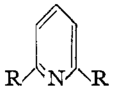
to convert the methyl groups of 2,6-lutidine (I) into substituents which would be suitable for further transformations toward the desired bicyclic system. Oxidation to dipicolinic acid was the only procedure which gave satisfactory yields of a useful intermediate. The transformations described in this report produced interesting substances but the yields were very low.

The dilithium salt of 2,6-lutidine reacted with bromine in ether to form small amounts of 2,6-di-(bromomethyl)-pyridine (II) and large quantities of an acid-soluble brown polymer. The reaction of N-bromosuccinimide with I also produced II along with some 6-bromomethyl-2-methylpyridine (III). Although Buu-Hoi[2] has stated that side-chain brominations in the heterocyclic series proceed easily with N-bromosuccinimide we have been able to obtain II in only 2% yield by this procedure.

When diethyl dipicolinate (IV) was reduced with lithium aluminum hydride a low yield of 2,6-di-(hydroxymethyl)-pyridine (V) was formed. Conversion of this diol to the dibromide II with hydrobromic and sulfuric acids served to confirm the structure of II.



I, R = CH_3
II, R = CH_2Br
IV, R = $COOC_2H_5$
V, R = CH_2OH

Dibromide II, even when analytically pure, melted over a range of 10 to 30° depending on the rate of heating. Melting was accompanied by the formation of a red color which remained after the sample cooled. It is believed that intermolecular quaternization may be taking place as the sample is heated. An attempt to hydrolyze II using silver oxide in aqueous ethanol did not yield diol V but a red substance similar to that obtained by heating II.

Experimental[3]

Diethyl Dipicolinate (IV).—Dipicolinic acid (25.0 g.) prepared by permanganate oxidation of 2,6-lutidine[4] was refluxed with 150 ml. of absolute ethanol while dry hydrogen chloride was introduced in a steady stream. When the acid had completely dissolved the excess ethanol was quickly distilled. The residual oil was then slowly heated on an oil-bath under full aspirator-vacuum until the product abruptly evolved hydrogen chloride.

The acid-free residue was distilled at 158° (1 mm.) to yield 20.0 g. (60%) of a sweet-smelling solid which melted at 41–42°.[5]

Anal. Calcd. for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87. Found: C, 59.22; H, 5.90.

2,6-Di-(bromomethyl)-pyridine (II). A.—A solution of phenyllithium in ether was prepared from 14.7 g. (2.12 moles) of lithium and 157 g. (1.0 mole) of bromobenzene. Fifty-five ml. (0.51 mole) of 2,6-lutidine was added to the ethereal solution and stirred overnight. To this mixture, cooled to 10°, 160 g. (1 mole) of bromine was rapidly added with vigorous stirring. Filtration from the solids and polymer left a very lachrymatory ethereal solution which was evaporated at room temperature to yield a dark oil. Rapid distillation at 0.5 mm. produced a white solid consisting of the dibrominated base and biphenyl. Four recrystallizations from petroleum ether produced about 750 mg. (1%) of pure 2,6-di-(bromomethyl)-pyridine which melted with decomposition from 66 to 76° or 66 to 99° depending on the rate of heating.

Anal. Calcd. for $C_7H_7NBr_2$: C, 31.73; H, 2.66; Br, 60.32. Found: C, 31.76; H, 2.64; Br, 60.37.

B.—A suspension of 62 g. (0.35 mole) of N-bromosuccinimide in 200 ml. of dry carbon tetrachloride was heated under reflux and illumination with 20 ml. (0.18 mole) of 2,6-lutidine. Boiling was continued for 15 hours while 1.2 g. of benzoyl peroxide was added in 4 portions. The remaining succinimide was filtered and the filtrate washed quickly with cold sodium bisulfite solution and water. Evaporation of the solvent left an oil which was distilled at 0.5 mm. The partially crystallized distillate was chilled, sucked as free as possible from adhering liquors and recrystallized three times from petroleum ether. About 1 g. (2%) of product was obtained which melted from 66 to 92°. A mixture of the dibromide and that prepared in (A) above, melted from 66 to 92° at the same rate of heating.

6-Bromomethyl-2-methylpyridine Picrate.—The adhering liquors from the crude dibromide II were dissolved in diethyl ether and an ethereal solution of picric acid was added until precipitation ceased. The picrate melted at 143° after four recrystallizations from ethanol.

Anal. Calcd. for $C_{13}H_{11}N_4O_7Br$: C, 37.61; H, 2.67; N, 13.49; Br, 19.25. Found: C, 38.18, 38.17; H, 2.90, 2.82; N, 13.50; Br, 19.12.

2,6-Di-(hydroxymethyl)-pyridine (V).—Diethyl dipicolinate (55.7 g., 0.25 mole) was added to a solution of lithium aluminum hydride (0.4 mole) in diethyl ether. An orange-red color developed immediately. The mixture was stirred overnight and water added to decompose the excess hydride. The ethereal layer was separated and evaporated leaving no residue. Carbon dioxide was passed into the aqueous suspension of solids to precipitate the lithium. The resulting suspension retained a yellow-colored substance which was polymeric. Filtration and distillation of the water-phase left a viscous oil (2 g., 5%) which crystallized upon the addition of ethyl acetate. Recrystallization from this solvent and a single sublimation produced the pure diol which melted at 114–118°. The diol was completely soluble in water and insoluble in dry ether.

Anal. Calcd. for $C_7H_9O_2N$: C, 60.41; H, 6.52. Found: C, 60.49; H, 6.43.

The hydrochloride, after being crystallized from methanol and sublimed, melted with decomposition at 153–160°.

Anal. Calcd. for $C_7H_{10}O_2NCl$: C, 47.87; H, 5.74. Found: C, 47.42; H, 5.66.

The diol was converted to the dibromide by the action of hydrobromic and sulfuric acids. After a small sample was boiled with an excess of 48% hydrobromic and concentrated sulfuric acids for 4 hours, the mixture was poured over ice-water, neutralized with dilute sodium hydroxide, and quickly extracted with ether. Removal of the dried solvents left the dibromide, which after recrystallization from petroleum ether melted from 66 to 74° with decomposition. A mixture of this dibromide and that prepared in (A) above melted from 63 to 76°.

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[2] N. P. Buu-Hoi, *Ann.*, **556**, 1 (1944).

[3] Microanalyses were by W. Manser, Zurich, Switzerland. All melting points are corrected and were determined using the Kofler Hot Stage.

[4] G. Black, E. Depp and B. B. Corson, *J. Org. Chem.*, **14**, 17 (1949).

[5] G. Crippa, M. Long and E. de Martini, *Gazz. chim. ital.*, **64**, 83 (1934), reported a m.p. of 28° for this compound. The difference may have been due to the presence of traces of moisture which appear to lower the m.p. markedly.

Studies in the Wagner Rearrangement. VII.[1] The Dehydration of 2-Phenyl-1-acenaphthenol-1-C^{14}

BY WILLIAM A. BONNER AND CLAIR J. COLLINS

RECEIVED JANUARY 21, 1953

Several isotopic investigations have been reported[2] in which migration ratios for various sub-

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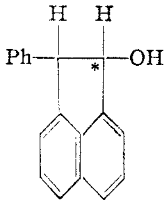
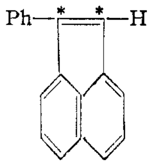
[1] This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] C. J. Collins and B. M. Benjamin, THIS JOURNAL, **75**, 1644 (1953) and previous papers.

stituted phenyl groups have been studied under the dehydrating conditions of the Wagner rearrangement. We have now attempted to extend these studies to the dehydration of the *cis*- and *trans*-isomers of 2-phenyl-1-acenaphthenol-1-C^{14} (I). The acenaphthene system appeared attractive because of the known migration[3-5] of phenyl caused by the action of acid on the 1,2-diphenyl-1,2-acenaphthenediols, the unusual *cis*-elimination observed in certain of its carbanion reactions[6] and the possibility that further information regarding symmetrical phenonium ions[7] might be obtained.

It was proposed to study the extent of phenyl migration during the dehydration of I by degradation of the dehydration product, 1-phenylacenaphthylene (II), to 8-benzoyl-1-naphthoic acid (III).


I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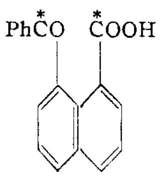
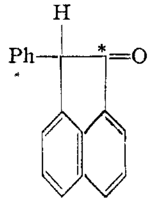

III


IV

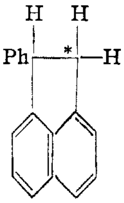
Decarboxylation of the latter would give products whose radioactivity assay would establish unambiguously the carbon-14 distribution in II.

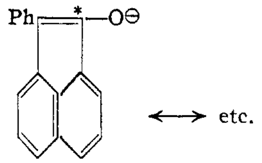
One of the desired isomers of the carbinol I was formed by the lithium aluminum hydride reduction of 2-phenylacenaphthenone-1-C^{14} (IV) in the manner previously described.[8]

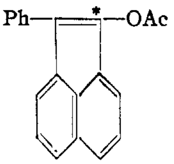
The action of phosphorus pentoxide on our isomer of carbinol I in inert solvent at elevated temperature led to immediate dehydration. The desired olefin II, however, was not the only product formed, and, in fact, could be isolated only in low yield. The bulk of the product was an amorphous yellow material of higher molecular weight and of apparently polymeric nature, from which the desired olefin II could be separated by fractional crystallization of its picrate. Decomposition of the picrate gave pure crystalline II having physical properties in agreement with those recorded in the literature. When an attempt was made to oxidize the olefin II to the acid III with neutral potassium permanganate no crystalline product could be obtained. The crude product was predominantly a neutral orange sirup, probably resulting from polymerization of the olefin II. Ozonization of II, however, followed by oxidative degradation of the ozonide led to the desired acid III in good yield. Decarboxylation of the acid so obtained yielded 1-benzoylnaphthalene containing 7.5% of the radioactivity of the parent acid. Thus phenyl migration occurred during or after the dehydration, I → II, to the extent of 7.5%.

Since the lithium aluminum hydride reduction of ketones is generally non-stereospecific in nature,[9] we have attempted to establish the geometrical configuration of our carbinol I and to prepare the second isomer by other means.

The experiments undertaken with these objectives are summarized as follows: (1) Catalytic reduction of the ketone IV with Adams catalyst or Raney nickel produced the same carbinol I obtained by means of lithium aluminum hydride reduction of the ketone. In the Raney nickel reduction a small amount of 1-phenylacenaphthene (V) also was formed. (2) Treatment of the ketone IV with alcoholic alkali led to a deep purple solution, presumably the consequence of the enolate anion VI and its resonance forms. Upon catalytic reduction these solutions absorbed far more than equimolar proportions of hydrogen, but no crystalline derivative could be isolated. (3) When the ketone IV was dissolved in pyridine an orange solution was formed, apparently owing to enol formation. This solution had a color identical with solutions of the olefin II. Treatment of such a solution with acetic anhydride led to the isolation of the enol acetate VII, an orange sirup capable of characterization through its crystalline picrate.


V


VI


VII

The structure of VII was confirmed by its ozonization in good yield to 8-benzoyl-1-naphthoic acid (III). Catalytic reduction of the enol acetate VII with Raney nickel produced only the hydrocarbon V. Similarly, the action of Raney nickel on the acetate of the carbinol I resulted in the hydrocarbon V, although the carbinol I itself was stable under similar conditions. (4) Reduction of the enol acetate VII using Adams catalyst led to a mixture of the hydrocarbon V and the acetate of the carbinol I. Thus the same geometrical isomer of I was produced by lithium aluminum hydride reduction and catalytic reduction of the ketone IV as by catalytic reduction of the enol acetate VII.

In view of the known *cis*-addition of hydrogen to olefins,[10,11] it was hoped that the catalytic reduction of the enol acetate VII would lead unambiguously to the *cis*-isomer of I. In the absence of the second geometrical isomer, however, we are unable to state that our isomer of I possesses the *cis*-configura-

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[3] P. D. Bartlett and R. F. Brown, This Journal, **62**, 2927 (1940).

[4] R. F. Brown, *ibid.*, **74**, 428 (1952).

[5] R. F. Brown, J. B. Nordmann and M. Madoff, *ibid.*, **74**, 432 (1952).

[6] S. J. Cristol, *ibid.*, **74**, 2193 (1952).

[7] D. J. Cram, *ibid.*, **71**, 3863 (1949), and subsequent papers.

[8] W. A. Bonner and C. J. Collins, *ibid.*, **75**, 2308 (1953).

[9] L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949); W. G. Brown, "Organic Reactions," Vol. VI, J. Wiley and Sons, New York, N. Y., 1951, p. 474.

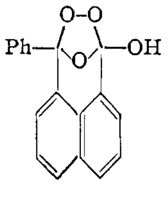
[10] R. P. Linstead and co-workers, This Journal, **64**, 1985, 1991, 2003, 2006, 2014, 2022 (1942).

[11] C. C. Price and J. V. Karabinos, *ibid.*, **62**, 1159 (1940).

tion, due to the possibility of *cis* → *trans* isomerization of I on the catalyst surface.

Our inability to obtain unequivocal evidence as to the configuration of our isomer of carbinol I, as well as our observation[12] that olefins formed by phosphoric anhydride dehydration may themselves undergo further rearrangement under conditions of the Wagner rearrangement, make it impossible for us to offer an unambiguous mechanistic interpretation of the present dehydration.

One point regarding the ozonization of VII is noteworthy. Assuming a normal structure for the ozonide, hydrolysis of the latter should yield an intermediate such as VIII. The structure VIII is vaguely suggestive of a hemiacetal, and might be expected to undergo spontaneous decomposition with loss of oxygen to give 8-benzoyl-1-naphthoic acid (III) directly. When the ozonide of the enol acetate was warmed with dilute alkali a gas was evolved and the acid III could be isolated by mere acidification, no oxidative treatment of the ozonide being necessary.



VIII

Experimental

1-Phenylacenaphthylene.—Phenylmagnesium bromide (20% excess) was prepared from bromobenzene (7.50 ml.) and magnesium (1.74 g.) in ether (100 ml.). To this solution was added dropwise with stirring over a 20-minute period a solution of acenaphthenone[13] (10.0 g.) in a mixture of benzene (70 ml.) and ether (40 ml.). The mixture was stirred for one hour under reflux, cooled slightly, and decomposed by the dropwise addition of excess water. The magnesium salts were filtered (Celite), and rinsed twice by slurrying with ether and refiltering. After washing and drying, the light orange ether layer was evaporated to yield 14.1 g. of yellow sirup. This was dissolved in hot ethanol (90 ml.) and treated with a solution of picric acid (14.2 g.) in hot ethanol (60 ml.). Crystallization was rapid, yielding 12.8 g. of 1-phenylacenaphthylene picrate, m.p. 122–123° in agreement with the recorded value.[14] The picrate was decomposed by dissolving in benzene (200 ml.) and passing the solution through a 2.8 × 45 cm. column of alumina, rinsing with benzene. Solvent evaporation from the effluent left 6.5 g. of yellow oil which readily crystallized. Recrystallization from ethanol (50 ml.) gave 4.6 g. of orange needles, m.p. 59–60°. Concentration of the mother liquors to *ca.* 12 ml. produced an additional 1.3 g., m.p. 55–56.5°, over-all yield from acenaphthenone 49%. The m.p. of 1-phenylacenaphthylene previously has been recorded as 57–58°[14] and 54–55°.[15] On standing for several weeks the crystalline material became noticeably gummy, possibly due to spontaneous polymerization. It was accordingly reconverted to the picrate and stored as such.

Attempted Oxidation of 1-Phenylacenaphthylene.—The above hydrocarbon (0.25 g.) was dissolved in acetone (10 ml.) and treated with a solution of potassium permanganate (0.35 g., 1 equiv.) and magnesium chloride hexahydrate (0.23 g., 1 equiv.) in water (4 ml.). The mixture was allowed to stand one hour, after which the MnO_2 was filtered and rinsed with acetone. The filtrate was concentrated and diluted with water then treated with ether and excess sodium bicarbonate. Evaporation of the ether layer left 0.15 g. of red neutral oil which failed to crystallize when seeded with starting material. Acidification of the bicarbonate layer, followed by extraction with ether and evaporation of the extract, produced only 0.03 g. of intractable gum which failed to crystallize on seeding with 8-benzoyl-1-naphthoic acid. It appears probable that the above oxidation conditions led only to polymeric material.

Ozonization of 1-Phenylacenaphthylene.—The above hydrocarbon (0.25 g.) was dissolved in acetone (15 ml.) and ozonized on a semimicro scale.[16] Ozonization was complete in four minutes, as indicated by disappearance of the orange color. The acetone solution of the ozonide was treated with a solution of potassium permanganate (0.25 g.) in water (5 ml.) and allowed to stand at room temperature for 20 hours. The MnO_2 was filtered, rinsed with acetone, and the oxidation mixture processed as described above. The neutral fraction gave only 0.02 g. of oil. The acidic fraction produced 0.33 g. (109%) of fluffy glass. This was recrystallized twice from a mixture of ether and ligroin giving 0.10 g. of pure 8-benzoyl-1-naphthoic acid, m.p. 131.5–132.5°.

Dehydration of 2-Phenyl-1-acenaphthenol-1-C^{14}.—The material employed in the present dehydration was a sample previously described[12] having m.p. 167.2–167.7° and showing a radioactive assay of 2.326 ± 0.016 mc./mole. This material (1.5 g.) was dissolved in hot anhydrous benzene (50 ml.), and the solution was treated with *ca.* 0.75 g. of phosphorus pentoxide. The orange color characteristic of 1-phenylacenaphthylene was immediately formed. The mixture was boiled with swirling for three minutes, cooled and washed twice with water. Solvent evaporation produced 1.47 g. of orange sirup. This was boiled with ethanol (15 ml.) and the solution was decanted from 0.60 g. of insoluble, presumably polymeric gum. The ethanol solution of the soluble fraction was treated with a solution of picric acid (0.9 g.) in ethanol (8 ml.). Chilling in ice produced 0.37 g. of 1-phenylacenaphthylene picrate, m.p. 121–123°. In a similar experiment the picrate isolated at this point had a radioactive assay of 2.303 ± 0.002 mc./mole. The above picrate was dissolved in benzene and decomposed on a small column of alumina. Evaporation of the effluent and washings left 0.20 g. of oil which readily crystallized on scratching with a small seed of 1-phenylacenaphthylene. The material was ozonized without recrystallization. In a parallel experiment, however, the 1-phenylacenaphthylene produced after decomposition of the picrate was recrystallized. The purified material had m.p. 54–55° and showed an assay of 2.303 mc./mole. In the present experiment no further pure 1-phenylacenaphthylene was obtained from subsequent picrate fractions obtained from the original mother liquors.

The above crude 1-phenylacenaphthylene (0.20 g.) was dissolved in acetone (12 ml.) and ozonized as described above. The neutral fraction obtained after permanganate oxidation of the ozonide weighed 0.03 g., while the crude acidic fraction weighed 0.14 g. The latter was recrystallized from a mixture of ether and ligroin to give a sample of 8-benzoyl-1-naphthoic acid of m.p. 132.5–133.5° showing an assay of 2.340 mc./mole. In order to have sufficient material for the decarboxylation described below, this acid was diluted with a quantity of non-radioactive 8-benzoyl-1-naphthoic acid calculated to give a lower potency sample having an assay of 1.139 mc./mole.

The above diluted 8-benzoyl-1-naphthoic acid (0.198 g.) was dissolved in quinoline (3 ml.) and treated with a pinch of copper chromite. The mixture was refluxed for 20 minutes, sweeping the carbon dioxide produced into warm barium hydroxide solution with the aid of a helium stream. The barium carbonate was filtered, rinsed with boiled water, ethanol and acetone, then dried; yield 0.12 g., assay, 1.003 ± 0.005 mc./mole. This value is slightly lower than that required on the basis of the benzoylnaphthalene assay below, presumably because of unavoidable contamination of the barium carbonate. The quinoline solution remaining after decarboxylation was cooled, poured into excess dilute hydrochloric acid, and the resulting mixture was continuously extracted with ether for 1.75 hours. The ether extract was treated with Norit and evaporated to give 0.17 g. of amber oil. The latter was crystallized from methanol (2 ml.) to give a sample of 1-benzoylnaphthalene having m.p. 76–77° and showing a radioactivity assay of 0.0852 ± 0.0000 mc./mole. This figure permits calculation that the extent of phenyl migration during or after the dehydration of 2-phenyl-1-acenaphthenol-1-C^{14} was 7.5%.

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(12) To be published in detail in the near future.

(13) L. F. Fieser and J. Cason, *ibid.*, **62**, 434 (1940).

(14) B. R. Brown and D. L. Hammick, *J. Chem. Soc.*, 1395 (1948).

(15) E. Ghigi, *Ber.*, **73B**, 677 (1940).

(16) W. A. Bonner, *J. Chem. Educ.*, in press.

1-Acetoxy-2-phenylacenaphthene-1-C^{14}.—2-Phenyl-1-acenaphthenol-1-C^{14} (0.20 g.) was dissolved in pyridine (5 ml.) and the solution treated with acetic anhydride (4 ml.). After standing at room temperature for 24 hours the mixture was poured into water, and the resulting solid extracted into ether. The ether extract was washed with water, dilute hydrochloric acid, more water, and then sodium bicarbonate solution. Solvent evaporation produced 0.24 g. of white solid. Two recrystallizations from ethanol gave a sample of m.p. 122.5–123°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.32; H, 5.59. Found: C, 83.35, 83.24; H, 5.67, 5.70.

Hydrogenation of 2-Phenylacenaphthenone-1-C^{14}.—The ketone (0.3 g.) was dissolved in ethanol (12 ml.) and treated with Raney nickel (*ca.* 0.6 g.). The mixture was stirred magnetically overnight under a 35 p.s.i. hydrogen atmosphere. Catalyst filtration and solvent evaporation produced a white solid which was fractionally crystallized from a mixture of acetone and ligroin. A total of 0.13 g. of 2-phenyl-1-acenaphthenol-1-C^{14} was obtained, m.p. 166–168°, no depression when admixed with an authentic sample. After removal of several intermediate impure fractions from the mother liquors, a small quantity of 1-phenylacenaphthene was isolated, m.p. 100–101°.

When 0.25 g. of 2-phenylacenaphthenone-1-C^{14} was reduced in ethanol using Adams catalyst, a total of 0.14 g. of 2-phenyl-1-acenaphthenol-1-C^{14}, m.p. 166–167° was obtained.

Action of Raney Nickel on 2-Phenyl-1-acenaphthenol-1-C^{14} and its Acetate.—The carbinol (0.14 g.) was dissolved in ethanol (18 ml.) and the solution treated with Raney nickel (*ca.* 1 g.). On stirring for 19 hours under 1 atmosphere of hydrogen, 17.5 ml. of hydrogen was consumed. On processing the hydrogenation mixture for products, 0.07 g. of unchanged starting material was recovered. While the mother liquors may have contained 1-phenylacenaphthene, none of this could be isolated in crystalline form.

The above 1-acetoxy-2-phenylacenaphthene-1-C^{14} (0.08 g.) was dissolved in ethanol (10 ml.) and treated with Raney nickel (0.6 g.). On stirring for 19 hours under one atmosphere of hydrogen, 8.0 ml. of hydrogen was consumed. The catalyst was filtered and rinsed, and the filtrate was evaporated to dryness. The resulting 0.06 g. of oil crystallized on scratching, and was recrystallized from 1.5 ml. of ethanol. The resulting needles, m.p. 103–104°, showed no mixed m.p. depression with 1-phenylacenaphthene.

Enol Acetate of 2-Phenylacenaphthenone-1-C^{14}.—2-Phenylacenaphthenone-1-C^{14} (0.50 g., radioactivity assay, 2.322 ± 0.002 mc./mole) was dissolved in pyridine (3 ml.) to give an orange solution. The latter was treated with acetic anhydride (2 ml.), and the mixture permitted to stand for about two hours, then diluted with excess water and allowed to stand about 15 minutes. The orange oil was extracted into ether, and the ether extract was washed with water, dilute hydrochloric acid, again with water, and finally with sodium bicarbonate solution. Solvent evaporation led to a quantitative yield of the sirupy enol acetate. A sample of this sirup (0.32 g.) was dissolved in hot ethanol (4 ml.) and treated with a solution of picric acid (0.30 g.) in hot ethanol (1 ml.). Formation of red needles of the picrate was almost instantaneous. These were filtered, 0.44 g., m.p. 144.5–146°. Recrystallization from ethanol (5 ml.) gave 0.33 g. of product having m.p. 145–146° and showing a radioactivity assay of 2.342 mc./mole.

Anal. Calcd. for $C_{26}H_{17}O_9N_3$: C, 60.60; H, 3.33; N, 8.16. Found: C, 60.15; H, 3.56; N, 8.26.

Ozonization of Enol Acetate of 2-Phenylacenaphthenone-1-C^{14}.—The above sirupy enol acetate (0.36 g.) was dissolved in ethanol (15 ml.) and ozonized on a semi-micro scale. Ozonization was complete in about 8 minutes, as indicated by disappearance of the original orange color. To the alcoholic solution of the ozonide was slowly added 10% sodium hydroxide solution (10 ml.), causing the gentle evolution of a gas, presumably oxygen. The solution was heated to boiling on the steam-bath, after which the solvent was evaporated in an air stream. The residue was diluted with water and the solution extracted with ether. Evaporation of solvent from the ether layer gave 0.05 g. of neutral gum which was not investigated. The alkaline layer was acidified with hydrochloric acid, extracted with ether, and the extract decolorized with Norit and evaporated to dryness to give 0.24 g. of amber glass. Crystallization from a mixture of ether and ligroin gave 0.16 g. of pure 8-benzoyl-1-naphthoic acid, m.p. 131–132°, unchanged on admixture with an authentic sample.

Hydrogenation of Enol Acetate of 2-Phenylacenaphthenone-1-C^{14}.—The above sirupy enol acetate (0.62 g.) was dissolved in ethanol (15 ml.) and Raney nickel added. Hydrogenation at atmospheric pressure and room temperature for 1.75 hours resulted in the uptake of 71 ml. of hydrogen and disappearance of the orange color.

Customary processing led to 0.47 g. of amber sirup which crystallized completely when scratched with 1-phenylacenaphthene. Three recrystallizations from methanol gave a sample of 1-phenylacenaphthene-2-C^{14} of m.p. 102–102.5°, radioactivity assay, 2.330 ± 0.010 mc./mole.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.30, 93.43; H, 6.18, 6.10.

This material showed no mixed m.p. depression with authentic 1-phenylacenaphthene, m.p. 103–104°, prepared by the Raney nickel catalyzed hydrogenation of our above sample of 1-phenylacenaphthylene. The m.p. for 1-phenylacenaphthene has been previously reported[14] as 105–106°. The structure of the above reduction product was further confirmed by the fact that it could be oxidized to 8-benzoyl-1-naphthoic acid with neutral permanganate in acetone.

In another experiment 0.59 g. of the above sirupy enol acetate was dissolved in 15 ml. of ethanol and treated with *ca.* 0.15 g. of freshly reduced Adams catalyst. Reduction was fairly rapid at room temperature and one atmosphere pressure. After an hour 61 ml. of hydrogen was consumed (theory, 57 ml.), and some orange color was left. The catalyst was filtered, rinsed with ethanol, and the filtrate was evaporated to dryness. Ligroin (25 ml.) was added to the residue, causing partial crystallization. The solution was evaporated to 8 ml. and the crystals filtered, 0.18 g., m.p. 115–118°. The filtrate was diluted with ligroin to 25 ml. and passed through a 1 × 20 cm. alumina column. The column was rinsed with ligroin (100 ml.) and the clear effluent was evaporated to dryness. There resulted 0.11 g. of oil which slowly crystallized. This was recrystallized from 2.5 ml. of ethanol to yield 0.04 g. of 1-phenylacenaphthene, m.p. 103–104°, mixed m.p. with an authentic sample undepressed. The alumina column was then rinsed white with ethanol (50 ml.) and the effluent was evaporated to 4 ml. Seeding with the above material of m.p. 115–118° produced 0.05 g. of solid, m.p. 112–114°. Evaporation of the filtrate gave 0.17 g. of orange oil, presumably unreduced enol acetate. The combined solid materials were recrystallized from a mixture of ethanol (2.5 ml.) and ligroin (3 ml.) to produce 0.11 g. of white needles, m.p. 122–123°, mixed m.p. with the above sample of 1-acetoxy-2-phenylacenaphthene, 121–122°.

For further characterization of the acetoxy product obtained on reduction of enol acetate, deacetylation was undertaken. Impure acetate (0.17 g.) from the recrystallization mother liquors of the above and a parallel reduction were dissolved in ether (10 ml.) and added to a stirred slurry of excess lithium aluminum hydride in ether. After stirring for 10 minutes the excess anhydride was destroyed by the cautious addition of acetone, then of water, and hydrochloric acid. The ether layer was decolorized (Norit) and evaporated to give 0.13 g. (90%) of crude 2-phenyl-1-acenaphthenol. Recrystallization from 3 ml. of ethanol gave 0.06 g. of needles, m.p. 165.5–167°, mixed m.p. with authentic carbinol 166.5–167.5°.

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The Resolution of a Bis-Tridentate Iron(II) Complex

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It is generally agreed that in the bis-2,2′,2″-terpyridyl metal complexes the two tridentate chelate groups are arranged in two equatorial planes at right angles so that the complex cation has a plane