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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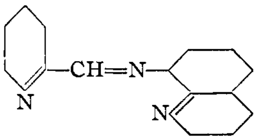
It is generally agreed that in the bis-2,2′,2″-terpyridyl metal complexes the two tridentate chelate groups are arranged in two equatorial planes at right angles so that the complex cation has a plane of symmetry.[1] The Schiff base (1) from 8-aminoquinoline and pyridine-2-aldehyde is structurally analogous to 2,2′,2″-terpyridyl and models show a high probability of similar coördination about metallic atoms. Since this molecule is a dissymmetrical tridentate chelate the complex cation should exist in enantiomeric forms. The addition of an alcoholic solution of (1) to aqueous ferrous sulfate was found to give such an intense green color that as little as one part of iron in two million could be detected by the reaction. The iron complex was resolved through the *d*-antimonyl tartrate. The enantiomeric iodides were stable at room temperature but racemized in two minutes at 100°.



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It is noteworthy that the sequence —N=C—C=N—C—C=N— in (1) is the same as in 2,2′,2″-terpyridyl so that similar possibilities exist for resonance and double bonding of the nitrogen and metal atoms. In the same way it can be inferred that the Schiff bases from pyridine-2-aldehyde and primary amines such as aniline and ethylenediamine should act, respectively, as bidentate and quadridentate molecules similar to 2,2′-dipyridyl and 2,2′,2″,2‴-tetrapyridyl. These compounds are being investigated.

Experimental

8-(α-Pyridylmethyleneamino)-quinoline.—Pyridine-2-aldehyde (5.35 g.) was added to a solution of 8-aminoquinoline (7.0 g.) in ethanol (5.4 ml.) and the mixture warmed for a few minutes on the water-bath. After cooling, ether was added and the product crystallized from ethanol. The minute cream needles melted at 123.5°. *Anal.* Calcd. for $C_{15}H_{11}N_3$: C, 77.2; H, 4.8; N, 18.0. Found: C, 76.2; H, 4.7; N, 18.3.

***d,l*-Bis-(8-(α-pyridylmethyleneamine)-quinoline) Iron (II) Iodide, Dihydrate.**—Ferrous sulfate heptahydrate (1.39 g.) in water (25 ml.) was treated with the tridentate (2.35 g.) in hot methanol (50 ml.) and the mixture heated to 70°. After dilution with 80 ml. of water, the intensely green colored solution was filtered and the iodide precipitated by the addition of sodium iodide. Recrystallized from hot water it gave fine black prisms. The perchlorate, sparingly soluble black needles, could not be oxidized to the iron(III) complex without complete decomposition. *Anal.* Calcd. for $C_{30}H_{26}N_6O_2I_2Fe$: C, 44.4; H, 3.2; N, 10.4; Fe, 6.9; I, 31.3. Found: C, 44.8; H, 3.5; N, 10.6; Fe, 6.9; I, 31.4.

***l*-Bis-(8-(α-pyridylmethyleneamino)-quinoline) Iron(II) Iodide Dihydrate.**—The *d,l*-iodide (2.0 g.) in hot water (40 ml.) was shaken with excess of freshly precipitated silver chloride. Filter pulp was added and the mixture filtered, washing the silver halide precipitate with a little hot water. The volume of the dark green solution was adjusted to 60 ml. and the substance cooled to 4°. Potassium *d*-antimonyl tartrate (0.9 g.) in water (15 ml.) was added with scratching of the sides of the vessel. The fine black precipitate was filtered off, washed with a little ice-water and dissolved in 10% sodium acetate solution (50 ml.) at 35–40°. After filtration the levo iodide was precipitated by the very slow addition of 10% sodium iodide solution. The active iodide which was much less soluble than the *d,l*-iodide was crystallized several times from warm methanol by the addition of ether, to give dark green nodular prisms. A 0.0025% solution in water gave α_D −0.05°, whence $[\alpha]^{20}_D$ −2000°, and $[M]^{20}_D$ −16,000°; a 0.005% solution gave α^{20}_{5461} −0.03°, whence $[\alpha]^{20}_{5461}$ −600°, and $[M]^{20}_{5461}$ −5,000°. *Anal.* Calcd. for $C_{30}H_{26}N_6O_2I_2Fe$: C, 44.4; H, 3.2; N, 10.4; I, 31.3. Found: C, 44.7; H, 3.3; N, 10.5; I, 31.4.

***d*-Bis-(8-(α-pyridylmethyleneamino)-quinoline) Iron (II) Iodide Dihydrate.**—The filtrate from the antimonyl tartrate precipitation was treated very slowly with 10% sodium iodide solution and the resulting precipitate of the impure *d*-iodide crystallized as above from warm methanol and ether.

A 0.0025% solution in water gave α_D +0.05°, whence $[\alpha]^{20}_D$ +2000°. *Anal.* Calcd. for $C_{30}H_{26}N_6O_2 \cdot I_2Fe$: C, 44.4; H, 3.2; N, 10.4; I, 31.3. Found: C, 44.7; H, 3.3; N, 10.5; I, 31.4.

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[1] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649 (1937).

Thermal Decomposition of Chlorate–Chloride Mixtures

BY A. VANDEN BOSCH AND A. H. W. ATEN, JR.

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As a result of kinetic measurements Glassner and Weidenfeld have recently suggested[1] that the formation of potassium perchlorate during the thermal decomposition of potassium chlorate should be due to a transfer of atomic oxygen from the chlorate ion to a chloride ion. If this assumption were correct, decomposition of ordinary chlorate in the presence of radioactive chloride would lead to the formation of labeled perchlorate.

We have performed experiments of this type, using sodium chlorate and sodium chloride because we encountered difficulties in the rapid recrystallization of potassium perchlorate formed in this way. A mixture of 5 g. of $NaClO_3$ with 0.6 to 0.8 g. of NaCl was kept at 505° during 30 minutes. The $NaClO_3$ had been dried at 120° and the NaCl had been irradiated with a mixed beam of slow and fast neutrons and contained both Cl^{34} and Cl^{38}. As irradiation of the chloride crystals is reported to influence the course of the chemical reaction[1] the NaCl was melted before use. The reaction mixture was dissolved in water, perchlorate was precipitated as $KClO_4$ by addition of KNO_3 and chloride was isolated as AgCl. Activities were measured with a mica window counter and corrections for the natural activity of potassium and for self-absorption were applied, although these were of minor importance. In four experiments at the end of the reaction period the mixture contained 15–22% of the total chlorine as ClO_4^-, 76–82% as Cl^- and 2–4% as ClO_3^-. For the ratio of the specific activities of the chlorine in ClO_4^- and in Cl^- from the reaction mixture the following successive figures were found: 0.013, 0.015, 0.004, 0.010.

In case the mechanism of Glasner and Weidenfeld were correct and if all the chloride ions in the mixture have an equal chance of participating in the reaction, this ratio should have been > 1. At the start of the reaction the perchlorate would have originated from the undiluted labeled chloride. However, as the reaction proceeded, the original radioactive chloride would have been diluted by new inactive chloride formed in the decomposition of the chlorate and therefore at the end the specific activity of the Cl^- in the reaction mixture should be lower than the specific activity of the chlorine in the perchlorate. (Both in our experiments and in those of Glasner and Weidenfeld part of the chloride may have remained solid from the start of the reaction, but at least an appreciable fraction must have been present in the melt. Incomplete melting of the chloride might have lowered the ratio to a value slightly less than unity, but not to a small fraction of 1.)

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[1] A. Glasner and L. Weidenfeld, THIS JOURNAL, **74**, 2464 (1952).