maximum yield of 0.07 g. It melted at 183° and was probably a monobasic hydroxy acid. This acid has not been available in sufficient quantity for satisfactory study.

Anal. Subs., 0.0520, 0.0520: CO_2, 0.1095, 0.1098; H_2O, 0.0272, 0.0266. Calcd. for $C_{10}H_{12}O_5$: C, 56.6; H, 5.66. Found: C, 57.41, 57.57; H, 5.81, 5.68. *Titration.* Subs., 0.0159: 0.7 cc. of $N/10$ KOH. Calcd. mol. wt.: 212. Found: 227.

Dehydrodihydroxyrotenonic Acid Ethyl Ester.—One gram of the acid was boiled for three hours in 10 cc. of 10% alcoholic sulfuric acid. The ester crystallized on cooling and was recrystallized from 95% alcohol. It crystallized in needles melting at 98°. The yield was nearly quantitative.

Anal. Subs., 0.0704: CO_2, 0.1692; H_2O, 0.0383. Calcd. for $C_{25}H_{28}O_8$: C, 65.78; H, 6.14. Found: C, 65.55; H, 6.04.

Summary

Derric acid of formula $C_{12}H_{14}O_7$ which is obtained by peroxide oxidation of dehydrodihydroxyrotenonic acid of formula $C_{23}H_{24}O_8$ is oxidized by permanganate to a new dibasic acid of formula $C_{11}H_{12}O_7$ having the properties of a dimethoxytartronic acid. It seems likely that the rotenone molecule contains the grouping corresponding to a dimethoxyphenylsuccinic acid. Such an assumption might explain the formation and properties of dehydrorotenone. A possible explanation of the formation of dehydrodihydroxyrotenonic acid by the addition of the elements of water to the double bond is open to theoretical objections.

Washington, D. C.

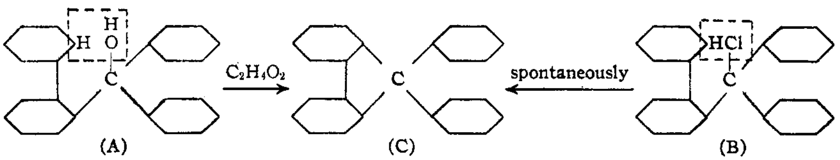
[Contribution from the Chemistry Laboratory of the University of Michigan]

SPIRANS WITH FOUR AROMATIC RADICALS ON THE SPIRO CARBON ATOM[1]

By R. G. Clarkson and M. Gomberg

Received February 24, 1930 Published July 3, 1930

Ullmann and Wurstemberger,[2] by heating the crude 2-phenyltriphenylcarbinol (A) with sulfuric acid, and Khotinsky and Patzewitch[3] by heating the same with acetic acid obtained 9,9-diphenylfluorene (C). We have now succeeded in preparing the carbinol pure and in crystalline state, but our attempts to convert it into carbinol chloride (B) resulted invariably



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[1] Part of a dissertation submitted by R. G. Clarkson to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Science, 1929.

[2] Ullmann and Wurstemberger, *Ber.*, **38**, 4105 (1905).

[3] Khotinsky and Patzewitch, *ibid.*, **42**, 3106 (1909).

in the formation of the same diphenylfluorene, even when the mildest conditions of procedure were employed.

We then prepared 9-(2-biphenyl)-9-fluorenol, anticipating greater stability both for this carbinol and its carbinol chloride. The fluorenol could indeed be recrystallized unchanged from acetic acid, but the addition of a drop of hydrochloric acid to the solution brought about an immediate closure of the ring. The compound so formed, *spiro*-bifluorene (Formula I, Table I), is the simplest possible representative of that class of spirans in which the spiro carbon atom is linked by all its four valencies to groups of the purely aromatic series. Very few examples of such spirans are described in the literature.[4] This proneness of the *o*-biphenyl and other similar groups toward ring closure we have now sought to utilize in extending our knowledge of the new type of spirans. A list of those which have been prepared is given in Table I, indicating the carbinols that give rise to the spirans. The names of the carbinols and the corresponding spirans are given in the experimental part.

Experimental

2-Phenyltriphenyl Carbinol.—2-Aminobiphenyl[5] was converted into 2-cyanobiphenyl by essentially the same procedure as has been since described by Schlenk and Bergmann;[6] b. p. 202–204° at 43 mm. As these authors give for their substance a melting point of 41°, and ours, after recrystallization, melted at 35–36°, we have further verified the constitution of the compound by synthesizing it from *o*-cyanodiazonium hydroxide and benzene.[7]

2-Phenylbenzophenone was obtained by the action of phenylmagnesium bromide upon 2-cyanobiphenyl with a yield of 76%. When reduced with magnesium–magnesium iodide mixture,[8] the ketone gives, instead of the expected pinacol, 9-phenylfluorene, but only in 25% yield.

A solution of 6.5 g. of 2-phenylbenzophenone in 50 cc. of ether was added to a solution of phenylmagnesium bromide obtained from 8 g. of bromobenzene. After refluxing overnight, the solid magnesium carbinol salt was filtered off and decomposed with an ice-cold solution of ammonium chloride. The crude solid carbinol was filtered from the aqueous solution of the salts, dried and recrystallized from a mixture of benzene and petroleum ether as large, slightly yellow clumps; m. p. 87–88°; yield, 5.2 g., or 63%.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.25; H, 6.00. Found: C, 89.05; H, 5.85. Mol. wt. (in benzene). Calcd.: 336. Found: 338.

The failure of previous investigators[2,3] to obtain this carbinol in the solid state may be attributed to the partial decomposition of the carbinol in their process of steam distillation. The substance can be safely steam distilled only if every trace of acid is previously removed.

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[4] Radulescu, in the "Publications de l'Institut Chimique de Cluj," **1926-1928**, Vols. I–V, supplies a fairly complete bibliography on spirans. We desire to express to Dr. Radulescu our appreciation for a copy of these publications.

[5] Graebe and Rateanu, *Ann.*, **279**, 257 (1894).

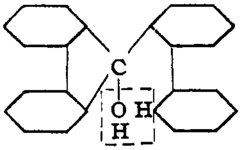
[6] Schlenk and Bergmann, *ibid.*, **464**, 33 (1928).

[7] Gomberg and Bachmann, This Journal, **46**, 2339 (1924).

[8] Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

TABLE I

FORMULAS OF COMPOUNDS



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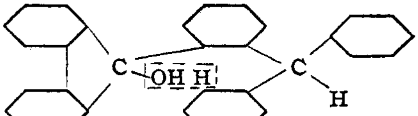

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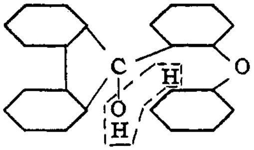

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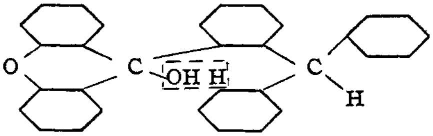

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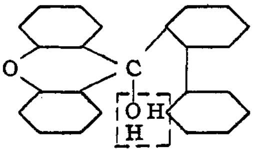

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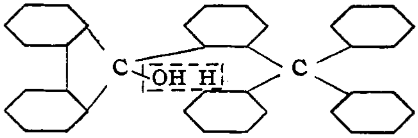

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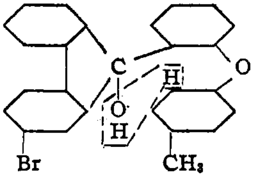

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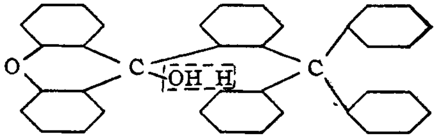

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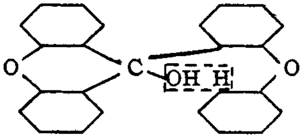

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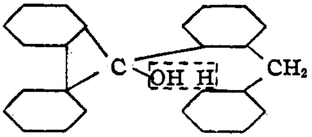

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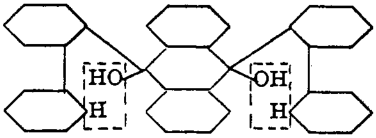

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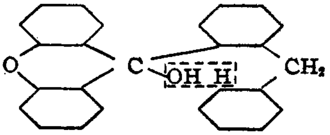

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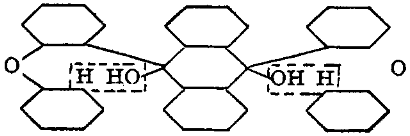


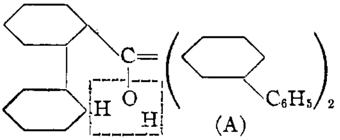
XII

When a solution of the carbinol in acetic acid is heated, an orange-red color develops; after a few minutes of boiling the liquid becomes filled with crystals of the colorless diphenylfluorene (Formula C) and the color of the solution fades completely.

All attempts to prepare the carbinol chloride yielded the same hydrocarbon (C). The chloride evidently passes over into the fluorene spontaneously, for treatment of the carbinol with acetyl chloride, even at 0°, produces the fluorene.

9,9-Di-(3-biphenyl)-fluorene

An analog of 2-phenyltriphenyl carbinol, namely, 2,3′,3′′-triphenyltriphenyl carbinol, was prepared from 3-bromobiphenyl and the ester of 2-phenylbenzoic acid. The crude carbinol resisted all efforts to obtain it crystalline. It was converted into 9,9-di-(3-biphenyl)-fluorene (A) by heating an acetic acid solution of the carbinol with a few drops of sulfuric acid and formed colorless crystals; m. p. 190–193°.



(A)

Anal. Calcd. for $C_{37}H_{26}$: C, 94.43; H, 5.57. Found: C, 94.09; H, 5.48. Mol. wt. (in benzene). Calcd.: 470. Found: 480.

9,9′-Spirobifluorene (I)

9-(2-Biphenyl)-9-fluorenol.—2-Iodobiphenyl was prepared from the amino compound by Sandmeyer's reaction, b. p. 183–186° at 32 mm. Our yield was usually 75%, and the iodide reacted directly with ordinary magnesium, requiring no agency for activation.[9] To the Grignard reagent from 14.0 g. of 2-iodobiphenyl was added 9 g. of fluorenone in small portions; the mixture was refluxed overnight on a steam-bath. The yellow precipitate was filtered, washed with a little absolute ether and decomposed with ice and ammonium chloride. The carbinol was filtered, dried and recrystallized from alcohol, or from a mixture of benzene and petroleum ether as colorless prisms; m. p. 169–170°; yield, 70%.

The compound is more stable than 2-phenyltriphenyl carbinol; a pure sample may be recrystallized unchanged from glacial acetic acid. The crude carbinol, which contains traces of adsorbed iodine, is converted to the spiran by such treatment.[10]

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.78; H, 5.43. Found: C, 90.05; H, 5.27. Mol. wt. (in benzene). Calcd.: 334. Found: 330.

The Spiran (I).—One drop of hydrochloric acid was added to a boiling solution of 5.0 g. of the above fluorenol in 10 cc. of acetic acid. Boiling was continued for a minute or two until the yellow color disappeared, and water was then added to the hot solution until the latter became turbid. After cooling the solution, the large glistening plates of spiran were filtered and dried. A further quantity of the product was obtained by diluting the filtrate with water. The compound may be recrystallized from alcohol or from a benzene–petroleum ether mixture; m. p. 198–199°; yield, 4.0 g.

The spiran was also obtained by allowing a benzene–acetyl chloride solution of the carbinol to stand overnight at room temperature. Evaporation of the solvent yielded large prisms of the hydrocarbon. The substance is not affected by boiling with zinc dust and acetic acid, and does not add bromine.

Anal. Calcd. for $C_{25}H_{16}$: C, 94.90; H, 5.10. Found: C, 95.07; H, 5.11. Mol. wt. (in benzene). Calcd.: 316. Found: 316.

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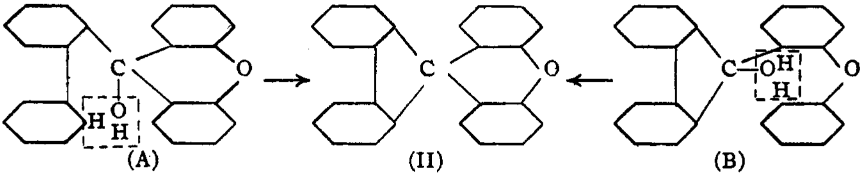
[9] Gilman, Kirby and Kinney, THIS JOURNAL, **51**, 2261 (1929), gave a yield of 51.7%, and used activated copper-magnesium alloy to start the Grignard reaction.

[10] Compare Ref. 8, p. 246.

Spiro-9-fluorene-9′-xanthene (II)

A definite proof concerning the course of our condensation reaction would be afforded if the same spiran (II) resulted (1) on the one hand from 9-(2-phenoxyphenyl)-9-fluorenol (A), and (2) on the other hand from 9-(2-biphenyl)-9-xanthenol (B). Such is the case.



(1) Synthesis of the Spiran (II) from 9-Flurenone

2-Iododiphenyl Ether.—The method of Jones and Cook[11] was used in preparing 2-nitrodiphenyl ether, except that *o*-chloronitrobenzene was substituted for the *o*-bromo compound and the reaction was carried out at 150 instead of 100°. The nitro ether was reduced to the amino ether, and through Sandmeyer's reaction converted into the iododiphenyl ether.

The iodide boils at 198–202° at 32 mm.; m. p. 54–56°.

Anal. Calcd. for $C_{13}H_9OI$: I, 42.72. Found: I, 42.88. Mol. wt. (in benzene). Calcd.: 296. Found: 289.

9-(2-Phenoxyphenyl)-9-fluorenol (Formula A).—It is necessary to use a large volume of ether in preparing the Grignard reagent from the above iodide since the halomagnesium compound is likely to crystallize from concentrated solutions upon the metal in large compact prisms. After boiling a solution of 8.9 g. of the 2-iodo compound in ether for two hours with 0.73 g. of magnesium, the metal had completely dissolved. A solution of 5.4 g. of fluorenone was added and the mixture was refluxed overnight. The insoluble magnesium product was filtered, washed with a little ether, and decomposed with ice and ammonium chloride. The recrystallized carbinol, slightly brown clumps, melted at 154°; yield, 5.7 g.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.68; H, 5.18. Found: C, 85.47; H, 5.02. Mol. wt. (in benzene). Calcd.: 350. Found: 354.

The Spiran (II).—Three g. of the carbinol was boiled for a few minutes with a mixture of 10 cc. of acetic acid and 3 cc. of acetyl chloride. Upon cooling the solution, glistening colorless crystals of spiran were obtained; m. p. 212–213°; yield, 2.2 g.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.33; H, 4.85. Found: C, 90.28; H, 4.70. Mol. wt. (in benzene). Calcd.: 332. Found: 325.

This spiran is the mother substance of the dihydroxycarboxylic acid described by Bischoff and Adkins.[12]

(2) Synthesis of the Spiran (II) from Xanthone

A solution of 4.9 g. of xanthone in 60 cc. of hot benzene was added to the Grignard reagent from 7 g. of 2-iodobiphenyl and the reaction mixture boiled overnight. The insoluble magnesium salt was separated and decomposed in the usual way, and the crude product purified. The pure material crystallized in colorless needles from a mixture of benzene and petroleum ether; m. p. 130°; yield, 4.3 g.

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[11] Jones and Cook, THIS JOURNAL, **38**, 1537 (1916).

[12] Bischoff and Adkins, *ibid.*, **45**, 1030 (1923).

Analysis indicated that the substance was not the expected xanthenol (B), but a molecular compound of (B) with xanthone in the ratio of one to one. Similar compounds have been reported by others.[13] In solution, dissociation into the components ensues, as is shown by the molecular weight determination made upon the complex. The free carbinol (B) could not be obtained directly from the double compound; but after conversion of the xanthenol component of the complex to the spiran (II), the xanthone, which remained unchanged, could be readily removed.

Anal. Calcd. for ($C_{25}H_{18}O_2 + C_{13}H_8O_2$): C, 83.29; H, 4.80. Found: C, 83.49; H, 4.82. Mol. wt. (in benzene). Calcd. for $(350 + 196) \div 2 = 273$. Found: 275.

One gram of the double compound was dissolved in 20 cc. of acetic acid and warmed on the steam-bath for three hours. Crystals of the spiran slowly separated, 0.52 g. being obtained. From the mother liquor 0.22 g. of pure xanthone was isolated. The spiro compound obtained in this way melted at 212°. Mixed with the spiran prepared from the fluorenol (A) it melted at 212–213°. The structure of the spiran is thus definitely established since it must contain both the fluorene and xanthene rings.

Spiro-9-(2-bromofluorene)-9′-(2′-methylxanthene) (III)

2-Iodo-4′-methyl-diphenyl Ether.—2-Nitro-4′-methyl-diphenyl ether was prepared[14] by a procedure similar to that for 2-nitrodiphenyl ether, from potassium *p*-cresylate and *o*-chloronitrobenzene. The amine was obtained from the nitro compound and was then converted into the iodide. The iodide distilled at 210–215° at 34 mm. and solidified to a mass of colorless needles; m. p. 41°; yield, 74%.

Anal. Calcd. for $C_{13}H_{11}OI$: I, 40.72. Found: I, 40.94. Mol. wt. (in benzene). Calcd.: 310. Found: 313.

9-(2-Phenyl *p*-Tolyl Ether)-6-bromo-9-fluorenol.—The direct bromination of fluorene[15] was used to prepare 2-bromofluorene. The employment of repeated crystallizations suggested by these authors was avoided by distilling the crude product under reduced pressure; b. p. 234–239° at 48 mm.; m. p. 110°; yield, 65%. The bromofluorene was oxidized with sodium dichromate and acetic acid, and the fluorenone twice recrystallized from glacial acetic acid as beautiful yellow needles; m. p. 143–145°.[16]

A solution of 15.5 g. of 2-iodo-4′-methyl-diphenyl ether in absolute ethyl ether was boiled with 1.2 g. of magnesium for four hours on a steam-bath. One hundred cc. of benzene was then added and 12.9 g. of 2-bromofluorenone was introduced in small portions. The mixture was refluxed overnight and the insoluble product was then filtered and decomposed in the usual way; yield, 14 g. The pure carbinol formed pale yellow cubical crystals and melts at 175°.

Anal. Calcd. for $C_{26}H_{19}O_2Br$: Br, 18.03. Found: Br, 18.04. Mol. wt. (in benzene). Calcd.: 443. Found: 441.

The Spiran (III).—Heating a concentrated solution of the above carbinol in glacial acetic acid, to which a few drops of concentrated hydrochloric acid had been added, produced the spiran as colorless needles; m. p. 201°.

Anal. Calcd. for $C_{26}H_{17}OBr$: Br, 18.90. Found: Br, 18.63. Mol. wt. (in benzene). Calcd.: 425. Found: 427.

We had hoped to convert the methyl group to a carboxyl group, which would enable us to form salts of the spiran with optically active bases, and thus perhaps re-

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[13] Schlenk and Hertzenstein, *Ann.*, **372**, 27 (1910); Ref. 8, p. 253.

[14] Cook and Sherwood, THIS JOURNAL, **37**, 1835 (1915).

[15] Courtot and Vignati, *Bull. soc. chim.*, [4] **41**, 58 (1927).

[16] Gomberg and Pernert, THIS JOURNAL, **48**, 1378 (1926), give 149°.

solve the acid into its stereoisomers. The effort was unsuccessful, since the methyl group could not be oxidized without destroying the spiran linkage.

9,9′-Spirobixanthene (IV)

9-(2-Phenoxyphenyl)-9-xanthenol.—To the Grignard reagent from 0.6 g. of magnesium and 7.4 g. of 2-iododiphenyl ether was added a solution of 4.9 g. of xanthone in 25 cc. of hot benzene. The mixture was refluxed on the steam-bath overnight and the precipitate filtered, washed and decomposed. The recrystallized carbinol, slightly brownish clumps of crystals, melted at 136–137°; yield, 6.3 g. No tendency toward formation of a complex with xanthone was noticed in the case of this carbinol.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.94; H, 4.95. Found: C, 81.72; H, 4.81. Mol. wt. (in benzene). Calcd.: 366. Found: 365.

The Spiran (IV).—Heating a solution of 3 g. of the carbinol in 15 cc. of acetic acid for three hours produced 2.2 g. of 9,9′-spirobixanthene; shining colorless needles; m. p., 283–284° (corr.).

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.18; H, 4.63. Found: C, 86.38; H, 4.86. Mol. wt. (in benzene). Calcd.: 348. Found: 349.

In this spiran there are two bridge oxygen atoms instead of one, as in xanthone. These oxygen atoms may, potentially, form so-called oxonium salts. In distinction from xanthone, in the case of the spiran, devoid as it is of C=O groups, no evidence of salt formation was noticed, neither with dry hydrogen bromide nor with perchloric acid.[17]

Spiro-9-fluorene-9′-(9,10-dihydro-anthracene) (V)

Attempts to prepare carbinols by the action of Grignard reagents from 2-iodobiphenyl and from 2-iododiphenyl ether upon anthrone were unsuccessful. The desired spirans were obtained in another way, by extending the ring closures to diphenylmethane derivatives.

2-Bromo-diphenylmethane.—2-Bromobenzophenone was reduced[18] with zinc amalgam to the corresponding diphenylmethane. The crude product was distilled and yielded a colorless liquid which neither solidified nor became viscous at 0°; b. p. 192–198° at 32 mm.; yield, 50%. A large amount also of higher-boiling material was formed during the reduction.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.35. Found: Br, 32.15. Mol. wt. (in benzene). Calcd.: 247. Found: 252.

9-(2-Benzylphenyl)-9-fluorenol.—An ether solution of 2-bromodiphenylmethane completely dissolved 1.21 g. of magnesium in the course of four hours of boiling. Nine grams of fluorenone was added and the mixture was refluxed overnight. The insoluble yellow product was filtered, washed with ether and decomposed. The recrystallized carbinol, large colorless prisms, melted at 132–133°; yield, 10.4 g.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.37; H, 5.91. Mol. wt. (in benzene). Calcd.: 348. Found: 351.

The Spiran (V).—Five grams of the carbinol was dissolved in 20 cc. of boiling acetic acid and one drop of concentrated hydrochloric acid was added. The solution became deep yellow and then decolorized after a few minutes of boiling. Beautiful white needles of the spiran crystallized from the cold solution; m. p. 207°; yield, 4.0 g.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.55; H, 5.61. Mol. wt. (in benzene). Calcd.: 330. Found: 327.

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[17] Gomberg and Cone, *Ann.*, **376**, 232 (1910).

[18] Clemmensen, *Ber.*, **47**, 681 (1914).

Spiro-9-xanthene-9'-(9,10-dihydro-anthracene) (VI)

9-(2-Benzylphenyl)-9-xanthenol.—The carbinol was prepared from 0.6 g. of magnesium, 6.2 g. of 2-bromodiphenylmethane and 4.9 g. of xanthone; colorless needles, from a mixture of ether and petroleum ether; m. p. 146°; yield, 6.9 g.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.52; H, 5.56. Mol. wt. (in benzene). Calcd.: 364. Found: 369.

The Spiran (VI).—The spiran was obtained by heating 3 g. of the xanthenol for two hours on the steam-bath with a mixture of 10 cc. of acetic acid and 3 cc. of acetyl chloride. Colorless leaflets, m. p. 257–259° (corr.).

Anal. Calcd. for $C_{26}H_{18}O$: C, 89.85; H, 5.24. Found: C, 89,57; H, 5.25. Mol. wt. (in benzene). Calcd.: 3.46. Found: 343.

Spiro-9-fluorene-9'-(10-phenyl-9,10-dihydro-anthracene) (VII)

Since 2-bromodiphenylmethane was found to react so readily with magnesium, it was decided to attempt the preparation of a Grignard reagent from 2-bromotriphenylmethane.

9-(2-Benzhydrylphenyl)-9-fluorenol.—Our 2-bromotriphenyl carbinol melted at 104–105°.[19] The carbinol was reduced to the methane by the use of concentrated hydriodic acid; m. p. 84–85°.

After twenty-four hours of boiling, a solution of 8.1 g. of 2-bromotriphenylmethane in 50 cc. of toluene and 50 cc. of ether had completely dissolved the equivalent amount of magnesium. Toluene is essential, owing to the slight solubility of the Grignard reagent in ether alone. Fluorenone, 4.5 g., was added and the mixture was refluxed overnight. The insoluble product was filtered from the cooled solution and decomposed in the customary way; yield, 51%. The recrystallized carbinol, colorless needles, melts at 192°.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.45; H, 5.81. Mol. wt. (in benzene). Calcd.: 424. Found: 429.

The Spiran (VII).—The corresponding spiran was obtained by boiling an acetic acid solution of the carbinol containing a few drops of concentrated hydrochloric acid until the brown color which first appeared had faded; white needles; m. p. 267–268° (corr.).

Anal. Calcd. for $C_{32}H_{22}$: C, 94.54; H, 5.46. Found: C, 94.26; H, 5.43. Mol. wt. (in benzene). Calcd.: 406. Found: 408.

Spiro-9-xanthene-9'-(10-phenyl-9,10-dihydro-anthracene) (VIII)

9-(2-Benzhydrylphenyl)-9-xanthenol.—The reaction mixture from 4.9 g. of xanthone and the Grignard reagent from 8.1 g. of 2-bromotriphenylmethane was worked up as described for the preceding carbinol. White needles from benzene–petroleum ether; m. p. 200–205° with decomposition. Analysis and molecular weight determination showed the product to be a molecular complex of xanthone with the new xanthenol, one to one.

The Spiran (VIII).—The spiran was obtained in the usual way from acetic and hydrochloric acids. Colorless needles from a mixture of xylene and acetic acid; m. p. 334–335° (corr.).

Anal. Calcd. for $C_{32}H_{22}O$: C, 90.96; H, 5.25. Found: C, 90.58; H, 5.33. Mol. wt. (in benzene). Calcd.: 422. Found: 431.

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[19] Gomberg and Van Slyke, THIS JOURNAL, **33**, 535 (1911). Tschitchibabin, *Ber.* **44**, 456 (1911), gives it as 158°.

Spiro-9-fluorene-9′-(10,10-diphenyl-9,10-dihydro-anthracene) (IX)

9-(2-Biphenyl)-10,10-diphenyl-9,10-dihydro-9-anthranol.—A hot solution of 6.9 g. of 10,10′-diphenylanthrone[20] in 50 cc. of toluene was added to the Grignard reagent from 5.6 g. of 2-iodobiphenyl and the mixture refluxed on the steam-bath overnight. The crude carbinol was extracted with petroleum ether, which removed any biphenyl present, and was crystallized from a mixture of benzene and petroleum ether; slightly yellow clumps; m. p. 231–234° with decomposition; yield, 55%.

Anal. Calcd. for $C_{38}H_{28}O$: C, 91.16; H, 5.64. Found: C, 90.98; H, 5.76. Mol. wt. (in benzene). Calcd.: 500. Found: 497.

The Spiran (IX).—Upon boiling a solution of the carbinol in acetic acid the liquid became red-brown and deposited the spiran in glistening white needles; m. p. 363–364° (corr.); yield, quantitative.

Anal. Calcd. for $C_{38}H_{26}$: C, 94.57; H, 5.43. Found: C, 94.87; H, 5.43. Mol. wt. (in benzene). Calcd.: 482. Found: 494.

Spiro-9-xanthene-9′-(10,10-diphenyl-9,10-dihydro-anthracene) (X)

9-(2-Phenoxyphenyl)-10,10-diphenyl-9,10-dihydro-9-anthranol.—The carbinol was obtained from 6 g. of 2-iododiphenyl ether, 0.5 g. of magnesium and 6.9 g. of diphenylanthrone by the method of preparation used for the preceding carbinol. The crude product was recrystallized by extraction with benzene in a Soxhlet extractor; colorless microscopic crystals, only slightly soluble in benzene or toluene, m. p. 276–278° (corr.); yield, 74%.

Anal. Calcd. for $C_{38}H_{28}O_2$: C, 88.34; H, 5.46. Found: C, 88.32; H, 5.59. Mol. wt. (in benzene). Calcd.: 516. Found: 511.

The Spiran (X.)—Boiling an acetic acid solution of the anthranol caused the formation of the spiran; minute crystals, m. p. 377–380° (corr.); yield, quantitative.

Anal. Calcd. for $C_{38}H_{26}O$: C, 91.53; H, 5.26. Found: C, 91.50; H, 5.16. Mol. wt. (in benzene). Calcd.: 498. Found: 511.

Di-spiro-9,9′-di-fluorene-9″9‴-(9,10-dihydro-anthracene) (XI)

9,10-Di-(2-biphenyl)-anthraquinol.—To the Grignard reagent from 15.6 g. of 2-iodobiphenyl, 5.8 g. of anthraquinone, finely divided,[21] was added in small portions. Two hundred cc. of dry toluene was then added and most of the ether was distilled. The mixture was boiled overnight under a reflux condenser, then decomposed in the customary manner and the precipitated anthraquinol was removed by filtration. The toluene layer was evaporated and the residue of this crude anthraquinol was extracted with petroleum ether, in order to remove biphenyl from the carbinol. The amount of biphenyl (3.7 g.) corresponded to 45% of the starting iodo product and indicated a very incomplete Grignard reaction. The combined two carbinol samples were repeatedly extracted with fresh portions of alkaline sodium hydrosulfite until the liquid was no longer colored. The residue, now free from anthraquinone, was washed with water and with alcohol and thoroughly dried. The anthraquinol, very slightly soluble in the usual organic solvents, was crystallized by extraction with xylene in a Soxhlet extractor; small pearly leaflets; m. p. 353–355° (corr.) with decomposition; yield, 3.6 g., which corresponds to 25%.

Anal. Calcd. for $C_{38}H_{28}O_2$: C, 88.34; H, 5.46. Found: C, 88.50; H, 5.35. Mol. wt. (in quinoline). Calcd.: 516. Found: 509.

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[20] Haller and Guyot, *Bull. soc. chim.*, [3] **17**, 877 (1897).

[21] Kovache, *Ann. Chim.*, [9] **10**, 227 (1918).

The Di-spiran (XI).—This was obtained by heating a suspension of the above anthraquinol in a mixture of acetic acid and acetyl chloride for four hours; microscopic needles; yield, quantitative. The compound was recrystallized from quinoline; m. p. 471–474° (corr.).

Anal. Calcd. for $C_{38}H_{24}$: C, 94.96; H, 5.04. Found: C, 94.83; H, 5.04. Mol. wt. (in quinoline). Calcd.: 480. Found: 454.

Di-spiro-9,9′-di-xanthene-9″,9‴-(9,10-dihydro-anthracene) (XII)

9,10-Di-(2-phenoxyphenyl)-anthraquinol.—The procedure of preparation was similar to that used for the preceding carbinol, using anthraquinone and the Grignard reagent from 2-iododiphenyl ether. The compound was crystallized from xylene, in which it is only slightly soluble; yield, 47%; shining colorless needles; m. p. 351–353° (corr.), with decomposition.

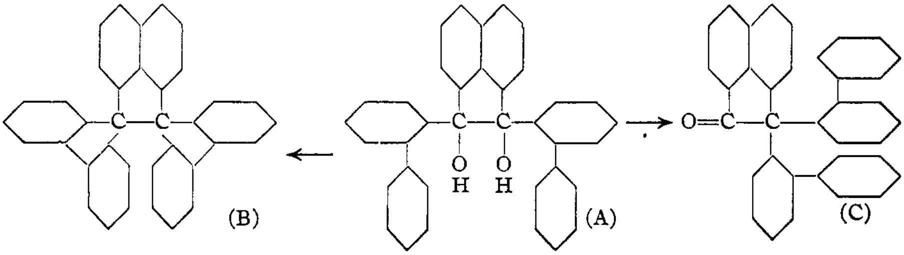
Anal. Calcd. for $C_{38}H_{28}O_4$: C, 83.18; H, 5.15. Found: C, 83.58; H, 5.21. Mol. wt. (in quinoline). Calcd.: 548. Found: 549.

The Di-spiran (XII).—The anthraquinol just described proved more refractory in eliminating water than any of the others here mentioned, a mixture of acetic acid and acetyl chloride producing no change. The di-spiran was obtained by heating 3 g. of the anthraquinol with a mixture of 20 cc. of acetic acid and 2 cc. of sulfuric acid for eight hours on the steam-bath. The substance was recrystallized from quinoline; m. p. 487–490° (corr.); yield, 70%.

Anal. Calcd. for $C_{38}H_{24}O_2$: C, 89.04; H, 4.72. Found: C, 88.70; H, 4.72. Mol. wt. (in quinoline). Calcd.: 512. Found: 489.

7,7-Di-(2-biphenyl)-8-acenaphthenone

We attempted to prepare a di-spiran of another type, by dehydrating 7,8-di-(2-biphenyl)-acenaphthodiol (A). Heating in the usual way with acetic acid and hydrochloric acids did not, however, produce the expected di-spiran (B), but instead the pinacolin (C).



7,8-Di-(2-biphenyl)-acenaphthodiol.—Finely divided acenaphthoquinone, 4.55 g., and the Grignard reagent from 14 g. of 2-iodobiphenyl in toluene were refluxed overnight. The gummy product was hydrolyzed and yielded a mixture of oil and solid. The oil was removed by washing the solid several times with cold alcohol, and the solid pinacol was recrystallized several times from a mixture of benzene and petroleum ether; slightly yellow powder; m. p. 168°; yield, 3.9 g., or 32%.

Anal. Calcd. for $C_{36}H_{26}O_2$: C, 88.14; H, 5.33. Found: C, 88.54; H, 5.30. Mol. wt. (in benzene). Calcd.: 490. Found: 485.

The Pinacolin (C).—Two grams of the pinacol, when heated on a steam-bath with 10 cc. of acetic acid containing a few drops of hydrochloric acid, began to deposit crystals. After four hours the color of the solution still persisted, but no further crystallization could be observed. The product was filtered and recrystallized from a mixture of xylene and acetic acid; colorless, shining plates; m. p. 265–267° (corr.); yield, 1.5 g.

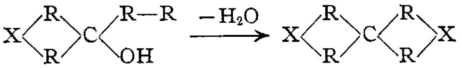
Anal. Calcd. for $C_{36}H_{24}O$: C, 91.50; H, 5.11. Found: C, 91.67; H, 5.05. Mol. wt. (in benzene). Calcd.: 472. Found: 480.

Treatment with alcoholic potash hydrolyzed the pinacolin[22] with the production of an acid; m. p. 252–254° (corr.). Apparently the rearrangement of the pinacol to the corresponding pinacolin takes place more readily than does spiran formation.

Summary

1. It has been found that the chlorides of tertiary aromatic carbinols containing the *o*-biphenyl group decompose spontaneously to give 9,9-disubstitution products of fluorene, which may be obtained by treating the carbinol with mild dehydrating agents.

2. This reaction has been extended to tertiary aromatic carbinols which contain, instead of the *o*-biphenyl group, the *o*-phenoxyphenyl-, *o*-benzylphenyl or *o*-benzhydrylphenyl group, respectively. The tendency toward ring closure on the part of these carbinols and carbinol chlorides has been utilized by us in preparing new spiro compounds



X is a valence, an O, a CH_2, a CH(Ph) or a $C(Ph)_2$

In all, twelve new spirans have been prepared, including two di-spirans. The spirocarbon atom has all its four valencies occupied by aryl groups—such spiro compounds being at present only little known.

The complex spirans, all beautifully crystalline, are characterized by unusually high melting points and by extreme insolubility. In accord with the views of Radulescu[4,23] the spirans were all found to be colorless.

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[22] Beschke and Kitaj, *Ann.*, **369**, 202 (1909).

[23] Löwenbein and Katz, *Ber.*, **59**, 1377 (1926).