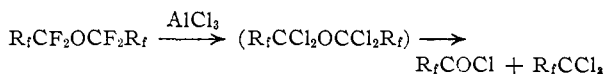


ported. Members of a series of perfluoro ( $\alpha$ -alkyl) cyclic ethers were treated with aluminum chloride to give simple replacement of the three alpha fluorine atoms by chlorine.

A quite different result was obtained when perfluoro di-( $n$ -alkyl) ethers were similarly treated. No  $\alpha, \alpha', \alpha'$ -tetrachloroethers were found, but instead the cleavage products corresponding to them were isolated, as illustrated by the equation



The absence of partially-reacted ethers or their cleavage products lends support to the postulation of the tetrachloro ether as a reaction intermediate. Although under these conditions the cyclic  $\alpha, \alpha', \alpha'$ -trichloroperfluoro ethers were stable,<sup>1b</sup> decachlorodiethyl ether on heating splits spontaneously to  $CCl_3COCl$  and  $C_2Cl_6$ .<sup>2</sup>

The reaction of ( $n$ - $C_4F_9$ )<sub>2</sub>O with aluminum chloride gave known products. The acyl chloride,  $n$ - $C_3F_7COCl$ ,<sup>3-5</sup> and the trichloride,  $n$ - $C_3F_7CCl_3$ ,<sup>6</sup> were identified by boiling points and infrared spectra. The acyl chloride  $n$ - $C_5F_{11}COCl$ ,<sup>5</sup> from cleavage of the ether ( $n$ - $C_6F_{13}$ )<sub>2</sub>O, was similarly identified. The trichloride,  $n$ - $C_5F_{11}CCl_3$ , is a new compound.

It is now possible to characterize perfluoro ethers and determine their structure by cleavage followed by preparation of a suitable derivative of the resulting perfluoroacyl chloride or chlorides. In the examples described here the amides were prepared. By mixed melting point determination with authentic samples of  $n$ - $C_3F_7CONH_2$ <sup>3-5</sup> and  $n$ - $C_5F_{11}CONH_2$ <sup>5</sup> these amides were shown to have the normal structure.

This work verifies that the perfluoro ethers have retained the normal structure of the hydrogen-containing ethers from which they were obtained by electrochemical fluorination.<sup>7,8</sup>

#### Experimental

**Perfluoro Ethers.**—The perfluoro ethers ( $n$ - $C_4F_9$ )<sub>2</sub>O and ( $n$ - $C_6F_{13}$ )<sub>2</sub>O used in this work had been prepared in these laboratories by electrochemical fluorination<sup>8</sup> of the corresponding ethers, ( $n$ - $C_4H_9$ )<sub>2</sub>O and ( $n$ - $C_6H_{13}$ )<sub>2</sub>O.<sup>9</sup> Their boiling points, refractive indices and infrared spectra indicated the absence of impurities.

**Reactions with Aluminum Chloride.**—Reactions and processing were very similar to those previously described.<sup>1b</sup> Minor differences are noted below.

**Reaction of ( $n$ - $C_4F_9$ )<sub>2</sub>O.**—Twenty grams of the perfluoro ether ( $n$ - $C_4F_9$ )<sub>2</sub>O and the theoretical amount of aluminum chloride (8.0 g.) were heated together at 175° for 16 hours in a rocking autoclave of 43-ml. volume. The autoclave was chilled and opened: volatile materials were caught in a liquid air trap on warming and partial evacuation. There

(2) Malaguti, *Ann. Chim.*, [3] **16**, 13 (1846); E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 224.

(3) Technical Bulletin, "Heptafluorobutyric Acid," Minnesota Mining and Manufacturing Company, New Products Division, St. Paul 6, Minnesota, 1949.

(4) D. R. Husted and A. H. Ahlbrecht, Abstracts, 116th A.C.S. Meeting, September, 1949, p. 10K.

(5) A. H. Ahlbrecht, D. R. Husted, T. S. Reid and G. H. Smith, Jr., *THIS JOURNAL*, **78**, in press (1956).

(6) G. V. D. Tiers, H. A. Brown and T. S. Reid, *ibid.*, **75**, 5978 (1953).

(7) J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, p. 414.

(8) J. H. Simons, U. S. Patent 2,500,388 (March 4, 1950).

was obtained 2.3 g. of material boiling above room temperature, with  $n_D^{25}$  1.2880 (reported<sup>3</sup> for  $n$ - $C_3F_7COCl$ ,  $n_D^{25}$  1.288). Infrared analysis showed this material to be fairly pure  $n$ - $C_3F_7COCl$ . The amide, prepared by direct reaction with ammonia gas and recrystallized from  $CCl_4$ , did not depress the melting point of an authentic sample of  $n$ - $C_3F_7CONH_2$ .<sup>5</sup> *Anal.* Calcd. for  $C_4H_2F_7NO$ : N, 6.57. Found: N, 6.64.

Distillation of the filtered reaction product gave several fractions, b.p. 87–98°, which contained both unreacted ( $n$ - $C_4F_9$ )<sub>2</sub>O and  $n$ - $C_3F_7CCl_3$ . By refractive indices and infrared spectra the amounts were determined to be 6.0 and 2.8 g., respectively. From this the ether conversion is calculated as 70%, and the yields of  $n$ - $C_3F_7COCl$  and  $n$ - $C_3F_7CCl_3$  are each 30% (based upon ether not recovered). In an otherwise identical reaction, run at 150° for 13 hours, the conversion was 45% but the yield of  $n$ - $C_3F_7CCl_3$  was only 8%;  $n$ - $C_3F_7COCl$  was not recovered. Some hexachloroethane was found in the distillation residues.

**Reaction of ( $n$ - $C_6F_{13}$ )<sub>2</sub>O.**—The ether ( $n$ - $C_6F_{13}$ )<sub>2</sub>O, 110 g. and aluminum chloride, 35 g. (120% of theory) were heated at 230° for 15 hours. Upon distillation of the filtered reaction mixture there was obtained  $n$ - $C_5F_{11}COCl$ , b.p. 87–93°,  $n_D^{25}$  1.2992 (reported<sup>5</sup> for  $n$ - $C_5F_{11}COCl$ , b.p. 90°,  $n_D^{25}$  1.310) yield 20.6 g. (43%). Infrared analysis showed this to be pure  $n$ - $C_5F_{11}COCl$ . *Anal.* Calcd. for  $C_6ClF_{11}O$ : Cl, 10.7. Found: Cl, 10.8.

The amide, recrystallized from  $CCl_4$ , did not depress the melting point of an authentic sample of  $n$ - $C_5F_{11}CONH_2$ .<sup>5</sup> *Anal.* Calcd. for  $C_6H_2F_{11}NO$ : N, 4.47; F, 66.8. Found: N, 4.40; F, 66.7.

There was also obtained a fraction which proved to be fairly pure  $n$ - $C_5F_{11}CCl_3$ : it had b.p. 140–144°,  $n_D^{25}$  1.3403 and weighed 28.5 g. (51%). It was, however, contaminated by some hexachloroethane; this was removed by means of the purification procedure previously described for the cyclic  $\alpha, \alpha', \alpha'$ -trichloroperfluoro ethers.<sup>1b</sup> Twenty grams of pure  $n$ - $C_5F_{11}CCl_3$ , b.p. 143°,  $n_D^{25}$  1.3383, was obtained. *Anal.* Calcd. for  $C_6Cl_3F_{11}$ : C, 18.6; Cl, 27.5. Found: C, 18.6; Cl, 27.5.

Sixteen grams (15%) of unreacted ( $n$ - $C_6F_{13}$ )<sub>2</sub>O was recovered. Yields are based on ether not recovered.

The reaction of 25 g. of ( $n$ - $C_6F_{13}$ )<sub>2</sub>O and 8 g. of  $AlCl_3$  at 185° for 14 hours went to the extent of 77%. The yields of  $n$ - $C_5F_{11}COCl$  and  $n$ - $C_5F_{11}CCl_3$  were 51 and 63%, respectively.

**Acknowledgment.**—I am indebted to Dr. H. E. Freier for the analytical data, to Dr. W. E. Keiser and Dr. J. McBrady for the infrared spectra, and to Mr. J. D. Keating for assistance with the autoclave reactions.

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### The Chemistry of Perfluoro Ethers. III. Synthesis of $\omega$ -Trichloromethylperfluoroacyl Chlorides by Cleavage of Cyclic Perfluoro Ethers<sup>1</sup>

BY GEORGE VAN DYKE TIERS

RECEIVED SEPTEMBER 8, 1955

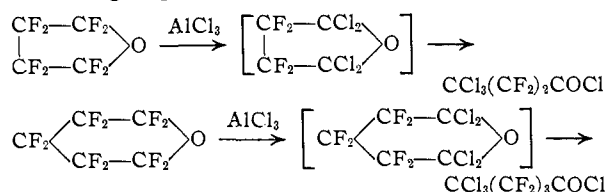
Perfluoro ( $\alpha$ -alkyl) cyclic ethers have been found to react with aluminum chloride to give simple substitution of the three  $\alpha$ -fluorine atoms by chlorine.<sup>2a</sup> Alpha substitution also occurred with perfluoro di-( $n$ -alkyl) ethers, but was then followed by cleavage of the ether.<sup>2b</sup>

This study has now been extended to two cyclic perfluoroethers which do not bear an  $\alpha$ -perfluoroalkyl group. These ethers split very much as had

(1) Presented at the 126th Meeting of the American Chemical Society, New York, N. Y., 1954, Abstracts, p. 27-M.

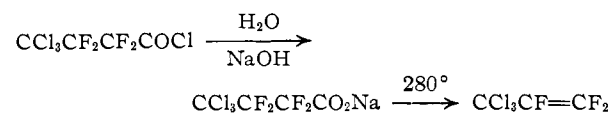
(2) (a) Part I, G. V. D. Tiers, *THIS JOURNAL*, **77**, 4837 (1955). (b) Part II, *ibid.*, **77**, 6703 (1955).

the non-cyclic ethers, but the cleavage product contains both the trichloromethyl and the acyl chloride groups, as illustrated by the equations



From the absence of symmetrical products such as  $\text{CCl}_3(\text{CF}_2)_2\text{CCl}_3$  or  $\text{ClCO}(\text{CF}_2)_3\text{COCl}$  it is reasoned that the chlorine shift (which accompanies splitting) is intramolecular. The ease of splitting of these ethers is in marked contrast to the stability of the  $\alpha, \alpha, \alpha'$ -trichloroperfluorocyclic ethers,<sup>2a</sup> and demonstrates that the mere presence of a five- or six-membered ring is not responsible for resistance to cleavage.

The  $\omega$ -trichloromethylperfluoroacyl chlorides are new compounds. They have been characterized by their physical properties and infrared spectra, and by conversion to their amides. They may be used to identify or to prove the structure of the parent ether, or alternatively as synthetic intermediates. An example of the latter is the preparation of the new trichlorotrifluoropropene  $\text{CCl}_3\text{CF}=\text{CF}_2$ , according to the scheme



The thermal decomposition of sodium salts of perfluorocarboxylic acids to give perfluoroolefins has been reported previously.<sup>3</sup>

The proposed structure,  $\text{CF}_2=\text{CF}-\text{CCl}_3$ , is confirmed by examination of the infrared spectrum. The carbon-carbon double bond absorption is found at  $5.63 \mu$ , as compared with  $5.56 \mu$  for  $\text{C}_3\text{F}_6$ .<sup>4a</sup> A shift to longer wave length has been found on passing from  $\text{CCl}_2=\text{CCl}-\text{CF}_3$  ( $6.30 \mu$ ) to  $\text{CCl}_2=\text{CCl}-\text{CCl}_3$  ( $6.46 \mu$ ).<sup>5</sup> These compounds also serve to illustrate the pronounced shift to longer wave length which accompanies replacement of vinylic fluorine by chlorine in perhaloolefins. This shift is  $0.20\text{--}0.25 \mu$  per substitution, and has been found to apply also to the substitution of vinylic fluorine by a perfluoroalkyl group.<sup>4b</sup>

The  $\alpha, \alpha, \alpha', \alpha'$ -tetrachloro ethers, postulated as intermediates in the cleavage reaction, are themselves known compounds. They have been synthesized by chlorination of the corresponding fluorohydro ethers, and have been treated with antimony trifluorodichloride to achieve the synthesis of the perfluoro cyclic ethers.<sup>6</sup> In the case of cyclo- $\text{C}_4\text{F}_8\text{O}$ , Henne and Richter obtained in fair yield a product which compared closely in physical

properties with the cyclo- $\text{C}_4\text{F}_8\text{O}$  used in this study. An extremely low yield was obtained in the case of cyclo- $\text{C}_5\text{F}_{10}\text{O}$ , but this was attributed to increased difficulty in fluorinating the tetrachloro ether cyclo- $\text{C}_5\text{Cl}_4\text{F}_6\text{O}$ . Henne and Richter commented that extensive decomposition occurred by way of breaking the ring, although decomposition products were not described; certainly the work reported in the present paper supports this view.

#### Experimental

**Perfluoro Ethers.**—Perfluorotetrahydrofuran and perfluorotetrahydropyran were prepared by electrochemical fluorination of the corresponding cyclic ethers.<sup>6-8</sup> The boiling point of cyclo- $\text{C}_4\text{F}_8\text{O}$  was in agreement with previously reported values.<sup>6,8</sup> In the case of perfluorotetrahydropyran, physical constants have been reported for a highly purified sample<sup>9</sup>: the boiling point,  $34.0^\circ$ , is somewhat higher than earlier values.<sup>6,8</sup> The ether sample used in this work was almost pure, as judged by its refractive index and its infrared spectrum: the isomeric cyclic ether, perfluoro-2-methyl-tetrahydrofuran<sup>9</sup> was not present.

**4,4,4-Trichlorotetrafluorobutyryl Chloride.**—Perfluorotetrahydrofuran, 21.6 g. (0.10 mole) and aluminum chloride, 13.3 g. (0.10 mole), were heated together at  $170^\circ$  for 13 hours in a 43-ml. rocking autoclave.<sup>2</sup> Volatile products were caught in a liquid air trap. After crude fractionation in a vacuum system, 9.1 g. of unreacted cyclo- $\text{C}_4\text{F}_8\text{O}$  was recovered and identified by molecular weight and infrared spectrum. The conversion was 57% based on cyclo- $\text{C}_4\text{F}_8\text{O}$ . (Note: insufficient  $\text{AlCl}_3$  was used.) A filtered solution of the reaction product in  $\text{C}_6\text{F}_{12}\text{O}$  was distilled to give 4,4,4-trichlorotetrafluorobutyryl chloride, b.p.  $148^\circ$ ,  $n_D^{25}$  1.4105, yield 8.6 g. (55%) based on unrecovered perfluoro ether. Pot residues contained hexachloroethane. *Anal.* Calcd. for  $\text{C}_4\text{Cl}_4\text{F}_4\text{O}$ : Cl, 50.3; Cl (hydr.), 12.6. Found: Cl, 50.1; Cl (hydr.), 12.3. The amide was prepared by reaction with ammonia gas, and was recrystallized from  $\text{CCl}_4$ , m.p.,  $126.5\text{--}127.0^\circ$  (cor.), not altered by further recrystallization. *Anal.* Calcd. for  $\text{C}_4\text{H}_2\text{Cl}_3\text{F}_4\text{NO}$ : Cl, 40.5; F, 29.0; N, 5.34. Found: Cl, 40.5; F, 28.7; N, 5.33.

**5,5,5-Trichlorohexafluoropentanoyl Chloride.**—Perfluorotetrahydropyran, 19.8 g. (0.075 mole), and aluminum chloride, 13.3 g. (0.10 mole), reacted at  $180^\circ$  for 13 hours. A filtered solution of the reaction product in  $\text{C}_6\text{F}_{12}\text{O}$  was fractionated and 6.0 g. of unreacted cyclo- $\text{C}_5\text{F}_{10}\text{O}$  was recovered and identified by infrared analysis. From this the conversion is estimated as 70%. As in the preceding example, there was little or no intermediate fraction, but pot residues contained hexachloroethane. There was obtained 5,5,5-trichlorohexafluoropentanoyl chloride, b.p.  $165^\circ$ ,  $n_D^{25}$  1.3966, yield 9.3 g. (54%), based on unrecovered perfluoro ether. *Anal.* Calcd. for  $\text{C}_5\text{Cl}_3\text{F}_6\text{O}$ : Cl, 42.7; Cl (hydr.), 10.7; F, 34.4. Found: Cl, 43.0; Cl (hydr.), 10.4; F, 33.9. The amide, recrystallized from  $\text{CCl}_4$ , had m.p.  $138.3\text{--}138.4^\circ$  (cor.) not altered by further recrystallization. *Anal.* Calcd. for  $\text{C}_5\text{H}_2\text{Cl}_3\text{F}_6\text{NO}$ : C, 19.2; N, 4.49. Found: C, 19.2; N, 4.61.

**4,4,4-Trichlorotetrafluorobutyric Acid.**—The acyl chloride  $\text{CCl}_3\text{CF}_2\text{CF}_2\text{COCl}$ , 30.0 g. (0.106 mole), was mixed with water, 1.91 g. (0.106 mole), in a narrow-necked flask and allowed to stand until about the theoretical weight loss (as HCl gas) had occurred. The reaction mixture was distilled to give pure 4,4,4-trichlorotetrafluorobutyric acid, b.p.  $212^\circ$ ,  $n_D^{25}$  1.4132, neutral equivalent 262, 264 (calcd. 263.5), yield 23.0 g. (81%). The sodium salt was prepared and was dried at  $110^\circ$ . *Anal.* Calcd. for  $\text{C}_4\text{Cl}_3\text{F}_4\text{NaO}_2$ : F, 26.6; Na, 8.08. Found: F, 26.2; Na, 8.26.

**3,3,3-Trichlorotrifluoropropene.**—Following the general procedure of LaZerte, *et al.*,<sup>3</sup> the sodium salt,  $\text{CCl}_3\text{CF}_2\text{CF}_2\text{CO}_2\text{Na}$ , 13.9 g. (0.049 mole), was found to decompose at  $250\text{--}280^\circ$  *in vacuo*. Volatile products were fractionally distilled to give 3,3,3-trichlorotrifluoropropene, b.p.  $89\text{--}91^\circ$ ,  $n_D^{25}$  1.4027, yield 4.8 g. (50%). *Anal.* Calcd. for  $\text{C}_3\text{Cl}_3\text{F}_3$ : F, 28.6. Found: F, 28.7.

(7) J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, p. 414.

(8) E. A. Kauck and J. H. Simons, U. S. Patent 2,594,572 (April 29, 1952).

(9) T. J. Brice and R. I. Coon, *THIS JOURNAL*, **75**, 2921 (1953).

(3) J. D. LaZerte, L. J. Hals, T. S. Reid and G. H. Smith, *THIS JOURNAL*, **75**, 4525 (1953).

(4) D. C. Smith, *et al.*, "Spectroscopic Properties of Fluorocarbons and Fluorinated Hydrocarbons," NRL Report 3567, Naval Research Laboratory, Washington, D. C., 1949; (a) p. 63 and p. 126, (b) p. 142.

(5) D. C. Smith, *et al.*, "Infrared Spectra of Fluorinated Hydrocarbons," NRL Report 3924, Naval Research Laboratory, Washington, D. C., 1952, p. 63 and p. 68.

(6) A. L. Henne and S. B. Richter, *THIS JOURNAL*, **74**, 5420 (1952).

**Acknowledgment.**—Mr. H. L. Anderson carried out the preparation of the 3,3,3-trichlorotrifluoropropene. I thank Dr. P. W. Trott for the pure isomer of cyclo-C<sub>6</sub>F<sub>10</sub>O used in this study. I am indebted to Dr. H. E. Freier for the analytical data, to Dr. W. E. Keiser for the infrared spectra, and to Mr. J. D. Keating for assistance with the autoclave reactions.

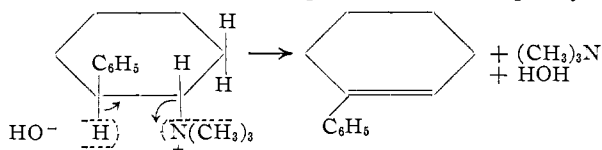
CONTRIBUTION NO. 101 FROM THE  
CENTRAL RESEARCH DEPARTMENT  
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### Elimination Reactions in Cyclic Systems. III. Mechanism of the Formation of 1-Phenylcyclohexene from Trimethyl-*trans*-2-phenylcyclohexylammonium Hydroxide

BY JOSEPH WEINSTOCK AND F. G. BORDWELL

RECEIVED SEPTEMBER 1, 1955

In a recent publication<sup>1</sup> it was shown that the product from a Hofmann degradation of trimethyl-*trans*-2-phenylcyclohexylammonium hydroxide was practically pure 1-phenylcyclohexene. Rather than assume that this product resulted from a direct *cis* elimination and that the reaction constituted an exception to the general rule that *trans* eliminations are favored,<sup>2</sup> the authors postulated that 3-phenyl-



cyclohexene was first formed in the reaction, by a *trans* elimination, and that this initial product was rearranged under the reaction conditions to 1-phenylcyclohexene.

Our investigations of elimination reactions in cyclic systems<sup>3-5</sup> suggested that the increased acidity of the hydrogen attached to the carbon holding the phenyl group might be sufficiently great to allow a *cis* elimination involving this hydrogen to occur more rapidly (giving 1-phenylcyclohexene) than the *trans* elimination involving a relatively non-acidic hydrogen (giving 3-phenylcyclohexene), which was suggested.<sup>1</sup> To test this hypothesis we have prepared 3-phenylcyclohexene and investigated its tendency to rearrange in the presence of base.

An attempt was made at first to obtain 3-phenylcyclohexene from *trans*-2-phenylcyclohexanol by the method of Price and Karabinos.<sup>6</sup> Since this method was found to give a mixture of products,<sup>7</sup> it was abandoned in favor of pyrolysis of the xan-

thate of *cis*-2-phenylcyclohexanol.<sup>8</sup> This sample of 3-phenylcyclohexene gave an infrared spectrum almost identical with that from the reaction of 3-bromocyclohexene with phenylmagnesium bromide.<sup>9</sup> Reduction of 3-phenylcyclohexene gave phenylcyclohexane identical with a sample obtained by reduction of 1-phenylcyclohexene. It is evident from the ultraviolet absorption spectrum of the sample of 3-phenylcyclohexene obtained by the xanthate method that no more than a small percentage of 1-phenylcyclohexene can be present. These results support the structure assignments and analyses of Alexander and Mudrak.<sup>8</sup>

The extent of rearrangement of 3-phenyl- to 1-phenylcyclohexene on treatment with bases was followed by changes in refractive index. Under the conditions used by Arnold and Richardson<sup>1</sup> for the Hofmann reaction no rearrangement was observed.

In order to be sure that the non-homogeneous nature of our reaction mixture was not responsible for the failure of rearrangement, 3-phenylcyclohexene was heated with potassium hydroxide in alcohol solution at 100°. After one-fourth hour the extent of rearrangement was 0%; after 24 hr., 4.5%; after 96 hr., 9.8%; after 192 hr., 14.2%.

A slow rate of isomerization for a similar system was observed by Quelet<sup>10</sup> for the base-catalyzed transformation of allyl-*p*-bromobenzene to propenyl-*p*-bromobenzene. Refluxing for 24 hours with a solution of potassium ethoxide in ethanol caused 40% isomerization; seven hours reflux with potassium amyloxide in amyl alcohol gave 75% isomerization. The slower rate of isomerization observed by us for 3-phenylcyclohexene is consistent with the fact the ionization of a hydrogen in an open-chain system, exemplified by ethyl acetoacetate, is about one hundred times as fast as in a comparable cyclic system, exemplified by 2-carboethoxycyclohexanone.<sup>11</sup> 1,4-Pentadiene also appears to be stable to alkali since it is formed from 1,5-diiodo- or 1,5-dichloropentane by treatment with alcoholic potassium hydroxide.<sup>12</sup>

The possibility that traces of silver oxide might in some way cause rearrangement of 3-phenylcyclohexene to 1-phenylcyclohexene also was eliminated, since 3-phenylcyclohexene was found to be unaffected by heating with a suspension of silver oxide under the reaction conditions.

It is highly probable that 1-phenylcyclohexene is formed in the Hofmann degradation<sup>1</sup> by a *cis* elimination, as indicated in the equation. This is then another example wherein increased acidity of the hydrogen being eliminated promotes a *cis* elimination in preference to a possible *trans* elimination.<sup>3-5</sup>

#### Experimental

**Materials.**—*cis*-2-Phenylcyclohexanol was prepared by the method of Price and Karabinos<sup>6</sup> as modified by Berti.<sup>13</sup>

(8) E. R. Alexander and A. Mudrak, *THIS JOURNAL*, **72**, 1810 (1950).  
(9) A. Berlande, *Bull. soc. chim.*, [5] **9**, 644 (1942). We wish to thank Dr. C. J. Collins for providing us with samples of 3-phenylcyclohexene made by this method.

(10) R. Quelet, *Bull. soc. chim.*, [4] **45**, 80 (1929).  
(11) R. G. Pearson and R. L. Dillon, *THIS JOURNAL*, **75**, 2439 (1953).  
(12) N. Demjanow and M. Dojarenko, *Ber.*, **40**, 2589 (1907); H. B. Dykstra, J. F. Lewis and C. E. Boord, *THIS JOURNAL*, **52**, 3396 (1930).  
(13) G. Berti, *THIS JOURNAL*, **76**, 1213 (1954).

(1) R. T. Arnold and P. N. Richardson, *THIS JOURNAL*, **76**, 3649 (1954).

(2) See the discussion in "Structure and Mechanism of Organic Chemistry," by C. K. Ingold, Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII.

(3) J. Weinstock, R. G. Pearson and F. G. Bordwell, *THIS JOURNAL*, **76**, 4748 (1954).

(4) F. G. Bordwell and R. J. Kern, *ibid.*, **77**, 1141 (1955).

(5) F. G. Bordwell and M. L. Peterson, *ibid.*, **77**, 1145 (1955).

(6) C. C. Price and J. V. Karabinos, *ibid.*, **62**, 1159 (1940).

(7) See C. J. Collins and H. J. Schaeffer, Abstracts of Minneapolis Meeting of the American Chemical Society, September, 1955, p. 56-O; C. C. Price, J. A. McCoy and E. Eliel, *ibid.*, p. 55-O.