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Alkylation of alkyl halides by diazo compounds where the carbene attacks the C-Hal bond belongs to the type of radical reactions and is sufficiently widely discussed in the literature. We should expect that such alkylation would occur easily with perfluoroalkyl iodides, which, as is known, are easily split homolytically. In the literature, such alkylation has been described only in the case of trifluoromethane with diazomethane, where a mixture is obtained in which 1,1,1-trifluoro-3-iodopropane predominates, along with 1,1,1-trifluoroiodoethane [1]. The reaction was carried out with irradiation by ultraviolet light in the gas phase

$\mathrm{CF_{3}I} + \mathrm{CH_{2}N_{2}} \rightarrow \mathrm{CF_{3}CH_{2}I} + \mathrm{CF_{3}CH_{2}CH_{2}I}$

We have carried out alkylation of perfluoroalkyl iodides by diazomethane in ether solution at room temperature, in daylight or in the dark in the case of 1,2-diiodoperfluoroethane and α,β -dichloro- ω -iodoperfluoroalkanes. In all cases, with excess CH₂N₂ or with excess alkane, we have obtained bismethylene homologs whose formation can be explained by homolytic splitting of the iodine-carbon bond.

 $I \operatorname{CF_2CF_2I} + 4\operatorname{CH_2N_2} \rightarrow I \operatorname{CH_2CH_2CF_2CH_2CH_2I} + 4\operatorname{N_2}$ $I \operatorname{(CF_2)_n} \operatorname{CFClCF_2Cl} + 2\operatorname{CH_2N_2} \rightarrow I \operatorname{(CH_2)_2} \operatorname{(CF_2)_n} \operatorname{CFClCF_2Cl} + 2\operatorname{N_2}$ n = 2, 4.

Perfluoroalkyl chlorides do not react with diazomethane under these conditions. The resulting 1,6-diiodo-3,3,4,4tetrafluorohexane gives no melting point depression with a sample previously obtained by reaction of diiodoperfluoroethane with ethylene [2]. $I(CH_2)_2(CF_2)_2CF ClCF_2Cl$ is identical with the product synthesized from ethylene and 1,2dichloro-4-iodoperfluorobutane in an autoclave at 250°. Neither diazoacetic ester catalyzed by cuprous chloride nor dichlorocarbene obtained by pyrolysis of sodium trichloroacetate in a solution of 1,2-dimethoxyethane react with iodoperfluoroalkanes.

EXPERIMENTAL

Reaction of Diazomethane with Perfluoroalkyl Iodides. In a two-neck flask fitted with a reflux condenser and dropping funnel we placed a solution of diazomethane in ether and at room temperature we gradually added the iodoperfluoroalkane. 2 h after the end of nitrogen evolution, we distilled off the ether and distilled the residue in a vacuum. In the case of diiodoperfluoroethane after distillation of the ether, the residue was twice extracted with hot heptane and the crystalline 1,6-diiodo-3,3,4,4-tetrafluorohexane was isolated. The physical properties and analytical results of the compound are given in the table.

Reaction of Ethylene with 1,2-Dichloro-4-iodoperfluorobutane. We placed in a 250 ml steel ampule 57 g of 1,2-dichloro-4-iodoperfluorobutane. The ampule was cooled in liquid nitrogen, evacuated, and 7 g of ethylene was condensed in it. We heated for 8h at 250°. The reaction mass was fractionated on a column. We obtained 47.5 g (77%) of 1,2-dichloro-6-iodo-5,5,6,6-tetrahydroperfluorohexane, b. p. 81° (8 mm), n_D^{20} 1.4290; d_4^{20} 1.987. Found: C 17.71; H 1.18; F 32.07%; MR 52.41. Calculated: C 17.69; H 0.98; F 32.68%. MR 52.32.

SUMMARY

By reaction of diazomethane in ether solution at room temperature with 1,2-diiodoperfluoroethane, 1,2-dichloro-4-iodoperfluorobutane, and 1,2-dichloro-6-iodoperfluorohexane, we have obtained the corresponding 1,6-

Polyfluorohalo- alkane	B.p., °C (p,mm Hg)	M. p.,°C	n_D^{20}	d_{20}^4	MR			Found, %			Calculated, %		
					found	calcu- lated	Yield, 껴	υ	Н	F	, Σ	н	£1
$I(CH_2)_2(CF_2)_2CFCICF_2CI 1(CH_2)_2(CF_2)_4CFCICF_2CI I(CH_2)_2CF_2CF_2(CH_2)_2 I$	86(13) 114(14)	$\left \frac{-}{114} \right $	1,4288 1,4035	1,987 1,987	52,73 62,34	52,32 61,74	48 62 20	17,50 18,96	0,64 0,76	33,08 41,75	17,69 18,93	0,98 0,78	32,67 41,22

diiodo-3,3,4,4-tetrafluorohexane, 1,2-dichloro-5,5,6,6-tetrahydro-6-iodoperfluorohexane, and 1,2-dichloro-7,7,8,8-tetrahydro-8-iodoperfluorooctane.

LITERATURE CITED

- 1. M. Hudlicky and V. König, Collec. Czechosl. chem. commun., 28, No. 10, 2824 (1963).
- 2. I. L. Knunyants, V. V. Shokina, and S. Khrlakyan, Dokl. AN SSSR, 154, 384 (1964).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.