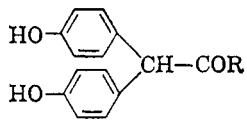
TABLE II



	R	M.P.	Yield, %	Formulas	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
VII	$-N(CH_3)_2$	238–241	86	$C_{16}H_{17}NO_3$	70.83	6.38	5.16	70.61	6.42	4.99
VIII	$-NH-C_6H_5$	210	95	$C_{20}H_{17}NO_3$	75.25	5.37	4.37	75.60	5.63	4.45
IX	$-N(CH_2-CH_2)_2O$	218–220	95	$C_{18}H_{19}NO_4$	69.00	6.25	4.41	69.17	6.37	4.30

Anal. Calcd. for $C_{23}H_{27}N_2O_5Cl$ (446): N, 6.27; Cl, 7.94; $COCH_3$, 19.22; tert. N, 3.13. Found: N, 6.07; Cl, 7.96; $COCH_3$, 18.9; tert. N, 3.33.

Bis(4-hydroxyphenyl)acetamides by hydrolysis of the corresponding bis(4-acetoxyphenyl)acetamides. General procedure. To 0.03 mole of the bis(4-acetoxyphenyl)acetamide dissolved in 250–300 ml. of methanol 72 ml. (0.18 mole) of 10% sodium hydroxide was added. After 1 hr. at room temperature with occasional stirring the solution was neutralized with 10% hydrochloric acid, diluted with 350 ml. of water and the methanol was removed *in vacuo*.

The crystalline product was collected and recrystallized from ethanol or ethanol-water mixture.

Bisglyceryl ether of bis(4-hydroxyphenyl)acetanilide. To a gently boiling solution of sodium ethoxide (from 7 ml. of absolute ethanol and 0.46 g. of metallic sodium) 3.19 g. of bis(4-hydroxyphenyl)acetanilide (VIII) dissolved in 9 ml. of absolute ethanol was added. After 10 min., 2.21 g. of glycerol-α-chlorohydrin were dropped in, the solution was refluxed for 1 hr., cooled, the sodium chloride formed was filtered off and alcohol was removed by distillation. The resinous residue was taken up with ethyl ether giving a white amorphous solid (5.5 g., 95%) melting at about 100° dec.

Anal. Calcd. for $C_{26}H_{29}NO_7$: N, 2.99; OH, 14.54. Found: N, 2.97; OH, 14.32.

The bisglyceryl ether of bis(4-hydroxyphenyl)acetomorpholide (IX), similarly obtained, is a hygroscopic, very light violet solid melting at about 100° dec.

Anal. Calcd. for $C_{24}H_{31}O_8N$: N, 3.04; OH, 15.25. Found: N, 2.85; OH, 14.7.

Acknowledgment. The author gratefully acknowledges the help of Prof. R. Fusco in discussing this work. He is also indebted for the analyses to Dr. G Pelizza (Organic Analytical Lab.) and to Mr. A. Restelli (Microanalytical Lab.).

MILAN, ITALY

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT AND THE CENTRAL RESEARCH DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Preparation of Some 9,10-Difunctional Derivatives of 9,10-Dihydro-9,10-ethanoanthracene[1a]

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Two routes to 9,10-diamino-9,10-dihydro-9,10-ethanoanthracene (I. X = NH_2) have been developed, in which ethylene is added to simple difunctional anthracene derivatives. For example, ethylene was added to 9,10-dinitroanthracene and the resulting product (I. X = NO_2) was hydrogenated. The diamine was converted to the diol (I. X = OH) and other difunctional derivatives. These intermediates have been converted into condensation polymers. Certain of the derivatives of the diamines including polymers have been shown to liberate ethylene upon heating and to revert to anthracene derivatives.

The synthesis of condensation polymers with unusual properties has been facilitated by the development of low temperature techniques[2] which permit the use of a wide range of reactive intermediates.

As ethylene is known to add to the 9,10-positions of substituted anthracenes[3–8] to give bridgehead

(1) (a) Presented at 138th ACS National Meeting, Sept. 12, 1960, New York. (b) Present address: Department of Chemistry, Harvard University.

(2) E. L. Wittbecker and P. W. Morgan, *J. Polymer Sci.*, **40**, 289–297 (1959) and following papers.

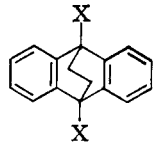
(3) C. L. Thomas, U. S. Patent **2,406,645**, August 27, 1946.

(4) J. S. Meek, V. C. Godefroi, and W. B. Evans, 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., April 1953.

(5) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952).

(6) M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta*, **40**, 2129 (1957).

compounds, it was felt that a study of the difunctional derivatives (I) might lead to some intermediates which would give polymeric products with unusual properties



I

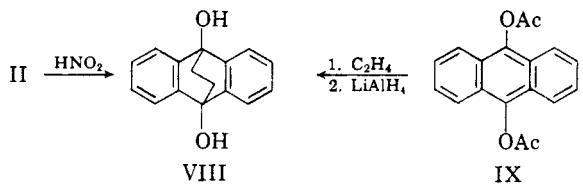
II. X = —NH_2
VIII. X = —OH
X. X = NCO

The 9,10-diamine (II) (X = NH_2) was made by the two independent routes, shown in Fig. 1.

In the first procedure, anthraquinone was converted to 9,10-bisformamidoanthracene (III) by refluxing with formamide.[9] This compound could not be condensed with ethylene, presumably because of lack of solubility in benzene, even at 220°. Hydrolysis to the diamine gave a product which was air sensitive and hard to work with. However, half-hydrolysis gave a product (IV) which condensed readily with ethylene to give the desired compound, II, after hydrolysis of the intermediate monoformyl derivative V.

In the second procedure, 9,10-dinitroanthracene (VI)[10,11] was condensed with ethylene to give VII, which was readily hydrogenated to II.

The diol VIII was obtained by the action of nitrous acid on the diamine, (II). It sublimed



VIII IX

easily near its melting point. The properties of both the diol and its diacetate agreed with the properties reported by J. S. Meek[12] for the product obtained by condensing ethylene with 9,10-diacetoxyanthracene (IX), and its lithium aluminum hydride reduction product, indicating no rearrangement during the deamination of II. The diisocyanate (X) was readily obtained by reaction of phosgene with the dihydrochloride of II in refluxing xylene.

As indicated above, 9,10-diminoanthracene (XI) is very sensitive to air oxidation. As the nature of the products of its air oxidation was not completely

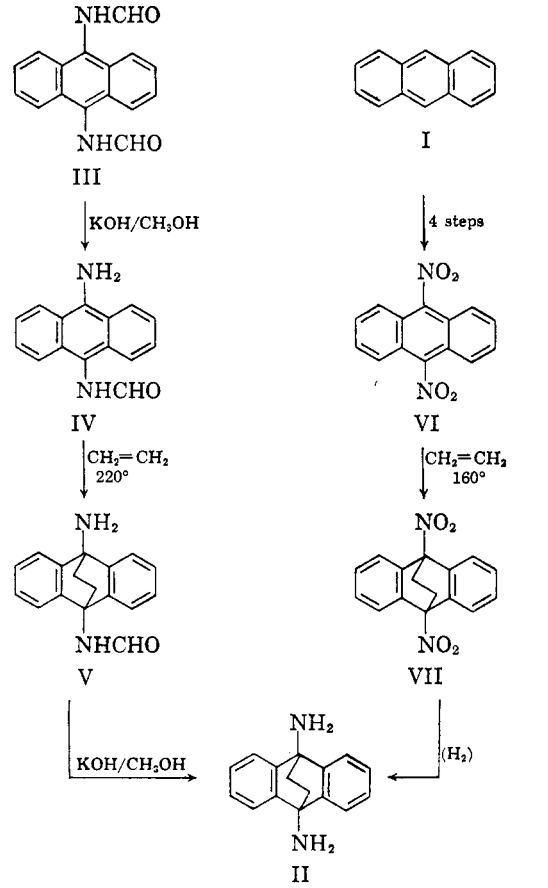
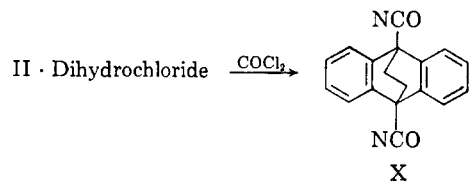


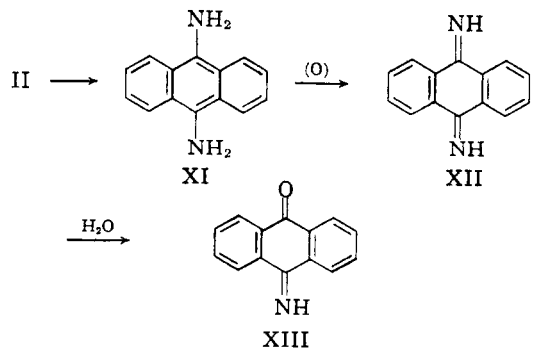
Fig. 1. Synthesis of 9,10-diamino-9,10-dihydro-9,10-ethanoanthracene



X

clear from a study of the literature,[13,14] they were examined briefly.

When a solution of XI in dimethylformamide was exposed to air, the orange color faded rapidly. The crystalline product agreed in properties with the bisimine (XII) prepared by Stein and von

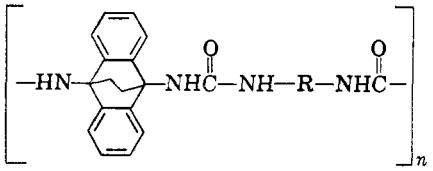


XI XII XIII

(7) J. S. Meek, B. T. Poon, and S. J. Cristol, *J. Am. Chem. Soc.*, **74**, 761 (1952).
(8) J. S. Meek, J. R. Dann, and B. T. Poon, *J. Am. Chem. Soc.*, **78**, 5413 (1956).
(9) B. Schiedt, *J. Prakt. Chem.*, **157**, 203 (1941).
(10) E. de B. Barnett, J. W. Cook, and H. H. Grainger, *J. Chem. Soc.*, **121**, 2059 (1922).
(11) E. de B. Barnett, *J. Chem. Soc.*, **127**, 2040 (1925).
(12) J. S. Meek, private communication.
(13) M. L. Stein and H. von Euler, *Gaz. chim. ital.*, **84**, 290 (1954).

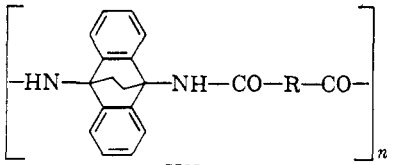
Euler[13] by silver oxide oxidation of XI. Recrystallization from aqueous dimethylformamide and then from methanol resulted in partial hydrolysis to the ketoimine (XII) which Stein and von Euler[13] obtained by a similar procedure.

High molecular weight polyureas (XIV) were prepared from the diisocyanate X and several diamines. Polyamides XV were prepared from



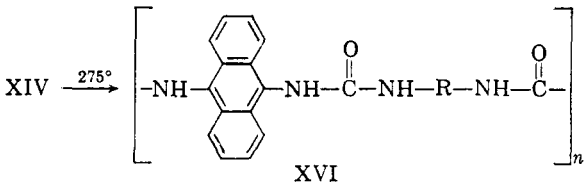
XIV

diamines both by melt and interfacial methods.[2] The first method gave discolored products, but colorless polymers were obtained from the latter procedure.



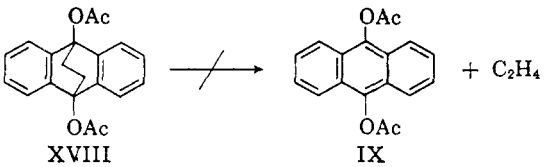
XV

It was noted that the polymers, when heated, foamed and turned bright yellow. Infrared analysis showed the evolved gas to be ethylene, indicating that the addition of ethylene is reversible. This means that the polymers, as for example XIV, can be converted after preparation to anthracene derivatives:



XVI

When the diamine II and its bisformamide derivative (III) were heated to 180° and 334° respectively, the characteristic ultraviolet absorption bands of anthracene could be observed. However, similar treatment of the diacetate of VIII produced no ethylene.



XVIII IX

(14) N. N. Vorozhtsov and V. P. Shkitin, *J. Gen. Chem., U.S.S.R.*, **10**, 883–893 (1940); *Chem. Abstr.*, **35**, 4375 (1941).

EXPERIMENTAL

9,10-Bisformamidoanthracene (III).[9] A mixture of 400 g. of anthraquinone and 3500 g. of redistilled formamide was refluxed for 4 hr. During that time, the solid initially present dissolved, then a second material began to separate, yielding eventually a thick slurry. When the reaction was complete, it was cooled and filtered. The straw-yellow solid was washed with water, then repeatedly with absolute alcohol and dried. The yield was 428 g. (84%). It showed no sign of melting or decomposing at temperatures below 400°.

9-Amino-10-formamidoanthracene (IV).[9] A mixture of 350 g. of 9,10-bisformamidoanthracene with 470 g. of potassium hydroxide in 3800 ml. of methanol was refluxed 2 hr., cooled in ice, filtered, and dried. The product was yellow-orange, and melted at about 300° (lit.[9] m.p. 292°). The yield of product was 70%. It was used without further purification.

Anal. Calcd. for $C_{15}H_{12}N_2O$: C, 76.3; H, 5.12; N, 11.9. Found: C, 76.0; H, 5.1; N, 11.5.

Autoxidation of 9,10-diaminoanthracene. About 1 g. of the monoformyl derivative was hydrolyzed to the diamine by refluxing under argon with 40% potassium hydroxide in methanol. It was isolated in the form of scarlet leaflets which were recrystallized from methanol. It was quite soluble in dimethylformamide, acetone, and other common solvents. A solution of 0.8 g. of diamine in 25 ml. of dimethylformamide rapidly turned colorless on exposure to air. This colorless solution, on addition of water, gave a fine precipitate (0.8 g.) of colorless needles of XII m.p. 155–165° (lit.[13] m.p. 153–154°).

Anal. Calcd. for $C_{14}H_{10}N_2$: N, 13.6. Found: N, 12.6, 12.7.

These crystals were recrystallized from aqueous dimethylformamide, then from methanol to give 0.5 g. of needles, m.p. 214–217° (lit.[13] m.p. 218°).

Anal. Calcd. for $C_{14}H_9NO$: N, 6.76. Found: N, 7.9.

9,10-Dinitroanthracene (VI). 9-Nitroanthracene[15] was converted to 9,10-dinitroanthracene by a combination of the procedures described by Meisenheimer and Connerade[16] and Barnett, Cook and Grainger.[10] Crude 9-nitroanthracene (128 g.) was dissolved in 1250 ml. of chloroform, and nitrogen dioxide gas was passed slowly into the stirred solution. A crystalline solid slowly separated. After about 40 hr. the stream of gas was stopped, and excess nitrogen dioxide was removed by passing a stream of nitrogen gas through the reaction mixture while maintaining the temperature at 40°. The solid product was removed by filtration and washed with pentane to yield 121.5 g. of 9,9,10-trinitro-9,10-dihydroanthracene. Addition of pentane to the filtrate caused an additional 23 g. of product to precipitate. The first crop of crystals was added to 453 g. of pyridine with vigorous stirring. When gas evolution ceased, the resulting yellow precipitate was removed by filtration and was washed thoroughly with water to yield 100 g. of 9,10-dinitroanthracene. A portion recrystallized from benzene melted sharply at 301° (lit. m.p. 294°, Ref. 16; 310°, ref. 11). The yield of 9,10-dinitroanthracene from 9-nitroanthracene was 77%.

9-Amino-10-formamido-9,10-dihydro-9,10-ethanoanthracene (V). In a typical experiment 100 g. of the monoformyl derivative and 750 ml. of benzene were heated in a bomb at 200 to 220° with maximum cylinder pressure of ethylene for 48 hr. The bomb was cooled and vented. The product consisted of a dark brown benzene solution mixed with a large mass of slightly discolored crystalline material. This mixture was filtered. The solid, which weighed 93 g. (83%) was essentially pure condensation product, m.p. 240°. A portion was sublimed in a high vacuum at 124°. The sublimate was recrystallized from decahydronaphthalene to give pure white needles melting sharply at 240°.

(15) C. E. Braun, C. D. Cook, C. Merritt, and J. E. Rousseau, *Org. Syntheses*, **31**, 77 (1951).

(16) J. Meisenheimer and E. Connerade, *Ann.*, **330**, 133 (1904).

Anal. Calcd. for $C_{17}H_{16}N_2O$: C, 77.3; H, 6.67. Found: C, 77.0, 77.3; H, 6.35, 6.52.

Evaporation of the benzene filtrate gave a few grams of a tarry material which was not examined further.

Several attempts were made to condense ethylene with diformamidoanthracene in benzene solution at 170–220°. Only starting materials were recovered.

9,10-Dinitro-9,10-dihydro-9,10-ethanoanthracene (VII). A mixture of 20 g. of 9,10-dinitroanthracene and 20 ml. of benzene was charged into a 100-ml. silver-lined autoclave and heated to 160° for 13 hr. under pressure of 1000 atm. of ethylene. When the resulting solution was evaporated, 19.8 g. (90%) of white crystalline ethylene adduct was obtained. A portion was recrystallized from acetone and was then sublimed for analysis (m.p. 247.5–248.5°).

Anal. Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.9; H, 4.1; N, 9.5; mol. wt., 296. Found: C, 65.1; H, 4.2; N, 9.5; mol. wt., 272, 280.

The infrared spectrum showed the presence of nitro groups and also exhibited the characteristic band at 760 $cm.^{-1}$ which is observed in many ethanoanthracene derivatives.[17]

9-Amino-10-formamido-9,10-dihydro-9,10-ethanoanthracene (V). Eighty grams of the monoformyl compound was refluxed for 6 hr. with 450 g. of potassium hydroxide in 750 ml. of methyl alcohol. The mixture was then cooled and diluted with 1 l. of water. The product crystallized well overnight. It was recrystallized using decolorizing carbon from aqueous alcohol to give 58 g. of a crystalline product. A 5-g. sample was recrystallized from benzene-cyclohexane mixture to give a product melting at 148–149°.

Anal. Calcd. for $C_{16}H_{16}N_2$: C, 81.4; H, 6.7. Found: C, 81.0, 81.6; H, 6.9, 7.1.

The infrared spectrum of the diamine, and direct combustion analysis for oxygen, suggested that there was still 1 to 2% of unhydrolyzed formamide linkages present.

To hydrolyze this material completely, a 2-g. sample was dissolved in 50 ml. of tetrahydrofuran and refluxed for 12 hr. with 50 ml. of 3*M* methylmagnesium bromide. The mixture was poured into ammonium chloride–water, and the crude diamine was removed by filtration. It was recrystallized from ethyl alcohol containing a trace of sodium hydroxide to yield 1.8 g. of a monohydrate which melted at 115–120° on the Kofler hot stage.

Anal. Calcd. for $C_{16}H_{18}N_2O$: C, 75.6; H, 7.13; N, 11.0. Found: C, 75.4; H, 6.96; N, 11.1.

The hydrate lost water when heated above 120° or when recrystallized from boiling benzene-cyclohexane to yield white crystals melting at 148–148.5°.

Anal. Calcd. for $C_{16}H_{16}N_2$: C, 81.4; H, 6.7; N, 11.9. Found: C, 81.4, 81.3; H, 6.9, 6.9; N, 11.7, 11.7.

The diamine formed a disulfate when treated with 50% sulfuric acid. The salt was insoluble in water and did not melt at 400°.

Anal. Calcd. for $C_{16}H_{16}N_2 \cdot 2H_2SO_4$: C, 44.4; H, 4.6; N, 6.5. Found: C, 44.4, 44.2; H, 4.7, 4.9; N, 6.4, 6.4.

Reduction of 9,10-dinitro-9,10-dihydro-9,10-ethanoanthracene. A solution of 29 g. of the dinitro compound in 100 ml. of dioxane was hydrogenated at 1000 psi at a temperature of 50° using a Raney nickel catalyst. After the calculated quantity of hydrogen had been absorbed, the solution was filtered under nitrogen, and the filtrate was evaporated under nitrogen to yield 29 g. of a white crystalline product which exhibited an infrared spectrum identical with that of the diamine hydrate described above. After recrystallization from ethanol, the melting point was 110–115° with remelting at 147–148°.

9,10-Bisacetamido-9,10-dihydro-9,10-ethanoanthracene. Ten milliliters of acetic anhydride was added to a solution of 0.25 g. of the diamine in 25 ml. of refluxing pyridine. Fine white needles gradually separated; after 30 min. the mixture was cooled and filtered. The fine needles (0.25 g.) melted without decomposition at about 400°. At slightly lower temperatures, sublimation occurred.

Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 75.0; H, 6.3; N, 8.7. Found: C, 74.7; H, 6.30; N, 8.7.

Preparation of 9,10-bisformamido-9,10-dihydro-9,10-ethanoanthracene. A solution of 10 g. of 9,10-diamino-9,10-dihydro-9,10-endoethanoanthracene in 100 ml. of formic acid was heated at reflux for 20 hr. After this period, water was added to the hot solution to the cloud point. On cooling a crystalline precipitate formed. This was collected, washed with ether and dried. The yield was 2.5 g., melting point *ca.* 330° on the hot bar.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: N, 9.6. Found: N, 9.5, 9.5.

9,10-Dihydroxy-9,10-dihydro-9,10-ethanoanthracene (VIII). Five grams of the diamine was dissolved in a mixture of 100 ml. of acetic acid and 100 ml. of water. The mixture was cooled in an ice bath, and 10 g. of sodium nitrite in 200 ml. of water was added over 30 min. Next day the mixture was heated on the steam bath and evaporated nearly to dryness. The slurry was cooled in ice, then filtered. The yield of gummy product was 4.9 g. and probably contained diol, mixed acetates, and other products. This was sublimed to give 4.3 g. sublimate at 250–275°/0.3–0.4 mm. The sublimate melted broadly. It was dissolved in tetrahydrofuran, and 50 ml. of 1*M* butyllithium was added. The mixture was warmed on the steam bath and the residue was acidified with dilute hydrochloric and collected. The solid was dried and recrystallized from 200 ml. of boiling benzene to give 2.7 g. of beautifully crystalline diol. This material melted at 274° on a preheated hot stage, and sublimed readily (lit.[12] m.p. 269–271°).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.6, 80.7; H, 5.98, 5.91.

9-10-Diacetoxy-9,10-dihydro-9,10-ethanoanthracene. A sample of 250 mg. of diol was heated on the steam bath with a mixture of 3 ml. of dimethylacetamide and 3 ml. of acetyl chloride for 4 hr. The solution was poured into ice water, filtered, and dried. Without purification, the fine needles melted at 206–209° (lit.[12] m.p. 207–209°).

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 74.4, 74.3; H, 5.5, 5.7.

9,10-Dihydro-9,10-ethanoanthracene-9,10-diisocyanate (X). Hydrogen chloride gas was passed into a stirred solution of 118 g. of 9,10-diamino-9,10-dihydro-9,10-ethanoanthracene in 1000 ml. of xylene (dried over calcium hydride). The dihydrochloride precipitated as a white, water soluble compound. The reaction mixture was heated to reflux, and a slow stream of phosgene was passed into it for a period of about 4 hr. (A longer reaction time would be desirable, as unchanged salt was recovered.) Nitrogen was passed through the solution to remove excess phosgene. The solution was filtered and solvent was distilled through a 25-cm. Vigreux column at water pump vacuum. The diisocyanate crystallized from the cooled residue and the remaining xylene was removed by the use of a rotary film evaporator at oil pump pressure. The crude yellow product weighed 72 g.

Sixty grams of the crude diisocyanate was dissolved in 900 ml. of boiling cyclohexane at the boil. The solution was treated with decolorizing charcoal and filtered under nitrogen. The solvent was evaporated at reduced pressure, to yield 48 g. of yellow solid (m.p. 75–78°) which after distillation at 188–192°/0.8 mm. melted at 83–85°.

Anal. Calcd. for $C_{18}H_{12}N_2O_2$: C, 75.0; H, 4.2; N, 9.7. Found: C, 75.0, 75.0; H, 4.3, 4.3; N, 9.4, 9.5.

The infrared spectrum was consistent with the proposed structure, and showed a strong isocyanate band at 4.44 μ.

The bispiperidine derivative was prepared by adding 5 ml. of piperidine to a solution of 1.00 g. of the diisocyanate in 25 ml. of benzene. The mixture was heated at reflux for 30 min., and then was cooled. The white crystalline precipitate was washed with ether and vacuum dried. The product weighed 1.3 g. and melted at 242–243°.

Anal. Calcd. for $C_{18}H_{34}N_4O_2$: C, 73.4; H, 7.42; N, 12.2. Found: C, 73.4, 73.5; H, 7.5, 7.5; N, 12.0, 12.1.

(17) W. R. Benson, *Dissertation Abstr.*, 19, 2750 (1959).

Thermal decomposition of 9,10-bisformamido-9,10-ethanoanthracene. A small sample of the ethano compound (m.p. 330°C.) was heated for 10 min. under nitrogen in a 334° vapor bath. The material melted, then changed with effervescence to a dark green powder. This did not melt below 400° (hot bar). Ultraviolet spectra of the untreated and heat-treated compound was determined. Characteristic bands of anthracene were observed in the spectrum of the heat-treated sample, while none appeared in that of the untreated one.

Thermal decomposition of 9,10-diamino-9,10-ethanoanthracene. Samples (1.0 g.) of the diamine were heated under nitrogen in a 140°, 155°, and 194° vapor bath. No visible changes were observed in the first two cases, while at 194° the originally clear, colorless melt effervesced and turned to a brilliant red, and on cooling deposited red crystals. These showed a characteristic anthracene spectrum in the ultraviolet.

A solution of the ethanoanthracene diamine in *o*-dichlorobenzene (b.p. 180°) was heated at reflux for 4 hr. under nitrogen. Strong anthracene bands developed in the ultraviolet spectrum of this solution.

Polymer from 9,10-dihydro-9,10-ethanoanthracene-9,10-diisocyanate. A solution containing 2.88 g. (0.01 mole) diisocyanate in 15 ml. of dimethyl sulfoxide was prepared. To it was added a solution of 1.16 g. (0.01 mole) of hexamethylenediamine in 10 ml. of dimethyl sulfoxide. After stirring at 40–50° under nitrogen for 1 hr., a clear viscous solution resulted. A film was cast, and the remaining portion was poured into water. The polymer was washed with water, and dried in a vacuum oven at 90°. It had a polymer melt temperature (PMT) of 294°[18] with gas evolution and foaming. The films were drawable about 1.5X at 150°. Drawn strips were boiled off, but showed no crystallinity by X-ray.

The polymer when heated at 250–275° turned yellow and showed anthracene bands in the ultraviolet. Small samples of the polymers were placed in a tube which was connected to an infrared gas cell and to a vacuum pump. The tube and cell were evacuated to *ca.* 1 mm. pressure, the tube was immersed into a 275° vapor bath for 2 min. The polymer discolored strongly. The cell was now closed, and the infrared spectrum of the contents was recorded. The characteristic band of ethylene was detected, indicating that this polymer converted quite readily to the corresponding anthracene polyurea.

Polymerization of the diisocyanate with 2,2-bis(4-aminophenylpropane). To a solution of 2.88 g. (0.01 mole) of diisocyanate in 25 ml. of dimethyl sulfoxide was added with stirring under nitrogen a solution of 2.26 g. of (0.01 mole) of 2,2-bis(4,4′-diaminodiphenyl)propane in 20 ml. of the same solvent. After 10 min., 4 drops of triethylamine was added as catalyst for the reaction. The solution was stirred 3 hr. and was then poured into water to precipitate the polymer. The polymer was collected, washed with water, and dried in a vacuum oven at 90°. It weighed 4.8 g. and melted at 298° with yellowing and effervescence.

Polymerization of the diisocyanate and tetramethyleneglycol. In a small polymer tube were placed 6.33 g. of the diisocyanate and 1.978 g. of tetramethyleneglycol. The mixture was heated in a 205° vapor bath; the initially thin melt became very viscous after *ca.* 15 min. and solidified to a mass after 1 hr. Heating was continued for an additional hour. The polymer had a melt temperature of 220–230°.

When heated to 245°, the pale yellow product of the above reaction foamed to about four times its original volume, and became brilliant yellow. The ultraviolet spectra of these two polymers were determined in dimethyl sulfoxide. The spectrum obtained from the "degraded" polymer showed two bands at 263 mμ and 269 mμ, respectively, while the original polymer did not show these bands.

Polymerization of the diamine (II) *with sebacoyl chloride.*[2] A solution of 1.83 g. freshly recrystallized diamine in 30 ml. of chloroform was placed in a high speed mixer. To this was added simultaneously with stirring 1.85 g. of sebacoyl chloride in 10 ml. of chloroform and 1.65 g. of sodium carbonate in 60 ml. of water. The mixture was stirred for 10 min. and the chloroform evaporated. The polymer was collected, washed with water and dried in a vacuum oven at 70°. The yield of polymer was 2.2 g., with a PMT[18] of 350°.

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Preparation of Some New Modifications of Diphenyltin[1]

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Preparations of diphenyltin described earlier[2,3] lead to yellow products of very high or very low solubility in benzene. The preparation of yellow modifications of intermediate solubility, and of two colorless modifications are described in this paper. Diphenyltin dihydride, whose preparation and characterization are described, decomposes in the presence of amines to produce yellow modifications of diphenyltin. Decomposition in methanolic solutions leads to a colorless modification of degree of polymerization of five or six. This modification in turn can be converted into a less soluble crystalline modification by dissolving in solvents such as dimethylformamide, dimethyl sulfoxide, and morpholine. It also undergoes thermal and photochemical transformations into yellow diphenyltin.

Diphenyltin has been prepared in two ways which are fundamentally different. Krause and Becker[2] prepared it by reaction of phenylmagnesium bromide with stannous chloride;

$$2\ C_6H_5MgBr + SnCl_2 \longrightarrow (C_6H_5)_2Sn + 2MgBrCl$$

The product was described as a bright yellow solid which softened at 126° and melted to a deep red liquid at 130°. It was monomeric, but its molecular weight increased over three days by a factor of three and over five months by a factor of about five. The elemental analyses agreed with the theoretical values. When Jensen and Clauson-Kaas attempted

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(2) E. Krause and R. Becker, *Ber.*, **53**, 173 (1920).

(3) E. Krause and R. Pohland, *Ber.*, **57**, 532 (1924).