SULFOTRIOXIDATION OF POLYCHLOROETHYLENES

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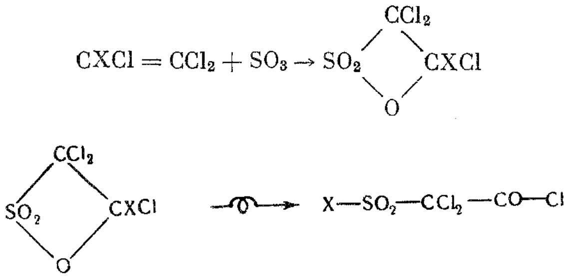
It is well known that the interaction of sulfur trioxide with tetrafluoroethylene [1, 2], trifluorochloroethylene [1-3], and symmetrical difluorodichloroethylene [3] is accomplished under relatively mild conditions and leads to the formation of the corresponding fluorine-contatining β-sultones. It has been found that the interaction of sulfur trioxide with fluorotrichloroethylene and tetrachloroethylene occurs only under comparatively rigorous conditions – when the reagents are heated in an autoclave at 160-180° and 180-200°, respectively. Moreover, in both cases no formation of halogen-containing β-sultones was observed; the reaction products were sulfur dioxide and fluorodichloroacetyl chloride in the first case and trichloroacetyl chloride in the second:

$$CXCl = CCl_2 + SO_3 \longrightarrow SO_2 + CXCl_2 - CO - Cl$$

The difficulties arising when the reaction of sulfur trioxide is carried out with polychloroethylenes in comparison with hydrogen-or fluorine-containing olefins, obviously are due to steric factors – shielding of the multiple bond of the olefin by chlorine atoms, the atomic volume of which considerably exceeds the atomic volumes of hydrogen and fluorine. The reaction may be described by a scheme including intermediate formation of a chlorine-containing β-sultone, its isomerization to a sulfoacetic acid derivative, and cleavage of the latter with liberation of sulfur dioxide:



$$X - SO_2 - CCl_2 - CO - Cl \longrightarrow SO_2 + X - CCl_2 - CO - Cl$$

The possibility of accomplishment of the first step of the reaction is based upon the well-known precedents of the reaction of sulfur trioxide with chlorine-containing olefins – 1,2-dichloroethylene [4] and trichloroethylene [5]. The postulation of the second step of the process – isomerization of the chlorine-containing ethane-β-sultone to a sulfohalodichloroacetyl chloride – is also based upon the well known fact of the analogous isomeric transformation of fluorine-containing β-sultones upon heating [6]. To demonstrate the reality of the third step of the process – desulfoxidation of sulfodichloroacetyl dihalide – we evaluated the thermal stability of compounds of this type. We found that sulfodichloroacetyldichloride breaks down almost entirely when heated to 100°, while sulfodifluoroacetyl chloride breaks down almost entirely when heated above 150°, with the elimination of sulfur dioxide and the formation of the corresponding trichloro- and trifluorochloroacetyl chlorides.

$$Cl - SO_2 - CX_2 - CO - Cl \longrightarrow SO_2 + CX_2Cl - CO - Cl$$

Dihalides containing a fluorine atom in the sulfonyl group are more stable to thermolysis: (e.g. fluorosulfofluoroacety chloride, fluorosulfodifluoroacetyl chloride, and fluorosulfodifluoroacetyl fluoride). In the first case, the elimination of sulfur dioxide is observed upon heating above 180°, in the second above 200°, and in the third above 250°. In all cases there is a predominant formation of the "normal" thermolysis products – the corresponding acetyl halides

$$F-SO_2-CX_2-CO-F \longrightarrow SO_2+CX_2F-CO-F$$

The acyl halides isolated in the desulfoxidation reaction were identified by successive conversion to esters and amides of the corresponding acids.

Thus, the observations and considerations cited permit us to assert that the direction of the reaction of polyhaloolefins with sulfur trioxide will be determined by several factors: the degree of shielding of the multiple bond of the olefin, the tendency of the corresponding halo-containing β-sultone to isomerize to a sulfonyl halide compound, and, finally, the thermal stability of the latter.

EXPERIMENTAL

Sulfotrioxidation of fluorotrichloroethylene. A mixture of 18.0 g sulfur trioxide and 16.0 g of fluorotrichloroethylene was heated in a steel autoclave at 160-180° for three hours. Fractionation of the reaction mixture isolated 5.5 g (86%) sulfur dioxide and 10.1 g (57.5%) fluorodichloroacetyl chloride with b.p. 74-75°. Found: C 13.48; F 10.22; Cl 61.12%. C_2OFCl_3. Calculated: C 13.70; F 10.82; Cl 60.72%.

The chloride was dissolved in ethanol. Fractionation of the solution isolated ethyl fluorodichloroacetate with b.p. 129-130°, which was converted to fluorodichloroacetamide with m.p. 125.5-126°. No depression of the melting point of a mixed sample with a preparation prepared from methyltrichloroacetate through methyfluorodichloroacetate was observed.

Sulfotrioxidation of tetrachloroethylene. A mixture of 18.0 g sulfur trioxide and 16.6 g tetrachloroethylene was heated in an autoclave at 180-200° for four hours. Fractionation of the mixture isolated 5.2 g (81%) sulfur dioxide and 10.2 g (56%) trichloroacetyl chloride with b.p. 117-119°. Found: C 14.69; Cl 85.03%. C_2OCl_4. Calculated: C 14.47; Cl 85.65%.

The chloride was dissolved in ethanol. Fractionation of the solution isolated ethyltrichloroacetate with b.p. 61° (11 mm), which was converted to the diethylamide of trichloroacetic acid with m.p. 26.5°. Found: N 6.21%. $C_6H_{10}ONCl_3$. Calculated: N 6.42%.

Thermolysis of chlorosulfodichloroacetyl chloride. A 24.6 g portion of chlorosulfodichloroacetyl chloride was heated on a boiling water bath until the cessation of evolution of gaseous products, which were condensed in a trap cooled to -20°. The condensate (5.9 g, 92%) was sulfur dioxide. Fractionation of the residue isolated 15.1 g (83%) trichloroacetyl chloride.

Thermolysis of chlorosulfodifluoroacetyl chloride. When 21.3 g of chlorosulfodifluoroacetyl chloride was heated to 150° with a reflex condenser, gaseous substances condensing at -20° were liberated, and the volatile liquid substances were distilled off. The condensate (5.6 g, 87.5%) was sulfur dioxide. Fractionation of the distillate isolated 11.0 g (74%) of difluorochloroacetyl chloride, with b.p. 49-50°. Found: C 15.88; F 25.00; Cl 47.93%. $C_2OF_2Cl_2$. Calculated: C 16.13; F 25.53; Cl 47.70%.

The chloride was dissolved in ethanol. Fractionation of the solution isolated ethyldifluorochloroacetate, with b.p. 96-97°, which was converted todifluorochloroacetamide, with m.p. 78°. Found: N 10.64%. $C_2H_2ONF_2Cl$. Calculated: N 10.82%.

Thermolysis of fluorosulfofluoroacetyl chloride. When vapors of 17.8 g of fluorosulfofluoroacetyl chloride were passed through a quartz tube 400 mm long and 8 mm in diameter, heated to 180-190°, the formation of gaseous substances condensing at -20° and volatile liquid substances collected at 0° was observed. The condensate (5.6 g, 87.5%) was sulfur dioxide. The distillate (8.7 g, 76%) proved to be difluoroacetyl chloride, with b.p. 24-26°.

The chloride was dissolved in ethanol. Fractionation of the solution yielded ethyldifluoroacetate with b.p. 69-70°. Found: C 38.96; H 4.63; F 30.15%. $C_4H_6O_2F_2$. Calculated: C 38.75; H 4.84; F 30.66%, and difluoroacetamide with m.p. 50-50.5°. Found: N 14.55%. $C_2H_3ONF_2$. Calculated: N 14.72%.

Thermolysis of fluorosulfodifluoroacetyl chloride. Vapors of 19.6 g fluorosulfodifluoroacetyl chloride were passed through a quartz tube heated to 200-210°: the reaction products were absorbed in 30 ml of dry methanol, cooled to -20°. Fractionation of the solution yielded 5.9 g (92%) sulfur dioxide and 11.4 g (89%) methyltrifluoroacetate, with b.p. 42-43°. The latter, when treated with ammonia in ether solution, was converted to trifluoroacetamide, with m.p. 74°. Found: N 12.58%; $C_2H_2ONF_3$. Calculated: N 12.38%. No depression of the melting point of a mixed sample with a preparation prepared from trifluoroacetic anhydride was observed.

Thermolysis of fluorosulfodifluoroacetyl fluoride. Vapors of 36 g of fluorosulfodifluoroacetyl fluoride were passed through a quartz tube heated to 250-270°; the reaction products were condensed in a trap cooled to -78°. Among the noncondensing waste gases, we detected carbon monoxide. Fractionation of the condensate isolated two fractions: with b.p. -60 to -50°, yield 21.5 g, and with b.p. -12 to -9°, yield 14.0 g.

Each of the fractions was dissolved in 20 ml of methanol, and the solutions obtained were fractionated. From the first solution we isolated 19.5 g (76%) methyltrifluoroacetate and 4.0 g (18%) dimethyl sulfite, with b.p. 125-126°. Found: C 22.06; H 5.65; S 29.34%; mol. wt. 108.0; equiv. wt. (iodometry) 57.2. $C_2H_6O_3S$. Calculated: C 21.80; H 5.45; S 29.07%; mol. wt. 110.2; equiv. wt. 55.1.

Fractionation of the second solution yielded 10.1 g (78%) sulfur dioxide and 3.5 g (15%) dimethyl oxalate with m.p. 53.5°. A mixed sample with the commercial recrystallized preparation gave no depression of the melting point.

SUMMARY

1. The sulfotrioxidation of fluorotrichloroethylene and tetrachloroethylene was studied.

2. The thermolysis of dihalides of substituted sulfoacetic acids, carried out with an elimination of sulfur dioxide, was studied.

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