FLUORINATED MONO- AND DIEPOXY COMPOUNDS*

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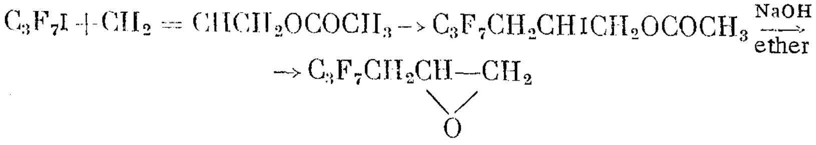
The previously described expoxides containing fluorinated groups were prepared either by the oxidation of the corresponding olefins [1, 2] or by the dehydrohalogenation of halohydrins [3, 4]. In 1962 Brace [5] prepared an epoxyheptafluorohexane by a somewhat unusual method, namely by the action of alkali on the product of the addition of perfluoropropyl iodide to allyl acetate:



$$C_3F_7I + CH_2 = CHCH_2OCOCH_3 \rightarrow C_3F_7CH_2CHICH_2OCOCH_3 \xrightarrow[\text{ether}]{NaOH} \rightarrow C_3F_7CH_2\underset{O}{\underbrace{CH{-}CH_2}}$$

In an analogous way, by the reaction of 1,2-dichloro-1,1,2,3,3,4,4-heptafluoro-4-iodobutane with allyl acetate in presence of azodiisobutyronitrile (ABN) or dicyclohexyl peroxydicarbonate (PODC) we obtained the addition product (I)

$$\begin{aligned} &CF_2ClCFClCF_2CF_2I + CH_2 = CHCH_2OCOCH_3 \longrightarrow \\ &\longrightarrow CF_2ClCFClCF_2CF_2CH_2CHICH_2OCOCH_3 \qquad \text{(I)} \end{aligned}$$

The reactions of octafluoro-1,4-diiodobutane with allyl acetate were found interesting. Our experiments showed that octafluoro-1,4-diiodobutane reacts with allyl acetate with liberation of heat, and in presence of ABN, as well as the monoadduct (II), the diadduct (III) is obtained in good yield:

$$\begin{aligned} &I(CF_2)_4I + CH_2 = CHCH_2OCOCH_3 \longrightarrow \\ &\longrightarrow I(CF_2)_4CH_2CHICH_2OCOCH_3 + CH_3COOCH_2CHICH_2(CF_2)_4\cdot \\ &\cdot CH_2CHICH_2OCOCH_3 \end{aligned}$$

When PODC is used as initiator, with allyl acetate the diadduct (III) is formed exclusively in 82% yield, but with allyl alcohol only the monoadduct (IV) is formed:

$$I(CF_2)_4I + CH_2 = CHCH_2OH \longrightarrow I(CF_2)_4CH_2CHICH_2OH \qquad \text{(IV)}$$

In presence of PODC the monoadduct (II) again reacts with allyl acetate with formation of the diadduct (III). When tetrafluoro-1,2-diiodoethane reacts with allyl acetate a diadduct analogous to (III) is not formed, but only the monoadduct $I(CF_2)_2CH_2CHICH_2OCOCH_3$ (V), which is obtained in about 12%; with allyl alcohol tetrafluoro-1,2-diiodoethane does not react at all. By the action of anhydrous sodium hydroxide in dry heptane on the mono- and diadducts (I) and (III) we obtained mono- and di-epoxy compounds: (see following page)

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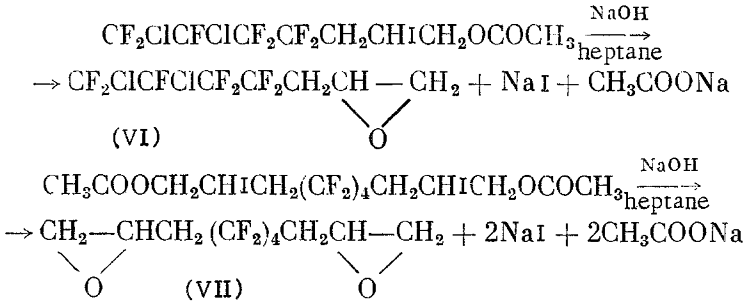


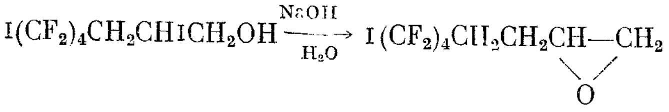
$$CF_2ClCFClCF_2CF_2CH_2CHICH_2OCOCH_3 \xrightarrow[\text{heptane}]{NaOH}$$
$$\rightarrow CF_2ClCFClCF_2CF_2CH_2\underset{O}{\underbrace{CH - CH_2}} + NaI + CH_3COONa$$

(VI)

$$CH_3COOCH_2CHICH_2(CF_2)_4CH_2CHICH_2OCOCH_3 \xrightarrow[\text{heptane}]{NaOH}$$
$$\rightarrow \underset{O}{\underbrace{CH_2 - CH}}CH_2(CF_2)_4CH_2\underset{O}{\underbrace{CH - CH_2}} + 2NaI + 2CH_3COONa$$

(VII)

By the action of aqueous sodium hydroxide on the monoadduct (IV) we obtained the epoxy compound (VIII):



$$I(CF_2)_4CH_2CHICH_2OH \xrightarrow[H_2O]{NaOH} I(CF_2)_4CH_2CH_2\underset{O}{\underbrace{CH - CH_2}}$$

(VIII)

EXPERIMENTAL

Addition of 1,2-Dichloro-1,1,2,3,3,4,4-heptafluoro-4-iodobutane to Allyl Acetate. A mixture of 37.9 g of 1,2-dichloroheptafluoro-4-iodobutane, 10 g of allyl acetate, and 0.33 g of ABN was heated with stirring at 80-90° in an atmosphere of nitrogen for five h. The reaction mixture was vacuum-distilled. After redistillation we obtained 31.1 g of 6,7-dichloro-4,4,5,5,6,7,7-heptafluoro-2-iodo-1-heptanol acetic ester (I) (yield 64.6%); b.p. 128° (6 mm); n_D^{20} 1.4418; d_4^{20} 1.8480. Found: C 22.85, 22.70; H 1.62, 1.60; F 28.10, 28.24%; MR 68.56. $C_9H_8F_7Cl_2O_2I$. Calculated: C 22.54; H 1.67; F 27.76%; MR 68.58 (AR_F 1.19).

Addition of Octafluoro-1,4-diiodobutane to Allyl Acetate. A mixture of 130.5 g of octafluoro-1,4-diiodobutane, 90 g of allyl acetate, and 1.9 g of ABN was heated with stirring at 80-90° in an atmosphere of nitrogen for five h. After 30 min an exothermic reaction was observed, and the temperature within the reaction mixture rose to 105°. The reaction mixture was vacuum-distilled, and we obtained: a) 30 g of unchanged octafluoro-1,4-diiodobutane; b) 48.4 g (36% on the octafluoro-1,4-diiodobutane that reacted) of 4,4,5,5,6,6,7,7-octafluoro-2,7-diiodo-1-heptanol acetic ester (II); b.p. 112-113° (3 mm); n_D^{20} 1.4542. Found: C 19.69, 19.79; H 1.67, 1.47; F 26.71, 26.68%; mol. wt. 535. $C_9H_8O_2F_8I_2$. Calculated: C 19.49; H 1.44; F 27.43%; mol. wt. 554; c) 55.1 g (41.3% on the octafluoro-1,4-diiodobutane that reacted) of the diadduct (III); b.p. 164-167° (0.03 mm); n_D^{20} 1.4680. Found: C 25.87, 25.73; H 25.87, 25.73; H 2.44, 2.52; F 23.02, 22.58%. $C_{14}H_{16}F_8O_4I_2$. Calculated: C 25.68; H 2.44; F 23.24%.

A mixture of 30 g of octafluoro-1,4-diiodobutane, 25 g of allyl acetate, and 1 g of PODC was heated in an atmosphere of nitrogen to 58°, at which temperature the mixture warmed up spontaneously to 67°; heating was then continued for five h at 58-60°. Excess of allyl acetate was driven off, and the product was vacuum-distilled. We obtained 35.6 g (81.9%) of the diadduct (III); b.p. 164-167° (0.03 mm); n_D^{20} 1.4680.

Addition of 4,4,5,5,6,6,7,7-Octafluoro-2,7-diiodo-1-heptanol Acetate (II) to Allyl Acetate. The reaction was for the preceding experiment. From 11.1 g of (II), 2.5 g of allyl acetate, and 0.5 g of PODC we obtained 1.5 g of unchanged (II), b.p. 112-114° (2 mm) and n_D^{20} 1.4558, and 9.7 g [93.8% on the monoadduct (II) that reacted] of the diadduct (III); b.p. 178-180° (2 mm); n_D^{20} 1.4660.

Addition of Octafluoro-1,4-diiodobutane to Allyl Alcohol. A mixture of 40 g of octafluoro-1,4-diiodobutane, 14.3 g of allyl alcohol, and 3 g of freshly reprecipitated PODC was heated with stirring in an atmosphere of nitrogen. When the temperature reached 57-58° it rose further spontaneously to 69°, and heating was continued for five h at 58-60°. Excess of allyl alcohol was driven off, and we obtained 21.2 g (47% on the octafluoro-1,4-diiodobutane taken for reaction) of the monoadduct (IV); b.p. 110-111° (3.5 mm), m.p. 38° (from petroleum ether). Found: C 16.71; H 1.32; F 29.75%. $C_7F_8H_6OI_2$. Calculated: C 16.4; H 1.17; F 29.60%.

Addition of Tetrafluoro-1,2-diiodoethane to Allyl Acetate. A mixture of 36.4 g of tetrafluoro-1,2-iodoethane, 38 g of allyl acetate, and 2.5 g of ABN was heated at 80-85° in an atmosphere of nitrogen for five h. Unchanged allyl acetate (b.p. 103°) and tetrafluoro-1,2-diiodoethane (b.p. 112°) were distilled off, and we obtained 5.5 g (11.8% on the tetrafluorodiiodoethane taken for reaction) of 4,4,5,5-tetrafluoro-2,5-diiodo-1-pentanol acetic ester (V);

b.p. 54-55° (95 mm); n_D^{20} 1.4464. Found: C 18.37, 18.15; H 1.96, 1.81; F 16.78, 16.9%. $C_7F_4H_8O_2I_2$. Calculated: C 18.50; H 1.78; F 16.73%.

Analogously, from 17.7 g of tetrafluoro-1,2-diiodoethane, 15 g of allyl acetate, and 1.43 g of PODC we obtained 2,25 g (10% on the tetrafluorodiiodoethane taken for reaction) of (V).

1,2-Dichloro-6,7-epoxy-1,1,2,3,3,4,4-heptafluoroheptane (VI). A mixture of 11.3 g of 6,7-dichloro-4,4,5,5,6,7,7-heptafluoro-2-iodo-1-heptanol acetate (I) and 70 ml of dry heptane was prepared in a four-necked round-bottomed flask fitted with mechanical stirrer and reflux condenser protected by a calcium chloride tube, and 1.84 g of anhydrous sodium hydroxide was added with stirring in the course of 30 min. The reaction mixture was heated for 7-8 h at 85°, and the solution was then filtered. The precipitate was washed with a little heptane, and the filtrate was washed with water until neutral and dried with magnesium sulfate. After the removal of solvent we obtained a) 3.8 g [100% on the adduct (I) that reacted] of (VI); b.p. 78-80° (12 mm); n_D^{20} 1.3833; d_4^{20} 1.627. Found: C 27.36, 27.47; H 1.47, 1.51; F 41.9, 42.58%; MR 44.33. $C_7F_7Cl_2H_5O$. Calculated: C 27.18; H 1.61; F 43.04%; MR 44.33 (AR_F 1.19); b) 5.4 g of unchanged (I).

1,2:9,10-Diepoxy-4,4,5,5,6,6,7,7-octafluorodecane (VII). 10 g of dry sodium hydroxide was added to a solution of 32.7 g of (III) in 70 ml of heptane at 50-60° in the course of 30 min. The reaction mixture was heated at 85° for four h and then cooled, and 100 ml of water was added to the thick mass. The heptane layer was separated, washed several times with water until neutral to litmus, and dried with magnesium sulfate. The resinous mass which had not dissolved in water or heptane was dissolved in ether, and the ether solution was washed with water until neutral and dried with magnesium sulfate. The residue remaining after the removal of ether and heptane was distilled, and we obtained: a) 6.6 g [46.1% on the diadduct (III) that reacted] of (VII); b.p. 110-112° (5 mm); n_D^{20} 1.3809; d_4^{20} 1.5150. Found: C 37.32, 37.45; H 3.30, 3.30; F 47.31, 47.67%; MR 48.11. $C_{10}H_{10}F_8O_2$. Calculated: C 38.21; H 3.15; F 48.4%; MR 48.00 (AR_F 1.19); b) 3 g of starting substance.

6,7-Epoxy-1,1,2,2,3,3,4,4-octafluoro-1-iodoheptane (VIII). A solution of 3 g of sodium hydroxide in 7 ml of water was boiled in a three-necked flask fitted with mechanical stirrer, condenser, and dropping funnel, and 26 g of (IV) was added slowly. The mixture was heated for two h in a boiling water bath. When cool, the reaction mixture was diluted with water and extracted with ether, and the extract was washed with water until neutral to litmus and dried with magnesium sulfate. After removal of ether we obtained 12 g (61.5%) of (VIII); b.p. 86-88° (12 mm); n_D^{20} 1.4077. Found: C 22.47; F 40.19; H 1.44%. $C_7H_5F_8OI$. Calculated: C 21.87; F 39.58; H 1.30%.

SUMMARY

1. The addition of α-iodo and α,ω-diiodo-fluoroalkanes to allyl acetate was effected in presence of azodiisobutyronitrile and dicyclohexyl peroxydicarbonate.

2. From the addition products the following mono- and di-epoxy compounds were prepared 1,2-dichloro-6,7-epoxy-1,1,2,3,3,4,4-heptafluoroheptane, 1,2:9,10-diepoxy-4,4,5,5,6,6,7,7-octafluorodecane, and 6,7-epoxy-1,1,2,2,3,3,4,4-octafluoro-1-iodoheptane.

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