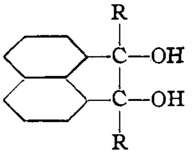
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

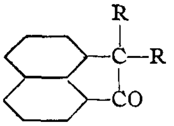
The Pinacol–Pinacolone Rearrangement. VIII. The Rearrangement of 7,8-Diarylacenaphthenediols

BY W. E. BACHMANN AND EDITH JU-HWA CHU[1]

Recently[2] we reported the results obtained on the rearrangement of a number of 9,10-diaryldihydrophenanthrenediols; in these compounds the simple aryl groups migrated exclusively and 9,9-diarylphenanthrones were formed. We have now turned our attention to the rearrangement of another class of cyclic pinacols, the 7,8-diarylacenaphthenediols (I).



I

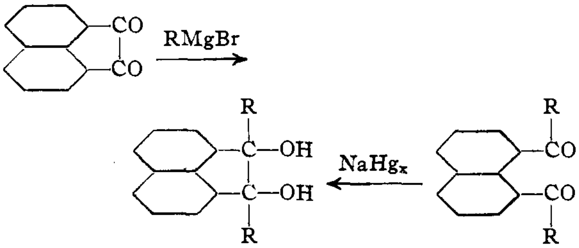


II

Acree[3] prepared 7,8-diphenylacenaphthenediol (I, R = phenyl) and reported that the compound remained unchanged when it was heated with acetyl chloride. Later, Beschke[4] obtained 7,7-diphenylacenaphthenone (II, R = phenyl) by heating the pinacol with acetic acid containing a small amount of hydrochloric acid.

We have now prepared seven new pinacols of this type in which the aryl groups, R, are *m*-tolyl, *p*-tolyl, *p*-biphenyl, *p*-anisyl, *p*-phenetyl, *p*-chlorophenyl and *p*-fluorophenyl. All of these pinacols were obtained from acenaphthenequinone through the Grignard reaction.

Since reduction of 2,2′-diacylbiphenyls by sodium amalgam gave 9,10-diaryldihydrophenanthrenediols which are diastereoisomers of the pinacols obtained by the Grignard reaction from phenanthrenequinone,[2] we have prepared several 7,8-diarylacenaphthenediols (I, R = phenyl, *p*-tolyl, *p*-chlorophenyl and *p*-fluorophenyl) by a similar reduction of 1,8-diacylnaphthalenes (III). Here, too, the pinacols prepared by reduction were diastereoisomers of those prepared by the Grignard reaction. It is of interest that solutions of the disodium salts of the diarylacenaphthenediols, like those of the diaryldihydrophenanthrenediols, are colorless, an indication that no appreciable dissociation into ketyl radicals takes place.[5]

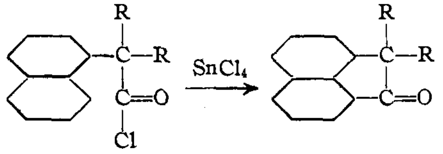


III

The yields and properties of the pinacols are shown in Table I.

Rearrangement of the Pinacols.—All of the pinacols were found to rearrange when they were heated with a solution of iodine in acetic acid. In every case the simple aryl group R was found to migrate exclusively with the formation of 7,7-diarylacenaphthenones (II). In the reaction the five-membered ring of the acenaphthene derivative was retained; no evidence of any tendency to form a four-membered ring was found. The stereoisomeric pinacols gave the same diarylacenaphthenone. The yields and the properties of the pinacolones are presented in Table II.

Two of the pinacolones, 7,7-diphenylacenaphthenone and 7,7-di-*p*-biphenylacenaphthenone, were synthesized by ring closure of diphenyl-α-naphthylacetyl chloride (IV, R = phenyl) and di-*p*-biphenyl-α-naphthylacetyl chloride (IV, R = *p*-biphenyl), respectively, by means of stannic chloride.



IV

7,8-Diarylacenaphthylenes.—The low yields of diarylacenaphthenones from the *p*-chlorophenyl and *p*-fluorophenyl pinacols were due to the formation of diarylacenaphthylenes (VI) through a side reaction. These compounds probably resulted through the action of hydrogen iodide present in the mixture of iodine and acetic acid; the pinacol is converted to the intermediate iodide (V) which yields the acenaphthylene (VI) by loss of a molecule of iodine.

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[1] From part of the Ph.D. dissertation of Edith Ju-Hwa Chu.

[2] Bachmann and Chu, THIS JOURNAL, **57**, 1095 (1935).

[3] Acree, *Am. Chem. J.*, **33**, 186 (1905).

[4] Beschke, *Ann.*, **369**, 200 (1909).

[5] Compare Bachmann, THIS JOURNAL, **55**, 1179 (1933).

TABLE I

7,8-DIARYLACENAPHTHENEDIOLS (I)

All of the compounds are colorless

-Acenaphthenediol	Recryst. solvent	Cryst. form	Yields, % Grignard reaction	Yields, % $NaHg_x$ reduction	M. p., °C.	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
Diphenyl	Acet. + alc.	Fine needles	43		154.3–155.3			[a]	
Diphenyl	Alcohol	Needles		10	173.5–175.6			[b]	
Di-*p*-biphenyl	Acetone	Fine needles	49		220	88.2	5.3	87.7	5.4
Di-*p*-tolyl	Acet. + alc.	Prisms	45		182–182.5	85.2	6.0	85.1	6.0
Di-*p*-tolyl	Acetone	Fine needles		52	154.3–155.3	85.2	6.0	84.6	5.8
Di-*m*-tolyl	Acet. + bz.	Fine needles	36.5		152.3–153.3	85.2	6.0	85 4	5.8
Dianisyl	Acetone	Prisms	34		168–169	78.4	5.5	77.8	5.2
Diphenetyl	Acetone	Needles	24		144.5–145.5	78.9	6.1	78.5	6.1
Di-*p*-chlorophenyl	Bz. + acet.	Plates	29		222–223	Cl	17.4		16.9
Di-*p*-chlorophenyl	Acetone	Hexagonal plates		37	78–79.5				17.5
Di-*p*-fluorophenyl	Acet. + bz.	Prisms	38		220–221	F	10.2		10.0
Di-*p*-fluorophenyl	Acet. + alc.	Tetragonal plates		86	153.5–154.5				10.4

[a] Acree, *Am. Chem. J.*, **33**, 186 (1905). [b] Wittig, Leo and Wiemer [*Ber.*, **64**, 2405 (1931)] reported 171–173° for the melting point of 7,8-diphenylacenaphthenediol which they obtained by interaction of 1,8-dibenzoylnaphthalene and phenylmagnesium bromide.

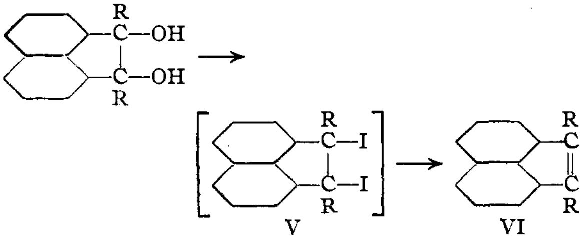
TABLE II

7,7-DIARYLACENAPHTHENONES (II)

All of the compounds are colorless

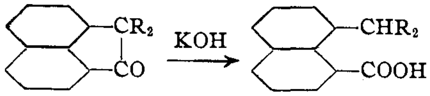
-Acenaphthenone	Recryst. solvent	Cryst. form	Yield, %	M. p., °C.	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
Diphenyl	Acet. + alc.	Needles	94	171.3–172.4			[a]	
Di-*p*-biphenyl	Acet. + bz.	Prisms	99	248–249	91.	5.15	91.0	5.2
Di-*p*-tolyl	Acetone	Plates	99	128.5–129.5	89.7	5.7	89.9	5.8
Di-*m*-tolyl	Acetone	Tetragonal plates	100	147.5–148.5	89.7	5.7	89.5	5.7
Dianisyl	Acetone	Needles	100	151.5–152.5	82.1	5.3	81.5	4.9
Diphenetyl	Acet. + alc.	Prisms	100	122.8–123	OC_2H_5	22.1		22.0
Di-*p*-chlorophenyl	Acetone	Prisms	62	145.5	Cl	18.2		18.1
Di-*p*-fluorophenyl	Acetone	Prisms	68	127.5–128.5	F	10.7		10.7

[a] Beschke, *Ann.*, **369**, 200 (1909).



The structures of the acenaphthylenes were established by synthesis. The pinacols were converted to the corresponding dichlorides by reaction with hydrogen chloride; when the dichlorides were heated with an acetone solution of sodium iodide the diarylacenaphthylenes were formed. In this manner we prepared five diarylacenaphthylenes (R = phenyl, *p*-biphenyl, *p*-tolyl, *p*-chlorophenyl and *p*-fluorophenyl) as shown in Table III. Usually some pinacolone as well as the dichloride was formed by interaction of the pinacol with hydrogen chloride and in the case of dianisylacenaphthenediol and diphenetylacenaphthenediol the pinacolones were the sole products.

Scission of 7,7-Diarylacenaphthenones to 8-(Diarylmethyl)-1-naphthoic Acids.—The 7,7-diarylacenaphthenones were transformed into 8-(diarylmethyl)-1-naphthoic acids (VII) either by fusion with potassium hydroxide or by refluxing with 25% potassium hydroxide solution in methanol. Their yields and properties are listed in Table IV.



VII

Oxidation of 7,8-Diarylacenaphthenediols to 1,8-Diacylnaphthalenes.—The 7,8-diarylacenaphthenediols were oxidized to 1,8-diacylacenaphthalenes (III) by a hot solution of chromic acid in acetic acid. The yields and the properties of these diketones are presented in Table V.

Table III

7,8-DIARYLACENAPHTHYLENES (VI)

All of these hydrocarbons are deep-orange in color

-Acenaphthylene	Recryst. solvent	Cryst. form	Yield, %	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Diphenyl	Acetone	Needles or prisms	95	161.3			[a]	
Di-*p*-biphenyl	Benzene	Needles	45	189.5–190.5	94.7	5.3	94.3	5.2
Di-*p*-tolyl	Acet. + alc.	Prisms	44	137.2–137.7	94.0	6.0	93.8	5.9
Di-*p*-chlorophenyl	Acetone	Needles	29	204.5–205.5	Cl, 19.0		18.8	
Di-*p*-fluorophenyl	Acetone	Needles	36	153.5–154.5	F, 11.2		11.1	

[a] See reference *b* under Table I.

Table IV

8-(DIARYLMETHYL)-1-NAPHTHOIC ACIDS (VII)

All of the compounds are colorless

-Methyl-naphthoic acid	Recryst. solvent	Cryst. form	Fusion temp., °C.	Time, min.	Yields, % Fusion	Yields, % 25% KOH	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Diphenyl	Bz. + acet.	Needles	250	10	74	74	226			[a]	
Di-*p*-biphenyl	Bz. + acet.	Needles	320	10	52	59	247–248	88.2	5.3	87.7	5.1
Di-*p*-tolyl	Acetone	Prisms	250	20	15	45	159.3–160.3	85.2	6.0	85.1	5.8
Di-*m*-tolyl	Acetone	Rect. prisms	250	20	30	65	189.5–190.5	85.2	6.0	84.9	6.0
Dianisyl	Acetone	Prisms	250	10	39	56	173.5–174.5	78.4	5.5	78.3	5.2
Diphenetyl	Acetone	Needles	250	10	34	54	170–171	OC_2H_5		21.1	20.9
Di-*p*-chlorophenyl	Acetone	Hex. heavy plates	250	20	10	3.5	225–226	Cl		17.4	17.2
Di-*p*-fluorophenyl	Acet. + alc.	Hex. plates	250	10	16	23	221–222	F		10.2	10.2

[a] See reference *a* under Table II.

Table V

1,8-DIACYLNAPHTHALENES (III)

All of the diketones are colorless

-Naphthalene	Recryst. solvent	Cryst. form	Yield, %	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Dibenzoyl	Acet. + alc.	Heavy plates	72	186.5			[a]	
Di-(*p*-phenylbenzoyl)	Acetic acid	Fine needles	75	219–220	88.5	4.9	88.1	5.0
Di-*p*-toluyl	Acet. + bz.	Plates	64	181.5–182.5	85.7	5.5	85.3	5.5
Di-*m*-toluyl	Acetic acid	Feather-like crys.	57	157.3–158.3	85.7	5.5	85.3	5.5
Dianisoyl	Acetone	Prisms	65	215–216	OCH_3	15.4		15.6
Diphenetoyl	Bz. + acet.	Plates	75	197–197.5	79.3	5.7	79.2	5.8
Di-*p*-chlorobenzoyl	Acetone	Prisms	54	188	Cl	17.5		17.4
Di-*p*-fluorobenzoyl	Acet. + alc.	Diamonds	64	166.5–167.5	F	10.2		10.2

[a] See reference *a* under Table II.

Experimental

Preparation of 7,8-Diarylacenaphthenediols. (a) Grignard Reaction.—To the Grignard reagent prepared from 0.14 mole of aryl bromide (bromobenzene, *p*-bromobiphenyl, *p*-bromotoluene, etc.) in 50 cc. of anhydrous ether was added a benzene solution of 10 g. of acenaphthenequinone. The mixture was refluxed on a steam-bath for twenty-four hours except in the case of diphenylacenaphthenediol for which only four hours were allowed. By hydrolysis of the reaction mixture with dilute acetic acid and recrystallization of the product, the pinacols were obtained as colorless crystals.

(b) Reduction by Sodium Amalgam.—One gram of 1,8-diacylnaphthalene (obtained by oxidation of the pinacols prepared by the Grignard reaction) in a mixture of ether and benzene was shaken with 114 g. of 1% sodium amalgam at room temperature for twenty days, the mixture was filtered and the filtrate was treated with dilute acetic acid in order to hydrolyze the disodium salts of the pinacols. The product was a mixture of the pinacol and some unreacted diacylnaphthalene from which the pinacol was obtained by repeated recrystallization.

Rearrangement of the Pinacols.—A mixture of 0.0045 mole of pinacol, 1 g. of iodine and 100 cc. of acetic acid was refluxed for thirty minutes. The diarylacenaphthenones, which were precipitated by pouring the solution into an aqueous solution of sulfur dioxide, were purified by recrystallization, forming colorless crystals.

In order to detect if any of the isomeric pinacolone, $C_{10}H_6C(R)COR$ was formed, 1 g. of the crude pinacolone was refluxed with a solution of 25 g. of potassium hydroxide in 100 cc. of methanol for three days. After removal of the solvent by distillation under reduced pressure, the residue was stirred with cold water and filtered. In the filtrate no trace of acids (benzoic, *p*-toluic, etc.) could be detected. By washing with dilute hydrochloric acid, purification through the ammonium salts and then recrystallization the residue gave colorless crystals of 8-(diarylmethyl)-1-naphthoic acids.

Synthesis of 7,7-Diphenylacenaphthenone.—A mixture of 0.50 g. of diphenyl-α-naphthylacetic acid[6] and 1 g. of thionyl chloride was refluxed for an hour. After removal of the excess of thionyl chloride, the acid chloride was dissolved in carbon disulfide and treated with 5 cc. of stannic chloride and heated on a steam-bath. From the products of hydrolysis there was isolated a solid which after repeated recrystallization from benzene and acetone gave crystals of 7,7-diphenylacenaphthenone, which proved to be identical with the pinacolone obtained by rearrangement.

Di-*p*-biphenyl-α-naphthyl-acetic Acid.—A mixture of 1.5 g. of di-*p*-biphenyl-α-naphthylchloromethane[7] and 5.1 g. of 45% sodium amalgam was shaken in 20 cc. of ether and 30 cc. of benzene for two hours. A stream of dry carbon dioxide was passed through the intensely colored solution of the triarylmethylsodium compound until the color disappeared completely. The di-*p*-biphenyl-α-naphthylacetic acid crystallized from benzene in colorless prisms; yield, 66%; m. p. 216–217° with decomposition.

Anal. Calcd. for $C_{36}H_{26}O_2$: C, 88.2; H, 5.3. Found: C, 88.1; H, 5.0.

Synthesis of 7,7-Di-*p*-biphenylacenaphthenone.—This compound was obtained by cyclization of di-*p*-biphenyl-α-naphthylacetyl chloride (prepared by means of thionyl chloride) in the same method that was used for the phenyl analog. The 7,7-di-*p*-biphenylacenaphthenone was identical with the pinacolone obtained by rearrangement.

Scission of 7,7-Diarylacenaphthenones by Potassium Hydroxide.—One-tenth gram of pinacolone was fused with 1 g. of potassium hydroxide in a metal bath at the temperature shown in Table V. After the mass had been dissolved in acetone and water, the 8-(diarylmethyl)-1-naphthoic acid was precipitated by dilute hydrochloric acid. For purification the acid was dissolved in ammonium hydroxide, precipitated again by dilute hydrochloric acid and then recrystallized.

Oxidation of the Pinacols.—A mixture of 0.003 mole of pinacol, 0.25 g. of chromic acid anhydride in 12 cc. of acetic acid was heated on a steam-bath for thirty minutes. The 1,8-diacylnaphthalene was precipitated by addition of cold water and then purified by recrystallization.

Synthesis of 7,8-Diarylacenaphthylenes.—A stream of dry hydrogen chloride was passed through an ice-cold solution of 0.001 mole of pinacol in chloroform for thirty minutes. After the solvent had been removed, the dichloride crystallized when it was stirred with a little acetone and petroleum ether.

A mixture of 0.0003 mole of the dichloride and 0.12 g. of sodium iodide in a few cc. of acetone was refluxed for thirty minutes. The solution became yellow and then dark red due to the liberation of iodine during the reaction. The mixture was poured into an aqueous solution of sulfur dioxide and the orange-colored solid was refluxed with 25% potassium hydroxide solution in methanol for two days in order to destroy the pinacolone which was present. The product after this treatment was digested with dilute ammonium hydroxide in order to dissolve the diarylmethylnaphthoic acid and the residue of diarylacenaphthylene was filtered, washed with water and recrystallized.

By treating 7,8-di-*p*-chlorophenylacenaphthylene dichloride with sodium iodide, 1,8-di-*p*-chlorobenzoylnaphthalene was formed instead of 7,8-di-*p*-chlorophenylacenaphthylene. However, by refluxing a mixture of 0.001 mole of the dichloride, 10 cc. of hydrogen iodide (d. 1.7) and 20 cc. of acetic acid for two hours the acenaphthylene was obtained mixed with a small amount of pinacolone. The compound was also obtained in 27% yield by refluxing an ether solution of the dichloride with zinc dust.

Summary

Seven new 7,8-diarylacenaphthenediols have been synthesized and subjected to rearrangement. It was found that in each case the simple aryl group migrates exclusively with respect to the acenaphthyl group; the products of the rearrangement are 7,7-diarylacenaphthenones.

The 7,7-diarylacenaphthenones are cleaved into 8-(diarylmethyl)-1-naphthoic acids either by treatment with 25% potassium hydroxide solution in methanol or by fusion with potassium hydroxide.

The 7,8-diarylacenaphthenediols are oxidized to 1,8-diacylnaphthalenes by chromic acid.

Four new 7,8-diarylacenaphthylenes have been synthesized from the 7,8-diarylacenaphthenediols.

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[6] Conant and Wheland, THIS JOURNAL, **54**, 1219 (1932).

[7] Schlenk and Bomhardt, *Ber.*, **46**, 1482 (1913).