

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, RESEARCH DIVISION, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Extensions of the Willgerodt Reaction. II

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The Willgerodt reaction has been extended to include a series of alkyl substituted aromatic hydrocarbons. Amides were obtained, but the carbon skeleton was altered in certain cases. The reaction was also carried out on benzyl chloride.

Discussion

In a previous paper we discussed the extension of the Willgerodt reaction to certain unsaturated aliphatic hydrocarbons and *n*-butylamine.¹ This work led us to believe that alkyl substituted aromatic hydrocarbons might also lend themselves to this reaction.

It is known that small amounts of H₂S are formed when sulfur is heated with materials such as toluene and that under vigorous conditions thiophene derivatives are formed.²

This suggests the possible formation of sulfuretted materials from alkyl substituted aromatics which might react further to give amides in the Willgerodt system.

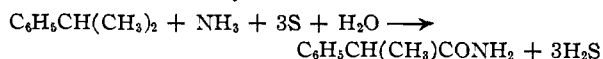
Isopropylbenzene was chosen for initial study since it contains a tertiary hydrogen atom which should be quite susceptible to attack by sulfur. Reaction was accomplished at 235°. The reaction was then extended to other alkylated benzenes. Table I lists the hydrocarbons investigated and approximate yields to the products listed.

TABLE I

COMPOUNDS EXAMINED IN THE WILLGERODT REACTION

Reactant	Product	Approx. yield to amide (mole %)
Toluene	Benzamide	15-20
Isopropylbenzene	Benzamide + phenylacetamide + α -phenylpropionamide	20
Ethylbenzene	Benzamide + phenylacetamide	20
<i>p</i> -Xylene	Terephthalamide + benzamide	10-20
Benzyl chloride	Benzamide	60

The stoichiometry of the reaction is



Although the Willgerodt reaction classically does not alter the carbon skeleton of the reactants, such was not the case with alkyl substituted aromatics. The conditions used in these cases were quite vigorous (235-320°), and the degraded products represented removal of single carbon atoms from the side chain. Thus, the isolation of α -phenylpropionamide, phenylacetamide and benzamide from reaction of isopropylbenzene suggests degradation by loss of single carbon atoms. Whether this occurred by decarboxylation of hydrolyzed amide or whether C-C cleavage occurred before amide formation, is not clear; however, it was established that higher temperatures caused greater alteration in the carbon skeleton.

(1) M. A. Naylor and A. W. Anderson, *THIS JOURNAL*, **75**, 5392 (1953).

(2) M. M. L. Aronstein and A. S. Van Nierop, *Rec. trav. chim.*, **21**, 448 (1902).

No attempt was made to establish optimum reaction conditions or to determine accurate yields on the systems where mixed amides were obtained. Emphasis was placed on identification of reaction products in these cases, and generous losses were incurred during the fractional crystallization procedures used. In all cases considerable quantities of unreacted hydrocarbons were recovered so ultimate yields should be much higher than reported in Table I. Reaction on materials such as benzyl chloride might well be expected to take place in view of the ease of either hydrolysis or attack by sulfur at the chlorine atom.

Experimental

Equipment.—The equipment used in this work was the same as that described in the previous paper.¹

Reaction with Toluene.—A mixture of 46 g. of toluene (0.5 mole), 64 g. (2 moles) sulfur and 150 ml. of concentrated aqueous ammonia (2.2 moles) reacted for 2 hours at 250-260°. The initial pressure of 95 atm. rose to 130 atm. After cooling and bleeding off H₂S, the product consisted of two layers. The upper layer contained mainly unreacted toluene (*ca.* 20 g.) and on evaporation gave 4 g. of crystallized product plus some sulfur. The lower aqueous layer contained 5 g. of solid recovered by filtration.

After several recrystallizations and charcoal treatment in water, white crystalline benzamide was obtained with m.p. 115-120°. Further recrystallization from benzene gave benzamide with m.p. 125°, lit. 128°, mixed m.p. 125°.

Anal. Calcd. for C₇H₇NO: N, 11.56. Found: N, 11.53, 11.46.

Reaction with Isopropylbenzene.—A mixture consisting of 60 g. of isopropylbenzene (0.65 mole), 64 g. of sulfur (2 moles) and 150 ml. of concentrated aqueous ammonia (2.2 moles) was run at 235-245° for one hour. Pressure rose from 81 to 102 atm. The product was obtained in two layers containing some solid which was filtered off. This was combined with 5 g. of solid obtained upon the evaporation of unreacted isopropylbenzene from the upper layer. The total crude amide represented about 20% conversion of isopropylbenzene to mixed amides.

The crude solid was dissolved in benzene, treated with charcoal, cooled to 25° and filtered. The crystals so obtained softened at 110° and melted at 128°. Fractional crystallization of this solid from benzene (*ca.* 4 g. in 50-60 ml.) gave two crops of crystals on filtration at 40° and on further cooling the filtrate to 15°.

Another recrystallization from benzene of the less soluble material with filtration at 50° gave white, crystalline phenylacetamide, m.p. 153-154°, lit. 155°.

Anal. Calcd. for C₈H₉NO: N, 10.37. Found: N, 10.51, 10.51.

The second more soluble crop of crystals obtained on cooling to 15°, mentioned above, melted at 102-103°. The filtrate from these crystals was evaporated to 5 ml. giving white α -phenylpropionamide which melted at 94°, lit. 92°.

Anal. Calcd. for C₉H₁₁NO: N, 9.39. Found: N, 9.57.

In a second run made as above but at 250-260° for 2 hours a final pressure of 238 atm. was observed. The solid filtered directly from the two-layer reaction product was recrystallized five times in benzene and gave benzamide crystals with m.p. 126°.

Anal. Calcd. for C₇H₇NO: C, 69.39; H, 5.82; N, 11.56. Found: C, 69.26, 68.92; H, 6.08, 6.19; N, 11.60, 11.70.

The benzene filtrate from recrystallization contained more soluble material presumed to be a mixture of phenylacetamide and α -phenylpropionamide.

Reaction with Ethylbenzene.—When a mixture of 53 g. of ethylbenzene (0.5 mole), 64 g. of sulfur (2 moles) and 150 ml. of concentrated aqueous ammonia (2.2 moles) was heated at 250–260° for 2 hours, the initial pressure went from 115 to 225 atm. The solid filtered directly from the reaction mixture was recrystallized and decolorized with charcoal in water. This product, 11.7 g., melted from 106–111° and contained 11.3% nitrogen—a value suggesting a mixture of benzamide (11.56% N) and phenylacetamide (10.37% N).

Reaction with *p*-Xylene.—This reaction was carried out to see whether a diamide could be prepared. A mixture of 26 g. of *p*-xylene (0.5 mole), 64 g. of sulfur (2 moles) and 150 ml. of aqueous ammonia (2.2 moles) was treated at 300° for one hour. A light yellow solid was filtered from the reaction mixture which was insoluble in boiling water. The solid weighed 10.5 g. after being extracted three times with boiling, 200-ml. portions of water. Further extraction of the solid (8 times with a total of 200 ml. of boiling carbon disulfide) yielded 8.0 g. of tan-colored product. This material did not melt below 260°, gave off NH₃ when warmed with caustic and compared with terephthalamide as follows:

Anal. Calcd. for C₈H₈N₂O₂: C, 58.53; H, 4.91; N, 17.05. Found: C, 58.52, 58.81; H, 4.90, 5.31; N, 16.63, 16.72.

For further identification of the above product as terephthalamide, 2.00 g. of the material was boiled 1 hour with 30 ml. of 20% sodium hydroxide. Dilution of the resulting slurry to 100 ml. gave a yellow solution containing a trace of black solid. Decolorization with charcoal resulted in a

colorless solution from which a white solid was filtered after acidifying with concd. HCl. This precipitate was boiled with water, filtered, and washed several times with water and methanol. The solid product (1.98 g.) compared with terephthalic acid as follows:

Anal. Calcd. for C₈H₆O₄: C, 57.77; H, 3.64. Found: C, 58.08, 58.12; H, 3.71, 3.80.

The filtrate from the original reaction mixture was combined with the 500 ml. of water used to extract and wash the terephthalamide. Evaporation to dryness on a steam-cone gave 53.8 g. of dark yellow solid. Two extractions of this material with 300 ml. of boiling water left 24.1 g. of sulfur. Cooling of this filtrate to 0° gave a total 2.1 g. of tan solid which did not melt below 300° and was not characterized further.

Reaction with Benzyl Chloride.—One-half mole of benzyl chloride (63.3 g.) was treated as above at 190° for 3.75 hours. The product was evaporated to dryness. The residue was extracted three times with hot water, and 35.2 g. of benzamide was obtained on crystallization from the water. After several recrystallizations from water, the product melted at 125–126°.

Anal. Calcd. for C₇H₇NO: N, 11.56. Found: N, 11.61.

We plan to publish data on the application of the Willgerdt reaction to saturated aliphatic hydrocarbons in a future paper.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Low Temperature Halogenation of Isobutylenes

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The direct chlorination of pure methylenecyclohexane (I) in the presence of anhydrous sodium bicarbonate at 0° has been examined. Two products, 1-chloromethylcyclohexene (II) and 1-chloromethyl-1-chlorocyclohexane (III), were isolated in yields of 38–48% and 12–19%, respectively. A cyclic transition state is proposed for the formation of the allylic monochloride and an ionic mechanism for the dichloride. Bromination of methylenecyclohexane gives the simple addition compound (XVII) as the major product.

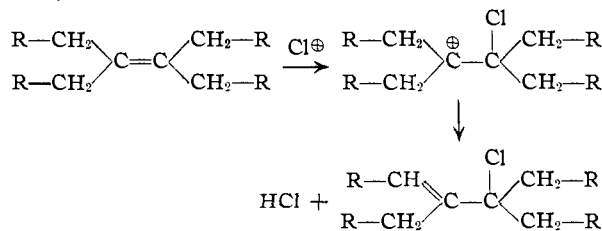
That simple olefins can react with chlorine to give substitution products was first observed by Sheshukov,² but for fifty years this reaction received little attention.

Tishchenko,³ as a result of an extensive investigation, proved that the chlorine atom of the allylic chloride so formed is bonded directly to one of the original unsaturated carbon atoms of the olefin molecule and that a shift of the carbon-carbon double bond takes place.

The chlorination of isobutylene and related hydrocarbons is now carried out on a commercial scale, and the reaction has received a great deal of attention in the research laboratories of the Shell Development Company.⁴

In a recent paper, Taft⁵ has given an excellent bibliography, has summarized the evidence which serves to exclude a radical mechanism, and has

proposed a two-step mechanism for the chlorination, as follows.



It is generally accepted that the first and rate-determining step in the reaction of many A-B type molecules with olefins involves the addition of an active cation to the double bond. In such reactions with α - and β -pinene, a Wagner-Meerwein rearrangement occurs, and products having a camphane skeleton are produced. Thus, with each of these terpenes, hydrogen chloride yields⁶ bornyl chloride (IV), and α -pinene reacts with bromine to give 2,6-dibromocamphane (V).⁷

(6) J. L. Simonsen, "The Terpenes," Vol. II, Cambridge Univ. Press, Cambridge, 1949, pp. 170 and 202.

(7) J. L. Simonsen, ref. 6, p. 168.

(1) Taken from the Ph.D. Thesis of William W. Lee, July, 1952.

(2) Sheshukov, *J. Russ. Phys. Chem. Soc.*, **16**, 478 (1884).

(3) D. V. Tishchenko, *J. Gen. Chem. (U.S.S.R.)*, **3**, 1326 (1938); *C. A.*, **33**, 4190 (1939).

(4) J. Burgin, W. Engs, H. P. A. Gross and G. Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939).

(5) R. W. Taft, Jr., *THIS JOURNAL*, **70**, 3364 (1948).