[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

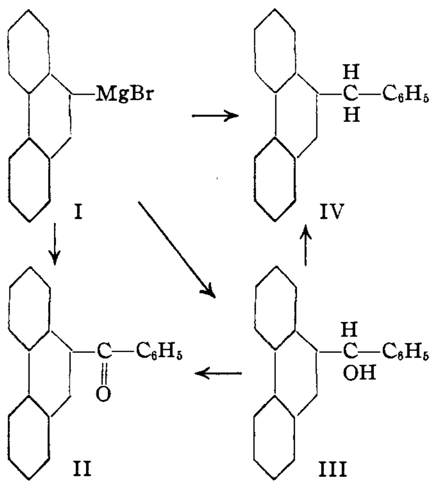
Syntheses of Phenanthrene Derivatives. I. Reactions of 9-Phenanthrylmagnesium Bromide

BY W. E. BACHMANN

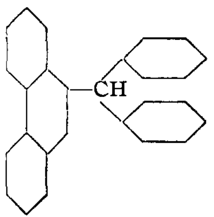
The importance of compounds containing the phenanthrene group makes it desirable to have methods of synthesis leading to derivatives of definite structure. The Friedel and Crafts reaction with phenanthrene which has been employed on a number of occasions for making phenanthrene derivatives has the disadvantage of giving isomeric derivatives which are often difficult to separate and whose structures must subsequently be determined. Specifically, we needed 9-benzoylphenanthrene in an investigation. Willgerodt and Albert[1] reported that 9-benzoylphenanthrene (m. p. 127°) is formed by the action of benzoyl chloride on phenanthrene in the presence of aluminum chloride, although they offered no proof of the structure of their product. Recently Mosettig and van de Kamp[2] from their experience with the condensation of phenanthrene with acetyl chloride expressed the view that the entering of the benzoyl group into the 9-position was doubtful. We decided to prepare the ketone by a method which would leave no doubt of the structure of the final product and we turned to the Grignard reagent from 9-bromophenanthrene. This Grignard reagent has been employed previously on only three occasions.[3] We have now carried out a number of experiments with 9-phenanthrylmagnesium bromide in order to determine its value for introducing the 9-phenanthryl group into molecules.

Synthesis of 9-Benzoylphenanthrene.—By interaction of 9-phenanthrylmagnesium bromide (I) and benzonitrile, followed by hydrolysis of the ketone-imine that is formed, 9-benzoyl phenanthrene (II) is obtained in the form of colorless needles melting at 89–90° instead of 127° as reported by Willgerodt and Albert. The identical product (m. p. 89–90°) is obtained from 9-cyanophenanthrene and phenylmagnesium bromide and also by oxidation of phenyl-9-phenanthrylcarbinol (III) which has been prepared from 9-phenanthrylmagnesium bromide and benzaldehyde. We are now engaged in synthesizing the isomeric benzoylphenanthrenes for comparison with the product of Willgerodt and Albert.

By reduction of their ketone Willgerodt and Albert obtained "9-benzylphenanthrene" as colorless leaflets melting at 91–92°. We have prepared 9-benzylphenanthrene (IV) by interaction of 9-phenanthrylmagnesium bromide and benzyl chloride and also by reduction of phenyl-9-phenanthrylcarbinol; both methods give a product crystallizing in prisms which melts at 153–154°. The relationships are apparent from the following scheme.



Reaction with Alkyl Halides.—The Grignard reagent reacts with alkyl halides to give 9-alkylphenanthrenes. In addition to benzyl chloride we tried the action of methyl iodide, diphenylbromomethane and 9-bromofluorene. The last three reagents give 9-methylphenanthrene, diphenyl-9-phenanthrylmethane (V) and biphenylene-9-phenanthrylmethane (VI), respectively. Triphenylchloromethane reacts rapidly with 9-phenanthrylmagnesium bromide but no crystalline product could be obtained from the reaction mixture.



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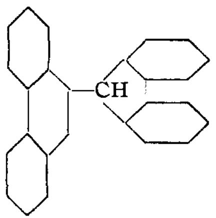

VI

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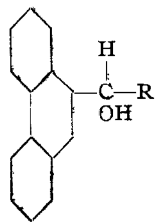
[1] Willgerodt and Albert, *J. prakt. Chem.*, [2] **84**, 383 (1911).

[2] Mosettig and van de Kamp, THIS JOURNAL, **55**, 3442 (1933).

[3] Pschorr, *Ber.*, **39**, 3128 (1906); Salkind and Lubinskaja, *ibid.*, **61**, 269 (1928); Shoppee, *J. Chem. Soc.*, 37 (1933).

Reaction with Aldehydes and Ketones.—9-Phenanthrylmagnesium bromide reacts normally with formaldehyde to give 9-phenanthrylcarbinol and with acetaldehyde and benzaldehyde to give secondary alcohols of formula VII (in which R is CH_3, C_6H_5). Reaction of the Grignard reagent with fluorenone gives biphenylene-9-phenanthrylcarbinol (VIII); with benzophenone diphenyl-9-phenanthryl-carbinol (IX) is formed.



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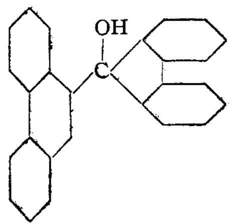
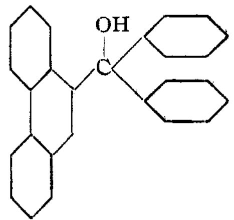


VIII



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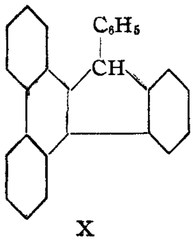
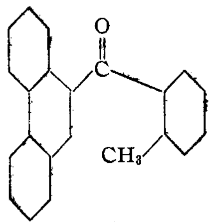


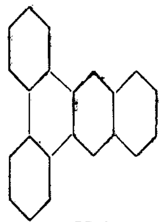
X

Biphenylene - 9 - phenanthrylcarbinol (VIII) is reduced by hydriodic acid quantitatively to biphenylene-9-phenanthrylmethane (VI). When diphenyl-9-phenanthrylcarbinol (IX) is heated with hydriodic acid, two products are formed; one of these is the normal reduction product diphenyl-9-phenanthrylmethane (V); the other product is formed not by reduction but by loss of the elements of water since the same compound is obtained in nearly quantitative yield when the carbinol is warmed with sulfuric acid in acetic acid. Triarylcarbinols frequently undergo dehydration to give 9-arylfluorenes and it was considered that such a reaction had taken place in this instance. Of the two likely compounds VI and X that could be formed in this manner only X (1,2,3,4-dibenzo-9-phenylphenanthrene) remained when it was found that the product was different from VI that had been prepared from 9-phenanthrylmagnesium bromide and 9-bromofluorene. Structure X was confirmed when it was found that the compound was identical with 1,2,3,4-dibenzo-9-phenylfluorene that was synthesized recently by Koelsch.[4]

Synthesis of *o*-Tolyl-9-phenanthryl Ketone (XI) and 1,2,3,4-Dibenzoanthracene (XII).—By hydrolysis of the ketone-imine that is produced by interaction of 9-phenanthrylmagnesium bromide and *o*-tolunitrile there is obtained *o*-tolyl-9 phenanthryl ketone (XI). This synthesis is of special interest inasmuch as Clar[5] was unable to isolate the ketone from the mixture of isomers that was obtained by condensation of *o*-toluyl chloride and phenanthrene. We have found that the pure *o*-tolyl-9-phenanthryl ketone is converted to 1,2,3,4-dibenzoanthracene (XII) when it is heated at its boiling point. Since Clar obtained this dibenzoanthracene by heating his mixture of ketones our results show that he actually had *o*-tolyl-9-phenanthryl ketone and also furnish proof of the structure of the dibenzoanthracene.



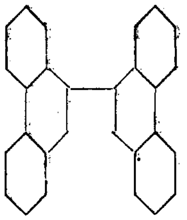
XI



XII

Reaction of the Grignard Reagent with Carbon Dioxide and with Chloroethyl Carbonate.—With carbon dioxide the Grignard reagent gives a good yield of phenanthrene-9-carboxylic acid and the method ranks with the recent process of Mosettig and van de Kamp[6] as a convenient method of preparing this acid. With chloroethyl carbonate the Grignard reagent gives the ethyl ester of phenanthrene-9-carboxylic acid. This reaction offers another method of obtaining rapidly phenanthrene-9-carboxylic acid (by hydrolysis of the ester) in excellent yield (90% based on the bromophenanthrene).

9-(9'-Phenanthryl)-phenanthrene.—The reaction between an aromatic Grignard reagent RMgX and anhydrous cupric chloride usually yields the hydrocarbon RR; 9-phenanthrylmagnesium bromide likewise gives the corresponding hydrocarbon 9-(9'-phenanthryl)-phenanthrene



XIII

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(4) Koelsch, This Journal, 56, 480 (1934).

(5) Clar, Ber., 62, 350, 1574 (1929).

(6) Mosettig and van de Kamp, This Journal, 54, 3328 (1932).

(XIII). Attempts to prepare the compound from 9-bromophenanthrene by reaction with copper and with sodium have so far been unsuccessful.

Chemiluminescence of the Grignard Reagent.—9-Phenanthrylmagnesium bromide exhibits a splendid chemiluminescence when it is exposed to air. In a dark room the greenish-blue light emitted when the solution is swirled in a flask open to the air is sufficient for reading several lines of journal type. When air is passed through the solution heat is developed and the salt of 9-hydroxyphenanthrene is formed. In a number of experiments we employed the disappearance of chemiluminescent property of the solution as an indication of the end of the reaction between the Grignard reagent and a reactant.

Conclusion.—In addition to the compounds mentioned the Grignard reagent reacts with a number of other substances, including sulfur. We are also extending our study to the isomeric bromophenanthrenes, some of which may prove useful in synthesizing compounds leading to cholesterol and ergosterol. We plan to determine the migration aptitude of the phenanthryl group in the pinacol rearrangement and also the effect of the group on the dissociation of hexaarylethanes and of pentaarylethanes.

Experimental

9-Bromophenanthrene.—The 9-bromophenanthrene obtained by heating phenanthrene dibromide was purified by distillation under reduced pressure followed by recrystallization from ligroin (60–80°); our product melted at 65–66° while the value usually reported in the literature is 63°. If the bromophenanthrene is not quite pure a dark green color and some red precipitate is formed at the start of the reaction with magnesium; the pure bromide gives a transparent light-brown solution without intermediate color effects.

Preparation of the Grignard Reagent.—Pschorr used a mixture of ether and anisole as the solvent in the preparation of the Grignard reagent because with ether alone the reagent separates as a solid. We have found that a mixture of ether and benzene keeps the reagent in solution; moreover, the benzene is more easily removed from the final product than is anisole. For the experiments listed in Table I a mixture of 6.45 g. of 9-bromophenanthrene, 0.65 g. of magnesium ribbon, 0.05 g. of iodine, 15 cc. of ether and 15 cc. of benzene was refluxed on a steam-bath for four to five hours; numerous quantitative experiments showed that 95–98% of the theoretical amount of magnesium reacts in this length of time. Since the reagent reacts with oxygen, the reaction mixture was always protected from free access of air by means of a mercury trap and the reaction was often run in an atmosphere of nitrogen. The excess of magnesium (about 0.05 g.) was removed from the clear solution and the 9-phenanthrylmagnesium bromide was then treated with a reactant. When the reaction was complete the product was hydrolyzed. The essential data are given in Table I. In all cases the products were obtained as colorless crystals. The analyses were carried out by W. S. Struve.

Preparation of 9-Benzoylphenanthrene.—(a) From 9-phenanthrylmagnesium bromide and benzonitrile: see Table I.

(b) From 9-cyanophenanthrene: 9-cyanophenanthrene was prepared in excellent yield from 9-bromophenanthrene and cuprous cyanide according to the directions of Mosettig and van de Kamp;[6] the product after separation from inorganic material by extraction with chloroform was purified by distillation and recrystallization from chloroform and alcohol; the 9-cyanophenanthrene was obtained as needles which melted at 109.5–110°. Werner reported 103° and Mosettig and van de Kamp gave 103–104° for the melting point.

A mixture of 5.4 g. of 9-cyanophenanthrene and a solution of phenylmagnesium bromide prepared from 6 g. of bromobenzene was refluxed for five hours. The reaction mixture was then worked up as described in note (a) under Table I; yield of 9-benzoylphenanthrene, 3 g. (42%); m. p. 89–90°.

(c) By oxidation of phenyl-9-phenanthrylcarbinol. The secondary alcohol was oxidized to the ketone by making the bromomagnesium salt RR'CHOMgBr and reaction of the salt with benzaldehyde, which abstracts H and MgBr.[7] To a cold filtered solution of ethylmagnesium bromide which had been prepared from 0.8 g. of ethyl bromide in 10 cc. of ether was added 5 cc. of benzene and then phenyl-9-phenanthrylcarbinol until no further evolution of ethane gas occurred; 1.53 g. of carbinol was required; after a short time a large amount of the bromomagnesium salt of the carbinol precipitated. Two cc. of benzaldehyde was added and the resulting mixture was refluxed on a steam-bath for one hour; hydrolysis gave 1.0 g. (66%) of 9-benzoylphenanthrene (m. p. 89–90°) which was identical with the product obtained by methods (a) and (b).

The ketone was also prepared conveniently from 9-bromophenanthrene without isolation of the intermediate carbinol. Thirteen grams of 9-bromophenanthrene was converted to the Grignard reagent; the solution was cooled to −5° and treated gradually with a solution of 5 g. of benzaldehyde in 25 cc. of benzene, the temperature being kept below 0°. The mixture was kept cold for twelve hours; during this time a large amount of the carbinol salt precipitated. The liquid was decanted and to the residual solid was added 10 cc. of benzaldehyde; after the mixture had been refluxed for one hour it was hydrolyzed. The ketone was purified by distillation under reduced pressure (b. p. 235–240° (1 mm.)) and recrystallization; yield, 6.2 g.

Reduction of Phenyl-9-phenanthrylcarbinol to 9-Benzylphenanthrene.—A mixture of 0.5 g. of the carbinol, 0.5 g. of iodine, 0.5 g. of red phosphorus, 1 cc. of water and 10 cc. of acetic acid was refluxed for one hour, filtered hot and poured into water. By recrystallization from acetic

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[7] Gomberg and Bachmann, This Journal, 52, 4967 (1930); Shankland and Gomberg, *ibid.*, 52, 4973 (1930).

TABLE I

REACTIONS OF 9-PHENANTHRYLMAGNESIUM BROMIDE

Abbreviations: alc, alcohol; bz, benzene; chl, chloroform; ac, acetone; lig, ligroin; MeOH, methyl alcohol; tolu, toluene; s, soluble; sls, slightly soluble; vs, very soluble; i, insoluble; h, hot.

Reagent added		Reaction time, hrs.			Yield					Solubility					Analyses, %	
Name	G.	Cold	Hot	Product	G.	%	M. p., °C.	Recryst. solvents	Cryst. form	Alc.	Ac.	Bz.	Color with H_2SO_4	Formula	Calcd.	Found
Benzonitrile[a]	3.2		5	9-Benzoylphenanthrene	4.6	65	89.5–90	Bz + lig	Broad needles	s	vs sls (lig.)	vs	Deep orange	$C_{21}H_{14}O$	88.9 5.1	89.4 5.0
o-Tolunitrile[b]	3.2		10	o-Tolyl 9-phenanthryl ketone	5.2	70	88–90	Alc + ac	Triangular prisms	sls	vs		Deep orange	$C_{22}H_{16}O$	89.2 5.4	89.5 5.5
Methyl iodide[c]	5		22	9-Methylphenanthrene	3.5	73	90–91	MeOH	Prisms							
Benzyl chloride	4		9	9-Benzylphenanthrene	4.8	72	153–154	Bz or HAc	Prisms	sls		s(h)	None	$C_{21}H_{16}$	94.0 6.0	93.2 5.9
Diphenylbromomethane[d]	6.5		10	Diphenyl-9-phenanthrylmethane	6.5	72	175–176	Bz + alc	Needles	sls		sls vs(h)	None	$C_{27}H_{20}$	94.2 5.8	94.4 5.9
9-Bromofluorene	6.5		6	Biphenylene-9-phenanthrylmethane	4.2	50	197–198	Bz	Diamonds	sls		s(h)	None	$C_{27}H_{18}$	94.7 5.3	93.9 5.3
Formaldehyde[e]	Exc.	12		9-Phenanthrylcarbinol	2.6	50	149	Bz + ac	Needles	s	vs	sls	Green-black			
Acetaldehyde[f]	1.8	6		Methyl-9-phenanthrylcarbinol	4.0	75	134–135	Bz	Needles	s	vs	sls	Black			
Benzaldehyde[g]	2.5	0.5 +	1	Phenyl-9-phenanthrylcarbinol	5.1	72	139.5–140.5	Bz + lig	Prisms	i(lig.)		sls vs(h)	Blue-green	$C_{21}H_{16}O$	88.3 5.8	88.7 5.7
Benzophenone[h]	5		6	Diphenyl-9-phenanthrylcarbinol	7.0	76	173–174	Bz + lig	Clusters of prisms		vs	s(h)	Green-blue	$C_{27}H_{20}O$	90.0 5.6	89.1 5.6
Fluorenone[i]	4		4	Biphenylene-9-phenanthrylcarbinol	4.8	60	189	Bz + lig	Prisms	i(lig.)		s vs(h)	Green	$C_{27}H_{18}O$	90.5 5.0	90.2 5.1
Carbon dioxide[j]	Exc.	5		Phenanthrene-9-carboxylic acid	3.9	70	251–252	Tolu + HAc								
Chloroethylcarbonate[k]	4		0.3	Ethyl ester of phenanthrene-9-carboxylic acid	3.1	50	58	Lig	Prisms							
Cupric chloride[l]	10		2	9-(9′-Phenanthryl)-phenanthrene	2.4	54	184–185	Chl + MeOH	Plates	i	sls	sls	None	$C_{28}H_{18}$	94.9 5.1	94.8 5.1
Oxygen[m]	Exc.	1		9-Hydroxyphenanthrene	1.1	23	144–146		Needles							

[a] The reaction mixture was hydrolyzed with cold dilute acetic acid; the aqueous layer was discarded and the ether–benzene solution of the ketone-imine was shaken with concentrated hydrochloric acid. The ketone-imine hydrochloride which precipitated in crystalline form was filtered off and was hydrolyzed to the ketone by heating it with 100 cc. of water for one hour. The 9-benzoylfluorene crystallizes slowly.

[b] The reaction mixture was treated as described in (*a*); the imine hydrochloride precipitated as an oil but solidified after a few minutes. The ketone which was obtained on hydrolysis did not crystallize when it was cooled; when, however, a few cc. of benzene was added the ketone crystallized immediately, apparently because of the formation of a complex with benzene; the latter is an excellent solvent for recrystallizing the ketone. For analysis a sample of ketone was kept at 150° at 1 mm. for two hours.

[c] A 90% yield of product melting at 84–86° was obtained; purification was accomplished by distillation and recrystallization.

[d] An immediate exothermic reaction took place as soon as the diphenylbromomethane was added and in a short time a considerable amount of precipitate appeared.

[e] Mosettig and van de Kamp, THIS JOURNAL, 55, 2998 (1933), obtained this carbinol (m. p. 149–149.5) by catalytic reduction of phenanthrene-9-aldehyde.

[f] Pschorr obtained this carbinol by the same reaction but did not mention the yield; Mosettig and van de Kamp[2] prepared it (m. p. 135.5–136°) by catalytic reduction of 9-acetylphenanthrene.

[g] The Grignard reagent was kept below 0° throughout the slow addition of 2.5 g. of benzaldehyde in 10 cc. of benzene; after a short time a large amount of the colorless crystalline salt of the carbinol precipitated.

[h] The diphenyl-9-phenanthrylcarbinol crystallizes with benzene of crystallization; these crystals melt at 128–129° with bubbling, the melt solidifies and the resulting solid melts at 172–174°. The solvent can be removed by heating the compound at 100° under reduced pressure.

[i] The product holds benzene of crystallization tenaciously; the solvent can be removed by heating the compound at 120°.

[j] Shoppee obtained this acid in 50% yield by the same reaction; he used a mixture of ether and anisole as solvent in the preparation of the Grignard reagent.

[k] The amount of ester actually formed is greater than 50%; the lower yield results from losses in purification. This was shown in another experiment by hydrolyzing the crude reaction product with warm alcoholic potassium hydroxide solution; 5.0 g. (90%) of phenanthrene-9-carboxylic acid was obtained.

[l] An immediate reaction occurred on addition of the anhydrous cupric chloride. *Mol. wt.* of 9-(9′-phenanthryl)-phenanthrene. Calcd. 354. Found (Menzies method in benzene): 365, 354, 359.

[m] Thirty cc. of benzene was added to the Grignard reagent; the latter was cooled and dry air free from carbon dioxide was passed into the solution; after half an hour only a slight chemiluminescence was visible. The mixture was hydrolyzed with dilute acid and the 9-hydroxyphenanthrene was extracted from the ether–benzene solution by dilute alkali.

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.

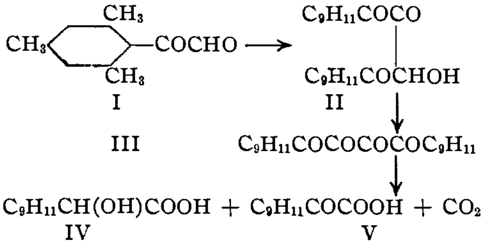
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

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).