[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, PENNSYLVANIA STATE UNIVERSITY]

A SYNTHESIS OF HYDROPHENANTHRENES[1]

N. C. DENO AND HARRY CHAFETZ

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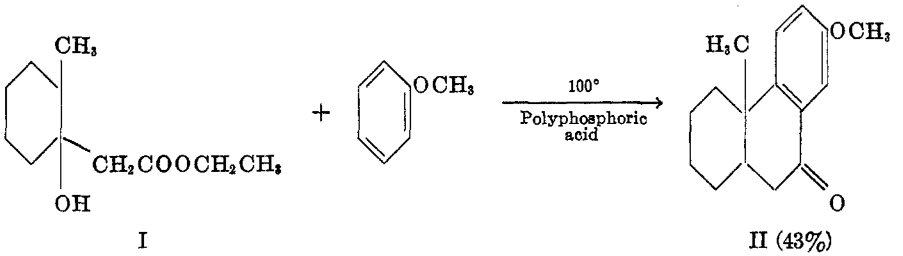
Several of the reported syntheses of partially hydrogenated phenanthrenes have employed a Friedel-Crafts type of alkylation or acylation. This paper reports a synthesis in which these two reactions have been combined into a single step.

Several cases have already been reported where an aromatic nucleus has been alkylated and acylated in a single step. Benzene has been treated with α,β-unsaturated acids to form indanones (1, 2). Benzene and alkylbenzenes have been treated with lactones to yield indanones and tetralones (3, 4). The application of this type of reaction to the synthesis of phenanthrenes has not been previously reported.

The following reaction has now been effected. The structure of II (1,2,3,4,9,10,11,12-octahydro-12-methyl-9-keto-7-methoxyphenanthrene) was demonstrated by the following observations. 2-Methoxyphenanthrene was formed in 13% yield by reduction of II with lithium aluminum hydride followed by heating with palladium at 325°. The b.p. of II was 155–162°/0.45 mm., which is in the range expected for structure II. The keto group was indicated by preparation and analysis of an oxime and a 2,4-dinitrophenylhydrazone. The infrared absorption spectrum showed a strong absorption at 5.95 μ characteristic of a conjugated carbonyl and also strong absorption at 6.23 μ and 6.71 μ characteristic of the aromatic ring. The complete infrared absorption spectrum appears elsewhere (5).



II (43%)
and product III (19%)

A second ketone was also obtained in impure form. The b.p. of this ketone (III) was 142–160°/0.45 mm., which is in the range expected for an isomer of II. The presence of the keto group and the isomerism of II and III were indicated by the preparation and analysis of the 2,4-dinitrophenylhydrazone. When III was reduced with lithium aluminum hydride followed by heating at 325° with palladium, an oil was obtained in about the same yield as from II, but which failed to crystallize on seeding with 2-methoxyphenanthrene. The evidence indicates that III is either a stereoisomer of II or the isomeric spiran structure.

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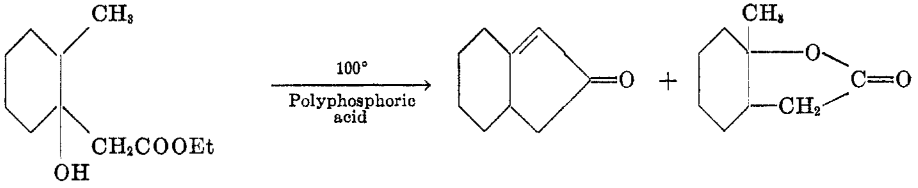
The above alkylation-acylation reaction was extended to 1,3-dimethoxybenzene. A product was obtained which had a b.p. of 160–165°/0.4 mm., which is in the range expected. However, the structure of this product cannot be analogous to structure II or III. No keto group was present as indicated by the absence of any carbonyl band in the infrared absorption spectrum and by the failure of the product to form an oxime, semicarbazone, or 2,4-dinitrophenylhydrazone. The aromatic ring was present as indicated by the infrared absorption at 6.24 μ and 6.65 μ. There was some indication of the presence of a double bond, both from the spectrum and from the fact that the product rapidly reduced 2 % aqueous potassium permanganate in contrast to II which was oxidized only at a very slow rate. The analysis (*cf.* experimental) had a lower per cent of C and H than that which would be expected for a cyclized structure. This fact coupled with the absence of a carbonyl group suggests that possibly only alkylation and not acylation took place.

Attempts to extend the reaction to hydroquinone, 4-methoxyphenol, 1,4-dimethoxybenzene, 4-bromoanisole, 2-chloro-1,4-dimethoxybenzene, and 2-methyl-1,4-dimethoxybenzene failed to yield any product distilling in the expected range.

The action of polyphosphoric acid on I by itself led to an interesting internal cyclization shown below.



I IV (18%) V (48%)

The identity of IV, bicyclo[4.3.0]non-6-ene-8-one, was demonstrated by the b.p. of 121–124°/17 mm., the m.p. of 221–223° for the semicarbazone, and the m.p. of 197–199° for the 2,4-dinitrophenylhydrazone, all of which agree with the corresponding values reported (6). Only the n_D^{20} 1.5081 varied somewhat from the reported value of n_D^{19} 1.5190 (6). The identity of IV was further confirmed in the following way. Sommer and Webster (7) prepared IV by the base-catalyzed cyclization of 2′-ketocyclopentylacetone. The semicarbazone and 2,4-dinitrophenylhydrazone prepared from each of the two samples of IV showed no depression in m.p. when mixed. IV had been originally synthesized by alkylating 2-carboethoxycyclopentanone with propargyl bromide followed by cyclization (6).

The formation of IV involves a double bond migration but otherwise resembles other internal cyclizations of lactones (8).

The identification of V as the lactone of 2-methyl-2-hydroxycyclohexane-1-acetic acid was demonstrated by the b.p. and refractive index which agreed with previously reported values (9). Compound V was also hydrolyzed to the free hydroxy acid which was identified by its neutral equivalent and m.p. (9).

It was not determined whether the lactone V was an intermediate in the formation of IV. Both IV and V are by-products in the preparation of II and III.

EXPERIMENTAL

Preparation of II *and* III. Polyphosphoric acid was prepared by heating 700 g. of phosphorus pentoxide with 400 ml. of 85% phosphoric acid for several hrs. at 100° to effect solution. A solution of 6.9 g. (0.064 mole) of anisole and 13.7 g. (0.068 mole) of ethyl 2-methyl-1-hydroxycyclohexane-1-acetate (I) in 320 g. of polyphosphoric acid was heated for 80 min. at 100°. The deep orange-red solution was hydrolyzed with ice and water and extracted with ether. The ether solution after washing with water and aqueous sodium hydrogen carbonate was dried over calcium chloride and distilled through a small fractionating column. The product (II), b.p. 155–162° (mainly 155–157°)/0.45 mm. weighed 6.7 g. (43%). The product (III), b.p. 142–160°/0.45 mm. weighed 2.9 g. (19%). The yield of residual polymer which did not distil below 180°/0.45 mm. was 1.3 g.

When the reaction was conducted at temperatures above 100°, the yield of II and III were lowered.

Product II was obtained as a viscous yellow oil which decolorized permanganate in acetone only at a very slow rate. It was analyzed as its oxime and 2,4-dinitrophenylhydrazone. The oxime was prepared by refluxing II with an excess of hydroxylamine hydrochloride in pyridine-ethanol solution for 20 hrs. Most of the solvent was removed by blowing a stream of air on the solution heated at 100°. Several recrystallizations of the precipitated solid from methanol-water gave white needles, m.p. 144–146°.

Anal. Calc'd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.15.
Found: C, 73.73; H, 8.02.

The 2,4-dinitrophenylhydrazone was prepared by treating a solution of II in ethanol with a solution of 2,4-dinitrophenylhydrazine in 80% sulfuric acid. It was obtained in 90% yield as an orange powder, m.p. 165° (sintered)–186–189°. It exhibited an unusual m.p. behavior on recrystallization from ethyl acetate. The first recrystallization raised the m.p. to 194.5–197°, but two further recrystallizations gave orange crystals, m.p. 185–187°. At least two crystalline forms are involved. During the observation of the m.p., the orange crystals change to red crystals before melting.

Anal. Calc'd for $C_{22}H_{24}N_4O_5$: C, 61.15; H, 5.85.
Found: C, 61.12; H, 5.84.

Product III was also a viscous yellow oil. It formed a 2,4-dinitrophenylhydrazone, m.p. 98–171°, in 95% yield. Several recrystallizations from ethyl acetate gave small yellow crystals, m.p. 176–178°.

Anal. Calc'd for $C_{22}H_{24}N_4O_5$: C, 61.15; H, 5.85.
Found: C, 61.30; H, 5.80.

The low m.p. of the crude 2,4-dinitrophenylhydrazone of III indicates that III was not a pure isomer.

2-Methoxyphenanthrene from II. A solution of 0.617 g. of II in ether was reduced with excess lithium aluminum hydride. The reaction mixture was hydrolyzed and ether-extracted. After removal of the ether, the residual oil was heated for 2½ hrs. with 0.4 g. of 10% palladium on charcoal at 250–325°. After cooling, the reaction mixture was dissolved in acetone and the catalyst was removed by filtration. Evaporation of the acetone left 0.389 g. of oil which partially crystallized when triturated with pentane to give 0.070 g. (13%) of white crystals, m.p. 60–78°. Two recrystallizations from ethanol-water gave white leaflets. The m.p., 95–96.5°, is in substantial agreement with the m.p. of 100–101° reported for pure 2-methoxyphenanthrene (10). The *picrate* was also prepared. It melted at 121–122.5°, reported 124–125° (10).

When III was similarly treated, the oil produced after dehydrogenation would not crystallize on seeding with 2-methoxyphenanthrene.

Reaction of I *with 1,3-dimethoxybenzene.* The reaction and isolation of products was conducted in a manner identical to that used in the preparation of compounds II and III. The yield of product, b.p. 160–165°/0.4 mm., was 3.9 g. from 10.5 g. (0.076 mole) of 1,3-dimethoxybenzene and 16 g. (0.08 mole) of I. The product failed to form a 2,4-dinitrophenylhydrazone, semicarbazone, or oxime and instantly decolorized permanganate in aqueous acetone.

The yield of product was considerably increased by using polyphosphoric acid made from 620 g. of phosphorus pentoxide per 400 ml. of 85% phosphoric acid, a reaction time of eight hrs., and stirring throughout the reaction time. Under these conditions 14.2 g. of product, b.p. 160–168°/0.4 mm., was obtained from 20 g. of 1,3-dimethoxybenzene and 31 g. of I. This product appeared to be identical to that obtained under the other reaction conditions.

Anal. Found: C, 70.28; H, 7.88.

The above analysis has too low a percentage of C and H for any reasonable cyclized structure. Coupled with the absence of a carbonyl group, it is suspected that I alkylated 1,3-dimethoxybenzene and then possibly one of the methoxy groups was hydrolyzed. The analysis calculated for this speculation is C, 70.6, and H, 8.5.

Internal cyclization of I *to* IV *and* V. A solution of 50 g. of I in 750 g. of polyphosphoric acid (same composition as used in the preparation of II and III) was heated at 100° for three hrs. The solution was hydrolyzed with ice and water and extracted four times with ether. The ether extract was washed with water and 5% aqueous sodium carbonate. The ether solution was dried over calcium chloride and distilled through a small fractionating column. The product boiling at 113–128°/17 mm. (6.4 g., 18%) was mainly IV although it was refractionated to get purer samples, b.p. 121–124°/17 mm. The product boiling at 134–136°/17 mm. was V (18.4 g., 48%).

SUMMARY

Ethyl 2-methyl-1-hydroxycyclohexane-1-acetate (I) in the presence of polyphosphoric acid reacts internally to give the lactone (V) and a cyclopentenone derivative (IV). When anisole is also present, alkylation and acylation of the anisole take place to yield a phenanthrene derivative (II) in 43% yield and an isomeric compound (III) in 19% yield which may also be a derivative of phenanthrene. The ready availability of the starting materials makes this an attractive synthetic method. Attempts to extend this reaction to several other methoxybenzenes were unsuccessful with the possible exception of 1,3-dimethoxybenzene. In this case the structure of the product is not yet established.

State College, Penna.

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