tion of the State University of New York. The author also wishes to express his thanks to the Foundation for a Summer Research Fellowship.

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STATE UNIVERSITY OF NEW YORK
NEW YORK STATE COLLEGE FOR TEACHERS
ALBANY, N. Y.

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(1) C. D. Gutsche, *Org. Reactions*, **VIII**, 364 (1954).

(2) A. H. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

(3) The molar quantities were chosen to give a slight excess (about 10%) of the diazoalkane (based on the average yields of diazoalkane given by Wilds and Meader[2]). In an experiment conducted by Mr. E. Otremba in these laboratories, it was established that 3-pentanone does not react with etheral diazoethane at room temperature. Thus, it was assumed that the ketonic product would not react with excess diazoalkane. A polar solvent is evidently necessary to promote the reaction of acyclic ketones with diazoalkanes (ref. 1, p. 375).

Reaction of Aluminum Phenoxide with Nitriles

H. W. JOHNSTON

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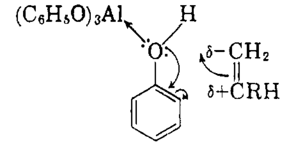
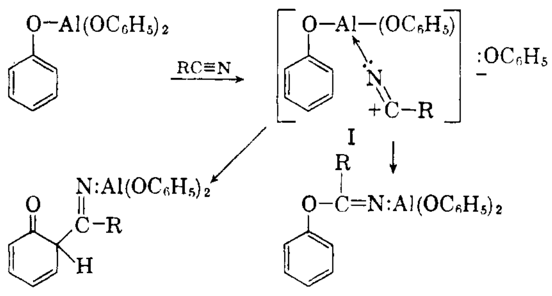
In a previous report it was shown that the cyanoethylation of phenol in the presence of anhydrous aluminum chloride and dry hydrogen chloride gave a small amount of the *ortho-* addition product, the δ-lactone of β-(*o*-hydroxyphenyl) propionic acid.[1] Our interest in the possibility of increasing the yield of this *ortho-* isomer was prompted by the work of Kolka, Napolitano, and Ecke, who found that alkylation of the phenolic salt of aluminum with alkenes at temperatures of 240° to 320° and pressures of 200 to 800 p.s.i. gave unusually high yields of *ortho-* alkylated products.[2] However, in our laboratory when acrylonitrile and aluminum phenoxide were caused to react together under similar conditions, a resin was obtained as the principal reaction product, and neither dihydrocoumarin nor *p*-hydroxyphenylpropionitrile were isolated. An infrared spectral examination of the resin showed that the cyano-group had completely disappeared, and strong aromatic carbonyl bands appeared, indicating that, under these relatively severe reaction conditions, polymerization of the olefin had taken place with considerable cross linking of the resin through the formation of carbonyl groups linked to the aromatic ring. Bands corresponding to both *ortho-* and *para-* substitution were noted. That cross linking of the polymer took place in a Hoesch-type reaction of the nitrile was confirmed in an experiment in which acetonitrile was substituted for acrylonitrile in the reaction with aluminum phenoxide. *o*-Hydroxyacetophenone and *p*-hydroxyacetophenone were recovered in yields of 3 and 4%, respectively based upon equivalents of aluminum consumed.

In the alkylation of phenol with ethylene or propylene the suggestion is advanced that a cyclic concerted mechanism operates, in which aluminum phenoxide is coordinated with excess phenol with simultaneous attack of the olefin upon the *ortho-* position of the benzene ring:[2]



However, this mechanism as constructed here implies an electron shift toward the ring though opposed by both the coordination of aluminum and the proton of phenol. A suggested mechanism more applicable to the aluminum phenoxide-nitrile system might be the displacement of a phenoxide ion from aluminum phenoxide by the nitrogen atom and its electron pair. An attack is then possible upon the *ortho-* position of the new phenoxide complex (I) to give an *ortho-* substituted dienone (II) or, alternately, upon the oxygen atom of the displaced phenoxide ion to form an imidic ester complex (III). Cleavage of the latter would permit amidation of the *para-* position of phenol.



II III

An interesting study of the Fries rearrangement parallels the above suggestion. Cullinane and Edwards[3] have studied the rate of rearrangement of substituted phenyl acetates and have found that the kinetics were consistent with a mechanism which assumes the displacement of the acyl group from the oxygen atom by a second mole of catalyst. The acyl carbonium ion attack upon the *ortho-* or *para-* position of the phenolic moiety is said to be irreversible, contrary to the results obtained by Rosenmund and Schnurr.[4]

Finally, in some experiments with aluminum phenoxide and ethyl acrylate a small amount of β-phenoxypropionic acid was isolated indicating

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(1) H. W. Johnston and F. J. Gross, *J. Org. Chem.*, **22**, 1264 (1957).

(2) H. J. Kolka, J. P. Napolitano, and G. Ecke, *J. Org. Chem.*, **21**, 712 (1956).

(3) W. M. Cullinane and B. F. R. Edwards, *J. Chem. Soc.*, 434 (1958) and *J. Chem. Soc.*, 3016 (1957).

(4) K. W. Rosenmund and W. Schnurr, *Ann.*, **460**, 56 (1928).

the definite possibility of 1,4-addition of phenoxide ion to the acrylic ester. Also, in the presence of diphenyl ether as a solvent instead of excess phenol, phenyl acrylate was isolated in 20% yield based on consumed phenol. This ester-interchange reaction tends to support the proposal that in the analogous reaction of aluminum phenoxide and acrylonitrile the nitrilo-group displaces phenoxide ion from the aluminum complex.

EXPERIMENTAL

Reaction of acetonitrile with aluminum phenoxide. Eighteen g. (0.67 mole) of aluminum turnings was added in small portions over a period of 3 hr. to 184 g. (2 moles) of freshly distilled phenol held at 172–185° under an atmosphere of nitrogen gas. The addition of aluminum metal was carried out conveniently in glass apparatus until a temperature of 185° was noted for the molten mass, at which time it was transferred to a 1-l. stainless steel bomb. The bomb was heated to 195° with the remaining aluminum until no more phenol was lost through the vent.

The bomb was cooled to room temperature and opened. Eighty-two g. (2 moles) of freshly distilled acetonitrile was added and the bomb-head replaced. Air was purged from the bomb by means of nitrogen after which the reaction mixture was heated to 185° with constant mechanical shaking for a period of 6 hr. A maximum pressure of 115 p.s.i. was noted. Heating and shaking were continued for an additional 2 hr. at 220° and 165 p.s.i., after which the bomb was cooled to room temperature and opened. The mixture, consisting of a watery liquid and a brittle crystalline solid, was poured over 1 kg. of cracked ice containing 150 ml. of concentrated hydrochloric acid (*d*, 1.2). (Two g. of unreacted aluminum was recovered at this point.)

The organic phase was separated and steam-distilled. The distillate was shaken with sodium chloride and the oils were recovered by extraction with three 50-ml. portions of toluene. The hydrocarbon solution was washed three times with 50-ml. portions of saturated sodium chloride, separated, and distilled through a 100-cm. modified Claisen column. One hundred and thirty g. of phenol (0.57 mole) was recovered at 89° and 24 mm. after which the residue was transferred to a Claisen flask of 10 ml. capacity. Three g. (0.04 mole) of colorless liquid was recovered at 95–99° at 18 mm. which was identified as *o*-hydroxyacetophenone (oxime, m.p. 114–116° uncorr., which is in agreement with the literature).[5]

The residual tar which was involatile in steam was taken up in ether and separated from the aqueous phase. Benzene was added and the solvents distilled until a thick oil was obtained. A small amount of hot 3:1 alcohol-benzene mixture was added and crystallization took place upon standing in an ice chest. Seven g. (0.05 mole) of *p*-hydroxyacetophenone, m.p. 104–106°, was obtained.[6]

Reaction of acrylonitrile with aluminum phenoxide. In a procedure similar to that described for acetonitrile and aluminum phenoxide, 9 g. (0.37 mole) of aluminum turnings was caused to react with 282 g. (3 moles) of phenol at 170–172° under nitrogen. Since an excess of phenol was present as a solvent it was unnecessary to transfer the mixture to the bomb until all the aluminum has been dissolved. Fifty-three g. (1 mole) of freshly distilled phenol was added and the mixture was held with continual shaking at 172–180° for 9 hr. From the dark red oil 177 g. (1.2 moles) of phenol was recovered and a viscous dark brown resin remained which was undistillable.

Examination of the infrared spectrum of a resin-potassium bromide-pellet showed practically complete disappearance of the nitrile bond at 2251 cm.$^{-1}$ and the appearance of strong aromatic ketone bands at 1578, 1641, 1223, and 1169 cm.$^{-1}$

Reaction of ethyl acrylate with aluminum phenoxide. In a procedure similar to that employed for the reaction of phenol and acrylonitrile 282 g. (3 moles) of phenol, 9.0 g. (0.37 mole) of aluminum turnings and 900 g. of ethyl acrylate gave a yellow oil from which ethyl acrylate and phenol were removed by distillation. The residue consisted of rubbery red crumbs. Extraction with toluene followed by vacuum stripping of this solvent gave 9 g. of a tan fusible residue, which was recrystallized from hot water to a melting point of 85–93°. Further recrystallization from benzene gave needles of β-phenoxyproprionic acid, m.p. 93–96°,[7] identified by conversion into the semicarbazone of 4-chromanone, m.p. 223–226°. Louden and Razden[8] report a melting point of 227° for this derivative.

In a second experiment, 18 g. (0.67 mole) aluminum turnings was caused to react with 184 g. (2 moles) of phenol in 75 ml. of diphenyl ether. Two hundred g. (2 moles) of ethyl acrylate was added to the salt and held at 175–182° for 11 hr. under pressures of 40 to 60 p.s.i. Decomposition of the reaction mixture in acid followed by isolation of distillable products as described above gave 52 g. (0.35 mole) of phenyl acrylate, b.p. range, 65° at 15 mm. to 71° at 14 mm. Redistillation of this fraction at ordinary pressures gave a product of b.p. 106–168° at 712 mm., sp. gr., 0.975 20°/4°. Infrared analysis showed strong bands at 1610, 1590, 1500, 1480, 1300, 1240, 1180, 1120, 1050, 690 cm.$^{-1}$ A ferric chloride test was negative; bromine was strongly absorbed.

In addition, 24 g. of phenol was recovered to complete recovery of the diphenyl ether. A gelatinous material, presumably polyethyl acrylate and its cross-linked phenolic derivatives, was noted.

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WHITWORTH COLLEGE
SPOKANE, WASH.

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(6) E. M. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds, Order I*, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 229.

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(8) J. D. Louden and R. K. Razden, *J. Chem. Soc.*, 4289 (1954).

An Attempted Synthesis of Dipyrazolo[*def*, *qrs*]flavanthrene-8,16-dione

W. L. MOSBY AND W. L. BERRY

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Fusion of pyrazolanthrone (I) with alkali produces a dye known as "pyrazolanthrone yellow," for which, at one time, structure II was proposed.[1]

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