PERFLUOROALKYLATION OF ISOBUTYLENE AND TOLUENE

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The thermal addition of allyl systems to the activated double bonds of olefins, as well as to activated bonds of acetylenes, has been well studied [1, 2]. Reactions of this kind have not been carried out with fluoroolefins. Perfluoroisobutylene reacts with isobutylene at the temperature 300°, and forms a linear dimer 1,1-bis-trifluoromethyl-2,2-difluoro-4-methylpentene-4 in 80% yield. The structure is confirmed by the PMR and IR spectra:

$$(CF_3)_2C=CF_2+(CH_3)_2C=CH_2\longrightarrow(CF_3)_2CHCF_2CH_2C(CH_3)=CH_2$$

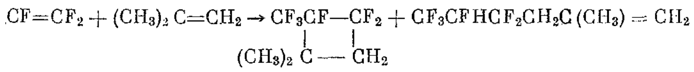
The adduct is readily dehydrofluorinated by dry alkali in ether solution, forming 1,1-bistrifluoromethyl-2-fluoro-4-methylpentadiene-1,4 and readily adds one molecule of bromine in chloroform solution.

$$(CF_3)_2CHCF_2CH_2C(CH_3)=CH_2\xrightarrow{-HF}(CF_3)_2C=CFCH_2C(CH_3)=CH_2\underset{Zn}{\overset{Br_2}{\rightleftarrows}}$$

$$(CF_3)_2C=CFCH_2CBr(CH_3)CH_2Br$$

$$(CF_3)_2CHCF_2CH_2C(CH_3)=CH_2\xrightarrow{Br_2}(CF_3)_2CHCF_2CH_2CBr(CH_3)CH_2Br$$

Perfluoropropylene reacts with isobutylene at 380°, forming two products — a cyclodimer with b.p. 99° and a linear adduct, which by analogy with the adduct of φ-isobutylene and isobutylene, may be ascribed the structure — 1,1,1,2,3,3-hexafluoro-5-methylhexene-5, with b.p. 95°.

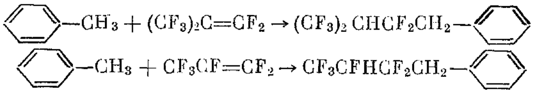


$$CF=CF_2+(CH_3)_2C=CH_2\rightarrow\begin{array}{c}CF_3CF-CF_2\\ \quad|\qquad|\\ (CH_3)_2C-CH_2\end{array}+CF_3CFHCF_2CH_2C(CH_3)=CH_2$$

$$CF_3CFHCF_2CH_2C(CH_3)=CH_2\underset{Zn}{\overset{Br_2}{\rightleftarrows}}CF_3CFHCF_2CH_2C(CH_3)BrCH_2Br$$

The cyclodimer and linear dimer are separated by bromination in chloroform solution. Cyclodimerization of φ-propylene with isobutylene occurs according to the "head to head" type, which is confirmed by the nature of the splitting of the signal of the CH_2 group in the NMR spectrum (Fig. 1).

In the region from 2 to 3 p.p.m., CH_2 represents a doublet, split on the nucleus of one fluorine atom, situated along the diagonal of the ring [3]. The reaction of φ-isobutylene and φ-propylene with toluene proceeds under more rigorous conditions than that with isobutylene, at a temperature of 400-450°, forming 2-trifluoromethyl-3-benzyl-1,. , 1,1,3,3-pentafluoropropane and 3-benzyl-1,1,1,3,3-hexafluoropropane



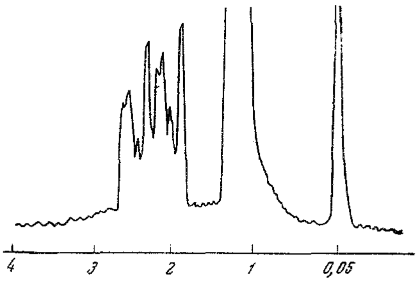


Fig. 1

The structure of the adduct of perfluoroisobutylene with toluene was demonstrated by dehydrofluorination, followed by oxidation of the benzylperfluoroisobutylene obtained to phenylacetic acid. Whereas 2-trifluoromethyl-3-benzyl-1,1,1,3,3-pentafluoropropane

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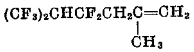
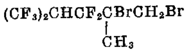
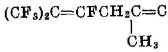
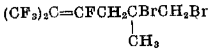
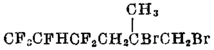
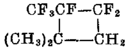
TABLE 1

	Yield,%	B. p., °C p, mm Hg)	n_D^{20}	d_4^{20}	Found					Calculated				
					MR	C,%	H,%	F,%	Br,%	*MR*	C,%	H,%	F,%	Br,%
 $(CF_3)_2CHCF_2CH_2\underset{\substack{\mid\\ CH_3}}{C}{=}CH_2$	80	112	1.3315	1.3470	38.98	37.39	3.14	59.44	—	39.47	37.47	3.12	59.41	—
 $(CF_3)_2CHCF_2\underset{\substack{\mid\\ CH_3}}{C}BrCH_2Br$	80	91 (14)	1.4185	1.8980	55.29	22.99	1.93	37.16	39.40	55.46	23.07	1.92	36.56	38.46
 $(CF_3)_2C{=}CFCH_2\underset{\substack{\mid\\ CH_3}}{C}{=}CH_2$	66	107	1.3405	1.2760	38.81	39.93	3.30	55.67	—	39.18	40.67	2.96	56.35	—
 $(CF_3)_2C{=}CFCH_2\underset{\substack{\mid\\ CH_3}}{C}BrCH_2Br$	84	81 (8)	1.4236	1.8500	55.70	25.19	2.19	34.37	40.94	55.16	24.24	1.76	33.58	40.44
$(CF_3)_2CHCF_2CH_2C_6H_5$	69	66 (8)	1.4010	1.4230	49.86	45.21	2.80	51.93	—	50.19	45.20	2.74	52.05	—
$(CF_3)_2C{=}CFCH_2C_6H_5$	42	71 (10)	1.4185	1.3790	49.76	48.62	2.86	48.75	—	49.52	48.53	2.57	48.89	—
 $CF_3CFHCF_2CH_2\overset{\substack{CH_3\\ \mid}}{C}{=}CH_2$	12,4	95	1.3365	1.2394	34.48	40.34	3.90	56.44	—	34.91	40.77	3.88	55.33	—
 $CF_3CFHCF_2CH_2\overset{\substack{CH_3\\ \mid}}{C}BrCH_2Br$	—	86 (14)	1.4338	1.8560	51.31	23.54	2.23	30.15	44.50	50.89	22.95	2.18	31.14	43.71
	28,6	99	1.3325	1.2975	32.76	39.99	3.71	55.52	—	33.40	40.77		55.33	—
$CF_3CFHCF_2CH_2C_6H_5$	48	70 (16)	1.4128	1.3310	46.08	49.56	3.24	46.64	-	45.59	49.58	3.30	47.10	—

splits out a molecule of hydrogen fluoride under the action of alkali hydroxides in the cold in ether solution, the adduct of φ-propylene with toluene does not split out hydrogen fluoride, neither when heated with potassium hydroxide at 200°, nor with dimethylaniline.

EXPERIMENTAL

Reaction of Perfluoroisobutylene with Isobutylene. In a 50 ml metallic ampule were placed 20 g perfluoroisobutylene, 11 g isobutylene, and 0.1 g hydroquinone, and the mixture was heated for 8 h at the temperature 300°. Distillation yielded 21 g of the adduct. IR spectrum: ν_{max} 3090 cm^{-1} ($> C = CH_2$). PMR spectrum in CCl_4 (standard HMDS), $\delta (CH_3)$ 1.8; $\delta (CH_2)$ 2.8 (triplet); $I(CH_2 - F)$ 18Hz, $\delta (CH_2 =)$ 9.5 (doublet); I6Hz; $\delta (> CH -)$ 3.5 (heptet); I (HF) 8 Hz. 1,1-Bistrifluoromethyl-2,2-difluoro-4-methylpentene-3 adds a molecule of bromine in chloroform, forming the dibromide.

Dehydrofluorination of 1,1-Bistrifluoromethyl-2,2-difluoro-4-methylpentene-4. $(CF_3)_2-CHCF_2CH_2C\cdot(CH_3)=CH_2$ was gradually added with mixing to a suspension of potassium hydroxide in abs. ether. Distillation yielded $(CF_3)_2C=CFCH_2C(CH_3)=CH_2$. IR spectrum: ν_{max} 3095 cm^{-1} ($>C=CH_2$) and 1700-1710 cm^{-1} ($>C=CF$) $\cdot$ $(CF_3)_2C=CFCH_2C(CH_3)=CH_2$ adds one molecule of bromine in chloroform, forming $(CF_3)_2C=CFCH_2C(CH_3)BrCH_2Br$. When it was treated with zinc dibromide in boiling acetone, $(CF_3)_2C=CFCH_2C(CH_3)=CH_2$ was obtained. IR spectrum: ν_{max} 3095 cm^{-1} ($>C=CH_2$), 1700 cm^{-1} ($>C=CF-$).

Reaction of Perfluoropropylene with Isobutylene. In a 250 ml metallic ampule were placed 40 g isobutylene, 120 g perfluoropropylene, and 1 g hydroquinone. The mixture was heated for 8-10 h at a temperature of 380°. The reaction mass was brominated in chloroform solution at room temperature. The excess bromine was decolorized with sodium bisulfite. Distillation yielded: 35 g of a cyclodimer with b.p. 98-99° and 25 g of $CF_3CFHCF_2CH_2CBr(CH_3)CH_2Br$ with b.p. 86°, 14 mm. The IR spectrum of the cyclodimer of perfluoropropylene with isobutylene: ν_{max} 1440 cm^{-1} ($-CH_2-$), with no absorption band in the region of 3100 cm^{-1} ($> C = CH_2$).

A mixture of 5 g granulated zinc and 25 g $CF_3CFHCF_2CH_2CBr(CH_3)CH_2Br$ was boiled in a methanol solution with a reflux condenser for 1 h. The reaction mass was poured out into water. The oil that stratified was dissolved in ether, washed with water, with bicarbonate solution, and again with water. It was dried with calcium chloride. Distillation yielded 5.4 g $CF_3CFHCF_2CH_2C(CH_3) = CH_2$ with b.p. 94-95°. IR spectrum: ν_{max} 3090 cm^{-1} ($> C = CH_2$).

Reaction of Toluene with Perfluoroisobutylene and Perfluoropropylene. A mixture of 0.1 mole of the φ-olefin and 0.25 mole of toluene was heated in a metallic ampule with a 50 ml capacity for 14 h at a temperature of 400° in the case of φ-isobutylene and 450° in the case of φ-propylene. Distillation yielded the adduct.

Dehydrofluorination of the Adduct of Toluene with Perfluoroisobutylene. $C_6H_5CH_2CF_2CH(CH_3)_2$ was gradually added with mixing to a suspension of potassium hydroxide in abs. ether. Distillation yielded benzylperfluoroisobutylene. IR spectrum: ν_{max} 1685 cm^{-1} ($> C = CF$).

Oxidation of Benzylperfluoroisobutylene. A 10 g portion of benzylperfluoroisobutylene was dissolved in 80 ml of acetone, and with mixing at 20-25°, 4 g of $KMnO_4$ was added in portions. After this, the mixture was mixed for another 6 h at 30-35°. The precipitate was washed with hot water, and the aqueous solution extracted with ether and acidified with conc. HCl. The acid mother liquor was extracted several times with ether. From the ether solution we obtained 1.8 g phenylacetic acid (40%, calculated on the basis of the reacted alkene).

The constants and analyses of the compounds obtained are cited in Table 1.

CONCLUSIONS

1. The thermal alkylation of isobutylene with perfluoroisobutylene was carried out, and a linear dimer was obtained. As a result of thermal alkylation of isobutylene with perfluoropropylene, a cyclodimer and a linear dimer were obtained.

2. Cyclodimerization of φ-propylene with isobutylene proceeds according to the "head to head" type.

3. Thermal alkylation of toluene with φ-isobutylene and φ-propylene is accomplished at the methyl group, forming 2-trifluoromethyl-3-benzyl-1,1,1,3,3-pentafluoropropane and 3-benzyl-1,1,1,2,3,3-hexafluoropropane, respectively.

LITERATURE CITED

1. C. J. Albisetti, N. G. Fischer, M. J. Hogsed, and R. M. Joyce, J. Amer. Chem. Soc., 78, 2637 (1956).
2. J. C. Sauer and G. N. Sausen, J. Organ. Chem., 27, 2730 (1962).
3. C. M. Iharts and J. D. Roberts, J. Amer. Chem. Soc., 79, 1008 (1957).