

2-amino gives none the 2-oxy gives a strong color.

There is marked similarity in ultraviolet absorption of (I) and (III), respectively, to the 6-amino- and 6-oxypyrimidines. A correspondence of the ultraviolet absorption of one of Windaus' oxidation products of the vitamin to that of a 6-oxypyrimidine has been noted by Smakula.<sup>5</sup> This similarity does not extend to the 2-amino- and 2-oxypyrimidines (Figs. 1 and 2).

The authors are grateful to Dr. H. T. Clarke and Dr. Oskar Wintersteiner for microchemical and spectrographic facilities at the Department

(5) A. Smakula, *Z. physiol. Chem.*, **230**, 231 (1934).

of Biochemistry of the College of Physicians and Surgeons. We are also indebted to the Carnegie Corporation for financial support through the Carnegie Institute of Washington.

### Summary

The acidic product of sulfite cleavage,  $C_6H_9N_3SO_3$  (I), has the chemical characteristics and ultraviolet absorption of a 6-aminopyrimidine.

Strong hydrochloric acid converts this product into a second substance,  $C_6H_8N_2SO_4$  (III), having the properties of a 6-oxypyrimidine.

NEW YORK, N. Y.

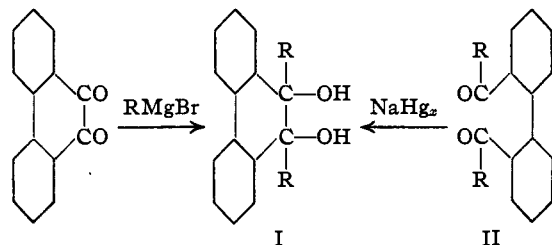
RECEIVED MARCH 28, 1935

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

## The Pinacol-Pinacolone Rearrangement. VII. The Rearrangement of 9,10-Diaryldihydrophenanthrenediols<sup>1</sup>

BY W. E. BACHMANN AND EDITH JU-HWA CHU

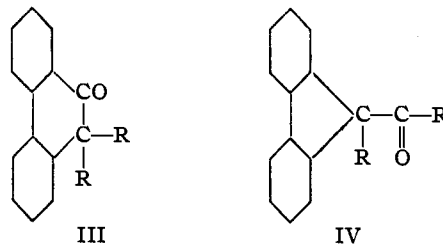
In a previous paper<sup>2</sup> of this series the preparation and rearrangement of three 9,10-diaryldihydrophenanthrenediols were described; in these pinacols the phenyl, *p*-tolyl and anisyl groups were the aryl radicals R (Formula I). We are now reporting the results obtained on six new pinacols of this type in which the aryl groups are *m*-tolyl, *p*-biphenyl,  $\alpha$ -naphthyl, phenetyl, *p*-chlorophenyl and *p*-fluorophenyl. These compounds were prepared in two ways: by interaction of phenanthrenequinone and a Grignard reagent and by reduction of 2,2'-diacylbiphenyls (II) by sodium amalgam.



Actually, the two methods yielded two different pinacols in each case; the products are probably diastereoisomers. The yields and properties of these pinacols are presented in Table I.

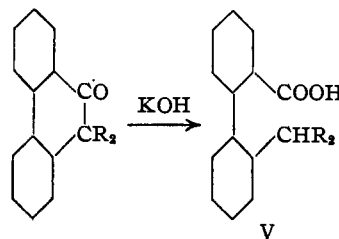
**Rearrangement of the Pinacols.**—By treatment with a hot solution of iodine in acetic acid, the diaryldihydrophenanthrenediols lost a molecule of water and were rearranged to 9,9-diaryl-

phenanthrones (III) exclusively; in no instance was there any rearrangement to the isomeric pinacolone, acyl-aryl-fluorene (IV). The stereoisomeric pinacols gave the same diarylphenanthrone.



In all, nine groups, phenyl, *m*-tolyl, *p*-tolyl, anisyl, phenetyl, *p*-chlorophenyl, *p*-fluorophenyl, *p*-biphenyl and  $\alpha$ -naphthyl, have been found to migrate during the rearrangement of diaryldihydrophenanthrenediols in preference to a transformation taking place from a phenanthrene to a fluorene ring. The diarylphenanthrones are listed in Table II.

**Scission of 9,9-Diarylphenanthrones to 2-(Diarylmethyl) - 2' - carboxylbiphenyls.**—By



(1) From part of the Ph.D. dissertation of Miss Chu.

(2) Bachmann, *THIS JOURNAL*, **54**, 1969 (1932).

TABLE I  
 9,10-DIARYLDIHYDROPHENANTHRENEEDIOLS

-Dihydrophenanthrenediol	Recryst. solvent	Cryst. form	Yields, %		M. p., °C.	Calcd.		Analyses, %	
			Grignard reaction	NaHg <sub>2</sub> reduction		C	H	Found C	Found H
Diphenetyl-	Acetone	Heavy plates	33		140.5-141	79.6	6.2	79.5	6.2
Diphenetyl-	Acetone	Tetrag. prisms		59	155.5			80.1	6.1
Di- $\alpha$ -naphthyl	Acetone	Long needles	31		263-264	87.9	5.2		<sup>a</sup>
Di- $\alpha$ -naphthyl-	Propanol	Fine prisms		70	204-204.5			87.7	5.2
Di- <i>p</i> -biphenyl-	Carb. tetr.	Granules	65		192-192.5	88.4	5.4	88.5	5.5
Di- <i>p</i> -biphenyl-	Acet. + alc.	Prisms		56	159-160			88.2	5.5
Di- <i>p</i> -chlorophenyl-	Carb. tetr.	Fine needles	44		187-188	Cl,	16.4		16.7
Di- <i>p</i> -chlorophenyl-	Acet. + alc.	Prisms		86	223				16.1
Di- <i>p</i> -fluorophenyl-	Chloroform	Needles	30		180-181.5	F,	9.5		9.5
Di- <i>p</i> -fluorophenyl-	Alcohol	Prisms		71	210-211				9.5
Di- <i>m</i> -tolyl-	Chloroform	Prisms	40	<sup>b</sup>	148.5-149	85.7	6.1	85.6	6.1

<sup>a</sup> Jezierski, *Roczniki Chem.*, **13**, 44 (1933), prepared this compound.

<sup>b</sup> Reduction of 2,2'-di-*m*-toluylbiphenyl gave an oil which did not crystallize; with the rearranging agent this oil yielded the pinacolone, 9,9-di-*m*-tolylphenanthrone.

 TABLE II  
 9,9-DIARYLPHENANTHRONES

-Diarylphenanthrone	Recryst. solvent	Cryst. form	Yield, %	M. p., °C.	Calcd.		Analyses, %	
					C	H	Found C	Found H
Diphenetyl-	Acetone	Needles	98	136-137		<sup>a</sup>		
Di- $\alpha$ -naphthyl-	Chlorobz.	Needles	98	258.5-259	91.5	4.9	90.9	4.9
Di- <i>p</i> -biphenyl-	Bz. + acet.	Cubes	98	253-253.5	91.6	5.2	91.3	5.2
Di- <i>p</i> -chlorophenyl-	Acetone	Plates	100	138-139	Cl,	17.1		16.8
Di- <i>p</i> -fluorophenyl-	Acetone	Prisms	98	170-170.5	F,	10.0		10.0
Di- <i>m</i> -tolyl-	AcOH	Plates	100	197-198		<sup>b</sup>		

<sup>a</sup> Bachmann and Sternberger, *THIS JOURNAL*, **55**, 3819 (1933). We have now synthesized this compound in 77% yield from di-*p*-hydroxyphenyl-phenanthrone [Goldschmidt, Vogt and Bredig, *Ann.*, **445**, 123 (1925)]; the disodium salt of the latter compound was shaken with diethyl sulfate and a slight excess of 10% sodium hydroxide for two days.

<sup>b</sup> See reference in Note *a*.

 TABLE III  
 2-(DIARYLMETHYL)-2'-CARBOXYLBIPHENYLS

-Methyl-2'-carboxylbiphenyl	Recryst. solvent	Cryst. form	Fusion temp., °C.	Time, min.	Yield, %	M. p., °C.	Calcd.		Analyses, %	
							C	H	Found C	Found H
Diphenetyl-	Alcohol	Fine needles	245	10	76	97-98	79.6	6.2	79.7	6.4
Di- $\alpha$ -naphthyl-	Alcohol	Fine prisms	300	10	83	215	87.9	5.2	87.7	5.1
Di- <i>p</i> -biphenyl-	Carb. tetr.	Rhomboid prisms	300	30	81	197-198	88.4	5.4	87.9	5.4
Di- <i>p</i> -chlorophenyl-	Alcohol	Needles	225	10	54	205-206	Cl	16.4		16.5
Di- <i>p</i> -fluorophenyl-	Alcohol	Needles	200	10	48	162	F	9.5		9.4
Di- <i>m</i> -tolyl-	Alcohol	Needles	245	10	86	90	85.7	6.1	86.1	6.1

fusion with potassium hydroxide the 9,9-diarylphenanthrones were converted to 2-(diaryl-methyl)-2'-carboxylbiphenyls (V) (see Table III). We are investigating whether these 2,2'-disubstituted biphenyls exist in optically active forms.

**Oxidation of Diaryldihydrophenanthrenediols to 2,2'-Diacylbiphenyls.**—A hot solution of chromic acid in acetic acid oxidized the pinacols to 2,2'-diacylbiphenyls (II). The structures of these diketones were established by synthesis; the compounds were obtained by running an Ullmann reaction on *o*-bromo-acyl-benzene, which had been prepared either by the Grignard reac-

tion or Friedel and Crafts reaction. The yields and properties of these compounds are shown in Tables IV and V.

### Experimental

**Preparation of 9,10-Diaryldihydrophenanthrenediols.**  
 (a) **Grignard Reaction.**—To the Grignard reagent prepared from 0.2 gram mole of aryl bromide (*p*-bromophenetole,  $\alpha$ -bromonaphthalene, etc.) in 120 cc. of ether was added 100 cc. of benzene and then 10.4 g. of phenanthrenequinone; the mixture was then refluxed on a steam-bath for twenty-four hours except in the case of diphenyldihydrophenanthrenediol for which only six hours were allowed. The product which was obtained by hydrolysis crystallized when it was stirred with methyl alcohol, alone

TABLE IV  
 2-BROMO-ACYL-BENZENES

-Benzophenone	Temp.	Recryst. solvent	Cryst. form	Yield, %		M. p., °C.	Analyses, %			
				F. & C. react.	Grig. react.		Calcd. Br	Cl, F	Found Br	Cl, F
2-Bromo-3'-methyl-	Refluxed	Acet. + lig.	Heavy plates	82	2	54.4	29.1		28.6	
2-Bromo-4'-ethoxy-	0°C.	Propanol	Diamonds	52	1.5	81	26.2		26.1	
2-Bromo-4'-phenyl <sup>a</sup>	Refluxed	Benzene	Heavy plates	63	2	90.5-91				
2-Bromo-4'-chloro-	Refluxed	Acet. + alc.	Needles	75	2	49-49.5	27.1	12.0	26.9	12.1
2-Bromo-4'-fluoro-	Refluxed	Acet. + alc.	Prisms	45	16	49.5-50	28.6	6.8	28.4	6.8
2-Bromophenyl $\alpha$ -naphthyl ketone <sup>b</sup>	Refluxed	Alcohol	Prisms	79	20	87				

<sup>a</sup> Gomberg and Bailar, THIS JOURNAL, 51, 2229 (1929), found a m. p. of 88.5°.

<sup>b</sup> Knoll and Cohn, *Monatsh.*, 16, 208 (1895), prepared this compound by the Friedel and Crafts reaction.

 TABLE V  
 2,2'-DIACYLBIPHENYLS

-Biphenyl	Recryst. solvent	Cryst. form	Yields, %		M. p., °C.	Analyses, %			
			Oxid. react.	Ulim. react.		Calcd. C	H	Found C	H
Di- <i>m</i> -toluyl-	AcOH	Prisms	63	38	105-106	86.1	5.6	85.8	5.6
Diphenetoyl-	Acetone	Rhomboid prisms	78	57	137-138	80.0	5.8	79.8	5.7
Di- $\alpha$ -naphthoyl-	AcOH	Plates	62	66	200 <sup>a</sup>				
Di- <i>p</i> -phenylbenzoyl-	Acet. + bz.	Threads	85	22	209.5-210	88.7	5.1	88.6	5.1
Di- <i>p</i> -chlorobenzoyl-	Acetone	Prisms	89	0	139-140	Cl	16.4		16.2
Di- <i>p</i> -fluorobenzoyl-	Acetone	Cubes	75	30	136.5-137.5	F	9.6		9.6

<sup>a</sup> Jezierski, Table I, Note a, reported 204.5-205°.

or mixed with acetone. All of the pinacols were obtained as colorless crystals by recrystallization.

(b) **Reduction by Sodium Amalgam.**—Two grams of 2,2'-diacylbiphenyl in 60 cc. of anhydrous ether was shaken with 114 g. of 1% sodium amalgam at room temperature for one week. Hydrolysis of the ether solution of the disodium pinacolate with dilute acetic acid gave the pinacol.

**Rearrangement of the Pinacols.**—A mixture of 0.003 gram mole of pinacol, 0.5 g. of iodine and 50 cc. of acetic acid was refluxed for an hour, cooled and poured into an aqueous solution of sulfur dioxide. The diarylphenanthrones were obtained as colorless crystals by recrystallization. All of the pinacols can be rearranged to the diarylphenanthrones by a mixture of acetyl chloride and acetic acid but in certain cases this reaction is slow.

In order to determine whether even a small amount of aryl-acylfluorene (IV) was formed, the crude rearrangement product in each case was heated for three days with a 25% solution of potassium hydroxide in methanol, a reagent capable of cleaving such pinacolones into arylfluorene and acid (phenetic, naphthoic, etc.); not even a trace of such acids could be detected.

**Oxidation of the Pinacols.**—A mixture of 0.03 gram mole of pinacol, 6 g. of chromic acid anhydride, 4 cc. of water and 150 cc. of acetic acid was heated on a steam-bath for one hour and was then refluxed for half an hour. The diketone which precipitated when the mixture was poured into water was obtained as colorless crystals by recrystallization.

**Preparation of 2-Bromo-acyl-benzenes.**—For the Grignard reaction a solution of 5 g. of *o*-bromocyanobenzene in 30 cc. of benzene was added to the Grignard reagent prepared from 0.054 gram mole of aryl bromide (*m*-bromotoluene, *p*-fluorobromobenzene,  $\alpha$ -bromonaphthalene) in 35 cc. of ether; after being refluxed for the time indicated

in Table IV, the mixture was treated with water and the imine was hydrolyzed to the ketone by hot dilute hydrochloric acid. The 2-bromo-3'-methylbenzophenone was distilled under reduced pressure (b. p. 180-181° at 5 mm.) before it was recrystallized.

In the Friedel and Crafts reaction 27 g. of aluminum chloride was added in portions to a solution of 16.3 g. of *o*-bromobenzoyl chloride and 0.074 gram mole of the compound to be coupled (biphenyl, phenetole, chlorobenzene) in 150 cc. of carbon disulfide (with chlorobenzene the carbon disulfide was omitted). After the reaction was complete (Table IV), the mixture was hydrolyzed and steam distilled.

**Synthesis of 2,2'-Diacylbiphenyls.**—A mixture of 2 g. of copper powder and 0.5 g. of 2-bromo-acyl-benzene was heated in a metal bath for one-half hour at 200° ( $\alpha$ -naphthyl, *p*-biphenyl-, *p*-fluorophenyl) or 250° (*m*-tolyl, phenetyl). The diketone was obtained from the cooled reaction mixture by extraction with acetone. We were unable to obtain the diketone from 2-bromo-4'-chlorobenzophenone.

**Cleavage of 9,9-Diarylphenanthrones by Potassium Hydroxide.**—One gram of 9,9-diarylphenanthrone was fused with 2 g. of potassium hydroxide in a metal-bath at the temperature shown in Table III. The cooled mass was digested with warm acetone and transferred to dilute hydrochloric acid. The free biphenyl acids were purified through their ammonium salts and finally by recrystallization. The acids hold water tenaciously.

**Analysis for Fluorine.**—A 0.25-g. sample (diaryldihydrophenanthrenediol, diarylphenanthrone, bromo-acyl-benzene) was fused with 0.25 g. of sucrose, 0.5 g. of potassium nitrate and 7 g. of sodium peroxide in a bomb. The melt was dissolved in water, nearly neutralized with hydrochloric acid and the filtered solution was made up to 250 cc. A 25-cc. portion was titrated with standard

thorium nitrate according to the modified procedure of Armstrong.<sup>3</sup>

### Summary

Six 9,10-diaryldihydrophenanthrenediols have been synthesized.

9,9-Diarylphenanthrones are formed by rear-

(3) Armstrong, *THIS JOURNAL*, **55**, 1741 (1933).

rangement of the pinacols.

The 9,9-diarylphenanthrones are cleaved into 2-(diarylmethyl)-2'-carboxylbiphenyls by fusion with potassium hydroxide.

The diaryldihydrophenanthrenediols are oxidized to 2,2'-diacylbiphenyls by chromic acid.

ANN ARBOR, MICHIGAN

RECEIVED APRIL 8, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BUREAU OF DAIRY INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

## The Addition of Mercaptans to Certain Double Bonds

BY BEN H. NICOLET

Some time ago the writer reported<sup>1,2</sup> the ready addition of *p*-tolylmercaptan to certain rather reactive double bonds (in  $\alpha,\beta$ -unsaturated ketones and esters) in the presence of sodium alcoholates. More recently, the sodium salt of benzalpyruvic acid proved so insoluble that the addition of mercaptans could not be carried out by this method.

It was, however, noted that Kohler<sup>3</sup> had found that sulfinic acids sometimes add to unsaturated ketones as such, without the addition of alkali. The corresponding experiment with mercaptans was most successful. Benzalacetophenone and either *p*-tolyl or benzyl mercaptan, when heated together on the water-bath without any catalyst, showed quite complete reaction in five minutes, though *not* in two minutes. The product was, as expected,  $\text{PhCH}(\text{SR})\text{CH}_2\text{COPh}$ , where R was either *p*-tolyl or benzyl. The corresponding addition of these mercaptans to benzalpyruvic acid,  $\text{PhCH}=\text{CHCOCOOH}$ , occurs about equally readily.

The addition of hydrogen sulfide to unsaturated ketones of this type has been reported in the presence of alkali as weak as sodium carbonate in alcohol suspension.<sup>4</sup> The writer has, however, found that hydrogen sulfide adds readily to benzalacetophenone in alcohol without even this amount of alkali.

Methyl cinnamate also presents a double bond of somewhat (although decidedly less) enhanced reactivity. Without catalyst, the addition of either of the mercaptans mentioned was doubtful

after five hours at 100°. With the addition, however, of 0.1 cc. of piperidine for 5 g. of ester, a good yield was obtained after two hours (but *not* after half an hour) at 100°.

Additions of these mercaptans to  $\alpha$ -acetylaminoacrylic acid, and to other aminoacrylic acid derivatives, are being reported elsewhere, in connection with a new synthesis of cystine which may have biological significance. The work described was undertaken primarily to throw light on the probability of the assumption of an addition of hydrogen sulfide or methyl mercaptan to methylenepyruvic acid,  $\text{CH}_2=\text{CHCOCOOH}$  (as yet unknown), as an early stage in a possible biological synthesis of methionine and homocystine. This point will be discussed further in another place.

On reëxamination of the literature, after completion of the work reported, it seems proper to call attention to the almost incredible reactivity of thioglycolic acid found by Holmberg,<sup>5</sup> and also to the unsaturated mercaptans of v. Braun and Plate,<sup>6</sup> which polymerize on standing.

### Experimental Part

$\beta$ -Phenyl- $\beta$ -benzylmercaptopropiophenone.—Equivalent quantities of benzalacetophenone and benzylmercaptan were mixed and heated for five minutes on the steam-bath. A good yield of pure product (m. p. 71°) was obtained after crystallization from alcohol. A reaction time of two minutes gave a much poorer yield.

*Anal.* (Parr bomb) Calcd. for  $\text{C}_{22}\text{H}_{20}\text{OS}$ : S, 9.64. Found: S, 9.78, 9.84.

Under similar conditions, but using *p*-tolylmercaptan, altogether similar results were obtained. The known  $\beta$ -phenyl- $\beta$ -*p*-tolylmercaptopropiophenone was obtained, m. p. 113°.<sup>1</sup>

(5) Holmberg, *Ber.*, **65**, 1349 (1932); Axberg and Holmberg, *ibid.*, **66**, 1193 (1933).

(6) V. Braun and Plate, *ibid.*, **67**, 281 (1934).

(1) Nicolet, *THIS JOURNAL*, **53**, 3066 (1931).

(2) Nicolet, *J. Biol. Chem.*, **95**, 389 (1932).

(3) Kohler and Reimer, *Am. Chem. J.*, **31**, 163 (1904).

(4) See Hooper, Macbeth and Price, *J. Chem. Soc.*, 1147 (1934), for a summary of the literature.