Certain salts and derivatives of the resulting hydroxy and amino esters were prepared.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Studies in the Rearrangements of Phenyl Ethers. The Action of Aluminum Chloride on Butyl Phenyl Ethers

BY RICHARD A. SMITH

The action of aluminum chloride on phenyl ethers has been studied extensively; this reaction is now reasonably clear and is known as the Fries migration.[1]

The isomerization of phenyl ethers to substituted phenols has received but little study; the two rearrangements appear, at the present time, to have many characteristics in common. There are undoubtedly many recorded instances of reactions in which phenyl ether isomerization took place due to the presence of an aluminum chloride catalyst. The transitory nature of the ether in most cases prevented the observation of the rearrangement as such. In 1892 Hartmann and Gattermann[2] in utilizing the action of aluminum chloride at elevated temperatures to hydrolyze phenyl ethers to phenols and alkyl halides noticed, in one case, the formation of a small quantity of a substituted phenol. This will be referred to in greater detail later. Ether rearrangements with the aid of aluminum chloride have been reported by Huston.[3] The author has reported the synthesis of thymol and an isomer by the catalytic isomerization of isopropyl *m*-cresyl ether with aluminum chloride.[4]

In this communication it is desired to show extensions of the method to rearrangements of different types of alkyl phenyl ethers. Ethers in which the carbon atom of the alkyl group attached to the ether oxygen was, respectively, primary, secondary and tertiary were studied. The three butyl ethers, iso, secondary and tertiary, were selected. A second purpose is to attempt to clarify contradictory evidence in the literature pertaining to para iso and tertiary butyl phenols.

The first purpose of the report was fulfilled by synthesizing the three designated butyl phenyl ethers in a conventional manner. The isobutyl phenyl ether has been prepared previously.[2,5]

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(1) Kraenzlein, "Aluminiumchlorid in der organischen Chemie," Verlag Chemie, G. m. b. H., Berlin, 1932.

(2) Hartmann and Gattermann, *Ber.*, **25**, 3531 (1892).

(3) R. C. Huston, Indianapolis Meeting of the American Chemical Society, 1931.

(4) Smith, THIS JOURNAL, **55**, 849 (1933).

(5) Riess, *Ber.*, **3**, 780 (1870); Bamberger, *ibid.*, **19**, 1820 (1885); Perkin, *J. Chem. Soc.*, **69**, 1250 (1896); Senkowski, *Ber.*, **24**, 2974 (1891).

The three ethers were treated in the cold with anhydrous aluminum chloride and the reaction products isolated and identified as substituted phenols.

Hartmann and Gattermann in reporting the small quantity of substituted phenol they obtained from isobutyl phenyl ether state it to be *p*-isobutylphenol. The melting point they cite is in agreement with that in the literature for *p*-isobutylphenol. Kraenzlein[1] in commenting on their work states that the action is a splitting off of isobutylene and readdition of this compound and phenol to yield *p*-tertiary-butylphenol. The compound prepared by Hartmann and Gattermann is reported as the tertiary product in Beilstein's "Handbuch." The situation is complicated by the data appearing in the literature concerning the two phenols in dispute. The methods of synthesis of *p*-tertiary-butylphenol leave but little doubt as to its structure.[6]

Senkowski and earlier workers[7] have reported the synthesis of *p*-isobutylphenol from the action of zinc chloride on isobutyl alcohol and phenol. The product so prepared has physical constants almost identical with those of the tertiary derivative. Senkowski notes this. Evidence of this communication, and earlier ones, indicates that the isobutylphenol has never been prepared, the product being tertiary-butylphenol.

The experimental evidence of the present communication indicates that both tertiary and isobutyl phenyl ether isomerize to the same product, *p*-tertiary-butylphenol. This is an agreement with the experimental results of the previous workers but not with their conclusions. The present findings support the mechanism of Kraenzlein. The fact that isobutyl phenyl ether leads to a tertiary-butylphenol strongly indicates the need of a mechanism involving scission of the ether with readdition of the subsequent products. The apparent necessity for such a mechanism in this one case does not prove that all such reactions are not intramolecular, as it is conceivable that a compound may change to an isomer, with a decrease in free energy, by more than one path. The mechanism of these isomerizations is at present under further study.

Secondary-butyl phenyl ether was found to rearrange to *p*-secondary-butylphenol, which has been previously prepared.[8]

The behavior of tertiary-butyl phenyl ether is worthy of note. This compound isomerizes very readily to *p*-tertiary-butylphenol by the application of heat alone. It cannot be distilled at atmospheric pressure without rearrangement taking place. The pyrolysis of this ether is described.

Experimental

Preparation of the Ethers.—The phenyl ethers were prepared by the action of the alkyl bromides on a solution of sodium phenolate in alcohol. An equivalent of sodium

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[6] Studer, *Ber.*, **14**, 1474 (1881); *Ann.*, **211**, 242 (1882); Senkowski, *Ber.*, **23**, 2418 (1890); Gurewitsch, *ibid.*, **32**, 2428 (1895); Lewis, *J. Chem. Soc.*, **83**, 329 (1903).

[7] Senkowski, *Ber.*, **24**, 2974 (1891); Liebmann, *ibid.*, **14**, 1842 (1881); **15**, 150 (1882).

[8] Estreicher, *ibid.*, **33**, 442 (1900).

was added to excess alcohol; an equivalent of phenol was added to the clear solution so obtained. An excess of the alkyl halide was then added and the whole refluxed for six to eight hours. In the case of the tertiary butyl derivative the time of refluxing was shortened to twenty minutes to minimize isomerization. The excess alcohol and alkyl halide were removed by evaporation, the sodium bromide was washed out with water, the phenolic compounds were removed with 15% sodium hydroxide solution, and the remaining organic material was water-washed, dried and distilled. The yields of the isobutyl and secondary butyl ethers ranged from 80–90%. The yields of the tertiary-butyl phenyl ether were poor. The analytical data and physical properties of these compounds appear in Table I. The tertiary-butyl product was obtained as long white needles insoluble in 15% potassium hydroxide, and with no action on aqueous or alcoholic ferric chloride. The product was recrystallized from benzene. The pure recrystallized product melted under water. Due to rearrangement to the phenol, no accurate melting point could be determined. Prolonged heating in the melting point tube gave the melting point of the *p*-tertiary-butylphenol.

Catalytic Rearrangement of the Ethers.—Each ether was rearranged to the phenol by allowing it to stand a few days at room temperature with an equal weight of aluminum chloride. The catalyst was always added to the ether in small portions with external cooling. The aluminum chloride in each case dissolved in the ether with the formation of a viscous dark red mass. After standing, the products were decomposed with ice, water and hydrochloric acid. The organic products were separated, water-washed and extracted with 15% potassium hydroxide. The quantity of unrearranged ether was always very small. The alkaline solutions were neutralized with hydrochloric acid. The product from secondary-butyl phenyl ether was a liquid which was purified by distillation. The other two ethers yielded solid products which were purified by recrystallizations from water. Long white needles of the same melting point and the same mixed melting point were obtained. Yields were always in excess of 50%.

Pyrolytic Rearrangement.—The secondary and isobutyl phenyl ethers did not rearrange on ten hours of refluxing. Tertiary-butyl phenyl ether isomerized entirely to an alkali-soluble product on a few hours of refluxing. The boiling point rose from 192 to 230° in three hours. The product was recrystallized from water. The mixed melting points with the products obtained by catalytic ether rearrangement were identical.

TABLE I

BUTYL PHENYL ETHERS AND BUTYLPHENOLS

Sec-butyl phenyl ether has been rearranged to the phenol by means of a sulfuric–acetic acid rearranging mixture by Natelson (Ph.D. Thesis, N. Y. U., 1931) and Siegel (M.Sc. Thesis, N. Y. U., 1933). The product they obtained is the same as that reported here.

Phenyl ethers	Ref. index n_D^{24}	Density	B. p., °C.	Formula	Analyses, % Carbon	Analyses, % Hydrogen
				Calcd.:	80.0	9.3
(a) Isobutyl	1.4932	d^{24} 0.924	196	$C_6H_5OCH_2CH(CH_3)_2$	80.4	9.4
(b) *Sec*-butyl	1.4943	d^{21} .973	193	$C_6H_5OCH(CH_3)(C_2H_5)$	80.7	9.2
					80.1	9.8
(c) Tert-butyl	....	......	192	$C_6H_5OC(CH_3)_3$	79.9	9.8
P-*sec*-butylphenol	1.5182	d^{21} .986	236	$HOC_6H_4CH(C_2H_5)(CH_3)$	80.2	9.3
p-Tert-butylphenol						
(a) By the action of heat on *t*-butylphenol ether	....	......	230 (m. p. 100)	$HOC_6H_4C(CH_3)_3$	79.6	9.5
(b) By catalytic rearrangement of *t*-butyl phenyl ether	....	......	230 (m. p. 100)	$HOC_6H_4C(CH_3)_3$	79.4	9.4
(c) By catalytic rearrangement of isobutyl phenyl ether	....	......	230 (m. p. 100)	$HOC_6H_4C(CH_3)_3$	79.3	9.7

The author wishes to acknowledge his indebtedness to Miss R. T. Roth for the analyses performed.

Summary

1. Iso, secondary and tertiary-butyl phenyl ethers have been prepared and catalytically rearranged to phenolic compounds.

2. The rearrangement of tertiary-butyl phenyl ether by the action of heat has been described.

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Studies on the Rearrangement of Tertiary-butylmethylcarbinol (Pinacolyl Alcohol). II.[1] Dehydration

BY FRANK C. WHITMORE AND P. L. MEUNIER[2]

A primary alcohol containing the grouping R_3CCH_2OH can be dehydrated only with rearrangement.[3] On the other hand, a related tertiary alcohol, $R_3CC(OH)R_2$, is dehydrated mainly without rearrangement.[4] Conceivably a secondary alcohol, $R_3CCHOHR$, could be dehydrated either with or without rearrangement.[5] Until the present study, only rearranged products had been reported from the dehydration of such secondary alcohols.[1,6] The simplest of these alcohols, tertiaryl-butylmethylcarbinol, has been dehydrated by many workers.[7] The products obtained have been rearranged olefins, tetramethylethylene (b. p. 72°), and *unsym*-methylisopropylethylene (b. p. 54°). Previous work in this Laboratory has shown that the intermediate fraction, b. p. 65–67°, observed by some workers, is a mixture of the same two olefins.[1] The only preparations of the normal dehydration product, *tert*-butylethylene, have been made indirectly by the thermal decomposition of the xanthate of pinacolyl alcohol[8] and of the acetate.[1]

In the present work the pinacolyl alcohol was purified by repeated distillation and fractional crystallization and a large quantity was dehydrated at high pressure and temperature over a catalyst of phosphoric acid on silica gel. The usual rearranged olefins, tetramethylethylene and *unsym*-methylisopropylethylene, were obtained but, in addition, a small

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(1) Whitmore and Rothrock, THIS JOURNAL, **55**, 1106 (1933).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932); Whitmore and Church, *ibid.*, **55**, 1119 (1933).

(4) Whitmore and Laughlin, *ibid.*, **54**, 4011 (1932).

(5) Whitmore, *ibid.*, **54**, 3274 (1932).

(6) Whitmore and Houk, *ibid.*, **54**, 3714 (1932); Whitmore and Krueger, *ibid.*, **55**, 1528 (1933).

(7) See citations to literature in Ref. 1.

(8) Fomin and Sochanski, *Ber.*, **46**, 244 (1913).