197° and a mixture of the two at 196°–198° with softening at 189°.

Methyl 4,4′-Diacetamidodiphenylacetate (XIV).—A. From the nitro ester (VIII). Hydrogenation and acetylation of the nitro-ester was accomplished by shaking for several hours (initial temperature of 75°) a solution of 0.80 g. (0.0025 mole) of the nitro compound in about 140 ml. of glacial acetic acid and 1 ml. of acetic anhydride under 40 lb. of hydrogen pressure in the presence of 0.2 g. of platinum on carbon catalyst. Filtration and evaporation of the solvent yielded 0.84 g. (98%) of light brown crystalline amide which, on heating, shrank at about 240° and finally melted at 275°. Recrystallization several times from acetic acid yielded pure white product which melted at 284–286° (on the block).

Anal. Calcd. for $C_{19}H_{20}O_4N_2$: N, 8.24. Found: N, 8.08.

B. **From Heller's Acid.**—Esterification of Heller's acid with methanol and dry hydrogen chloride yielded an oil which failed to crystallize. Acetylation of the oil afforded an excellent yield of white crystals melting at 284–287° and showing no depression (284–286°) when mixed with material from procedure A (above).

4,4′-Dibromodiphenylacetic Acid.—When 6.0 g. (0.014 mole) of 1,1,1-trichloro-2,2-bis-(*p*-bromophenyl)-ethane was hydrolyzed according to Grummitt,[13] 1.4 g. (27%) of fairly pure acid resulted. Recrystallization from ethanol afforded the pure acid, m. p. 188–189.2° (literature, 187–188°[34]). The material insoluble in the hydrolysis mixture was recrystallized from ethanol to yield 1.78 g. (39%) of pure 4,4′-dibromodiphenylmethane, m. p. 62–63.8° (literature, 64°[35]).

4,4′-Diiododiphenylacetic Acid.—(a) Hydrolysis of 3.00 g. (0.0056 mole) of 1,1,1-trichloro-2,2-bis-(*p*-iodophenyl)-ethane (m. p. 175.2–176.6°),[36] according to Grummitt[13] produced 1.63 g. (69%) of fairly pure 4,4′-diiododiphenylmethane, m. p. 87.5–93°, as the insoluble product. Recrystallization from 50 ml. of ethanol afforded 1.18 g. of the pure methane, m. p. 91.6–93° (literature: 92–93°,[37] 93–93.5°[38]). Acidification of the alkaline filtrate from the hydrolysis yielded 0.42 g. of crude acidic material which was not purified.

(b) Hydrolysis of 4.3 g. (0.0080 mole) of the ethane for three hours produced 1.81 g. of insoluble material. Acidification of the alkaline filtrate as before caused the formation of a white emulsion which on standing one month in a refrigerator gradually deposited 0.43 g. (12%) of brownish solid, m. p. 176–186°. Recrystallization (charcoal) from aqueous ethanol left 0.20 g. of pure acid as a fine white powder, m. p. 192.5–195.5° (uncor.).

Anal. Calcd. for $C_{14}H_{10}O_2I_2$: I, 54.70; neut. equiv., 464. Found: I, 54.88[28]; neut. equiv., 458.

Summary

Nitration of diphenylacetic acid (I) has produced as the major isolable substance the 3,4′-dinitrodiphenylacetic acid (II), while nitration under similar conditions of the corresponding methyl ester, VII, afforded the 4,4′dinitro isomer, VIII. Acid hydrolysis of VIII yielded the corresponding acid, IX. The structures of II and IX have been proved by degradations to previously known materials while reduction of IX to the diamino acid produced a material identical with that prepared by Heller from dichloroacetic acid and aniline. The identity of the two has been further confirmed by the preparation of derivatives.

The method used for hydrolyzing DDT was modified and extended with varying degrees of success to the preparation of diphenylacetic acid (I) and its 4,4′-dibromo and 4,4′-diiodo derivatives.

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[34] Biltz, *Ber.*, **43**, 1815 (1910).

[35] Goldthwaite, *Am. Chem. J.*, **30**, 447 (1903).

[36] Chattaway and Muir (ref. 14) listed 172°.

[37] Nastukoff and Scheljagin (ref. 14).

[38] Menon, *Quart. J. Indian Chem. Soc.*, **4**, 437 (1927).

BETHLEHEM, PA. RECEIVED MARCH 4, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

The Aromatic Elimination Reaction. I. Mechanism of the Decarboxylation of Mesitoic Acid

BY W. M. SCHUBERT

The decarboxylation of mesitoic acid[1] and other hindered aromatic acids[2] in solutions of strong acids appears to be a manifestation of a general aromatic elimination reaction. Probably occurring by a similar mechanism are such reactions as desulfonation, the cleavage of hindered aromatic ketones in boiling sirupy phosphoric acid,[1,3] the reverse Fries rearrangement[4] and similar acyl wanderings, and migrations of the sulfonic acid group. A profound influence is exerted on these reactions by bulky substituents *ortho* to the group being eliminated. Thus the decarboxylation of alkylbenzoic acids in boiling sirupy phosphoric acid occurred only when two alkyl substituents were substituted *ortho* to the carboxyl group.[1] Acyl cleavage requires the presence of at least one *ortho* alkyl group,[1] and in the reverse Fries rearrangement the presence of an alkyl substituent *ortho* to the wandering acyl group is necessary.[4] Similarly, the desulfonation reaction is enhanced considerably by the presence of *ortho* methyl substituents.[5]

These acid-catalyzed reactions appeared to be, on the surface at least, the reverse of aromatic electrophilic substitution. It appeared also that resonance inhibition is involved. With a view toward elucidating the mechanism of these processes, a kinetic study was made of the decarboxylation of mesitoic acid in strong sulfuric acid solution. Of all the aromatic elimination reactions,

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[1] Klages, *Ber.*, **32**, 1549 (1899).

[2] Buning, *Rec. trav. chim.*, **40**, 327 (1921).

[3] Arnold and Rondestvedt, THIS JOURNAL, **68**, 2176 (1946).

[4] Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928).

[5] Crafts, THIS JOURNAL, **23**, 236 (1901).

the decarboxylation reaction appeared to lend itself most readily to a quantitative study, since the reaction could be easily followed by measuring the rate of evolution of carbon dioxide.

Experimental

Materials.—Mesitoic acid, prepared by the method of Barnes,[6] was recrystallized from ligroin, then glacial acetic acid, m. p. 152–153°. Methyl mesitoate was made by the method of Newman,[7] b. p. 115.5–112° (7 mm.), n^{20}_{D} 1.5077. Solutions of 81.8, 83.3, 84.7, 86.1, 88.2, 91.3, and 94.4% sulfuric acid were made by diluting C. P. concentrated sulfuric acid. Solutions of 96.9 and 100% strengths were made by mixing appropriate amounts of concentrated sulfuric and fuming sulfuric acid. The strengths of these solutions were determined by titrations of aliquot portions of diluted samples against standard alkali.

Apparatus and Method.—A schematic diagram of the reaction vessel and the shaking device is shown in Fig. 1. The bulb A varied in capacity from 15 to 40 ml. and the reservoir B was of 10-ml. capacity. The reaction vessel was fastened to a pendulum arm which pivoted at C. The pendulum arm was fastened to a shaker arm which pivoted at D. The vessel was shaken back and forth so that the bulb A swung through an arc of 4 inches at the rate of 200 swings per minute. The whole was immersed in a constant temperature oil-bath up to the point D. The maximum variation in the bath temperature at 90° was ±0.05°.

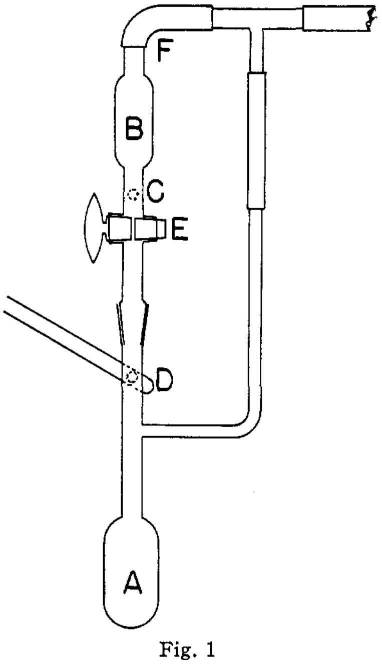

Fig. 1

When a run was to be made, 0.2–0.3 g. of finely powdered mesitoic acid was introduced into the bulb A through a funnel. Two or three short pieces of 3-mm. glass rod were introduced to facilitate mixing. The entire apparatus was then assembled and placed in the bath. Sulfuric acid of appropriate strength was prewarmed in the bath and then 10 ml. was introduced into the reservoir B by means of a fast flowing pipet, the stopcock E being closed. The connection at F was quickly made, the stopcock E opened, and the shaker and timer turned on.

The gas escaping from the reaction vessel was passed through a water-cooled spiral condenser and then was collected over water saturated with carbon dioxide in a 50-ml. gas buret. A diagram of the buret and the leveling device is shown in Fig. 2. The gas was led into the buret at G with stopcock H open to the reaction vessel, the gas buret and the leveler I. Water was run out of the buret J at a rate such that the levels of water in I were the same. At the instant a reading was to be made the stopcock H was closed to G, but kept open to the gas buret and the leveler I. The water levels in I were quickly adjusted, the gas volume read, and then the stopcock H reopened to the reaction vessel.

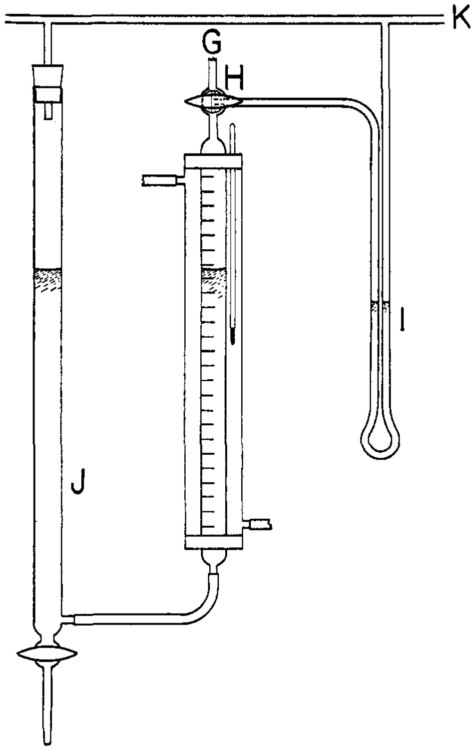

Fig. 2.

Before a run was begun the entire apparatus was swept out with carbon dioxide. During a run an atmosphere of carbon dioxide at atmospheric pressure was kept over the water being displaced by allowing a slow stream of carbon dioxide to enter through K.

Results

In Table I are summarized the results of duplicate runs on the rate of decarboxylation of mesitoic acid in 83.3% sulfuric acid at various temperatures. The values of *k* are those calculated for a first order process. In the last line of the table is the result of a run made at 80.0° with methyl mesitoate. Duplicate runs were made in all instances with the exception of methyl mesitoate. The calculations for *k* were based on the first volume reading that indicated equilibrium conditions (*e. g.*, complete solution of the mesitoic acid) had been attained. At 90.0°, eighty seconds elapsed, and nearly half the volume of carbon dioxide had been evolved before the readings were significant. At 50.0°, nine-hundred seconds elapsed, and about 9% of the gas was evolved before the first significant volume reading was made. The results of a

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(6) Barnes, *Org. Syntheses*, **21**, 77 (1941).

(7) Newman, This Journal, **63**, 2431 (1941).

typical run are shown in Table II. In Table III are summarized the results of duplicate runs on the effect of changing acid concentration on the rate constant. The effect of percentages of sulfuric acid lower than 81.8% could not be investigated because the solubility of mesitoic acid fell off markedly below this percentage.

TABLE I

DECARBOXYLATION OF MESITOIC ACID IN 83.3% SULFURIC ACID

Temp., °C.	$k \times 10^3$ sec.$^{-1}$	
50.0	0.123	0.119
60.0	0.486	0.482
70.0	1.61	1.47
80.0	4.82	5.04
90.0	13.7	14.0
80.0	4.79[a]	

[a] This run was made on methyl mesitoate.

TABLE II

DECARBOXYLATION OF MESITOIC ACID IN 83.3% SULFURIC ACID AT 60.0°

t (sec.) $\times 10^{-2}$	$V_\infty - V$ ml. CO_2	$k \times 10^3$ sec.$^{-1}$
0	37.25	
3	33.23[a]	
6	28.78	0.483
9	24.92	.479
12	21.46	.486
15	18.52	.487
21	13.69	.492
27	10.19	.493
33	7.55	.494
48	3.65	.491

[a] Values of k calculated on basis of this volume as zero point.

TABLE III

DECARBOXYLATION OF MESITOIC ACID AT 80.0° IN VARIOUS STRENGTHS OF SULFURIC ACID

H_2SO_4, %	$k \times 10^3$ sec.$^{-1}$	
81.8	4.73	4.53
83.3	4.82	5.04
84.7	4.95	4.95
86.1	4.85	4.70
86.1[a]	4.95	
88.2	4.25	4.51
91.3	3.03	3.10
94.4	1.40	1.37
96.9	0.184	0.185
100	0	

[a] Anhydrous sodium sulfate (2.0 g.) was added to this run.

Individual values of k for any particular run varied from the average by 0.5 to 2.6%. The average yield of carbon dioxide for all runs was 91%, not taking into account the gas remaining dissolved in the reaction mixture. To determine the yield of mesitylene, 20 g. of mesitoic acid was heated with 150 cc. of 83.3% sulfuric acid at 80° for ninety minutes. The mixture was cooled and the upper layer was separated carefully and diluted with ether. The ether solution was washed with aqueous sodium bicarbonate and then dried over calcium chloride. The ether was removed by distillation and the residue distilled at atmospheric pressure in a modified Claisen flask. The yield of mesitylene, b. p. 161–161.5°, $n^{20}\text{D}$ 1.4992 was 12.2 g., 84%. There was no forerun or residue.

Mesitylenesulfonic Acid.—The formation of mesitylenesulfonic acid as a secondary product of the elimination reaction was detected in the 83.3 to 96.9% sulfuric acid solutions. Cooling of the reaction mixture of the run made in 83.3% sulfuric acid caused deposition of a very small amount of crystals. A definite layer of mesitylene was formed. In stronger acid solutions the layer of mesitylene became successively smaller and the amount of crystals deposited after the mixture was cooled became greater until in 88.2% sulfuric acid no layer of mesitylene was obtained. In sulfuric acid between 91.3 and 96.8% strength no crystals separated from the cooled reaction mixture; dilution with weaker sulfuric acid caused the sulfonic acid to separate. The sulfonic acid obtained in some of the runs was recovered by suction filtration through a sintered glass funnel. It was then triturated with cold concentrated hydrochloric acid, suction filtered, washed with concentrated hydrochloric acid, and dried over potassium hydroxide. After being allowed to come to equilibrium with the atmosphere, it melted at 75–76.5°. This is apparently the dihydrate, reported as melting at 77°.[5,8] It was identical with a sample prepared by shaking mesitylene (0.4 cc.) with 86.1% sulfuric acid (10 cc.) at 80.0° for forty minutes.

Treatment of the sulfonic acid (0.4 g.) with 83.3% sulfuric acid (5 cc.) at 45° for eight hours caused no discernible separation of a mesitylene layer. Mesitoic acid (0.4 g.), treated in the same manner, yielded a definite layer of mesitylene (0.1–0.2 cc.).

Hydrolysis of Methyl Mesitoate.—Methyl mesitoate (6 g.) was dissolved in 50 cc. of 83% sulfuric acid and the solution left standing at room temperature for twenty minutes. The solution was poured onto crushed ice. The white precipitate was removed by suction filtration and was washed thoroughly with water. The yield of mesitoic acid, m. p. 150–152°, was 5.0 g., 91%. When a small amount of methyl mesitoate was shaken in a test-tube with 75% sulfuric acid and warmed slightly on the steam-bath, the insoluble oily ester was replaced by a white precipitate of mesitoic acid in a few minutes.

Discussion

The decarboxylation of mesitoic acid in strong sulfuric acid is a pseudo first order process, the rate varying with changing acid concentration. Methyl mesitoate likewise was decarboxylated in a pseudo first order process. The decarboxylation of the ester proceeded via preliminary hydrolysis

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(8) Rose, *Ann.*, **164**, 55 (1872).

to mesitoic acid rather than by elimination of the entire carbomethoxy group. Preliminary hydrolysis to the acid was suggested by the fact that the pseudo first order rate constant *k* for carbon dioxide evolution from the ester in 83.3% sulfuric acid at 80.0° had essentially the same value as the constant for mesitoic acid under the same conditions (see Table I). It was then found that methyl mesitoate was hydrolyzed to the acid rapidly and completely within a few minutes when dissolved in 83.3% sulfuric acid. Hydrolysis occurred even in warm 75% sulfuric acid in which the ester was not very soluble. Thus the use of sulfuric acid of around 100% strength to hydrolyze the alkyl esters of mesitoic acid[7,9] is not essential.

In sulfuric acid above 83.3% an increasing amount of the mesitylene liberated in the decarboxylation reaction was sulfonated to give mesitylenesulfonic acid. That the mesitylenesulfonic acid is not an intermediate in the formation of mesitylene was shown by the fact that mesitylene was obtained from methyl mesitoate (the ester rather than the acid was used because of its more ready solubility) under conditions that failed to affect mesitylenesulfonic acid. Thus, when both methyl mesitoate and mesitylenesulfonic acid were treated with 83.3% sulfuric acid at 45° for eight hours, the former gave a definite layer of mesitylene; the latter did not.

The effect of changing acid concentration on the pseudo first order constant *k* is summarized in Table III. No straight line relationship between log *k* and the Hammett acidity function, H_0, is found. Consequently, the rate of the reaction is not proportional to the concentration of the conjugate acid of mesitoic acid, BH^+, alone, and the rate-determining step is not a first order decomposition of BH^+.[10a,10b]

The change in pseudo first order rate constant with acid concentration is interpretable on the basis that the rapid and reversible formation of the conjugate acid, BH^+, as shown in step a, is followed by the rate determining step b, the reaction of BH^+ with water to yield mesitylene, M, and carbon dioxide, and regenerate oxonium ion. Actually, the mechanism a + b is indistinguishable from c, but in either instance the transition state would contain water as well as hydrogen ion and mesitoic acid.

$$\text{(a)}\quad B + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} BH^+ + H_2O$$

$$\text{(b)}\quad BH^+ + H_2O \xrightarrow{k_2} M + H_3O^+ + CO_2$$

$$\text{(c)}\quad B + H_3O^+ \xrightarrow{k_3} M + H_3O^+ + CO_2$$

$$\text{(d)}\quad M + H_2SO_4 \longrightarrow MSO_3H + H_2O$$

The reasoning applied by Zucker and Hammett[10a,c] to the enolization of acetophenone in perchloric acid solutions up to 3.6 *M* may be employed here, for in this enolization the rate-determining step is the reaction of the conjugate acid of the ketone with water. Accordingly, the Brönsted rate equation for the rate-determining step in the decarboxylation of mesitoic acid is

$$v = k_2 a_{BH^+} a_{H_2O} / f_{x^+}$$

$$v = k_2 K_1 a_B a_{H_3O^+} / f_{x^+} \text{ since } a_{BH^+} a_{H_2O} = K_1 a_B a_{H_3O^+}$$

hence

$$k = \frac{v}{C_B} = \frac{k_2 K_1 C_{H_3O^+} f_B f_{H_3O^+}}{f_{x^+}}$$

where *f* is the activity coefficient and x^+ refers to the transition complex. The assumption is made that

$$f_B f_{H_3O^+} / f_{x^+} = \text{constant}$$

as was done by Zucker and Hammett in the enolization of acetophenone, for the same components are present in the transition complex as in the reactants. It follows that if *b* is the rate-determining step then *k* is proportional to $C_{H_3O^+}$. Changes in *k* thus should parallel changes in oxonium ion concentration with per cent. sulfuric acid. Oxonium ion concentration in strong sulfuric acid has to date not been measurable. However, the variation in *k* with concentration of sulfuric acid parallels what would be expected to be the changes in oxonium ion concentration. An examination of Table III discloses little variation in the rate constant with change in sulfuric acid concentration in the region of a one to one molar ratio of sulfuric acid and water, with the maximum value of the rate constant at monohydrate strength. One would expect the point of maximum concentration of oxonium ion to be at about the point of molar equivalence of water and sulfuric acid (see, for example, the statements of Hammett[11]). Furthermore, the concentration of oxonium ion would not be expected to vary much about this point. For example, a slight increase in sulfuric acid concentration should lead to a greater tendency to form oxonium ion but this would be compensated for by a decrease in the water concentration. Similarly a slight increase in water concentration would by mass action tend to increase the concentration of oxonium ion, but this is compensated for by a decrease in the sulfuric acid concentration. As the concentration of water is decreased the rate constant begins to drop off almost linearly, as might be expected. However, if the rate constant is proportional to oxonium ion concentration, then it might also be expected that the rate would drop off linearly to zero at 100% sulfuric acid concentration, but instead the rate constant dips down to nearly zero in the region of 97% acid. The fact that the rate constant drops off more rapidly than oxonium ion concentration is probably due to the fact that the concentration of one of the reactants, BH^+, is reduced by formation of the ion, $(CH_3)_3C_6H_2CO^+$, which apparently exists to a large ex-

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(9) Hammett and Treffers, THIS JOURNAL, **59**, 1708 (1937).

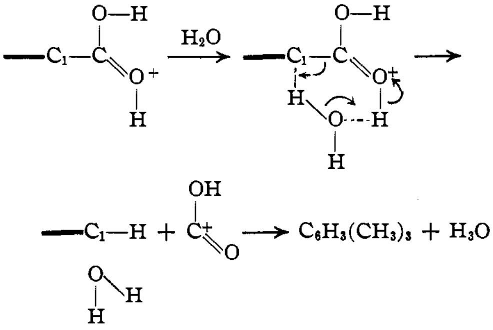
(10) (a) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 273-281; (b) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932); (c) Zucker and Hammett, *ibid.*, **61**, 2791 (1939).

(11) Hammett, *Chem. Reviews*, **16**, 68 (1935).

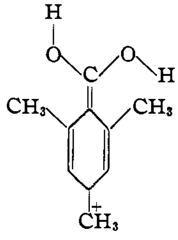
tent even in 97% sulfuric acid. Hammett and Treffers,[9] as well as Newman,[7] have clearly demonstrated the presence of this ion in 100% sulfuric acid solutions of mesitoic acid.

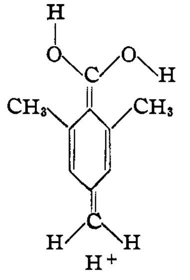
The concentration of bisulfate ion could conceivably follow the same sort of variation as the values of *k* in Table III. However, if the pseudo first order rate constant were proportional to bisulfate ion concentration, it would imply that the rate-controlling step in the decarboxylation is a reaction between mesitoic acid and the bisulfate ion. It is difficult to conceive of a mechanism whereby this could occur. Furthermore, the decarboxylation occurs in other acids, such as sirupy phosphoric acid.[1] A run was made in which excess bisulfate ion was introduced by the addition of sodium sulfate. The rate constant was virtually unchanged (see Table III). This is to be expected if the reaction follows the scheme a + b or c, since excess bisulfate ion increases the concentration of water and B, and decreases the concentration of oxonium ion and BH^+. If bisulfate ion enters the rate equation the velocity should have been substantially increased.

Since the indicated proportionality between the pseudo first order rate constant *k* and $C_{H_3O^+}$ shows the probable presence of water in the transition state, it is suggested that the reaction may take the following steric course. The heavy line represents the mesitylene nucleus, and the carbon atom attached to the carboxyl group is C_1, with the carboxyl group being out of the plane of the ring



A shift of electrons as indicated by the arrows would then lead to the formation of the products. The necessary presence of bulky *ortho* substituents thus would have two functions, both the result of steric inhibition of coplanarity of the protonated carboxyl group and the mesitylene nucleus. Firstly, resonance interaction of this group with the ring is damped. That is to say, resonance structures such as I and II are inhibited. This results in a weakening of the bond holding the carboxyl group due to decreased double-bond character of the bond. Secondly, the group is forced into a favorable geometric position for the transition complex pictured to form. The electrophilic hydrogen in the water molecule next to C_1 is thus situated in a position where it may complex readily with the field of the π-orbital[12] (*i. e.*, favorably situated for electrophilic attack at C_1).[13]





II

In Fig. 3 are plotted log *k* against 1/*T* for the decarboxylation in 83.3% sulfuric acid. From this plot an activation energy of 27.4 kilocalories for the reaction is calculated. The *PZ* factor is 4.4 × 10^{14}.

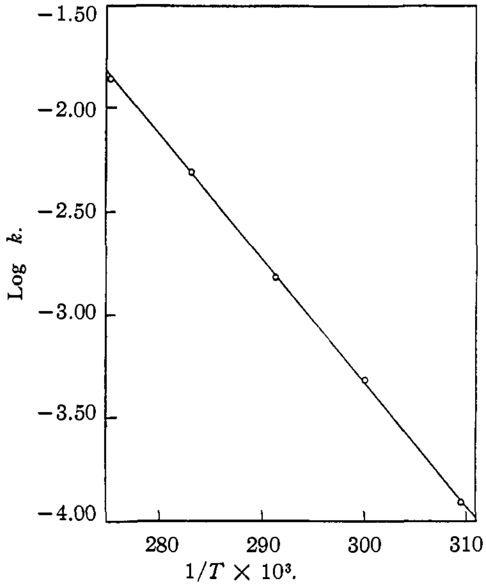


Fig. 3.

A study of the elimination of other groups and a possibility of using this type of reaction as a measure of oxonium ion concentration in strong sulfuric acid solutions is in progress.

The author wishes to thank Mr. H. K. Latourette for invaluable assistance in preparing the diagrams and graphs.

Summary

1. A kinetic study was made of the decarboxylation of mesitoic acid in 81.8 to 100% sulfuric acid solutions by following the rate of carbon dioxide evolution. The reaction is a pseudo first order process, the rate varying with changing acid concentration. The activation energy is 27.4 kilocalories in 83.3% sulfuric acid.

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[12] Dewar, *J. Chem. Soc.*, 781 (1946).

[13] It appears likely that allyl mesitoate should by a similar mechanism undergo a rearrangement to allylmesitylene and carbon dioxide.

2. The change in the pseudo first order constant with percentage sulfuric acid follows changes expected for oxonium ion concentration, taking into consideration the formation of the carbonyl ion, $(CH_3)_3C_6H_2CO^+$. From this it can be concluded that the probable rate-controlling step is the reaction between the conjugate acid of mesitoic acid and water.

3. The decarboxylation of methyl mesitoate in strong sulfuric acid was shown to proceed by way of intermediate hydrolysis to mesitoic acid.

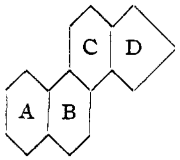
RECEIVED FEBRUARY 2, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Use of 4-Substituted Hydrindenes in the Preparation of Cyclopentanophenanthrene Derivatives[1]

BY RODERICK A. BARNES[2] AND LOUIS GORDON[3]

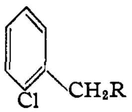
The synthesis of substances having the cyclopentanophenanthrene nucleus has usually been carried out by building up rings C and D starting with a substituted benzene or naphthalene.



The alternate approach involving construction of rings A and B from a hydrindene derivative has not been previously employed.[4] The 5-substituted hydrindenes which are the major products of the usual aromatic substitution reactions on hydrindene could cyclize in either of two ways.[5] In the present work this alternate approach has been applied by starting with 4-substituted hydridenes, which can cyclize only at the desired position.

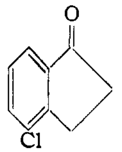
The starting material 4-chlorohydrindene[6] was most conveniently prepared in large quantity from *o*-chlorotoluene.

The conversion of I to the *o*-chlorobenzyl halides (II, III) was effected by bromine, N-bromosuccinimide, and sulfuryl chloride in 98, 82 and 76% yields, respectively.[7] The reaction of sodiomalonic ester with either II or III produced the desired ester (IV) in 76% yield; in addition there was isolated a crystalline by-product, m. p. 79°, which is believed to be the dialkylation product, ethyl di-(*o*-chlorobenzyl)-malonate. The acid (V) was produced in nearly quantitative yield by refluxing IV with a mixture of acetic and hydrochloric acids. The cyclization of V to 4-chloro-1-hydrindone (VI) and subsequent reduction to VII were carried out according to the method of Fieser and Hershberg.[6] Catalytic reduction of the ketone (VI) with platinum and hydrogen also produced VII in good yield; however, the chlorine atom was hydrogenolyzed if the reduction was allowed to proceed after the theoretical amount of hydrogen had been absorbed. The over-all yield of 4-chlorohydrindene (VII) by this procedure was 55%.

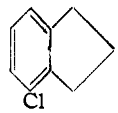


I, R = H
II, R = Br
III, R = Cl

IV, R = CH(COOEt)$_2$
V, R = CH$_2$COOH

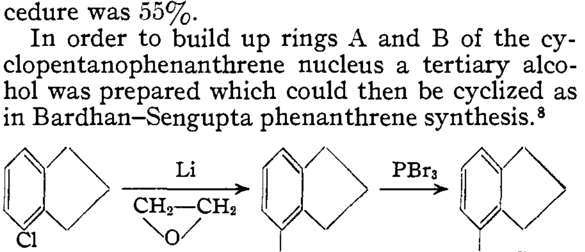


VI



VII

In order to build up rings A and B of the cyclopentanophenanthrene nucleus a tertiary alcohol was prepared which could then be cyclized as in Bardhan–Sengupta phenanthrene synthesis.[8]



VII VIII IX

The reaction of 4-hydrindenyl lithium with ethylene oxide takes place more readily and in better yield (82%) than is usually the case with analogous Grignard reagents; this is undoubtedly due

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[1] Presented in part at the New York meeting of the A. C. S., September, 1947.

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[3] Submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, Department of Chemistry, Columbia University, June, 1948.

[4] By analogy with some natural steroids it might be anticipated that an aromatic ring C would be difficult to reduce to the perhydro system.

[5] The cyclization of γ-5-hydrindenylbutyric acid yields only the linear ketone, 5,6,7,8-tetrahydrobenz[f]indanone-5, Sengupta, *J. Ind. Chem. Soc.*, **16**, 89 (1939).

[6] Fieser and Hershberg, THIS JOURNAL, **59**, 394 (1937), have prepared this substance in ca. 45% over-all yield from *o*-chlorobenzaldehyde.

[7] *o*-Chlorobenzyl chloride is now commercially available.

[8] This general method for preparation of the phenanthrene ring system was first described by Bardhan and Sengupta, *J. Chem. Soc.*, 2520 (1932), and was later elaborated by others; (a) Cook and Hewett, *ibid.*, 1098 (1933); (b) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 288 (1936); (c) Kon, *J. Chem. Soc.*, 1081 (1933).