[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Synthetic Studies in the Dihydropyrene Series[1]

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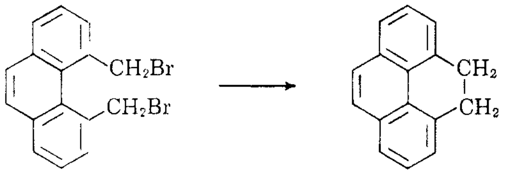
A new synthesis of 4,5-dihydropyrene is reported. Synthetic experiments designed to produce 1,6-dihydropyrene yielded pyrene, apparently because of the ease of autoxidation of this dihydropyrene. Some experiments designed to yield 1,8-dihydropyrene are reported, but the synthesis was not completed.

The reported copolymerization of pyrene with butadiene[2] made it desirable to have available the dihydropyrene types which might be formed by a free radical attack on pyrene so that their ultraviolet absorption characteristics could be determined. 4,5-Dihydropyrene had been prepared by Coulson[3] by the catalytic reduction of pyrene. However, molecular orbital calculations[4] have indicated that free radical attack on pyrene might be expected to produce 1,6- or 1,8-dihydropyrene derivatives, and these were desired as well.

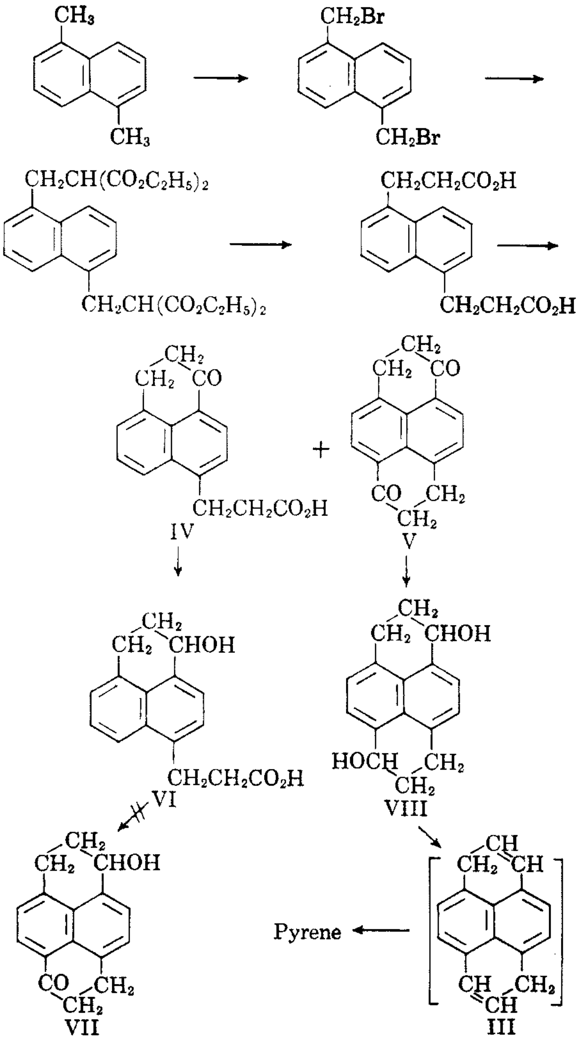
4,5-Dihydropyrene (I) has now been synthesized by the action of lithium phenyl on 4,5-bis(bromomethyl)phenanthrene (II), which was prepared by the method of Badger and co-workers.[5] Our dihydropyrene was identical with that reported by Coulson.[3] This type of ring closure of a dibromide has often been accomplished with lithium phenyl on biphenyl derivatives to yield dihydrophenanthrenes,[6,7] but does not appear to have been applied to phenanthrene derivatives before this time. The structure of the dibromide (II) has been definitely established by the work of Bergmann and Pelchowicz.[7]



II I

Another possible route to 4,5-dihydropyrene that was investigated was the cyclodehydration of β-(4-phenanthryl)ethanol, a compound which has been described by Bendas and Djerassi.[8] The attempted dehydration produced only a very low molecular weight polymer of 4-vinylphenanthrene.

The following series of reactions was selected for the synthesis of 1,6-dihydropyrene (III):



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[1] The work discussed herein was begun as a part of the synthetic rubber research project under the auspices of the National Science Foundation and completed under contract number AF-33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, Lt. L. E. Coleman and Lt. Paul D. Shaw, project engineers.

[2] C. S. Marvel and W. S. Anderson, *J. Am. Chem. Soc.*, **76**, 5434 (1954).

[3] E. A. Coulson, *J. Chem. Soc.*, 1298 (1937).

[4] N. P. Buu-Hoi, R. Dandel, and C. Vroelant, *Bull. soc. chim. (France)*, 211 (1949); C. W. Scherr, *J. Chem. Phys.*, **21**, 1582 (1953).

[5] G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 2326 (1950).

[6] D. M. Hall and E. E. Turner, *Nature*, **163**, 537 (1949); D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 711 (1950); E. D. Bergmann and J. Szmuszkovica, *J. Am. Chem. Soc.*, **73**, 5153 (1951); G. M. Badger, P. R. Jeffries, and R. W. L. Kimber, *J. Chem. Soc.*, 1837 (1957).

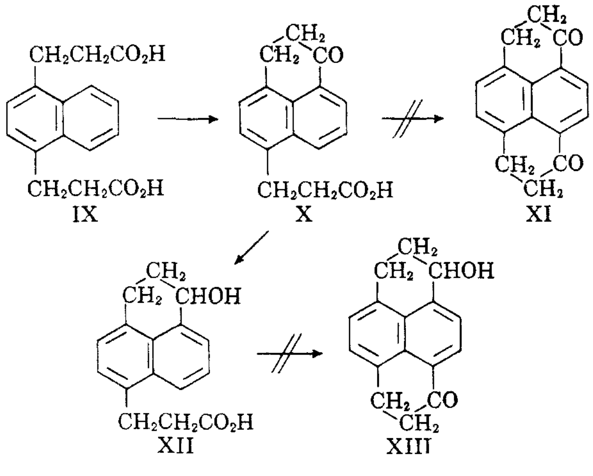
[7] E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 2663 (1953).

[8] H. Bendas and C. Djerassi, *J. Am. Chem. Soc.*, **78**, 2474 (1956).

It was impossible to proceed by steps IV to VI to VII because this last cyclization could not be achieved. The conversion of the diketone (V) to the dihydroxy compound (VIII) went smoothly. Dehydration of VIII was expected to yield the desired 1,6-dihydropyrene (III) but instead pyrene was produced. The labile nature of this dihydro derivative might perhaps have been predicted on the basis of the experience of Bergmann and Bograchov,[9] who found that the dilithium adduct of pyrene on hydrolysis gave only pyrene, due to autoxidation. However, in view of the stability of the 4,5-dihydro compound we had not expected this ease of oxidation and had not tried to avoid contact of our reaction mixture with air.

Work on the synthesis of the 1,6-dihydropyrene was abandoned at this point when polymerization experiments cast doubt on the ability of pyrene to participate in free radical initiated polymerization.[10]

Before the final step in the above synthesis was reached, some preliminary work had been done toward the synthesis of intermediates needed for the preparation of 1,8-dihydropyrene. 1,4-Dimethylnaphthalene was converted to 1,4-bis(bromomethyl)naphthalene and this in turn through the malonic ester synthesis to 1,4-naphthalenebispropionic acid (IX). This acid was converted to the known 2,3-dihydro-1-oxo-1*H*-phenalene-6-propionic acid (X). This keto acid could not be cyclized to the diketone (XI). It was reduced to the known alcohol acid[11] (XII), but all attempts to cyclize XII to the tetracyclic ketone (XIII) failed.



EXPERIMENTAL[12]

4,5-Dihydropyrene (I). A 500-ml. three necked flask, condenser, and fritted stick were dried at 130° and assembled, capping the condenser with a drying tube, and covering the third neck of the flask with a rubber diaphragm made from a section of inner tube. In the cooled flask were placed 50 ml. of dry benzene, 200 ml. of dry ethyl ether, and 548 mg. (1.51 mmoles) of 4,5-bis(bromomethyl)phenanthrene (II). The mixture was stirred magnetically until all of the dibromide was in solution. Meanwhile, purified nitrogen was bubbled through the solution for 20 min. and then the fritted stick was raised so that the nitrogen flowed over the liquid layer.

Lithiumphenyl was prepared and standardized by the Organic Reactions procedure.[13] The lithium phenyl solution (6.0 ml. of 0.40*N* solution, 2.4 mmoles) in a syringe was then added to the stirred solution of dibromide dropwise over a 20-min. period, by injection through the rubber diaphragm. The solution in the flask became cloudy due to precipitation of lithium bromide almost as soon as addition of the lithium phenyl was begun.

The mixture was stirred at ambient temperature for 1 hr. and was then heated under gentle reflux for 2 hr. At the end of this period, the reaction was terminated by the rapid addition of 150 ml. of 0.25% sulfuric acid. The phases were separated and the aqueous phase was washed once with a benzene-ether mixture. The combined organic phases were washed once with 5% sodium bicarbonate solution, once with water, and dried over sodium sulfate.

The solvent was removed and the residue was taken up in hot ethanol, filtered of a small amount of gummy residue, and concentrated to a small volume. There was obtained 278 mg. (90.5%) of crude 4,5-dihydropyrene, m.p. 128–131°. Repeated recrystallization from absolute ethanol gave an analytical sample, m.p. 132–132.5°. Literature[3] m.p. 132°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.12; H, 6.09. C, 93.05; H, 6.32.

In order to eliminate the persistent oxygen containing impurity, the material was chromatographed on alumina, using benzene as eluent, and then recrystallized three times from ethanol, m.p. 132–132.5°.

Anal. Found: C, 93.82; H, 6.13.

The *picrate* was prepared by standard methods[14] and purified by repeated recrystallization from absolute ethanol; m.p. 146.5–147°. Literature[3] m.p. 147°.

Anal. Calcd. for $C_{22}H_{15}O_7N_3$: C, 60.97; H, 3.49; N, 9.70. Found: C, 60.97; H, 3.56; N, 9.61.

The infrared spectrum (10% solution in carbon disulfide) showed the following important bands: 2835, 2890, 2940, and 3065 cm.$^{-1}$ (carbon-hydrogen stretching frequencies; all are of medium intensity); 726, 757, and 831 cm.$^{-1}$ (1,2,3-tri- and 1,2,3,4-tetrasubstituted benzene; all are of very strong intensity). There is almost no absorption between these two extremes. The aromatic region, of course, was blocked out by the solvent.

The ultraviolet spectrum was obtained in absolute ethanol solution. The reported[15] spectrum in heptane is shown for comparison in the table.

Attempts to cyclize β-(4-phenanthryl)ethanol. One g. of this alcohol was dissolved in a mixture of 15 ml. of concentrated sulfuric acid and 5 ml. of water and heated on the steam cone with occasional stirring for 30 min. The reaction was terminated by dilution with water. Extraction with benzene gave a white powder. This material was electrostatic and in general acted like a low molecular weight polymer. It softened at about 110° but was not fully liquid until 180°. A molecular weight determination by the Rast method showed this material to be an oligomer with a molecular weight of 7.2×10^2. This corresponds to an average chain length of 3.5 units. The inherent viscosity (0.25% in benzene) of this material was found to be 0.009. The infrared

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(9) E. D. Bergmann and E. Bograchov, *J. Am. Chem. Soc.*, **62**, 3016 (1940).

(10) C. S. Marvel and B. D. Wilson, *J. Org. Chem.*, **23**, 1479 (1958).

(11) G. Lock and E. Walter, *Chem. Ber.*, **75B**, 1158 (1942).

(12) All melting points are corrected.

(13) H. Gilman and Millir, *Org. Reactions*, **VI**, 353 (1951).

(14) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Fourth Edition, John Wiley & Sons, Inc., New York, N. Y., 1956, p. 229.

(15) H. Fromherz, L. Thaler, and G. Wolf, *Z. Elektrochem.*, **49**, 387 (1943).

$2.259 \times 10^{-3}M$ in Ethanol[a]		$2.259 \times 10^{-3}M$ in Heptane	
λ_{max} (mμ)	Log ϵ	λ_{max} (mμ)	Log ϵ
351	1.93	—	—
345	2.17	345	2.12
342	2.19	342	2.11
335	2.41	338	2.13
329	2.31	331	2.19
(327)	2.27	327	2.18
320	2.38	323	2.18
(318)	2.35	317	2.15
(312)	2.30	(310)	2.22
$2.259 \times 10^{-5}M$ in Ethanol[a]			
298	4.08	299	4.10
286	4.07	287	4.05
281	4.11	280	4.06
(272)	4.14	—	—
258	4.64	258	4.65
214	4.63	—	—

[a] Inflection points are enclosed in parentheses.

spectrum (in Nujol) was compatible with a poly-4-vinylphenanthrene structure. The ultraviolet spectrum (in carbon tetrachloride) showed absorption maxima at 352, 336, 301, and 260 mμ. This is in fair agreement with the spectrum of 4-ethylphenanthrene.[8]

Attempted cyclization of the alcohol in polyphosphoric acid or by use of anhydrous aluminum chloride failed to give any product.

1,4-Dimethylnaphthalene. A clean and dry three-liter flask was equipped with stirrer, condenser, and addition funnel. In the flask were placed 3.77 g. (0.0933 mole) of lithium aluminum hydride and 11.4 g. (1.1 mole of 80% pure material) of lithium hydride. These were slurried in 150 ml. of dry tetrahydrofuran added through the funnel. In the funnel was placed 87.1 g. (0.380 mole) of 5,8-bis(chloromethyl)tetralin (prepared by chloromethylation of tetralin[16]) dissolved in 400 ml. of dry tetrahydrofuran. The flask was heated to reflux temperature, with stirring, and the external heat source was then removed. The dihalide solution was added dropwise to the stirred hydride suspension at a rate necessary to maintain a moderate reflux rate. The addition required 1 hr. The mixture was then heated under gentle reflux for 1 hr. and then cooled to 15° (a thermometer was added down the condenser) by external cooling. Twenty-five ml. of tetrahydrofuran was diluted with an equal volume of water and added dropwise to the mixture at such a rate to keep the temperature in the range 15–20°. Next 1 l. of 5% aqueous sulfuric acid was added at a rate to maintain the temperature in the range 20–25°.

Ether was added and the phases were separated. The aqueous phase was extracted once with ether. The combined ethereal solutions were washed once with dilute hydrochloric acid, once with water, and dried over sodium sulfate–potassium carbonate. Removal of the solvent and distillation of the product yielded 54.5 g. (89.5%) of 5,8-dimethyltetralin, b.p. 51–54°/0.12–0.15 mm.; n_D^{25} 1.5466.

In a 100-ml. sidearm flask equiped with an air condenser were placed 32.1 g. (0.200 mole) of 5,8-dimethyltetralin and 3.2 g. of 10% palladium on charcoal. A slow stream of purified nitrogen was introduced through the sidearm. The flask was then heated at 260 ± 3° for 2 hr. The catalyst was filtered off the cooled mixture and well washed with ether. Distillation of the filtrate and washings gave 28.3 g. (95.8%) of 1,4-dimethylnaphthalene, b.p. 72–79°/0.5–0.7 mm., n_D^{20} 1.6116. Literature[17] n_D^{20} 1.6127.

1,4-bis(Bromomethyl)naphthalene. In a dry 500-ml. quartz flask was placed a solution of 31.2 g. (0.200 mole) of purified 1,4-dimethylnaphthalene in 300 ml. of reagent grade carbon tetrachloride. Benzoyl peroxide (0.60 g.) and 71.4 g. (0.401 mole) of *N*-bromosuccinimide were powdered, mixed well, and added to the flask. The solution was refluxed and irradiated with an ultraviolet source for 1.5 hr. and then allowed to sit overnight at ambient temperature. It was then warmed on a steam cone and filtered hot. The crude succinimide residue was then digested several times with hot carbon tetrachloride to remove all remaining product. The yield was 44.0 g. (70.0%) of 1,4-bis(bromomethyl)naphthalene, m.p. 178–186°. Repeated recrystallization of the product from benzene, chloroform, or carbon tetrachloride gave an analytical sample, m.p. 191–191.5°.

Anal. Calcd. for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21; Br, 50.89. Found: C, 46.32; H, 3.25; Br, 50.82.

The infrared spectrum (in Nujol) showed the following important bands: 754 and 733 cm.$^{-1}$ (*o*-disubstituted benzene; the band is split), 849 cm.$^{-1}$ (1,2,3,4-tetrasubstituted benzene), 1450 cm.$^{-1}$ (methylene), 1520 and 1591 cm.$^{-1}$ (aromatic bands).

Diethyl α,α'-dicarbethoxy-1,4-naphthalenebispropionate. A 5-l. three necked flask, stirrer, condenser, and addition funnel were dried at 120°, assembled, and the outlets capped by drying tubes. When the apparatus had cooled, 1 l. of absolute ethanol was placed in the flask, followed by 46 g. (2.0 g. at.) of sodium metal. When all of the sodium had reacted, 500 ml. (3.29 moles) of redistilled malonic ester, b.p. 89–91°/12 mm., was added dropwise over 1 hr. to the stirred solution. During this stage, it was important to maintain a brisk reflux temperature in order to prevent the sodiomalonic ester from precipitating from solution. The solution was heated under reflux for an additional 3 hr. after addition was completed. In the addition funnel 195 g. (0.621 mole) of 1,4-bis(bromomethyl)naphthalene was slurried in 800 ml. of dry benzene and added to the reaction mixture over a 45-min. period. Two hundred ml. of benzene was then used to wash in the residual dibromide. Sodium bromide precipitation began almost immediately after addition of the dibromide was begun. The pale yellow mixture was kept at reflux temperature and stirred for an additional 5 hr. and then allowed to stand overnight at ambient temperature.

The mixture was hydrolyzed by 500 ml. of water, followed by 500 ml. of 20% aqueous hydrochloric acid. The phases were separated and the aqueous phase was washed well with ether. The combined organic phases were washed well with 5% aqueous sodium bicarbonate solution and water, and dried over sodium sulfate.

The solvents and excess malonic ester were removed *in vacuo.* The residue (286 g.) was diluted with 500 ml. of hot absolute ethanol and filtered hot of a small residue. From the cooled solution there was obtained 203 g. (69.3%) of diethyl α,α'-dicarbethoxy-1,4-naphthalenebispropionate, m. p. 67–68°. Recrystallization from absolute ethanol raised the melting point of the product to 68.5–69°. Lock and Walter prepared this ester from the corresponding dichloromethyl compound and reported its melting point as 66.5°.[11] Later Badger, Cook and Crosbie[16] reported the melting point as 68.5–69°.

1,4-Naphthalenebispropionic acid (IX). Saponification and decarboxylation of diethyl α,α'-dicarbethoxy-1,4-naphthalenebispropionate by the procedure of Lock and Walter[11] gave a 97.4% yield of 1,4-naphthalenebispropionic acid, m.p. 257–258°. Literature[11] m.p. 258°.

2,3-Dihydro-1-oxo-1H-phenalene-6-propionic acid (X). The ring closure was found to proceed in liquid anhydrous hydrogen fluoride after several unsuccessful attempts, using essentially the procedure of Lock and Walter.[11] It

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[16] G. M. Badger, J. W. Cook, and G. W. Crosbie, *J. Chem. Soc.*, 1432 (1947).

[17] National Bureau of Standards-American Petroleum Institute Research Project 44.

was necessary to keep the temperature low during the mixing step, and also for some time thereafter in order to get the reactions to take place. Also, the ring closure was found to go best by using only small samples (1–2 g.) of IX in 15 to 25 g. of hydrogen fluoride. Polyethylene containers were used in place of silver vessels. By this procedure, a consistent yield of 97.0–98.0% of crude X, m.p. 194–198° was obtained. Literature[11] m.p. 205°. No attempt was made to purify the free acid.

The attempts at ring closure of X to XI were unsuccessful in either polyphosphoric acid or sulfuric acid.

Ethyl 2,3-dihydro-1-oxo-1H-phenalene-6-propionate. Crude X (4.53 g., 17.9 mmoles) and 90 ml. of absolute ethanol were placed in a flask. The suspension was stirred magnetically and 1 ml. of concentrated hydrochloric acid was added from a syringe. The mixture was heated under reflux for 30 min. and allowed to stand at room temperature for 1 hr. The ethanol was then removed *in vacuo*. The residue was extracted twice with 50 ml. each of hot cyclohexane. The combined cyclohexane extracts were treated with charcoal and the solvent was removed. There remained 3.80 g. (75.4%) of yellow-orange ethyl 2,3-dihydro-1-oxo-1*H*-phenalene-6-propionate, m.p. 82–85°. Repeated recrystallization from cyclohexane yielded 2.5 g. (50%) of bright orange crystals, m.p. 92–92.5°. Literature[11] m.p. 90°.

2,3-Dihydro-1-hydroxy-1H-phenalene-6-propionic acid (XII). In a 300-ml. flask were placed 7.98 g. (28.3 mmoles) of ethyl 2,3-dihydro-1-oxo-1*H*-phenalene-6-propionate and 150 ml. of 0.5*N* sodium hydroxide. The mixture was heated to reflux and this temperature maintained for 20 min. in order to saponify the ester, and then the mixture was cooled to 30°. To this mixture there was added in several portions 1.50 g. (39.6 mmoles) of sodium borohydride. This mixture was heated at 65° for 1 hr. and then cooled. The reaction was terminated by careful addition of dilute hydrochloric acid. Gas evolution occurred and soon after it ceased precipitation of 2,3-dihydro-1-hydroxy-1*H*-phenalene-6-propionic acid (XII) occurred. There was obtained 6.86 g. (94.8%) of a light brown powder, m.p. 171–173°. Lock and Walter[18] have obtained this compound by the catalytic reduction of the keto acid (X) and reported the m.p. 182°. No purification was attempted on our reduction product. The infrared spectrum (in Nujol) of this crude acid showed the following important bands: 3300–3200 cm.$^{-1}$ (broad, alcohol), 2960 cm.$^{-1}$ (carboxylic acid), 1710 cm.$^{-1}$ (aliphatic carboxylic acid), 1604 and 1519 cm.$^{-1}$ (aromatic bands), 948 cm.$^{-1}$ (carboxylic acid), 822 cm.$^{-1}$ (1,2,3,4-tetrasubstituted benzene) and 764 and 684 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

The ethyl ester was prepared for identification purposes. In a 100-ml. flask 500 mg. (1.77 mmoles) of ethyl 2,3-dihydro-1-oxo-1*H*-phenalene-6-propionate was dissolved in 45 ml. of absolute ethanol. Then 250 mg. (6.61 mmoles) of sodium borohydride was added all at once to the stirred solution. The color of the solution changed rapidly from the bright orange of the keto ester to the reddish brown color. The solution was stirred at ambient temperature for 1 hr. and then at 50° for an additional hour. The reaction was terminated by careful addition of 20 ml. of 10% aqueous hydrochloric acid. The product was extracted into benzene. The extract was washed with bicarbonate solution, water, and dried over sodium sulfate. Removal of solvent left a brownish residue of 435 mg. (86.5%) after an estimated 5–10% mechanical loss. Repeated recrystallization from cyclohexane gave a yellow product, m.p. 107.5–108.5°, which failed to analyze correctly. Two further recrystallizations from ethanol gave a white product, m.p. 110–111°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.80; H, 7.12.

The infrared spectrum (in Nujol) showed the following important bands: 3300 cm.$^{-1}$ (alcohol), 1728 cm.$^{-1}$ (aliphatic ester), 1603 and 1521 cm.$^{-1}$ (aromatic bands), 1103 cm.$^{-1}$ (alcohol), 828 cm.$^{-1}$ (1,2,3,4-tetrasubstituted benzene) and 769 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

The attempted cyclization of XII to XIII in liquid anhydrous hydrogen fluoride gave in poor yield a material which was not readily purified, plus large amounts of carbonaceous material. The infrared spectrum of this crude product (in Nujol) indicated the possible presence of a tetrahydropyrenone, but nothing definite concerning the product could be determined on the sample available.

1,5-Dimethylnaphthalene. To an excess of methylmagnesium iodide solution (approximately 0.24 mole) there was added 26.9 g. (0.168 mole) of 5-methyltetralone-1, prepared from *o*-bromotoluene by the procedures of Newman and Cline,[19] in ether solution. The crude alcohol obtained on hydrolysis and workup of the addition product was mixed with 10% of its weight of 10% palladium on charcoal, which served both as a dehydration[20] and as a dehydrogenation[21] catalyst. The flask was placed in a bath at 200° and a stream of dry nitrogen was passed through the flask. The temperature was raised to 270° over a period of 0.5 hr. At *ca.* 210° dehydration began and at *ca.* 240° dehydrogenation began. The temperature was held at 270° for 1.5 hr. The cooled product was dissolved in benzene, the catalyst removed by filtration, and the solvent removed *in vacuo*. Distillation of the residue gave 23.1 g. (88.3%) of 1,5-dimethylnaphthalene, b.p. 68–69°/0.15–0.30 mm.; m.p. 76–79°. Recrystallization from methanol raised the melting point to 81–82°. Literature[11] m.p. 82°.

1,5-bis(Bromomethyl)naphthalene. Bromination of 1,5-dimethylnaphthalene by the same procedure used to prepare the 1,4-isomer gave a 57.8% yield of 1,5-bis(bromomethyl)-naphthalene. Repeated recrystallization from benzene gave an analytical sample, m.p. 215.5–216° (dec.).

Anal. Calcd. for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21; Br, 50.89. Found: C, 45.78; H, 3.46; Br, 50.45.

The infrared spectrum (in Nujol) showed the following important bands: 695 and 789 cm.$^{-1}$ (1,2,3-trisubstituted benzene), 1454 cm.$^{-1}$ (methylene), 1520 and 1599 cm.$^{-1}$ (aromatic bands), and 2840 and 2920 cm.$^{-1}$ (methylene).

Diethyl α,α'*-dicarbethoxy-1,5-naphthalenebispropionate.* This compound was prepared in 73.1% yield by the same procedure used to prepare the 1,4-isomer. Repeated recrystallization of the product from absolute ethanol gave an analytical sample, m.p. 72.5–73.5°.

Anal. Calcd. for $C_{22}H_{32}O_8$: C, 66.09; H, 6.82. Found: C, 66.20; H, 7.07.

The infrared spectrum (10% solution in carbon disulfide) showed the following important bands: 1751 and 1736 cm.$^{-1}$ [split (malonic type) ester], 1599 cm.$^{-1}$ (aromatic band) and 790 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

1,5-Naphthalenebispropionic acid. Saponification of diethyl α,α'-dicarbethoxy-1,5-naphthalenebispropionate (101.9 g., 0.216 mole) was carried out by the same procedure as used for the 1,4- isomer. The crude tetracarboxylic acid (99.7 g.) was dried and then decarboxylated by heating at 210 ± 5° for 5.5 hr. Only slight loss of carbon dioxide occurred at 190 ± 5° for 4 hr., the conditions for decarboxylation of the 1,4-isomer.

The crude product was recrystallized from refluxing nitrobenzene, dissolved in base, treated with charcoal, filtered, and reprecipitated with acid. The product was collected on a Buchner funnel, washed well with water, and dried. There was obtained 39.6 g. (67.5% over-all) of a light brown powder, m.p. 302–305° (dec.). Elemental analysis was not attempted on this compound because of the difficulties of purification. Like the 1,4-isomer, this compound appears to be insoluble in all ordinary solvents.

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(18) G. Lock and E. Walter, *Chem. Ber.*, **77B**, 286 (1944).

(19) M. S. Newman and W. K. Cline, *J. Org. Chem.*, **16**, 934 (1951).

(20) W. E. Bachmann and A. L. Wilds, *J. Am. Chem. Soc.*, **60**, 624 (1938).

(21) E. W. J. Butz, *J. Am. Chem. Soc.*, **62**, 2557 (1940).

The infrared spectrum (in Nujol) showed the following important bands: 2595 and 2515 cm.$^{-1}$ (carboxyl OH stretching frequencies), 1707 cm.$^{-1}$ (aliphatic carboxylic acid), 1605 and 1516 cm.$^{-1}$ (aromatic bands), 1301 cm.$^{-1}$ (carboxyl CO stretching frequency), 948 cm.$^{-1}$ (carboxylic acid), 793 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

The diethyl ester was prepared for identification purposes. Twenty ml. of absolute ethanol and 1.00 g. (3.67 mmoles) of 1,5-naphthalenebispropionic acid were mixed in a flask and 0.60 ml. of concentrated hydrochloric acid was added to the stirred mixture. The suspension was then heated to reflux temperature and this temperature maintained for 1.5 hr. The mixture became clear at about 1.25 hr. The hot solution was treated with charcoal and filtered. The filtrate yielded a precipitate on cooling. The yield was 0.95 g. (79%). Repeated recrystallization from ethanol followed by several recrystallizations from cyclohexane gave an analytical sample, m.p. 94.5–95°.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 72.90; H, 7.50.

The infrared spectrum (10% solution in carbon disulfide) showed the following important bands: 1737 cm.$^{-1}$ (aliphatic ester), 1600 cm.$^{-1}$ (aromatic band), 1178 and 1165 cm.$^{-1}$ (diester), and 789 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

2,3-Dihydro-3-oxo-1H-phenalene-6-propionic acid (IV). Using the same conditions as used for the hydrogen fluoride catalyzed ring closure of the 1,4-isomer, 1,5-naphthalenebispropionic acid did not give the corresponding excellent results obtained for the 1,4-isomer. The yield varied from 87 to 94% and there was a significant amount of base insoluble material, which was collected from the various runs. Purification of the crude 2,3-dihydro-3-oxo-1*H*-phenalene-6-propionic acid (IV), m.p. 148–151°, was not attempted.

The infrared spectrum (in Nujol) showed the following important bands: 1729 cm.$^{-1}$ (aliphatic carboxylic acid), 1663 cm.$^{-1}$ [aromatic ketone (?)], 833 cm.$^{-1}$ (1,2,3,4-tetrasubstituted benzene), 768 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

The ethyl ester was prepared for identification purposes. Crude IV was esterified by the same procedure used to prepare the ethyl ester of X. There was obtained by extraction with cyclohexane 62% of a dark colored residue, m.p. 45–47°. Repeated recrystallization from a cyclohexane-ethanol mixture gave an analytical sample of colorless crystals of ethyl 2,3-dihydro-3-oxo-1*H*-phenalene-6-propionate, m.p. 46.5–47°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.48.

The infrared spectrum (10% solution in carbon disulfide) showed the following important bands: 1739 cm.$^{-1}$ (aliphatic ester), 1694 cm.$^{-1}$ (aromatic ketone), 850 cm.$^{-1}$ (1,2,3,4-tetrasubstituted benzene) and 768 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

2,3-Dihydro-3-hydroxy-1H-phenalene-6-propionic acid (VI). Direct reduction of crude IV to 2,3-dihydro-3-hydroxy-1*H*-phenalene-6-propionic acid was carried out so as to eliminate the two steps of esterification and saponification, as well as the large product loss on esterification.

In a 100-ml. flask 1.00 g. (3.93 mmoles) of IV was dissolved in 50 ml. of 0.1*N* sodium hydroxide. To the stirred solution there was added all at once 500 mg. (13.2 mmoles) of sodium borohydride. The mixture was stirred at ambient temperature for 0.5 hour and then at 50° for 1 hr. The reaction was terminated by careful addition of 10% aqueous hydrochloric acid to the cooled solution. Addition of excess mineral acid precipitated the product. The yield was 0.84 g. (85%). The product was found to be slightly soluble in water, which could account for the lower than expected yield. A two-fold recrystallization from aqueous methanol gave a yellow product of m.p. 114–116° which gave a low carbon analysis (found 72.24; calcd. 74.98) but was not further purified. The infrared spectrum (in Nujol) showed the following important bands: 2680, 2600, and 2550 cm.$^{-1}$ (carboxylic acid OH stretching frequencies), 3300 and 3160 cm.$^{-1}$ (alcohol), 1725 cm.$^{-1}$ (aliphatic carboxylic acid), 1635, 1604, and 1519 cm.$^{-1}$ (aromatic bands), 842 cm.$^{-1}$ (1,2,3,4-tetrasubstituted benzene) and 763 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

The ethyl ester was prepared for identification purposes. Ethyl 2,3-dihydro-3-oxo-1*H*-phenalene-6-propionate (390 mg., 1.38 mmoles) was reduced with sodium borohydride to ethyl 2,3-dihydro-3-hydroxy-1*H*-phenalene-6-propionate by the same procedure as used to prepare the 1-hydroxy derivative. The yield of crude material was 122%. Purification began by chromatography on alumina, using 10% ethanol in cyclohexane as eluent. Next a threefold recrystallization from a cyclohexane ethanol mixture was carried out. Finally the product was recrystallized five times from aqueous ethanol; m.p. 61–62°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.24; H, 7.15. C, 75.18; H, 7.16.

The infrared spectrum (in Nujol) showed the following important bands: 3260 cm.$^{-1}$ (alcohol), 1736 cm.$^{-1}$ (aliphatic ester), 1603 and 1518 cm.$^{-1}$ (aromatic bands), 1172 cm.$^{-1}$ (ester CO stretching frequency), 1104 cm.$^{-1}$ (secondary alcohol), 839 cm.$^{-1}$ (1,2,3,4-tetrasubstituted benzene), and 766 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

The attempts at ring closure of VI to VII were unsuccessful in either liquid anhydrous hydrogen fluoride or polyphosphoric acid. Also, attempted cyclization of the benzoate of VI was unsuccessful in liquid anhydrous hydrogen fluoride.

1,2,3,6,7,8-Hexahydropyrene-1,6-dione (V). In view of the failure to cyclize 2,3-dihydro-3-hydroxy-1*H*-phenalene-6-propionic acid to a known or unequivocal structure, it was decided to go back and investigate the by-product obtained from the preparation of IV.

The combined base insoluble material from all the runs of cyclization of 1,5-naphthalenebispropionic acid weighed 1.47 g. This material was extracted twice with benzene and the benzene filtrates concentrated somewhat. A bright yellow precipitation then occurred. Repeated recrystallization from benzene gave 757 mg. of bright yellow plates of 1,2,3,6,7,8-hexahydropyrene-1,6-dione, m.p. 239.5–240.5°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.55; H, 5.39.

The infrared spectrum (in Nujol) showed the following important bands: 1675 and 1203 cm.$^{-1}$ (aromatic ketone), 1588 and 1519 cm.$^{-1}$ (aromatic bands), and 850 cm.$^{-1}$ (1,2,3,4-tetrasubstituted benzene).

1,2,3,6,7,8-Hexahydropyrene-1,6-diol (VIII). Reduction of V was carried out, using sodium borohydride in ethanol solution. Ethanol proved to be a poor solvent choice, for both starting material and product proved to be insoluble in it. For any future work, tetrahydrofuran is recommended as a better solvent choice and either lithium aluminum hydride or sodium borohydride could be used.

In a 200-ml. flask there were placed 633 mg. (2.68 mmoles) of IV, 75 ml. of absolute ethanol, and 500 mg. (13.2 mmoles) of sodium borohydride. The suspension was stirred magnetically and over a period of several minutes the color changed from an original orange-yellow of the dione through a red color. At this stage, the material was almost completely in solution. Then reprecipitation began, this time of a cream-colored material.

The mixture was stirred at 50° for 1.5 hr. and then cooled to room temperature. The reaction was then terminated by careful addition of 20 ml. of 10% aqueous hydrochloric acid. The precipitation was collected and dried. The yield was 516 mg. (80.1%) of a slightly brownish powder, m.p. 240–242°, insoluble in ordinary organic solvents.

The infrared spectrum (in Nujol) showed the following important bands: 3260 cm.$^{-1}$ (alcohol), 1673 cm.$^{-1}$ (weak, a trace of the ketonic material remaining), 1600 and 1519 cm.$^{-1}$ (aromatic bands), 1304 and 1086 cm.$^{-1}$ (secondary alcohol), 848 and 837 cm.$^{-1}$ (both are of equally strong intensity; at least one is assignable to 1,2,3,4-tetrasubstituted benzene).

Attempts to prepare 1,6-dihydropyrene (III). VIII was found to be somewhat soluble in glacial acetic acid, so recrystallization from this solvent was attempted. After warming to get the material in solution, none would come out. Finally the solvent was removed by freeze drying, leaving a residue, m.p. 112–123°, which was soluble in benzene and ethanol. Chromatography of this material on alumina, using benzene as the eluent, gave a fast-moving band (characteristic of hydrocarbons) red in color. The material was recrystallized five times from petroleum ether (b.p. 60–68°)-hexane, m.p. 146–147°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. For $C_{16}H_{10}$: C, 95.19; H, 4.81. Found: C, 94.56; H, 5.40.

The ultraviolet spectrum (1.382 mg./l. in absolute ethanol) showed the material to be identical to pyrene. It was calculated that there was 89% pyrene in the sample. The infrared spectrum (10% solution in carbon disulfide) also was very like that of pure pyrene.

Chromatography of this material on alumina was begun in an attempt to identify the colored material by separation of the hydrocarbon components. Elution with petroleum ether (b.p. 60–68°)-hexane[22] was used. The pyrene fractions came off first as a white solid, m.p. 146–148°. (Pyrene when purified has a melting point of 150°.) A pale yellow band followed, but the amount of material recovered was not great enough to allow any physical measurements except a qualitative ultraviolet spectrum in ethanol solution. The spectrum again was that of pyrene so it is probable that autoxidation had occurred.

URBANA, ILL.

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[22] E. M. Charlet, K. P. Lanneau, and F. B. Johnson, *Anal. Chem.*, 26, 861 (1954).

[CONTRIBUTION FROM POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Synthesis of α-Hydroxyisobutyric Acid from Isobutylene

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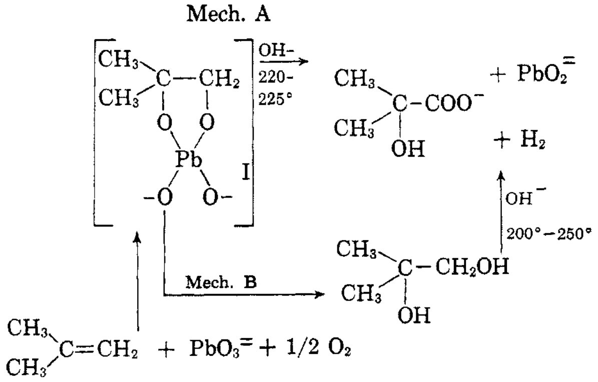
Isobutylene is oxidized with air in the presence of sodium plumbate/sodium hydroxide catalyst to α-hydroxyisobutyric acid. α-Hydroxyisobutyric acid is also obtained in good yields from isobutylene glycol and sodium hydroxide at 200–250°.

The air oxidation of isobutylene under a variety of conditions has been reported to give such products as methacrolein[1] and isobutylene glycol,[2] as well as compounds with fewer than four C-atoms.

We have found that sodium plumbate–sodium hydroxide mixtures are unique catalysts for the direct oxidation of isobutylene to α-hydroxyisobutyric acid (obtained as the sodium salt). The optimum conditions determined in this work employed a benzene solution of isobutylene, air at 1000 p.s.i. and temperatures of 200–250°. The yield varied markedly with the proportions of the reaction components and the preparation of the catalyst. Higher air pressures caused further oxidations; oxalic acid was detected under these conditions, probably resulting from oxidation of the benzene. Lower air pressures gave oily acids of low α-hydroxyisobutyric acid content. Satisfactory results were obtained only with the ratio of sodium plumbate–sodium hydroxide in the ranges 1:7 to 1:10.

The mechanism of the oxidation step of this reaction probably parallels that for permanganate oxidations. Wiberg[3] has recently offered evidence for an intermediate cyclic permanganate ester. In analogy we may write a cyclic plumbate ester (I), the formation of which requires 0.5 mole of oxygen. This accounts for the observation that no reaction takes place in the absence of oxygen even when molar amounts of sodium plumbate were used. The dehydrogenation step of this reaction may follow either of two mechanisms. The cyclic plumbate ester (I) may be dehydrogenated directly to α-hydroxyisobutyrate (Mech. A). Alternately, the plumbate ester (I) may be decomposed by direct alkaline cleavage to isobutylene glycol which is then dehydrogenated. Primary alcohols are known to be dehydrogenated to acids by heating with anhydrous alkali.[4] We have been able to demonstrate that isobutylene glycol is dehydrogenated to α-hydroxyisobutyrate when heated with alkali to 250°.



Although α-hydroxyisobutyric acid is the major product in this oxidation, it is not the only com-

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[1] A. Clark and R. S. Shutt, U. S. Patent 2,383,711 (1945).

[2] C. E. Schweitzer, U. S. Patent 2,644,837 (1953).

[3] K. B. Wiberg, Abstracts of papers, page 60-P, 132nd American Chemical Society meeting, New York, N.Y., September 1957.

[4] J. Dumas and J. S. Stas, *Ann. Chim. Phys.* (2), 83, 113, *Ann.*, 35, 129 (1840).