## CONCLUSIONS

1. The x-ray diffraction analysis of the structure of E-benzylidene(diphenylmethylene)succinic anhydride has been carried out.

2. The direction of the photo- and thermochromic cyclization reaction of this compound is controlled by steric factors; the phenyl substituent of the diphenylmethylene fragment appears to be drawn closer to the reactive methylene center corresponding to it in comparison with the phenyl substituent of the benzylidene fragment.

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#### FLUOROINDENES.

COMMUNICATION 9.\* PREPARATION OF BROMINATED POLYFLUOROINDENES AND THEIR REACTION WITH OLEUM

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Polyfluoroindenes react with electrophiles at the double bond and/or the geminal node [2-5]. In the reaction with oleum, the extents to which these reactions occur depend on the substituents in the five-membered ring [3, 5]. Specifically, as the number of chlorine atoms increases, the reaction at the geminal node becomes predominant [3]. In order to establish the more general behavior of this process, it was of interest to examine the reaction of oleum with other halogenated polyfluoroindenes, especially with the hitherto unknown polyfluorobromoindenes. Information is available for the synthesis of polyfluorochloroindenes, by the reaction between polyfluoroindenes and AlCl<sub>3</sub> [1, 3, 5], and by dehalogenating polyfluorochloroindanes [1, 2] obtained from polyfluoroindanes and AlCl<sub>3</sub> [6].

For this reason, in order to obtain indenes containing bromine atoms, and also in continuation of studies of the reactions of polyfluorinated indanes and indenes with Lewis acids, we here examine the reactions of polyfluoroindanes and perfluoroindene (I) with  $AlBr_3$ , together with the reactions of bromoindenes with oleum.

It has been shown that perfluoroindane (II) reacts with  $AlBr_3$  to give 1,1-dibromooctafluoroindane (III) and 1,1,3,3-tetrabromohexafluoroindane (IV). The latter is formed together

\*For communication 8, see [1]. +Deceased.

1883

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with the indane (III) even in the early stages of the reaction. Indane (IV) is obtained in high yields using a ratio of (II) to  $AlBr_3$  of ~3:4. When an excess of  $AlBr_3$  is used, l,l,2,3-tetra-bromotetrafluoroindene (V) is obtained. It is noteworthy that when (II) is reacted with an excess of  $AlCl_3$ , the fluorines in the 2-position are not attacked, replacement of F by Cl taking place in the aromatic ring [6]



The formation of bromoindenes also takes place when many other polyfluoroindanes react with an excess of  $AlBr_3$ . For instance, 5,6-dichloro-octafluoroindane (VI) reacts with  $AlBr_3$  to give 1,1,2,3-tetrabromo-5,6-dichlorodifluoroindene (VII). The reaction of 5-chloronona-fluoroindane (VIII) with  $AlBr_3$  gives a mixture of 1,1,2,3-tetrabromo-5-chlorotrifluoroindene (IX) and 1,1,2,3-tetrabromo-6-chlorotrifluoroindene (X), the latter predominating. In an analogous reaction, 5H-nonafluoroindane (XI) undergoes both replacement of F by Br atoms in the five-membered ring, and replacement of H by Br, giving a mixture of 1,1,2,3,6-pentabromotrifluoroindene (XIII), the latter predominating. These results suggest the high thermodynamic stability of the indenes (X) and (XIII) as compared with indenes (IX) and (XII) (cf. the reaction of polyfluoroindenes with  $AlCl_3$  [2]).



Polyfluoroindanes react with  $AlBr_3$ , in all probability, via the formation of indanyl cations (crypto-ions), as in the reaction of the indane (II) with  $AlCl_3$  [6]. The formation of bromoindenes in these reactions may be represented, in the case of (IV), as follows. In the indane (IV), replacement of the F atoms in the 2-position by Br takes place, followed by the reactions:



It was shown in a separate experiment that the indene (I), under the conditions of the reaction of (II) with  $AlBr_3$ , is converted, depending on the amount of  $AlBr_3$  used, into the indene (XIV) or (V). It is noteworthy that in the reaction of (I) with an excess of  $AlCl_3$ , the fluorines in the 2-position are unaffected [3].

TABLE 1. <sup>19</sup>F NMR Spectra of Brominated Polyfluorindenes



Com-	ð, ppm					
pound	<b>F</b> <sup>2</sup>	<b>F</b> <sup>4</sup>	F2	F <sup>6</sup>	F7	$F = F, \Pi Z$
(V)		14,6	11,7	8,5	24,2	$ \begin{bmatrix} J_{45} = 2,0 & J_{46} = 3, & J_{47} = 15,5, \\ J_{56} = 18, & J_{57} = 7, & J_{67} = 20 \end{bmatrix} $
(VII) *		38,2			46,3	$J_{47} = 16,5$
(IX)		36,2		31,0	23,4	$J_{47} = 16, J_{67} = 20$
(X)		14,1	34,1		45,0	$J_{45} = 20, J_{47} = 16, J_{57} = 3,5$
(XII)		44,1		39,1	23,6	$J_{47} = 16,5, J_{67} = 22$
(XIII)		14,4	42,0		52,4	$J_{45}=21, J_{47}=16, J_{57}=3$
(XIV)	35,8	12,5	12,5	7,9	23,6	

\*The spectrum of (VII) was obtained in  $CH_2Br_2$  (~4 mole %).

The differences in the reactions of the indane (II) with an excess of  $AlCl_3$  [6] and  $AlBr_3$  may be explained in terms of the intermediate cation A, with two  $CBr_2$  groups at the cationic center, being more stable than B, which contains the more acceptor  $CCl_2$  groups [7]. In addition, on passing from 1,1,3,3-tetrachlorohexafluoroindane to the cation B, displacement interactions of the F and Cl atoms disappear, and on passing from the indane (IV) to the cation A, the interactions of the F atoms with the more bulky bromine atoms also disappear, which also contributes to the higher stability of A as compared with B.



X = Br (A), C1 (B).

This explanation is in accordance with the reaction of perfluorotetralin (XV) with  $AlBr_3$  to give 1,1,4,4-tetrabromooctafluorotetralin (XVI). Note that the fluorine atoms in (XVI) in the 2- and 3-positions are not attacked, even under conditions somewhat more severe than in the reaction of the indane (II) with  $AlBr_3$ . This is apparently due to the stability of cation C being lower than that of A (the  $CF_2$  group has higher acceptor properties than  $CBr_2$  [7] and, in addition, the gain in energy as a result of the removal of displacement interactions on passing from (XVI) to the cation C must be less than in the case of (IV), cf. [8]).



The bromoindenes (V), (VII), (IX), and (X) react readily with oleum to give the indane-1,3-diones. For example, the reaction of (V) with 20% oleum gives 2,2-dibromotetrafluoroindane-1,3-dione (XVII), reaction of (XVII) and (VII) gives 2,2-dibromo-5,6-dichlorodifluoroindane-1,3-dione (XVIII), and of a mixture of (IX) and (X), 2,2-dibromo-5-chlorotrifluoroindane-1,3-dione (XIX). (See scheme below.)

These reactions may be represented as follows, taking (V) as an example. The reaction evidently first involves the geminal node, with the formation of the 2,3-dibromotetrafluoro-

		Four	nd/Calcu	lated, %			IR spectru cm	·n	
Compound	M.P. C	U	Br	Cl Cl a	F4	empineat formula	Farom	c=0 (c=c)	UV spectrum, λ <sub>max</sub> , um (lg ε)
(111)		26,20	38,10 2006		36,15	$C_9Br_2F_8$	1644, 1518		
(IV)	93–94,7 b	19,92	30,00 59,34		21,00	$C_{6}Br_{4}F_{6}$	1639,		274 pl (3,14), 283 pl (3,07)
. (A)	95–96 b	21.23	62,64	(206)	14,69	$C_9Br_4F_4$	1497	(1554)	326 (3,53)
(ÌII)	120,2–121,2 c	21,46	03,40 - 59,24 - 50,54	(£0€)	15,09	$\mathrm{C_0Br_4Cl_2F_2}$	1447	(1549).	338 (3,56)
(X) + (X1)		20,14	09,30 61,47		10,32	C <sub>6</sub> Br <sub>4</sub> ClF <sub>3</sub>	1484	(1548)	332 (3,66)
(IIIX) + (IIX)		20,78	70,68		10,34	$C_9Br_5F_3$	1477	(1557)	332 (3,72)
(XIV)	44-45 b	19,14 24,62	53.41		21,46	C,Br3F,	1501	(1648)	311 (3,28), 323 pl (3,25)
(XVI)	110,3-111,3 b	24,41 20,48	04,14 53.42 57.02		21,45 25,48	$\mathrm{C}_{10}\mathrm{Br_4F_8}$	1636,		288 (3,41), 293 pl (3,39)
(IIIAX)	109,2–110,2 c	28,71	42,20	(373)	20,05	$C_9Br_2F_4O_2$	1627,	1781, 1750	253 p1 (3.96), 298 (3.21), 349 (3.37),
(IIIIAX)	120,2-121,2 c	26,30 26,44		17.39	8,84 9,29	$C_9Br_3Cl_2F_2O_2$	1594, 1553	1774 1742	270 p1 (4,19), 278 p1 (4,08), 305 p1 (3.20), 317 (3.47).
(XIX)	96–96,7 c	27,23		8,72 9,04	$\frac{14,70}{14,53}$	$C_9Br_2ClF_3O_2$	1606,	1774, 1744	333 $(3.66)260$ pl $(4,10)$ , $269$ nn $(4,02)$ ,
(XX)	109,2-110,1 d	29,86 30,03	$\frac{44,30}{44,41}$	(353) (360)	$\frac{21,44}{21,12}$	$\mathrm{C_9Br_2F_4O}$	1489 1637, 1504	1745 (1560)	307 (3,377), 320 (3,53) 316 Pl (3,21), 327 (3,38), 338 Pl (3,27), 343 (3,33),
						•			388 P1 (3,12), 404 (3,15), 418 P1 (3,09)

TABLE 2. Properties of Compounds Obtained

a) Molecular weights were measured by vapor phase osmometry (solvent CHCl<sub>3</sub>).
b) After crystallization from alcohol.
c) Crystallized from CCl<sub>4</sub>.
d) Crystallized from hexane.

TABLE 3. Conditions for and Results of Reactions of (I), (II), (VI), (VIII), (XI), and (XV) with  $AlBr_3$ 

Compound,	AlBr3, g	CH2Br2, m1	T, C (time, h)	Yield of product, g
$\begin{array}{c} (1) - 1, 1 \\ (1) - 1 \\ (1) - 0, 3 \\ (11) - 30 \\ (VI) - 2 \\ (VIII) - 2 \\ (XI) - 0, 5 \\ (XV) - 0, 3 \\ (XV) - 0, 3 \end{array}$	$1,24 \\ 1,64 \\ 0,47 \\ 59 \\ 3,7 \\ 3,8 \\ 1,64 \\ 0,76 \\ 0,71$	4 8 3 115 9 8,5 5 3 3	$\begin{array}{r} -20 \div -15 \ (0,5) \\ 25-30 \ (3) \\ 15-20 \ (2) \\ 25-30 \ (4) \\ 45-50 \ (2) \\ 45-50 \ (2,5) \\ 20 \ (1,5) , \text{then} 50 \ (0,5) \\ 15-20 \ (2) \\ 25-30 \ (1) , \text{then} 50-55 \ (3,5) \end{array}$	$\begin{array}{l} (XIV) - 1,39 \\ (V) - 1,77 \\ (V) + (XIV)a - 0,42b \\ (V) - 50,2 \\ (VII) - 3,15 \\ (IX) + (X)c - 3,2 \\ (XII) + (XIII)d - 0,7 e \\ (XVI) f - 0,43b \\ (XVI) - 0,44 \end{array}$

a) (V):(XIV) ~ 1:1 (<sup>19</sup>F NMR).

b) Weight of product after purification on a column (silica gel, hexane).

c) (IX):(X) ~ 1:1.6 (<sup>19</sup>F NMR).

d) (XII):(XIII) ~ 1:1.6 (<sup>19</sup>F NMR).

e) Weight of product after purification on a column (silica gel, light petroleum).

f) <sup>19</sup>F NMR spectrum of (XVI) at 10°C ( $\delta$ , ppm): 71.1 (FA<sup>2.3</sup>) and 43.8 FB<sup>2,3</sup>, JAB ~ 245 Hz; 38.1 (F<sup>5,8</sup>), 14.4 (F<sup>6,7</sup>).



indenone (XX) (cf. the reaction of 1,1,3-tri-chloropentafluoroindene with oleum [3]). This reacts with  $Br_2$ , formed under the reaction conditions, to give 2,2,3,3-tetrabromotetrafluoro-indanone (XXI), which then reacts with oleum to give the indandione (XVII).



It was shown in a separate experiment that (XX) in the oleum- $Br_2$  system gives (XVII), but on treatment with an excess of bromine in the absence of oleum it is apparently converted into (XXI) (<sup>19</sup>F NMR spectrum). Compound (XX) was obtained by hydrolyzing the product of the reaction of (V) with  $SbF_5$ .

The structures of the products were confirmed by their elemental analyses and spectral data. The <sup>19</sup>F NMR spectral data of the brominated indenes (Table 1) are in agreement with those of other polyfluoroindenes [1, 9]. Examination of the <sup>19</sup>F NMR spectra of (III), (IV), and (XVI)-(XIX) was carried out as in [6]. The IR spectra of the polyfluorobromoindenes showed, as is also the case for chlorinated polyfluoroindenes [1], a considerable decrease

in the frequencies of the stretching vibrations of the double bonds as compared with perfluoroindene (I) [1]. It is noteworthy that the IR spectra of halogenated ethylenes also show a decrease in the frequency of the stretching vibrations of the double bond when fluorine is replaced by chlorine or bromine [10].

### EXPERIMENTAL

<sup>19</sup>F NMR spectra were obtained on a Varian A-56/60A instrument (56.4 MHz) in CCl<sub>4</sub> (11 mole %), or in the cases of the indenone (XX) and indandiones (XVII)-(XIX) in CH<sub>2</sub>Cl<sub>2</sub> (5-10 mole %). Shifts are given to lower field from  $C_6F_6$  (internal standard). IR spectra were obtained on a UR-20 in CCl<sub>4</sub>, and UV spectra on a Specord UV-VIS in heptane. The data for the compounds are given in Table 2.

<u>1,1,3,3-Tetrabromohexafluoroindane (IV)</u>. To a mixture of 1 g of the indane (II) and 2 ml of  $CH_2Br_2$  was added with stirring at 20-25°C over 0.5 h a solution of 1.32 g of AlBr<sub>3</sub> in 5 ml of  $CH_2Br_2$ . The mixture was stirred for 5 h at 25°C, then treated with 30 ml of 5% hydrochloric acid. The organic layer was separated, dried over MgSO<sub>4</sub>, and transferred to a clock glass to give 1.7 g of the indane (IV). <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 71.4 (F<sup>2</sup>), 24.7 (F<sup>1,7</sup>), 15.4 (F<sup>5,6</sup>).

<u>1,1-Dibromooctafluoroindane (III)</u>. The indane (II) (20 g) was treated with stirring at 0°C over 0.5 h with a solution of 2.4 g of AlBr<sub>3</sub> in 4 ml of  $CH_2Br_2$ , and the mixture stirred for 2 h at 24°C. It was then treated with 5% hydrochloric acid (50 ml), and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure (15-20 mm) together with some of the indane (II) (16 g). The residue (5.6 g) was filtered to give crystals (1.7 g) of the indane (IV). The filtrate contained (II), (III), and (IV) in a ratio of 9:2:1 (<sup>19</sup>F NMR spectrum). The indane (II) was distilled off under reduced pressure (15-20 mm). Molecular distillation of the still residue (100°C, 15 mm) gave 0.42 g of the indane (III). <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 55.7 (F<sup>3</sup>), 49.8 (F<sup>2</sup>), 26.1 (F<sup>7</sup>), 23.0 (F<sup>4</sup>), 18.7 (F<sup>6</sup>), 15.6 (F<sup>5</sup>).

The reactions of the other polyfluoroindanes together with (I) and (XV) with  $AlBr_3$  were carried out as in the first experiment. The experimental data are given in Table 3.

2,3-Dibromotetrafluoroindenes (XX). To a solution of 4.45 g of  $SbF_5$  in 10 ml of  $SO_2$  at  $-50^{\circ}C$  was added 2.59 g of the indene (V), and the mixture stirred at  $-50^{\circ}C$  until all the (V) had dissolved. The mixture was transferred to ice water, extracted with chloroform, dried over MgSO<sub>4</sub>, and the solvent removed to give 2.16 g of solid product, which on column chromatography (silica gel, hexane) gave 1.25 g of (V) and 0.86 g of the indenone (XX). <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 26.6 (1F), 19.1 (2F), 12.3 (1F).

 $\frac{2,2-\text{Dibromo-5,6-dichlorodifluoroindane-1,3-dione (XVIII)}{\text{and 2 ml of 20\% oleum was stirred for 3 h at 50-55°C.}$  The mixture was then transferred to ice water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over MgSO<sub>4</sub>, and the solvent removed to give 1.5 g of (XVIII). <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 53.2.

<u>2,2-Dibromo-5-chlorotrifluoroindane-1,3-dione (XIX)</u>. Obtained as in the preceding example, from 2.1 g of a mixture of indenes (IX) and (X) (~1:1.6) and 2.1 ml of 20% oleum, yield 1.55 g. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 52.3 (F<sup>4</sup>), 47.0 (F<sup>6</sup>), and 28.3 (F<sup>7</sup>).

 $\frac{2,2-\text{Dibromotetrafluoroindane-1,3-dione (XVII)}{2 \text{ g of (V) and 2 ml of 20% oleum, yield 1.5 g XVII.} a) Obtained as in the preceding example, from 2 g of (V) and 2 ml of 20% oleum, yield 1.5 g XVII. <sup>19</sup>F NMR spectrum (<math>\delta$ , ppm): 30.5 (F<sup>4</sup>,<sup>7</sup>) and 26.2 (F<sup>5</sup>,<sup>6</sup>). The <sup>19</sup>F NMR and IR spectra and melting point of (XVII) were identical with those given in [11].

b) A solution of 0.1 g of the indenone (XX) and 0.014 ml of  $Br_2$  in 0.2 ml of 20% oleum was heated in a sealed ampul for 3 h at 50-55°C, then worked up as in the preceding example to give 0.07 g of (XVII).

c) To a solution of 0.1 g of the indenone (XX) in 0.4 ml of  $CH_2Br_2$  in an NMR ampul was added 0.044 ml of  $Br_2$  and the mixture heated at 50-55°C for 12.5 h. The <sup>19</sup>F NMR spectrum of the reaction mixture showed signals for the starting material, and four signals of the same intensity at  $\delta$  27.5, 26.2, 23.8, and 15.1 ppm, apparently attributable to the indanone (XXI) [ratio of (XX) to (XXI), 1:3]. The mixture was transferred to a clock glass to give 0.12 g of product. This was dissolved in  $CH_2Br_2$  and its <sup>19</sup>F NMR spectrum obtained. The ratio of (XX) to (XXI) was 1:2. The mixture was heated for 1 h at 50-55°C, when the proportion of (XX) to (XXI) was 1.5:1 (<sup>19</sup>F NMR spectrum). This was transferred to a clock glass, and heated for 3 h at 50-55°C to give 0.09 g of starting material (XX) (<sup>19</sup>F NMR spectrum).

#### CONCLUSIONS

1. 1,1,3-Tribromopentafluoro- and 1,1,2,3-tetrabromotetrafluoroindene have been obtained from perfluoroindene and  $AlBr_3$ .

2. 1,1,3,3-Tetrabromohexafluoroindane and 1,1,2,3-tetrabromotetrafluoroindene have been obtained from perfluoroindane and  $AlBr_3$ . 1,1,2,3-Tetrabromopolyfluoroindenes are also obtained by treating other polyfluoroindanes with excess  $AlBr_3$ .

3. Hydrolysis of the product of the reaction of 1,1,2,3-tetrabromotetrafluoroindene with  ${\rm SbF}_5$  has given 2,3-dibromotetrafluoroindenone.

4. Reaction of 1,1,2,3-tetrabromopolyfluoroindenes with 20% oleum, and of 2,3-dibromotetrafluoroindenone with oleum in the presence of  $Br_2$ , has given the corresponding 2,2-dibromopolyfluoroindane-1,3-diones.

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