Identification of the Isomers of Ditrifluoromethylhexafluorocyclobutane

By B. Atkinson and P. B. Stockwell

The dimer of perfluoropropene has been separated into three fractions. Evidence from mass spectra and nuclear magnetic resonance shows that the fractions, identified by infrared bands, are: 9.39 µ, trans-1,2-; 9.59 µ, cis-1.2-; 10.53 µ, 11.84 µ, a mixture of cis- and trans-1,3-ditrifluoromethylhexafluorocyclobutane.

THE preparation of ditrifluoromethylhexafluorocyclobutane (DMC) by dimerisation of perfluoropropene has been described by Brown¹ and Hauptschein, Fainberg, and Braid.² The product can be separated into three fractions, A, B, C, in order of decreasing boiling point.² These were thought to be three of the four isomers of DMC² annexed. Both physical and chemical evidence indicated 1,2- and 1,3-formulations for isomers A and C, respectively, but the structure of isomer B was not established. In connection with kinetic studies of the isomerisation and dissociation of DMC³ we found it necessary to study the isomeric content of the dimer of perfluoropropene and definitely to assign structures.

We separated three fractions by gas chromatography and studied their n.m.r., infrared, and mass spectra. We conclude that A is trans-1,2-DMC, B is cis-1,2-DMC, and C is a mixture of cis- and trans-1,3-DMC.

EXPERIMENTAL

Materials.-The dimer of perfluoropropene was supplied by E. I. du Pont de Nemours and Co., Inc. It showed all the infrared peaks characteristic of the dimers prepared by Hauptschein et al. (Found: C, 24.6; F, 75.8%; M, 301. Calc. for C_6F_{12} : C, 24.0; F, 76.0%; M, 300).

Gas chromatography using conventional esters, Silicone elastomer E301, or Fluorolube S-30 as stationary phase gave only one peak. Partial separation into three overlapping peaks was obtained by using 45% w/w of chlorofluorobutanes on 60-80 mesh Celite at 20°. The chlorofluorobutanes (C, 15; Cl, 62; F, 23%) were supplied by Imperial Chemical Industries Limited, General Chemicals Division. Columns were 5.4 m. long, 14 mm. diam. for preparative use, 3 mm. diam. for analysis. The order of elution was C, B, A, which corresponds to the order of increasing b. p. found by Hauptschein et al.² By taking cuts and re-cycling each portion separately for two or three passes per portion 98% A, 95% B, and 80% C were prepared. Small quantities of pure A (B not detectable), 99% B (1% C), 94% C (6% B) were prepared by taking narrow cuts. Impurities taken up from the stationary phase were removed by passing products through a 1.6 m. column of dibutyl phthalate on Celite.

The original material was $55 \cdot 5\% A$, $41 \cdot 6\% B$, $2 \cdot 9\% C$.

Infrared Spectra.-These were recorded at high resolution on a Grubb-Parsons " Spectromaster."

Nuclear Magnetic Spectra.—¹⁹F spectra were recorded at 56.4 Mc./sec. on a Varian Associates H.R. 60 spectrometer. Fraction C was also examined at 40 and at 94.1 Mc./sec. Pure liquid was used unless a solvent is mentioned. Trifluoroacetic acid was used as external reference. Ratios A:B:C in mixtures were determined by area measurements on CF peaks. Mass Spectra.—These were recorded on an A.E.I. M.S.9

spectrometer at a resolving power of 1000.

RESULTS

Infrared Spectra.-Line positions and absorbancies for the fractions A, B, and C were in good agreement with the results and conclusions of Hauptschein et al.² Details will be supplied on request. There is a general similarity between the three spectra but variations at about 11 μ are striking. Both A and B have strong bands at 11.01 and 11.37 μ : C has bands of similar strength at 10.53 and



Nuclear magnetic resonance spectra: (a) A, (b) B, (c) C, all at 56.4 Mc./sec.; (d) C at 94.1 Mc./sec. The scale marking on each peak is 10 c.p.s Chemical shifts are given in p.p.m.

11.84 μ , with little absorption between. A has characteristic lines at 9.39 and 13.62μ . B has characteristic lines at 9.59 and 13.81μ .

Nuclear Magnetic Resonance Spectra.—At 56.4 Mc./sec. the original mixture gave a composite $-CF_3$ peak, six $>CF_2$ peaks, and four CF peaks. Each of the fractions separated by gas chromatography gave peak-area ratios $CF_3: CF_2: CF$ of 3:2:1, as expected for a DMC isomer. Individual spectra are illustrated in the Figure.

Chemical shifts for isomer A (Figure a) are -2.9 p.p.m. (-CF₃), 51.7 p.p.m. ()CF₂), 115 p.p.m. ()CF). The fine structure of the $-CF_3$ signal corresponds fairly well to a doublet splitting of 7.1 c./sec. and a quintet of 4.7 c./sec. The \rightarrow CF line was described by Hauptschein *et al.*² as a

¹ H. C. Brown, J. Org. Chem., 1957, 22, 1256. ² M. Hauptschein, A. H. Fainberg, and M. Braid, J. Amer. Chem. Soc., 1958, 80, 842.

³ P. B. Stockwell, Thesis, University of London, 1965.

doublet but it conforms better with a quartet splitting of 7.1 c./sec.

Isomer *B* has the following features (Figure *b*) -2.9 p.p.m. (-CF₃); quartet from AB pair (>CF₂), coupling constant 240 c./sec., chemical shifts 49.7, 53.7, 116.5 p.p.m.; (>CF). The low-field lines from the AB pair have a well defined quartet splitting of 10 c./sec.

Chemical shifts for fraction C at 56.4 Mc./sec. (Figure c) are $-3\cdot3$ p.p.m. (-CF₃), $49\cdot5$ (>CF₂), $112\cdot5$ (=CF), 114 (=CF). The unsymmetrical >CF₂ band is resolved at $94\cdot1$ Mc./sec. (Figure d) into two lines, both septets (46.35, 6.3 c./sec.; 46.6 p.p.m., 7.3 c./sec., in solution in CCl_4). The areas are not equal. The separation between the two CF lines is 1.5 p.p.m. (40 Mc./sec.), 1.54 p.p.m. (56.4 Mc./sec.). Within experimental error these separations are concordant. In CCl₄ the corresponding CF shifts are 109.7, 111.3 p.p.m. and the separation is 1.58 p.p.m. (56.4 Mc./sec.), 1.59 p.p.m. (94.1 Mc./sec.). Again the separations are concordant. The fact that in a fixed solvent the separation between the lines in p.p.m. is independent of frequency shows that the lines have different chemical shifts and that they are not spin-coupled signals. The two \geq CF lines are from different compounds. Area ratios for the lines 46.35: 109.7 and for 46.6: 111.3 are both approximately 2:1. These observations prove that fraction C contains two isomers, C_1 , with lines at $-3\cdot3$, $49\cdot27$, 112.5 p.p.m. $(-4.95, 46.35, 109.7 \text{ in } \text{CCl}_4)$ and C_2 with $-3\cdot3$, 49.52, 114 p.p.m. ($-4\cdot95$, 46.6, 111.2 in CCl₄). The fractions examined contained more C_2 than C_1 .

Mass Spectra.—These are summarised in Table 1 (ionising voltage 70 v) and Table 2 (ionising voltage 15 v). Samples 1 and 4 are >99.5% A; 2 and 5 are >99% B; 3 and 6 are >80% C. Fragmentation peaks of abundance less than 1% of the base peak have been omitted.

TABLE 1

Mass spectra of isomers of ditrifluoromethylhexafluorocyclobutane. Ionising voltage 70 v

. .

	Mass	Abundances		
Ion		1(A)	2 (B)	3 (C)
C ₆ F ₁₂	300	0.1	0.12	0.11
C.F.1	281	14	14	6
C, F,	231	84	85	5
C, F,	212	2	2	3
C ₅ F,	193	6	5	3
C, F,	181	83	75	14
C.F	162	4	4	2
C.F	150	53	46	95
C,F,	143	8	8	4
C.F	131	49	46	100
C.F	121	4	3	2
C.F	119	6	7	0.4
C.F.	112	4	4	3
C.F	105	4	4	1
C.F.	100	100	100	65
C.F	93	21	20	13
C.F	81	9	5	4
C.F	74	5	5	4
CF,	69	91	80	63
C . F .	62	2	3	3
C,F	55	2	3	3
CF,	50	10	10	
CF	31	18	16	13

The 70 v mass spectra of A and B have three metastable peaks at 189.9, 141.8, and 94.8. With the aid of the nomo-

⁴ J. H. Beynon, "Mass Spectrometry," Elsevier Publishing Co., New York, 1960.

741

TABLE	2
Mass spectra of isomers.	Ionising voltage 15 v

		Abundances	8
Ion	$\overline{4(A)}$	5 (B)	6 (C)
C ₅ F ₁₈	0.5		0.6
C ₆ F ₁₀	2		1
C ₅ F,	39	42	11
$C_{5}F_{8}$	2		5
C ₄ F ₇	100	100	2
$C_{a}F_{b}$	94	73	100
$C_{3}F_{5}$	_		23
$C_{2}F_{4}$	53	48	6
CF ₃	2		

grams given by Beynon⁴ it was found that the peaks corresponded to the processes,

$$\begin{split} & C_{6}F_{11}{}^{+} = C_{5}F_{9}{}^{+} + CF_{2} \\ & C_{5}F_{9}{}^{+} = C_{4}F_{7}{}^{+} + CF_{2} \\ & C_{4}F_{7}{}^{+} = C_{3}F_{5}{}^{+} + CF_{2} \end{split}$$

At 70 v samples of C gave just one metastable peak at 66.67 corresponding to the process,

$$C_3F_6^+ = C_2F_4^+ + CF$$

The results show that A and B have virtually identical ion-abundance distributions. These two substances are clearly geometrical isomers which yield the same initial ion. Major products are $C_2F_4^+$, $C_4F_7^+$, CF_3^+ , $C_5F_9^+$, $C_3F_6^+$, $C_3F_5^+$. Samples of C yield $C_3F_6^+$, $C_3F_5^+$, $C_2F_4^+$, CF_3^+ . At low ionising voltages the contrast between the high yield of $C_4F_7^+$ from A and B and the low yield from C is striking.



A and B give the C_2 , C_3 , and C_4 fragments to be expected from the alternative modes of cleavage of the ring in the 1,2-DMC structure. C gives the single breakdown product expected from cleavage of the ring in a 1,3-DMC structure. There is a general similarity between the behaviour of these compounds and that of hexafluorocyclobutanes.⁵

Chemical Properties.—We have made quantitative studies of isomerisation and dissociation of A and B at 420— 500°.³ We confirm that A isomerises to B and vice-versa.² They do not form C. A and B dissociate to perfluoropropene very much more rapidly than does C.

DISCUSSION

The mass spectra show that A and B are 1,2-isomers, and C_1 and C_2 are 1,3-isomers. The pairing of A and B⁵ J. R. Majer, "Advances in Fluorine Chemistry," vol. 2, Butterworths, London, 1961, p. 74. as geometrical isomers is supported by the similarities in the infrared spectra and by their modes of isomerisation. Isomerisation between the 1,2-geometrical isomers has been observed in both 1,2-dimethylcyclobutane ⁶ and 1,2-dichlorohexafluorocyclobutane.⁷

The nuclear magnetic resonance spectra have an unexpected simplicity in the >CF₂ resonance. Of the four isomers only trans-1,3-DMC has a centre of symmetry and a predictable identity of properties for the two fluorine atoms in the CF₂ group. It was expected that the CF_2 groups in the other three isomers would form AB pairs and give the characteristic group of four lines. This behaviour has been observed in the 1,2-dichlorohexafluorocyclobutanes.7 In fact only one isomer, B, gives an AB quartet. The low-field lines of this quartet show a clear quartet splitting indicating that only one fluorine atom of each pair couples strongly with only one CF_3 group. This confirms that B is a 1,2-isomer. It was observed with 1,2-dichlorohexafluorocyclobutane⁷ that the AB quartets for the geometrical isomers have the same average chemical shift. Thus a further confirmation of the geometrical relation between A and B is provided by the observation that the >CF₂ shifts of B average to 51.7 p.p.m., the observed shift for A. Similarly the $\supset CF_2$ lines for C_1

⁶ H. R. Gerberich and W. D. Walters, J. Amer. Chem. Soc., 1961, **83**, 3935, 4884.

J. Chem. Soc. (B), 1966

and C_2 are only 0.25 p.p.m. apart. Both the C_1 and C_2 lines are good septets, as expected for a strongly coupled pair of equivalent fluorine atoms located symmetrically between two CF₃ groups.

The unexpected equivalence of the fluorine atoms within the >CF₂ pair in three isomers A, C_1 , and C_2 , makes the identification of the geometric isomers difficult. It appears that substitution of a fluorine atom by a CF₃ group does not produce asymmetry of shielding on the adjacent CF₂ group. This contrasts sharply with the effect of substitution by chlorine. In the only isomer of DMC that shows asymmetry of shielding there must be a special feature producing it. We deduce that B is *cis*-1,2-DMC and that the cause of asymmetry of shielding is the strain associated with the presence of adjacent CF₃ groups.

As no major difference between the properties of 1,3-DMC isomers, C_1 and C_2 , has been found we cannot complete the identification.

We thank Dr. E. S. Waight for help with mass spectra, Dr. L. F. Thomas of the University of Birmingham for n.m.r. measurements at $94 \cdot 1$ Mc./sec., and the S.R.C. for a maintenance grant to P. B. S. We acknowledge gifts of chemicals by E. I. du Pont de Nemours and Co., Inc., and Imperial Chemical Industries Limited, General Chemicals Division.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON S.W.7. [6/137 Received, February 2nd, 1966]

⁷ B. Atkinson and M. Stedman, J. Chem. Soc., 1962, 512.