carboxylation of the corresponding 1-phenylcycloparaffin - 1 - carboxylic acids. Of these, phenylcyclobutane has not previously been reported.

2. The preparation of 1-phenylcyclopentane and -cyclohexane-1-carboxylic acids and of 2-phenylhydrindene-2-carboxylic acid is described.

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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 Course of the Reaction in the Presence of Foreign Aromatic Bodies

BY RICHARD A. SMITH

The mechanism of the rearrangement of phenyl ethers to substituted phenols is still an open question despite some twenty years of study of the reaction. Discussions of possible mechanisms are to be found in publications of Claisen and Tietze,[1] Kursanoff,[2] Niederl and Storch,[3] and Sowa, Hinton and Nieuwland.[4]

In the present communication it will be shown that these rearrangements in the presence of anhydrous aluminum chloride appear to be intermolecular instead of intramolecular. The isomerizations of isopropyl phenyl and *p*-cresyl ethers, and isobutyl phenyl ether have been studied. Isopropyl phenyl ether isomerizes to mono- and di-isopropyl substituted phenol; when this ether was treated with aluminum chloride in the presence of a foreign aromatic compound, diphenyl ether, the yield of isopropylphenols was halved. The other products were *p*-isopropyl diphenyl ether and its isomer, the *o*-substituted ether. Similarly, isopropyl *p*-cresyl ether isomerizes to *o*-isopropyl-*p*-cresol; in the presence of diphenyl ether less of this product was obtained, and the substituted diphenyl ethers were again obtained. In the presence of benzene very little of the substituted phenol was obtained; instead a fair yield of cumene was observed. Isobutyl phenyl ether isomerizes to *p*-butylphenol; in the presence of benzene, however, the primary product was *t*-butylbenzene.

Experimental

Preparation of the Ethers.—The alkyl phenyl ethers were prepared by the same general method. An equivalent of sodium was added to excess ethyl alcohol (95%); an equivalent of the phenol was added to the resulting solution. A 10% excess of the appropriate alkyl bromide was then added and the whole refluxed for six hours. Excess of alkyl halide and alcohol were then removed by distillation on a steam-bath. The sodium bromide was washed out with water, and the phenolic compounds with 15% sodium hydroxide. The remaining material was water washed, dried with anhydrous sodium sulfate and purified by distillation. The yields varied from 80–90%. The ethers have been prepared by previous workers and the agreement in physical properties is satisfactory. The physical properties and references to earlier preparations are listed in the table.

Rearrangement of the Ethers.—Each phenyl ether was rearranged to the corresponding substituted phenol with anhydrous aluminum chloride. To one mole of the ether in a round-bottomed flask surrounded by a cooling bath was added in small portions one mole of aluminum chloride. The heat generated was absorbed by the external cooling bath of cold water. The whole was then allowed to stand for twenty-four hours at room temperature. Hydrolysis was accomplished by pouring the resulting viscous mass on chopped ice; hydrochloric acid was used to complete the hydrolysis and to keep the aluminum in solution. The organic products were separated, water washed, and extracted with 15% sodium hydroxide. The quantity of unrearranged ether was always small. The alkaline solution was neutralized with hydrochloric acid and the organic liquid which separated removed, washed with water, dried with anhydrous sodium sulfate, and purified by distillation. In each case the resulting phenol, or phenols, has been prepared previously and the agreement in physical properties is satisfactory. The physical properties and references to former preparations appear in the table.

Rearrangements in the presence of a foreign aromatic body were performed in a similar manner. The aluminum chloride was added to a solution of the alkyl phenyl ether in benzene or diphenyl ether. The subsequent working up of products was the same except that the alkali insoluble liquid was also worked up. This was water washed, dried with anhydrous sodium sulfate and separated into its components by fractional distillation. In one case two solid products were obtained; di-*t*-butylbenzene, which was distilled and recrystallized from alcohol; and tri-*t*-butylbenzene, which remained as a residue upon distillation and was recrystallized from alcohol. All products obtained, except two, have been previously obtained and the agreement in physical properties is satis-

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(1) Claisen and Tietze, *Ber.*, **58**, 275 (1925).

(2) Kursanoff, *J. Russ. Phys.-Chem. Soc.*, **46**, 815 (1914); *C. A.*, **9**, 1753 (1915).

(3) Niederl and Storch, THIS JOURNAL, **55**, 284 (1933).

(4) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933).

PHYSICAL CONSTANTS AND ANALYSES OF THE COMPOUNDS PREPARED

Compound	Formula	B. p., °C.	Sp. gr.	n_D
Isopropyl phenyl ether[1,2]	$C_6H_5OCH(CH_3)_2$	178	0.978_{20°	1.4992_{20°
Isopropyl *p*-cresyl ether[1,2]	$CH_3C_6H_4OCH(CH_3)_2$	194	$.925_{20^\circ}$	1.4955_{20°
Isobutyl phenyl ether[3]	$(CH_3)_2CHCH_2OC_6H_5$	196	$.924_{24^\circ}$	1.4932_{24°
2-Hydroxy-1-isopropylbenzene[1,2]	$C_6H_4(OH)CH(CH_3)_2$	212–214	1.012_{20°	1.5315_{20°
4-Hydroxy-1-isopropylbenzene[2]	$C_6H_4(OH)CH(CH_3)_2$	223–225	0.990_{20°	1.5228
4-Hydroxy-1-methyl-3-isopropylbenzene[1,2]	$C_6H_3(OH)(CH_3)(CH(CH_3)_2)$	233–234	$.988_{20^\circ}$	1.5275_{20°
4-*t*-Butylphenol[3]	$C_6H_4(OH)C(CH_3)_3$	230 (m. p. 100°)	....	......
4-Isopropylphenyl phenyl ether[4]	$C_6H_5OC_6H_4CH(CH_3)_2$	288.90	1.041_{24°	1.5609_{24°
2-Isopropylphenyl phenyl ether[5]	$C_6H_5OC_6H_4CH(CH_3)_2$	263.4	1.053_{24°	1.5688_{24°
Isopropylbenzene	$C_6H_5CH(CH_3)_2$	154	0.859_{24°	1.4930_{25°
Tetiary butylbenzene[6]	$C_6H_5C(CH_3)_3$	166–168	$.868_{24^\circ}$	1.4942_{23°
1,4-Di-*t*-butylbenzene[6]	$(C_6H_4(C(CH_3)_3)_2$	238 (m. p. 76°)	....	......
1,4,6-Tri-*t*-butylbenzene[6]	$C_6H_3(C(CH_3)_3)_3$	(m. p. 128°)	....	......
2-Isopropylphenoxyacetic acid[1]	$C_6H_4(OCH_2COOH)CH(CH_3)_2$	(m. p. 130°)	....	......
2-Isopropyl-4-methylphenoxyacetic acid[1]	$C_6H_4(OCH_2COOH)(CH_3)CH(CH_3)_2$	(m. p. 128°)	....	......

(1) Niederl and Natelson, THIS JOURNAL, **53**, 1932 (1931).

(2) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3406 (1933).

(3) Smith, *ibid.*, **55**, 3720 (1933).

(4) Calculated for $C_{15}H_{16}O$: C, 84.9; H, 7.5. Found: C, 84.7; H, 7.9.

(5) Calculated for $C_{15}H_{16}O$: C, 84.9; H, 7.5. Found: C, 84.7; H, 7.0.

(6) Senkowski, *Ber.*, **23**, 2413, 2420 (1890).

factory; as before the properties and references to previous preparations appear in the table. The analysis of the two new compounds also appears.

The acetic acid derivatives were prepared by allowing molar quantities of the phenol and bromoacetic acid in a solution of 20% sodium hydroxide to stand for a few hours. The alkaline solutions were then acidified and the resulting products purified by recrystallization from 60% alcohol. The two derivatives so prepared are in agreement with those previously reported.

The general procedure has been outlined; the specific results will now be briefly described.

I. Isopropyl Phenyl Ether Rearrangements

(a) Isopropyl phenyl ether when treated with aluminum chloride yielded three alkali-soluble products; they consisted of *o*- and *p*-isopropylphenol, and di-isopropylphenol. A small quantity of higher boiling material was neglected. A one-third molar quantity yielded 65% of phenolic products of which 10% was di-isopropylphenol and 5% higher boiling material. The *p*-isomer predominated over the *o*-. The acetic acid derivative of the *o*- was prepared.

(b) The above reaction performed in the presence of a one-third molar quantity of diphenyl ether yielded the same products in a 30% yield. Free phenol in a 33% yield was obtained; this figure is not accurate due to loss of phenol by water washing. The alkali-insoluble materials were unreacted diphenyl ether and two mono isopropyl substituted diphenyl ethers, probably *o*- and *p*-. The yield of substituted diphenyl ethers accounted for the decreased quantity of isopropylphenols.

II. Isopropyl *p*-Cresyl Ether Rearrangements

(a) With aluminum chloride alone, a 70% yield of the *o*-substituted cresol was obtained. The acetic acid derivative was prepared.

(b) Isopropyl *p*-cresyl ether when treated with aluminum chloride in the presence of a three times volume of benzene yielded *p*-cresol as the predominant alkali-soluble material. The alkali insoluble material consisted of excess benzene, cumene and a small quantity of higher boiling materials; the yield of cumene was about 60%.

(c) Isopropyl *p*-cresyl ether was also rearranged in the presence of an excess of diphenyl ether. There was an 8–10% yield of the isomerization product, and about 40% of isopropyl substituted diphenyl ether. Some 50% of the ether was converted to *p*-cresol.

III. Isobutyl Phenyl Ether Rearrangements

The isomerization of this product to *p*-*t*-butylphenol has been described in a previous publication. In the presence of excess benzene the yield was only 5–6%, 70% of the ether being converted to *t*-butylbenzene and some di- and tri-*t*-butylbenzene.

Summary

1. Isopropyl phenyl ether has been isomerized to *o*- and *p*-isopropylphenol with aluminum chloride.

2. Isopropyl *p*-cresyl ether has been similarly isomerized to a substituted *p*-cresol.

3. The two isopropyl ethers when treated with aluminum chloride in the presence of diphenyl ether yield decreased quantities of substituted phenols, isopropyl substituted diphenyl ether being obtained instead.

4. Isopropyl *p*-cresyl ether and isobutyl phenyl ether when treated with aluminum chloride in the presence of benzene, yield very little substituted phenol, and yield isopropyl and *t*-butylbenzene.

5. It may be concluded that in the cases of phenyl ether isomerizations reported in this communication the primary course of the reaction is intermolecular in character and the reaction, therefore, involves scission.

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