Additional chloroform solution, 110 ml., containing 6.6 g. (0.048 mole) of peroxybenzoic acid was added. After 4 hr. at room temperature, 0.044 mole of peracid was still present. The chloroform solution was then washed repeatedly with sodium carbonate solution and dried over anhydrous sodium sulfate. The chloroform was removed at atmospheric pressure and the residual oil was distilled to yield 12.0 g. (80%) of IV as a colorless oil, b.p. 50–51.5° (0.7 mm.), n_D^{28} 1.5031.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.0; H, 9.39. Found: C, 80.0; H, 9.50.

The infrared spectrum of IV showed a characteristic 1,2-epoxide peak at 11.84 μ.[10]

exo-5,6-Cyclopentano-exo-2-norborneol (octahydro-exo-4,7-methanoinden-exo-5-ol, VI). Lithium aluminum hydride, 3.8 g. (0.1 mole) was dispersed in 50 ml. of tetrahydrofuran by refluxing with stirring, 5.0 g. (0.033 mole) of epoxide IV was added, and the reaction mixture was heated at reflux for 5 days. The excess lithium aluminum hydride was destroyed with 10 ml. of ethyl acetate and the complex was decomposed with 100 ml. of water. Extraction of both the solid and liquid phases with pentane, drying and evaporation of the solvents, and, finally, distillation yielded 1.15 g. of a forerun, b.p. 50–73° (0.5 mm.), which was about 65% epoxide by infrared analysis, and 3.14 g. (62%) of impure alcohol VI, b.p. 75–79° (0.7 mm.), which solidified, m.p. 37–46°.

The *acid phthalate* derivative was prepared by heating 1.0 g. (6.6 mmoles) of the reduction product with 1.27 g. (8.6 mmoles) of phthalic anhydride in 15 ml. of pyridine on the steam bath. Water and 6*N* hydrochloric acid were added and the precipitated oil was taken up in ether. The ethereal solution was dried over anhydrous sodium sulfate and the solvent was evaporated to yield 1.9 g. (96%) of product, m.p. 151–153.5°. Crystallization from acetone gave 0.81 g. of pure acid phthalate, m.p. 157.5–158°; mixed m.p., 157.5–158°, with the acid phthalate of authentic VI.[1,6,7]

Treatment of 0.5 g. (3.3 mmoles) of the alcohol with 0.73 g. (3.9 mmoles) of *p*-nitrobenzoyl chloride in 5 ml. of pyridine yielded 0.6 g. (60%) of crude product, m.p. 86–90°. Two crystallizations from hexane gave 0.25 g. of *p*-nitrobenzoate, m.p. 91.5–93°; mixed m.p. 93.5–94° with the *p*-nitrobenzoate of authentic VI[1,6] (m.p. 94–94.5°).

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL SCIENCE, KANSAS STATE COLLEGE]

Condensation Reactions of Carbon Monoxide with Aluminum Chloride and Aromatic Systems

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Carbon monoxide reacts with aromatic hydrocarbons in the presence of molar quantities of aluminum chloride at 60° and a pressure of 50 p.s.i. to give substituted anthracenes. Toluene gives a dimethylanthracene, diphenylmethane gives a dibenzylanthracene, and *p*-xylene yields 1,4,5,8-tetramethylanthracene. Diphenyl ether forms xanthydrol at 80°.

Aromatic aldehydes, benzyl alcohol, and benzhydrol are cleaved in the presence of excess aluminum chloride to give carbon monoxide. If an aryl hydrocarbon is present, polynuclear systems are formed.[3–7] Carbon monoxide should then react with aromatic hydrocarbons to form derivatives of anthracene.

In the present investigation, carbon monoxide under 50 p.s.i. pressure was shaken with various aromatic hydrocarbons and diphenyl ether in the presence of aluminum chloride over a period of 12–18 hours. Pressure drops of 5–15 pounds were noted in most cases.

At 60°, toluene reacts with carbon monoxide to form a mixture of dimethylanthracenes which is regarded as a eutectic mixture of the 2,6- and 2,7-isomers.[8] Diphenylmethane gives a dibenzylanthracene, while *p*-xylene gives a tetramethylanthracene, probably the 1,4,5,8 isomer.[4]

The dimethyl and dibenzylanthracenes were analytically and spectroscopically identical with the products obtained from the reactions of benzaldehyde with toluene and diphenylmethane.[3,4,6] Each is regarded as a mixture of the 2,6- and 2,7-isomers[8].

The reaction is temperature dependent. At 30°, toluene reacts to give some *p*-tolualdehyde along with dimethylanthracene. At 40°, only a trace of aldehyde is observed. The yield of dimethylanthracene increases to a maximum at 60° (Table I). A comparison of this reaction with the Gattermann-Koch reaction was carried out.[9] Toluene, saturated with dry hydrogen chloride, failed to give increased yields of dimethylanthracene at 60°.

Diphenyl ether is unique in that the carbon monoxide bridges the *ortho*- positions to give xanthydrol.

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(2) From the master's thesis of R. C. Horn, Kansas State College, Pittsburg, Kan.

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TABLE I

EFFECT OF TEMPERATURE ON YIELD OF DIMETHYLANTHRACENE[a]

Temperature. °C.	*p*-Tolualdehyde, g.	Dimethylanthracene, g.
30	3.86	0.7
40	0.10	2.1
50	0.10	2.7
60	0.10	3.0

[a] 60 ml. toluene; 12 hours.

Diphenyl ether has been reported[7] previously to react with benzaldehyde and aluminum chloride to give 9-phenylxanthydrol.

As evidence that the anthracenes are substituted on the benzenoid positions, the dimethyl- and dibenzylanthracenes were oxidized to the corresponding anthraquinones. In each case the disubstituted anthraquinone was obtained, indicating that the groups could not be on the 9 or 10 position.

EXPERIMENTAL

The reaction of toluene and carbon monoxide in the presence of aluminum chloride. Toluene (60 ml., 0.65 mol.) and 25 g. (0.2 mol.) of aluminum chloride were placed in the reaction flask of a Parr hydrogenation apparatus. The system was filled with carbon monoxide to 50 p.s.i. The reaction mixture was agitated and allowed to react for 12 hr. at 60°. The reaction mixture was then decomposed with ice and hydrochloric acid and steam distilled.

The solid residue from the steam distillation was removed by filtration and dried by azeotroping with benzene and sublimed under vacuum (1 mm.). Crystallization of this product from ligroin (b.p. 60–90°) gave 2.1 g. of a dimethylanthracene which melted at 223–225°.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.10; H, 6.80. Found: C, 92.87; H, 6.69.

Dimethylanthraquinone. Dimethylanthracene (0.45 g.), dissolved in 7 ml. of glacial acetic acid, was refluxed gently over a low flame. A solution of 2.0 g. of chromic anhydride in 2.0 ml. of water and 8 ml. of acetic acid was added during 1 hr. The solution was cooled, diluted with 200 ml. of water, and filtered. The crude green solid was washed with water, dilute aqueous sodium hydroxide, and again with water. Crystallization from 95% ethanol gave yellow needles of dimethylanthraquinone (0.41 g., 79%) which melted at 154–155°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.30; H, 5.08. Found: C, 81.04; H, 4.89.

The reaction of diphenylmethane and carbon monoxide with aluminum chloride. Diphenylmethane (60 ml.) and aluminum chloride (25 g.) when shaken with carbon monoxide at 50 p.s.i. for a period of 12 hr. at 60° gave, after decomposition, 10 g. of solid which was vacuum sublimed (1 mm.). Crystallization from ligroin (b.p. 60–90°) gave 3 g. of a dibenzylanthracene which melted at 191–192°.

TABLE II

ULTRAVIOLET DATA

	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ
Anthracene	252	5.30	322	3.50	338	3.80	355	4.00	375	3.90
Dimethylanthracene	257	5.10			340	3.60	359	3.71	378	3.60
Tetramethylanthracene	259	5.38			343	3.69	359	3.79	380	3.69
Dibenzylanthracene	253	5.46	324	3.75	339	4.06	356	4.24	375	4.20
Xanthydrol	249	3.75	284	3.33						

Anal. Calcd. for $C_{28}H_{22}$: C, 93.85; H, 6.15. Found: C, 93.61; H, 6.00.

Dibenzoylanthraquinone. Oxidation of 1 g. of the dibenzylanthracene with 4 g. of chromic anhydride, 28 ml. of glacial acetic acid, and 4 ml. of water gave 1.09 g. (98.1%) of dibenzoylanthraquinone which melted at 241–242° (from 95% ethanol).

Anal. Calcd. for $C_{28}H_{16}O_4$: C, 80.70; H, 3.85. Found: C, 80.47; H, 3.61.

The reaction of toluene with carbon monoxide and hydrogen chloride in the presence of aluminum chloride at 60°. Toluene (60 ml.) was saturated for 1 hr. with dry hydrogen chloride gas. This toluene and 25 g. of aluminum chloride were treated with carbon monoxide at 50 p.s.i. and 60°. The mixture was agitated for 12 hr. The reaction mixture was worked up in the usual way and gave no aldehyde. The solid material weighed 4.7 g. from which 1.10 g. of dimethylanthracene were obtained.

The reaction of toluene with carbon monoxide in the presence of aluminum chloride at 30°. Toluene (60 ml.) and 25 g. of aluminum chloride were treated with carbon monoxide as previously described. The reaction mixture was agitated for 12 hr. at 30°. The distillate from the steam distillation was positive to the Schiff reagent. The organic layer was separated and treated with saturated aqueous sodium bisulfite. The solid formed was removed by filtration, dried, and decomposed with concentrated hydrochloric acid. *p*-Tolualdehyde (3.86 g., 0.032 mol.) was recovered. The 2,4-dinitrophenylhydrazone melted at 233–235°, lit.[10] m.p. 232–234°.

The solid from the steam distillation was removed by filtration, dried, and sublimed under vacuum (1 mm.). Crystallization from ligroin gave 0.7 g. of dimethylanthracene, m.p. 223–225°.

The same reaction carried out at 40° gave 0.1 g. of *p*-tolualdehyde and 2.1 g. of dimethylanthracene. At 50°, 0.1 g. of aldehyde and 2.7 g. of dimethylanthracene were obtained.

The reaction of diphenyl ether and carbon monoxide with aluminum chloride. Diphenyl ether (60 ml.) and aluminum chloride (25 g.) were shaken at 80° for 16 hr. with carbon monoxide at 50 p.s.i. Steam distillation gave first unchanged diphenyl ether and later white crystals of xanthydrol. The xanthydrol was removed by filtration and weighed 2.1 g. It melted at 120–122°, lit.[10] m.p. 121°. The dixanthyl urea derivative melted at 260–261°, lit.[10] m.p. 260°.

The reaction of p-xylene and carbon monoxide with aluminum chloride. *p*-Xylene (60 ml.) and aluminum chloride (25 g.) were shaken at 60° for 16 hr. with carbon monoxide at 50 p.s.i. The solid remaining after steam distillation weighed 16.00 g. Vacuum sublimation gave 8.5 g. of a tetramethylanthracene which melted at 268–269° (from ligroin b.p. 60–90°). Ellison and Hey[4] have prepared 1,4,5,8-tetramethylanthracene, m.p. 270°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.37; H, 7.63. Found C, 92.16; H, 7.45.

Absorption spectra. The ultraviolet absorption spectra

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were carried out in spectra grade cyclohexane with a Beckmann Model DU spectrophotometer.

The values for maxima and minima of the anthracenes are in good agreement with the proposed effects of groups.[11] The dimethyl and tetramethylanthracenes show a bathochromic effect with some loss of fine structure, with respect to anthracene. Dibenzylanthracene shows a fine structure effect, with a hyperchromic shift, no loss in fine structure and no bathochromic shift.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY]

N-Alkylation of Nitriles with Benzyl Alcohol, Related Alcohols, and Glycols[1]

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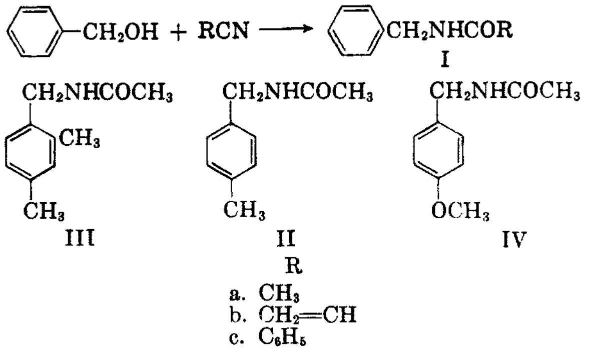
Nitriles are readily *N*-alkylated under mild conditions with primary alcohols related to benzyl alcohol and with glycols of the di(hydroxymethyl)benzene type to give good yields of *N*-aralkylamides and *N,N'*-bisaralkylamides, respectively.

In the reaction of nitriles with olefins and alcohols,[2,3] ethers,[4] esters,[5] and halides,[6] the alkylating compound is ordinarily restricted to those which can form a secondary or tertiary carbonium ion in an acidic medium.[7] An exception may be noted in the case of the primary halides which are known to form *N*-substituted nitrilium complexes with nitriles in the presence of Lewis acids.[8] Recently, Lora-Tamayo, Madronero, and Munoz reported that nitriles may be alkylated with β-phenylethyl chloride in the presence of stannic chloride to give derivatives of dihydroisoquinoline.[9] However, it has been asserted that primary alcohols are unreactive toward nitriles notwithstanding recourse to prolonged reaction times, elevated temperatures, and the use of fuming sulfuric acid as catalyst.[3c]

It was therefore noteworthy to observe in this laboratory that primary alcohols and glycols of the aralkyl type were condensed smoothly with nitriles under mild conditions to give *N*-aralklyamides and *N,N'*-bisaralkylamides in good yields. Thus, careful addition of benzyl alcohol to a large excess of acetonitrile containing substantial proportions of sulfuric acid resulted in a spontaneous reaction at 5–30° which afforded *N*-benzylacetamide[10] (Ia) in good yield. *N*-Benzylacrylamide[11] (Ib) was prepared from acrylonitrile, and, in similar manner, *N*-(4-methylbenzyl)acetamide[12] (II), *N*-(2,4-dimethylbenzyl)acetamide[13] (III), and *N*-(4-(methoxybenzyl)acetamide[14] (IV) were prepared



from the corresponding alcohols (Table I). The reaction was readily extended to glycols of the arenedimethanol type to produce several new difunctional amides. The reaction of 4,6-dimethyl-1,3-di(hydroxymethyl)-benzene with excess acetonitrile afforded *N,N'*-diacetyl-4,6-dimethyl-1,3-di(amino-

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