ω-PHENYLPERFLUORO-α-OLEFINS AND ω-PHENYLPERFLUOROALKANOIC ACIDS

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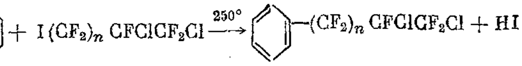
In 1960 Tiers [1] showed that at 250° perfluoroheptyl iodide alkylates benzene with formation of (perfluoroheptyl) benzene and bis(perfluoroheptyl)benzene. The position of the second alkyl group was not elucidated.

By using the ω-iodo-α,β-dichloroperfluoroalkanes prepared by us earlier [2] as alkylating agents, we prepared a number of ω-phenyl-α,β-dichloroperfluoroalkanes.

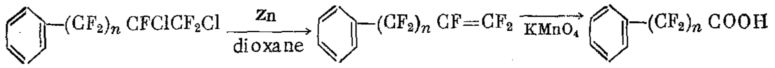


$$I(CF_2)_nCFClCF_2Cl + HI \rightarrow H(CF_2)_nCFClCF_2Cl + I_2$$

$n=2, 4, 6$

The hydrogen iodide formed in the reaction partially reduced the iodoalkanes with replacement of iodine with hydrogen, which greatly reduced the yields of phenylhaloalkanes. By using sodium acetate to bind the hydriodic acid we succeeded in raising the yields of phenylhaloalkanes from 30-40 to 70%.

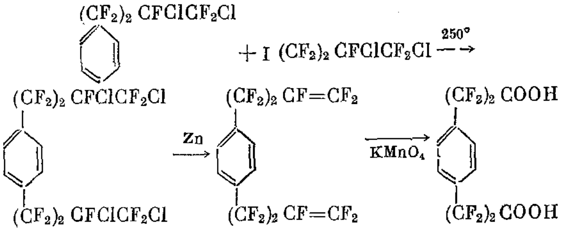
The dechlorination of the ω-phenyl-α,β-dichloroperfluoroalkanes with zinc in dioxane led to ω-phenylperfluoro-α-olefins, and the oxidation of the latter with potassium permanganate led to the corresponding ω-phenylperfluoroalkanoic acids.



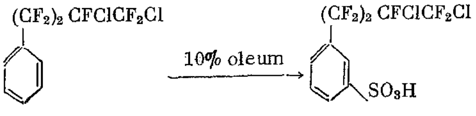
$n = 2, 4, 6$

From the acids we prepared esters, amides, nitriles, and amidines by the usual methods.

The further action of iododichloroperfluoroalkanes led to dialkylbenzenes, which made it possible to pass to a new type of fluorinated diolefins and dicarboxylic acids. The presence of one single peak in the PMR spectrum, both for the dialkyl derivative and for the dicarboxylic acid prepared from it (solution in CF_3COOH), indicates that the second alkyl group enters the para position.



(Polyfluoroalkyl) benzenes are readily sulfonated. Thus, by the action of 10% oleum on (3,4-dichloroheptafluorobutyl) benzene we obtained a quantitative yield of (3,4-dichloroheptafluorobutyl) benzenesulfonic acid.



EXPERIMENTAL

ω-Phenyl-α,β-dichloroperfluoroalkanes. A 250-ml steel ampule was charged with 135 ml of benzene and 0.1 mole of the ω-iodo-α,β-dichloroperfluoroalkane. The ampule was heated at

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TABLE 1. ω-Phenyl-α,β-dichloroperfluoroalkanes

Dichloroper-fluoroalkane	Yield, %	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	MR		Found, %			Calculated, %		
					found	calculated	C	H	F	C	H	F
(3,4-Dichloroheptafluorobutyl)benzene	68,0	207(760) 111(33)	1,4301	1,537	55,31	55,49	35,29	1,71	39,79	36.47	1,52	40,43
1,2-Dichloroundecafluoro-6-phenylhexane	72	137(33)	1,4050	1,616	65,05	65,29	33,77	1,21	48,24	33,57	1,17	48,71
1,2-Dichloropentadecafluoro-8-phenyloctane	62	138(17)	1,3941	1,691	74,83	75,09	31,89	1,09	53,59	31,77	0,95	53,86
p-Bis(3,4-dichloroheptafluorobutyl)benzene	46	124(6)	1,4173	1,732	84,26	84,67	28,81	0,69	44,21	28,96	0,69	45,86

TABLE 2. ω-Phenylperfluoro-α-olefins

Phenylperfluoroalkene	Yield, %	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	MR		Found, %			Calculated, %		
					found	calculated	C	H	F	C	H	F
Heptafluoro-4-phenyl-1-butene	69	70(33)	1,4102	1,418	44,98	45,3	46,51	2,15	50,80	46,51	1,94	51,55
Undecafluoro-6-phenyl-1-hexene	73	99(32)	1,3910	1,544	55,09	55,10	40,02	1,41	57,47	40,22	1,40	58,38
Pentadecafluoro-8-phenyl-1-octene	65	120(25)	1,3760	1,6211	64,83	64,09	36,45	1,29	62,41	36,69	1,09	62,22
p-Bis(heptafluoro-3-butenyl)benzene	59	100(15)	1,3901	1,618	64,18	64,29	38,08	0,99	59,40	38,36	0,91	60,73

TABLE 3. ω-Phenylperfluoroalkanoic Acids and Their Derivatives

Acid and its derivatives	Yield, %	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	Found		Calculated		Found, %			Calculated, %		
					MR	neut. equiv.	MR	neut. equiv.	C	H	F	C	H	F
α,α,β,β-Tetrafluorohydrocinnamic acid	70	150(29)	—	—	—	214,6	—	222	48,53	2,69	33,80	48,65	2,70	34,23
ethyl ester	94	125(20)	1,4390	1,263	52,07	—	51,64	—	53,20	4,02	30,51	52,80	4,00	30.40
amide	93	m.p. 146-147							49,08	2,95	34,02	48,87	3,17	34,39
nitrile	87	146	1,4219	1,2604	40,63	—	40,48	—	53,62	2,73	38,25	53,20	2,46	37,44
amidine	95	m.p. 112	—	—	—	—	—	—	49,00	3,54	33,31	48,99	3,64	34,54
Octafluoro-5-phenylvaleric acid	87	167(35)	—	—	—	324,1	—	322	40,65	1,94	47,89	40,99	1,87	47,20
ester	85	142(24)	1,4100	1,408	61,59	—	61,42	—	44,68	2,99	42,75	44,57	2,86	43,49
amide	93	m.p. 108	—	—	—	—			40,97	1,88	47,50	41,25	1,88	47,50
nitrile	92	103(65)	1,3930	1,426	50,54	—	50,28	—	43,32	1,43	51,48	43,57	1,65	50,17
amidine	98	m.p. 72	—	—	—	—	—	—	41,48	2,59	47,74	41,25	2,50	47,50
Dodecafluoro-7-phenylheptanoic acid	72,5	164(18)	—	—	—	422,5	—	422	36,86	1,52	54,25	36,97	1,42	54,03
Octafluoro-p-benzenedipropionic acid	63	m.p. 172	—	—	—	190,4	—	183	39,68	1,81	40,92	39,34	1,64	41,53

250° for 8 h. Benzene was distilled off through an efficient column, and the residue was diluted with ether. The solution was washed with saturated sodium thiosulfate solution and water, dried with magnesium sulfate, and distilled. The yields and constants of the ω-phenyl-α,β-dichloroperfluoroalkanes obtained are given in Table 1.

p-Bis(3,4-dichloroheptafluorobutyl)benzene. A steel ampule was charged with 49.5 g of (3,4-dichloroheptafluorobutyl)benzene and 114 g of 1,2-dichloroheptafluoro-4-iodobutane. The ampule was heated for 6 h at 250°. The reaction product was extracted with ether, and the extract was washed with saturated sodium thiosulfate solution and water, dried with magnesium sulfate, and distilled through a column of 12-plate efficiency. We obtained: 1) 24 g of 4H-1,2-dichloroheptafluorobutane, b.p. 82-83°; n_D^{20} 1.3282; d^{20} 1.669. Found %: C 19.06; H 0.80; F 53.25; MR 30.77. $C_4HF_7Cl_2$. Calculated %: C 18.97; H 0.40; F 52.57; MR 31.38. 2) 40 g of p-bis(3,4-dichloroheptafluorobutyl)benzene, b.p. 124° (6 mm). 3) Residue (15 g), probably poly(dichloroheptafluorobutyl)benzene.

ω-Phenylperfluoro-α-olefins. A flask fitted with reflux condenser, stirrer, and dropping funnel was charged with 19.5 g of zinc dust and 100 ml of dioxane, and with vigorous stirring at the boiling point 0.1 mole of the phenyldichloroperfluoroalkane was added gradually. The reaction mixture was stirred at the boiling point for 6 h. The reaction product was steam-distilled off, dried, and distilled. The yields and constants of the olefins obtained are given in Table 2.

ω-Phenylperfluoroalkanoic Acids. A three-necked flask fitted with stirrer, dropping funnel, and thermometer was charged with 30 ml of water, 30 ml of acetone, and 4.8 g of potassium permanganate. A solution of 0.015 mole of the phenylperfluoroalkene in 15 ml of acetone was added gradually with maintenance of the temperature at 20°. Stirring was continued for 5 h. The precipitate was filtered off and washed with hot water. The filtrate was decolorized with sulfur dioxide, vacuum-evaporated down to 20 ml, and made strongly acid with 50% sulfuric acid. The layer which separated and the ether extract were dried with magnesium sulfate and distilled. Analogously, from p-bis(heptafluoro-3-butenyl)benzene we obtained $\alpha,\alpha,\alpha',\alpha',\beta,\beta,\beta',\beta'$,-octafluoro-p-benzenedipropionic acid. The yields and constants of the acids and their derivatives are given in Table 3.

Phenylperfluoroalkanoic Esters. A mixture of 0.25 mole of the ω-phenylperfluoroalkanoic acid, 70 ml of absolute ethanol, and 3 ml of fluorosulfuric acid was refluxed for 90 min. The reaction mixture was cooled, poured onto ice, and extracted with ether. The ethereal solution was washed with sodium bicarbonate solution and water and dried with magnesium sulfate. The residue remaining after the removal of ether was vacuum-distilled. The yields and constants of the esters obtained are given in Table 3. The bicarbonate solution was made strongly acid with sulfuric acid (Congo Red), and unchanged acid was recovered.

Phenylperfluoroalkanamides. Dry ammonia was passed into an ice-cooled solution of 0.2 mole of the ethyl ω-phenylperfluoroalkanoate in twice the volume of dry ether until no more was absorbed. Ether was driven off, and the amide was recrystallized from benzene.

Phenylperfluoroalkanenitriles. Equal weights of the ω-phenylperfluoroalkanamide and diphosphorus pentoxide were mixed carefully, and the mixture was heated in a Wurtz flask. The nitrile formed was collected in the receiver and distilled through a column.

Phenylperfluoroalkanamidines. 70 ml of liquid ammonia was introduced into a two-necked flask fitted with reflux condenser cooled with a mixture of acetone and solid carbon dioxide, and with cooling with the same mixture 0.1 mole of the ω-phenylperfluoroalkanenitrile was added rapidly. The reaction mixture was left with cooling for 2 h, and then ammonia was evaporated and the residue was crystallized from heptane.

(3,4-Dichloroheptafluorobutyl)benzenesulfonic Acid. 16.5 g of (3,4-dichloroheptafluorobutyl)benzene was added with vigorous stirring to 80 ml of 10% oleum. The reaction mixture was stirred at room temperature for 1 h and then poured into a cold saturated solution of sodium chloride. The layer which separated was diluted with 30 ml of ether and dried with magnesium sulfate. Ether was driven off, and we obtained 18 g of a thick oil, from which after neutralization with KOH we obtained a quantitative yield of the potassium salt. The potassium salt is soluble in water, ether, and alcohol. The carefully dried salt was recrystallized from alcohol; m.p. 260° (decomp.). Found %: C 26.63; H 0.71; F 27.52. $C_{10}H_4F_7Cl_2SO_3K$. Calculated %: C 26.85; H 0.89; F 29.75.

CONCLUSIONS

1. When ω-iodo-α,β-dichloroperfluoroalkanes were heated with benzene at 250°, ω-phenyl-α,β-dichloroperfluoroalkanes were obtained. By the further action of ω-iodo-α,β-dichloroperfluoroalkanes on these monoalkylbenzenes dialkylbenzenes were obtained, and it was shown by the PMR method that the second alkyl group enters the para position relative to the first.

2. By the action of zinc in dioxane the phenyldichloroperfluoroalkanes were converted into the corresponding ω-phenylperfluoro-α-olefins and phenylenediolefins.

3. By oxidation of the olefins ω-phenylperfluoroalkanoic acids were obtained.

4. Phenylperfluoroalkanes are sulfonated by oleum in the cold with formation of (perfluoroalkyl)-benzenesulfonic acids.

LITERATURE CITED

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2. O. L. Knunyants and Li Chih-yüan, Izv. AN SSSR. Otd. khim. n., 1961, 1462.