(4.7 g.). This was removed by filtration and washed with methylene chloride.

Recrystallization proved difficult and the material was analyzed as such.

*Anal.* Calcd. for $C_5H_7I_5N_2OS$: C, 7.7; H, 0.9; I, 81.6; N, 3.6. Found: C, 7.7; H, 0.6; I, 79.6; N, 4.1.

A specimen (0.5 g.) of this material treated with a mixture of sodium hydrogen carbonate and sodium thiosulfate solutions afforded 4-acetaminothiazole (82 mg., 91%), m.p. 175–178°.

**4-Acetamino-5-(2,4-dichlorophenyl)thiazole.** (**a**).—To α-cyano-2,4-dichlorobenzyl thiocyanate (1.2 g.) suspended in glacial acetic acid (10 ml.) there was added dropwise at 5° a solution (12 g.) of hydrogen iodide (10–12%) in the same solvent. After an additional 30 min. at this temperature, acetic anhydride (3 ml.) was added and the liquid allowed to stand for 2 hr. at room temperature, then poured into 20% sodium acetate solution. Extraction with methylene chloride afforded a noncrystallizable gum which was redissolved in methylene chloride and percolated through a silica gel (5 g.) column. The initial eluate yielded an oil which slowly crystallized affording 2,4-dichlorobenzyl cyanide (50 mg.), m.p. 57–58° (reported[19] m.p. 58–59°). The infrared spectrum of this material had a band at 7.07 μ characteristic of a methylene group in a benzyl cyanide system.

Further elution of the column with ethyl acetate led to a second oil which when recrystallized from methylene chloride–ether afforded 4-acetamino-5-(2,4-dichlorophenyl)thiazole (0.35 g.), m.p. 115–116°. This material did not depress the melting point of a specimen prepared according to the procedure following.

*Anal.* Calcd. for $C_{11}H_8Cl_2N_2OS$: C, 46.0; H, 2.8; Cl, 24.7; N, 9.8; S, 11.2. Found: C, 46.0; H, 2.6; Cl, 24.5; N, 9.7; S, 11.2.

(**b**).—4-Acetamino-2-bromo-5-(2,4-dichlorophenyl)thiazole (1.0 g.) was dissolved in ethanol (60 ml.) containing potassium hydroxide (0.23 g.) and the resulting solution stirred under hydrogen in the presence of a 10% palladium-on-charcoal catalyst (0.15 g.). Hydrogen absorption had almost ceased after 2 hr. and the catalyst and solvent were removed by the usual methods. The residue was extracted with methylene chloride, and the extract concentrated and diluted with ether. Cooling to 5° caused crystallization of the product (0.45 g., 59% yield). A further crystallization from ethyl acetate gave the pure substance, m.p. 116–117°. Its infrared spectrum was identical with that of the material prepared by method a.

**The Action of Hydrogen Chloride on Cyanomethyl Thiocyanate.**—Cyanomethyl thiocyanate (0.1 g.) in ether (5 ml.) was saturated at room temperature with hydrogen chloride. After 1 hr. the yellow precipitate was removed and heated with acetic anhydride (~5 ml.) until solution was complete. The mixture was then poured into sodium acetate solution and the product isolated by methylene chloride extraction. Crystallization of the latter from acetone–petroleum ether (b.p. 66–67°) led to fine white needles, m.p. 202–206° (20 mg.).

*Anal.* Calcd. for $C_5H_6N_2O_2S$: C, 38.0; H, 3.8; N, 17.7; S, 20.3. Found: C, 38.1; H, 3.6; N, 17.5; S, 20.3.

**Solvolysis Experiments with 4-Amino-2-bromothiazole Hydrobromide.** (**a**).—The hydrobromide (1.0 g.) was stirred vigorously with water (15 ml.) for 15 min. and the undissolved solid removed by filtration and dried (0.5 g.), m.p. >280°. Its infrared spectrum showed bands at 5.92 and 6.20 μ.

*Anal.* Calcd. for $C_3H_5BrN_2OS$: C, 18.3; H, 2.6; Br, 40.6; N, 14.2; S, 16.3. Found: C, 18.4; H, 2.5; Br, 40.4; N, 14.1; S, 16.0.

(**b**).—The hydrobromide (4.0 g.) was added, with stirring, in one portion to 10% sodium hydrogen carbonate solution (200 ml.). As soon as effervescence had subsided, the solid was removed and, while still damp, added to a mixture of pyridine (20 ml.) and acetic anhydride (20 ml.) and the resulting mixture stirred for 1 hr. The clear solution was poured into water and the product isolated by methylene chloride extraction. The resulting brown gum crystallized easily from methanol and gave a highly crystalline solid (1.0 g.), m.p. 178–180° (effervesces at 110–120°). Two further crystallizations afforded the pure material, m.p. 184–185°, as large diamonds. Its infrared spectrum showed absorption at 2.97, 3.05, 3.11, 3.12, 5.92, and 6.52 μ.

*Anal.* Calcd. for $C_8H_{13}BrN_4O_6S_2$: C, 23.7; H, 3.2; Br, 19.7; N, 13.8; S, 15.8. Found: C, 23.5; H, 3.2; Br, 20.0; N, 13.8; S, 16.0.

(**c**).—The hydrobromide (0.5 g.) was refluxed with 5 *N* hydrochloric acid (10 ml.) for 3 hr. Evaporation of the solution to dryness followed by crystallization of the residue from ether–petroluem ether (b.p. 30–60°) afforded colorless prisms of thiazolidine-2,4-dione, m.p. 126–127° undepressed on admixture with an authentic specimen.

**The Action of Hydrogen Bromide on α-Cyano-2,4-dichlorobenzyl Selenocyanate.**—The selenocyanate (0.4 g.) was suspended in glacial acetic acid (4 ml.) and stirred while hydrogen bromide in acetic acid (1 g., 30% hydrogen bromide) was added dropwise. The reaction mixture immediately became homogeneous and turned a dark brown color. After 30 min., an excess of acetic anhydride was added and the solution then allowed to stand a further 3 hr. The mixture was poured into 20% sodium acetate solution and deposited selenium removed by filtration. The filtrate was processed by methylene chloride extraction which led to a small amount of a sirup. On standing in the refrigerator, this deposited crystals (6 mg.), m.p. 170° (softening at 160°). Its infrared spectrum showed bands at 3.09 and 6.00 μ.

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# Hydrogenation of Diels–Alder Adducts of Anthracene[1]

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In the presence of ruthenium catalyst, hydrogen attacks selectively only one aromatic ring in 9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride (I). Several diesters and an N-substituted imide were prepared from the resulting hydrogenation product (II). In the presence of Raney nickel, the action of hydrogen on I is nonselective. In contrast to I, hydrogenation of 11-methylol-9,10-dihydro-9,10-ethanoanthracene in the presence of ruthenium catalyst proceeds with attack on both aromatic rings. This difference is attributed to steric effects.

The Diels–Alder condensation of anthracene with dienophiles is a reversible, temperature-dependent reaction.[2] At higher temperatures, usually above 200°, the equilibrium is shifted in favor of the polycyclic hydrocarbon.[3] Pyrolysis of anthracene adducts has been suggested as a means of purifying anthracene or unsaturated alcohols.[4] The low thermal stability of these adducts excludes their use as potential starting materials for the preparation of polymers. It was thought that hydrogenation of one or both benzene

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(1) Paper presented before the Division of Fuel Chemistry, 143rd National Meeting of the American Chemical Society, Cincinnati, Ohio, January, 1963.

(2) For numerous references, see M. C. Kloetzel, *Org. Reactions*, **4**, Chap. 1 (1948).

(3) (a) W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **60**, 481 (1938); (b) R. Norman Jones, C. J. Gogek, and R. W. Sharpe, *Can. J. Research*, **26B**, 719 (1948).

(4) C. W. Smith and R. T. Holm, U. S. Patent 2,761,883 (1956).

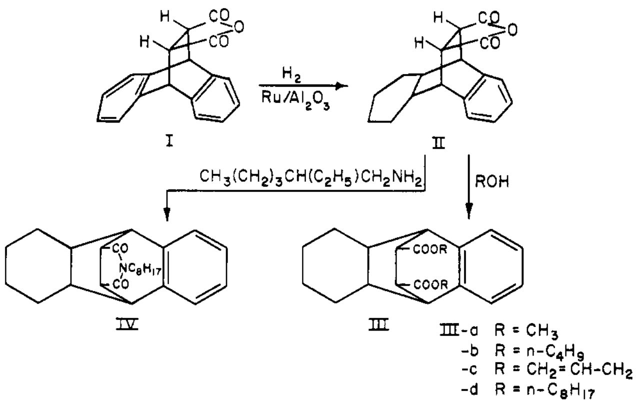
Table I

Diesters (III) and N-Substituted Imide (IV)

| Formula | Yield, % | B.p., °C. and $n^{25}_D$ | M.p., °C. | Molecular formula | Calculated | | Found |
|---|---|---|---|---|---|---|---|
| III-a | 77 | | 145–147[a] | $C_{20}H_{24}O_4$ | C | 73.14 | 73.49 |
| | | | | | H | 7.37 | 7.53 |
| III-b | 85 | 220–225 | | $C_{26}H_{36}O_4$ | C | 75.69 | 75.13 |
| | | (1.5 mm.) | | | H | 8.80 | 8.62 |
| | | 1.5710 | | | | | |
| III-c | 72 | 201–203 | | $C_{24}H_{28}O_4$ | C | 75.76 | 75.86 |
| | | (0.5 mm.) | | | H | 7.42 | 7.62 |
| | | 1.5420 | | | | | |
| III-d | 88 | 245–248 | | $C_{34}H_{52}O_4$ | C | 77.82 | 77.67 |
| | | (0.4 mm.) | | | H | 9.99 | 10.01 |
| | | 1.5025 | | | | | |
| IV | 76 | 190–232 | 72–74[b] | $C_{26}H_{35}NO_2$ | C | 79.34 | 79.36 |
| | | (0.6 mm.) | | | H | 8.96 | 9.08 |
| | | | | | N | 3.56 | 3.30 |

[a] Recrystallized from hexane–ethyl acetate (10:1). [b] Recrystallized from petroleum ether (30–60°).

rings in these adducts would prevent the pyrolytic reversal reaction and produce compounds of higher thermal stability. This was found to be the case when two anthracene adducts, 9,10-dihydroanthracene-9,10-*endo*-$\alpha,\beta$-succinic anhydride (I)[5] and 11-methylol-9,10-dihydro-9,10-ethanoanthracene (VIII),[6] were hydrogenated in the presence of ruthenium catalyst. Hydrogenation of adduct I under high pressure at 145–150° in the presence of ruthenium-on-alumina catalyst led to the absorption of three moles of hydrogen per mole of I, producing 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10-$\alpha,\beta$-succinic anhydride (II).



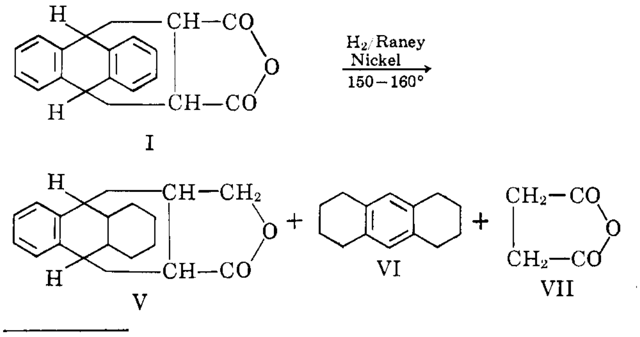
The infrared and ultraviolet spectra were consistent with structure II. The ultraviolet spectrum was that of an *ortho*-disubstituted benzene, and the infrared showed absorption bands characteristic of anhydride and *ortho*-disubstituted benzene groups.

Under the conditions employed, only one benzene ring was hydrogenated. The failure of the second benzene ring to undergo hydrogenation can be explained by steric effects as follows. The molecule of adduct I, which contains a *meso*-dihydroanthracene skeleton, is nonplanar. It has been shown that 9,10-dihydroanthracene is bent about the line joining carbon atoms 9 and 10, each half of the molecule being planar but the two halves inclined to each other at an angle of approximately 145°.[7,8] Assuming that addition of hydrogen to the benzene rings requires a flatwise adsorption of the unsaturated ring against the catalytic surface, it is likely that, due to the bent configuration of adduct I and to the hindering effect of the bulky anhydride group, only one of the benzene rings can be hydrogenated.[9] Inspection of the Godfrey molecular model of the adduct (I) confirms these expectations.

The hydrogenated adduct II, m.p. 145–165°, was a mixture of stereoisomers, and no attempt was made to separate them and determine their configuration. Several derivatives of interest as potential plasticizers or pesticides, such as the diesters (III-a, -b, -c, -d) and the N-substituted imide (IV), which were prepared by standard procedures from II, are listed in Table I.

The foregoing results show that in the presence of a ruthenium catalyst, a selective hydrogenation occurred, resulting in the reduction of the aromatic ring but not affecting the succinic anhydride group of the adduct (I). In contrast, the anhydride group is attacked when a substituted succinic anhydride[10,11] is hydrogenated in the presence of palladium or platinum catalyst, the products obtained being hydroxylactones, lactones, and $\beta$-methyl acids. The reduction of adduct I in the presence of Raney nickel at 160° was also nonselective, providing a mixture of compounds. These were 1,2,3,4,4a,9,9a,10-octahydro-9,10-ethanoanthracene-11-methylol-12-carboxylic acid lactone (V), produced by an attack on the aromatic ring and the anhydride group; s-octahydroanthracene (VI); and succinic anhydride (VII).

Products VI and VII could have been formed either by hydrogenolysis or thermal decomposition of the



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(5) O. Diels and K. Alder, *Ann.*, **486**, 191 (1931).

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(9) For a discussion of the effect of steric hindrance on catalytic hydrogenation of polycyclic aromatic compounds, see R. P. Linstead, W. Doering, S. B. Davis, P. Levine, and R. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985–2026 (1942), and R. P. Linstead and R. R. Whetstone, *J. Chem. Soc.*, 1428 (1950).

(10) F. Michael and W. Peschke, *Chem. Ber.*, **75**, 1603 (1942).

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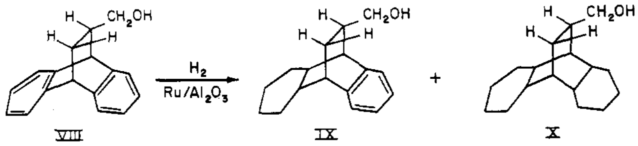
adduct (I) followed by hydrogenation of the intermediates.

The lactone (V), m.p. 125–145°, was a mixture of stereoisomers.

In contrast to I, the hydrogenation of 11-methylol-9,10-dihydro-9,10-ethanoanthracene (VIII) in the presence of ruthenium catalyst proceeds further, with some reduction of both aromatic rings, affording a mixture of 11-methylol-9,10-ethano-1,2,3,4,4a,9,9a,10-octahydroanthracene (IX) and 11-methylol-9,10-ethanoperhydroanthracene (X) in a variable ratio depending upon the reaction time.



Hydrogenation of both aromatic rings of VIII occurred, since the hindering effect of the hydroxymethyl group is smaller than that of the rigid and bulky anhydride group of I. As in the previous case, no attempt was made to separate the stereoisomers.

## Experimental

**1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10-α,β-succinic Anhydride (II).**—A mixture of 83 g. of 9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride (I) (m.p. 261–262°),[3a] 250 ml. of dioxane, and 6.0 g. of 5% ruthenium-on-alumina catalyst was placed in an "Aminco" autoclave, and hydrogen was admitted up to 1350 p.s.i. The vessel was shaken and heated for 16 hr. at 145–148°, after which the absorption of hydrogen ceased. The amount of hydrogen absorbed corresponded to about 3 moles of hydrogen per mole of I. After cooling, the catalyst was removed by filtration and washed with acetone. The filtrate and the washing were combined, and the solvents were removed by distillation, first at atmospheric pressure, then under vacuum. The solid residue, after washing with petroleum ether (30–60°), gave 71 g. (84%) of 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10-α,β-succinic anhydride (II), m.p. 145–165°. A sample of the anhydride, crystallized from ethyl acetate–petroleum ether, melted at 175–177°. Infrared absorption maxima: 5.45, 5.70, and 13.0 μ. Ultraviolet absorption spectrum in methylene chloride: $\lambda_{max}$ 247 mμ (ε 248), 253 (270), 260 (297), 263 (216), and 267 (230).

*Anal.* Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; mol. wt., 282.3. Found: C, 76.67; H, 6.57; mol. wt. (alkaline titration), 283.3.

In order to determine its heat stability, II was heated for 6 hr. in air to 230–240°. A slight discoloration, but no degradation, occurred.

In a second experiment, a modified procedure was employed for purifying the crude hydrogenation product. After separation from the catalyst and removal of the solvent, the solid residue was heated with 5% sodium hydroxide for 5 min. on a steam bath. After cooling and washing with ether to remove the nonacidic products, the aqueous layer was acidified with 15% hydrochloric acid. The precipitated solid, after washing with water and drying, gave the adduct (II) in a yield of 85%.

**Hydrogenation of 9,10-Dihydroanthracene-9,10-α,β-succinic Anhydride in the Presence of Raney Nickel.**—An "Aminco" bomb was charged with 27.6 g. of the adduct (I), 250 ml. of ethyl alcohol, and 10 ml. of Raney nickel catalyst, and hydrogen was admitted under 1330 p.s.i. at 25°. The bomb was shaken and heated at 160° for 20 hr. The amount of hydrogen absorbed corresponded to about 13.5 moles of hydrogen per mole of the starting adduct. After cooling, the solution of the hydrogenated product was separated from the catalyst by filtration, and the catalyst was washed with ether. The filtrates were combined and the solvents removed, first at atmospheric pressure, then under vacuum. The residue, composed of an oil and a solid, was treated with ethyl alcohol. The solid, insoluble in alcohol, was separated by filtration to give 4.8 g. of s-octahydroanthracene. The filtrate, after removal of the solvent by distillation, gave 20 g. of an oil.

In order to separate acidic products from nonacidic, the oil (18 g.) was heated on a steam bath with 120 ml. of 10% sodium hydroxide solution for 2 hr., and, after cooling, was extracted with ether. The nonacidic product, after elimination of ether, gave an additional 5.6 g. of s-octahydroanthracene. The total of s-octahydroanthracene isolated from the reaction mixture amounted to 10.4 g., or 56%. The alkaline solution was acidified with concentrated hydrochloric acid, and the precipitated solid was separated by filtration. The aqueous filtrate, after ether extraction and removal of the solvent, afforded 0.4 g. of succinic acid. The precipitated solid (6.0 g.) was crystallized several times from ethyl acetate to yield 1,2,3,4,4a,9,9a,10-octahydro-9,10-ethanoanthracene-11-methylol-12-carboxylic acid lactone, m.p. 125–145°. Infrared absorption maxima: 5.7 (lactone) and 13.0 μ (*ortho*-disubstituted benzene ring).

*Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 79.74; H, 7.67.

**Hydrogenation of 11-Methylol-9,10-dihydro-9,10-ethanoanthracene (VIII).**—A mixture of 54 g. (0.228 mole) of 11-methylol-9,10-dihydro-9,10-ethanoanthracene (m.p. 105–108°) (VIII),[12] 250 ml. of ethyl alcohol, and 4.0 g. of 5% ruthenium-on-alumina catalyst was placed in an autoclave, and hydrogen was admitted up to 1630 p.s.i. The vessel was shaken and heated for 6 hr. at 150°, after which the absorption of hydrogen ceased. The amount of hydrogen absorbed corresponded to about 3.8 moles of hydrogen per mole of adduct. After removal of the catalyst and solvent, the residue was distilled to yield 46 g. (84%) of a colorless oil, b.p. 150–175° (0.6 mm.), $n^{25}D$ 1.5480, consisting of a mixture of 11-methylol-9,10-ethanol-1,2,3,4,4a,9,9a,10-octahydroanthracene and 11-methylol-9,10-ethanoperhydroanthracene in an approximate ratio of 3 to 1.

*Anal.* Calcd. for $3(C_{17}H_{22}O) + C_{17}H_{28}O$: C, 83.89; H, 9.70; mol. wt., 244. Found: C, 83.87; H, 10.20; mol. wt., 248. (From determination of the hydroxyl content by acetylation method.)

Upon cooling, the oil solidified partially. The separated solid, 11-methylol-9,10-ethanoperhydroanthracene, crystallized from hexane, melted at 102–104°. The infrared and ultraviolet spectra of the solid product showed complete disappearance of the aromatic ring.

*Anal.* Calcd. for $C_{17}H_{28}O$: C, 82.80; H, 11.36. Found: C, 82.71; H, 11.59.

A thermal stability test of the hydrogenated adducts IX and IX + X was conducted as follows: Samples of the products were heated separately in air for 4 hr. at 235–240°. The products became colored, and according to infrared spectra, partial oxidation to the aldehydes occurred (infrared, 5.85 μ). However, no change in the carbon skeleton of the products was observed.

In a similar hydrogenation run, the crude product was separated from the catalyst, a fresh portion of the catalyst (4.0 g.) was added, and the mixture was hydrogenated further at 160° for an additional 17 hr. The reaction mixture contained approximately 30% of IX and 70% of X.

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[12] Prepared by the method of H. Krzikalla and E. Woldan, German Patent 740,142 (1943).