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

2,2a,3,4-Tetrahydro-1H-cyclopent[cd]indene

BY HENRY RAPOPORT AND JOSEPH Z. PASKY

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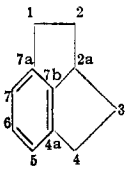
The fused tricyclic compound containing one six- and two five-membered rings, 2,2a,3,4-tetrahydro-1H-cyclopent[cd]-indene (I), has been synthesized by pyrolysis of the lead salt of 7-carboxy-1-indanacetic acid (IV) followed by reduction of the resulting ketone. Yields in the pyrolysis step were 40–50% when precautions were taken to prepare a normal lead salt. To prepare the 1,7-disubstituted indan, indene was condensed with methyl acrylate, the substituted propionic acid was converted to 2a,3,4,5-tetrahydro-5-acenaphthenone (XII), and this was ring-opened by Beckmann rearrangement after oximation. Except for its striking ease of catalytic hydrogenation, compound (I) displayed the properties expected of a normal aromatic compound.

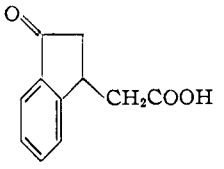
The synthesis of the 6,5,5-tricyclic fused ring system of 2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (I) has been the subject of considerable effort as reported in the literature. Although there have been occasional unsubstantiated claims to its syn-



I

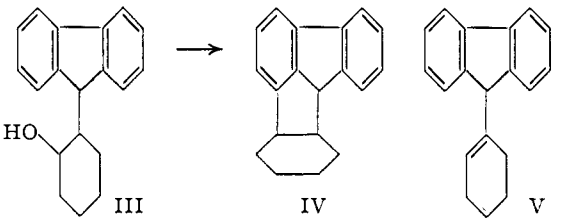
thesis (to be discussed below), this effort has been unsuccessful and has led to the frequent conclusion that this highly-strained ring system may be incapable of existence.[1–7] In the present report, the synthesis of compound I and some of its properties were described.

The unsuccessful attempts reported in the literature invariably involved cyclizations of β-phenylglutaric acids. Ring-closure to the 3-keto-1-indanacetic acid (II) took place readily and under a variety of conditions such as the action of sulfuric acid on the acid,[2] aluminum chloride on the acid chloride,[1–3,5] and hydrogen fluoride on the acid.[4,5] However, in no instance could the cyclizations be continued to the tricyclic cyclopent[cd]indene ring system. In several cases, the 3-keto group was reduced to methylene and the 1-indanacetic acid was subjected to ring-closure reactions. These also failed.[3,4,8]



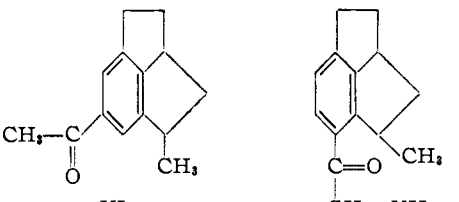
II

There have been three previous claims to the preparation of the cyclopent[cd]indene ring system. Hurd and Mold[9] suggested that the action of phosphoric acid on 2-(9-fluorenyl)-cyclohexanol (III) resulted in the cyclopentindene IV, since the product was unreactive toward bromine and alkaline permanganate. However, Cook and Hunter[7] established the structure of the product as 9-(1-cyclohexenyl)-fluorene (V) by hydrogenation to 9-cyclohexylfluorene, formation of an epoxide and oxidation to a diol with osmium tetroxide.



III IV V

Lagidze[10] has reported the reaction of benzene and 1,3,5-triacetoxyhexane under Friedel–Crafts conditions gave compound VI[10a] or VII.[10b] This seems highly unlikely, particularly since on oxidative degradation of the product presumably with structure VII, 1,2,4-benzenetricarboxylic acid was obtained.



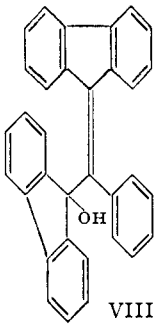
VI VII

The third claim to have prepared a cyclopent[cd]-indene ring system is an older one which has been frequently overlooked. Koelsch[11] subjected compound VIII to the action of a mixture of sulfuric and acetic acids and assigned structure IX to the product. The data presented are consistent with structure IX as the probable structure but do not appear to be sufficient to establish it uniquely.

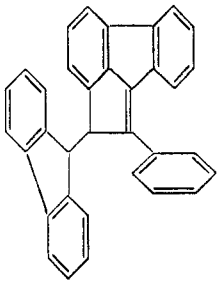
In considering the 1-indanacetic acid cyclization attempts, it was felt that the failure of these procedures to give a cyclopent[cd]indene might not necessarily be due to the strained nature of this ring system. A study of models and a scale drawing with carbon atoms 2 and 3 deviating slightly from coplanarity do not indicate excessive strain. Using normal bond lengths, models can be made with relatively small (*ca.* 10°) angular distortions,

(1) J. v. Braun and J. Reutter, *Ber.*, **59**, 1922 (1926).
(2) J. G. Jackson and J. Kenner, *J. Chem. Soc.*, 573 (1928).
(3) J. v. Braun and K. Weisbach, *Ber.*, **64**, 1785 (1931).
(4) G. M. Badger, J. E. Campbell and J. W. Cook, *J. Chem. Soc.*, 1084 (1949).
(5) D. H. Hey and D. H. Kohn, *ibid.*, 3177 (1949).
(6) A. G. Anderson and H. F. Greef, THIS JOURNAL, **74**, 5124 (1952), footnote 2.
(7) J. W. Cook and L. Hunter, *J. Chem. Soc.*, 3168 (1952).
(8) J. v. Braun, E. Danziger and Z. Köhler, *Ber.*, **50**, 56 (1917).
(9) C. H. Hurd and J. D. Mold, *J. Org. Chem.*, **13**, 339 (1948).
(10) (a) R. M. Lagidze, *Doklady Akad. Nauk S.S.S.R.*, **77**, 1023 (1951); (b) R. M. Lagidze and B. S. Potskhverashvili, *Soobshcheniya Akad. Nauk Gruzin. S.S.R.*, **14**, No. 8, 473 (1953).
(11) C. F. Koelsch, THIS JOURNAL, **54**, 4744 (1932).

which if correct do not imply a prohibitive amount of strain.



VIII

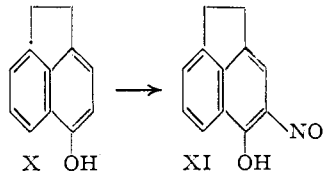


IX

Cyclization may have been prevented by the steric impositions of the Friedel–Crafts type reactions used. If the attacking group must enter the benzene ring at an angle following or simultaneously with aromatic carbon–hydrogen bond rupture, the short two-carbon chain of indanacetic acid may be unable to accommodate this requirement and still approach near enough to make the bond. Particularly would this be a very difficult and crowded approach if complexing with the Lewis acid catalyst is involved, as it most likely is.

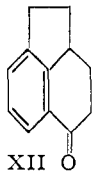
Therefore, the approach chosen to circumvent this difficulty of cyclizing into the benzene ring was to use a 1,7-disubstituted indan. Bond formation would then not involve electrophilic substitution in the aromatic nucleus and a variety of intramolecular cyclization methods would be available in a more flexible system.

To prepare the appropriate 1,7-disubstituted indan a number of methods were considered. Nitrosation of 5-acenaphthenol (X)[12] gave 4-nitroso-5-acenaphthenol (XI). However, yields on the nitrosation were poor and no product could be identified from ring-opening attempts *via* Beckmann re-



X OH XI OH

arrangement. 2a,3,4,5-Tetrahydro-5-acenaphthenone (XII) then became the key intermediate since conceivably this could be oximinated and then opened to the desired 1,7-disubstituted indan.



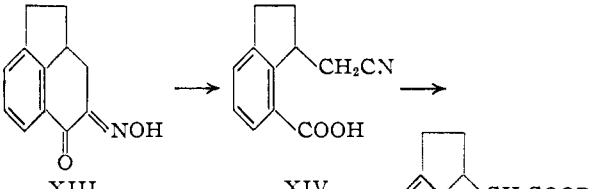
XII O

The synthesis of XII has been twice reported in the literature,[1,13] both methods proceeding through 1-indaneacetic acid, extending the carbon chain by standard reactions, and then cyclizing the resulting propionic acid. In addition to the steps in the chain-extension, 1-indanacetic acid itself had to be prepared from 1-indanone, making this synthesis of XII not particularly attractive for the preparation of the anticipated large amounts of material.

An alternative approach to XII was the hydrogenation of 5-acenaphthenol (X) to 2a,3,4,5-tetrahydro-5-acenaphthenol followed by oxidation to the ketone. The combined difficulty of securing quantities of 5-acenaphthenol and the only fair yield obtained on hydrogenation led to abandonment of this route.

A procedure which should easily give the indan substituted with a propionic acid side chain is Michael condensation of the readily available indene with methyl acrylate. However, a search of the literature revealed a discouraging report[14] on this method. With indene, acrylonitrile gave only di- and tricyanoethylation products, and the reaction with acrylic esters was reported to be unsuccessful. Because of its obvious advantages, this reaction was re-investigated and by using a large excess of indene, which was recoverable, an 85% yield of the mono-condensation product with methyl acrylate was obtained. Hydrogenation, hydrolysis, acid chloride formation and ring-closure then gave 2a,3,4,5-tetrahydro-5-acenaphthenone (XII) in excellent yield and unlimited quantity.

To proceed to the 1,7-disubstituted indan, the ketone XII was oximinated with butyl nitrite in the presence of potassium *t*-butoxide (acid catalysis gave only resinous material) and the oximino-ketone XIII was ring-opened to the cyano-acid XIV with benzenesulfonyl chloride in pyridine. These reactions proceeded in 60 and 70% yield, respectively, and thus concluded an extremely facile process for converting indene to 7-carboxy-1-indanacetonitrile.



XIII XIV XV

Several methods were examined to complete the ring closure to the tricyclic cyclopent[cd]indene system. Dieckmann cyclization applied to the dimethyl ester XV, even under conditions of extreme high dilution,[15] gave as the only product essentially complete recovery of starting ester. Heating the dibasic acid XV with acetic anhydride both in the absence and presence of potassium cyanide[16] also failed to give ring formation. Starting acid and some cyclic anhydride were the products in each case.

Pyrolysis of heavy metal salts of the dibasic acid then was investigated in some detail. Since there is little basis for prediction as to the most efficacious metallic salt, a number were tried. The thorium salt on pyrolysis gave a 3% yield of the ketone XVI

(12) H. Rapoport, T. P. King and J. B. Lavigne, THIS JOURNAL, 73, 2718 (1951).
(13) A. G. Anderson and R. H. Wade, *ibid.*, **74**, 2274 (1952).
(14) H. A. Bruson, *ibid.*, **64**, 2457 (1942).
(15) N. J. Leonard and R. C. Sentz, *ibid.*, **74**, 1704 (1952).
(16) F. Uhle, *ibid.*, **71**, 761 (1949).

as a crystalline sublimate; the calcium salt similarly gave a 2% yield. On turning to the lead salt, the yield unexpectedly rose to 20%, but repetition of the process showed the yield to be quite erratic and unpredictable, varying from 10% to as high as 50%.

There seemed to be one correlation with the yield and that was the composition of the lead salt. In those cases where analysis indicated the presence of appreciable basic lead salt, the yields were low. However, when the material was pure normal lead salt, the yields were consistently 40–50%.

A reliable procedure for preparing the normal lead salt was developed from the following considerations. The species of lead ions present in an aqueous solution are determined by equation 1. From the value of this equilibrium constant, the distribu-

$$Pb(OH)^+ = Pb^{++} + OH^-;\ K = 3 \times 10^{-8}\ ^{17} \quad (1)$$

tion of the lead in solution between $Pb(OH)^+$ and Pb^{++} as a function of the *p*H has been calculated and is shown in Table I. Thus, when a solution of

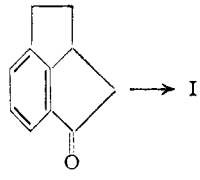
TABLE I

SPECIES OF LEAD IONS IN SOLUTION AS A FUNCTION OF *p*H

*p*H	7	6	5
$Pb(OH)^+$, %	77	25	3
Pb^{++}, %	23	75	97

lead nitrate is added to a neutralized (*p*H 7–7.5) solution of a carboxylic acid, the initial precipitate very probably contains some basic lead salt. By carrying out the addition of lead nitrate solution (*p*H 4.3) very slowly (four hours) and with vigorous stirring, this initial precipitate has an opportunity to dissolve as the $Pb(OH)^+$ concentration decreases and then to reprecipitate as the normal salt.

This procedure consistently gave the normal lead salt of the dibasic acid XV, whereas rapid addition of the lead nitrate solution resulted in material containing considerable basic lead salt. It is apparent that the composition of the lead salt depends on its mode of precipitation, and the yield of ketone XVI, in turn, is profoundly affected by the lead salt composition.



XVI

The hydrocarbon 2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (I) then was obtained from the ketone XVI by a modified Wolff–Kishner procedure. That the synthetic compounds actually had the 6,5,5-fused ring structures I and XVI was established by elemental analysis and molecular weight determinations. The high volatility of these compounds is also consistent with a monomeric structure. Oxidation of each compound gave hemimellitic acid, characterized as the trimethyl ester, and the ultraviolet and infrared spectra are consistent with these structures.

The ultraviolet absorption spectra of the ketone XVI and the hydrocarbon I are shown in Figs. 1 and 2, together with those of the corresponding 6,5,6-fused tricyclic ring compounds 2a,3,4,5-tetrahydro-5-acenaphthenone (XII) and 2a,3,4,5-tetrahydroacenaphthene. Taking the acenaphthene derivatives as models for a normal trisubstituted aromatic system of this type, there is very little departure from normality in the case of the 6,5,5-tricyclic compounds XVI and I. This indicates very little if any departure from planarity in the benzene ring as a result of the attachment of the fused five-membered rings.

The same type of normal spectra were found in the infrared.[18] The 6,5,5-ketone XVI and the 6,5,6-ketone XII have their carbonyl bands at the same wave lengths as 1-indanone and 1-tetralone, 5.81 and 5.92 μ, respectively.

Attempts were made to detect strain in this ring system and any resulting decrease in benzene resonance stabilization as might be reflected in a difference in chemical reactivity. For this purpose, the reactions of the 6,5,5-hydrocarbon I and the 6,5,6-hydrocarbon with perbenzoic acid, maleic anhydride and hydrogen were investigated. With perbenzoic acid in chloroform at room temperature both compounds react very slowly and at the same rate. After seven days, 50 mole % of perbenzoic acid had been consumed. With maleic anhydride, no reaction took place until a temperature of 130° was reached and then no identifiable product could be isolated from either compound.

However, on catalytic hydrogenation there was a striking difference. With a palladized carbon catalyst in ethanol at room temperature and atmospheric pressure, 2a,3,4,5-tetrahydroacenaphthene was completely inert, as was expected. On the other hand, 2,2a,3,4-tetrahydro-1H-cyclopent[cd]-indene very rapidly absorbed exactly three moles of hydrogen and gave a crystalline perhydro compound of m.p. 50°. Models indicate perhydrocyclopent[cd]indene has a plane of symmetry through carbons 2a, 7b and 6, and this symmetry probably accounts for its high melting point.

Thus we may conclude that compound I is not a highly strained ring system, incapable of existence, as previously imagined. Spectrally, it shows only a very slight, if any, departure from normal properties, and its chemical reactions seem normal except for catalytic hydrogenation. Since the latter is a surface reaction, it may be unique in discerning small differences in stability.

Experimental[19]

Methyl β-(1-Indanyl)-propionate.—Indene (233 g., 2 moles) and methyl acrylate (43 g., 0.5 mole), both of which had been redistilled at 20 mm., were added to a solution of 11.5 g. (0.5 mole) of sodium in 500 ml. of absolute methanol and the solution was heated under reflux for 20 hours in a nitrogen atmosphere. The cooled solution was added to one liter of 0.5 *N* acetic acid, the organic phase was removed, and the aqueous phase was extracted with two 100-ml. portions of benzene. After being dried over magnesium sulfate, the solution was fractionally distilled and the unsaturated ester was obtained in 85% yield (86 g.) boiling at 105–120° (2–4 mm.). This ester (90 g., 0.45 mole), dis-

(17) I. M. Korenman, *Zhur. Obshchei Khim.*, **21**, 1961 (1951).

(18) Infrared spectra were determined on 0.4 *M* solutions in chloroform with a Baird spectrophotometer.

(19) All melting points are corrected and those above 200° were taken in evacuated capillaries; microanalyses were performed by the Microchemical Laboratory, University of California.

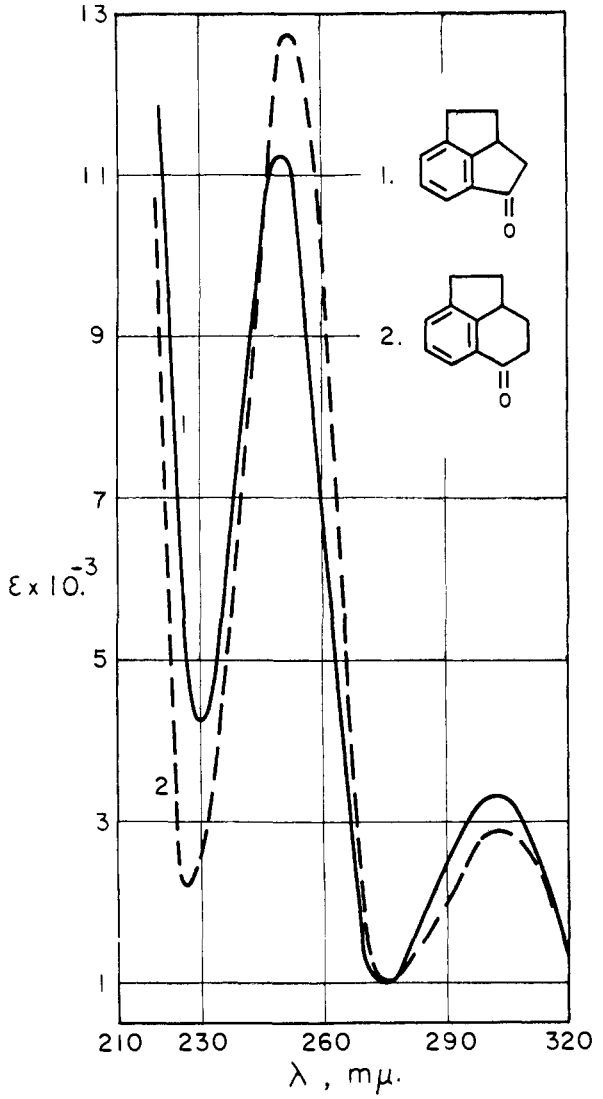


Fig. 1.—Ultraviolet absorption spectra in 95% ethanol: ——, 2,2a,3,4-tetrahydro-1-keto-1H-cyclopent[cd]indene (XVI); ------, 2a,3,4,5-tetrahydro-5-acenaphthenone (XII).

solved in absolute ethanol (150 ml.), was shaken in the presence of 2 g. of 5% palladized carbon at room temperature and 3 atm. hydrogen pressure. After hydrogen absorption ceased (overnight) with the uptake of 100 mole % of hydrogen, the mixture was filtered and the filtrate was distilled. Methyl β-(1-indanyl)-propionate was collected in quantitative yield, b.p. 144–154° (10 mm.), 126° (2.5 mm.) (reported[13] b.p. 144–154° (10 mm.)), m.p. 17–18°, $n^{20}D$ 1.5220.

2a,3,4,5-Tetrahydro-5-acenaphthenone (XII).—Methyl β-(1-indanyl)-propionate was saponified, the acid was converted to acid chloride with phosphorus pentachloride, and the acid chloride was cyclized, all according to the procedure of Anderson and Wade.[13] 2a,3,4,5-Tetrahydro-5-acenaphthenone of m.p. 85–86° was obtained (reported m.p. 85–86°,[1] 83–84°[13]).

2a,3,4,5-Tetrahydro-4-oximino-5-acenaphthenone (XIII).—A solution of 6.9 g. (0.04 mole) of 2a,3,4,5-tetrahydro-5-acenaphthenone and 4.12 g. (0.04 mole) of *n*-butyl nitrite in 40 ml. of *t*-butyl alcohol was added slowly to an ice-cooled solution of 1.6 g. (0.04 mole) of potassium in a mixture of 40 ml. of *t*-butyl alcohol and 40 ml. of dry ether. Stirring was continued for 12 hours at 5–10° after which most of the *t*-butyl alcohol was evaporated under reduced pressure and the residue was poured into 200 ml. of water. Extraction of the aqueous solution with three 50-ml. portions of benzene afforded 1% of recovered acenaphthenone in the

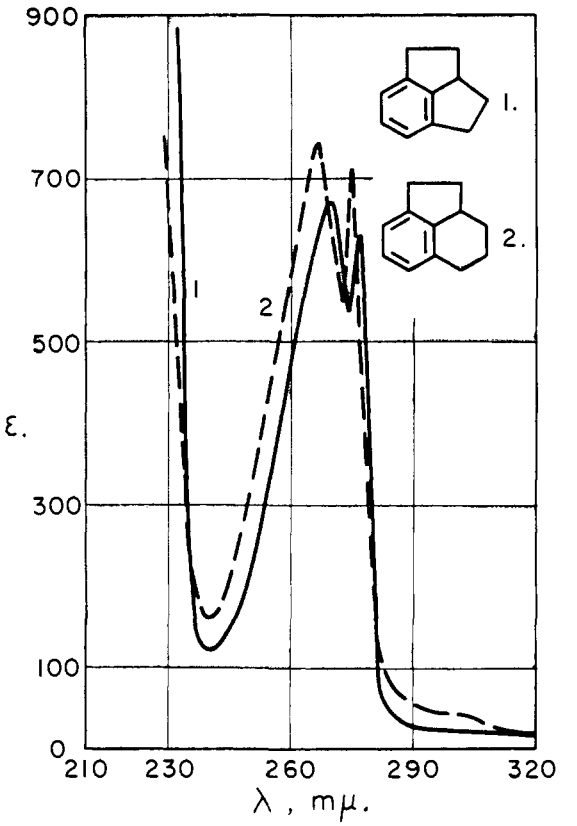


Fig. 2.—Ultraviolet absorption spectra in 95% ethanol: ——, 2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (I); ------, 2a,3,4,5-tetrahydroacenaphthene.

benzene extracts, and saturation of the aqueous solution with carbon dioxide caused precipitation of a yellow solid. Crystallization from acetone–water gave pale yellow needles of 2a,3,4,5-tetrahydro-4-oximino-5-acenaphthenone in 60% yield, m.p. 183° dec.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.6; H, 5.5; N, 7.0. Found: C, 71.4; H, 5.4; N, 6.8.

7-Carboxy-1-indanacetonitrile (XIV).—While maintaining the internal temperature at 20–30° by external cooling, a solution of 22 g. (0.125 mole) of benzenesulfonyl chloride in 20 ml. of pyridine was added over one hour with stirring to 25 g. (0.125 mole) of 2a,3,4,5-tetrahydro-4-oximino-5-acenaphthenone dissolved in 60 ml. of pyridine. After addition had been completed, the reaction mixture was stirred for an additional half-hour at 20–30°, it was acidified to congo red with 6 *N* sulfuric acid, and it was stirred for another half-hour. Filtration removed the precipitate which was washed well with water and digested with 2 *N* aqueous potassium carbonate. When most of the precipitate had gone into solution after several hours of digestion, decolorizing carbon was added, the mixture was filtered, and the filtrate was acidified with concd. hydrochloric acid to *p*H 2. There was thus obtained 17.5 g. (70% yield) of 7-carboxy-1-indanacetonitrile which could be recrystallized from water, m.p. 133–135°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.6; H, 5.5; N, 7.0; equiv. wt., 201. Found: C, 71.9; H, 5.3; N, 7.1; equiv. wt., 199.

7-Carboxy-1-indanacetic Acid (XV).—7-Carboxy-1-indanacetonitrile was hydrolyzed by boiling 50.4 g. (0.25 mole) in 500 ml. of 3.5 *N* potassium hydroxide in a nitrogen atmosphere. After 12 hours, when the ammonia evolution had reached 95% of theoretical, the solution was cooled, acidified to *p*H 2, and filtered. The precipitate of 7-carboxy-1-indaneacetic acid was crystallized from water, m.p. 190–191°, and the yield was practically quantitative.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.5; H, 5.5; equiv. wt., 110. Found: C, 65.3; H, 5.3; equiv. wt., 110.

Lead Salt of 7-Carboxy-1-indanacetic Acid.—A solution of 110 g. (0.5 mole) of the dibasic acid XV in 270 ml. of ethanol was adjusted to *p*H 7.5 with 1 *N* aqueous sodium hydroxide and to it a warm solution of 277 g. (0.84 mole) of lead nitrate in two liters of water was added over the course of four hours with rapid stirring. The finely divided, precipitated lead salt was removed by filtration, washed with water (3 × 200 ml.) and ethanol (2 × 500 ml.), and dried to constant weight at 100° and 20 mm. pressure. The yield was quantitative.

Anal. Calcd. for $C_{12}H_{10}O_4Pb$: C, 33.9; H, 2.4; Pb, 48.6. Found: C, 34.0; H, 2.5; Pb, 48.4.

2,2a,3,4-Tetrahydro-1-keto-1H-cyclopent[cd]indene (XVI).—Pyrolysis of not more than 0.25″ thick layers of the lead salt of 7-carboxy-1-indanacetic acid at 350–380° (20 mm.) gave yields of 40 to 50% of ketone as a crystalline sublimate. This was resublimed at 60° (20 mm.) to give diamond-shaped crystals, m.p. 63°.

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.5; H, 6.6; mol. wt., 158. Found: C, 83.6; H, 6.6; mol. wt. (Rast), 148.

The 2,4-dinitrophenylhydrazone of XVI was prepared in the usual manner and was recrystallized from ethanol; m.p. 255–257° dec.

Anal. Calcd. for $C_{17}H_{14}O_4N_4$: C, 60.4; H, 4.2; N, 16.6. Found: C, 61.0; H, 4.6; N, 16.5.

2,2a,3,4-Tetrahydro-1H-cyclopent[cd]indene (I).—Application of the modified Wolff–Kishner procedure of Anderson and Wade[13] to 3.96 g. (0.025 mole) of 2,2a,3,4-tetrahydro-1-keto-1H-cyclopent[cd]indene, resulted in an 80% yield, 2.9 g., of the hydrocarbon, b.p. 91° (10 mm.), $n^{20}D$ 1.5629.

Anal. Calcd. for $C_{11}H_{12}$: C, 91.6; H, 8.4. Found: C, 91.7; H, 8.5.

2a,3,4,5-Tetrahydroacenaphthene was prepared in a similar manner from 2a,3,4,5-tetrahydro-5-acenaphthenone in 84% yield and it boiled at 114–115° (10 mm.), $n^{20}D$ 1.5607 (reported[20] b.p. 115–116° (10 mm.), $n^{25}D$ 1.5582).

Oxidation Experiments.—Following the directions of Anderson and Greef,[6] potassium permanganate oxidations were performed on 2,2a,3,4-tetrahydro-1-keto-1H-cyclopent[cd]indene (XVI), 2,2a,3,4-tetrahydro-1H-cyclopent-[cd]indene (I) and 2a,3,4,5-tetrahydroacenaphthene. In each case, after esterification, trimethyl hemimellitate of m.p. 100–101° was obtained (reported[21] m.p. 100–101).

(20) J. v. Braun and G. Kirschbaum, *Ber.*, **55**, 1680 (1922).

(21) L. Schmid and F. Tadros, *Monatsh.*, **63**, 210 (1933).

From the ketone, a 15% yield was obtained; however, the two hydrocarbons gave yields of 1 and 4%, respectively.

Hydrogenation of 2,2a,3,4-Tetrahydro-1H-cyclopent[cd]-indene (I).—A solution of 2 g. (14 mmoles) of I in 20 ml. of absolute ethanol was hydrogenated at room temperature and atmospheric pressure using 0.4 g. of 5% palladized carbon as catalyst. After two hours and the consumption of 300 mole % of hydrogen, hydrogen absorption ceased and the mixture was filtered. Evaporation of the filtrate gave an 85% yield of **perhydrocyclopent[cd]indene** which sublimed easily on the steam-bath at atmospheric pressure, m.p. 50°.

Anal. Calcd. for $C_{11}H_{18}$: C, 88.0; H, 12.0. Found: C, 87.8; H, 12.0.

Application of the same conditions, even in the presence of perchloric acid, resulted in no hydrogenation of 2a,3,4,5-tetrahydroacenaphthene.

4-Nitroso-5-acenaphthenol (XI).—5-Acenaphthenol[12] (5 g., 0.03 mole) was dissolved in a warm solution of 1.2 g. (0.03 mole) of sodium hydroxide in 30 ml. of water. To the cooled (6–7°) solution, 2.2 g. (0.031 mole) of sodium nitrite was added and then 12 ml. of 6 *N* sulfuric acid was added over a 15-minute period with stirring. After being stirred for another 15 minutes, the mixture was filtered and the washed and dried precipitate was digested with ten 25-ml. portions of boiling cyclohexane. Concentration to 35 ml. and cooling gave material of m.p. 172–174° dec.

Anal. Calcd. for $C_{12}H_9O_2N$: C, 72.4; H, 4.6; N, 7.0. Found: C, 72.2; H, 4.4; N, 6.7.

Hydrogenation of 5-Acenaphthenol (X).—5-Acenaphthenol[12] (6.8 g., 0.04 mole) was dissolved in 75 ml. of absolute ethanol, 3 g. of Raney nickel[22] was added, and the mixture was hydrogenated at 25° and a pressure of 40 p.s.i. until 110 mole % of hydrogen was absorbed. The mixture was then filtered, the ethanol was flash-distilled from the filtrate, and the residue was dissolved in 300 ml. of ether. Thorough extraction with 0.5 *N* aqueous sodium hydroxide solution removed phenolic material (50% recovery) after which the ether was evaporated and the residue was distilled to yield 2a,3,4,5-tetrahydroacenaphthene (see above) (15%) and 2a,3,4,5-tetrahydro-5-acenaphthenol, b.p. 158–160° (18 mm.)[1] (35%).

(22) R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE A. M. TODD CO.]

The Isolation of Piperitone Oxide from *Mentha sylvestris*

BY ROBERT H. REITSEMA AND VERNERS J. VARNIS

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From a species of mint, *Mentha sylvestris*, there has been obtained a ketone corresponding to the formula $C_{10}H_{16}O_2$. Through conversion to diosphenol and progressive degradation studies, the structure of this material has been shown to be *l*-piperitone oxide.

Essential oils from the mint species generally contain predominantly monocyclic terpenes. The oxygenated constituents appear to have oxygen in either the 2-position (the spearmints) or the 3-position (the peppermints) of the *p*-menthane ring. One of the few mint oils which appeared to be distinct from this generalization was the oil from *Mentha sylvestris*. Chromatography indicated that a ketone was present in rather high concentration which was different from the common mint constituents.[1] Since *M. sylvestris* was of interest in a hybridizing program, the structure of this new ketone was investigated.

Analysis of the ketone and the semicarbazone indicated the empirical formula to be $C_{10}H_{16}O_2$. Steam distillation of the ketone or the semicarbazone from an acid media gave diosphenol (I). This and the general infrared spectrum[2] indicated the presence of a *p*-menthane carbon skeleton. The second oxygen was probably not present as a hydroxyl or ester group on the basis of the infrared spectrum and the failure to obtain hydroxyl group derivatives. A possibility was an ether group which would be cyclic since all ten carbons are used in the menthane structure. The formation of diosphenol showed the location of oxygen functions at carbons 2 and 3. The isolation of diosphenol and not a ma-

(1) R. H. Reitsema, *J. Am. Pharm. Assoc. (Sci. Ed.)*, **43**, 414 (1954).

(2) A. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).