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Dibenzo (g,p)chrysene: A Challenging Experiment in Organic Synthesis

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SYNOPSIS: Directions are given for the four-step synthesis of dibenzo(g,p)chrysene from fluoren-9-one. The intermediate products are 9,9'-bifluorene-9,9'-diol, spiro[fluorene-9,9'-(10'H)-phenanthren]-10'-one, and spiro[fluorene-9,9'-(10'H)-phenanthren]-10'-01 in that order. The experiment is designed to illustrate

This experiment focuses on a problem which often perplexes the beginning student of organic chemistry: the conceptualization of the process of structural rearrangement during chemical reaction. In the beginning organic course nowadays much emphasis is placed on the reactions of carbonium ions. This experiment is concerned with two types of carbonium ion rearrangements—the pinacol rearrangement and the reverse "retropinacol" rearrangement. Active metal induced bimolecular reduction, as well as the reduction of a carbonyl group to an alcohol group by a hindered Grignard reagent, are also illustrated in this sequence.

The preparation which we have chosen is that of dibenzo(g,p)chrysene (I) from fluoren-9-one. The reactions used are outlined in Charts 1-4, and may be followed by use of molecular models, if desired. The properties of this compound, I, which are described below, are of considerable interest. Chemically, the amount of double bond character in the central double bond of I has been the subject of debate, with evidence from MO calculations, x-ray studies, and chemical methods giving contradictory results. Such results raise the basic question of the applicability of MO methods and their limitations. Also of interest is the strong blue fluorescence of the molecule, its ability to be oxidized to a cation radical, and its interesting nmr spectrum.

The experimental details are relatively simple, and require no special equipment except a small ultraviolet lamp for monitoring the chromatographic separation of the final product. We have found that the experiment can be done in four or five three-hour laboratory periods, although the apportioning of time must be somewhat flexible to allow the students to read some of the original literature, to construct models, and possibly to design further experiments. The experiment is recommended for students, who have had at least one semester of organic laboratory or who are in a senior research or independent study type of situation.

THE SYNTHESIS OF DIBENZO(G,P)CHRYSENE

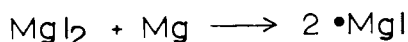
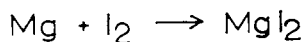
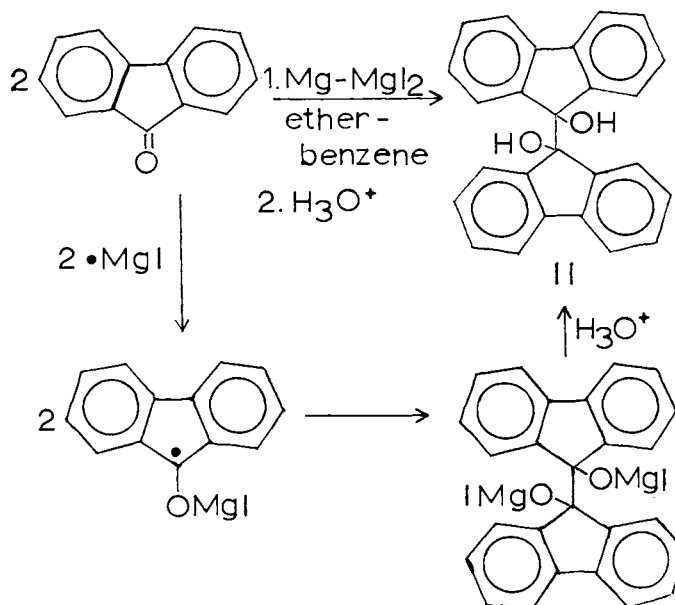
Active Metal Induced Bimolecular Reduction. In this reaction fluoren-9-one is reduced to 9,9'-bifluorene-9,9'-diol

carbonium ion rearrangements and reductions as well as the properties of some interesting compounds to the experienced undergraduate student.

INDEX DESCRIPTORS: Dibenzo (g,p)chrysene, synthesis of Fluoren-9-one, reduction of 9,9'-Bifluorene-9,9'-diol Spiro[fluorene-9,9'-(10'H)-phenanthren]-10'-one Spiro[fluorene-9,9'-(10'H)-phenanthren]-10'-01 Student Experiment

(fluorenopinacol) (II) by the action of a mixture of magnesium iodide and magnesium metal as shown in Chart 1. This pinacol II was first synthesized by Gomberg and Bachmann (1). In fact, they used this method of synthesis in their work. The senior author, Moses Gomberg, was a pioneer in the chemistry of free radical reactions. The very reasonable mechanism outlined in Chart 1 involves the attack of mag-

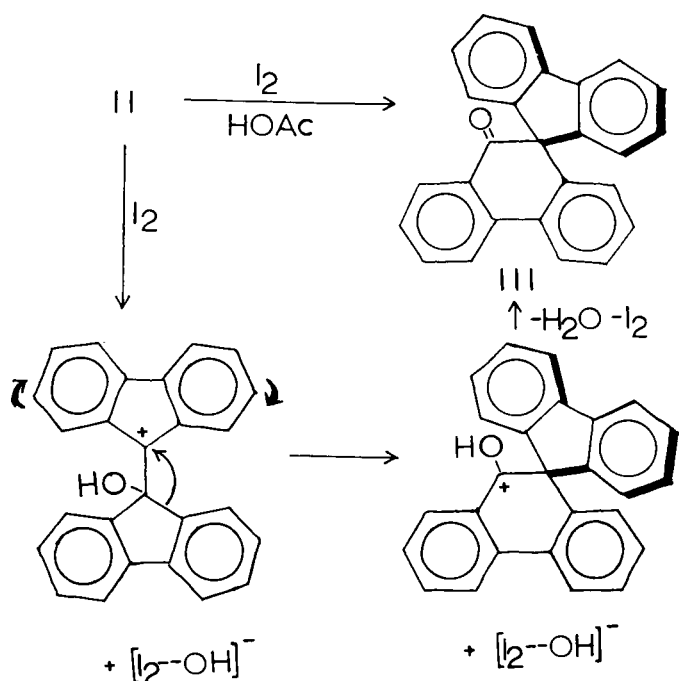
Chart 1



nesium on the carbonyl group. Magnesium is apparently monovalent and acts as a free radical in this reaction. Two of the free radicals resulting from the attack on the carbonyl

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Chart 2



group couple to give the magnesium alkoxide derivative of the pinacol II. Protonation of the alkoxide with hydrochloric acid leads to the product. This scheme is merely a modern representation of the type of reaction sequence proposed (1) by Gomberg and his students.

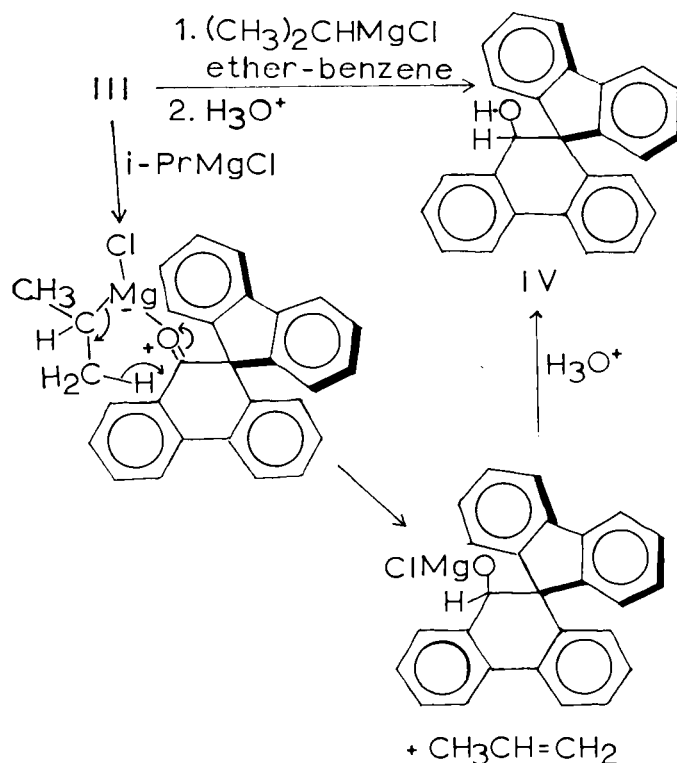
Another interesting possible method of preparing II involves the photochemical reduction of the ketone in the presence of a hydrogen donor. With benzophenone this type of reduction in the presence of 2-propanol is the basis for a particularly dramatic experiment (2) on the synthesis of benzopinacol. Unfortunately, this type of reduction has been unsuccessful for fluorene-9-one with alcohols (3,4). There is apparently some chance for success, however, with an amine as the hydrogen donor (4,5).

The Pinacol Rearrangement. The migration of a pair of electrons bonding a benzene ring to a central carbon atom of II is the key step in the production of the pinacolone, spiro[fluorene-9,9'-(10'H)-phenanthren]-10'-one (10,10-diphenylene-9-phenanthrone) (III), as shown in Chart 2. The usual catalyst for this type of rearrangement is strong acid which Gomberg and Bachmann (1) used in their synthesis. We have chosen to use molecular iodine which also can act as an electron acceptor and complex with a lone pair on the oxygen atom of the pinacol (II). This complexing would be expected to make the hydroxyl a better leaving group and the rearrangement could be formulated as outlined in Chart 2. This action of the iodine was suggested to us by the work of Andrews and Keefer (6) and we prefer it to the heterolytic dissociation of molecular iodine suggested in the work of Evans, Jones, and Thomas (7). As we have outlined the mechanism in Chart 2 the hydroxyl group complexed with the iodine leaves and a carbonium ion is formed. The re-

arrangement follows and I_2-OH which we have preferred to leave intact abstracts a proton from the rearranged carbonium ion to give III, molecular iodine, and water. It is possible that I_2-OH could dissociate to HOI and I^- which could abstract the proton and lead to the same products. It is also possible that the entire process of the group leaving and the rearrangement could be relatively concerted.

Reduction of a Carbonyl Group by Means of a Grignard Reagent. A Grignard reagent will generally add to the carbonyl group of a ketone forming an addition product which can be hydrolyzed to a tertiary alcohol. If, however, the ketone and/or the Grignard reagent are too sterically hindered about the point of attack, the ketone will abstract a hydride ion beta to the magnesium grouping, and will thus be reduced to a magnesium alkoxide. At the same time the alkyl group of the Grignard reagent will be oxidized to the corresponding alkene (4). This reaction of the hindered ketone (III) with isopropylmagnesium chloride is outlined in Chart 3. In this case the reduced alcohol, spiro[fluorene-9,9'-(10'H)-phenanthren]-10'-ol (10,10-diphenylene-9-phenanthrol) (IV), and propylene are formed (8).

Chart 3

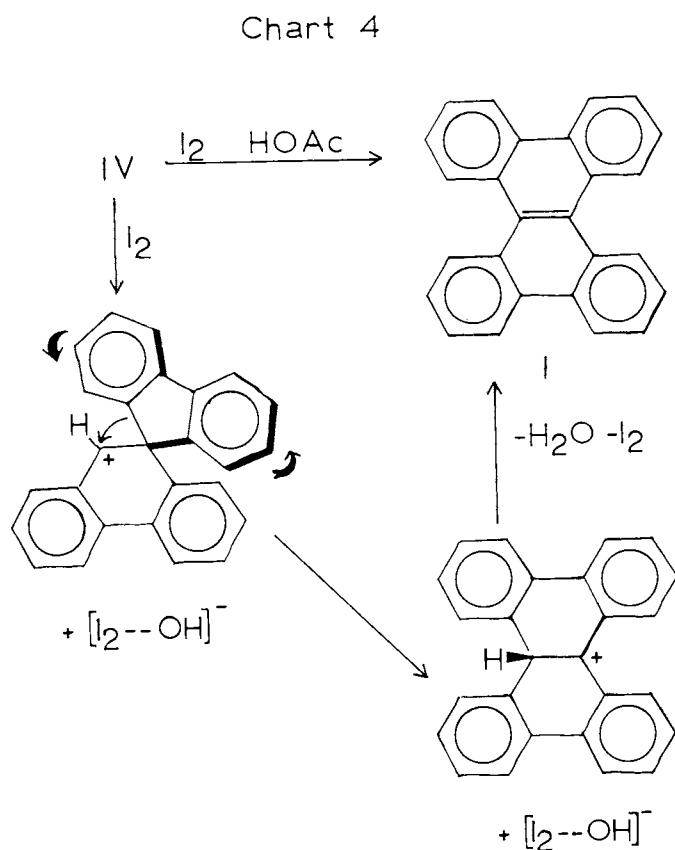


The Wagner-Meerwein or Whitmore Rearrangement. As applied to a pinacol alcohol such as IV this reaction is often called the retopinacol or retopinacolone rearrangement (9). It generally proceeds by a mechanism similar to that of the pinacol rearrangement. The rearrangement as applied to IV

is outlined in Chart 4. As in the pinacol rearrangement of Chart 2 the iodine makes the hydroxyl group a better leaving group and a carbonium ion is generated. A benzene ring shift followed by the loss of a proton completes the reaction as in the pinacol rearrangement of Chart 2. The resulting product in this reaction is the desired final product of our synthetic series: dibenzo(g,p)chrysene (dibenzo(a,c)triphenylene or 9,10-diphenylene phenanthrene) (I).

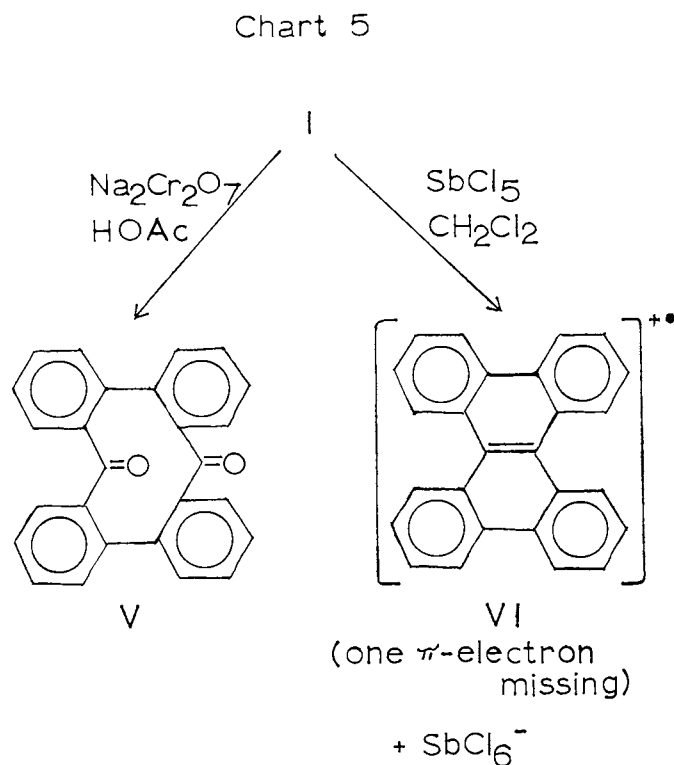
THE CHEMICAL PROPERTIES OF DIBENZO(G,P)CHRYSENE

Double Bond Character of the Central Bond. One of the most interesting features of the structure of dibenzo(g,p)chrysene I is the nature of the central bond. Some molecular orbital calculations (10,11) have predicted less double bond character for the central bond than for the bonds on the outer rings which are analogous to the 1,2-bonds of naphthalene. In fact this view of the structure is seemingly borne out by a determination of the crystal structure by means of X-ray diffraction (12). In this determination the central bond was found to be considerably longer than these outer bonds. On the other hand another molecular orbital calculation (13) predicted just the reverse: namely, that the inner central bond would have more double bond character and be shorter than any of the other bonds. This latter predicted structure is supported by the chemistry of I which has been



reported by Erickson and Schnipp (14). These authors found that the central bond reacted with an ozone molecule to the apparent exclusion of any other bond in the molecule.

The ozonolysis reaction, ozone followed by potassium iodide reduction, yielded the diketone tetrabenzo(a,c,f,h)cyclodecen-9, 18-dione (V). This same diketone can be formed by an oxidation experiment with dichromate in acetic acid as shown in Chart 5. The handling conditions in this experiment are somewhat less sophisticated than those for the ozonolysis, and this oxidation is recommended as an added experiment which the student might carry out on I after he has consulted the original literature (15).



Another reaction which attests to the double bond character of the central bond of I is the reaction (14) with osmium tetroxide² in pyridine-ether. The pyridine-osmium tetroxide complex when reduced with sodium sulfite yielded 8b,16b-dihydrodibenzo(g,p)chrysen-8b,16b-diol (VII) (14). The compound can be visualized from the structure of I with a hydroxyl group attached at each end of the central bond which would, then, no longer be double as shown in Chart 6. It is interesting that this diol VII could also be synthesized by an active metal reduction of the diketone V (16). This reaction must be a kind of an internal "bimolecular" reduction of the two carbonyl groups quite analogous to the reaction outlined in Chart 1. The hydroxyl groups on this diol would be expected to be *cis* to each other on the basis of the osmium tetroxide synthesis. This stereochemistry is also supported by the characteristics of the cleavage of this diol with lead tetraacetate (17). The diol derived from I was found (14) to undergo the pinacol rearrangement to give III, as shown in Chart 6. A reasonable mechanism can

² Students should be warned not to use osmium tetroxide unless special precautions are taken. The compound is very toxic.

be formulated for this conversion which is analogous to that outlined in Chart 2 for the conversion of II to III.

ical cation VI which is apparently deep blue. Another characteristic of the radical cation VI is its definitive electron spin resonance spectrum (20). In Chart 5 is outlined the oxidation of I by antimony pentachloride in methylene chloride to give VI. The structure of VI has been drawn exactly like that of I because the missing electron can be visualized as delocalized over the entire π system. This oxidation of I is a relatively simple experiment and could be carried out by a student with I and excess antimony pentachloride in methylene chloride. The esr measurements were made (20) with just such a solution kept free of oxygen and at a low temperature in order to get well resolved hyperfine splitting in the esr spectrum.

Chart 6

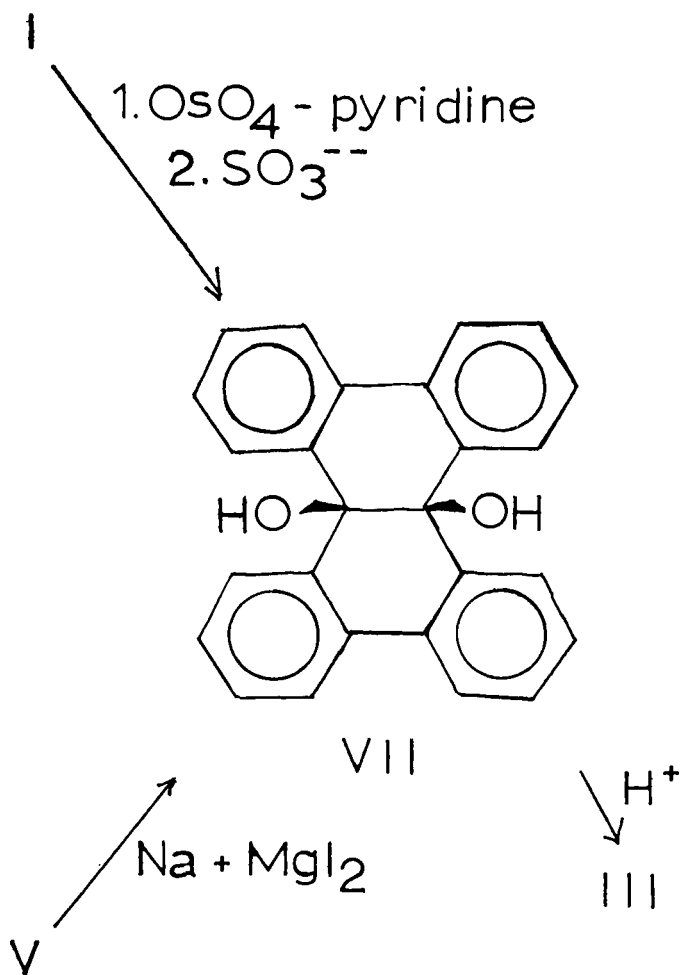


TABLE I. RESULTS OF THE SYNTHESIS OF DIBENZO(G,P)CHRYSENE (I)

Compd	mp (obs °C)	mp (lit °C)	Ref	% Yield	Ir Bands (nujol, cm ⁻¹)
II	185-186 ^a	190-192 ^a	1	90 ^b	3460, 3280, 1600, 765, 735, 725
III	255-256	255	1	58 ^c	1670, 1590, 1250, 772, 741 ^d , 724 ^d
IV	177-178	177-178	9	70 ^b	3460, 3400, 1470, 771, 746, 736, 718
I	214	218 214-215	19 16	85 ^c	1480, 1040, 750, 719

^a Mp with decomposition.

^b Yield before purification.

^c Yield after two crystallizations.

^d Band includes several maxima and inflection points.

SPECTRAL CHARACTERISTICS OF DIBENZO(G,P)CHRYSENE

Preparations of I, which are reasonably pure, tend to be nearly white—just slightly yellow. Even so the compound has been reported to absorb extensively in the near ultraviolet region (15,18,19). Relatively intense absorption bands have been reported (18) at 270, 288, 301, 336, 351, and 338 nm. Bands closely approximating these are given in the other references (15,19). Of even more interest is the dramatic bright blue fluorescence with a maximum emission around 420 nm (19). The fluorescence spectrum is particularly definitive in thin films at low temperatures. Another dramatic color change can be observed when I is oxidized to the rad-

The infrared absorption spectrum of I was measured for one of our samples. The main bands are given in Table I. The nmr spectrum of I in chloroform-d consisted of a symmetrical pattern with two separated multiplets of equal intensity. These multiplets were centered at $\delta = 7.55$ ppm and $\delta = 8.62$ ppm which check very well with the literature values (21) of 7.57 ppm and 8.63 ppm. This nmr pattern approximates the AA'BB' pattern of naphthalene (22) in appearance except that for naphthalene the two halves of the pattern are much closer together at $\delta = 7.38$ ppm and $\delta = 7.68$ ppm. With dibenzo(g,p)chrysene I the protons at positions 1, 4, 5, 8, 9, 12, 13, and 16 (like the α - positions of naphthalene) on the one hand, and the protons at positions 2, 3, 6, 7, 10, 11, 14, and 15 (like the β - positions of naphthalene) on the other hand, approximate each other very closely as to magnetic environment. Such a coincidence of chemical shifts and coupling constants leads to the approximate AA'BB' pattern. As with naphthalene (22) the downfield multiplets have been assigned (21) to the " α " protons. This is logical since these protons would be expected to experience a more pronounced deshielding by ring currents than would be the case for the " β " protons. In fact it would also be expected that such deshielding would be greater for I than for naphthalene especially for the " α " protons as has been observed.

STUDENT PROCEDURES

Reduction of Fluoren-9-one. Into a 250 ml round-bottomed flask, fitted with a reflux condenser, are placed 50 ml of dry ether, 150 ml of benzene, and 5 g of magnesium turnings. While stirring the mixture magnetically, add 15 g of iodine in small portions. Gentle heat may be required to start the reaction which, once started, proceeds with the evolution of heat and the slow decolorizing of the solution. Occasionally the reaction becomes difficult to start, in which case a few drops of ethyl bromide may be added to etch the surface of the magnesium and start the reaction.

When all of the iodine has been added and the brown color of the solution has become lighter, begin the addition of fluoren-9-one. In all, 20 g of fluorenone is added in several portions over a period of about twenty minutes. Stir the mixture rapidly during this time. After this addition the mixture is stirred gently at room temperature for an additional twelve hours before the magnesium complex is decomposed. During the first part of the reduction an orange precipitate may form, but this should mostly all dissolve to give a deep orange solution by the end of the reaction time.

After the twelve hours of stirring add the dark orange solution to 500 ml of 1 M hydrochloric acid. Stir the solution well to dissolve all inorganic salts, and boil it on a steam bath to evaporate all of the ether and benzene. The crude pinacol II is obtained by filtration. This crude pinacol is pure enough for the next step of the synthesis. A sample may be purified further, however, by recrystallizing it once or twice from ethanol.

The Pinacol Rearrangement. The crude pinacol II (15 g) with 0.1 g of iodine is suspended in 150 ml of glacial acetic acid. Stir the mixture and heat it to reflux temperature. The mixture is heated gently under reflux for an hour. Pour the reaction mixture into a liter of water and filter it through a filter crucible with a fritted disk of medium porosity. The resulting solid is twice recrystallized from benzene to give white crystals of the pinacolone III.

Reduction of the Pinacolone. A Grignard reagent is prepared from 7.0 ml of 2-chloropropane and 2.0 g of magnesium turnings in a mixture of 20 ml of dry benzene and 20 ml of dry ether. To the reagent is added 8.0 g of the pinacolone III in small portions at such a rate that the reaction does not become too vigorous. During the addition stir the mixture and heat it under reflux. After the addition is completed continue the heating and stirring for an additional hour. The addition product is then decomposed by 250 ml of 1 M hydrochloric acid. The solid phenanthrol IV is filtered, dried, and used directly in the next step. A small sample may be purified by recrystallizing once or twice from a 1:1 mixture of ethanol and acetone.

The Retropinacol Rearrangement. The phenanthrol IV (5.0 g) is heated with 0.1 g of iodine and 50 ml of glacial acetic acid under reflux for an hour as described for the

pinacol rearrangement. Pour the mixture into 250 ml of water, and separate the product by filtration. Dissolve the crude hydrocarbon in 50 ml of benzene, and pour the solution through a small alumina column. The chrysene I comes down the column first as benzene is used as an eluant. It can be detected by its blue fluorescence under an ultraviolet lamp. When no more fluorescent material is passing through the column, the elution is stopped. Evaporate the solvent from the solution. The product is then recrystallized twice from acetic acid to give white crystals of dibenzo(g,p)-chrysene I.

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