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## The Cyclization of Di- and Triaryl Carbinols. I. Contribution to the Mechanism of Cyclization Reactions

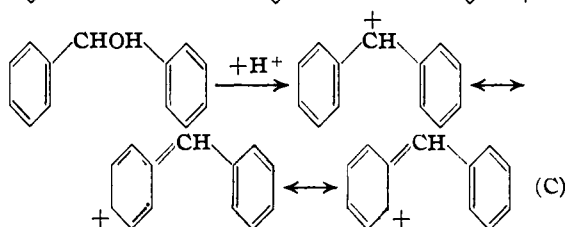
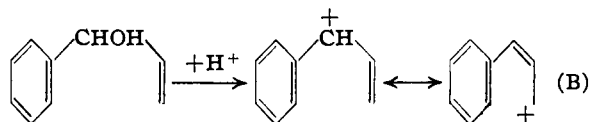
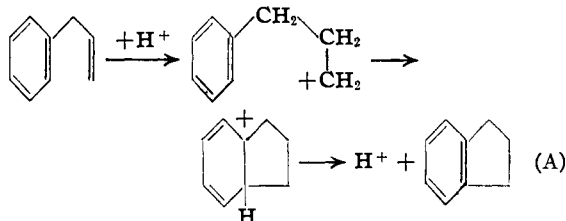
BY FELIX BERGMANN AND SHALOM ISRAELASHWILI<sup>1</sup>

In a previous paper<sup>2</sup> we reported that di-(9-phenanthryl)-carbinol cannot be cyclized to tetrabenzfluorene. In continuation of our studies on the participation of the 9,10-double bond of phenanthrene in cyclization reactions, we have now investigated other di- and triaryl-carbinols containing one or two phenanthrene nuclei.

The Grignard reaction between  $\alpha$ -naphthylmagnesium bromide and phenanthrene-9-aldehyde gave directly two hydrocarbons, one of m. p. 133°, which crystallizes in colorless prisms, and the other of m. p. 236° (brown needles). On the basis of their ultraviolet absorption spectra the structures I and II have been ascribed to them, respectively.<sup>3</sup> Oxidation of II with chromic acid in acetic acid gave a product which, according to its analysis, represents the diacetate III of the hydrated ketone.

The interaction of 9-phenanthrylmagnesium bromide with  $\alpha$ -benzoylnaphthalene readily yielded the carbinol, IV. When this was boiled with hydrobromic acid, a yellow bromine containing product appeared quickly. (With hydrochloric acid the corresponding chloride was obtained.) It was first considered to be a triaryl-methyl bromide, derived from IV. The bromine atom proved, however, extremely resistant to concentrated sulfuric acid or sodium ethylate (with sodium butylate in boiling butanol, debromination to an undefined product took place), and only by treatment with zinc in boiling acetamide,<sup>4</sup> a hydro-

carbon (V, X = H) was obtained which also formed directly in the described Grignard reaction. In later experiments (V, X = H) resulted directly from the treatment of IV with hydrobromic acid. As triarylmethyl halogenides contain easily ionizable halogen<sup>5</sup> and—in suitable cases—are



easily cyclized, whereas 9-phenyl-9-halogenofluorenes are quite resistant to hydrolysis, it is concluded, that the hydrocarbon is 9-phenyl-1,2,3,4,7,8-tribenzfluorene (V, X = H) and that the halogen compounds constitute its 9-halogeno derivatives (V, X = Hal).<sup>6</sup> Direct bromination of the hydrocarbon (V, X = H) did not give the

(1) Part of a thesis submitted to the Hebrew University, Jerusalem, 1945.

(2) F. Bergmann and Israelashwili, *THIS JOURNAL*, **67**, 1951 (1945).

(3) Jones, *ibid.*, **67**, 1956 (1945). From ethyl benzoate and 9-phenanthrylmagnesium bromide, too, a substance was obtained as by-product, which is probably di-(9-phenanthryl)-methane (see Experimental).

(4) Heyl and Cope, *ibid.*, **65**, 669 (1943).

(5) Pinck and Hilbert, *ibid.*, **59**, 8 (1937); Williamson, Anderson and Watt, *ibid.*, **65**, 49 (1943).

(6) The spectrographic data discussed by Jones (ref. 3) are consistent with this assumption.

9-bromo derivative (V, X = Br) but a compound the structure of which has not been further elucidated.

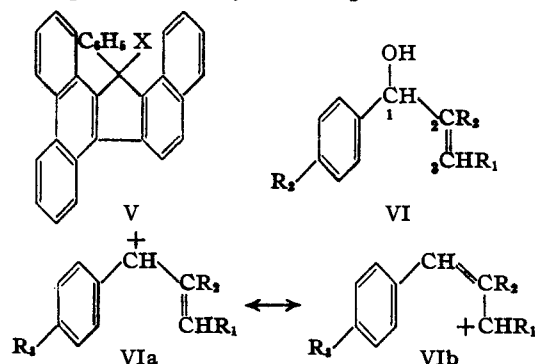
In contrast to the successful synthesis of the fluorenes (II) and (V, X = H) by dehydration of the appropriate carbinols, phenyl-di-(9-phenanthryl)-carbinol could not be cyclodehydrated: hydrobromic or sulfuric-acetic acid mixtures were without influence; a mixture of sulfuric acid and acetic anhydride acetylated the hydroxyl group. This behavior recalls the inertness of di-(9-phenanthryl)-carbinol.<sup>3</sup>

It appears that from these results and some literature data, certain conclusions can be drawn as to the factors governing the cyclodehydration of di- and tri-aryl carbinols.

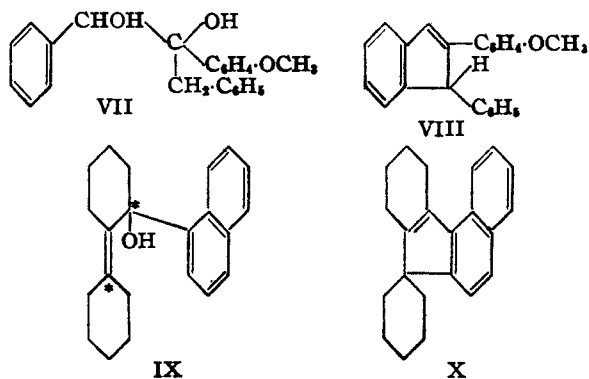
(a) We start from the cyclo-isomerization of allylbenzene and related compounds, in which<sup>7</sup> electrophilic reagents share the extra electron pair of the double bond and produce a positive charge at the  $\gamma$ -carbon atom, enabling it to attack the aromatic ring, as expected from a cationoid group (scheme A).

(b) If the allyl group is hydroxylated, the positive charge is produced, preferentially, according to scheme B; the resulting positive ion has *two* resonance structures; its stability is increased, especially in cases in which both these structures are identical.<sup>8</sup> Essentially the same mechanism applies to the formation of 1,2-diaryl-indenes from substituted hydrobenzoines, e. g., the formation of 1-phenyl-2-(*p*-methoxy-phenyl)-indene (VIII) from 1,3-diphenyl-2-(*p*-methoxy-phenyl)-propane-2,3-diol (VII), as the reagent used will first convert VII into VI ( $R_2 = H$ ,  $R_3 = p$ -methoxyphenyl,  $R_1 = \text{phenyl}$ ).<sup>9</sup> Cases in which

diols such as 1,2-di-(*p*-methoxy-phenyl)-3-phenylpropane-2,3-diol fail to react analogously,<sup>10</sup> find an explanation on similar lines. The resonance structure corresponding to VIa, ( $R_2 = p$ -methoxy-phenyl,  $R_1 = \text{phenyl}$ ,  $R_3 = \text{methoxy}$ ) does not cyclize because of the additional resonance involving the methoxy group  $R_3$ , and the resonance structure VIb fails to cyclize because the methoxy group  $R_3$  decreases the activity of the ortho-position required for the cyclization process. A similar

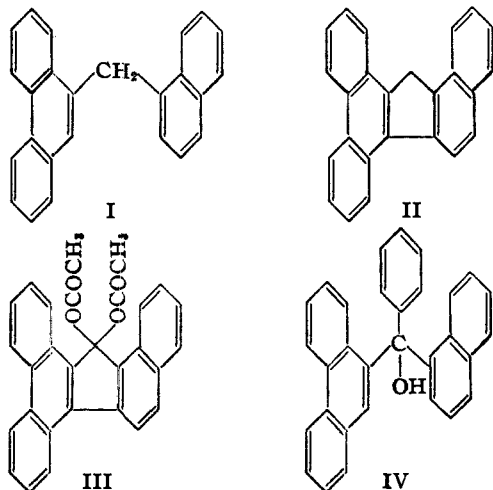


mechanism applies to the formation of the spiran (X) from IX.<sup>11</sup> The intermediate is a carbonium ion in which the positive charge resonates between the 2 carbon atoms marked with asterisks.



(c) When diaryl carbinols react with electrophilic reagents, the charge of the resulting carbonium ion can be distributed over all available *o*- and *p*-positions (scheme C). Cyclization occurs if the following conditions are fulfilled<sup>12</sup>: (1) The resonance structure in which the *o*-carbon atom is positively charged, must be formed to an appreciable degree. (2) This resonance structure must still contain an aromatic ring susceptible to attack by an electrophilic substituent.

In Table I we summarize the literature data and our own experiments on the behavior of diaryl carbinols. The following facts emerge: (a) If one of the aryls is a phenyl group, no cyclization occurs. Obviously, condition 1 is not fulfilled. (b) Cyclization is possible only, if *both* aryl groups exhibit a degenerated aromatic character, i. e., if



(7) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 310.

(8) The problem raised in a previous paper (*J. Org. Chem.*, **6**, 543 (1941)), as to whether in 1,2,3-triphenyl-allyl alcohol (VI,  $R_1 = H$ ,  $R_2 = R_3 = C_6H_5$ ) carbon atom 1 or 3 participates in the ring closure to 1,2-diphenyl-indene, loses its significance; the two processes are identical.

(9) O. Blum-Bergmann, *J. Chem. Soc.*, 723 (1938); see, also, *ibid.*, 1020 (1935).

(10) O. Blum-Bergmann, *Ber.*, **65**, 109 (1932).

(11) F. Bergmann and Eschinazi, *This Journal*, **66**, 183 (1944).

(12) Berliner, *ibid.*, **64**, 2894 (1942).

they are able to undergo such shifts as indicated in scheme C, and if the resonance structures are stabilized by participation of *both* aryl nuclei in the distribution of the charge (cases 4, 5, 6 and 8). Thus a third prerequisite for successful ring closure can be added: (3) *Resonance of the carbonium ion must involve at least two aromatic nuclei.*

TABLE I

## CYCLIZATION OF DIARYL CARBINOLS, RCHOHR'

R	R'	Result
1 Phenyl	Phenyl	No cyclization
2 Phenyl	$\alpha$ -Naphthyl	No cyclization
3 Phenyl	$\beta$ -Naphthyl	No cyclization
4 $\alpha$ -Naphthyl	$\alpha$ -Naphthyl	1,2,7,8-Dibenzfluorene
5 $\beta$ -Naphthyl	$\beta$ -Naphthyl	(3,4,5,6-Dibenzfluorene ?) <sup>a</sup>
6 $\alpha$ -Naphthyl	$\beta$ -Naphthyl	1,2,5,6-Dibenzfluorene <sup>b</sup>
7 Phenyl	9-Phenanthryl	No cyclization <sup>c</sup>
8 $\alpha$ -Naphthyl	9-Phenanthryl	1,2,3,4,7,8-Tribenzfluorene <sup>d</sup>
9 9-Phenanthryl	9-Phenanthryl	No cyclization <sup>e</sup>

<sup>a</sup> Schmidlin and Huber, *Ber.*, **43**, 2824 (1910), give m. p. 190°, whereas Martin (see the following footnote), who prepared the hydrocarbon by a different method, reports 152°. He could not duplicate the experiment of Schmidlin and Huber. <sup>b</sup> Martin, *J. Chem. Soc.*, 679 (1941). <sup>c</sup> Bachmann, *THIS JOURNAL*, **56**, 1363 (1934). <sup>d</sup> Present authors. <sup>e</sup> See footnote 2.

being obtained in the naphthyl nucleus. The results of Table II, which summarizes cyclization experiments with triaryl carbinols, can be explained in an analogous manner.

We see from Table II that introduction of an additional phenyl group into the aryl-phenyl-carbinols permits ring closure. This means that the accumulation of phenyl radicals increases the probability of their participation in the resonance of the carbonium ion. The additional factor coming into play will become clear from a consideration of, *e. g.*, case 11. The resonating ion has the structure XIa,b, and the right part of formula XIb is comparable with 1,1-diphenylethylene, which is known to behave as a true diene.<sup>14</sup> Inspection of a molecular model of this ethylene shows, that the ortho hydrogen atoms of the phenyl rings interfere. This interference can lead to two phenomena; the angle between the C-phenyl bonds may become larger or the rings may assume a non-coplanar arrangement. Coates and Sutton<sup>15</sup> have calculated from the dipole moments of *p,p'*-disubstituted 1,1-diphenylethylenes, that that angle is  $125 \pm 3^\circ$ , as compared

TABLE II

## CYCLIZATION OF TRIARYL CARBINOLS

R	R'	R''	Results	Remarks
10 Phenyl	Phenyl	Phenyl	(9-Phenylfluorene + triphenylmethane) <sup>a</sup>	Reaction temp. 400°
11 Phenyl	Phenyl	$\alpha$ -Naphthyl	9-Phenyl-1,2-benzfluorene <sup>b</sup>	—
12 Phenyl	Phenyl	$\beta$ -Naphthyl	9-Phenyl-3,4-benzfluorene <sup>b</sup>	—
13 Phenyl	$\alpha$ -Naphthyl	$\alpha$ -Naphthyl	9-Phenyl-1,2,7,8-dibenzfluorene <sup>c</sup>	No isomer
14 Phenyl	$\beta$ -Naphthyl	$\beta$ -Naphthyl	9-Phenyl-3,4,5,6-dibenzfluorene <sup>d</sup>	No isomer
15 Phenyl	$\alpha$ -Naphthyl	$\beta$ -Naphthyl	9-Phenyl-1,2,5,6-dibenzfluorene <sup>d</sup>	No isomer
16 Phenyl	Phenyl	9-Phenanthryl	9-Phenyl-1,2,3,4-dibenzfluorene <sup>e</sup>	No isomer
17 Phenyl	$\alpha$ -Naphthyl	9-Phenanthryl	9-Phenyl-1,2,3,4,7,8-tribenzfluorene <sup>f</sup>	No isomer
18 Phenyl	9-Phenanthryl	9-Phenanthryl	No reaction <sup>f</sup>	—

<sup>a</sup> Kliegl, *Ber.*, **38**, 284 (1905). This experiment, however, is not taken into account here, as the excessive reaction temperature and the formation of triphenylmethane as by-product "in appreciable quantities" make it doubtful, whether this cyclization can be compared with the other cases tabulated. <sup>b</sup> Ullmann and Mouraviev-Winogradoff, *Ber.*, **38**, 2213 (1905). <sup>c</sup> Schoepfle, *THIS JOURNAL*, **44**, 188 (1922). <sup>d</sup> Berliner, footnote 14. In this paper the product resulting from phenyl-di-( $\beta$ -naphthyl)-carbinol is erroneously designated as 9-phenyl-1,2,7,8-dibenzfluorene and that from the corresponding  $\alpha$ -naphthyl derivative as 9-phenyl-3,4,5,6-dibenzfluorene. <sup>e</sup> Bachmann and Kloetzel, *J. Org. Chem.*, **2**, 356 (1937). <sup>f</sup> Present authors.

Case 8 shows that the 9-phenanthryl radical is able to participate in the distribution of the charge of the resonating ion. If nevertheless no reaction occurs in case 9 (two phenanthryl groups!), then the reason must be seen in the lack of aromaticity of the 9,10-double bond in phenanthrene, *i. e.*, condition 2 is not fulfilled. This corresponds to the failure of many cationoid reagents to attack this bond.<sup>18</sup> We can thus formulate the general result of Table I in the following way: The ability of aromatic nuclei to accept the electric charge of an adjacent carbon atom, is directly proportional to their ability to form active dienes by conjugation with an exocyclic double bond. But with increasing conjugating power the aromatic character fades, an optimum of both features

with  $115 \pm 5^\circ$  for diphenylmethane. In the latter compound, the repulsion between the *o*-hydrogen atoms just enlarges the normal tetrahedral angle. In 1,1-diphenylethylene, with its conjugated exocyclic double bond, resonance leads to partial double bond formation between either of the benzene rings and the  $\alpha$ -carbon atom, and thereby to a coplanar arrangement of either ring with the ethylenic system. But in order to become coplanar, the phenyl rings must form a valency angle of  $160^\circ$ . The actual value of  $125^\circ$  indicates that the phenyl groups are twisted about  $30^\circ$  out of the common plane. A simple model would be given by XII, where one phenyl group forms a double bond with the  $\alpha$ -carbon atom and the second one is twisted about  $30^\circ$  out of the

(18) Fieser, "Chemistry of Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1936, p. 7.

(14) Wagner-Jauregg, *Ber.*, **63**, 3213 (1930); *Ann.*, **491**, 1 (1931).

(15) Coates and Sutton, *J. Chem. Soc.*, 567 (1942).

plane. Naturally, the phenyl groups can interchange their positions.

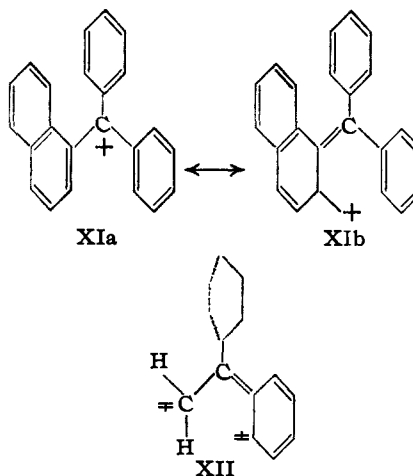
In applying these considerations to the present problem, it becomes clear, that in XI (and related triaryl-carbinols) one phenyl group must be distorted out of the plane, and that thereby the other one is forced to participate actively in the resonance of the carbonium ion (XIa) and, to this end, to assume a position coplanar with the naphthyl residue. Taking into account this last effect, we may formulate condition 3 above more broadly, thus:

(3) *At least two aryl nuclei must participate in the resonance, thus stabilizing the positive charge and assuming a coplanar position.* Cases 11, 12 and 16 are thus understandable. The very puzzling observation of Schoepfle, that phenyl-di-( $\alpha$ -naphthyl)-carbinol exclusively cyclizes to 9-phenyl-1,2,7,8-dibenzfluorene and that no trace of the isomeric 9-( $\alpha$ -naphthyl)-1,2-benzfluorene is formed, has been explained by Berliner<sup>12</sup> through the following statement: "The possibility of reaction in the phenyl instead of the naphthyl group to form the 9-naphthyl-benzfluorene is less likely because of the relative inertness of the phenyl group." But in Table II a number of cases show the ready participation of the phenyl group in ring closures, and the same applies to the similar cyclization reaction of *o*-benzylphenones.<sup>16</sup> On the basis of our above statements we can now give a simple explanation for the "inertness" of the phenyl group in phenyl-di-( $\alpha$ -naphthyl)-carbinol. It can be seen from case 4, that there exists complete resonance between the two forms in which the naphthyl rings bear the positive charges; and from the general difference in aromaticity between benzene and naphthalene it is clear, that the former will participate much less in the resonance of the carbonium ion than the latter, and therefore will preferably be the one aryl group which is not coplanar. On the other hand, this non-coplanar phenyl group will enforce a coplanar arrangement of the two naphthyl rings and, thereby, facilitate cyclization. This is in accord with the experimental facts. On the same basis, we have ascribed to the cyclization product of phenyl-( $\alpha$ -naphthyl)-(9-phenanthryl)-carbinol the structure of 9-phenyl-1,2,3,4,7,8-tribenzfluorene (V, X = H).

We can now conclude that in phenyl-di-(9-phenanthryl)-carbinol (case 18), it will be again the phenanthryl groups which participate preferably in the resonance so that again the phenyl ring is twisted out of the plane. Such an arrangement however, does not lead to ring closure, as has been shown in case 9.

It is thus clear, that a combination of electronic and steric factors—which, of course, influence each other—determines the course of the action of electrophilic reagents on di- and triaryl-carbinols. Their knowledge permits predictions as to the

possibility of ring closure in every case. Various applications of the theory here developed are now being investigated.



### Experimental

All melting points are uncorrected.

1. **1,2,3,4,7,8-Tribenzfluorene (II) and (9-Phenanthryl)-( $\alpha$ -naphthyl)-methane (I).**—To a Grignard solution prepared from  $\alpha$ -bromonaphthalene (20 g.) and magnesium (2.8 g.) was added at 0° a benzene solution of 9-phenanthraldehyde (20 g.). The mixture was refluxed for three hours. After decomposition with ammonium chloride, the oily product was fractionated. The fraction, b. p. 250–300° (0.2 mm.), was collected, dissolved in boiling acetic acid and precipitated with acetone. A brown-yellow precipitate was obtained. From butyl acetate, light-brown needles, m. p. 236–237° (II). The solutions exhibit violet fluorescence.

*Anal.* Calcd. for  $C_{25}H_{16}$ : C, 94.9; H, 5.1. Found: C, 94.6; H, 5.1.

From the mother liquor of II, a yellowish substance precipitated after some days, which, after recrystallization from acetic acid, formed colorless prismatic rods, m. p. 133° (I). With hot concd. sulfuric acid, it gives a violet color reaction.

*Anal.* Calcd. for  $C_{25}H_{18}$ : C, 94.3; H, 5.7; mol. wt., 318. Found: C, 94.6; H, 5.2; mol. wt., 298.

The picrate was prepared in acetic acid solution and recrystallized from the same solvent. The yellow-brown rods gave a melting point of 111°.

*Anal.* Calcd. for  $C_{31}H_{21}O_7N_3$ : C, 68.0; H, 3.8. Found: C, 68.4; H, 3.8.

When 0.7 g. of I in acetic acid was heated with chromic acid (0.3 g.) in water (2 cc.) on a boiling water-bath for two hours, water precipitated a yellow compound, which formed, after recrystallization from petroleum ether (130°), brown prisms, m. p. 158° (III).

*Anal.* Calcd. for  $C_{20}H_{20}O_4$ : C, 80.6; H, 4.6. Found: C, 80.85; H, 4.2.

2. **9-Phenyl-1,2,3,4,7,8-tribenzfluorene (V, X = H).**—To a Grignard solution prepared from 9-bromophenanthrene (50 g.) and magnesium (5 g.) was added, under cooling, a solution of  $\alpha$ -benzoylnaphthalene (45 g.) in benzene (100 cc.). After heating for two hours, 200 cc. of xylene was added and the low-boiling solvents distilled off on the water-bath. The xylene solution was refluxed for one hour and decomposed with dilute sulfuric acid. Distillation *in vacuo* gave a brown sirup, b. p. 300–320° (0.3 mm.), which crystallized immediately upon trituration with acetone-petroleum ether (80°). After two recrystallizations from butyl acetate, shiny plates of the carbinol (IV) were obtained, m. p. 201°. The yield was 12 g., 14.5%. Warm, concentrated sulfuric acid gave a deep ink-blue solution.

*Anal.* Calcd. for  $C_{21}H_{19}O$ : C, 90.7; H, 5.4. Found: C, 91.0; H, 5.2.

When the carbinol IV (2 g.) was refluxed with a mixture of acetic acid (45 g.) and 48% hydrobromic acid (45 cc.), a green-yellow precipitate appeared after about ten minutes. After two hours, the solution was cooled and the green substance recrystallized first from butyl acetate, then from xylene. Intensely yellow prisms, m. p. 278°, (V, X = Br); yield, quantitative. With sulfuric acid, a deep blue-violet color is obtained, which changes slowly to red-brown. The same color develops when the substance is heated above its melting point.

*Anal.* Calcd. for  $C_{21}H_{19}Br$ : C, 79.0; H, 4.0. Found: C, 78.8; H, 4.0.

The carbinol IV (2 g.) and a mixture of acetic acid (45 cc.) and hydrochloric acid (5 cc.) were treated as above. The product (V, X = Cl) formed light-yellow prisms, from butyl acetate, m. p. 282–283°; yield, quantitative.

*Anal.* Calcd. for  $C_{21}H_{19}Cl$ : C, 87.3; H, 4.5. Found: C, 87.0; H, 4.3.

The bromide (V, X = Br) (5 g.) and zinc dust (25 g.) were heated in boiling acetamide (50 g.). After some minutes, a violent exothermic reaction set in. Thereafter, the mixture was refluxed for four hours, then treated with hydrochloric acid and ether. The ether solution, after evaporation of the solvent, left a white residue, which was recrystallized twice from xylene as elongated plates, m. p. 238–239°. Cold concd. sulfuric acid gives a green color, which changes to wine-red, upon heating. Solutions of the substance exhibit intense violet fluorescence.

*Anal.* Calcd. for  $C_{21}H_{20}$ : C, 94.9; H, 5.1. Found: C, 94.8; H, 5.2.

The same compound was obtained later-on directly as by-product of the Grignard reaction described above. Thus one-tenth mole of  $\alpha$ -benzoylnaphthalene yielded 2.5 g. of carbinol (IV) and, from the mother liquor, 6 g. of the fluorene (V, X = H). Also the reaction of the carbinol (IV) with hydrogen bromide, as described before, gave later-on only the fluorene hydrocarbon. The bromide (V, X = Br) was not attacked by boiling aqueous sodium hydroxide or sodium ethylate in boiling ethanol. When it was heated for twelve hours with sodium butylate in butanol, sodium bromide precipitated slowly. No definite product could, however, be isolated from the reaction mass.

The carbinol (IV) (2 g.) was recovered unchanged, when heated with 90% hydrofluoric acid (10 cc.) in acetic acid (10 cc.) or with a mixture of sulfuric and acetic acid on the water-bath for twenty-four hours. It was likewise not affected, when dissolved in 60% oleum and left at 0° for twelve hours; at room temperature, sulfonation took place, leading to water-soluble products. Sixty per cent. perchloric acid was without effect at room temperature or at 100°. When 2 g. of the carbinol (IV) in acetic acid (30 cc.) was boiled with a solution of phosphorus pentoxide (2 g.) in the same solvent (10 cc.), a brown precipitate was obtained, which was the fluorene hydrocarbon (V, X = H) in not quite pure form.

*Bromination* of this hydrocarbon did not give (V, X = Br): 2 g. (V, X = H) was dissolved in chloroform (25 cc.) and a 1.5 N bromine solution in the same solvent (12.5 cc.) was added at room temperature. Evolution of hydrobromic acid started soon, and after some minutes a crystalline precipitate appeared. It was first recrystallized from acetic anhydride, then from xylene. The light-yellow rods, m. p. 303°, are neutral to litmus. It gives first a wine-red, then a violet color reaction with concd. sulfuric acid.

*Anal.* Calcd. for  $C_{21}H_{19}BrO_2$ : C, 74.0; H, 3.8.  $C_{21}H_{19}BrO_2$ : C, 73.7; H, 4.2. Found: C, 74.3; H, 4.3.

3. *Phenyl-di-(9-phenanthryl)-carbinol.*—To a Grignard solution, prepared from 9-bromophenanthrene (25 g.) and magnesium (2.5 g.), ethyl benzoate (15 g.) in benzene (50 cc.) was added. The solvents were distilled off and the residue was heated for five hours on the water-bath. After decomposition with dilute sulfuric acid, a brown sirup was obtained, which was fractionated *in vacuo*: Fraction

(a) had b. p. 240–250° (0.01 mm.), yellow oil, crystallizing upon trituration with petroleum ether (80°); m. p. 113°, probably di-(9-phenanthryl)-methane. Fraction (b) had b. p. 350–360° (0.05 mm.), brown resin which was dissolved in boiling propanol with addition of a little ethyl acetate. On cooling, a brownish crystalline precipitate appeared, which was recrystallized from ethyl benzoate. The microcrystalline prisms had m. p. 300–301°, yield 20%. It is of interest, that this substance, which is the desired carbinol, gives no color reaction with concd. sulfuric acid.

*Anal.* Calcd. for  $C_{33}H_{24}O$ : C, 91.3; H, 5.2. Found: C, 91.4; H, 5.1.

The carbinol was recovered unchanged after heating with concd. sulfuric acid to 80°; at 100°, decomposition occurred. Likewise, no reaction took place with sulfuric-acetic acid or with phosphorus and iodine in acetic acid. However, when the carbinol I (2 g.) was boiled in acetic anhydride (20 cc.), with addition of one drop of sulfuric acid, for thirty minutes, a black solution resulted. After filtration from a small amount of tar, water precipitated a grayish powder. From a mixture of butyl acetate and xylene (1:1), the acetyl derivative crystallized in beautiful, yellowish bricks, m. p. 345–347°.

*Anal.* Calcd. for  $C_{27}H_{20}O_2$ : C, 88.4; H, 5.2. Found: C, 88.4; H, 5.3.

4. *Attempted Synthesis of 1,2,3,4,5,6-Tribenzfluorene.*—To a Grignard solution from 9-bromophenanthrene (18 g.) and magnesium (2 g.),  $\beta$ -naphthaldehyde (11 g.) in benzene (50 cc.) was added. After refluxing it for four hours, the mixture was decomposed in the usual way and the crude sirup fractionated. The highest fraction, b. p. 300–310° (1.5 mm.), crystallized upon trituration with ethanol-ethyl acetate. Two grams of a yellow powder was obtained, m. p. 156–157°. After two recrystallizations from acetic acid and two from butyl acetate, the m. p. rose to 182°. The substance, according to its physical properties and analysis, is *sym*-di-( $\beta$ -naphthyl)-ethane.<sup>17</sup>

*Anal.* Calcd. for  $C_{22}H_{18}$ : C, 93.6; H, 6.4. Found: C, 93.7; H, 6.4.

### Summary

1. 1,2,3,4,7,8-Tribenzfluorene (II) and 9-phenyl-1,2,3,4,7,8-tribenzfluorene (V, X = H) are easily formed from the corresponding carbinols under the influence of electrophilic reagents. Phenyl-di-(9-phenanthryl)-carbinol, like di-(9-phenanthryl)-carbinol, is incapable of cyclo-dehydration.

2. The mechanism of the cyclization reaction is discussed for the following cases: (a) allyl-benzenes; (b)  $\alpha$ -hydroxy-allyl-benzenes; (c) diaryl-carbinols; (d) triaryl-carbinols and the following prerequisites are established for the cyclo-dehydration of the last two groups of compounds: I. *The electrophilic reagent must convert the carbinol into a carbonium ion, in which at least two aromatic rings participate strongly by their o-carbon atoms in the resonance of the positive charge, thus stabilizing the ion and assuming a coplanar position.* II. *Among the aromatic rings, which participate in the resonance, there must be at least one susceptible to attack by an electrophilic substituent at the ortho position.*

It is shown that these rules are sufficient for the explanation of all known data, positive or negative, pertaining to the cyclization reactions investigated.

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(17) Friedmann, *Ber.*, **49**, 1352 (1916); Schorigin, *ibid.*, **59**, 2510 (1926); Clar and Wallenstein, *ibid.*, **64**, 2076 (1931).