The flask was warmed slightly to aid solution and the material was transferred as quickly as possible to the autoclave. (In order to facilitate transfer of the material into the autoclave, it is found best to break the unmelted material into small pieces and to pour the mixture of liquid and solid into the autoclave, thus decreasing the period of preliminary heating.) The flask was washed with 5 ml. more of anhydrous dimethylformamide to make the transfer complete. The autoclave was flushed with dry nitrogen and quickly closed after which it was filled with carbon monoxide up to a pressure of 415 atmospheres, the temperature being 33°. The autoclave was then heated to 150° and shaken for 4.0 hours at this temperature. Upon cooling, the autoclave contents were diluted with a liter of water, and after standing for a few minutes, 22.5 g. of sodium hydroxide was added and the mixture refluxed for 2.0 hours, dimethylamine being given off copiously. The mixture was then steam distilled to remove unreacted indole and the residue was diluted to approximately 3 liters with water, charcoal added, heated to reflux and filtered. The filtrate was cooled to room temperature and placed in the refrigerator overnight. The product was filtered, washed several times with water and dried, 8.0 g. This latter filtrate was concentrated to 500 ml. and then cooled, whereupon 0.3 g. more of the product separated. The reaction mixture can be processed in an alternate manner. The mixture from the bomb was placed in a 100-ml. Claisen flask and distilled at 12 mm. pressure. After collecting 40–45 ml. of the solvent boiling in the range 48° to 52°, the distilling flask was allowed to cool leaving a viscous residue. Fifty ml. of water was added and the mixture heated, the viscous mass reacted slowly with the water to give a brown-colored precipitate. The mixture was further diluted to 1 liter and steam distilled to remove any indole present. The remaining steps were the same as above; yield 8.3 g., 57% of the theoretical; 193–195°, mixed melting point with an authentic sample, 193–195°; conversion of the product to the 3-indolalacetophenone[7] gave a m.p. of 165.5–166.5°, lit. 166–167°.[7]

3-Indolecarboxaldehyde by Reaction of Dimethylformamide on Indole in the Presence of Phosphorus Oxychloride.—To a flask protected from atmospheric moisture, fitted with a mechanical stirrer, and containing 1.18 mole of dimethylformamide cooled to −5°, 30.68 g. (0.2 mole) of phosphorus oxychloride was added with stirring so that the temperature did not rise above 10°. After completion of addition, 11.7 g. (0.10 mole) of indole was added in portions at temperature 23–27° followed by additional stirring at 25° for 0.5 hour. Then 40 g. of finely divided calcium carbonate was added to the mixture and the temperature gradually was raised to 30–35° whereupon the heat of reaction kept the temperature rising slowly, the external source of heat being removed. The temperature should be controlled by cooling of the flask with ice from time to time in order that the temperature reaches 55–60° in approximately 0.5 hour. The mixture was then cooled externally to 10° with ice and 200 ml. of a 30% solution of sodium acetate was poured into the flask with stirring, followed by dilution with water to 1.0 liter. After addition of 47.2 g. (1.18 moles) of sodium hydroxide, the mixture was refluxed for 3 hours, dimethylamine evolved copiously. The mixture was then steam-distilled to remove any unreacted indole and then diluted to 3.5 liters with water, heated to reflux, filtered, the filtrate being treated as above; yield 10.4 g. representing 72% of the theoretical; m.p. 193–195°, mixed m.p. with authentic sample, 193–195°; the product was converted to 3-indolalacetophenone,[7] m.p. 165.5–166.5°, lit. 166–167°.

Acknowledgments.—This work was supported in part by a Grant from the Committee on Research and Publications of Temple University. We are indebted to E. I. du Pont de Nemours and Company for the dimethylformamide and indole used in this work.

PHILADELPHIA, PENNA. RECEIVED AUGUST 20, 1951

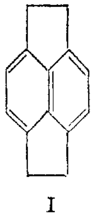
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

The Synthesis of Pyracene[1]

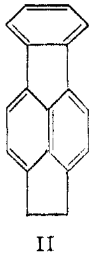
BY A. G. ANDERSON, JR., AND ROBERT H. WADE

An attempted synthesis of pyracene *via* 5-acenaphtheneacetic acid is presented and the failure to effect ring closure of the acid to 1-pyracenone is briefly discussed. The synthesis of pyracene from 1-indanone is reported.

The synthesis of 1,2-dihydrocyclopenta[fg]acenaphthene or pyracene (I) was first attempted by Mayer and Kaufmann[2] in 1920 and since that time a number of workers have investigated the preparation of compounds containing two five-membered rings fused to the opposite *peri*-positions of naphthalene. The literature dealing with these studies has been summarized by Kloetzel and Chubb[3] who synthesized 1,2-dihydrocyclopenta[cd]fluoranthene or 1,2-benzpyracene (II) and found it to be a stable compound.



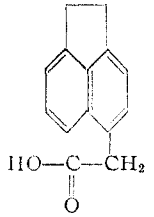
I



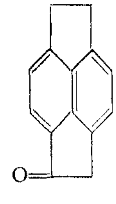
II

In this paper are reported first, the preparation of 5-acenaphtheneacetic acid (III) and our unsuccessful attempts to convert this acid to 1-pyracenone (IV) and second, the successful synthesis of pyracene from 1-indanone (V).

Since the treatment of the chloride or bromide of 1-naphthaleneacetic acid with aluminum chloride yields 1-acenaphthenone,[4] the cyclization of 5-acenaphtheneacetic acid (III) to 1-pyracenone (IV) seemed worthy of attempt.[5] Indeed, Mayer



III



IV

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[1] From the Ph.D. Thesis of Robert H. Wade.

[2] F. Mayer and W. Kaufmann, *Ber.*, **53**, 289 (1920).

[3] M. C. Kloetzel and F. L. Chubb, THIS JOURNAL, **72**, 150 (1950).

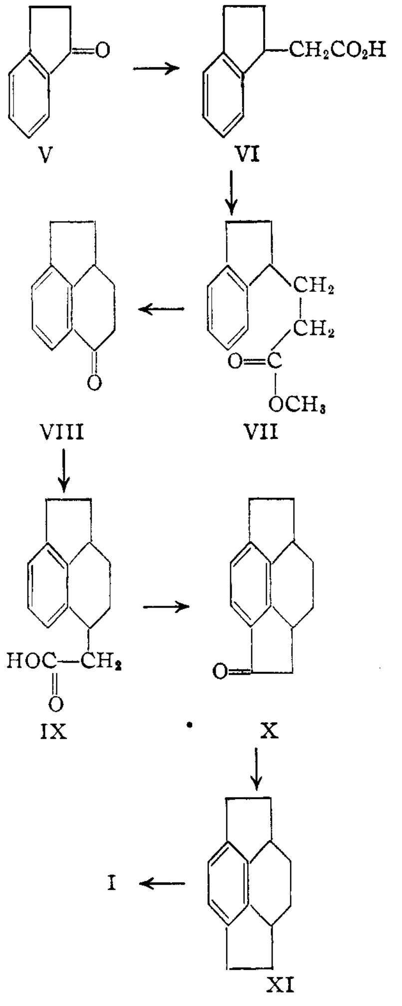
[4] Bad. Anilin- and Soda-Fabr., German Patent 230,237 (Oct. 23, 1909).

[5] The work of Kloetzel and Chubb (reference 3), wherein the analogous 3-fluorantheneacetyl chloride resisted cyclization, was reported after this portion of our work had been completed.

and Kaufmann[2] had considered this route to pyracene but were unable to prepare the intermediate acid. We were unable to repeat the preparation of this acid from acenaphthene and α-chloroacetic acid as described by Wolfram, *et al.*,[6] and attempts to obtain the compound *via* a 5-chloromethyl derivative of acenaphthene were also unsuccessful. However, a Willgerodt reaction or, better, the Kindler[7] modification of this reaction on 5-acenaphthenyl methyl ketone followed by hydrolysis of the amide proved to be a satisfactory method. Treatment of the acid with 80% sulfuric acid or with anhydrous hydrogen fluoride gave no ketonic product. Attempts to effect cyclization of the corresponding acid chloride by means of Friedel–Crafts reactions with stannic chloride, aluminum chloride, or by fusion with aluminum chloride and sodium chloride also failed.

As the formation of a *peri* six-membered[8] or seven-membered[9] ring on acenaphthene occurs readily, the size of the second *peri*-ring to be formed is apparently a critical factor. Since one five-membered *peri*-ring on the naphthalene nucleus may be obtained by direct cyclization,[4] the failure of a second five-membered *peri*-ring to form under the same conditions may be interpreted as evidence that the 5- and 6-positions of acenaphthene are farther apart than the 1- and 8-positions of naphthalene. In view of the values reported for the bond angles and bond distances in the *peri*-ring of acenaphthene,[10] there must be considerable strain in the molecule and it is possible that there is a resultant increase in the distance between the 5- and 6-positions.[11] If this is the case, and if the distance between the *peri*-positions in naphthalene is the maximum which will permit formation of a five-membered ring, the increased distance in acenaphthene would prevent the closure of the second five-membered ring.

It seemed probable that cyclization of a second five-membered ring could be effected with the partially saturated acenaphthene ring system[12] present in 2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid (IX). For the synthesis of this acid, 1-indanone (V) was prepared by a Friedel–Crafts cyclization of β-phenylpropionyl chloride. A Reformatsky reaction of the indanone with ethyl α-bromoacetate gave, after dehydration, ethyl indanylideneacetate which was converted to 1-indanacetic acid (VI) (in 75% yield from indanone) by catalytic hydrogenation and then saponification. Application of the Arndt–Eistert reaction as described by Newman and Beall[13] to the acid chloride of the indanacetic acid afforded methyl β-(1-indanyl)-propionate (VII) in good yield. Conversion of this ester to the corresponding acid chloride and cyclization to 2a,3,4,5-tetrahydro-5-acenaphthenone (VIII) was readily accomplished with either stannic chloride or aluminum chloride as the condensing agent.



The tricyclic ketone (VIII) was subjected to a Reformatsky reaction with ethyl α-bromoacetate and the crude product dehydrated and hydrolyzed to give a dihydro-5-acenaphtheneacetic acid in which the position of the double bond was not determined. Catalytic hydrogenation of the unsaturated acid proceeded quantitatively and the resulting 2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid (IX) was readily cyclized *via* its acid chloride to 2a,3,4,4a-tetrahydro-1-pyracenone (X).

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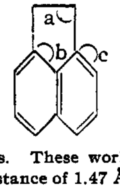
(6) A. Wolfrom, L. Schornig and E. Hausdorder, U. S. Patent 1,951,686 (March 20, 1934).

(7) M. S. Newman, *J. Org. Chem.*, **9**, 521 (1944); von K. Kindler, *Ann.*, **431**, 193, 222 (1927); *Arch. Pharm.*, **265**, 389 (1927).

(8) K. Fleischer, H. Hittel and P. Wolff, *Ber.*, **53**, 1847 (1920).

(9) L. F. Fieser and M. A. Peters, THIS JOURNAL, **54**, 4347 (1932).

(10) The values found by K. Banerjee and K. L. Sinha (*Indian J. Phys.*, **11**, 21 (1937)) are 97° for the internal aliphatic angle (a), 114° for the internal (b) and 126° for the external (c) angles between the aromatic and aliphatic bonds. These workers also reported an aromatic carbon–carbon bond distance of 1.47 Å. and an aliphatic carbon–carbon bond distance of 2.01 Å. The latter value was corrected to 1.8 Å. by A. I. Kitaigordoskii (*J. Phys. Chem.* (*U. S. S. R.*), **21**, 1085 (1947)).



(11) From the viewpoint of the Mills–Nixon theory, the bonds common to the *peri*- and naphthalene rings would assume single bond character. This "bond fixation" would result in a single rather than aromatic bonds between the opposite *peri*-positions with a consequent increase in the distance between these positions.

(12) This was confirmed while our studies were in progress by Kloetzel and Chubb (reference 3) in their synthesis of 1,2-benzpyracene.

(13) M. S. Newman and P. F. Beall, THIS JOURNAL, **72**, 5163 (1950).

Reduction of the ketone (X) by the usual procedure for the Huang-Minlon[14] modification of the Wolff–Kishner reaction resulted in a fair yield of 2a,3,4,4a-tetrahydropyracene (XI) but considerable decomposition also occurred. By delaying the addition of the alkali until the formation of the hydrazone was complete and low boiling substances had been removed,[15] a 92% yield of nearly colorless hydrocarbon was obtained. The compound did not form a derivative with either picric acid or trinitrobenzene and was inert to dilute potassium permanganate. Catalytic dehydrogenation of XI afforded pyracene (I) as colorless needles in 67% yield.

The structure of this new compound was proven by analysis, comparison of its ultraviolet absorption spectrum with that of acenaphthene (Fig. 1) and oxidation to the known 1,4,5,8-naphthalenetetracarboxylic acid. This acid was identified by a series of characteristic transformations first performed by von Bamberger and Philip[16] and later confirmed by Fieser and Peters.[9] The acid is also unique in that neither it nor any of its known derivatives have characteristic melting points.

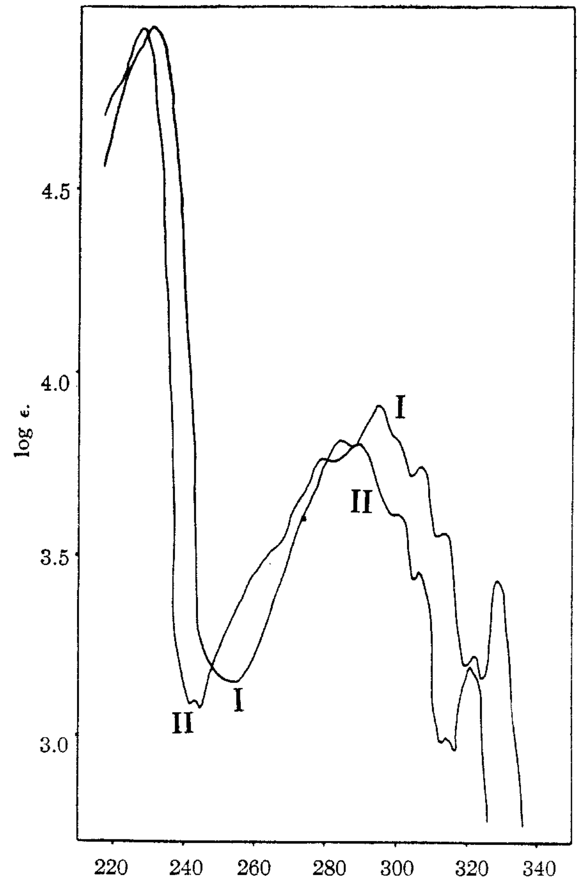


Fig. 1.—Ultraviolet absorption spectra of pyracene (I) and acenaphthene (II).

Pyracene readily formed both a picrate and a trinitrobenzene derivative, was inert to dilute potassium permanganate, and was not reduced by hydrogen in the presence of a catalyst at room temperature and atmospheric pressure. An attempt to introduce a double bond into each of the *peri*-rings in pyracene to form the non-alternant hydrocarbon pyracylene is in progress.

Experimental[17]

5-Acenaphthenyl Methyl Ketone.—Acenapthene was converted by acetylation to 5-acenaphthenyl methyl ketone in the manner described by Graebe.[18] The product, after recrystallization from ligroin, melted at 68–68.5° whereas the value reported[18] is 75°. Identification was provided by preparation of the oxime, m.p. 162–163°, and the picrate, m.p. 93–94°, in agreement with the literature.[18]

5-Acenaphtheneacetic Acid (III).—In a Kindler modification of the Willgerodt reaction,[7] 5-acenaphthenyl methyl ketone (39 g., 0.2 mole) and sulfur (9.6 g., 0.3 mole) were dissolved in 26 ml. (0.3 mole) of morpholine and the solution heated under reflux for 16 hours. The hot solution was then poured into 100 ml. of warm alcohol and the almost black product (82 g.) which precipitated on cooling was separated by suction filtration. The crude thiomorpholide was washed with 50 ml. of cold alcohol and heated under reflux with 168 ml. of glacial acetic acid, 26 ml. of sulfuric acid and 37 ml. of water for five hours. The reaction mixture was poured while hot into 600 ml. of water; a red-brown precipitate formed in the aqueous solution and a black residue remained in the flask. The brownish precipitate was separated and combined with the black residue and the total solids digested with sodium hydroxide (20 g., 0.5 mole) in 400 ml. of water. After separation of insoluble material, the filtrate was acidified with hydrochloric acid. Upon cooling 20 g. (48%) of crude product separated as a brown solid. Repeated treatment of an ethanolic solution of this material with Norite and finally crystallization gave colorless needles, m.p. 179–180°. The value reported is 187°.[6] The product had a neutral equivalent of 213 as compared to a calculated value of 212.

Attempts to effect the cyclization of the 5-acenaphtheneacetic acid to 1-pyracenone (IV) with 80% sulfuric acid or anhydrous hydrogen fluoride or *via* the acid chloride by Friedel–Crafts reactions with stannic chloride, aluminum chloride, or by fusion with aluminum chloride and sodium chloride were unsuccessful.

Ethyl 1-Indanylideneacetate.—A solution of 132 g. (1.0 mole) of 1-indanone (prepared from β-phenylpropionyl chloride by the procedure of Johnson and Glenn)[19] in 275 ml. of dry benzene and 275 ml. of absolute ether was allowed to undergo a Reformatsky reaction with ethyl α-bromoacetate (166 ml., 1.5 moles) and twenty-mesh zinc (65 g., 1 mole) under a nitrogen atmosphere. The procedure for the reaction and the isolation of the product was that of Bachmann and Dreiding.[20] To the crude hydroxy ester thus obtained was added 50 mg. of *p*-toluenesulfonic acid and distillation of this mixture gave 154 g. (82%) of the unsaturated ester as the fraction boiling at 148–162° at 8 mm. A boiling point of 166–168° at 10 mm. has been reported by von Braun, *et al.*[21]

Ethyl 1-Indanacetate.—An ethanolic solution of ethyl 1-indanylideneacetate (154 g., 0.76 mole) was allowed to react with hydrogen in the presence of a 10% palladium-on-charcoal catalyst at a pressure of 2–3 atmospheres. The theoretical quantity of hydrogen was absorbed in approximately eight hours. The reaction mixture was worked up in the usual manner to give 147 g. (95%) of the saturated ester as a colorless oil, b.p. 140–143° at 10 mm. (reported, 149–150° at 12 mm.),[21] n^{25}_{D} 1.5141.

1-Indanacetic Acid (VI).—Ethyl 1-indanacetate (39.2 g., 0.192 mole) was heated with 160 ml. of 10% sodium hy-

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[14] Huang-Minlon, This Journal, **68**, 2487 (1946).

[15] J. A. Nelson, Ph.D. Thesis, University of Washington, 1950. This procedure has been found to give good results in several other cases wherein decomposition and lower yields were observed with the usual method.

[16] E. von Bamberger and M. Philip, *Ann.*, **240**, 147 (1877.)

[17] All melting points are corrected. Boiling points are uncorrected.

[18] von C. Graebe, *Ann.*, **327**, 77 (1903).

[19] W. S. Johnson and H. J. Glenn, This Journal, **71**, 1092 (1949).

[20] W. E. Bachmann and A. S. Dreiding, *J. Org. Chem.*, **13**, 317 (1948).

[21] J. von Braun, E. Danziger and Z. Koehler, *Ber.*, **50**, 56 (1917).

droxide until the solution became clear (45 minutes). The cooled solution was extracted with ether, treated with Norite, filtered and the filtrate acidified with cold, dilute hydrochloric acid. The yield of crude, cream colored acid was 34 g. (100%) after drying in a vacuum desiccator. After one recrystallization from water the product melted at 59–60°.[21]

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 74.97; H, 6.87. Found: C, 74.86; H, 6.98.

Methyl β-(1-Indanyl)-propionate (VII).—1-Indanacetic acid (132 g., 0.75 moles) was treated with thionyl chloride (544 ml., 7.5 moles) at room temperature for 30 minutes, the excess thionyl chloride removed and the residue distilled. 1-Indanacetyl chloride (129 g., 87%) was obtained as the fraction boiling at 134–135° at 10 mm.[21] To the acid chloride (19.5 g., 0.1 mole) dissolved in 25 ml. of absolute ether was added dropwise an ethereal solution of diazomethane prepared from 42 g. of N-nitroso-N-methylurea. After standing overnight the solvent was removed under reduced pressure at room temperature. The residual yellow diazoketone was dissolved in 165 ml. of absolute methanol and a solution of silver benzoate (3 g.) in 37 ml. of triethylamine[18] added in small portions with stirring. Ninety-six per cent. of the theoretical amount of nitrogen was evolved as measured with a wet test meter. The solution was then boiled with charcoal, filtered, and the solvent removed on a steam-bath under reduced pressure. Distillation of the residue afforded 18.4 g. (98%) of crude methyl β-(1-indanyl)-propionate as the fraction boiling at 144–154° at 10 mm. Redistillation of a portion of this product gave a more pure sample of the ester (b.p. 150–154° at 12 mm., $n^{20}D$ 1.5234).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.52; H, 8.05.

Saponification of this sample yielded β-(1-indanyl)-propionic acid, m.p. 57–59° (reported, 50°),[22] which formed an amide melting at 89–92°.[22]

β-(1-Indanyl)-propionyl Chloride.—Methyl β-(1-indanyl)-propionate (102 g., 0.5 mole) was heated under reflux with a solution of sodium hydroxide (40 g., 1.0 mole) in 360 ml. of water under a nitrogen atmosphere for 90 minutes. Upon acidification of the cooled red homogeneous solution with hydrochloric acid an oil separated which did not solidify on standing overnight in the cold. A dried benzene solution of the oil was added dropwise to phosphorus pentachloride (114 g., 0.55 mole) and, after one hour at room temperature, the solvent was removed under reduced pressure on a steam-bath. On distillation 85.2 g. (82%) of the acid chloride was collected as a yellow oil, b.p. 138–142° at 11 mm. The boiling point reported is 155° at 16 mm.[22]

2a,3,4,5-Tetrahydro-5-acenaphthenone (VIII). Method A.—β-(1-Indanyl)-propionyl chloride (10 g., 0.05 mole) was converted to 2a,3,4,5-tetrahydro-5-acenaphthenone in the presence of anhydrous aluminum chloride (8 g., 0.06 mole) by the procedure of Johnson and Glenn.[19] The yield of crude ketone (m.p. 74–77°) recrystallized once from methanol was 7.4 g. (86%). An analytical sample melted at 83–84°.[22]

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.81; H, 7.14.

The semicarbazone was obtained as colorless flakes, m.p. 226–228°.[22]

Method B.—β-(1-Indanyl)-propionyl chloride (115 g., 0.55 mole) was converted to 2a,3,4,5-tetrahydro-5-acenaphthenone by cyclization in the presence of stannic chloride (142 ml., 1.2 moles) in the manner described by Fieser and Novello.[23] The yield of crude ketone was 83.5 g. (88.3%).

Dihydro-5-acenaphtheneacetic Acid.—2a,3,4,5-Tetrahydro-5-acenaphthenone (17.2 g., 0.1 mole) dissolved in 100 ml. of dry benzene and 200 ml. of dry toluene was subjected to a Reformatsky reaction with ethyl α-bromoacetate (55.6 ml., 0.5 mole) and a total of 32.7 g. (0.5 mole) of twenty-mesh zinc, under a nitrogen atmosphere in accordance with the procedure of Bachmann and Dreiding.[20] Dehydration of the crude hydroxy ester was accomplished by distillation from 20 mg. of β-naphthalenesulfonic acid and the unsaturated ester (16 g., 67%) collected as the fraction boiling at 140–150° at 3.5 mm. This product was saponified directly by boiling with potassium hydroxide (7.8 g., 0.14 mole) in 70 ml. of ethanol for one hour. Water (400 ml.) was then added, the mixture extracted with ether and the aqueous solution acidified with dilute hydrochloric acid. The yield (15 g.) of crude dihydroacenaphtheneacetic acid (m.p. 92–97°) obtained was quantitative. A sample recrystallized four times from 60% ethanol and sublimed *in vacuo* melted at 103–104°. The ultraviolet absorption spectrum of an ethanolic solution displaced maxima (in mμ) at 221 (log ε 4.83) and 260 (log ε 4.55).

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.76; H, 6.83.

2a,3,4,5-Tetrahydro-5-acenaphtheneacetic Acid (IX).—An ethanolic solution of the dihydro-5-acenaphtheneacetic acid (22.6 g., 0.105 mole) took up the theoretical quantity of hydrogen at 2–3 atmospheres pressure in the presence of a 10% palladium-on-charcoal catalyst. After removal of the catalyst and solvent, a quantitative yield of the crude saturated acid, which solidified on standing in a refrigerator, was obtained. An analytical sample (recrystallized four times from petroleum ether) melted at 101–102° alone and at 77–90° when mixed with the dihydro-5-acenaphtheneacetic acid. The ultraviolet absorption spectrum of an ethanolic solution showed the following peaks: λ_{max} in mμ at 258 (log ε 3.52) and 275 (log ε 3.48).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.75; H, 7.53.

The S-benzylisothiuronium salt was obtained as glistening colorless plates from 25% ethanol, m.p. 143–144°.

Anal. Calcd. for $C_{22}H_{26}N_2O_2S$: C, 69.08; H, 6.85. Found: C, 69.31; H, 6.92.

The amide crystallized as colorless flakes from dilute ethanol, m.p. 168–169°.

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96. Found: C, 78.11; H, 8.39.

2a,3,4,4a-Tetrahydro-1-pyracenone (X).—2a,3,4,5-Tetrahydro-5-acenaphtheneacetic acid (20 g., 0.093 mole) was heated carefully with 73 ml. of thionyl chloride for 15 minutes and the excess thionyl chloride then removed under reduced pressure. A solution of the residual acid chloride in 60 ml. of nitrobenzene was added to a cold (0°) solution of anhydrous aluminum chloride (29.2 g., 0.22 mole) in 300 ml. of nitrobenzene and the mixture allowed to stand overnight in a refrigerator. The dark red complex was hydrolyzed with ice and hydrochloric acid, the nitrobenzene removed by steam distillation, the dark residue dissolved in benzene and this solution washed with 6 *N* hydrochloric acid, water, 10% sodium hydroxide and finally with saturated sodium chloride solution. After drying the organic solution and removing the solvent, a dark oil remained which solidified on cooling. The yield of crude ketone was 16 g. (87%). Purification was accomplished by heating with three separate portions of 70–90° ligroin (10 ml. of solvent per gram of ketone) and decantation from the insoluble tar. The tan solid (m.p. 95–99°) obtained on removal of the ligroin was used in the next step without further purification. A portion recrystallized three times from 70–90° ligroin and once from ethanol formed light tan needles, m.p. 103–104°. The ultraviolet absorption spectrum of an ethanolic solution showed maxima at 221 mμ (log ε 4.36) and 265 mμ (log ε 4.11).

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.92; H, 7.40.

The 2,4-dinitrophenylhydrazone was obtained as glistening red plates, m.p. 248–249°.

Anal. Calcd. for $C_{20}H_{18}N_4O_4$: C, 63.48; H, 4.79. Found: C, 63.47; H, 5.05.

2a,3,4,4a-Tetrahydropyracene (XI).—A mixture of 2a,3,4,-4a-tetrahydro-1-pyracenone (5 g., 0.025 mole), 25 ml. of 85% hydrazine hydrate and 18 ml. of ethanol was heated under reflux for one hour. The condenser was then removed, 25 ml. of diethylene glycol added and the heating continued until the temperature of the mixture rose to 170°. Potassium hydroxide (3.3 g., 0.06 mole) was then added to the cooled solution and the mixture heated under reflux until the evolution of nitrogen had ceased (*ca.* three hours).[15] The reaction mixture was worked up in the usual manner[14] followed by chromatography of a hexane solution of the product on an alumina column to give 4.25 g. (92.4%) of nearly colorless oil which solidified on standing. Recrystallization of a sample from ethanol–butanol, then from eth-

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[22] J. von Braun and J. Reutter, *Ber.*, **59**, 1922 (1926).

[23] L. F. Fieser and F. C. Novello, *ibid.*, **62**, 1855 (1940).

anol and, finally, sublimation *in vacuo* gave colorless feathery needles, m.p. 46–47°. The ultraviolet absorption spectrum of an ethanolic solution displayed a single maximum at 266 mμ (log ε 3.05). The hydrocarbon did not react with 2% potassium permanganate in acetone.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.46; H, 9.01.

Pyracene (I).—2a,3,4,4a-Tetrahydropyracene (4.55 g., 0.025 mole) was heated at 300–320° under a nitrogen atmosphere with 200 mg. of 10% palladium-on-charcoal catalyst until the evolution of hydrogen ceased (*ca.* 90 minutes). The product was dissolved in benzene, the catalyst removed by filtration, and, after removal of most of the solvent, the collected material recrystallized from benzene to give 3.0 g. (67%) of colorless needles which sintered at 206° and melted at 212–216°. Further recrystallization, twice from benzene and once from butanol, followed by sublimation *in vacuo* raised the melting point to 214.5–217.5°.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.38; H, 6.68.

The trinitrobenzene derivative crystallized from benzene as bright orange needles, m.p. 206–207°.

Anal. Calcd. for $C_{20}H_{15}N_3O_6$: C, 61.07; H, 3.84. Found: C, 61.09; H, 3.84.

The picrate was obtained from a benzene solution as dark red needles, m.p. 206–207°.

Anal. Calcd. for $C_{20}H_{15}N_3O_7$: C, 58.68; H, 3.69. Found: C, 59.10; H, 4.01.

Pyracene is only slightly soluble in ethanol, insoluble in hexane, and dissolves in hot benzene to give a solution having a blue fluorescence. The hydrocarbon showed no reaction with 2% potassium permanganate in acetone and was recovered quantitatively from an attempted hydrogenation in ethanol in the presence of a palladium-on-barium sulfate or platinum oxide catalyst at room temperature and atmospheric pressure. The ultraviolet absorption spectrum of an ethanolic solution showed the following peaks: λ_{max} in mμ at 231 (log ε 4.95), 284 (log ε 3.82), 295 (log ε 3.92), 307 (log ε 3.75), 313 (log ε 3.57), 322 (log ε 3.23) and 329 (log ε 3.44). This spectrum, along with that of acenaphthene, is shown in Fig. 1.

1,4,5,8-Naphthalenetetracarboxylic Acid.—Sodium dichromate (25 g.) was added in portions to a solution of pyracene (1.9 g.) in 50 ml. of acetic acid at a temperature of 90° and the resultant mixture heated under reflux for three hours. The cooled reaction mixture was poured into 150 ml. of cold dilute sulfuric acid and the precipitated acid collected by suction filtration. The crude product was then heated for 15 minutes in an alkaline solution containing 0.5 g. of potassium permanganate. On acidification of the decolorized, filtered solution, crystalline 1,4,5,8-naphthalenetetracarboxylic acid precipitated. The yield was 1.12 g. (35%). This acid had no characteristic melting point and was further identified by a series of specific transformations first described by Bamburger and Philip[16] and later confirmed by Fieser and Peters.[9]

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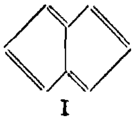
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Syntheses of Some Bicyclo[3.3.0]octane Derivatives

BY JOHN D. ROBERTS AND WILLIAM F. GORHAM[1]

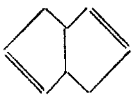
As part of a projected synthesis of pentalene (bicyclo[3.3.0]octatetraene), bicyclo[3.2.0]-2-hepten-6-one prepared by condensation of ketene and cyclopentadiene was converted by the Tiffeneau–Demjanov ring expansion procedure to a mixture of bicyclo[3.3.0]-2-octen-6-one and bicyclo[3.3.0]-2-octen-7-one. The ketonic mixture was reduced with lithium aluminum hydride and the resulting alcohols were converted to a mixture of tetrahydropentalenes by the Chugaev method. Unsuccessful attempts were made to transform the tetrahydropentalene mixture into pentalene by catalytic dehydrogenation procedures. Some of the steps in the Linstead synthesis of *cis*- and *trans*-bicyclo[3.3.0]octanes have been improved.

The question of the possible existence and stability of pentalene (bicyclo[3.3.0]octatetraene (I)) is of considerable interest since the substance would be a completely conjugated planar cyclic polyolefin without the (2 + 4 *n*) π-electrons[2] characteristic of the usual stable planar cyclic conjugated systems. The pentalene ring system seems to be known only as various derivatives of 1,2,4,5-dibenzpentalene,[3] and although a number of attempts have been made recently to synthesize 1,2-benzpentalene and its derivatives,[4] only Barrett and Linstead[5] have recorded an attempt to prepare the parent hydrocarbon (by catalytic dehydrogenation of *cis*-bicyclo[3.3.0]octane). Current theoretical opinion seems to be divided as to the possible stable existence of I.[6]

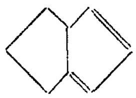


I

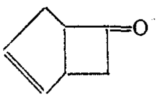
The principal objective of the present investigation was the synthesis and study of a tetrahydropentalene with an unconjugated double bond in each ring. Such a compound (as II) was expected to be somewhat more stable than an isomeric cyclopentanocyclopentadiene like III.[7] The synthesis started with bicyclo[3.2.0]-2-hepten-6-one (IV) which was obtained by addition of ketene to cyclopentadiene.[8] The structure of IV is indicated by the non-identity of its 2,4-dinitrophenylhydrazone with that of dehydronorcamphor[9] (the expected 1,4-adduct), the



II



III



IV

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[1] James Flack Norris Memorial Fellow, 1950–1951.

[2] E. Hückel, "Grundzüge der Theorie ungesättiger and aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, pp. 77–85.

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[9] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).