

288 *cis-* and *trans*-2 : 3-Dichlorohexafluorobut-2-ene.

By (Mrs.) F. DICKINSON, R. HILL, and J. MURAY.

2 : 3-Dichlorohexafluorobut-2-ene has been prepared by dechlorination of 2 : 2 : 3 : 3-tetrachlorohexafluorobutane by means of zinc. The *cis*- and the *trans*-isomer were separated by gas-liquid chromatography, and the stereoisomers identified on the basis of chemical analyses, molecular-weight determinations, and mass-spectrometric, nuclear magnetic resonance, and infrared spectroscopic examinations of the materials.

Some physical properties of the two isomers are given.

HENNE and his co-workers described the preparation of 2 : 3-dichlorohexafluorobut-2-ene from octachlorobut-2-ene and a mixture of antimony trifluoride and antimony dichlorotrifluoride<sup>1,2</sup> and by the dehydrochlorination of 2 : 3 : 3-trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane.<sup>3</sup> The structure of the products, mixtures of *cis*- and *trans*-2 : 3-dichlorohexafluorobut-2-ene, was confirmed by quantitative oxidation to trifluoroacetic acid.

We now describe the preparation, separation, and identification of the stereoisomers. Gas-liquid chromatography was applied on a preparative scale in their separation and mass-spectrometry and infrared and nuclear magnetic resonance spectroscopy in their identification. Dechlorination of 2 : 2 : 3 : 3-tetrachlorohexafluorobutane was chosen because it could yield only the desired compound.

TABLE I. *Physical properties of the isomers.*

	Isomer I ( <i>trans</i> )	Isomer II ( <i>cis</i> )		Isomer I ( <i>trans</i> )	Isomer II ( <i>cis</i> )
B. p. ....	66.2°	67.9°	V. p. (mm. Hg) at 25° ...	157	146
F. p. ....	-53	-108	" "	429	403
$n_D^{20}$ .....	1.3477	1.3471	" "	731	689

The results obtained in the measurements of vapour pressures (in mm.) in the temperature range 15—70° fitted the equations:

Isomer I (*trans*)  $\log p = 7.8432 - 1684/T$ ; isomer II (*cis*)  $\log p = 7.8621 - 1699/T$  where  $T$  is given in °K.

*Preparation, Separation, and Physical Properties of the Isomers.*—The isomers could not be separated by fractional distillation through a 15-plate column. Gas-liquid chromatography showed that various cuts of the 2 : 3-dichlorohexafluorobut-2-ene fraction consisted of two different entities in proportions varying from cut to cut. Subsequently, these components were proved to be *trans*- and *cis*-2 : 3-dichlorohexafluorobut-2-ene.

The isomers were, however, separated by gas-liquid chromatography on a preparative scale. Although separation was better at low temperatures, the retention times were too high to make this practicable on a larger scale and working at 85° was considered advantageous.

Chemical analyses and molecular weights of the isomers were in good agreement with theory; some physical properties are given in Table I.

*Identification of the Stereoisomers.*—The mass-spectrometric results (Table 2) showed that the two materials had similar but not identical cracking patterns. Since the possibility of ion-rearrangements could not be ruled out, the similarity of the patterns was not sufficient evidence to show that the two materials were stereoisomers.

Only a single <sup>19</sup>F peak, but at different field strength in each case, was obtained in the nuclear magnetic resonance spectra. The single peaks indicated that all the fluorine atoms were at equivalent sites in the molecules; there must therefore be two CF<sub>3</sub> groups in the molecule of each. This suggestion was confirmed by the absence of any multiplet fine-structure of the <sup>19</sup>F peaks. A fine structure would have appeared had the fluorine atoms

<sup>1</sup> Henne and Trott, *J. Amer. Chem. Soc.*, 1947, **69**, 1820.

<sup>2</sup> Henne and Newby, *ibid.*, 1948, **70**, 130.

<sup>3</sup> Henne *et al.*, *ibid.*, 1945, **67**, 1906.

been attached to adjacent carbon atoms. The structure of both compounds must accordingly be  $\text{CF}_3\cdot\text{CCl}\cdot\text{CCl}\cdot\text{CF}_3$ .

The evidence needed for identifying the isomers was provided by infrared spectroscopy. The results show C=C absorption at  $6.2\ \mu$  in isomer II but not in isomer I. The absence of this absorption shows isomer I to have the symmetrical *trans*-configuration, where no

TABLE 2. Some ion peaks of the mass spectra of the isomers.

Mass No.		Relative intensity of peak		Mass No.		Relative intensity of peak	
		Isomer I ( <i>trans</i> )	Isomer II ( <i>cis</i> )			Isomer I ( <i>trans</i> )	Isomer II ( <i>cis</i> )
232	$\text{C}_4\text{Cl}_2\text{F}_6$	81	73	132	$\text{C}_2\text{Cl}_2\text{F}_2$	0.4	0.3
213	$\text{C}_4\text{Cl}_2\text{F}_5$	16	21	93	$\text{C}_3\text{F}_3$	31	26
197	$\text{C}_4\text{ClF}_6$	27	26	85	$\text{CClF}_2$	8	8
182	$\text{C}_3\text{Cl}_2\text{F}_4$	4	3	69	$\text{CF}_3$	79	76
163	$\text{C}_3\text{Cl}_2\text{F}_3$	100	100	66	$\text{CClF}$	0.9	0.8
147	$\text{C}_3\text{ClF}_4$	36	33	50	$\text{CF}_2$	1	1
143	$\text{C}_4\text{F}_6$	4	4	47	$\text{CCl}$	2	2

change in dipole moment would be associated with the C=C stretching vibration. Examination of models shows that the *cis*-configuration would be strained at this bond and a change of dipole moment would accompany the C=C stretching vibration, resulting in infrared absorption.

It is therefore concluded that isomer I is *trans*-, and isomer II *cis*-2 : 3-dichlorohexafluorobut-2-ene.

#### EXPERIMENTAL

*Dechlorination of 2 : 2 : 3 : 3-Tetrachlorohexafluorobutane.*—The chlorofluorocarbon was added dropwise to the stirred mixture of zinc dust (about 400 g.), *n*-butyl alcohol (1.2 l.), and glacial acetic acid (5 ml.), at  $85-95^\circ$ ; in no run were more than 2 g. of the chlorofluorocarbon used per g. of zinc dust. The product passed through a fractionating column kept at  $55^\circ$  and was collected in traps at  $0^\circ$  and  $-80^\circ$ .

*Purification.*—The product (obtained in 88% yield) was refluxed for  $1\frac{1}{2}$  hr. over phosphoric oxide, cooled, filtered, and fractionally distilled in a still of 15 theoretical plates efficiency at the rate of 10–15 g. of distillate per hr. The fractions were examined by gas-phase chromatography, a Griffin Mark I V.P.C. unit being used with di-(3 : 5 : 5-trimethylhexyl) phthalate on kieselguhr ("Celite") as stationary phase, and their refractive indices and molecular weights determined.

Of the product (418 g.) which had been refluxed with phosphoric oxide, 3.5% distilled at  $32-34^\circ$ , 12.5% at  $34-67^\circ$ , 70% at  $67-68.5^\circ$ , and 5% at  $69^\circ$ , the rest being hold-up and residues. The main fraction, b. p.  $67-68.5^\circ$ , which was a mixture of *trans*- and *cis*-2 : 3-dichlorohexafluorobut-2-ene, had  $n\ 1.347$ ,  $M\ 234.4 \pm 0.5$ .

*Separation of Stereoisomers.*—A column, 16 ft. long, 1.46 in. diam., packed with "Celite" 545 (1990 g.), graded <sup>4</sup> by elutriation with water and impregnated with dibutyl phthalate (853 g.) was used. About 8 g. of the mixture of isomers were injected into the column at  $85^\circ$ , the inlet and outlet pressures being respectively 840 and 755 mm., through which nitrogen was passed at the rate of 20 l./hr. measured at  $20^\circ$  at 760 mm. A thermal conductivity cell was used for detection, and the fractions were collected in liquid-air traps. From 16 runs, 28 g. of pure *trans*-, 43 g. of practically pure *cis*-, and 24 g. of a mixture of the two isomers were isolated. Part of the *cis*-sample was recycled, giving 19 g. of pure material. The maximum of the peak for the *trans*-isomer appeared after 54.5 min. from the time of injection, and that of the *cis*-after 65.5 min. The corresponding time for argon was 11.8 min. The separated materials were examined by gas-liquid chromatography, a number of stationary liquid phases being used including dinonyl phthalate, polyethylene glycol 400, and silicone oil MS 550. No band due to impurity was detected by these materials. (Found, for the *trans*-isomer: C, 21.1; Cl, 30.7; F, 48.7%;  $M$ ,  $233.5 \pm 0.5$ . For the *cis*-isomer: C, 21.2; Cl, 30.5; F, 48.5%;  $M$ ,  $234.0 \pm 0.5$ . Calc. for  $\text{C}_4\text{Cl}_2\text{F}_6$ : C, 20.6; Cl, 30.5; F, 48.9%;  $M$ , 233.)

<sup>4</sup> James and Martin, *Biochem. J.*, 1952, **50**, 679.

*Determination of Properties and Identification of Isomers.*—The vapour pressures were measured in the temperature range 15—70° with a static isoteniscope by using a standard procedure,<sup>5</sup> and the freezing points on 2 ml. samples with a calibrated thermocouple.

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IMPERIAL CHEMICAL INDUSTRIES LIMITED, GENERAL CHEMICALS DIVISION,  
RESEARCH DEPARTMENT, WIDNES LABORATORY,  
WIDNES, LANCs.

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<sup>5</sup> Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412.

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