methyl-dihydrotrimesic acid by sulfuric acid has been found to proceed by loss of the carboxyl carbon atom as carbon monoxide, not carbon dioxide. The formation of di- and tetrahydrovitic acids in this reaction is therefore questioned.

4. It is shown that pyruvic acid synthesized from acetyl bromide-1-C¹⁴ via pyruvonitrile may be contaminated with 50% of radioactive acetic acid.

* This paper is based on work performed under Contract #W-7405-Eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory, University of California, Berkeley, California.

- I. THE SYNTHESIS OF TOLUENE-1,3,5-C¹⁴ AND OXALIC ACID-C¹⁴
FROM PYRUVIC ACID- α -C¹⁴
- II. THE MECHANISMS OF THE REACTIONS

By

Dorothy M. Hughes and James C. Reid

Radiation Laboratory and Department of Chemistry
University of California, Berkeley (1)

September 15, 1948

For the purpose of carrying out many types of tracer studies, it is necessary to have aromatic compounds labeled in the ring with isotopic carbon. A useful intermediate for the synthesis of such compounds would be toluene. At the suggestion of Prof. Melvin Calvin, the authors have investigated the feasibility of synthesizing toluene-C¹⁴ by decarboxylating uvitic acid (II), prepared from pyruvic acid- α -C¹⁴ via methyldihydrotrimesic acid (I). A valuable feature of this scheme is the formation of oxalic acid, a useful compound, which should be labeled if the scheme which has been postulated (2) for the condensation of pyruvic acid to methyldihydrotrimesic acid is correct. Although there is no reason to doubt the correctness of the essential features of this postulate, it was thought to be of interest to apply those checks which tracer technique affords, since

(1) This paper is based on work performed under Contract No. W-7405-Eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory, University of California, Berkeley, California.

(2) L. Wolff, Ann., 305, 125 (1899).

there are still comparatively few instances in which mechanisms formulated from considerations of the classical types have been directly checked with isotopic carbon. Accordingly, the specific activities of the intermediate compounds have been determined, and the mechanisms of all the reactions involved in the synthesis checked with respect to the fate of the tracer carbon atoms.

The reaction sequence is described in Fig. 1, which includes the previously postulated (2) course of the reactions leading to the formation of uvitic acid (equations A and B). It will be shown that equation B is in error with respect to the minor products. Positions expected to be labeled are marked with an asterisk.

Experimental

The radioactivity measurements were made by converting each organic sample to barium carbonate, which was mounted on a thin aluminum disc and counted with a G-M counter of the end window type. The techniques employed are described elsewhere. (3) All samples were counted long enough to reduce the statistical error to 1% or less.

Methyldihydrotrimesic Acid and Sodium Oxalate from Pyruvic Acid: -

A 0.4802 g. portion of pyruvic acid- α -C¹⁴ (4) which had been prepared

(3) W. G. Dauben, J. C. Reid, and P. E. Yankwich, *Anal. Chem.*, **19**, 828(1947).

(4) We are indebted to Mr. R. M. Lemmon for the synthesis of the radioactive pyruvic acid. The method of synthesis, described in outline in another place (R. M. Lemmon and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1232 (1947)) utilizes the following reaction sequence:



three weeks previously and stored in a refrigerator, was diluted with 10.124 g. of freshly distilled inactive pyruvic acid. The mixed acid (0.121 mole) was added dropwise to a solution of 22 g. (0.55 mole) of sodium hydroxide in 39 ml. of water, which was contained in a 125 ml. Erlenmeyer flask cooled in ice. The acid was added slowly to the solution, which was swirled to minimize local heating; the time required was about one half hour. If local heating was excessive, or if the order of mixing was reversed, the yield was lowered. After the acid had been added, the pale yellow solution was heated 3.5 hours on a steam bath. During this time, the color became deep orange, and a precipitate of sodium oxalate appeared. The mixture was chilled and the sodium oxalate was collected on a sintered glass filter, where it was washed with three 5 ml. portions of 12 M sodium hydroxide. The bulk of the product was left in crude form for future use; the total amount of oxalic acid present was determined by permanganate titration of an aliquot to be 84% based on pyruvic acid.

To obtain a pure specimen for radioactive assay, a portion of the crude sodium oxalate was dissolved in 1 M acetic acid, carbon dioxide was boiled out of the solution, and the oxalic acid was precipitated as its barium salt. The barium oxalate was dissolved in 3 M hydrochloric acid and the solution was evaporated to dryness on a steam bath. The residue was transferred to a small sublimation apparatus, and the oxalic acid was recovered by vacuum sublimation. The sublimed acid was crystallized twice from water and dried in air.

Methyldihydrotrimesic acid was precipitated from the filtrate left after removal of sodium oxalate by acidification with concentrated hydro-

chloric acid. The solution was cooled in ice during the acidification, and the acid was added slowly enough to prevent the temperature from rising above 60° as a precaution against decomposition of the methyl-dihydrotrimesic acid. A total of 50 ml. of hydrochloric acid was added; then the mixture was filtered. Sodium chloride was washed out of the white solid on the filter with 25 ml. of water in 3-4 ml. portions. The yield of acid, dried in high vacuum at room temperature, was 4.97 g.; 67.5% based on pyruvic acid. The principal impurity in the crude product was sodium chloride; purification of a sample for radioactivity assay was accomplished by crystallization from dilute ethanol at a temperature below 60°. The purified acid absorbs atmospheric moisture to form a monohydrate; drying in high vacuum gives the anhydrous compound. The radioactivity measurement was performed on the hydrate.

The filtrate left after removal of the methyl-dihydrotrimesic acid was subjected to continuous ether extraction for 8 hours. Evaporation of the ether left a syrup. When this was dried in vacuum a brittle brown material was obtained, which weighed 1.60 g.; it readily absorbed moisture from the atmosphere and again became syrupy. The material was burned in toto to determine its activity. (5)

-
- (5) Several experiments were performed to investigate the behavior of this substance on decarboxylation. Subjection of the material to decarboxylating conditions with several catalysts gave, in the most favorable cases, mixtures of volatile liquid products which were largely olefinic in nature. The amounts formed were small, and the mixtures were complex; consequently, no use except isotope recovery was made of the syrup.
-

The water solution from the ether extraction operation was neutralized with sodium hydroxide and evaporated. The activity of the residue was determined by heating an aliquot in a combustion train until all the carbonaceous materials were burned out of the rather large amount of salt present. The carbon dioxide was recovered as barium carbonate; this is referred to in Table 1 as Barium Carbonate I.

Uvic Acid from Methylidihydrotrimesic Acid: - The decarboxylation apparatus consisted of a 125 ml. conical flask bearing two ground necks. The center neck was fitted with a compensated dropping funnel, and the side neck carried a tube to conduct gas out of the flask. The tube extended a short distance into the flask and its end, which was drawn to small diameter, was bent up to serve as a spray trap. Provision was made for introducing a current of nitrogen, purified by passage through a preburner and a carbon dioxide absorber, into the system through the mouth of a dropping funnel. A stopcock was situated in the line just ahead of the dropping funnel. After leaving the flask, the gas passed through an absorber containing 1 M sodium hydroxide, then over copper oxide heated to 550°, and finally through a second absorber containing alkali. Atmospheric carbon dioxide was excluded from the system by a guard tube attached at the outlet.

Into the flask was placed 4.74 g. of dry crude methylidihydrotrimesic acid, and 20 ml. of concentrated sulfuric acid was placed in the funnel. The apparatus was assembled, and the air was swept out with nitrogen. The stopcock was closed and the acid was run into the flask from the dropping funnel. The mixture was heated in an oil bath to 120°, and decarboxylation commenced. When the initial evolution of carbon monoxide

had subsided, the stopcock was opened to admit a current (25 cc./min.) of nitrogen, and the temperature of the bath was raised to 150° C where it was held for 2 hours. At the end of this time, the reaction mixture was cooled somewhat and poured into 100 ml. of water; this caused the uvitic acid to separate. The mixture was allowed to become hot, for by this procedure a product was obtained which was less difficult to filter than one prepared in the cold. The crude, gray uvitic acid was collected on a sintered glass filter and carefully washed free of sulfate. (6). The yield of crude vacuum dried acid was 3.53 g.; 100% based on methyldihydrotrimesic acid.

To obtain a pure specimen for radioactivity assay, an aliquot was crystallized from dilute ethanol, with the use of charcoal, then crystallized again from dilute ethanol and dried under high vacuum. The neutralization equivalent of a specimen so purified was 90.5; calculated for anhydrous uvitic acid, 90.1.

To the alkali in each of the absorbers was added excess barium chloride solution and the precipitates were collected. The material from the first absorber weighed 0.149 g. after subtraction of the blank; 3.9% of the theoretical quantity based on methyldihydrotrimesic acid. It was shown by permanganate titration to contain 6% barium sulfite; the rest was carbonate. This specimen is referred to in Table 1 as Barium Carbonate II.

After correction for blank, the barium carbonate obtained from the second absorber weighed 3.689 g., 96.8% of theoretical. This specimen is referred to in Table 1 as Barium Carbonate III.

(6) Unless sulfate was completely removed, the toluene obtained by decarboxylation of the uvitic acid contained sulfur dioxide.

Toluene from Uvitic Acid: - The apparatus used for the decarboxylation of uvitic acid is shown in Fig. 2. The reaction vessel A is a 2 x 23 cm. Pyrex tube with a side arm, which terminates in a 10/30 ground joint, attached a short distance below the mouth. Provision is made for admitting purified nitrogen through a 24/40 ground joint, whose inner member has an extension which protrudes into the vessel to a point a few millimeters above the side arm. The tube is heated by a salt bath; a Transite disc B prevents the silicone lubricant in the ground joints from becoming excessively hot. The vessel is connected to the unit D which consists of a fore trap, whose capacity is about 5 ml., sealed to a second trap consisting of six turns of 7 mm. Pyrex tubing terminating in a 5 ml. receptacle r. The outlet of D is connected to a carbon dioxide absorber (not shown) containing 1 M sodium hydroxide. A guard tube to exclude atmospheric carbon dioxide completes the train. A Transite shield C protects D from the heat of a thermostatically controlled electric heater used to heat the salt bath.

Vessel A was charged with 3.44 g. of dry crude uvitic acid, 0.50 g. of powdered cupric oxide, and 10 ml. of freshly distilled synthetic quinoline; it was then connected to the train. The air was swept out of the system with nitrogen, and the stopcock at the entrance to A was closed. A Dry Ice-isopropanol mixture was placed around the spiral trap and the temperature of the contents of A was raised from 150° to 265° C over a period of one hour. The stopcock was then opened, and a current of purified nitrogen was passed through the apparatus for 3 hours, while the salt bath was held at 265 ± 5°. The fore trap was not cooled; it collected some water and toluene, and most of the small amount of quinoline which distilled with them. This partial removal of extraneous substances reduced difficulty from plugs of frozen material in the coils of the spiral trap.

The spiral trap was watched closely and the cooling bath was removed for a brief time if necessary, to allow plugs to melt and fall into the receptacle. Toward the end of the reaction, toluene in the fore trap was driven into r by stroking the trap with a soft flame.

When the reaction was finished, barium carbonate was precipitated from the absorber solution. The yield was 7.45 g. after correction for blank; 98.5% of the theoretical. This specimen is referred to in Table 1 as Barium Carbonate IV.

The toluene was purified with the aid of the apparatus shown in Fig. 3. This consists of a high vacuum manifold to which are attached vessels D, F, and G. A trap H is situated in the line. The unit D contains the crude toluene; the entrance to the fore trap is closed by a ground glass plug. Vessel F contains about 10 g. of phosphorus pentoxide, and G is a receptacle made by sealing a 3 mm. straight bore stopcock to a 15 ml. graduated conical centrifuge tube. The stopcock and the ground joint by which the receptacle is attached to the manifold are sealed to the centrifuge tube on a lathe, to insure that all the segments are coaxial; it is then possible to insert a long capillary pipet into the tube to withdraw portions of toluene for use, and the receptacle can be used as a storage vessel.

The contents of the spiral trap were frozen in liquid nitrogen and the pressure in the entire system reduced to 5 microns; stopcocks 2 and 3 were then closed. The toluene was transferred to F by cooling that vessel with liquid nitrogen while D was allowed to warm up. When most of the toluene had distilled, D was warmed in a bath of water at 40°. A pressure of about 50 microns developed during the transfer as the materials in the system released entrained gases; toward the end of the operation these gases interfered with the diffusion of toluene. To obtain the last of the

toluene, 2 was opened and the system was re-evacuated. The residual toluene condensed in H, which was cooled in liquid nitrogen. Stopcock 1 was then closed and the toluene in H was distilled into F.

Stopcocks 4, 5, and 7 were closed and F was removed from the line. By gently shaking the vessel, the phosphorus pentoxide and toluene were distributed in a layer over the entire inside wall area except the region near the stopcock. The vessel was again attached to the manifold and the toluene was distilled into G. A soft flame was passed a few times over F to drive out the last of the toluene.

The yield was 1.610 g.; 91.5% based on uvitic acid, or 62% based on pyruvic acid. The purity of the product was investigated with a sample prepared in a pilot run with inactive pyruvic acid. The boiling range was 110.6-111.1; n_D^{20} , 1.4978. Mass spectrometric analysis (7) showed the total amount of impurities in the range of mass numbers 0 to 200 to be about 0.2%. Regions scanned with particular attention were those corresponding to benzene, xylene, methylcyclohexane and methylcyclohexene. The height of the toluene peak corresponded to 100.2 \pm 0.2% toluene.

Discussion

The radioactivity measurements are recorded in Table 1. The molar specific activity to which reference is made in the heading of the third column is the specific activity of the compound multiplied by its mole-

(7) We wish to thank Dr. N. Bauer and the California Research Corporation for the mass spectrometric analysis.

cular weight. The ratios are calculated with the molar specific activity of the methylidihydrotrimesic acid as the denominator; each ratio has been multiplied by three to obtain integral values. Each value so calculated expressed, for the compound to which it refers, the number of carbon atoms in the molecule which were ketonic carbon atoms in pyruvic acid, assuming

Table 1
Radioactivity Measurements on the Reaction Products

Compound	Sp. Act. cts./min./mg.	Molar Sp. Act. Molar Sp.Act. MDTA	Total Act. as % of Initial
Undiluted active pyruvic acid	9420	--	100
Diluted pyruvic acid	427 (a)	2.08	100
Methylidihydrotrimesic acid Monohydrate	223	3.00	24.5
Oxalic acid Dihydrate	150	1.04	11.3
Syrup	464	--	16.5
Barium Carbonate I	66.3	--	8.82
Uvitic acid	302	2.98	23.7
Barium Carbonate II	.68	~ 0	.0022
Barium Carbonate III	.049	~ 0	.0029
Toluene	589	2.98	21.0
Barium Carbonate IV	.07	~ 0	.010
(a) Not measured directly; computed from the amount by which the active acid was diluted.			

that three of the ketonic atoms have been incorporated into methylidihydrotrimesic acid. Why the specific activity of pyruvic acid is not made the denominator of the ratio will be made clear below. The ratios show that for each ketonic carbon atom which appears in oxalic acid, three appear in methylidihydrotrimesic acid, and that these three are not lost in the succeeding reactions which lead to toluene. These facts are in accord with the mechanisms implied by the equations in Fig. 1. It is on the strength of this that the assignment of the positions of the tracer atoms has been made.

The molar specific activity ratio for pyruvic acid should be unity; actually it is 2.08. The explanation of this discrepancy is contained in the activity totals tabulated in the fourth column of Table 1. These numbers show that the sum of the total activities of the methylidihydrotrimesic acid, oxalic acid, and syrup is only 52% of the total activity of the pyruvic acid. Since the total weight of these three substances accounts for substantially all of the pyruvic acid, the radioactive (undiluted) preparation must have contained radioactivity impurity, which amounted to about 50% by weight.

A potentiometric titration of the pyruvic acid gave an equivalent weight corresponding to 90% pyruvic acid; the impurity is therefore acidic, although only one break was detectable on the titration curve. The fact that the final residue of salts contained a small part (18%) of the missing activity means that the impurity is extracted from acid solution by ether, but only slowly. Since the syrup did not contain an appreciable amount of the activity extracted, the impurity is a volatile substance, which was lost when the syrup was dried in vacuum.

-15-

To verify these observations, a confirmatory experiment was performed. In this run, a sample of the diluted pyruvic acid was subjected to radioactivity assay to check the specific activity of the undiluted preparation. The specific activity values obtained by direct measurement and by calculation from the dilution factor agreed within 3%. After isolation of methyldihydrotrimesic acid and sodium oxalate, an aliquot of the filtrate was subjected to radioactivity assay; the ether extraction was omitted. The activity measurements are tabulated in Table 2.

Table 2

Radioactivity Measurements Obtained in the
Confirmatory Experiment

Specimen	Total Activity as % of Initial	Weight as % of Theoretical
Diluted pyruvic acid	100	100
Methyldihydrotrimesic acid	19.1	58 (a)
Oxalic acid	9.7	79 (b)
Filtrate	63.9	--
Total	92.7	

(a) Theoretically equivalent to 43.5% of the total initial activity.
(b) Theoretically equivalent to 19.8% of the total initial activity.

Again, the large discrepancy was observed between the sum of the percentages of pyruvic acid converted to methyldihydrotrimesic and oxalic acids and the sum of the percentages of the total initial activity which were found in these compounds; most of the missing activity was found in

the liquor left after their removal. Although it is clear from the total activity values in Table 1 that the impurity did not participate in the reactions under study, it was identified definitely as a matter of interest.

The method used to synthesize the pyruvic acid (4) suggested that the impurity was acetic acid, as did the observations just recorded concerning its behavior. The identification was made by determining the Duclaux numbers of the acid distillable from the liquor obtained in the confirmatory experiment after removal of methyldihydrotrimesic and oxalic acids. The liquor was freed of chloride by treatment with silver oxide, then was filtered and adjusted to pH 3 with sulfuric acid. The Duclaux numbers are given in Table 3. The specific activities of the first and last fractions of the distillate were found (8) to be 8.8×10^5 and 9.0×10^5 cts/min/meq respectively; in contrast to these values the specific activity of the diluted pyruvic acid was 3.26×10^4 cts/min/meq. There was 0.799 milliequivalent of acetic acid in the 50 ml. of distillate collected.

Table 3

Duclaux Numbers for the Contaminant

Total Volume of Distillate, ml.	Acid Content as % of Total Distilled	% Expected for Acetic Acid
10	20.7	18.7
20	39.9	38.2
30	59.4	57.4
40	79.6	78.6
50 (a)	100	100
(a) The distillation was interrupted when 50 ml. of distillate had been collected because the large amount of sodium sulfate present caused unmanageable bumping.		

(8) by evaporating an aliquot of the solution on a glass plate and counting the sodium acetate directly

This should be about 34% (9) of the acetic acid originally present in the liquor; from this it can be calculated that the liquor contained 7.2×10^5 cts/min of acetic acid, and the undiluted pyruvic acid contained about 47% acetic acid by weight, a value in satisfactory agreement with the estimate of 52% mentioned earlier.

The Duclaux identification was confirmed by converting the acetic acid to its anilide. To a portion of the Duclaux distillate containing 11.1 mg. of active sodium acetate was added inactive acetic acid equivalent to 334 mg. of sodium acetate (both values were determined by titration). Sodium acetate was obtained by evaporating the solution and converted to acetanilide; the purified derivative had a specific activity of 264 cts/min/mg; calculated, 212. The discrepancy can reasonably be attributed to a slightly low value in the direct count of sodium acetate.

It was found that in the formation of uvitic acid (equation B) methyldihydrotrimesic acid loses its carboxyl carbon atom as carbon monoxide, not carbon dioxide as reported in the earlier work of Wolff. That the gas evolved is carbon monoxide is shown by the fact that very little barium carbonate, and still less sulfite, was recovered from alkali through which the gas had passed; by passage over hot copper oxide, however, carbon dioxide was formed in essentially quantitative yield.

In order for methyldihydrotrimesic acid to form uvitic acid by loss of carbon dioxide, the extra hydrogen atom attached to the number two position of the ring must be disposed of in some way; the opinion expressed in the earlier work is that a certain amount of di- and tetrahydrovitic

(9) A. A. Morton, "Laboratory Technique in Organic Chemistry", p. 132. First edition (1938), McGraw-Hill Book Company, New York.

acid, and perhaps analogous methyltrimesic acids are formed. Such materials were thought to compose the bulk of certain syrups obtained under various decarboxylation conditions, although in general the syrups were difficult to work with and this fact precluded the isolation of pure compounds from them. The high yield of uvitic acid obtained when concentrated sulfuric acid is used as the decarboxylation catalyst is stated (1) to be due to its ability to oxidize the extra hydrogen and thereby prevent the formation of the hydrogenated acids. Since the sulfuric acid does not function in the reaction as an oxidizing agent, yet the yield is quantitative, it is questionable, in view of the apparent inadequacy of the analytical method which must have been used to identify the evolved gas, to what extent the formation of di- and tetrahydro acids occurs.

(10) Wolff, loc. cit., p. 129.

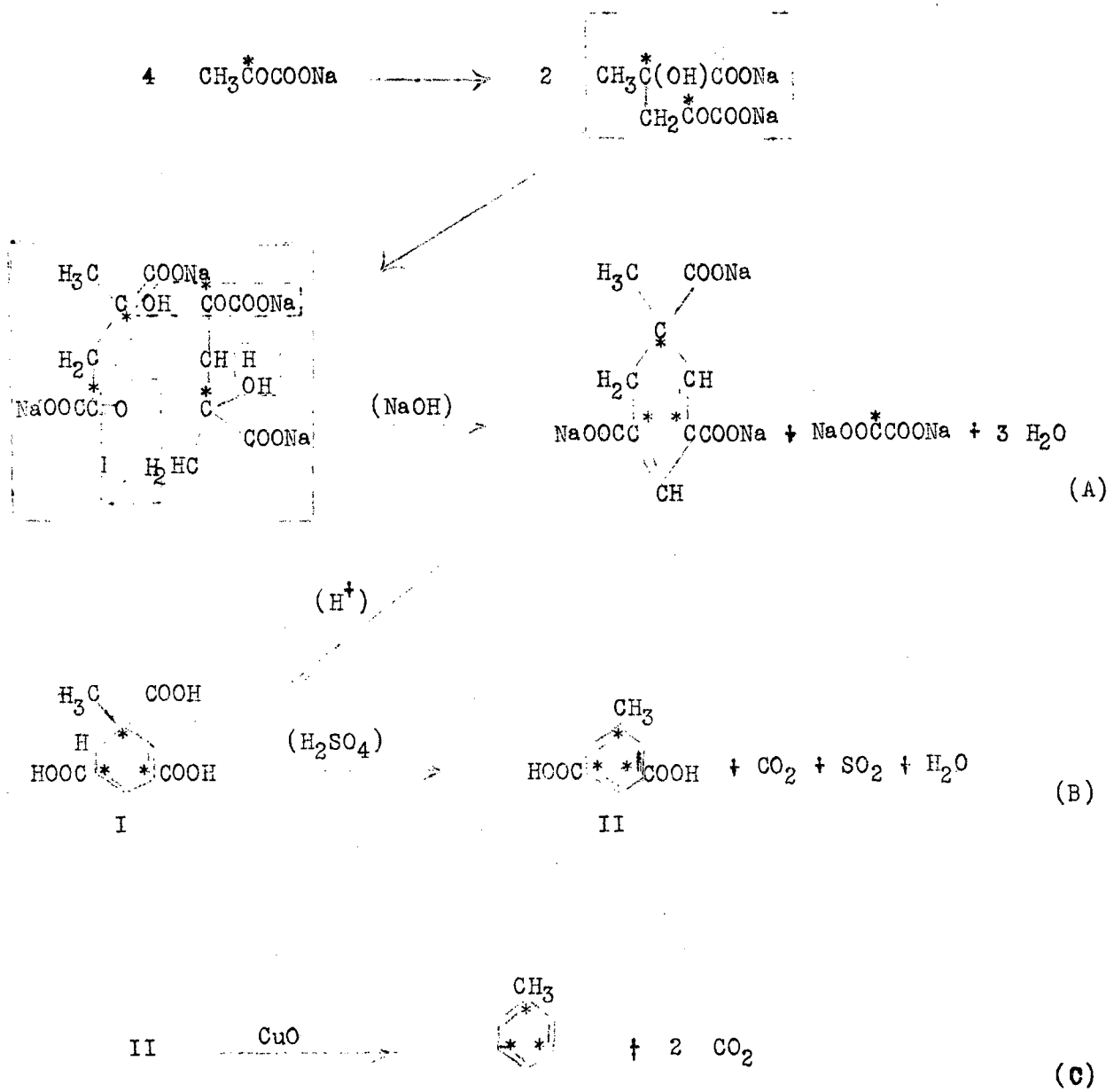


Figure 1

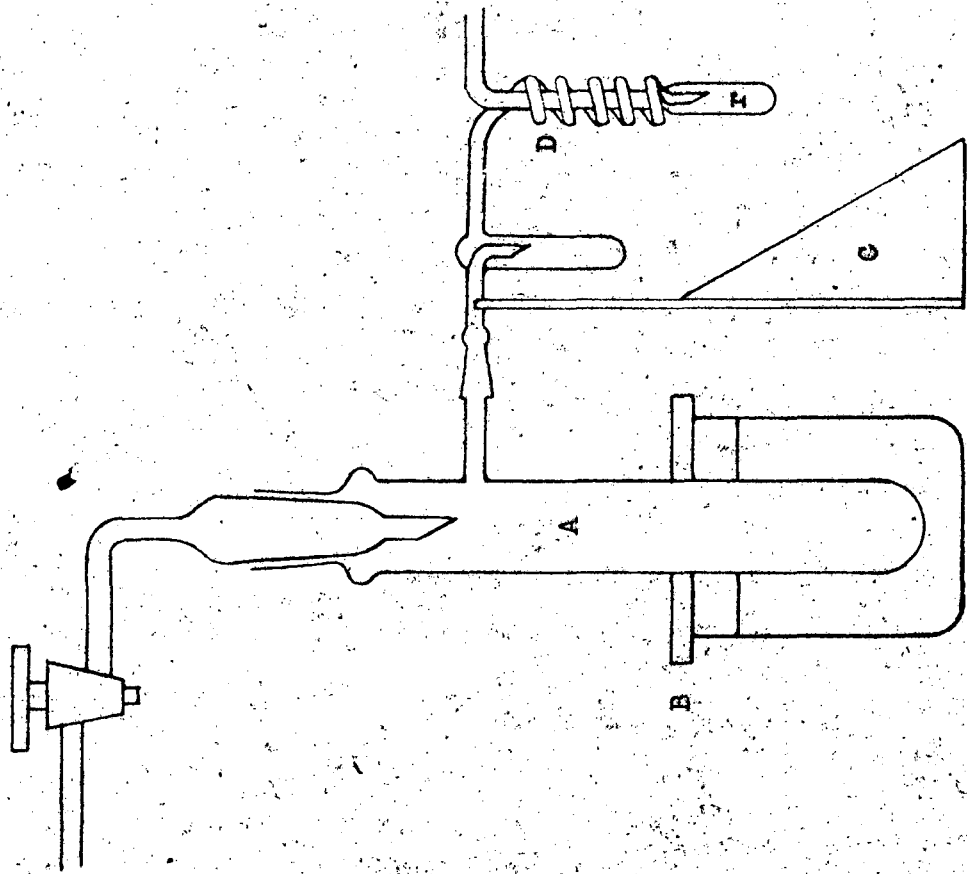


Fig. 3. Decarboxylation apparatus.

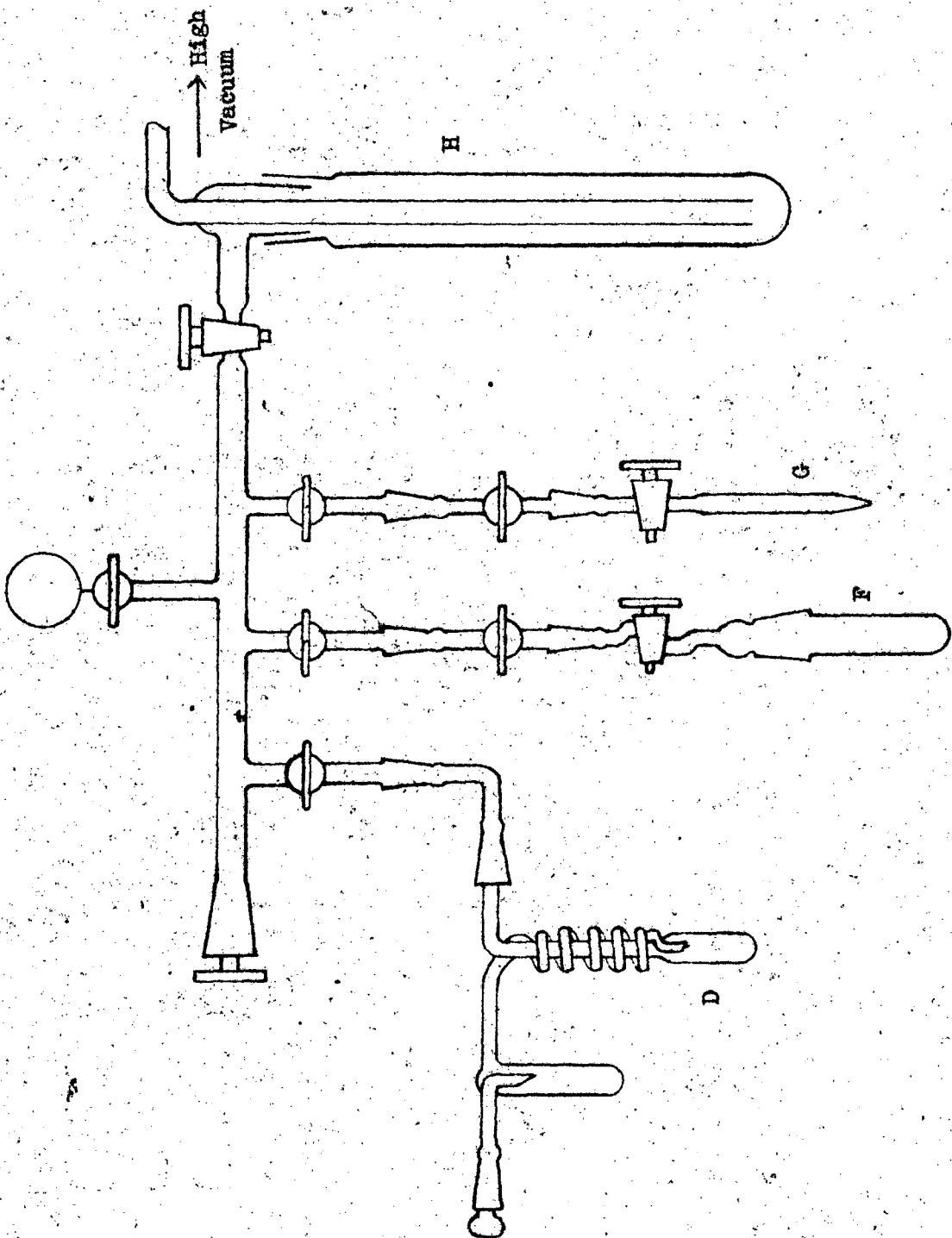


Fig. 3 Apparatus for Purification of Toluene.

~~RESTRICTED~~

CLASSIFICATION CANCELLED BY AUTHORITY
OF THE DISTRICT ENGINEER
BY THE DECLASSIFICATION COMMITTEE