acid the product (0.4 g.) was obtained in the form of colorless prisms which melted at 153–154° alone or when mixed with 9-benzylphenanthrene obtained from 9-phenanthrylmagnesium bromide and benzyl chloride.

Reaction of Diphenyl-9-phenanthrylcarbinol with Hydriodic Acid.—The carbinol (0.5 g.) was dissolved in 10 cc. of warm acetic acid, 1 cc. of hydriodic acid (d. 1.7) was added and the mixture was refluxed for one-half hour; the mixture of hydrocarbons which precipitated was filtered off; wt. 0.4 g. (no color with concentrated sulfuric acid). By recrystallization from toluene and from acetic acid the mixture was separated into approximately equal amounts of diphenyl - 9 - phenanthrylmethane (m. p. 175–176°) and the less soluble 1,2,3,4-dibenzo-9-phenylfluorene (m. p. 210–211°). The dibenzophenylfluorene crystallized from toluene in fine colorless needles; the melting point was unchanged when the compound was mixed with a sample of dibenzophenylfluorene which was synthesized by Koelsch[8] from 9-(α-hydroxybenzyl)-10-phenyl-phenanthrene and obtained by him from 1-biphenylene-3-phenylindene. The identity of the two hydrocarbons was further established by making the 9-benzoyl derivative by reaction of the hydrocarbon with sodium amalgam and benzoyl chloride; the benzoyl derivative of our hydrocarbon melted at 225–228° alone and when mixed with the 1,2,3,4-dibenzo-9-benzoyl-9-phenyl-fluorene of Koelsch.

Dehydration of Diphenyl-9-phenanthrylcarbinol (IX) to 1,2,3,4-dibenzo-9-phenylfluorene (X).—To a solution of 0.5 g. of the carbinol (IX) in 10 cc. of acetic acid was added 5 drops of concentrated sulfuric acid and the mixture was boiled. In a few seconds the intense green color of the solution changed to a brilliant red color and a large amount of colorless cubes precipitated; after five minutes of boiling all of the cubes had gone into solution and shortly after the clear hot solution deposited the hydrocarbon (X) in the form of fine needles; wt. 0.4 g.; m. p. 208–209°. The nature of the intermediate cubes has not been determined; the crystals melt at 156° and are converted at that temperature to the dibenzophenylfluorene (X).

Reduction of Biphenylene-9-phenanthrylcarbinol (VIII) to Biphenylene-9-phenanthrylmethane (VI).—The carbinol (VIII) (0.5 g.) was heated with 10 cc. of acetic acid containing 1 cc. of hydriodic acid (d. 1.7) for one hour; the product (0.45 g.) which precipitated was biphenylene-9-phenanthrylmethane (VI); m. p. 196–197° alone or when mixed with the product obtained from 9-phenanthrylmagnesium bromide and 9-bromofluorene.

1,2,3,4-Dibenzoanthracene (XII) from *o*-Tolyl-9-phenanthryl Ketone (XI).—The ketone (0.6 g.) was heated at its boiling point for forty-five minutes and then distilled at ordinary pressure; the solid distillate after recrystallization from xylene and from acetic acid yielded 0.2 g. of long straw-colored needles; m. p. 200–202°; Clar[5] reported 196–197°. In agreement with Clar the dibenzoanthracene gives a pale violet-red color with concentrated sulfuric acid; it yields a red picrate (m. p. 205°) and on oxidation with chromic acid gives 1,2,3,4-dibenzoanthraquinone.

Summary

A study has been made of the reaction of 9-phenanthrylmagnesium bromide.

Nine new 9-substituted phenanthrene derivatives have been synthesized by means of the Grignard reagent.

ANN ARBOR, MICHIGAN RECEIVED FEBRUARY 28, 1934

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[8] Dr. Koelsch kindly prepared the benzoyl derivative and compared it and the hydrocarbon with samples of the corresponding compounds that he had synthesized.

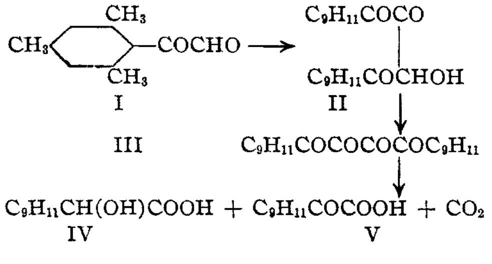
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Highly Activated Carbonyl Group. Dimesityl Tetraketone

BY ARZY R. GRAY AND REYNOLD C. FUSON

The search for compounds containing highly activated carbonyl groups whose properties can be studied[1] conveniently has been extended to the polyketones. The great reactivity of these compounds shows the remarkable cumulative effect of several carbonyl groups when placed in adjoining positions. It has now been possible to prepare dimesityl tetraketone—a compound which presents this same enhanced reactivity combined with a presumptive inertness of the terminal carbonyl groups.

The synthesis of dimesityl tetraketone was made possible by the discovery that mesitylglyoxal (I) undergoes a condensation of the benzoin type to give the corresponding acyloin (II). The acyloin dissolves in aqueous alkali but is reprecipitated upon acidification of the solution. With ferric chloride solution it gives a coloration. The acyloin is easily oxidized by nitric acid, which converts it into the tetraketone (III). The latter is a bright orange-red solid melting at 133–134°.



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[1] Gray and Fuson, THIS JOURNAL, **56**, 739 (1934).

It is readily hydrated, rapidly losing its color in contact with water. The hydrate, however, has not been obtained in a pure state.

The result obtained with phenylhydrazine is of great interest. Instead of being converted by this reagent into the expected phenylhydrazone or osazone, the tetraketone was *reduced* to the original acyloin. This is the reverse of the normal behavior of this reagent; phenylhydrazine has, however, been known to exhibit reducing properties in a few instances. Thus, alloxan is reduced to alloxantine by phenylhydrazine.[2] The tetraketone was unaffected by sulfur dioxide.

Attempts to prepare derivatives with hydroxylamine, semicarbazide and *o*-phenylenediamine have so far proved unavailing because these reagents are used in alkaline solutions. In the presence of alkali the tetraketone undergoes a complicated reaction which involves rearrangement and cleavage of the carbon chain. Four products have been isolated from this reaction. Two of these are acids and have been identified as mesitylglycolic acid (IV) and mesitylglyoxylic acid (V). The identification involved the reduction of mesitylglyoxylic acid to mesitylglycolic acid and the preparation of the methyl ester of the latter. A third product of the reaction is carbon dioxide. In addition to these three products there was formed a yellow solid which melted at 112.5–113.5°. This compound has not yet been identified.

Experimental

1,4-Dimesityl-3-ol-1,2,4-butanetrione.—To a solution of 5 g. of mesitylglyoxal in 10 cc. of 95% alcohol was added 0.2 g. of potassium cyanide and the mixture was stirred. The solution developed a red color and after two minutes began to deposit bright yellow crystals of the acyloin. After nine minutes the latter was separated on a filter and recrystallized from absolute alcohol. There was obtained a yield of 3.5 g. of product melting at 188.5–189.5°. An alcoholic solution of the acyloin produced a blue-green coloration with ferric chloride. The acyloin dissolved slowly in aqueous 5% sodium hydroxide solution at 70° to produce a bright red solution. Acidification of this solution by means of hydrochloric acid precipitated the original acyloin.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 75.0; H, 6.9. Found: C, 75.0; H, 6.7.

Dimesityl Tetraketone.—Fourteen and nine-tenths grams of 1,4-dimesityl-3-ol-1,2,4-butanetrione was added portionwise over a period of five minutes to 30 cc. of concentrated nitric acid. The mixture was stirred during the addition and at the end was gently heated until nitrogen oxides were no longer evolved. Water was added and the product was collected in a sintered glass crucible. After recrystallization from carbon disulfide the red tetraketone melted at 133.0–134.0°; yield, 92% of the theoretical amount.

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.4; H, 6.3. Found: C, 75.4; H, 6.3.

Hydrate.—A small amount of pure tetraketone was dissolved in glacial acetic acid and to the hot solution water was gradually added until the solution became turbid. The color of the solution changed from red to yellow and when cooled it deposited yellow crystals, but these were too unstable to be purified.

Action of Phenylhydrazine.—To a solution of 0.35 g. of dimesityl tetraketone in 25 cc. of 95% alcohol was added 0.54 g. of phenylhydrazine followed by 5 cc. of rinse alcohol. The solution, which rapidly became yellow, was heated almost to boiling and kept at this temperature for fifteen minutes. When allowed to cool the solution deposited 0.13 g. of 1,4-dimesityl-3-ol-1,2,4-butanetrione. The identity of the latter was confirmed by the method of mixed melting points and by the fact that nitric acid reconverted it into the tetraketone. Similar results were obtained when dry ether was used as solvent.

Rearrangement of the Tetraketone.—To 40 cc. of hot 20% potassium hydroxide solution was added gradually over a period of six minutes 7.8 g. of dimesityl tetraketone. During the addition, which was accompanied by shaking, heat was evolved and the tetraketone gradually went into solution. The solution was warmed for fifteen minutes, cooled, and then acidulated with hydrochloric acid. A color change from red to yellow was observed as well as the evolution of carbon dioxide. By ether extraction a yellowish-brown oil was obtained. By extraction with petroleum ether in a Soxhlet apparatus this oil was separated into two portions. The insoluble material was a solid melting at 152–153° and proved to be **mesitylglycolic acid.** The yield was 1.7 g.

The petroleum ether solution deposited crystals melting at 115–116.5° and whose neutral equivalent was 192.5 (calculated for mesitylglyoxylic acid, 192.1). It was identified as **mesitylglyoxylic acid** by a mixed melting point with an authentic specimen. Also, by reduction with sodium amalgam, it was converted into mesitylglycolic[3] acid. The yield of mesitylglyoxylic acid was 2.6 g.

From the petroleum ether mother liquor after the removal of the mesitylglyoxylic acid was isolated a bright yellow solid melting at 112.5–113.5°. It was soluble in most organic solvents and crystallized readily from alcohol or methanol. The yield was 1.2 g. This compound is being studied.

Summary

Mesitylglyoxal condenses to the corresponding acyloin ($C_9H_{11}COCH(OH)COCOC_9H_{11}$), from which dimesityl tetraketone is produced by oxidation.

The tetraketone is reduced to the acyloin by the action of phenylhydrazine.

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[2] Bogert and Davidson, *Proc. Nat. Acad. Sci.*, [3] **18**, 215 (1933); Pelizzari, *Gazz. chim. ital.*, **17**, 254 (1887).

[3] Feith, *Ber.*, **24**, 3542 (1891).

Alkali converts the tetraketone into a mixture which upon acidification yields carbon dioxide, mesitylglycolic acid, mesitylglyoxylic acid and a neutral compound which has not been identified.

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

The Nitration of α-Chloro and α-Bromoacetophenone

BY CHARLES BARKENBUS AND JOHN PHILIP CLEMENTS

m-Nitro-α-chloroacetophenone has been prepared with low yields by the action of diazomethane on *m*-nitrobenzoyl chloride[1] and by the chlorination of *m*-nitroacetophenone[2] though no yields were given. Since this compound was needed in fairly large amounts we have found that it can be prepared easily in good yields by the direct nitration of α-chloroacetophenone.

The nitration reaction has been widely used in studying orientation in the benzene ring. The most recent and interesting rule proposed for determining orientation in the benzene series is that of Latimer and Porter.[3] Since this rule neglects the influence of atoms beyond the so-called key atom the effect on nitration of the substitution of chlorine or bromine in the alpha position of acetophenone has been investigated. The results, listed in Table I, show that the introduction of chlorine or bromine does have some effect. This effect is not as large as that found in the nitration of esters of phenylacetic acid.[4]

TABLE I

PERCENTAGE OF META AND ORTHO–PARA ISOMERS FORMED DURING NITRATION

	Meta, %	Ortho–para, %
Acetophenone	65.5	34.5
α-Chloroacetophenone	68.5	31.5
α-Bromoacetophenone	69.4	30.6

These results are the average of several determinations.

Experimental

The method of determining the percentage of the different isomers formed during nitration has been worked out by Flurscheim and Holmes.[5] A modification of this method[4] was used though no consistent correction factor could be obtained and the extraction method had to be resorted to at that point. The data for a typical run on each of the three compounds are listed in Table II. The results stated in Table I are the average of at least three duplicate runs.

TABLE II

THE NITRATION, OXIDATION AND DETERMINATION OF THE ISOMERS

Substance	Acetophenone	α-Chloroacetophenone	α-Bromoacetophenone
Nitrated, g.	5.8576	7.3381	6.9592
Nitrated product obtained, g.	7.8530	9.3380	8.4880
Yield, %	97.6	98.5	99.4
Nitrated product oxidized, g.	2.8497	3.0000	3.5000
Acids obtained, g.	2.4802	2.0817	2.0680
Yield, %	86.0	83.0	86.5
Oxidation mixture, g.	0.4144	0.3610	0.3406
Nitrated product found by titration, g.	.4048	.3388	.3200
Unnitrated material present, g.	.0096	.0222	.0206
Unnitrated material (benzoic acid), %	2.32	6.15	6.05
2,4,6-Tribromoaniline obtained, g.	0.2760	0.2090	0.1941
Ortho and para nitrobenzoic acids, %	34.6	31.2	30.7
m-Nitrobenzoic acids, %	65.4	68.8	69.3

Preparation of *m*-Nitro-α-chloroacetophenone.—To 100 cc. of 96% sulfuric acid in a 500-cc. three-necked flask equipped with a dropping funnel and stirrer were added several pieces of carbon dioxide ice. The temperature dropped to at least −20° without outside cooling and could be easily kept at that temperature by further additions of the cooling agent. To this cold acid, 25 g. of α-chloroacetophenone of m. p. 57–58° was added slowly. When all of the solid had dissolved, a mixture of 20 cc. of 96% sulfuric acid and 15 cc. of fuming nitric acid (sp. gr. 1.50), cooled with carbon dioxide ice, was added rather rapidly, the temperature being kept below −20°. This required about twelve minutes and a longer period of addition was found to be detrimental. The solution was stirred for ten minutes at this temperature and then poured rapidly onto 500 g. of ice to which had been added some carbon dioxide ice. About 1200 cc. of ice water was then added and the light yellow solid filtered with suction and washed free from acid. The crude dry solid weighed 33 g. and was contaminated with unchanged α-chloroacetophenone, ortho and para isomers, and some benzoic acid.

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(1) Dale and Nierenstein, *Ber.*, **60**, 1026 (1927).

(2) Baker, *J. Chem. Soc.*, **134**, 2416 (1931).

(3) Latimer and Porter, THIS JOURNAL, **52**, 206 (1930).

(4) Yabroff and Porter, *ibid.*, **54**, 1199, 2507 (1932).

(5) Flurscheim and Holmes, *J. Chem. Soc.*, **131**, 448 (1928).