[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Diels–Alder Reactions of 9-Substituted Anthracenes.[1] IV. 9-Nitroanthracene and 9-Anthramide

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9-Nitroanthracene gave both possible adducts with acrylic acid, acrylyl chloride, acrylonitrile and acrylamide in the Diels–Alder reaction. With the first two the non-vicinal 9-nitro-11-substituted-9,10-dihydro-9,10-ethanoanthracene predominated. With allyl alcohol and methyl acrylate only one adduct was isolated and in each case it was the non-vicinal isomer. 9-Anthramide when heated with acrylic acid gave mainly 9,10-dihydro-9,10-ethanoanthracene-9,12-dicarboximide and some 9-carboxamido-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid. With allyl alcohol 9-anthramide gave 12-methylol-9,10-dihydro-9,10-ethanoanthracene-9-carboxylic acid lactone as the major product along with some non-vicinal adduct.

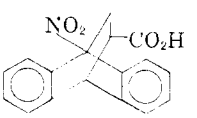
The condensation of 9-anthraldehyde with various monosubstituted ethylenes as dienophiles in the Diels–Alder reaction gave only vicinally substituted adducts,[2] while 9-cyanoanthracene[3] and the methyl acetal of 9-anthraldehyde[4] gave in some cases both the vicinal and non-vicinal adducts. In only one case did the non-vicinal 9,11-disubstituted-9,10-dihydro-9,10-ethanoanthracene predominate over the vicinal 9,12-disubstituted adduct. 9-Anthroic acid and acrylic acid as well as their salts have been reported to give only the non-vicinal or *meta* type adduct.[5] The isolation of non-vicinally substituted adducts is quite rare and no 1-substituted aliphatic diene such as piperylene,[6] 1-phenyl-,[7] 1-*p*-nitrophenyl-,[8] 1-acetoxy-[9] and 1-cyanobutadiene[10] or 2,4-pentadienoic acid[11] has been found to give with a monosubstituted ethylene a 3,5-disubstituted cyclohexene as the major adduct.

In the work reported here an exception to this general rule is 9-nitroanthracene. It was studied with the six monosubstituted ethylenes and with four of these the major or only product was the non-vicinal adduct.

With 9-nitroanthracene acrylic acid, acrylyl chloride, acrylamide and acrylonitrile gave both possible 9,10-ethanoanthracenes but with methyl acrylate and allyl alcohol only one adduct was isolated.

9-Anthramide was not as reactive a diene as the nitro analog and the ordinary vicinal type condensation predominated with acrylic acid and allyl alcohol.

The two acrylic acid adducts of 9-nitroanthracene melted at 225 and 268°. The relative amounts were quite variable but the lower melting isomer predominated in all our runs. The acrylonitrile adducts were hydrated to amides and the lower melting nitrile gave the higher melting acid and amide. The acrylyl chloride adducts could not be separated and were solvolyzed with formic acid to give a mixture in which the 225° acid predominated. The pure acid chlorides were prepared from the separated acids and the lower melting acid chloride was obtained from the lower melting acid. In turn the lower melting acid chloride gave the lower melting amide which was the predominate product of 9-nitroanthracene and acrylamide in acetone but not in xylene. The lower melting acid was obtained by hydrolyzing the methyl acrylate adduct and by oxidizing the allyl alcohol–9-nitroanthracene adduct. In this way a major lower melting and a minor higher melting series were established, but efforts to find which series had substituents in the 11 I or 12 II position failed until the study of 9-anthramide was undertaken.



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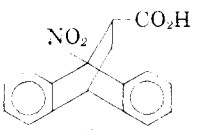

II

9-Anthramide upon heating with acrylic acid gave two products. The major one was insoluble in sodium bicarbonate but was soluble in sodium hydroxide, while the other was soluble in both. The major product was identified as the imide resulting from the vicinal adduct losing water at the high temperature required for the Diels–Alder reaction. It gave the known 9,12-dicarboxylic acid on hydrolysis.[3] The minor product was identified as 9-carboxamido-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid by its hydrolysis to the previously reported 9,11-dicarboxylic acid.[3,5] The amide-acid was degraded to an amino acid and an amino acid was prepared by reducing the lower melting adduct of 9-nitroanthracene and acrylic acid. Both decomposed about 245° with no observable difference when mixed. Each gave the same methyl ester which melted without decomposition. This established the major series as 9-nitro-11-substituted adducts.

9-Anthramide when condensed with allyl alcohol at 170–175° gave two products of which the major one was the known 12-methylol-9,10-ethanoanthracene-9(10H)-carboxylic acid lactone.[3] The other was identified by heating with acetic anhydride which gave the previously prepared 9-cyano-9,10 - dihydro - 9,10 - ethanoanthracene - 12-methanol acetate.[3]

The lactone may have been formed by solvolysis of 9-anthramide to give allyl 9-anthroate which then underwent an intramolecular Diels–Alder

(1) This work was supported by the Office of Naval Research.

(2) J. S. Meek, B. T. Poon and S. J. Cristol, THIS JOURNAL, **74**, 761 (1952).

(3) J. S. Meek, J. R. Dann and B. T. Poon, *ibid.*, **78**, 5413 (1956).

(4) J. S. Meek and J. R. Dann, *J. Org. Chem.*, **21**, 968 (1956).

(5) K. Alder and K. Heimbach, *Chem. Ber.*, **86**, 1312 (1953).

(6) J. S. Meek, J. W. Ragsdale, THIS JOURNAL, **70**, 2502 (1948).

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(9) K. Alder and M. Schumacher, *Ann.*, **565**, 148 (1949).

(10) H. R. Snyder and G. I. Poos, THIS JOURNAL, **72**, 4104 (1950).

(11) K. Alder, M. Schumacher and O. Wolff, *Ann.*, **564**, 79 (1949).

reaction. More likely the latter reaction occurred first and the adduct then lost ammonia to give the lactone. If the solvolysis was rapid in comparison with the diene synthesis, then only the lactone would have been isolated. However, the formation of the non-vicinal adduct showed solvolysis did not predominate and the two-to-one ratio of products was typical of ordinary Diels–Alder reactions involving 9-substituted anthracenes.

The nitro group in 9-nitroanthracene is reported to be in a plane almost perpendicular to the anthracene ring.[12] This of course would give some hindrance to vicinal adduct formation, but the hindrance from a nitro group should be less than a carboxamido group where vicinal adducts predominate. Again the cyano group being linear should give less hindrance than the aldehyde group, but 9-cyanoanthracene gives some non-vicinal adducts whereas so far none have been found for 9-anthraldehyde. Thus it appears that the negative group in the 9-position of anthracene plays an important role in determining which of two isomeric adducts will predominate.

The more negative is the group, the more likely it is that the non-vicinal adduct will form. The negativity of the substituent on the dienophile seems unimportant as the results with allyl alcohol and acrylic acid are equivalent with the same 9-substituted anthracene. The picture is partially obscured by temperature and solvent effects.

Experimental

9-Nitroanthracene.—Modified methods of Dimroth[13] and Barnett, Cook and Matthews[14] were used to prepare 9-nitroanthracene. The intermediate nitrodihydroanthranyl chloride melted at 170–171°, reported[13] 163°.

9-Nitroanthracene and Acrylic Acid.—Ten grams (0.045 mole) of 9-nitroanthracene, 6.3 g. (0.088 mole) of glacial acrylic acid, a trace of hydroquinone and 15 ml. of xylene were heated in a sealed tube at 150–160° for 20 hours. On cooling and removal from the tube, the xylene mixture was extracted with four 100-ml. portions of 5% potassium hydroxide solution. No unreacted 9-nitroanthracene was recovered from the separated xylene layer. The combined alkaline extracts were washed with three 50-ml. portions of benzene. The acid adduct mixture precipitated on acidification of the aqueous layer with 20% hydrochloric acid. It was filtered, washed with 50 ml. of water and 12.3 g. (93%) of white product was recovered, which darkened at 200°, and melted at 203–208°. Temperatures of 185–190° gave a 47% yield which was almost entirely the lower melting adduct. Anthraquinone and 9-nitroanthracene were found at the end of 20-hour runs at the higher temperature.

The crude material was dissolved in hot benzene and by slow evaporation of the solvent at room temperature two distinct crystalline forms were observed. The crystals were separated manually after decantation of the supernatant liquid. The lower melting isomer, 224–225°, consisted of large translucent prisms whereas the higher melting form, 267–268°, existed as small prisms. Both forms dissolved in benzene only after prolonged boiling of the solvent, with the higher melting isomer the more insoluble of the two. Xylene and acetonitrile proved to be effective recrystallization solvents. From acetonitrile, the lower melting isomer separated as very large, orthorhombic-type crystals in contrast to the observed twinned, elongated prismatic forms of the higher melting component.

Each isomeric adduct gave a correct neutralization equivalent. Mixed melting points of the two showed marked depressions.

Isomer, m.p. 225° (9-nitro-11-carboxylic acid). *Anal.* Calcd.: C, 69.15; H, 4.44; N, 4.74; neut. equiv., 295. Found: C, 69.30; H, 4.44; N, 4.85; neut. equiv., 296.

Isomer, m.p. 267–268° (9-nitro-12-carboxylic acid). *Anal.* Found: C, 69.39; H, 4.44; N, 4.86; neut. equiv., 295.

Each acid adduct was refluxed with an excess of thionyl chloride for 45 minutes. The remaining thionyl chloride was removed by evaporation under reduced pressure leaving solid acid chlorides. They were found to be readily soluble in dry benzene and carbon tetrachloride, slightly soluble in cyclohexane, and difficultly soluble in petroleum ether (30–60°) and *n*-hexane. After recrystallizations from cyclohexane the chloride of the low melting acid adduct was obtained in 94% yield, m.p. 109–109.5°. A similar derivative of the higher melting isomeric acid melted at 145–146° (90%).

Anal. (Isomer, m.p. 109–109.5° 11-acid chloride) Calcd. for $C_{17}H_{12}ClNO_3$: C, 65.08; H, 3.86. Found: C, 65.10; H, 3.87. (Isomer, m.p. 146° 12-acid chloride) Found: C, 64.98; H, 3.72.

Each acid chloride was converted to the amide by first dissolution in dry benzene and then saturation of the solution with dry ammonia gas over a period of one hour. Decantation of the heated benzene and extraction of the ammonium chloride gave the results: (a) acid chloride, m.p. 109°, yielded an amide, m.p. 230–231° (74%); (b) acid chloride, m.p. 146°, gave an amide derivative, m.p. 246–247° (73%).

9-Nitroanthracene and Acrylamide.—Of the procedures that were tried, the best yield of adduct was obtained when two grams (0.009 mole) of 9-nitroanthracene, 0.72 g. (0.01 mole) of acrylamide, a trace of hydroquinone and 10 ml. of xylene were heated in a sealed tube at 160–170° for 48 hours. The xylene solution was evaporated to dryness by means of a jet of compressed air and the residue was dissolved in hot benzene. Unreacted acrylamide selectively precipitated on cooling and slow evaporation of the solution, and thus allowed for facile recovery by filtration. The dienophile could also be effectively removed from the other constituents of the mixture by washing the benzene extract with water. Removal of the solvent from the benzene layer, dissolution of the remaining contents in hot methanol and gradual evaporation of the alcoholic solution resulted in the precipitation of orange, rod-shaped 9-nitroanthracene crystals and colorless prisms of adduct. These substances were mechanically separated after decanting the solvent.

Contrasting geometric crystal forms permitted the isolation of isomeric acrylamide adducts. A nearly quantitative manual separation of the two amides could be made after allowing a methanolic solution of the adduct mixture to slowly evaporate to dryness at room temperature. The one isomer, m.p. 230–231°, had very sharp cleavage planes and appeared to have characteristics common to triclinic crystallographic forms. The higher melting amide, 247–248°, consisted of tabular, diamond-shaped crystals with radial streaks as a distinguishing feature. This particular form had a tendency to clump readily and exist as aggregates. Mixed melting points of the two adducts with similarly melting amide derivatives obtained from the acrylic acid adducts gave no depression. The combined crude yield was 39% and the ratio of low melting to high melting amide was 0.6.

Anal. (Isomer, m.p. 231°, 11-carboxamido) Calcd. for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.50; H, 4.85; N, 9.61. (Isomer, m.p. 248°, 12-carboxamido) Found: C, 69.50; H, 4.88; N, 9.52.

9-Nitroanthracene and Acrylyl Chloride.—A mixture of 3.0 g. (0.013 mole) of nitroanthracene, 12 ml. of freshly distilled acrylyl chloride and a trace of hydroquinone was heated in a sealed tube at 135–140° for 24 hours. The excess acrylyl chloride was distilled from the moderately fluorescent reaction mixture. Fruitless attempts were made to isolate the crystalline acid chloride adducts by successive treatments of the residual viscous material with dry benzene and cyclohexane.

Thirty milliliters of formic acid (Matheson 98–100%) and the above crude adduct mixture dissolved in 20 ml. of isopropyl ether were heated at 70–80° for one hour with stirring. After cooling, the contents were extracted with three 15-ml. portions of 5% sodium hydroxide solution. The combined alkaline extracts after separation from the ether layer were acidified with dilute hydrochloric acid. The

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(13) O. Dimroth, *Ber.*, **34**, 219 (1901).

(14) E. Barnett, J. W. Cook and M. A. Matthews, *J. Chem. Soc.*, **123**, 1994 (1923).

white, acidic material which precipitated was filtered, dried and amounted to 3.1 g. (78%), m.p. 200–210°.

The isomeric acids of this mixture were isolated by using the more or less irregular fractional crystallization technique previously described for the separation of 9-nitroanthracene–acrylic acid adducts. The following fractions represent a 67% recovery of hydrolyzed product from the condensation of 9-nitroanthracene and acrylyl chloride: (a) low melting acid, 224–225°, 2.05 g.; (b) high melting acid, 267–268°, 0.37 g.; (c) unidentified fraction, presumably a mixture of the two isomers, m.p. 203–210°, 0.24 g.

9-Nitroanthracene and Methyl Acrylate.—One and a half grams (0.0067 mole) of 9-nitroanthracene, 11.6 g. (0.14 mole) of methyl acrylate and a trace of hydroquinone were heated in a sealed tube at 135–140° for 24 hours. The reaction mixture was exposed to a jet of compressed air to remove the excess and unreacted volatile dienophile. The remaining viscous substance was dissolved in 50 ml. of hot methanol and by cooling the alcoholic solution in an ice-water-bath a light-colored material precipitated. The crude product was filtered and amounted to 1.2 g. (60%), m.p. 100–105°. Recrystallization from methanol resulted in the formation of colorless prisms of ester adduct and small, orange crystals of 9-nitroanthracene. The two components were separated by manual means; 0.7 g. (35%) of ester adduct was recovered, m.p. 111.5–112.5°, as well as 0.07 g. of unreacted diene.

Anal. Calcd. for $C_{18}H_{15}NO_4$: C, 69.90; H, 4.88. Found: C, 70.05; H, 5.07.

One hundred and fifty-five milligrams of ester upon methanolic saponification gave 137 mg. of acid, m.p. 224–225° (97%). A mixed melting point with the similar melting acrylic acid adduct isomer gave no depression.

9-Nitroanthracene and Acrylonitrile.—By similar methods to the cases above, 1.5 g. of 9-nitroanthracene and 2 g. of acrylonitrile gave 0.312 g. of prisms, m.p. 175–176°, and 0.398 g. of needles, m.p. 159–160°, by recrystallizing 1.5 g. of crude product, m.p. 112–134°.

Anal. (Isomer, m.p. 176°, 11-cyano) Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38. Found: C, 74.12; H, 4.44. (Isomer, m.p. 160°, 12-cyano) Found: C, 73.79; H, 4.43.

Treatment of 100 mg. of the 176° nitrile with concentrated sulfuric acid and then ice led to 25 mg. of the 229° amide. When the same amount of the nitrile was heated in methanolic potassium hydroxide for 40 hours 40 mg. of the same amide was obtained on cooling. Acidification gave 54 mg. of the 11-carboxylic acid, m.p. 224–225°, which was the same as isolated previously from other sources.

Methanolic potassium hydroxide treatment of the 160° nitrile in a similar fashion gave 50 mg. (47%) of amide, m.p. 247–248° and 40 mg. of unchanged nitrile was recovered. Only a trace of acidic material was found and this indicated a more hindered nitrile. By the use of ethylene glycol as a solvent in place of methanol, 0.1 g. of nitrile gave 65 mg. (61%) of acid, m.p. 267–268°, which was identical to the high melting adduct of acrylic acid.

9-Nitroanthracene and Allyl Alcohol.—From 1.5 g. of 9-nitroanthracene and 7.8 g. of allyl alcohol which had been heated for 20 hours in a sealed tube at 190–195° there was obtained 0.157 g. of nearly white material, m.p. 151–153°. Crystallization from petroleum ether gave 0.11 g. (6%), m.p. 159–161°.

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.79; H, 5.54; N, 4.92.

Sixty milligrams of the alcohol was treated with sodium bromate in glacial acetic acid for three weeks at room temperature. Work up of the mixture gave 17 mg. (19%) of acid, m.p. 224–225°, and a mixed melting point with the low melting acrylic acid adduct was not depressed.

9-Anthramide.—A mixture of 9.7 g. of 9-cyanoanthracene,[15] 8.5 g. of potassium hydroxide dissolved in 5 ml. of water and 37 ml. of methyl Cellosolve was refluxed for 4 hours. Diluting with water gave 9.7 g. (92%) of 9-anthramide, m.p. 217–219°, reported[16] 215–216°.

9-Anthramide and Acrylic Acid.—A mixture of 14.5 g. of 9-anthramide and 14 g. of acrylic acid were heated with a trace of hydroquinone for 3 hours under a reflux condenser at 125–130°. Cooling gave a dark viscous sirup. Upon warming for 10 minutes in 25 ml. of 20% sodium hydroxide it dissolved. Acidification with hydrochloric acid gave a white viscous oil which was partially soluble in 5% sodium bicarbonate solution. The soluble portion was crystallized from ether and gave 1.69 g. of white crystals, m.p. 254–255°. The crystals seemed to retain solvent and swelled without melting when heated between 120–150° and an indifferent analysis was obtained.

Anal. Calcd. for $C_{18}H_{15}NO_3$: C, 73.70; H, 5.15. Found: C, 73.01; H, 5.36.

The compound was identified as 9-carboxamido-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid by saponification to give 9,10-dihydro-9,10-ethanoanthracene-9,11-dicarboxylic acid. A mixed melting point with a previously prepared sample[3] was not depressed and melted at 268–270°.

The sodium bicarbonate-insoluble material weighed 2.90 g. and melted at 210–211° after crystallization from ethanol.

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.13; H, 5.05; N, 4.88.

From this analysis and from the fact that saponification led to the known 9,10-dihydro-9,10-ethanoanthracene-9,11-dicarboxylic acid[3,5] the compound was identified as the half amide of this acid.

9-Hydroxylamino-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid.—Catalytic reduction in glacial acetic acid with Adams catalyst of the 9-nitro-11-carboxylic acid, m. p. 225°, resulted in 80% of the theoretical amount of hydrogen being absorbed when hydrogenation ceased after 15 hr. After removal of catalyst and solvent the residual oil was dissolved in hot benzene. A flocculent precipitate formed on cooling and was found to sinter at 155° and melt at 160–165°.

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.31; H, 5.91; N, 5.11.

9-Hydroxylamino-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic Acid.—Attempted reductions of the higher melting acrylic acid adduct isomer with Adams catalyst under similar conditions were ineffective. No hydrogen uptake was observed when methanol was used as the solvent. Glacial acetic acid was unsuitable due to the insolubility of the compound in this solvent at room temperature.

The catalytic reduction of the potassium salt of the acid with Raney nickel was found to be a satisfactory method for reducing the nitro group to the hydroxylamine. One-half gram (0.0017 mole) of adduct was treated with an alkaline solution of 0.2 g. potassium hydroxide in 15 ml. of water and approximately 0.1 g. of Raney nickel (wet) was added to the mixture. Reduction was carried out in an atmosphere of hydrogen at room temperature and pressure. After about an hour and a half the theoretical amount of hydrogen had been absorbed and there was no more uptake after an additional two hours. The catalyst was filtered and a white precipitate formed on neutralizing the alkaline solution; 0.43 g. of material was recovered on filtration, m.p. 203–207°. Recrystallization from water gave 0.37 g. (78%) of the hydroxylamino acid, m.p. 208–210°. Neither hydroxylamino compound appeared to cyclize on heating above its melting point.

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.69; H, 5.49; N, 5.02.

9-Amino-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid.—The catalytic reduction of the potassium salt of the low melting acrylic acid adduct with Raney nickel afforded a convenient means of reducing the nitro group to the amino group. It is noteworthy that under similar reduction conditions this isomer can be reduced to the amino acid whereas the higher melting isomeric acid is selectively reduced to the hydroxylamino acid.

Using like quantities of materials the theoretical amount of hydrogen was absorbed after about 10 hours. The catalyst was removed by filtration and a white precipitate formed on adjusting the *p*H of the alkaline filtrate to 4.5–5.5 with 20% hydrochloric acid. The material after filtering and drying amounted to 0.43 g. (96%), m.p. 153–157°. It was observed in recrystallizations from water that if the ratio of solvent to compound were relatively large, rectangular plates were formed, m.p. 153–158°, which on further heating solidified to give a product, m.p. 245–246°. When a

(15) L. F. Fieser and J. L. Hartwell, THIS JOURNAL, **60**, 2555 (1938).

(16) E. L. May and E. Mosettig, *ibid.*, **70**, 1077 (1948).

limited amount of water was used, tiny crystals precipitated, m.p. 245–247°. It seemed likely that the lower melting form probably constituted the hydrated amino acid.

Purification attempts by means of copper salt formation were unsuccessful. Treatment of the acid with a dilute ferric chloride solution failed to give a red coloration characteristic of some amino acids.

Evidently the water of crystallization was held very tenaciously by the amino acid since the melting point of the material, 153–158°, was not altered after drying in the Abderhalden apparatus over phosphoric anhydride or under vacuum at the reflux temperature of *n*-butyl acetate for 2.5 days. Approximately the theoretical loss of one molecule of hydration was observed upon heating a small amount of the material in an oil-bath maintained at 175–180° for 25 minutes. The resulting dehydrated product, m.p. 247–248°, was analyzed.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.72; H, 5.82; N, 5.48.

By the use of bromine and sodium hydroxide 0.291 g. of 9-carboxamido-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid, m.p. 255–256°, was degraded to 0.231 g. of crude amino acid, m.p. 220–250° dec. Upon recrystallization from water the material decomposed at 240–245° and its decomposition point was not depressed when mixed with the amino acid prepared from the nitro acid. Both amino acids when treated with acetic anhydride gave a derivative soluble in 2.5% sodium hydroxide and insoluble in hydrochloric acid, m.p. 285–289°. No observable depression of the decomposition point was observed when they were mixed and further investigation was not undertaken.

Thirty-two milligrams of the amino acid from the Hofmann degradation was esterified with methanol acidified with sulfuric acid and gave 14.7 mg. of product from 170 mg. of starting material, m.p. 133–135° (39%). Recrystallization from methanol raised the melting point to 137–139°. Reduction of the adduct of 9-nitroanthracene and methyl acrylate gave the same amino ester and mixed melting points were not depressed.

Anal. Calcd. for $C_{18}H_{17}NO_2$: N, 5.00. Found: N, 4.95.

9-Anthramide and Allyl Alcohol.—From 6.3 g. of 9-anthramide and 30 g. of allyl alcohol which had been heated in a sealed tube at 170–175° for 17 hours was isolated 3.24 g. of material, m.p. 222–224° (40%), and 1.7 g., m.p. 146–147° (22%). A mixed melting point with 9,10-dihydro-9,10-ethano-12-methylol-9-carboxylic acid lactone[3] with the higher melting product gave no depression.

The lower melting product gave a poor analysis and was converted into material melting at 118–119° when refluxed with acetic anhydride. A mixed melting point with authentic 9-cyano-9,10-dihydro-9,10-ethanoanthracene-11-methanol acetate was 121–121.5°.

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BOULDER, COLO.

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

Steroidal Hormone Analogs. VI. Synthesis of 3'-Acetyl-1',2':1,2-cyclopentano-1,2,3,4-tetrahydro-6-methoxynaphthalene[1]

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The preparation and determination of the configuration at the ring junction of an isomer of 3'-acetyl-1',2':1,2-cyclopentano-1,2,3,4-tetrahydro-6-methoxynaphthalene (VIII) is described. Conversion of VIII to 3'-oxo-1',2':1,2-cyclopentano-1,2,3,4-tetrahydro-6-methoxynaphthalene (Xa) (*cf.* 1-hydrindanone) was carried out under conditions which should not affect the ring junction, and equilibration of this material resulted in recovery of unchanged starting material. In view of the fact that *cis*-1-hydrindanone is more stable than *trans*-1-hydrindanone, the equilibration studies suggest that Xa and consequently VIII probably have the *cis* configuration at the ring junction.

In a previous paper[5] we reported the total synthesis of *dl*-18,19-dinorprogesterone[6] utilizing a tricyclic starting material representing the A, B and C rings of the final product. At the time the work was being carried out we were also investigating an approach to 18,19-dinorprogesterone involving the synthesis of a tricyclic intermediate representing the B, C and D rings to which ring A could be attached.[7] The present paper reports this work. The preparation of an isomer of 3'-acetyl-1',2':1,2-cyclopentano-1,2,3,4-tetrahydro-6-methoxynaphthalene (VIII) is described together with studies of the stereochemistry of its ring fusion. The five-membered ring of VIII was elaborated by methods similar to those described previously.[5,8]

Alkylation of 2-hydroxymethylene-6-methoxy-1-tetralone (I)[9] with sodium hydride and methallyl iodide in dimethylformamide solution[5] gave 74% of 2-methallyl-6-methoxy-1-tetralone (II). When the direct alkylation of 6-methoxy-1-tetra-

(1) Abstracted in part from the thesis of J. C. Wollensak, submitted to the Massachusetts Institute of Technology, 1958, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and from the theses of J. B. Hester, Jr. (1955), R. L. Foltz (1956) and J. I. Brauman (1959) submitted in partial fulfillment of the requirements for the degree of Bachelor of Science.

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(5) N. A. Nelson and R. B. Garland, THIS JOURNAL, **79**, 6313 (1957).

(6) Two reports have since appeared on the preparation of *d*-18,19-dinorprogesterone; see W. F. Johns, *ibid.*, **80**, 6456 (1958), and G. Stork, H. N. Khastgir and A. J. Solo, *ibid.*, **80**, 6457 (1958).

(7) Methods by which ring A could be attached have already been described; see, for example, G. Stork, H. J. E. Loewenthal and P. C. Mukharji, *ibid.*, **78**, 501 (1956), and L. J. Chinn and H. L. Dryden, Jr., Abstracts of Papers presented at the Chicago Meeting of the American Chemical Society, September 7–12, 1958, p. 14-O.

(8) (a) L. H. Sarett, W. F. Johns, R. E. Beyler, R. M. Lukes, G. I. Poos and G. E. Arth, THIS JOURNAL, **75**, 2112 (1953); (b) G. E. Arth, G. I. Poos, R. M. Lukes, F. M. Robinson, W. F. Johns, M. Feurer and L. H. Sarett, *ibid.*, **76**, 1715 (1954); (c) W. F. Johns, R. M. Lukes and L. H. Sarett, *ibid.*, **76**, 5026 (1954).

(9) D. K. Banerjee, S. Chatterjee, C. N. Pillai and M. V. Bhatt, *ibid.*, **78**, 3769 (1956).