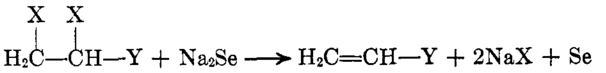
sulfates also react with sodium selenide to give symmetrical selenides. The procedure has been used for the preparation of spiro derivatives.[2] Cyclic selenides are made from polymethylene dibromides and alcoholic sodium selenide.[3] No cases of elimination of halogen from vicinal dihalides by sodium selenide have been reported.

We wish to report the convenient preparation of alkenes from vicinal dihalides by treatment with sodium selenide in dimethylformamide or dimethyl sulfoxide solution. Terminal alkenes are prepared in good to excellent yields from either vicinal dichloro- or dibromoalkanes. The following reaction illustrates our findings.



$$\overset{X}{H_2C}-\overset{X}{CH}-Y + Na_2Se \longrightarrow H_2C{=}CH-Y + 2NaX + Se \quad (1)$$

Table I summarizes the data obtained for a series of 1,2-dihalogen-substituted alkanes. The ease of removal of halogen is I > Br > Cl. The effect of added substituents on the elimination is to reduce the apparent yield of the alkene. Yields were based upon the amount of gas evolved. All gases were analyzed by gas chromatography[4] and found to be only the expected alkene in each case.

TABLE I

EFFECT OF SUBSTITUENTS ON DIHALIDE ELIMINATION REACTION

Dihalide		Alkene yield, %	
X	Y	Dimethylformamide	Dimethyl sulfoxide
I	H	85.2	88.0
Br	H	77.7	72.7
Br	CH_3	52.6	64.6
Br	C_2H_5	46.6	54.2
Cl	H	75.0	70.6
Cl	CH_3	50.5	57.4
Cl	C_2H_5	28.1	33.3

As the above reaction is exceedingly simple to perform, it can be suggested as a convenient new alternative to either prepare or purify alkenes.[5] Further work is in progress to determine the stereochemistry of this reaction and elucidation of its mechanism.

Experimental Section

The dihalides were obtained in high purity from the following sources: 1,2-dibromoethane, 1,2-dichloroethane (Fisher Scientific Co.); 1,2-diiodoethane, 1,2-dibromobutane, 1,2-dichlorobutane (City Chemical Co.); 1,2-dibromopropane, 1,2-dichloropropane (Matheson Coleman and Bell).

A representative experimental procedure is as follows. The dihalide in dimethylformamide (or dimethyl sulfoxide) is added to a rapidly stirred suspension of sodium selenide (ground to <100 mesh) in dimethylformamide (or dimethyl sulfoxide) at 70–75°. The reaction commences almost immediately and is evidenced by rapid gas evolution and a gradual darkening of the reaction mixture. Evolved gases are collected over water and analyzed by gas chromatography. Reaction is essentially complete after 1 hr. Each reaction was repeated several times and the results were reproducible. The yields of olefin are given in Table I.

Acknowledgment.—The authors gratefully acknowledge the support of the Selenium-Tellurium Development Association, Inc.

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[2] H. J. Backer and H. J. Winter, *Rec. Trav. Chim.*, **56**, 492 (1937).

[3] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1096, 1497, 2197 (1929); 1497 (1930).

[4] A 50-ft di-*n*-butylmaleate column was used.

[5] This elimination reaction may also be carried out in acetone with similar results. For example, 1,2-dibromoethane results in a 78.6% yield of ethylene.

The Synthesis and Resolution of 1- and 2-Methylcholanthrene[1]

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The idea of testing optical isomers of cancer-producing hydrocarbons is not new,[3] but prior to this work such optically active isomers had not been prepared.[4] In this paper we report on the synthesis of 1-methylcholanthrene (I) and 2-methylcholanthrene (II) and the resolution of each into optical antipodes.[5]

The synthesis of I was modeled after, but not the same as, the method described.[6] Modifications were needed in several steps because of the increased size of runs, our inability to reproduce reported[6] results, and the desire for higher yields.

The preparation of β-(3-phenanthroyl)propionic acid (III, Scheme I) was essentially that described[7] except for the purification procedure (see Experimental Section). The reduction to γ-(3-phenanthryl)butyric acid (IV) was effected[8] in markedly improved (94%) yield. Ring closure to V in hydrogen fluoride went in 94% yield.

As implied by Bachmann[9] the Reformatsky reaction of V was erratic. In our hands many attempts to duplicate Bachmann's result failed completely; yet, after many runs had failed, a few succeeded, although the yields was never so high as Bachmann reported for a 2-g run. On a larger scale (30 g of V), success was attained when the reactions were carried out in pure dry benzene, but occasionally, the reaction could not be started despite careful attention to details. The hydroxy ester was dehydrated without purification, the crude unsaturated ester was dehydrogenated by heating with sulfur, and the crude ester was hydrolyzed to the acid (VIa) in an over-all yield of 80% from V. Cyclization of VIa to VIIa proceeded well (83%) in hydrogen fluoride.

The conversion of VIIa to I was not so easy as anticipated. The best route involved condensation

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[1] Part of the work herein presented was taken from the Ph.D. thesis of R. W. Wotring, Jr., The Ohio State University, 1965.

[2] Postdoctoral Fellow on funds supplied by a grant from the National Institutes of Health, Bethesda, Md.

[3] L. F. Fieser and A. M. Seligman [*J. Am. Chem. Soc.*, **57**, 1377 (1935)] mention the interest and they synthesized, 2,3-dimethylcholanthrene but made no attempt at securing the optical isomers.

[4] The above 2,3-dimethylcholanthrene was reported to be carcinogenic by M. J. Shear, *Am. J. Cancer*, **28**, 334 (1936). One attempt to prepare it in optically active form failed; see M. S. Newman and J. Linsk, *J. Org. Chem.*, **14**, 480 (1949).

[5] The testing of these isomers for carcinogenic activity is being carried out by Dr. Charles Huggins, Ben May Laboratory for Cancer Research, Chicago, Ill., Dr. James Miller, McArdle Laboratory for Cancer Research, Madison, Wis., and Professor E. Von Haam, The Ohio State University. These workers will report their results independently.

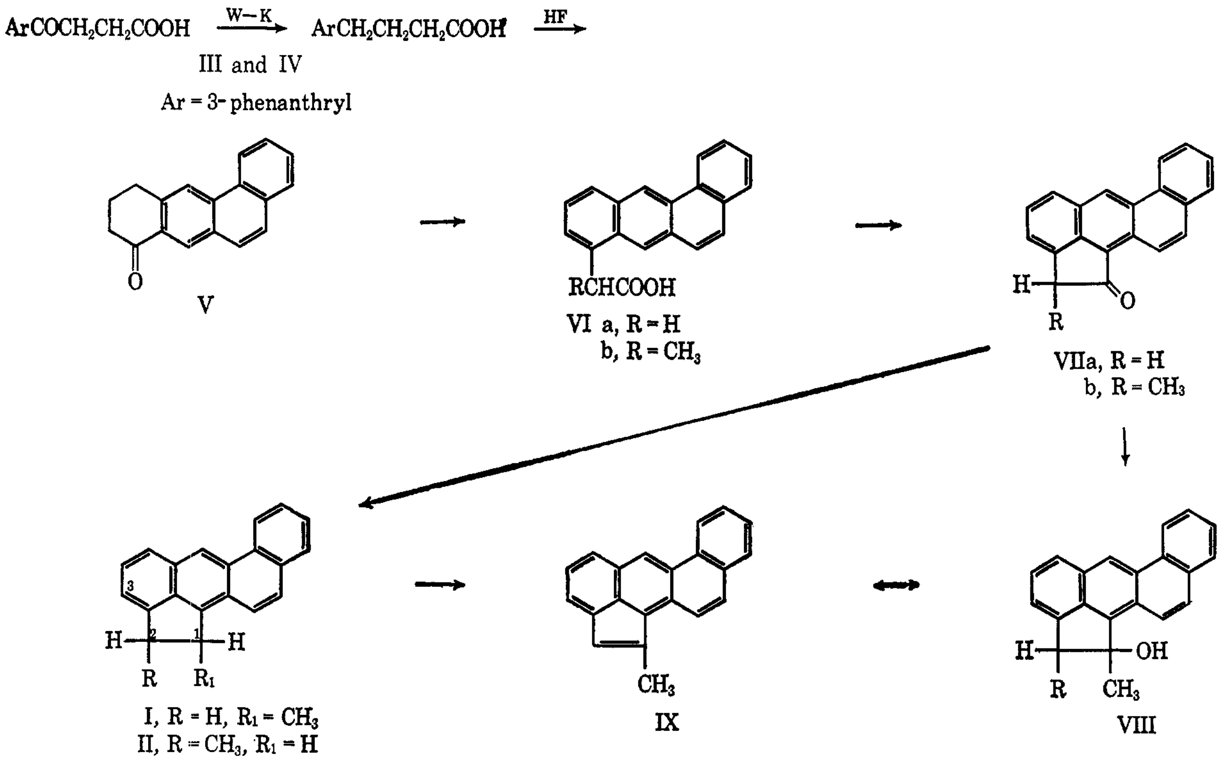
[6] W. E. Bachmann and S. R. Safir, *J. Am. Chem. Soc.*, **63**, 2601 (1941).

[7] R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 1012 (1933).

[8] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

[9] W. E. Bachmann, *J. Org. Chem.*, **3**, 434 (1938).

SCHEME I



of VIIa with methylmagnesium iodide followed by dehydration of the crude carbinol (VIII) to IX and catalytic reduction of the latter to I. On reduction of VIII with lithium aluminum hydride–aluminum chloride reagent,[10] I could be obtained in fair yield but a small amount of 2-methylcholanthrene (II) was isolated by chromatography. Since some rearrangement had occurred this method of reduction should be applied with caution in certain cases.

Condensation of V with methyl α-bromopropionate followed by dehydration, dehydrogenation with sulfur, and hydrolysis afforded VIb. Cyclization of the latter with hydrogen fluoride to VIIb followed by reduction of VIIb with lithium aluminum hydride–aluminum chloride yielded II. Neither the Huang-Minlon–Wolff–Kishner nor the Martin modification of the Clemmensen[11] reduction yielded more than small amounts of II.

Purification of both I and II was difficult as they remained orange-red to red colored even after the usual methods of purification were applied. The best method involved subjection of pure solutions of I and II in ethyl acetate–acetic acid (5:1) to catalytic hydrogenation over a platinum catalyst. In this way only could pale yellow hydrocarbons be obtained.

The resolutions of I and II were effected by fractional crystallization of the complexes of I and II with (+)- and (−)-α-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid[12] (TAPA). By using (+)-TAPA, (−)-I and (−)-II were obtained from the more insoluble complexes. The resolution of I proved to be easier than that of II. Small amounts of the resolved hydrocarbons are available for testing.

Experimental Section[13]

β-(3-Phenanthroyl)propionic Acid (III).—To a stirred solution of 356 g of phenanthrene and 220 g of succinic anhydride in 1.4 l. of nitrobenzene in a 5-l., three-necked flask was added 587 g of aluminum chloride during 20 min, the temperature being held at 10–20° by an ice bath. The bath was removed and, after 30 min, the temperature was raised to 45° for 15 min. The cooled reaction mixture was then poured on 2 kg of ice and 400 ml of concentrated HCl. After the nitrobenzene had been removed by steam distillation, the aqueous portion was decanted from the dark solid. A solution of 350 g of potassium carbonate in 1 l. of water was added and steam distillation was resumed until all of the nitrobenzene was removed. The cooled solution was extracted three times with ether and was then slowly acidified with HCl. The solid was washed with water and dried. This solid was then extracted with boiling chloroform (7 ml/g or other ratio shown by trial to be best for the particular run). The remaining solid was almost pure β-(2-phenanthroyl)propionic acid (15% yield). Recrystallization from acetic acid yielded the pure acid mp 208–209°, as colorless crystals.[14] From the chloroform extracts 190 g (34%) of III,[7] mp 159–160°, was obtained after two recrystallizations from chloroform. After several recrystallizations, a purer sample of III, mp 162–163°, was obtained, but the 159–160° material was used in subsequent reactions.

γ-(3-Phenanthryl)butyric Acid (IV).—To a stirred solution at 90° of 30 g of KOH and 125 g of III in 1.2 l. of triethylene glycol was added 90 g of 85% hydrazine. After heating to 110°, 65 g of KOH was added and the temperature was then raised to 195° by slow distillation. After 30 min at 195° the mixture was cooled to 30° and poured into 600 ml of water. The resulting solution was poured into 2 l. of ice and water containing 225 ml of concentrated HCl. The well-washed solid which formed was dried and crystallized from benzene (Darco G-60, charcoal) to yield 112 g (94%) of IV,[15] mp 139–140°.

5-Keto-5,6,7,8-tetrahydro-1,2-benzanthracene (V).—To 300 ml of anhydrous HF in a 500-ml polyethylene bottle cooled in an ice

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[10] Compare J. Blackwell and W. J. Hickinbottom, *J. Chem. Soc.*, 1405 (1961). See also J. H. Brewster, H. O. Bayer, and J. F. Osman, *J. Org. Chem.*, **29**, 110 (1964).

[11] E. L. Martin, *J. Am. Chem. Soc.*, **58**, 1438 (1936).

[12] M. S. Newman and W. B. Lutz, *ibid.*, **78**, 2469 (1956).

[13] Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich. The phrase "worked up in the usual way" means that the organic solvent layer was washed with dilute acid and/or base as needed, with saturated sodium chloride solution, and the solvent was removed after filtration through MgSO₄. All melting points are uncorrected and were taken with standardized thermometers.

[14] In ref 7, this acid was reported to melt at 207–208°.

[15] W. E. Bachmann and J. T. Bradbury [*J. Org. Chem.*, **2**, 175 (1937)] give a melting point of 139–140°.

bath was slowly added 50 g of IV with swirling. The deep red solution was left in a hood for 24 hr and the remaining contents were treated with sodium bicarbonate solution. The neutral portion of the reaction product was dissolved in 360 ml of hot chloroform (charcoal) and diluted with 110 ml of ethanol. This solution, after concentration to 220 ml by distillation, afforded 43.8 g (94%) of V,[16] mp 182–183°.

1,2-Benzanthracene-5-acetic Acid (VIa).—In a typical reaction a solution of 30.0 g of V in 500 ml of thiophene-free benzene in a 1-l., three-necked flask was concentrated to 450 ml by distillation. To the boiling solution was added a solution of 19.6 g of freshly distilled methyl bromoacetate followed by 8 g of zinc strip freshly activated by swirling with 2 *N* HCl for 2 min, rinsing with dry acetone, and drying in an oven at 70° for 10 min, followed by rapid sandpapering. After 3.5 hr at reflux under nitrogen all of the zinc had reacted. An additional 2 g of zinc and 1 g of methyl bromoacetate were added and refluxing was continued for 20 min. The reaction mixture was treated with dilute HCl and worked up as usual. A small amount of *p*-toluenesulfonic acid was added and benzene was distilled until no further water was seen in the distillate. The benzene was removed to yield 37.2 g of crude ester. To this 4.0 g of sulfur was added, and the mixture was heated at 195–200° for 4 hr. Then 1 g of zinc dust was added and heating was continued for 5 min. The cooled mixture was treated with 300 ml of hot acetone and the resulting solution (charcoal) was filtered (Celite, Filter Aid) and concentrated to dryness. The residue was hydrolyzed by boiling with aqueous alcoholic KOH for 30 min. The organic acid fraction was crystallized from benzene to yield 28.0 g (80% from V) of colorless VIa,[17] mp 233–234°. Comparable results were obtained when ethyl bromoacetate was used in place of methyl bromoacetate in the above sequence.

Ethyl 7,8-Dihydro-1,2-benzanthraceneacetate.—Before we were able to get the above Reformatsky reactions to proceed, we treated V with ethoxyethynylmagnesium bromide to produce the desired unsaturated ester[18] as described. To a solution under nitrogen containing the ethoxyethynylmagnesium bromide prepared from 7.4 g of ethoxyacetylene in 200 ml of tetrahydrofuran and 90 ml of ether was added 19.7 g of V during 25 min. After heating at reflux for 3 hr and standing at room temperature overnight, the mixture was treated with dilute H_2SO_4. After the usual work-up the residue was *quickly* vacuum distilled at 0.1–1.0 mm to yield a light yellow oil which crystallized readily from 120 ml of ethanol to yield 19.2 g (76%) of the named ester, mp 93–95°. A pure sample, mp 97.5–98.0°, was obtained after five further recrystallizations.

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.5; H, 6.4. Found: C, 83.6; H, 6.4.

Dehydrogenation of 7.0 g of ester, mp 93–95°, by heating with 0.77 g of sulfur at 195–200° for 5 hr yielded 6.3 g (90%) of ethyl 1,2-benzanthracene-5-acetate. The analytical sample melted at 115.6–117.0° after recrystallization from alcohol. On saponification acid VIa was obtained in high yield.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.1; H, 5.8. Found: C, 84.2; H, 5.6.

1-Ketocholanthrene (VIIa).—To 40 ml of HF was added 4.0 g of VIa with swirling. After 15 hr the residue was ground and washed well with sodium carbonate solution. The neutral product was crystallized from benzene to yield 3.1 g (83%) of yellow needles of VIIa,[9] mp 230–231°. Cyclization of VIa *via* the acid chloride (prepared with PCl_5) by treatment with $AlCl_3$ in carbon disulfide at reflux for 1 hr yielded VIIa in comparable yield.

1-Hydroxy-1-methylcholanthrene (VIII).—To 15 ml of 3 *M* ethereal methylmagnesium bromide was added a solution of 2.0 g of VIIa in 400 ml of warm benzene. After treatment with ammonium chloride solution the mixture was worked up as usual to yield 2.13 g of orange solid, mp 70–80°. A solution of 1 g of similar material in 100 ml of ethanol deposited 0.25 g of solid which was recrystallized from acetone-benzene to yield pure VIII, mp 210–211°.

Anal. Calcd for $C_{21}H_{16}O$: C, 88.7; H, 5.7. Found: C, 88.9; H, 5.7.

1-Methylcholanthrene (I).—To a suspension of 0.5 g of lithium aluminum hydride in 20 ml of ether was added a solution of 8.7 g of aluminum chloride in 50 ml of ether followed by a solution of 2.13 g of crude VIII (see above) in 250 ml of ether. After refluxing for 30 min, 15 ml of ethyl acetate was added and then ammonium chloride solution. After the usual work-up the material was chromatographed over Woelm alumina using benzene. A small amount of a crystalline yellow compound, mp 167.0–167.5°, which analyzed for $C_{21}H_{18}$, was eluted first but not further examined. The second compound eluted proved to be 2-methylcholanthrene (II) mp and mmp 156–157° (see below). Only 50 mg of II was obtained. There was then obtained 1.35 g (68%) of I, mp 166–168°. Recrystallization from acetone–alcohol yielded 1.20 g (60%) of pure I,[6] mp 169–170°, as small orange crystals.

Finally, 0.1 g of a deep red substance, mp 175.5–176.5°, was obtained. On the basis of an infrared band at 6.20 μ and analysis, the structure was assumed to be that of the olefin, IX, corresponding to I, but no further proof of structure was attempted.

Anal. Calcd for $C_{21}H_{14}$: C, 94.7; H, 5.3. Found: C, 94.5; H, 5.5.

An alternate preferable synthesis of I involved treatment of freshly prepared methylmagnesium iodide, from 3.8 g of magnesium and 25.6 g of methyl iodide in 110 ml of ether, with a solution of 5.4 g of VIIa in 750 ml of benzene. After 2 hr at room temperature the reaction mixture was treated with a solution of 40 g of NH_4Cl in 200 ml of water. The usual work-up afforded 5.0 g of crude orange solid, mp 170–180°. A solution of 2.7 g of this solid in 160 ml of 17% acetic acid in ethyl acetate was reduced over Adam's platinum catalyst at 35 psi. After 15-min reduction was complete and the catalyst was removed by filtration. The products from three such reductions were combined and crystallized from acetone–alcohol to yield 6.0 g of pale yellow I, mp 166–168°. Recrystallization afforded crystals, melting point and mixture melting point with I above 169–170°.

α-(1,2-Benzanthracene-5)propionic Acid (VIb).—In a typical reaction as described for VIa, 20.0 g of V was treated with 15.6 g of methyl α-bromopropionate and 6.3 g of zinc. After dehydration of the crude product the crude ester was heated with 2.73 g of sulfur at 195–200° for 5 hr. Saponification of the aromatic ester with a solution of 40 g of potassium hydroxide in 250 ml of alcohol and 90 ml of water followed after 30 min at reflux with 500 ml of hot water and cooling yielded a suspension of the potassium salt. This was poured into 2 l. of ice and water containing 100 ml of concentrated HCl. The solid was collected and taken into boiling benzene and this solution was worked up as usual to yield a brown solid. This was recrystallized from acetone (charcoal) and benzene to yield 18.6 g (76% based on V) of colorless VIb, mp 181–182°.

Anal. Calcd for $C_{21}H_{16}O_2$: C, 84.0; H, 5.4. Found: C, 83.8; H, 5.6.

In a similar run involving 20.0 g of V and ethyl α-bromopropionate, the dehydrated ester was saponified and the unsaturated acid α-(7,8-dihydro-1,2-benzanthracene-5)propionic acid was isolated as colorless crystals, mp 176.0–176.5°, in 88% yield, on recrystallization from benzene–petroleum ether.

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.6; H, 6.2.

This acid was converted into the methyl ester, mp 96.0–96.5°, on crystallization from methanol.

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.5; H, 6.4. Found: C, 83.4; H, 6.4.

1-Keto-2-methylcholanthrene (VIIb).—To 150 ml of HF was added 15.0 g of VIb. After the HF had evaporated the usual work-up afforded 12.0 g (85%) of VIIb as yellow dense prisms, mp 214–215°. A sublimed sample melted at 201–202°.

Anal. Calcd for $C_{21}H_{14}O$: C, 89.3; H, 5.0. Found: C, 89.0; H, 5.0.

2-Methylcholanthrene (II).—In the best of several experiments in which the proportions of $AlCl_3$ to $LiAlH_4$ to VIIb were varied, a solution of 4.0 g of VIIb in 300 ml of ether was added to a solution obtained by adding 2.0 g of $LiAlH_4$ to a solution of 13.9 g of $AlCl_3$ in 600 ml of ether. The reaction mixture was treated with ethyl acetate and then was worked-up as usual to yield 3.6 g (95%) of pale orange II, mp 155–157°, from acetone–alcohol. The recrystallized analytical sample melted at 156–157°.

Anal. Calcd for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 93.9; H, 6.1.

Catalytic reduction as in the case of I afforded pale yellow II, mp 156–157°.

Resolution of 1-Methylcholanthrene (I).—A solution containing 1.340 g of I and 2.224 g of (−)-TAPA[12] in 500 ml of benzene

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[16] Reference 7 reports mp 179–180° for V.

[17] Reference 9 gives mp 233–234° for VIa.

[18] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p 225.

was concentrated to 350 ml by distillation.[19] The mother liquor was decanted from the dark complex which had separated after standing for 1 day. This complex was recrystallized from 100 ml of benzene and the resulting complex was decomposed by treatment with sodium bicarbonate solution to yield 0.32 g of (−)-I, $[\alpha]^{20}\mathrm{D}$ −91.3 ± 1° (*c* 1, benzene). In similar runs using (+)-TAPA, (+)-I having comparable positive rotation was obtained. Repetition of this process using 0.30 g of I having $[\alpha]^{20}\mathrm{D}$ −91° and 1 equiv of (−)-TAPA in 60 ml of benzene yielded 0.20 g of (−)-I, $[\alpha]^{25}\mathrm{D}$ −96 ± 1° (*c* 1, benzene). Since repetition of this process did not result in further change of rotation we assume that maximum rotation has been reached. Comparable results were obtained with (+)-TAPA and (+)-I had similar mp and rotation to (−)-I. The melting point of both (+)-I and (−)-I is 167–168° and there is no appreciable depression of the melting point on mixing with racemic I, mp 169–170°. Over 2 g each of pure (+)-I and (−)-I was obtained.

Resolution of 2-Methylcholanthrene (II).—The resolution of II was more difficult than that of I. A hot solution of 2.00 g of II and 3.32 g of (−)-TAPA in 600 ml of benzene was allowed to stand at room temperature[19] for 2 days. The solid complex (A) which had separated from the green solution was collected by filtration. The filtrate was concentrated to one-half volume and on standing a second crop of complex, B, was obtained. The above filtration and concentration procedure was repeated three times. Complex A was recrystallized and the filtrate was used to recrystallize B, etc. After a number of such treatments had been performed the hydrocarbon was isolated from the complex by alkaline extraction of the TAPA. In this way fractions amounting to 0.95 g of (−)-II, $[\alpha]^{20}\mathrm{D}$ −45 to −50° (*c* 1, in benzene), were obtained, combined, and treated with 1.60 g of (+)-TAPA in 175 ml of hot benzene. The complex which separated was collected and the *filtrate* was worked up to yield 0.20 g of (−)-II, $[\alpha]^{20}\mathrm{D}$ −58.5 ± 1° (*c* 1, benzene), mp 160–161°. This rotation was not increased by further treatments and we assume it to be the maximum. Melting points of (+)-II and (−)-II ,mp 160–161°, with racemic II, mp 156–157°, were intermediate.

Quantities of maximally resolved I and II have been sent to research workers in the cancer field.[5]

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[19] All operations involving TAPA were carried out in apparatus shielded from light as much as convenient.

Nature of the Complex Formed When Phenyl Grignard Is Added to Fenchone

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Complex formation between a carbonyl group and a Grignard reagent has frequently been invoked in the mechanism of the Grignard addition reaction.[1] If a relatively stable Grignard–ketone complex could be isolated and shown to be an intermediate in the addition reaction then its structure would be of value in delineating the mechanism of this reaction.

With this in mind we have surveyed the various literature reports of stable complexes and reinvestigated the "phenyl Grignard–fenchone complex."

Pfeiffer and Blank noted a precipitate when the Grignard reagent prepared from ethyl bromide was added to benzophenone.[2] Upon hydrolysis of this reaction mixture benzophenone was isolated. As Bikales and Becker have pointed out, the complex was not isolated and then hydrolyzed.[3] When Nesmeyanov and Sazanova repeated Pfeiffer and Blank's work, but isolated and hydrolyzed the precipitate, they found that the corresponding carbinol was formed.[4] Thus it appears that the precipitate noted by Pfeiffer and Blank is not a Grignard–ketone complex, but is the magnesium salt of the carbinol formed from the addition and reduction reactions.

Meisenheimer obtained a precipitate from the reaction of benzaldehyde and ethylmagnesium bromide which he isolated by filtration and found that the solid released ethane upon hydrolysis.[5] However, the quantity of ethane was relatively small (2–5 mole %).

Klages[6] believed he had isolated a complex of acetomesitylene and ethylmagnesium bromide; however, Kohler[7] showed that this precipitate was the enolate salt of acetomesitylene.

Other carbonyl–Grignard complexes have been reported but with the exception of the fenchone–Grignard complex most of the carbonyl compounds contained other functional groups.[1a] Fenchone, however, was reported to combine with several aryl Grignard reagents to give products insoluble in ether. Prolonged heating of this precipitate in excess Grignard reagent was reported to give low yields of the addition product.[8] Nesmeyanov and Sazanova isolated this complex and carried out a partial analysis.[4] They noted that fenchone was regenerated when this precipitate was isolated and hydrolyzed. They also observed that the magnesium/bromide ratio was 1:14.

We have found that this precipitate is easily obtained in a granular form by the addition of the Grignard reagent from bromobenzene prepared in ether to fenchone dissolved in ether. The quantity of complex formed was variable, but in initial experiments about 8 g of precipitate could be isolated and dried under nitrogen from 15 g (0.1 mole) of fenchone. On heating the solid in a sealed capillary, a liquid is given off at 160°, just above the boiling point of fenchone. A KBr pellet of the precipitate shows a carbonyl absorption at 1630 while pure fenchone shows a carbonyl absorption band at 1740 cm^{-1}. No phenyl bands were observed. The precipitate was found to dissolve readily in tetrahydrofuran. Furthermore, when phenyl Grignard in tetrahydrofuran and fenchone are mixed, no precipitate is formed and the infrared spectrum of the solution shows the normal uncomplexed carbonyl absorption at 1740 cm^{-1}. There was no apparent reduction in the carbonyl intensity even on allowing the solution to stand for several days.

Weighed portions of the nitrogen-dried precipitate were hydrolyzed with a known amount of dilute sulfuric acid. The solution was extracted with carbon tetrachloride to remove ether, benzene, and fenchone. Aliquots of the aqueous phase were then used for (a) back titration with standard base to determine the

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[1] (a) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954; (b) J. Miller, G. Gregoriou, and H. S. Mosher, *J. Am. Chem. Soc.*, **83**, 3966 (1961); (c) M. Anteunis, *J. Org. Chem.*, **27**, 596 (1962); **26**, 4214 (1961); (d) H. O. House and D. D. Traficante, *ibid.*, **28**, 355 (1963); (e) S. G. Smith, *Tetrahedron Letters*, **No. 7**, 409 (1963).

[2] P. Pfeiffer and H. Blank, *J. Prakt. Chem.*, **153**, 242 (1939).

[3] N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1963).

[4] A. N. Nesmeyanov and V. A. Sazanova, *Bull. Acad. Sci. URSS Classe Sci. Chim.*, 499 (1941).

[5] J. Meisenheimer, *Ann.*, **446**, 76 (1926).

[6] A. Klages, *Chem. Ber.*, **35**, 2633 (1902).

[7] (a) E. P. Kohler, J. F. Stone, and R. C. Fuson, *J. Am. Chem. Soc.*, **49**, 3181 (1927); (b) E. P. Kohler and R. Baltzly, *ibid.*, **54**, 4015 (1932).

[8] S. Leroide, *Compt. Rend.*, **148**, 1611 (1909).