in the distillate. It is probable then that xylene resulted from the dehydration accompanied by cyclization of an unsaturated octyl alcohol or aldehyde.

Summary

The reactions of acetaldehyde over a zinc chromite catalyst at 360° under a pressure of 210 atmospheres of hydrogen resulted in the formation of a complex mixture of saturated and unsaturated alcohols, aldehydes and esters. After hydrogenation of this product over nickel the following products were identified and estimated: *n*-butanol, *p*-xylene, *n*-hexanol and the esters of acetic, butyric and caproic acids. The chief components of the mixture were ethyl acetate, butyl acetate and ethyl caproate. There were also produced in considerable amounts higher alcohols, lactones, hydrocarbons and acids. The synthesis of these products may be accounted for as the result of aldol and Tischtschenko-like reactions accompanied by such dehydrations, hydrogenations, autoxidation–reductions and intramolecular rearrangements as have been demonstrated previously to occur over oxide catalysts.

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THE PREPARATION OF FLUORENONE FROM FLUORENE AND FROM DIPHENIC ACID

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In the extension of various studies in progress in this Laboratory[1] it became necessary to secure an adequate supply of fluorenone. Of the numerous reactions in which the formation of fluorenone has been noted, the most promising seemed to be the oxidation of fluorene. Since the published methods do not indicate the best results, we have studied the process in detail. Our results are expressed in the specific directions and accompanying notes in the Experimental Part.

During the course of the work, however, it was observed that fluorenone could be obtained in substantially quantitative yield merely by the action of heat upon diphenic acid. Since the latter is readily preparable from commercial anthranilic acid, this mode of formation of fluorenone has the advantage of starting with conventional intermediates. Careful search of the literature yielded no reference to the action of heat alone upon diphenic acid save the statement[2] that when heated 10° above its melting point, (*i. e.*, at 238°) for half an hour, no diphenic anhydride was isolated. The

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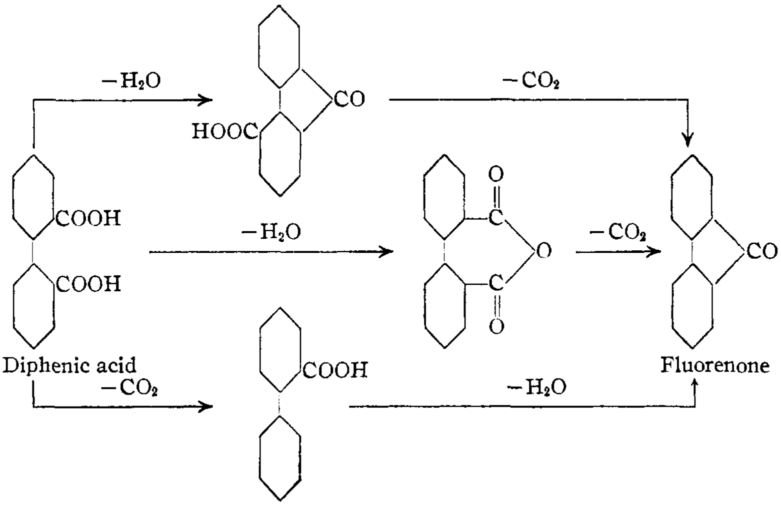
[1] Moore and Huntress, This Journal, **49**, 1324–1334, 2618–2624 (1927).

[2] Underwood and Kochmann, *ibid.*, **45**, 3071–7 (1923).

formation of fluorenone and carbon dioxide at higher temperature might be accounted for by several possible mechanisms, as follows:



Although our purpose was not to study the mechanism of the reaction, we have observed that the same result is obtained whether the starting material be diphenic acid, fluorenone-4-carboxylic acid or diphenic anhydride. Since a trace of diphenyl was found in the product, decarboxylation of diphenic acid evidently occurs very slowly as compared with ring closure. It seems probable, since the keto acid and diphenic anhydride can be interconverted under certain conditions, that both types of ring closure are involved.

By means of following the yields of carbon dioxide obtained upon heating fluorenone-4-carboxylic acid, it was found that a temperature of 360° sufficed for quantitative splitting out of carbon dioxide. Application of similar conditions to diphenic acid gave similar results. Acting on this preliminary study, runs were carried out on a larger scale, measuring the resultant fluorenone directly. It was found also that good results were obtained using a crude diphenic acid not subjected to the usual zinc dust–acetic acid purification.

Experimental Part

Fluorenone by Oxidation of Fluorene.—Equip a 3-liter ring-necked flask with an addition tube carrying a 500-ml. dropping funnel and a water condenser. Place in the flask 200 g. (1.2 moles)[2a] of technical fluorene (Note 1), add 400 ml. of technical glacial

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[2a] Since acceptance of this paper for publication, Mr. W. W. Hartmann, Department of Synthetic Chemistry, Eastman Kodak Company, has found that these directions may be applied to ten times the quantities here given, the oxidation being carried out in a 22-liter flask, and the final yield of pure recrystallized fluorenone amounting to 1450 g., or 66.8% of the calculated yield.

acetic acid and heat to gentle boiling. In another flask dissolve 600 g. of technical crystals of sodium bichromate (Note 2) in a warm mixture of 800 ml. of glacial acetic acid and 200 ml. of water. By means of the dropping funnel (Note 3) add this warm oxidizing solution in a slow steady stream to the boiling fluorene solution, so that boiling is never interrupted (Note 4) and no precipitation of lumps occurs. This will require about half an hour, as at first the reaction is quite vigorous. The mixed solutions are then refluxed for two and one-half hours more. The deep green liquid is then poured into 4 liters of ice water, allowed to stand for at least two hours and finally filtered through cloth on a 120-mm. Büchner funnel. The first wash water should contain a little sulfuric acid to avoid possible hydrolysis of the chromium salts, but the residue on the filter is presently washed free from all trace of chromic ion with pure water. If air dried at this point the bright yellow residue weighs 190–200 g.

Place the air-dried crude fluorenone in a 500-ml. Claisen distilling flask arranged to distil into an ordinary 300-ml. distilling flask, the Claisen side-arm serving as the only condenser. The Claisen flask is provided with the usual tube for the admission of air in vacuum distillations. The upper part of the Claisen may advantageously be wound with asbestos paper or twine. The flask is preferably heated with an electric cone heater as this facilitates smooth distillation. The receiver is connected to a vacuum pump (suitably protected from vapors and preferably arranged with pressure regulator) and the fluorenone distilled under reduced pressure. Toward the end of the distillation the clear bright yellow liquid will commence to acquire an orange tinge, the appearance of which serves as a convenient signal to stop distillation. The temperature range of distillation is not particularly important because its purpose is merely to remove rubicene and other highly colored impurities which cannot be separated by crystallization. Fluorene, if still present, is removed during the subsequent recrystallization.

The clear bright yellow distillate is dissolved in that number of ml. of benzene numerically equal to its weight in grams, this solution is warmed and to it is slowly added twice the benzene volume of petroleum ether, b. p. 30–60°, in such a way that no permanent separation of precipitate occurs. On allowing this solution to stand, extraordinarily beautiful crystals of fluorenone separate. These are filtered off, washed with petroleum ether and dried in the air. The yield based on the original crude fluorenone is 60–70% of crystals melting at 83.0–83.5°, uncorr.

Notes on the Preparation of Fluorenone

1. The purification of the technical fluorene prior to oxidation has no advantage. When fluorene which had been four times recrystallized from alcohol to a freezing point of 113° was used in this process, 70% of pure fluorenone was ultimately obtained. Precisely similar treatment of unrecrystallized hydrocarbon gave repeatedly 60–65% of final pure product. This slight difference in yield does not warrant the time and trouble required for preliminary purification. In this connection the recommendation of Thiele and Henle[3] that fluorene is best purified by recrystallization from alcohol containing sodium ethylate was tested, but the color and freezing points of the product from alcohol with or without sodium ethylate were substantially the same.

2. The use of a higher proportion of sodium dichromate is without advantage, since it does not affect either the yield or purity of the final product. The proportion here recommended is that originally proposed by Graebe and Rateanu and appears to represent about the minimum. Substitution of the equivalent quantity of potassium dichromate makes no difference in the yield or purity of the product, and because of the much smaller solubility in the aqueous acetic acid it does not completely dissolve and is therefore inconvenient to handle. Fanto's recommendation that 10% of sulfuric acid

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[3] Thiele and Henle, *Ann.*, **347**, 296 (1906).

be added to the oxidizing mixture was tested but since tar formation resulted its use was abandoned.

3. Since the solution of sodium dichromate in acetic acid and water crystallizes at room temperature, it is recommended that the stock oxidizing solution be kept warm in the second flask and added to the dropping funnel in small increments.

4. During the first part of the oxidation external heating may not be required. Care should be taken, however, to see that constant vigorous ebullition of the liquid is not interrupted, as otherwise an impenetrable lump of hydrocarbon precipitates which redissolves only with difficulty, and generally leads to much unchanged fluorene. With vigorous boiling, however, the use of a motor stirrer is unnecessary.

5. In the literature the recrystallization of fluorenone from alcohol is usually recommended for purification. This has the disadvantages, however, that the ketone separates first as liquid phase, and that any unchanged hydrocarbon is not completely removed. The precipitation of fluorenone from benzene by means of petroleum ether not only serves to remove every trace of hydrocarbon but also yields magnificent crystals. From the mother liquor additional fluorenone can be precipitated by more petroleum ether. An extensive crystallographic examination of fluorenone from alcohol has been made by Fittig and Schmitz.[4]

6. Distillation of the crude oxidation product prior to recrystallization is imperative. The process removes highly colored substances such as rubicene which otherwise follow the ketone through the purification process. Under atmospheric pressure fluorenone boils at 341.5°.

Fluorenone from Heating Diphenic Acid

Action of Heat upon Fluorenone-4-carboxylic Acid.—A 100-ml. distilling flask was arranged to be heated by fused potassium nitrate–sodium nitrate mixture contained in a hemispherical iron pan, and provided with a suitable thermometer. By means of an inlet tube reaching nearly to its bottom, a stream of air could be aspirated through the flask. This air was admitted through a Kunz spiral absorption bulb containing 50% potassium hydroxide solution. As the air left the reaction flask it passed through a U-tube containing glass beads and concd. sulfuric acid and thence through a glass wool plug into a second Kunz bulb with 50% potassium hydroxide solution. This bulb was protected from possible adventitious atmospheric carbon dioxide with a soda-lime tube. By heating a weighed quantity of substance in the reaction flask the carbon dioxide evolved was carried along by the air stream to the second Kunz bulb and absorbed. Results on fluorenone-4-carboxylic acid are as follows.

Expt.	Acid, g.	Time, min.	Temp., °C.	CO_2, g.	% of calcd.
2	2.0246	20	320	0.0130	3.3
3	2.1225	135	330	.0962	23.2
4	1.8855	135	340	.3255	88.2
5	1.5210	120	360	.2625	88.5

The fluorenone-4-carboxylic acid used was prepared by the action[5] of sulfuric acid on diphenic acid.

Action of Heat upon Diphenic Acid.—For Expt. 7 the apparatus described above was employed. For the other runs, in which the fluorenone obtained was measured rather than the accompanying carbon dioxide, a distilling flask of suitable size was heated in the same heating bath and the distillate condensed in a test-tube cooled by ice water. After heating as indicated, the temperature was raised until distillation occurred at

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[4] Fittig and Schmitz, *Ann.*, **193**, 117–119 (1878).

[5] Moore and Huntress, THIS JOURNAL, **49**, 1329 (1927).

atmospheric pressure; the use of diminished pressure is possible but unnecessary. The diphenic acid employed was all prepared by the method of Huntress.[6]

Expt.	Acid, g.	M. p., acid, °C.	Time, min.	Temp., °C.	CO_2, g.	% CO_2	Fluorenone		M. p., u. c. dist. formd.
							Wt.	% yield	
7	2.0607	226–228	105	360	0.3728	99.5	...	..	....
9A	2.005	213–215	90	360	....	..	1.22	82	83.5–84.5
9B	10.10	213–215	90	360	....	..	7.52	89	83.5–84.5
12	50.0	213–223	90	360	....	..	29.8	80	70–80
13	50.0	226–228	90	360	....	..	33.7	91	75–82
14	100.0	220–225	30	360	....	..	63.0	85	....

Notes.—1. Run 7 was made to verify for diphenic acid itself the optimum temperature which had been found for fluorenone-4-carboxylic acid.

2. Examination of the product from Expt. 13 showed that the principal impurity was diphenyl. This hydrocarbon is readily removed by the benzene–petroleum ether recrystallization.

3. Various grades of diphenic acid were purposely employed. In Expts. 9A, 9B, 12 and 14 diphenic acid was used which had not been subjected to the usual zinc dust–acetic acid purification. The use of copper diphenate instead of diphenic acid[7] gave only a low yield (36%).

Action of Heat upon Diphenic Anhydride.—During the course of the work one experiment was carried out on diphenic anhydride. When 2.152 g. of this substance was heated for one hundred and twenty minutes at 360° in the apparatus of Expt. 7, there was obtained 0.4061 g. of carbon dioxide corresponding to a 96% yield of fluorenone.

Solubility of Fluorenone and of Diphenyl.—A few solubilities were determined at 23° with results as follows, expressed as grams of substance per gram of solvent.

Solvent	Fluorenone	Diphenyl
Alcohol (95%)	0.075	0.054
Carbon tetrachloride	.19	.43
Ether	.31	.75
Benzene	.68	1.00

Summary

1. Heating diphenic acid at 360° causes rapid and nearly quantitative conversion to fluorenone and carbon dioxide. No previous observation of this fact could be found in the literature. The method is well suited for the preparation of either small or large quantities of fluorenone.

2. Under the same conditions both diphenic and fluorenone-4-carboxylic acids give similar results. Because of this fact no conclusion can at present be drawn regarding the mechanism of the reaction.

3. The preparation of fluorenone by oxidation of fluorene has been critically examined, and an improved procedure worked out which gives 60–70% yields of pure fluorenone, using ordinary apparatus.

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[6] Huntress, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1927**, Vol. VII, pp. 30–33.

[7] *Cf.* Dougherty, THIS JOURNAL, **50**, 571–573 (1928).