(2 + 3)-CYCLOADDITION REACTIONS OF OXIRANES AND THIIRANES

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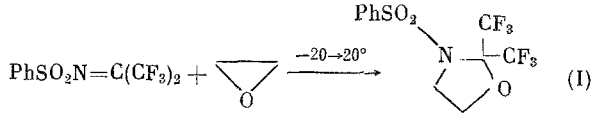
The presently known (2 + 3)-cycloaddition reactions of oxiranes and thiiranes are high-temperature and/or catalytic processes [1, 2]. Thus, their cycloadducts with carbon disulfide, carbon oxysulfide, isocyanates, and isothiocyanates form upon heating in the presence of bases (see [2], pp. 209-211). Their cycloaddition to nitriles of acids and ketenes has been carried out under electrophilic catalysis (see [2], pp. 266-267). Such highly electrophilic compounds as hexafluoroacetone and hexafluorodimethyl ketene form copolymers with three-membered heterocyclic compounds [3, 4]; however, (2 + 3)-cycloadducts were also obtained under the conditions for the thermal degradation of the latter. All these reactions are treated as stepwise (2 + 3)-cycloaddition processes, whose stereochemistry is controlled in a number of cases by the orbital symmetry of the strong intramolecular interactions in the intermediate particles.

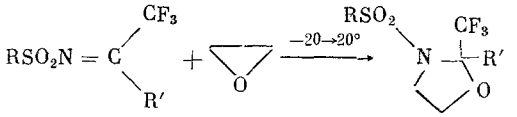
In this communication we shall examine the reactions of oxiranes and thiiranes with polyfluoroketone N-sulfonylimines. The latter compounds differ significantly from the aforementioned dipolarophiles. They undergo (2 + 2)-cycloaddition reactions under extremely mild conditions (−65 to 20°C) [5], as is characteristic of unsaturated compounds with a symmetrically drained π orbital. Accordingly, as was shown in [6], they form (2 + 4)-cycloaddition products with cis-1,3-dienes only at −78 to −50°C, at which their multiple bond is thermally inactivated. In addition, polyfluoroketone N-sulfonylimines were found to be mild π-acids. Thus, they add nucleophilic reagents more readily, the lower is their rigidity [7, 8]. π-Donors of electrons, such as dimethylaniline, anisole, and thiophene react with these compounds to form products of Michael reactions more readily, the higher is the polarizability of the π-donor [9]. The properties just cited characterize polyfluoroketone N-sulfonylimines as highly polarizable azomethines with a symmetrically drained, almost homolyzed π-orbital and were also the reasons for their selection as the dipolarophiles for the (2 + 3)-cycloaddition of oxiranes and thiiranes.

The preliminary study of the conversions in the hexafluoroacetone N-benzenesulfonylimine—ethylene oxide system showed that these reactions can be controlled only in dilute solutions [10]. The (2+3)-cycloaddition product in this case, i.e., oxazolidine I, could be obtained almost quantitatively at −20°C by mixing dilute solutions of the reagents. Under more severe conditions, as well as in the presence of water, copolymerization of the reagents takes place.



(I)

The reactions with chloropentafluoroacetone N-benzenesulfonylimine and hexafluoroacetone N-methanesulfonylimine are also realized smoothly under the optimal conditions for the synthesis of I:



R = Ph, R' = CF_2Cl (II), R = CH_3, R' = CF_3 (III).

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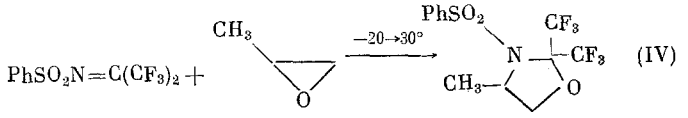
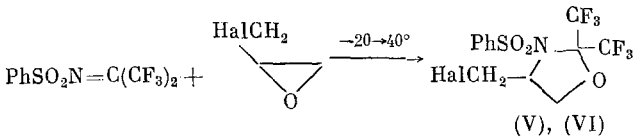
Hexafluoroacetone N-benzenesulfonylimine reacts more vigorously with propylene oxide than with ethylene oxide, and for this reason partial copolymerization of the reactants and a decrease in the yield of oxazolidine IV occur:



(IV)

As expected, the reactions of hexafluoroacetone N-benzenesulfonylimine with epichloro- and epibromohydrin, which have weaker π-donor properties, take place only with heating. At the same time, in these cases, too, the (2 + 3)-cycloadducts could be obtained only after mixing dilute solutions under mild conditions:

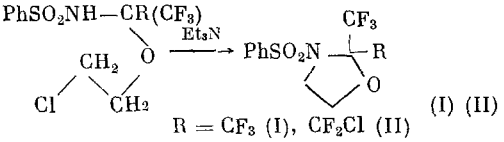


(V), (VI)

Hal = Cl (V), Br (VI).

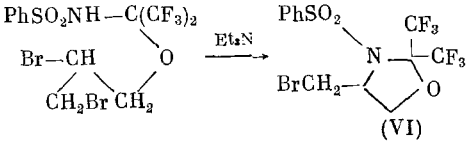
Apparently, selective cycloaddition occurs in the reactions under investigation only from the primarily formed π complexes as a result of the concerted transfer of an electron from the oxygen atom to the C=N bond and from the nitrogen atom of the latter to the two-carbon fragment in the oxirane ring.

In order to prove the structure, some of the oxazolidines considered above were synthesized by a back method. The synthesis of cycloadducts I and II was realized by cyclocondensation of the products of the reaction of the polyfluoroketone N-sulfonylimines with ethylenechlorohydrins:



(I) (II)

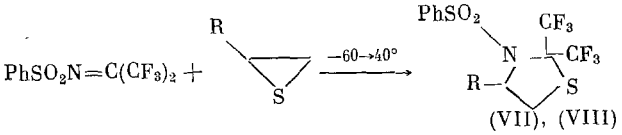
Oxazolidine IV was obtained with a high yield according to the scheme



(VI)

The physicochemical properties and spectral characteristics of the compounds obtained by the two methods were identical.

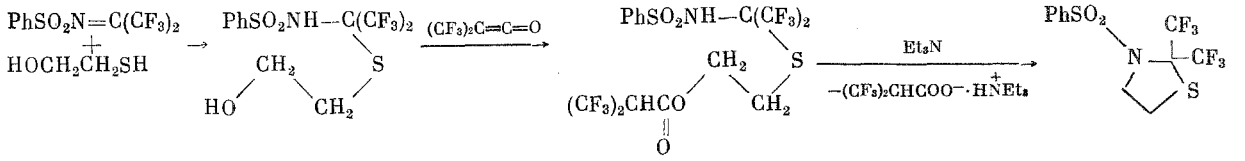
The reaction of hexafluoroacetone N-benzenesulfonylimine with thiiranes was more vigorous than that with the oxiranes. Ethylene sulfide and propylene sulfide were successfully involved in cycloaddition by mixing dilute solutions of the reactants at −60°C and then slowly heating the mixture to 30-40°C:



(VII), (VIII)

R = H (VII), CH_3 (VIII).

The ability of polyfluoroketone N-sulfonylimines to add thiols considerably more easily than alcohols [8] was utilized for the back synthesis of thiazolidine VII. For example, at −30 to −20°C 2-hydroxyethyl mercaptan smoothly reacts with hexafluoroacetone N-benzenesulfonylimine, and the N-[α-(2-hydroxyethylthio)hexafluoroisopropyl]benzenesulfamide formed was subjected after acylation by hexafluorodimethyl ketene to cyclocondensation. The compound obtained by this method was identical to thiazolidine VII considered above:



Unlike the polyfluoroketone N-sulfonylimines, hexafluoroacetone imine does not react with ethylene oxide under mild conditions, and a copolymer of these reagents forms in the presence of triethylamine. In addition, it has been shown that 3,3,3-trifluoropropylenesulfonyl fluoride, whose reactivity is close to that of the polyfluoroketone N-sulfonylimines, exothermically forms a donor–acceptor complex with ethylene oxide, which decomposed upon heating back to the original reactants. Thus, the ability of oxiranes and thiiranes to undergo (2 + 3)-cycloaddition is realized only with dipolarophiles which have a symmetrically drained π orbital and a high polarizability.

EXPERIMENTAL

Freshly prepared polyfluoroketone N-sulfonylimines, freshly redistilled propylene oxide, ethylene sulfide, and propylene sulfide, and ethylene oxide dried over a sodium wire were used in the reactions. The NMR spectra were recorded on a Perkin–Elmer R-20 spectrometer. The chemical shifts are given in the δ scale in parts per million relative to TMS for the ^1H nuclei and relative to CF_3COOH for the ^{19}F nuclei. The mass spectra were recorded on a Varian MAT CH-8 spectrometer with an ionizing energy of the electron beam equal to 70 eV.

2,2-Bis(trifluoromethyl)-3-benzenesulfonyl-1,3-oxazolidine (I). a) A solution of 6.1 g of hexafluoroacetone N-benzenesulfonylimine in 30 ml of diethyl ether at –20°C was given a dropwise addition of a solution of 1.0 g of ethylene oxide in 10 ml of the same solvent with stirring. The mixture was stirred at –20°C for 2 h, slowly heated to 20°C, held at that temperature for 24 h, and evaporated. This yielded 5.8 g (84%) of the compound, mp 59°C. Found: C 37.92; H 2.63; N 4.08; S 8.86%. Calculated for $C_{11}H_9F_6NO_3S$: C 37.83; H 2.60; N 4.01; S 9.18%. ^{19}F NMR spectrum (CCl_4): –3.9 (s, CF_3). ^1H NMR spectrum (CCl_4): 7.8–8.23 (m, C_6H_5), 3.95 and 4.95 (t, CH_2, J = 6.0 Hz). Mass spectrum: m/z 349 (M^+).

b) A solution of 13.3 g of N-[α-(2-chloroethoxy)hexafluoroisopropyl]benzenesulfamide in 40 ml of diethyl ether was given a dropwise addition of a solution of 3.5 g of Et_3N in 10 ml of the same solvent at –20°C with stirring. The mixture was heated to 20°C, held at that temperature for 4 h, and filtered, and the filtrate was evaporated. This yielded 10.7 g (87%) of the product, mp 59–60°C. ^{19}F NMR spectrum (CCl_4): –3.9 (s, CF_3). Mass spectrum: m/z 349 (M^+).

2-Trifluoromethyl-2-chlorodifluoromethyl-3-benzenesulfonyl-1,3-oxazolidine (II) was obtained under the conditions for the synthesis of I according to synthesis a) from 6.4 g of chloropentafluoroacetone N-benzenesulfonylimine and 1.0 g of ethylene oxide. The yield was 6.0 g (82%), and the mp was 43–44°C. Found: C 36.12; H 2.35; N 4.22; S 8.86%. Calculated for $C_{11}F_9F_5ClNO_3S$: C 36.20; H 2.46; N 3.84; S 8.75%. ^{19}F NMR spectrum (CCl_4): –6.7 (t, CF_3, J = 8.0 Hz), –19.6 (m, CF_2Cl). ^1H NMR spectrum (CCl_4): 7.4–8.0 (m, C_6H_5), 3.61 and 4.09 (t, CH_2, J = 6.0 Hz).

2,2-Bis(trifluoromethyl)-3-methanesulfonyl-1,3-oxazolidine (III) was obtained under the conditions for the synthesis of I according to synthesis a) from 4.85 g of hexafluoroacetone N-methanesulfonylimine and 1.0 g of ethylene oxide. The yield was 4.4 g (76%), and the mp was 29–30°C. Found: C 25.16; H 2.35; S 10.82%. Calculated for $C_6H_7F_6NO_3S$: C 25.08; H 2.44; S 11.19%. ^{19}F NMR spectrum (CCl_4): –3.46 (s, CF_3). ^1H NMR spectrum (CCl_4): 3.12 (s, CH_3), 3.78 and 4.69 (t, CH_2, J = 6.0 Hz). Mass spectrum: m/z 287 (M^+).

2,2-Bis(trifluoromethyl)-3-benzenesulfonyl-4-methyl-1,3-oxazolidine (IV) was obtained under the conditions of the synthesis of I from 6.1 g of hexafluoroacetone N-benzenesulfonylimine and 1.35 g of propylene oxide with the one difference that before the evaporation of the solvent the mixture was boiled for 2 h. The yield of IV was 5.2 g (72%), and the mp was 32–33°C. Found: C 39.43; H 2.98; N 3.76; S 8.29%. Calculated for $C_{12}H_{11}F_6NO_3S$: C 39.67; H 3.03; N 3.85; S 8.81%. ^{19}F NMR spectrum ($CHCl_3$): –5.74 and –2.95 (q, CF_3, J = 10.0 Hz). ^1H NMR spectrum (CCl_4): 7.9–8.44 (m, C_6H_5), 3.4–4.6 (m, CH, CH_2), 1.36 (d, CH_3). Mass spectrum: m/z 363 (M^+).

2,2-Bis(trifluoromethyl)-3-benzenesulfonyl-4-chloromethyl-1,3-oxazolidine (V). A solution of 6.1 g of hexafluoroacetone N-benzenesulfonylimine in 30 ml of diethyl ether was given an addition of a solution of 2.2 g of epichlorohydrin in 20 ml of the same solvent at −20°C with stirring. The mixture was slowly heated to boiling, boiled for 8 h, and evaporated. This yielded 5.0 g (64%) of the product, mp 75-76°C. Found: C 36.01; H 2.50; N 3.48; S 7.78%. Calculated for $C_{12}H_{10}F_6ClNO_3S$: C 36.22; H 2.51; N 3.52; S 8.05%. ^{19}F NMR spectrum (CCl_4): −4.72 (s, CF_3). ^1H NMR spectrum (CCl_4): 7.2-8.3 (m, C_6H_5), 4.2 and 3.55 (d, OCH_2 and $ClCH_2$, J = 8.6 Hz), 3.16 (t, CH, J = 9.2 Hz).

2,2-Bis(trifluoromethyl)-3-benzenesulfonyl-4-bromomethyl-1,3-oxazolidine (VI). a) The compound was obtained under the conditions for the synthesis of V from 3.05 g of hexafluoroacetone N-benzenesulfonylimine and 1.5 g of epibromohydrin. The yield was 3.65 g (78%), and the mp was 86-87°C. Found: C 32.76; H 2.24; N 3.07; S 7.01%. Calculated for: $C_{12}H_{10}F_6BrNO_3S$: C 32.70; H 2.27; N 3.18; S 7.25%. ^{19}F NMR spectrum (CCl_4): −4.5 (s, CF_3). ^1H NMR spectrum (CCl_4): 7.5-8.1 (m, C_6H_5), 4.4 and 3.8 (d, OCH_2 and $BrCH_2$, J = 8.0 Hz), 3.36 (t, CH, J = 9.0 Hz).

b) A solution of 5.8 g of N-[α-(2,3-dibromopropoxy)hexafluoroisopropyl]benzenesulfamide in 30 ml of diethyl ether was given an addition of 1.12 g of Et_3N at −20°C with stirring. The mixture was slowly heated to 20°C, held at that temperature for 4 h, and filtered, and the filtrate was evaporated. This yielded 4.2 g (86%) of the product, mp 85-87°C. ^{19}F NMR spectrum (CCl_4): −4.5 (s, CF_3).

2,2-Bis(trifluoromethyl)-3-benzenesulfonyl-1,3-thiazolidine (VII). a) A solution of 3.05 g of hexafluoroacetone N-benzenesulfonylimine in 15 ml of toluene was given an addition of a solution of 0.65 g of ethylene sulfide at −60°C with stirring. The mixture was slowly heated to 35-40°C, held at that temperature for 2 h, and fractionated. This yielded 2.1 g (55%) of the product, mp 30-31°C. Found: C 35.90; H 2.43; N 3.56; S 17.02%. Calculated for $C_{11}H_9F_6NO_2S_2$: C 36.16; H 2.46; N 3.83; S 17.53%. ^{19}F NMR spectrum ($CHCl_3$): −11.6 (s, CF_3). ^1H NMR spectrum ($CHCl_3$): 7.5-8.2 (m, C_6H_5), 3.9 and 5.16 (t, CH_2, J = 6.2 Hz). Mass spectrum: m/z 365 (M^+).

b) A solution of 6.1 g of hexafluoroacetone N-benzenesulfonylimine in 30 ml of diethyl ether was given a dropwise addition of a solution of 1.56 g of 2-hydroxyethyl mercaptan in 10 ml of the same solvent at a temperature from −40 to −30°C with stirring. The mixture was slowly heated to 20°C, and the solvent was evaporated in a vacuum. This yielded 7.66 g (100%) of technical-grade N-[α-(2-hydroxyethylthio)hexafluoroisopropyl]benzenesulfamide, mp 57-59°C. Found: C 34.15; H 2.75; N 3.83; S 16.24%. Calculated for $C_{11}H_{11}F_6NO_3S_2$: C 34.46; H 2.87; N 3.65; S 16.71%. ^{19}F NMR spectrum (CCl_4): −7.6 (s, CF_3).

A 2.5-g portion of hexafluorodimethylketene was bubbled into a solution of 3.83 g of N-[α-(2-hydroxyethylthio)hexafluoroisopropyl]benzenesulfamide in 25 ml of diethyl ether at −15 to −10°C with stirring. The mixture was stirred at −10 to −5°C for 1 h and left to stand for 24 h at 20°C. Then the reaction mass was cooled to −40°C, treated with a solution of 1.0 g of triethylamine in 10 ml of diethyl ether, slowly heated to 20°C, washed with water (three 20-ml portions), dried over sodium sulfate, and evaporated. This yielded 2.8 g (76%) of thiazolidine VII, mp 30-31°C. ^{19}F NMR spectrum: −11.6 (s, CF_3).

2,2-Bis(trifluoromethyl)-3-benzenesulfonyl-4-methyl-1,3-thiazolidine (VIII) was obtained under the conditions for the synthesis of VII according to procedure a) from 3.05 g of hexafluoroacetone N-benzenesulfonylimine and 0.8 g of propylene sulfide. The yield was 3.4 g (81%), and the bp was 92-93°C (0.01 mm). Found: C 38.34; H 2.90; N 3.41; S 16.69%. Calculated for $C_{12}H_{11}F_6NO_2S_2$: C 38.10; H 2.91; N 3.69; S 16.89%. ^{19}F NMR spectrum (CCl_4): −12.85 and −8.95 (q, CF_3, J = 9.8 Hz). ^1H NMR spectrum (CCl_4): 7.4-8.1 (m, C_6H_5), 3.3-4.2 (m, CH, CH_2), 1.17 (d, CH_3, J = 6.0 Hz).

CONCLUSIONS

1. The reactions of polyfluoroketone N-sulfonylimines with several oxiranes and thiiranes have been studied, and the unusually mild formation of 1,3-oxazolidines and 1,3-thiazolidines in these reactions has been demonstrated.

2. It has been established that selective cyclization takes place in the reactions studied only in dilute solutions under conditions which provide for the initial mild formation of donor–acceptor complexes of the reactants.

3. Theories regarding the role of the symmetry of the π orbital and the polarizability of the dipolarophile in the possibility of its mild involvement in cyclization with oxiranes and thiiranes have been advanced.

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NUCLEOPHILIC SUBSTITUTION OF HYDROXYL GROUPS IN 2-ALKYL(ARYL)-THIOETHANOLS

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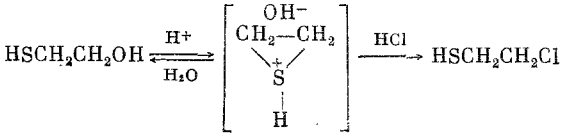
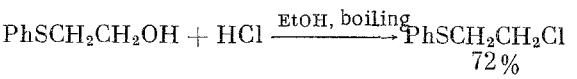
The features of the reactivity of 2-alkyl(aryl)thioalkanols in the nucleophilic substitution of the hydroxyl group have practically not been revealed, and the limited information on these conversions refers predominantly to reactions involving the replacement of the OH group by a halogen atom [1].

The possibility of the occurrence of such reactions was demonstrated for the first time in the example cases of the synthesis of di(2-chloroethyl) sulfide by reacting di(2-hydroxyethyl) sulfide with hydrochloric acid saturated with HCl upon heating [2]. 2-Chloroethyl mercaptan was obtained from 2-hydroxyethyl mercaptan by the same method under pressure in [3]. The comparatively mild replacement of the OH group by a chlorine atom in the reactions just cited is attributed to the ability of the original hydroxy compounds to form episulfonium ions upon protonation, which are opened not only by a hydroxide anion, but also by a chloride ion.



The low solubility of 2-alkyl(aryl)thioethanols in hydrochloric acid presents their exhaustive substitutive halogenation by the method considered above. It is possible to carry out such conversions exclusively only under homogeneous conditions, for example, in solutions of alcohols [4]:



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