

Benzoylcyanamide.—The ammonium salt obtained from 9.6 g. of benzoylisocyandichloride (above) was dissolved in 30 cc. of warm water, and the solution poured with shaking into 40 cc. of hot 3 *N* hydrochloric acid. An immediate precipitate of benzoylcyanamide was formed in a yield of 85%. It was purified by crystallization from water followed by drying *in vacuo* over concentrated sulfuric acid; m. p. 140°. ^{7,8} *Anal.* Calcd. for C₈H₈ON₂: N, 19.17. Found: N, 19.03.

(8) Diels and Wagner, *Ber.*, **45**, 876 (1912).

Summary

1. Benzoylisocyandichloride and ammonia do not interact to yield Traube's benzoylguanidine formed by the action of ethyl benzoate on guanidine.

2. It reacts with ammonia in both ether and alcohol solutions to form the ammonium salt of benzoylcyanamide in excellent yield.

NEW HAVEN, CONN.

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Catalytic Oxidations. II. Oxidations in the Cycloparaffin Series

BY NICHOLAS A. MILAS AND WILLIAM L. WALSH¹

In a previous paper² a technique was developed for the catalytic oxidation of compounds which readily polymerize on heating, of solids which decompose at their melting point and in general of compounds of low volatility. Inasmuch as very little work of this type has been done in the cycloparaffin series,³ we undertook to investigate the catalytic oxidation of cyclohexane and cyclopentane and some of their derivatives. We have found that in all cases the chief solid products were maleic acid and its anhydride. Table I summarizes some of our typical runs in this field together with the optimum conditions used. These results may be contrasted with those obtained when cyclohexene⁴ and cyclohexanol⁵ are oxidized in solution in which case adipic acid

inter alia is the chief product formed. However, at higher temperatures and under the conditions of our experiments adipic acid itself goes over to maleic acid. Apparently at relatively high temperatures maleic acid is one of the most stable products formed in catalytic oxidations of substances of four or more carbon atoms joined in a chain or a ring. This generalization is amply confirmed by the patent literature in this field.

Experimental Part

Apparatus and the Catalyst.—The apparatus was the same as that previously described² except for the addition of an extra spiral trap immersed in a carbon dioxide freezing mixture. This modification was found to trap completely all products condensable at the temperature of solid carbon dioxide. In various runs passage of the exit gases through two calcium chloride drying towers and a final weighed U-tube filled with silica gel showed no increase in weight of the latter.

The catalyst used throughout this work was vanadium pentoxide deposited on pumice. Its preparation and activation were also described in our first paper.

Organic Materials.—Most of the materials were those of the purest quality supplied by the Eastman Kodak Company, but further purified when their physical properties failed to agree with those recorded in the literature.

The cyclopentadiene was made by fractionating several times the technical grade cyclopentadiene through a 23-inch (58-cm.) Fenske column and the fraction boiling at 40–44° was collected and used in our experiments. To prepare cyclopentane, 80 g. of the purified cyclopentadiene was reduced in an Adams apparatus using 2 g. of platinum oxide catalyst. The product from this reduction was fractionated through a column and the fraction boiling at 48–50° showed no unsaturation and was therefore collected and used in our experiments.

Analytical Procedure.—To determine the unoxidized hydrocarbons the condensates in the various traps were combined into a special volumetric flask the neck of which

TABLE I
SUMMARY OF TYPICAL EXPERIMENTS

Substance	Optimum <i>t</i> , °C.	Molal ratio air/substance	Time of contact, sec.	% Yield of maleic acid	
Cyclohexane	350	205	3.6	19.7	19.78
Cyclohexene	410	109	1.6	30.94	30.89
Cyclohexanone ⁶	328	17	
Cyclohexanol ⁶	365	14.8	
Cyclopentane	410	135	1.6	25.46	25.50
Cyclopentadiene	410	126	1.6	32.4	
Adipic acid	410	...	1.6	15.64	

(1) Abstracted from Part II of the Ph. D. Dissertation of William L. Walsh, M. I. T., June, 1936.

(2) Milas and Walsh, *THIS JOURNAL*, **57**, 1389 (1935).

(3) Cf. Wilken-Jorden, *J. Chem. Met. Mining S. Africa*, **32**, 283 (1932); *C. A.*, **26**, 5406 (1932).

(4) Willstätter and Sonnenfeld, *Ber.*, **46**, 2952 (1913); Schrauth, U. S. Patent 1,921,101 (1933); Milas and Sussman, *THIS JOURNAL*, **59**, 2345 (1937).

(5) Ellis, "Organic Syntheses," Coll. Vol. 1, 1932, p. 18; Foster, *ibid.*, Vol. XIII, 1933, p. 110.

(6) Brooks, B. S. Thesis, M. I. T., June, 1935.

was graduated so that the volume of the unoxidized hydrocarbons could be read directly. In calculating the yields of maleic acid per pass this portion was deducted from the total amount passed. The maleic acid was determined both by titration and by the precipitation method described in the previous article. Absence of acidic products other than maleic acid in the reaction mixture was indicated by the close agreement between the amounts of this acid estimated by both methods.

In the oxidation of adipic acid, however, a modification of the usual procedure for the precipitation of barium maleate was necessary to prevent precipitation of the barium salt of any unoxidized starting material. This was accomplished by omitting the addition of alcohol for the complete precipitation of the barium salt which was collected and weighed as before. A correction for the small amount of barium maleate left in solution was applied using the solubility measurements of Weiss and Downs.⁷

To prove definitely that in every compound oxidized the acid formed was maleic acid, it was converted into fumaric acid under the influence of light and in the presence of bromine as the catalyst. The barium salt was also analyzed and two representative analyses are given below.

Anal. Calcd. for $C_4H_2O_4Ba \cdot H_2O$: Ba, 51.02. Found: Ba, 51.13, 50.78.

In the oxidation of cyclohexane and cyclohexene the presence of benzene in the unoxidized material was shown by conversion to *m*-dinitrobenzene with the usual nitrating mixture at the temperature of the steam-bath. Pure cyclohexane was unattacked under the same conditions. To estimate the benzene quantitatively in the presence of cyclohexane the following procedure was adopted. In a 30-cc. Pyrex flask with a 25-cm. neck graduated to 0.05 cc. was placed 5 cc. of the hydrocarbon mixture and 20 cc. of 10% fuming sulfuric acid added. The mixture was then shaken at room temperature for one-half hour, cooled to 0° and carefully diluted with successive small quantities of water until the unsulfonated hydrocarbon layer could be measured on the graduated neck of the flask. Blank experiments using a 50-50 mixture of benzene and cyclohexane gave an accuracy of 1%. Estimated by this procedure, the percentage of benzene in the hydrocarbon material recovered from the various runs with cyclohexane under different conditions of temperature, time of contact, etc., varied from 12 to 25% of the total. Recovered material from the oxidation of cyclohexene was saturated to bromine and consisted entirely of benzene.

Benzoquinone was identified in small quantities among the solid oxidation products of cyclohexane and cyclohexene. Formaldehyde and carbon dioxide were also identified in the exit gases of all oxidations herein reported.

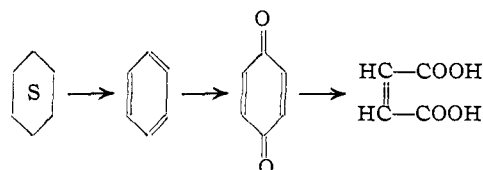
Discussion of Results

In addition to the runs recorded in Table I a complete study of the oxidation of cyclohexane was made at times of contact from one to three and six-tenths seconds, at temperature intervals of 30° from 320 to 470° and at molal ratios of air to cyclohexane from 31 to 245. Similar studies were made for each of the other hydrocarbons

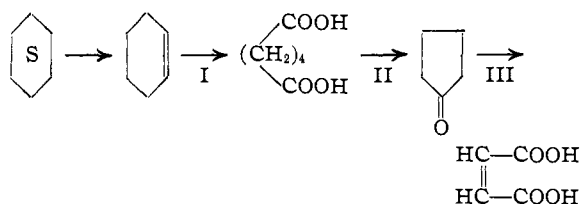
(7) Weiss and Downs, *THIS JOURNAL*, **45**, 2341 (1923).

listed in Table I and for complete data and curves the reader is referred elsewhere.¹

It already has been shown that in the oxidation of both cyclohexane and cyclohexene, benzene and quinone were isolated as two of the intermediate products. Furthermore, we have established that under the conditions of our experiments benzene is oxidized in part to maleic acid. It would appear, therefore, that the oxidation of cyclohexane may follow the course



However, inasmuch as the catalytic oxidation of adipic acid resulted in the formation of maleic acid and higher yields of the latter were similarly obtained from cyclohexene itself, one would tend to adopt an alternative view in which the oxidation proceeds via cyclohexene and adipic acid.



Furthermore, the production of formaldehyde is much more easily accounted for by this view than by the first. Step I of this series of reactions is in accord with similar oxidations of cyclohexene in the liquid phase; step II is a well known decarboxylation reaction, while we have confirmed step III by the catalytic oxidation under similar conditions of cyclopentanone. It is quite possible that the oxidation of cyclohexane proceeds by both of these mechanisms although a third possibility in which cyclohexane rearranges at the temperature of the reaction to methylcyclopentane and the latter oxidizes to maleic acid should not be excluded.

Summary

1. The catalytic oxidation of cyclohexane, cyclohexene, cyclohexanol, cyclohexanone, cyclopentane, cyclopentanone, cyclopentadiene and adipic acid using vanadium pentoxide as the catalyst to produce maleic acid as the chief solid product has been discussed.

2. Two alternative views with a possible

third one have been proposed to account for the cycloparaffin series.
course of the oxidation of hydrocarbons in the CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE SUBTROPICAL HORTICULTURE LABORATORY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Identification of Acetaldehyde in the Steam Distillate of the Peel of Citrus Fruits

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A preliminary study on the relation of acetaldehyde to physiological disorders of citrus fruits under cold storage conditions suggested the advisability of determining whether this substance is produced in the rind of the fruit. Vapors of acetaldehyde have been observed by Nelson² to produce brown spot and storage spot on oranges and grapefruit. Hall and Wilson³ have detected traces of this aldehyde in the aqueous residue from ether extraction of Valencia orange juice. Positive identification of acetaldehyde in the apple has been established by Power and Chesnut⁴ and by Thomas,⁵ and in the pear by Harley and Fisher.⁶ The latter have found an accumulation of larger quantities of aldehyde in pear tissue affected with scald and breakdown than in normal fruit. These facts, coupled with the demonstration of toxicity symptoms produced by acetaldehyde vapors, suggested the possibility that acetaldehyde may play an important role as an intermediate product in the oxidation of the respiratory substrates of citrus fruits.

Experimental

Samples of finely ground peel from 10 oranges, 15 lemons, and 6 grapefruit were steam distilled from a 5-liter flask in an all-glass apparatus. By using two receiving flasks in series containing a solution of 1.2% sodium bisulfite it was found that all the aldehyde was absorbed in the first receiver. Since total aldehyde was determined by Tomoda's⁷ modification of Ripper's⁸ procedure, the loss of bisulfite through the escape of sulfur dioxide or oxidation by air did not interfere.

Exact comparisons cannot be made between

(1) The assistance of the junior author was made available by a research grant from the California Fruit Growers' Exchange, Los Angeles.

(2) Nelson, *J. Agr. Research*, **46**, 695 (1933).

(3) Hall and Wilson, *THIS JOURNAL*, **47**, 2575 (1925).

(4) Power and Chesnut, *ibid.*, **42**, 1511 (1920).

(5) Thomas, *Biochem. J.*, **19**, 927 (1925).

(6) Harley and Fisher, *J. Agr. Research*, **35**, 983 (1927).

(7) Tomoda, *J. Soc. Chem. Ind.*, **48**, 76 (1929).

(8) Ripper, *Monatsh.*, **21**, 1079 (1900).

TABLE I
ALDEHYDE CONTENT OF CITRUS PEEL IN MILLIEQUIVALENTS

	Oranges		Eureka lemon	Marsh grapefruit
	W. navel	Valencia		
Grams peel	730	635	695	615
Fraction no. 1	0.302	0.352	0.529	0.391
2	.042	.077	.063	.053
3	.019	.072	.038	.030
4	.015	.042	.025	.030
5	.009			
Total	.387	.543	.655	.504
Per 100 g. of peel	.053	.086	.094	.082

the several varieties because of different stages of maturity of the samples. In the W. navel 800 ml. of distillate was obtained for all fractions, while in the other varieties 500 ml. was caught for each fraction. The rapid drop from the first fraction to the next suggests that most of the aldehyde is produced in the rind during the process of respiration and is not formed by the breakdown of substances during the course of distillation. In one case the rind residue after distillation was kept under sterile conditions for one week and then subjected to a second distillation. Each of the four fractions taken gave about the same amount of aldehyde as the last fraction of the first distillation. Further substantiating evidence on the formation of the aldehyde in the process of fruit metabolism has been obtained by collecting the vapors from air passed through frozen ground peel or over whole fruit and into bisulfite. In one case nearly 0.05 milliequivalent of aldehyde was recovered from each 100 g. of frozen ground lemon rind for a period of two weeks. The recovery of aldehyde from air passed over whole fruit was much less. Apparently the aldehyde is present in the fruit in a form which is more readily released by distillation.

For a colorimetric test of the aldehydes present in the steam distillate the Rimini reaction⁴ was employed. Indigo blue changing to yellow or brown indicates the presence of acetaldehyde,