Ethyl 2,4,5,6,7,8-hexahydroindene-2-one-8-carboxylate (IX). Potassium (12.0 g., 0.31 g.-atom) was dissolved in 500 ml. of dry *t*-butyl alcohol by heating under reflux. When the solution had cooled to room temperature, 60.7 g. (0.269 mole) of VII was added in one portion. A mild exothermic reaction ensued and a yellow precipitate formed. After standing for 25 min., the reaction mixture was poured into 500 ml. of ice water followed by the rapid addition of 26 ml. of concd. hydrochloric acid. After saturating the solution with sodium chloride, the organic layer was removed and the aqueous solution extracted four times with ether. The combined organic phases were dried, the solvent removed, and the residue distilled. The lower boiling fraction was 2,4,5,6,7,8-hexahydroindene-2-one (X), yield 2.8 g. (8%), b.p. 91–93° (2.8 mm.), n_D^{25} 1.5169, $\lambda_{max}^{C_2H_5OH}$ 230 mμ (ϵ 15,600 [lit.[16] b.p. 88° (4 mm.), n_D^{19} 1.5190, $\lambda_{max}^{C_2H_5OH}$ 228 mμ (ϵ 16,500)]. The semicarbazone was prepared and recrystallized from ethanol–carbon tetrachloride, m.p. 207.7–207.8° dec.

Anal. Calcd. for $C_{10}H_{15}N_3O$ (193.24): C, 62.15; H, 7.81; N, 21.75. Found: C, 62.47; H, 7.53; N, 22.08.

The higher boiling fraction was the desired IX, yield 21.8 g. (39%), b.p. 132–133° (2.8 mm.), n_D^{25} 1.5020, $\lambda_{max}^{C_2H_5OH}$ 230 mμ (ϵ 12,300). The semicarbazone was prepared and it was recrystallized from ethanol–carbon tetrachloride, m.p. 202.6–202.8° dec.

Anal. Calcd. for $C_{13}H_{19}N_3O_3$ (265.29): C, 58.85; H, 7.22; N, 15.84. Found: C, 59.02; H, 7.37; N, 16.08.

Ethyl cis-hexahydroindane-2-one-8-carboxylate. A solution of 13.5 g. (0.065 mole) of IX in 100 ml. of ethanol was hydrogenated over 0.5 g. of palladium-charcoal catalyst at 45 p.s.i. After 1 mole equivalent of hydrogen had been absorbed, the mixture was filtered, the filtrate concentrated and the residual oil distilled, b.p. 127–129° (2.8 mm.), n_D^{25} 1.4770, yield 12.7 g. (93%).

Anal. Calcd. for $C_{13}H_{18}O_3$ (210.26): C, 68.54; H, 8.63. Found: C, 68.39; H, 8.77.

The thiosemicarbazone was prepared by heating for 1 hr. a solution of 240 mg. (1.14 mmoles) of the ketone, 110 g. of thiosemicarbazide in 5 ml. of 70% ethanol. Upon cooling, there crystallized 320 mg. (98%) of product, m.p. 149–151°. Recrystallization from aqueous ethanol gave material with a m.p. of 150–151°.

Anal. Calcd. for $C_{13}H_{21}O_2N_3S$ (283.39): C, 55.08; H, 7.47; N, 14.83; S, 11.32. Found: C, 55.26; H, 7.33; N, 14.98; S, 11.42.

Similar results were obtained when the hydrogenation was conducted in methanol containing 1*N* hydrochloric acid, in 5% acetic acid in ethanol or in 0.2*N* ethanolic potassium hydroxide.

cis-Hexahydroindane-8-carboxylic acid (IV). A solution of the above ethyl *cis*-hexahydroindane-2-one-8-carboxylate (37.7 g., 0.179 mole), 36 g. of potassium hydroxide, 15 ml. of 85% hydrazine hydrate, and 250 ml. of diethylene glycol was heated at 190° under reflux for 1 hr. The excess hydrazine and water were distilled, the internal temperature raised to 210° and the heating continued for an additional 8 hr. The reaction solution was poured into 800 ml. of water and the basic solution extracted four times with ether. The combined extracts were dried and upon evaporation of the solvent an insignificant amount of material was obtained. The aqueous alkaline solution was then acidified with hydrochloric acid and extracted four times with ether. The combined extracts were dried, the solvent removed, and the residual oil upon cooling solidified, yield 29.2 g. (97%), m.p. 38–40°. Recrystallization from aqueous acetic acid yielded material with m.p. 43.5–44.5° (lit.[5] m.p. 43.5-45.5°, 49°).

Anal. Calcd. for $C_{10}H_{16}O_2$ (168.23): C, 71.40; H, 9.59. Found: C, 70.80; H, 9.36; neut. equiv., 168.2.

The acid was converted to the amide as described previously, m.p. 111–112°, mixed m.p. with authentic amide, 110–112°. In a similar fashion the *p*-promoanilide was prepared, m.p. 161–162°, mixed m.p. with authentic sample, m.p. 160–162°.

Diethyl α-acetonylpimelate (VIII). (*a*) *From ethyl α-acetonylcyclohexane-1-one-2-carboxylate* (VII). A solution of 2.80 g. (12.4 mmoles) of VII, 1.26 g. of sodium ethoxide and 60 ml. of anhydrous ethanol was heated under reflux for 24 hr. Water (125 ml.) was added, the mixture saturated with ammonium chloride, and then it was extracted several times with ether. The combined extracts were processed in the usual fashion and the residual oil distilled through a short path molecular still, fraction I, block temperature up to 110° (2 mm.), yield 1.28 g., n_D^{23} 1.4540; fraction II, block temperature 110–125° (2 mm.), yield 1.05 g., n_D^{23} 1.4455. A semicarbazone was prepared from fraction I and it was recrystallized from ethanol-water, m.p. 99.0–99.7°.

Anal. Calcd. for $C_{15}H_{27}O_5N_3$ (329.39): C, 54.69; H, 8.26; N, 12.76. Found: C, 54.76; H, 8.23; N, 12.59.

(*b*) *From diethyl α-propargylpimelate* (VI). To a suspension of 0.2 g. of mercuric oxide, 0.50 g. of VI, and 2 ml. of ethanol, there was added, dropwise, 0.8 ml. of concd. sulfuric acid. The solution then was poured into water, the material processed in the usual manner and the crude product converted directly to the semicarbazone, m.p. 98.7–99.4°, upon admixture with derivative prepared above, m.p. 98.9–99.6°.

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

11,12-Dimethylene-9,10-dihydro-9,10-ethanoanthracene

JOHN S. MEEK AND RICHARD D. STACY[1]

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11,12-Dimethylene-9,10-dihydro-9,10-ethanoanthracene was synthesized and found to undergo the Diels-Alder reaction as well as free radical polymerization.

A *trans* reduction of a carbon-carbon double bond by lithium aluminum hydride was discovered in the reduction of methyl 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate to *dl*-2,3-[9,10-anthrylene]-1,4-butanediol.

It was hoped that 2-butyne-1,4-diol would yield an adduct with anthracene and that this glycol (I) on treatment with hydroiodic acid would give 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene (II). If this succeeded then a similar route with bisanthracenes was to be tried to get reactive double dienes. These would be suitable

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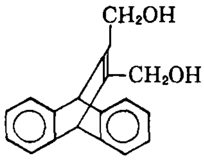
(1) Taken from part III of the Ph.D. thesis of R. D. Stacy, University of Colorado, 1957.



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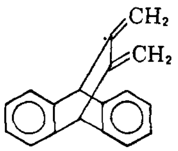
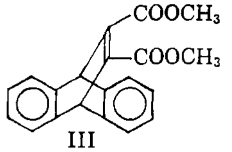


II

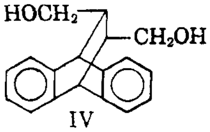
for condensation with bismaleimides in a Diels-Alder reaction to give polymeric adducts.

This simple route to compound II was abandoned when it was found that 2-butyne-1,4-diol did not condense readily with anthracene even at elevated temperatures. Almost all of the starting diol was easily recovered by extracting the reaction mixture with water. Johnson[2] was unable to condense cyclopentadiene with 2-butyne-1,4-diol and no other reference to its possible use as a dienophile seems to be reported.

The adduct[3] (III) of methyl acetylenedicarboxylate and anthracene seemed likely to give the diol I on reduction with lithium aluminum hydride. However, even the inverse addition of lithium aluminum hydride to compound III at −5° gave only a 15% yield of *dl*-2,3-[9,10-anthrylene]-1,4-butanediol (IV).



III

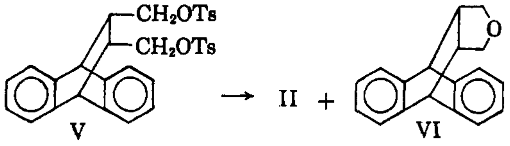


IV

Such a stereospecific ***trans*** reduction of a carbon-carbon double bond by lithium aluminum hydride does not seem to have been reported although ***trans*** reductions of acetylenic bonds to olefinic bonds are known.[4–6]

As IV is readily obtained by the reduction of the anthracene–fumaric acid adduct, it was prepared and converted into the toluenesulfonate following Walborsky's directions.[7] The *meso*-isomeric diol of IV was prepared by reducing the maleic anhydride anthracene adduct[7] and also condensing *cis*-2-butene-1,4-diol with anthracene.[8] The *meso* diol was converted into a *p*-toluenesulfonate (V).[7]

Treatment of the *dl* *p*-toluenesulfonate with boiling ethanolic sodium hydroxide for thirteen hours gave a sticky brownish material still containing sulfur. Compound V appeared to react more readily with base and gave a mixture which was separated into the hydrocarbon (II) and an ether (VI). Presumably saponification of one ester group in compound V gave an alkoxide ion which upon an intramolecular alkylation by the remaining *p*-toluenesulfonate group gave the ether. This ether had previously been obtained by the treatment of V with lithium aluminum hydride.[7]



The hydrocarbon II was identified as 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene since hydrogenation over 10% palladium on charcoal gave the known *cis*-11,12-dimethyl-9,10-dihydro-9,10-ethanoanthracene.[7]

A *cis*-addition of hydrogen is to be expected if 1,4-addition gave 11,12-dimethyl-9,10-dihydro-9,10-ethenoanthracene as an intermediate in the reduction. If hydrogen added 1,2- and then 3,4- the same *cis*-dimethyl compound would be expected if the intermediate 11-methyl-12-methylene-9,10-dihydro-9,10-ethanoanthracene were held on the catalytic surface for further hydrogenation. If it were not, the 11-methyl group would hinder one side of the ethano bridge and addition of hydrogen would again give the *cis*-isomer found.

Ozonolysis of II gave an orange diketone which yielded a quinoxaline with *ortho*-phenylenediamine. The diketone was decolorized by hydrogen peroxide in acetic acid but upon warming a yellow color appeared and anthraquinone was isolated. An attempt to run a benzilic acid rearrangement was given up when the work of Vaughn and Yoshimine appeared[9] which reported the synthesis of the diketone by a selenium dioxide oxidation of 11-keto-9,10-dihydro-9,10-ethanoanthracene. Treatment of the diketone with base gave them 9,10-dihydroanthracene-9-glyoxylic acid instead of a methanoanthracene by the expected benzilic acid rearrangement.

The olefin II gave a free radical polymerization. The polymeric product was fractionated and the molecular weights of the various fractions ranged from dimeric to decameric material. This type of polymer should be an all *cis* one. The olefin condensed readily with maleic anhydride.

EXPERIMENTAL

Attempted condensations of 2-butyne-1,4-diol with anthracene. Fluorescent anthracene (1.78 g.) was placed in 20 ml. of xylene together with 4.3 g. of butynediol and the mixture was boiled for 43 hr. The xylene solution was cooled, extracted with water and the two solutions were evaporated separately. The water insoluble fraction weighed 1.85 g. and after crystallization from benzene–petroleum ether (b.p. 85–99°) gave 1.50 g. of fluorescent anthracene. The water soluble fraction weighed 3.60 g.

When the same quantity of reactants was heated in ben-

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(2) A. W. Johnson, *J. Chem. Soc.*, 1009, (1946).

(3) O. Diels and K. Adler, *Ann.*, **486,** 191 (1931).

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(5) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954).

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(7) H. M. Walborsky, *Helv. Chim. Acta.*, **36,** 1251 (1953).

(8) H. Krzikalla, E. Woldan, and O. Dornheim, Ger. Pat. **736,024.** *Chem. Abstr.*, **38,** 4620^6 (1944).

(9) W. R. Vaughn and M. Yoshimine, *J. Org. Chem.*, **22,** 528 (1957).

zene at 200° for 12 hr. in a sealed tube, 3.81 g. of the butynediol was recovered plus 1.79 g. of crude anthracene.

Preparation of DL-*2,3[9,10-anthrylene]-1,4-butanediol.*

Thirteen grams of methyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate[8] in 150 ml. of tetrahydrofuran at −5° was reduced by a solution of 1.8 g. of lithium aluminum hydride in tetrahydrofuran. The addition of the lithium aluminum hydride was dropwise over a period of 1 hr. The temperature was maintained at −5° during the addition and for 3 hr. afterwards. Decomposition of the reaction mixture gave needles, m.p. 184–195°. One crystallization from benzene raised the melting point to 198–200°, reported 205–208°.[7] The purified needles weighed 1.61 g. (15%). The bisphenylurethane of the diol was prepared and after crystallization from acetonitrile melted at 251–253°, reported 252–254°.[7] The urethane when mixed with urethane supplied by Professor Walborsky showed no change in its melting point.

The fumaric acid adduct of anthracene was reduced as directed[7] and the resulting *dl*-diol melted at 199–201°. An almost identical melting point was observed for a mixture of this diol and the one obtained from the ester reduction.

11-12-Dimethylene-9,10-dihydro-9,10-ethanoanthracene.

The *meso*-2,3[9,10-anthrylene]-1,4-butanediol was prepared by reducing the maleic anhydride adduct of anthracene.[7] It was also prepared by heating 20 g. of anthracene with 45 ml. of *cis*-2-butene-1,4-diol in a sealed tube for 24 hr. at 180–185°.[8] The product was washed with water and crystallized from methanol and gave 24 g. (82%) of glistening white needles melting at 222–225°.

The *dl*- and *meso*-2,3[9,10-anthrylene]-1,4-butanediol were converted to their *p*-toluenesulfonates. Both sulfonates were treated with 7% ethanolic sodium hydroxide but the *dl* isomer failed to give a satisfactory product as it still contained sulfur. Thirty grams of the *meso*-*p*-toluenesulfonate (V) in 450 ml of 7% ethanolic sodium hydroxide was boiled under a reflux condenser for 13 hr. and then poured over ice. The light tan powder which formed was filtered and dried over phosphorus pentoxide, yield 16.7 g., m.p. 107–158°. A portion of this material was chromatographed by placing it on an alumina column with petroleum ether containing 5% benzene. Elution gave a 29% recovery of material melting at 150–157°. Further elution with absolute methanol gave a 61% recovery of material melting at 175–182°. Crystallization of the lower melting material from ethanol gave sparkling white needles of II, m.p. 151–153°.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.62; H, 5.98.

The higher melting material was crystallized from acetonitrile and melted at 180–182°. A crude preparation of 9,10,11,12,13,14 - hexahydro - 9,10[3′,4′[- furanothracene (VI) obtained from Dr. Walborsky[7] was crystallized from acetonitrile and then melted at 178–179°. A mixture of the two melted sharply in the same range.

Hydrogenation of 0.1 g. of compound II in ethanol over 10% palladium charcoal stopped in 10 min. with 93% of the calculated amount of hydrogen being absorbed. Removal of the catalyst and concentration of the ethanol gave 87 mg. of white plates, m.p. 168–170° which were identical with crystals of authentic *cis*-11,12-dimethyl-9,10-dihydro-9,10-ethanoanthracene[7] in melting point and infrared spectra comparisons.

A mixture of 0.117 g. of compound I and 0.278 g. of maleic anhydride was heated in 10 ml. of boiling benzene for 24 hr. A transient yellow color of a *pi* complex was observed. The solution was cooled and gave 0.128 g. of fine needles, m.p. 242–252°. Crystallization from acetone–petroleum ether gave glistening white needles of 1,2[9,10-anthrylene]-cyclohexene-*cis*-4,5-dicarboxylic anhydride, m.p. 251–252° dec.

Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.22; H, 5.01.

Ozonization of 1 g. of compound II in methanol led to bright orange crystals of 9,10-dihydro-9,10-ethanoanthracene-11,12-dione which were recrystallized from glacial acetic acid, yield 125 mg., m.p. 205–207°. The quinazoline derivative was prepared and melted at 298–299.5°. Both the diketone and the quinazoline derivative could be sublimed and the analytical data were satisfactory. Since then these compounds have been reported by Vaughn and Yoshimine to melt at 199–201.5° and 292°.[9]

The diketone on treatment with hydrogen peroxide following directions given for 1,2-diketo-[2.2.1]-bicycloheptane[11] led to the decolorization of the diketone. The colorless solution after a while gave a new yellow color and upon heating further a 34% yield of yellow anthraquinone was obtained.

A modification of the technique of Bailey and Golden[12] using heptyl mercaptan instead of lauryl mercaptan was used to polymerize compound II. The product was insoluble in boiling ethanol but soluble in benzene and melted from 185–195°. By diluting a solution in benzene with cold ethanol seven fractions were obtained totaling 1.05 g. Molecular weights (Rast) ranged from 2200 down to 652 and represented average values of 9.5 to 2.8 units of the diene per molecule in the polymer fractions.

Acknowledgment. The research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18(600)-648. The 2-butyne-1,4-diol and the 2-butene-1,4-diol were gifts of the General Aniline and Film Co.

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