The Reaction Between Certain Organometallic Reagents and Benzanthrone

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The action of certain organometallic reagents upon benzanthrone (7*H*-benz[*de*]anthracene-7-one) has been further investigated. Some of the components were identified, and the nature of hitherto unknown compounds was deduced. Phenylmagnesium chloride in tetrahydrofuran gave nearly double the yield of crystallizable products. The primarily-formed enol, formed by 1,4-addition and related to the principal product, 6-phenylbenzanthrone, was isolated and identified. In the presence of cuprous and cobaltous chlorides unexpected products were indicated. The formation of 3-phenylbenzanthrone is assumed to be the result of a 1,8-addition. Phenyllithium gave all the above and many others. Among them was the carbinol, formed by 1,2-addition, and a new hydrocarbon, 7-phenyl-7*H*-benzanthrene.

L'action de certains organo-métalliques sur la benzanthrone (benz[*de*]anthracène-7*H* one-7 a été étudiée de nouveau. Certains des constituants ont été identifiés et la nature de certains composés jusqu'alors inconnus en a été déduite. Le chlorure de phényl magnésium dans le tetrahydrofuranne a donné presque le double du rendement en produits cristallisables. L'énol principalement formé, obtenu par addition-1,4 et relié au produit principal, le phényl-6 benzanthrone, a été isolé et identifié. En présence des chlorures cuivreux et cobalteux des produits inespérés furent mis à jour. La formation du phényl-3 benzanthrone est semble-t-il, le résultat d'une addition-1,8. Le phenyllithium a donné tous les produits mentionnés et plusieurs autres. Parmi ceux-ci se trouvent le carbinol, formé par addition-1,2 et un nouveau hydrocarbone, le phényl-7 benzanthrène-7*H*. [Traduit par le journal]

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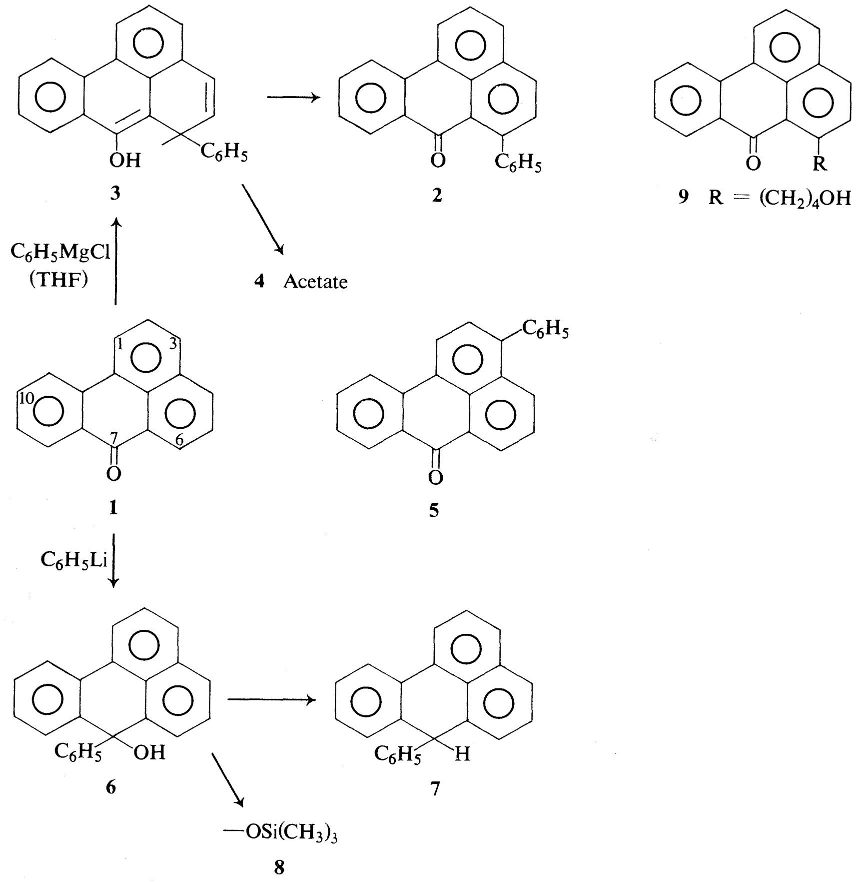
Earlier investigations (1–3) have shown that the product from the action of phenylmagnesium bromide on benzanthrone, under forcing conditions (ether–benzene), is the formation and isolation of 6-phenylbenzanthrone (**2**) in yields of 42–75%; this has also been formed by the use of phenylsodium (4). It was assumed that this substance resulted from an initial 1,4-addition to the double bond system, —(C=O)—CH=CH—. Because the yield was so low, it was considered worthwhile to reinvestigate the reaction making use of newly-available reagents and modern instrumental methods. The use of tetrahydrofuran as a solvent, and phenylmagnesium chloride, resulted in an initial isolation of at least an 80% yield of a solid product; this consisted not only of the aforesaid 6-phenylbenzanthrone, but a second substance which proved to be a primary adduct, the enol **3**. Furthermore, the latter relatively rapidly changed into the ketone **2** (see Scheme 1). An enol has not previously been isolated in the benzanthrone series. In practice, it was almost impossible to isolate other than the major component, the phenyl derivative **2**, except by a long, tedious, fractional crystallization. In order to avoid this, g.c. was applied to the entire reaction mixture; the ether was first treated with a silating agent to preserve the enol as its silated derivative. Interpretation of the results revealed not only a rough approximation of the amounts of the major constituent, but also the effect of changing the excess of Grignard reagent, as well as suggesting the presence of hitherto unrecognized components (Tables 1, 2).

A mixture of five known, expected components, including the hydrocarbon, $C_{28}H_{58}$, as an internal standard, for locating the various peaks, was prepared (*std.*). It will be noted that there is not much choice between the use of 3 (*372*) or 4 (*365*) equiv of the Grignard reagent. The total of silated enol plus ketone **2** is about 90 area %; this is not too far from the amount (80%) actually isolated, and indicates that our main purpose, to learn what and where the rest of the reaction products were, had been realized. The situation was similar with 5 (*379*) equiv of Grignard reagent, but there were more unidentifiable impurities. With 2 (*386*) equiv, however, there was much unused starting material. All these results as well as *385*, indicate that the enol had been formed first.

Despite the apparent separation of peaks on a



SCHEME 1

g.c. column, in practice it has proved extremely difficult to get rid of the main component, 6-phenylbenzanthrone (**2**) that accompanies attempted fractionation of crystalline products.

As it is well-known that the presence of copper in a Grignard reaction favors conjugate addition to an α,β-unsaturated ketone (5, 6), its effect was examined. Unexpectedly, an additional component, an isomeric ketone, was indicated in the g.c. It was assumed to be 3-phenylbenzanthrone (**5**) (old name, *Bz*-1-phenylbenzanthrone), because of g.c. and mass spectra (Table 3). In practice, it has not yet been possible to separate this isomer from the much more abundant **2**, because of their very similar solubilities.

In *399* the amount of cuprous chloride was doubled, and the mixture heated slightly longer. In an unsilated sample (*399*, footnote *a*, Table 1) *all* the enol had been converted to ketone **2**; the larger amounts of the ether masked the presence of isomer **5**, for it appears in the unsilated material (*399*).

Since 6-phenylbenzanthrone (**2**) is a product of 1,4-addition, the isomer **5** can be regarded as the result of conjugate, 1,8-addition. The carbon atom in the 3-position is at the end of the longest, unhindered conjugated system. 1,8-Addition is very rare; a few instances, involving the tropolone system, have been reported (8, 9).

The effect of cobalt (7) was also examined. The reaction was slowed down, as indicated by the larger amount of starting material recovered, and lesser formation of enol and ketone (*385*). Moreover, there was a new component **9**; interpretation of the mass spectral data (Table 3) indicates that the solvent, THF, had entered into its formation.

In order to ensure formation of the unknown carbinol **6**, a product of 1,2-addition, phenyllithium was employed. The situation was more complex, because of the multiplicity of products.

TABLE 1. Area % of reactions mixtures

Sample no.	Amount C_6H_5MgX and C_6H_5Li catalyst used	Ketone **5**	Ketone **2**	Enol **3**[c]	Carbinol **6**[a]	Hydrocarbon **7**	Carbinol **8**[c]	Unknowns[d] total	BA[e]
Std.	—	18.1[b]	40.4	12.5	0	0	0	0	25.5
379	5×	0	54.2	38.3	0	2.4	0	4.0	0.5
365	4×	0	55.4	37.6	0	1.3	0	2.9	2.8
378	3×	0	21.0	75.6	0	1.2	0	1.4	0.5
386[f]	2×	0	15.3	52.4	0	0	0	0.1	32.2
386[g]	2×	0	31.8	49.1	0	0	0	0.1	19.1
384	3×, Cu	5.5	35.0	50.0	0	3.5	0	0.7	5.3
399[a]	3×, Cu	0	90.0[j]	0	2.8	4.9	0	0.2	2.1
399	3×, Cu	2.5	35.8	52.4	0	6.5	0	0.1	2.8
385	3×, Co	7.3	9.2	47.1	0	3.3	1.7	16.4[h]	15
385R[i]	3×, Co	12.0	0	1.0	0	4.5	4.1	14.2	64.2
383[a]	3×, Li	[d]	45.7[j]	0	14.9	27	0	7.9	4.5
383	3×, Li	[d]	37.1	6.2	0	30.9	16	5.6	4.2
398[a,k]	3×, Li	[d]	47.3[j]	0	14.4	27.9	0	7.9	2.3
398[k]	3×, Li	[d]	43.0	3.3	0	18.7	28.6	4.4	2.0
390[l]	3×, Li, Cu	0	41.1	0	0	49.0	0	0.2	9.7

[a] Not silated.
[b] 3.4 Area % of 10-phenylbenzanthrone included here in standard.
[c] Silated enol or carbinol.
[d] Areas under 1% included in unknowns.
[e] BA = unused benzanthrone.
[f] Entire run.
[g] First crop.
[h] Includes 14–14.2% product 9, containing THF and possibly a trace of 10-phenyl-BA.
[i] RMgX added last.
[j] Includes enol.
[k] Ether only.
[l] Weak spectrum; 85% remains in column.

TABLE 2. Relative retentions of several components of the reaction mixture to benzanthrone

Elution order	t_R'/BA
Benzanthrone (BA) (**1**)	1.0
Silated carbinol (**8**)	1.36±0.01
Hydrocarbon (**7**)	1.60±0.03
Silated enol	2.39±0.01
Silated carbinol (**8**)	2.44±0.01
6-Phenyl-BA (**2**)	3.30±0.01
3-Phenyl-BA (**5**)	4.08±0.03
2-Phenyl-BA	4.71[a]
10-Phenyl-BA	5.00[a]

[a] Based on single chromatogram.

As before, unused benzanthrone, the 6-phenyl derivative **2**, and the same enol **3** were among products shown by t.l.c., and actually isolated. There was, probably, some of the 3-isomer also. Two new constituents were found; one was the expected carbinol **6**, for, after silation, the peak disappeared entirely, and a new one corresponding to its silated derivative **8**, and having a smaller retention time, appeared in a subsequent chromatogram. Mass spectrometric analysis of a trapped sample of the silyl derivative gave the calculated molecular ion at 380 m/e, with abundant fragment ions corresponding to the losses of silyl and phenyl groups.

The other new substance was the hydrocarbon **7**, 7-phenyl-7*H*-benzanthrene. The evidence favoring this structure is based on spectral data (u.v., i.r., mass spectrometry, and n.m.r.); the shape of the u.v. absorption curve is identical with that of 7*H*-benzanthrene (10), but the molar absorption is lower; this could be attributed to the "dilution effect" of the phenyl group. The i.r. is also similar (11); the bands at 13.4 (748 cm^{-1}) and 14.3 μ (697 cm^{-1}) suggest a monosubstituted benzene ring; the mass spectrum shows the molecular ion at 292 m/e, and fragment ions at 291 (24%) M − H, 289 (12%), 276 (5%), and 215 (100%) M − C_6H_5. Its n.m.r. shows 15 aromatic hydrogens to one tertiary hydrogen. The formation of 7-phenyl-7*H*-benzanthrene (**7**) presumably arises by reduction of the carbinol **6**. It appears to be present in quantity only in the organolithium runs in which the carbinol is formed.

TABLE 3. Mass spectra of benzanthrones

	Parent M		Fragment ions											
No.	Substituent[b]		M	%	M − H	%	M − OH	%	M − CO	%	M − HCO	%	M − H_2CO	%
1	None	D	230	100	229	1			202	45	201	22	200	25
	2-Phenyl	D	306	100	305	3.2	289	0.5	278	9.7	277	10	276	21
8	3-Phenyl	D		100		26		2		7		22		37
8	3-Phenyl[c]	H		100		21		1.2		6.6		19		27
8	3-Phenyl[d]	H		100		16		2		9		24		33
2	6-Phenyl	D		50		100		2[a]		8		3		8
	10-Phenyl	D		100		4		1.2		40		22		52
	X-Phenyl	H		100		15.3		1.3		22.4		30.7		35.9

[a] There is an additional peak at 287, (M − H_3O) 2%.
[b] D, DuPont 21-110B; H, Hitachi.
[c] Isolated in trap from g.l.c. of synthetic reference mixture.
[d] Separated from a Cu^+ catalyzed mixture.

Experimental

Owing to the great similarity in structures, the resemblances in physical properties of the possible isomeric benzanthrones are very close. Melting points fall in the same range. Solubilities do not differ markedly.

(I) Instrumental

Infrared Spectra

The spectra are much alike, except that of the 3-phenyl isomer **5**, which has a strong band at 7.23 μ (very difficult to detect in mixtures).

Nuclear Magnetic Resonance Spectra

These spectra are also much alike, except for the enol **3**, which has some non-aromatic bands. The n.m.r. spectra of the four available, phenyl-substituted benzanthrones are much alike, showing only aromatic hydrogen absorption, and were not decipherable in terms of individual assignments. Therefore, the position of the phenyl substitution could not be confirmed by n.m.r.

The spectrum of the enol **3** in acetone-d_6 has a complex multiplet from δ 8.0–8.8 (3H, aromatic), a complex multiplet from 7.0–7.9 (9H, aromatic). The remaining absorption is an AMX spectrum with $\delta_A = 6.67$ (1H), $\delta_M = 6.14$ (1H), $\delta_X = 5.52$ (1H), $J_{AM} = 9$, $J_{AX} = 1.5$, $J_{MX} = 5$ Hz. These do not allow distinction between the two possible allylic systems (12).

Mass Spectra

These spectra were determined by the use of two instruments, both at 7.0 eV, a DuPont-110B, and a Hitachi RMS-4. Four known phenylbenzanthrones and the parent **1** itself, as reference samples, were examined. Although the pure substances gave similar fragmentation patterns (Table 3) the relative intensities were not sufficiently different to permit their identification when they were components of a reaction mixture. All the phenylbenzanthrones are alike, except the 6-phenyl derivative **2**, which shows a fragment ion (100% at M − 1); this can be attributed to a linking with the adjacent carbonyl oxygen. A fragment at M − 28 is present in all; in this respect these ketones resemble 1-phenyl-9,10-anthraquinones (13). The fragmentation pattern of benzanthrone below 202 is entirely different from that of pure fluoranthene ($C_{16}H_{12}$).

The silated carbinol **8** gives a molecular ion at *m/e* 380 (14%) M, and fragment ions at 307 (1%) M − $(CH_3)_3Si$, 303 (100%) M − C_6H_5, 291 (15%), 289 (17%), 287 (5%), and 73 (32%) $(CH_3)_3Si$.

The enol acetate (7-acetoxy-6-phenyl-6-benz[*de*]anthracene (**4**) gives a molecular ion at *m/e* 350 (22%) M, and fragment ions at *m/e* 308 (44%) M − CH_2CO, 307 (61%) M − CH_3CO, 305 (72%) M − COOH, 291 (100%) M − $OCOCH_3$, 231 (83%), 202 (28%), and 43 (7%) CH_3CO.

The silyl derivative of the unknown substance, from the run in which phenylmagnesium chloride was "activated" with cobaltous chloride, gives a molecular ion at *m/e* 374 (80%) M, and fragment ions at 359 (40%) M − CH_3, 284 (100%) M − 90 (*i.e.*, M − $HOSi(CH_3)_3$), 256 (80%) M − 188 (loss of CO here), 215 (35%), and 73 (40%) $(CH_3)_3Si$. This is a reasonable fragmentation process for a silated derivative of a substance having the structure **9**. A partial interpretation of these observations suggests that the solvent, THF, has entered into one of the reaction products (14).

Gas Chromatography

A Barber–Colman 5000 instrument equipped with a flame ionization detector, and either an 8 ft × 1–8 in., 10% OV-1, or 4 ft, 5% Apiezon L on Chromosorb W-AWDMCS treated support, at 300 ISO, were used for all analyses. Relative retentions on either column were similar. Quantitative calculations (Tables 1, 2) were based on percentages of the volatiles, and response factors were assumed constant.

Although the reaction products were highly colored, sticky gums or hard waxes, from which, in most instances only a single crystalline component could be isolated, application of g.c. gave useful chromatograms, from which it was possible to calculate the area % of the components.

The four main fractions found in the Grignard runs were 3-phenyl- and 6-phenyl-benzanthrones, the enol of the latter, and unreacted benzanthrone. However, the lithium and cobalt runs (*383*, *385*, *398*) contained carbinols, which were estimated as their silated derivatives. Their structures were deduced by interpreting the i.r. and mass spectra. The new component **9** involving the solvent, THF, and present to the extent of about 14%, also trapped as a silated derivative, appears in the column of unknowns (*cf. 385*).

Thin-layer Chromatography

T.l.c. was of limited use. Most of the ketones were indistinguishable (had similar R_f values) on silica or alumina; the spots moved only half as fast on the latter. The solvent was benzene–chloroform, 3:1. The spot for 6-phenyl-benzanthrone (**2**), when illuminated by u.v. light (15) was brown, and masked most of the others.

(II) Preparation of Materials

Ten grams of benzanthrone (Aldrich, B 260), or Eastman's 7*H*-benz[*de*]anthracene-7-one, were recrystallized from a mixture of 70 ml of *o*-dichlorobenzene and 3.2 g of Norite, by boiling gently for 5 min and filtering through a folded filter. Alternatively, by the use of a large Soxhlet apparatus, an intimate mixture of 3 g of benzanthrone and 2 g of Norite, plus some scraps of filter paper, in the cup, was refluxed for 2 h; caking usually occurred in the bottom of the cup, and some product separated in the flask. The benzanthrone was lighter colored, and, after drying in an oven, melted at 175–176°, but the amount per run was limited to that stated. The product from dichlorobenzene was darker colored, m.p. 173–174°. Either way, the air-dried product was heated for 1 h in an oven at 93–95° before use. Other solvents (chlorobenzene, *p*-cymene, acetic or trifluoroacetic acids, dimethylformamide, and THF) were less satisfactory. 2-, 3-, and 10-Phenylbenzanthrones were prepared as given in the literature (23, 3, 24). Phenylmagnesium chloride was Fisher's (Certified reagent in THF, lot 765 225). THF was dried over sodium; air and nitrogen was bubbled through concentrated sulfuric acid. Melting points were determined on a Fisher–Johns block.

(III) The Grignard Reaction

The standardized procedure, adopted after several exploratory runs, using the usual type of apparatus, and swept with nitrogen follows: to a mixture of 25 ml of THF and 12 ml (3 equiv) of the phenylmagnesium chloride, was added 2.3 g (0.01 mol) of benzanthrone, rinsing in any adhering solid with 5 ml of THF. The solution turned a deep brown, but very little heat was evolved; the color was nearly black after 0.5 h. After the mixture had been refluxed for 1.5 h, the flask was cooled. A mixture of 6 ml of acetic acid and 16 ml of water, added cautiously at first, gave two layers. The organic solution was separated and the solvent removed. The sticky residue was taken up in chloroform and distilled with steam as long as any biphenyl (~2 g) came over.

The insoluble portion was taken up in a little chloroform. For g.c. estimation, an aliquot was dried over anhydrous calcium chloride, filtered, and the solvent evaporated; the residue was used directly or silated. To obtain the 6-phenylbenzanthrone (**2**) for further use, the insoluble residue after steam distillation was allowed to stand with a little acetone. Much of the product **2** soon crystallized; a second or even third crop might be obtained; this was followed by the enol **3**, although the separation was not sharp. Ether and methanol were helpful for removing the enol. Ether, ethyl acetate, acetone, benzene, and acetic acid were employed for recrystallization of **2**; the acid was preferred for large amounts, and acetone for small.

If the enol, which at first was isolated fortuitously, is desired, it is preferable to use a 2:1 ratio (*386*). It accumulated in the last fractions and was recrystallized from methanol; m.p., 146–147°.

Anal. Calcd. for $C_{23}H_{19}O$: C, 89.6; H, 5.8. Found: C, 89.8; H, 5.7.

The enol **3** is very readily converted to the ketone **2** (*a*) on simple standing at room temperature, and (*b*) fairly rapidly in most warmed solvents.

To show that the area percents from g.c. are reasonably similar to practical results the comparison (*379*) was made. The hard, colored residue (total weight, 3.35 g) was warmed with 6 ml of boiling acetone, the solution decanted, and the solid residue rinsed with two 4-ml portions of this solvent, followed by 6 ml of hot methanol. The residual solid (1.58 g) had a melting point of 184–185°. The acetone solution left a sticky pitch, which, after a hot ether extraction, left an additional 0.1 g of the same ketone, m.p. 183–184°, (total, 1.6 g 50%). This is in justifiable agreement with the g.c. estimation of 54.2%. It indicates that the use of results from the g.c. area percents are logical figures, and can be usefully employed.

The enol acetate **4** was prepared from 1 g of the mixture (*386*), by stirring it with 5 ml of acetyl chloride, decanting from insoluble material and allowing to cool. The crude ester was recrystallized twice, by boiling with propyl alcohol; it separated very rapidly on cooling. The pearly, yellow acetate melts at 168–169°, with very marked decomposition at 172–173°.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.7; H, 5.1. Found: C, 85.7; H, 5.4.

The insoluble portion, as well as residues from two recrystallizations were mixtures of the ketone **2**, and a trace of unchanged benzanthrone, identified by mixture melting points and t.l.c.

(IV) Effects of Copper and Cobalt Salts

These were employed for their possible catalytic property, *e.g.*, CuCl (5, 16) in *384* and *399*, and $CoCl_2$ (17) in *385* and *385R*. With 0.02 g of $CoCl_2$ (the hydrated reagent was allowed to stand for 10 min with 10 ml of acetyl chloride and the liquid was decanted) the residual, blue solid was rinsed into the reaction flask with 25 ml of THF, in portions. In a repeat (*385R*) of this run, with double the amount of $CoCl_2$, the phenylmagnesium chloride was inadvertently admitted last; this markedly affected the respective yields. There was no reaction with the copper and cobalt solutions by themselves, showing that the Grignard reagent was needed; this indicated that some sort of an intermediate was involved (17).

(V) Phenyllithium

This was prepared by the standard procedure (18), using 1.2 g of lithium, 90 ml of dry ether, and 12.4 g of bromobenzene (dried by distillation), to obtain 3 equiv of the reagent. To this with stirring was added, in two portions, 4.6 g of benzanthrone (0.02 mol); the second portion caused the brownish solution to boil. This was followed by 30 ml of THF, whereupon the solution became purple; all the solid dissolved without external heating, and a purple scum was formed. The ether was boiled off (10 min) on the steam bath, and the clear, dark brown solution was refluxed for 2 h without stirring. After cooling, a mixture of 5.5 ml of acetic acid and 13 ml of water was carefully added; the reaction was vigorous. The upper, ether layer was separated and distilled with steam; the residual black mass hardened. The solid from an acetone solution dispersed over silica gel (21, 22) was introduced into the top of a stainless steel column, and eluted with ligroine (b.p. 63–75°). The colored layer moved about two-thirds of the way down the column and stopped; the colorless eluate contained 1.8 g of crude tan hydrocarbon, m.p. 142–145°. Upon recrystallization from absolute alcohol, 0.6 g (m.p. 147–148°) was recovered. It was then purified by several thin layer purifications, scraping off the bluish-green (finally, blue) areas (following by u.v. light), and extracting each time with hexane until the m.p. was 155.5–156°; the analytical sample melted at 156.5°.

Anal. Calcd. for $C_{23}H_{16}$: C, 94.5; H, 5.5. Found: C, 94.6; H, 5.8.

Both solid and solutions in hexane, benzene, and absolute alcohol showed a blue fluorescence. In t.l.c. it gives a bright blue band on SiO_2 that moves with the solvent front (visible in u.v. light only). It did not form a picrate.

With the hope of isolating additional hydrocarbon, 1.5 g of accumulated residues from previous runs (C_6H_5Li, Cu^+ (19, 20)) were chromatographed, using Al_2O_3. By employing hexane as the eluent, a faintly colored band, which was easily visualized by the u.v. light, slowly moved down the column. In this way, the hydrocarbon was free from the otherwise persistent 6-phenylbenzanthrone (**2**). The yield was 5 mg, m.p. 155–156°.

An orange band was now eluted, employing a 3:1 benzene–chloroform mixture. The fractions were concentrated, in which a few orange needles separated. After warming with ethyl formate, additional solid crystallized, m.p. 203–204°, yield 2 mg. The substance appears to be an isomeric *x*-phenylbenzanthrone, (*x* probably = 4).

The carbinol **9** was detected only in the unsilated runs (in the absence of copper), because it was very easily transformed into the hydrocarbon **7**, as already mentioned. Trapped samples, collected by g.c., were used for structure determination (i.r., mass spectrometry).

The formation of so many products from the reactants in THF solution can be expected in view of the numerous reactive species present, and is evident from the multicolored chromatogram on silica gel (22 bands).

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