On reduction with $LiAlH_4$ in ether we obtained: from the methyl ester of 2,2,4,4-tetramethylpentanoic acid, 2,2,4,4-tetramethyl-1-pentanol, bp 76° (8 mm), n_D^{20} 1.4402, d_4^{20} 0.8427; from the methyl ester of 2-isopropyl-3,3-dimethylbutanoic acid, 2-isopropyl-3,3-dimethyl-1-butanol bp 75-78° (8 mm), n_D^{20} 1.4499, d_4^{20} 0.8745; from the mixture of esters from C_{13} acids, a mixture of C_{13} alcohols bp 141-145° (6 mm), n_D^{20} 1.4505.

CONCLUSIONS

BF_3 Complexes with acetic or propionic acid are highly active and stable catalysts for the carbonylation of olefins and alcohols and may be used repeatedly without lowering the initial activity.

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GENERATION AND PROPERTIES OF EPISULFONIUM COMPLEXES

COMMUNICATION 4*. PREPARATION OF EPISULFONIUM INTERMEDIATES FROM tert-BUTYLETHYLENE, AND THEIR REACTION WITH NUCLEOPHILIC REAGENTS AND REARRANGEMENT

É. A. Vorob'eva, M. Z. Krimer,
and V. A. Smit

UDC 542.91:547.379.2:547.313

In previous papers it was shown that the reaction of cyclohexene with cationoid reagents, like $C_6H_5SBF_4$ or CH_3SBF_4, leads to the formation of stable intermediates, which then are capable of reacting with various "external" intermediates [1-4]. These results made it possible to start broader studies, the purpose of which was to ascertain if analogous complexes can be obtained from other olefins and to study the characteristics of their structure and reactivity. In the present paper the study object is tert-butylethylene (I) (see [5] for preliminary communication), since the structure of this olefin made it possible to set up the problem regarding the regioselectivity of the addition of the attacking electrophile RS^+ and the "external" nucleophile Z, as well as the problem of whether rearrangements can be realized in the studied system.

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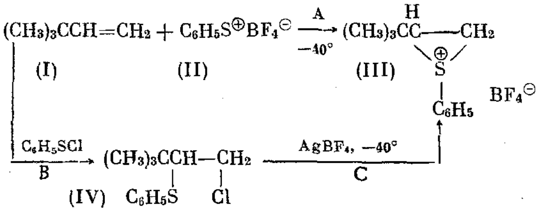
*See [1-3] for Communications 1-3.

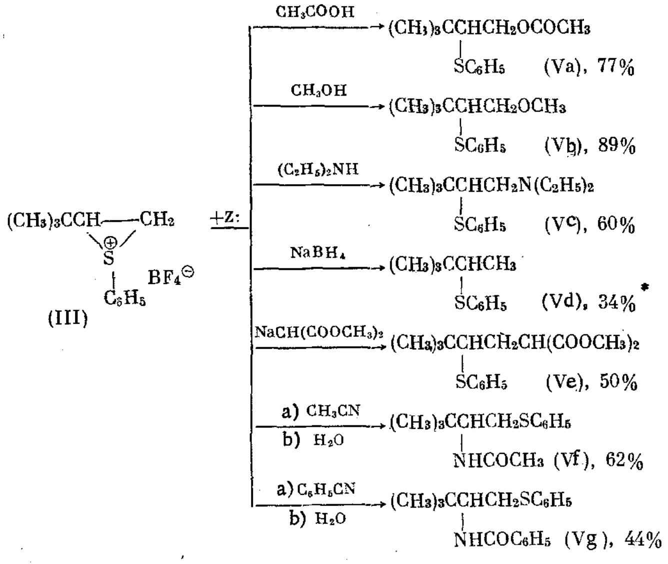
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, and the Institute of Chemistry of the Moldavian SSR, Kishinev. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1318-1325, June, 1976. Original article submitted June 11, 1975

We studied the reaction of (I) with $C_6H_5SBF_4$ (II) [obtained by the reaction: ($C_6H_5SCl + AgBF_4 \rightarrow C_6H_5SBF_4 + AgCl$]. It proved that this reaction proceeds quite easily and completely even at −40° C, in which connection the starting (I) is no longer detected in 10-15 min after mixing the reactants. A colored solution of the complex is obtained as a reaction result, which supposedly has the structure of the episulfonium ion (III). An alternate path [3] can be used to generate the complex (III), which includes the step of obtaining the covalent adduct (IV) (step B) and treatment of the latter with $AgBF_4$ (step C).



Complex (III) can be kept without change for several hours at −40 to −20° in solvents with a low nucleophilicity (CH_2Cl_2, $C_2H_4Cl_2$, CH_3NO_2, SO_2). This estimate is based on the yield of reaction products that is obtained when (III) is reacted with some external nucleophile. For example, the yield of the acetoxy adduct (Va) (obtained by treating (III) with AcOH, see below) did not change when the prior time of keeping complex (III) at −40° was varied from 10 min to 10 h. This stability made it possible to regard complex (III) as being a stable intermediate and make a broad study of its reaction characteristics under various conditions.

The principal property that determines the chemical behavior of complex (III) is its high electrophilicity. Thus, the reactions with nucleophiles of highly diverse nature, which are added to a solution of complex (III), proceed quite easily and, as a rule, are ended in 10-30 min even at −40 to −10°. The studied examples are enumerated in the following scheme.



The given structures of the adducts are based on the elemental analysis, IR, mass, and NMR spectral data. The fact that adducts (Va − g) are obtained in high or satisfactory yields serves as evidence that the main direction of the reaction of (III) with nucleophiles is attack on the carbon atom of the episulfonium ring. Here for most of the examples (Va − e) the regioselectivity of adding the nucleophiles corresponds to approach of the base from the sterically less shielded side of the bridge†. Violation of this rule was observed only when nitriles were used as the bases. When (III) is treated with nitriles it may be assumed that equilibrium is established between the episulfonium complex and the cyclic nitrilium salts (VI) and (VII) (similarly constructed intermediates were proposed previously for the reaction of obtaining Δ^2-thiazolines via the opening of episulfides by acids in the presence of nitriles [6]). Apparently, the predominant component in this mixture is the less hindered complex (VII) and this, according to the Markovnikov rule, is responsible for the

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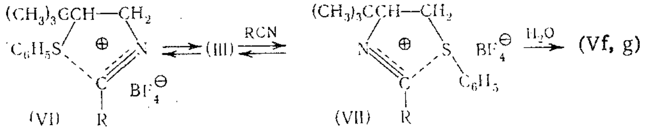
*Together with 35% of the corresponding hydroxy product (Vh).

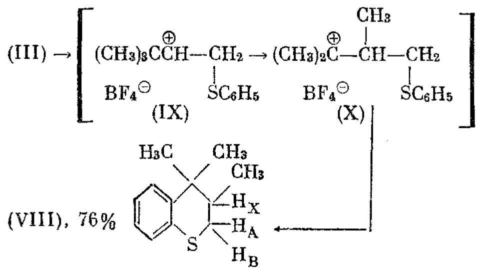
†Based on the NMR spectral data, contamination by the position isomers does not exceed 5-10% in the obtained adducts.



predominant formation of adducts (Vf) or (Vg) (when the reaction mixture is subsequently neutralized with aqueous $NaHCO_3$ solution). This postulated equilibrium can also explain the formation, together with amide products (Vf) and (Vg), of a substantial amount (up to 30%) of the usual (contrary to the Markovnikov rule) acetoxy adduct (Va), if the reaction mass is treated first with AcOH and then neutralized in the usual manner.

The ease with which (III) reacts with nucleophiles of variable nature, and the resulting predominant formation of the addition products of the nucleophilic moiety to the carbon center, show that complex (III) should be attributed to the discharge of cationoid intermediate of the carbonium-ion type. Especially indicative in this respect are the examples where (III) is reacted with such typical "supercaptors" of carbonium-ion intermediates as $NaBH_4$ [7] or nitriles [8]. The fact that both 2-phenylmercapto and 1-phenylmercapto derivatives can be obtained from complex (III) serves as clear evidence that the episulfonium bridge is present, which is apparently responsible for the stability of the intermediate.

It is known that the formation of substantial amounts of rearranged products is observed in most of the electrophilic addition reactions to (I) [9], in which connection the assumptions that cationoid intermediates take part in these reactions are based specifically on this fact. Consequently, it may be assumed that rearrangement products will also be formed in the reactions involving the cationoid complex (III). Nevertheless, a careful analysis of the products obtained when complex (III) is treated with various nucleophiles disclosed that (III) does not exhibit a tendency to rearrange at low temperatures (−40 to −20°), at least not for several hours. This signified that the episulfonium bridge in (III) is quite stable under these conditions, while the degree of localization of the positive charge on the carbon atoms of this system is small and, in any case, insufficient for the realization of carbonium-ion rearrangements. However, further studies disclosed that the reactivity character of complex (III) changes on going to higher temperatures. Thus, if a solution of (III), prepared at −40°, is heated up to room temperature and kept there for 1-2 h, then the (III) intermediate is converted almost completely to the covalent compound, which is incapable of reacting further with any external nucleophiles. The NMR, mass, and UV spectral data, and also the elemental analysis data, disclosed that this compound is 3,4,4-trimethyl [5, 6] benzothiochroman (VIII). The formation of adduct (VIII) can be explained if it is assumed that the (III) intermediate is converted by heat to the open carbcation (IX), which immediately undergoes the rearrangement usual for such systems to the carbonium ion (X), which then reacts with the aryl moiety by the intramolecular alkylation scheme.



In our opinion, the fact that heating by even 40-50° proves to be sufficient to "trigger" a typical carbonium-ion rearrangement indicates that the transition: bridge ion → open carbonium ion has a comparatively low activation energy value, which makes it possible to regard (III) and intermediates similar to it as being a peculiar kind of "masked" carbonium ion.*

It is obvious that the degree of stabilizing the cationoid intermediate (III) can be altered substantially by changing the nature of the aryl moiety on the sulfur. In particular, replacing phenyl by the 2,4-dinitrophenyl moiety destabilizes the episulfonium intermediate (XI) to such a degree that it is not detected even at −50° (products of the (V) type could not be obtained when the reaction mixture was treated with nucleophiles!), and practically the sole reaction product (in up to 65% yield) is the covalent fluorine-containing adduct (XII) with a rearranged skeleton (mass spectrum, ^1H and ^{19}F NMR spectra, elemental analysis). The formation of the latter can be described by the sequence of transformations: (I) → (XI) → (XIII) → (XIV) → (XII), which differs from the scheme for the formation of (VIII) only in that carbonium ion (XIV) is stabilized via the cleav-

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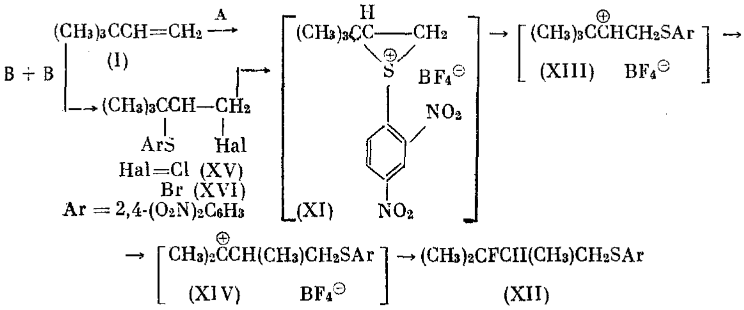
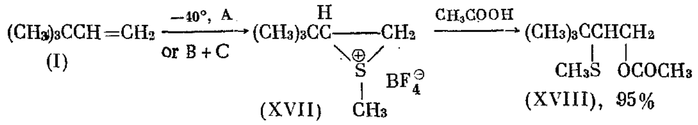
*The barrier of the transition: bridge ion → open ion proves to be even smaller if SbF_6^- is used as the counterion; in this case it is sufficient to hold at 0° for 1 h in order to completely convert (III) to (VIII).

age of fluorine from the complex BF_4^- anion, since alkylation in the aromatic ring is impossible in this case.



The formation of adduct (XII) is prevented completely when it is attempted to generate (XI) with a more stable complex anion SbF_6^- (by path A), but the main result is apparently polymerization. The sole product that could be isolated is oligomer (XIIa) of composition $2,4\text{-}(O_2N)_2C_6H_3S \cdot C_6H_{12} \cdot C_6H_{11}$ (mass spectrum).

We also studied the possibility of obtaining episulfonium complexes that contain an alkyl group on the sulfur atom. It proved that complex (XVII), which was obtained the same as (III), can also be attributed to the discharge of stable intermediates. Its reactions with nucleophiles proceed the same as shown in the scheme on p. 1268. A characteristic example is the formation of acetoxy adduct (XVIII), which corresponds to the anti-Markovnikov addition of the elements CH_3S^+ and CH_3COO^-. An attempt to effect rearrangement to complex (XVII) by heating at 20° proved unsuccessful; a complex mixture of products was formed, from which any pure compounds could not be isolated.



As a result, it was shown by us that the methods previously developed for the generation of episulfonium intermediates are not general enough. In particular, their use makes it possible to separate and make available for independent study the steps of adding an electrophile RS^+ and a nucleophile Z to the double bond. It is especially interesting that it was possible on the example of intermediate (III), which was obtained from (I), to clearly separate the steps of electrophilic attack and subsequent rearrangements of the skeleton. Finally, the problem of an accurate description of the structures of the obtained complexes cannot be considered as having been conclusively solved without making a detailed study of them employing the methods of physical organic chemistry. However, even by themselves, the obtained data on the reactivity of these intermediates serve as sufficiently unequivocal evidence in support of the validity of the proposed structures. It should be mentioned that a similar type of intermediate was obtained recently by the Dutch authors [10] based on the reaction of cis-di-tert-butylethylene sulfide with CH_3OSO_2F. Its structure was confirmed both by the data on the reactivity (formation of adducts of the (V) type when reacted with nucleophiles) and by a study of the ^1H and ^{13}C NMR spectra. The method used in [10] to obtain episulfonium intermediates unconditionally has interest, but apparently it has a narrower range of application than the methods developed by us, since it is mentioned in [10] that stable complexes could not be obtained by this method from trans-di-tert-butylethylene sulfide, cyclohexene, and tetramethylethylene.

The results of this and previous papers [1-5] require a revision of some of the usual concepts regarding the mechanism of the electrophilic addition reactions of covalent RSHal to multiple bonds. It is customary to assume [11] that intermediates of the type of episulfonium ions are formed in these reactions in the limiting step. However, as was shown by us, it is characteristic for this type of intermediates to have the ability to: a) react very easily with nucleophiles, and b) undergo skeletal rearrangements. At the same time, the complete absence of solvoaddition products is characteristic for the reactions with covalent RSHal compounds, even if they are run in either AcOH or CH_3CN as the medium, and also characteristic is the exclusive formation of nonrearranged products, for example, for the reactions with tert-butylethylene [12]. In our opinion, these data testify to the fact that under the usual conditions of the discussed reactions the formed intermediate should have a low polarity, and in its character should be closer to a covalent sulfuran (analogous to that discussed in [13]) than to the episulfonium ion.

The data obtained in [14] on the discussed problem are very interesting, where it was shown that in the presence of perchlorates the addition reaction of covalent RSHal compounds can give both solvoaddition products and rearrangement products. In other words, in its properties the intermediate, formed from covalent reactants, but under conditions that facilitate a separation of the charge (the presence of a high concentration of perchlorates), becomes completely analogous to the episulfonium complexes that were studied in our papers.

EXPERIMENTAL METHOD

The NMR spectra were taken in CCl_4 solution on a Varian DA-60 IL spectrometer, using HMDS as the internal standard. The chemical shifts are given on the δ scale in ppm. The IR spectra were recorded on a UR-10 instrument, while the mass spectra were recorded on a Varian CH-6 instrument. The reaction products (except (Vf), (Vg), and (XII)) were analyzed by GLC on an instrument equipped with a flame-ionization detector and a 200 × 3.5 mm column packed with 5% NSKT-33 deposited on Chromosorb W. The reaction products were isolated by preparative TLC on 24 × 24 cm plates.

General Method for Generating Intermediate (III) (path A). With stirring, a solution of 0.35 g of (I) in 4 ml of CH_2Cl_2 and 0.975 g of $AgBF_4$ in 3 ml of CH_3NO_2 were added in 5 min to a solution of 0.61 g (0.0042 mole) of C_6H_5SCl in 1.2 ml of abs. dichloroethane (DCE) and 4 ml of CH_2Cl_2, cooled to −45 to −50°. The mixture was kept at −45° for another 15 min, which was sufficient to obtain (III) (GLC analysis of a sample, treated with AcOH, disclosed the absence of (I) in the mixture).

Path B + C (step B, preparation of (IV)). With stirring, a solution of 0.61 g of C_6H_5SCl in 0.96 ml of abs. DCE and 4 ml of abs. CH_2Cl_2 was added in 5 min to a solution of 0.35 g of (I) in 4 ml of CH_2Cl_2, cooled to −20 to −30°, after which the mixture was kept at −10 to −20° for 15 min (the solution decolorized). After removal of the solvent the residue was vacuum-distilled. We obtained 0.76 g (79%) of (IV), bp 205-210° (2 mm); $n_D^{20.5}$1.5547. Found: C 62.90; H 7.65%. $C_{12}H_{17}SCl$. Calculated: C 63.02; H 7.44%.

Step C (generation of (III)). To a solution of adduct (IV) in CH_2Cl_2 at −45 to −50° was added 0.975 g of $AgBF_4$ in 3 ml of abs. CH_3NO_2. The obtained colored solution of (III) was kept at −15 to −10° for 10 min, which was sufficient for the complete precipitation of the AgCl and the formation of (III). Intermediate (III) was generated by similar procedures using C_6H_5SBr (see [3] for preparation).

Reactions of Intermediate (III) with Nucleophiles. All of the reactions were run using a standard sample and a solution of (III) that was obtained from 4.2 mmoles of (I) under the above described conditions. In all cases, after adding the necessary nucleophile, the reaction mixture was then treated with saturated $NaHCO_3$ solution and extracted with $CHCl_3$. After drying the extract over Na_2SO_4 the solvent was removed and the products were isolated by customary procedures. The NMR spectra of all of the adducts are given in Table 1.

a) Preparation of (Va). The treatment of (III) with glacial AcOH (20 ml) was run at −55 to −5° for 15 min. We isolated (Al_2O_3, petroleum ether: $CHCl_3$ = 11 :5) 0.8 g (78%) of (Va), n_D^{21} 1.5284. Found: C 67.89; H 8.17; S 12.33%. $C_{12}H_{20}O_2S$. Calculated: C 67.67; H 7.94; S 12.70%. Infrared spectrum: 1735 cm^{-1} ($OCOCH_3$).

b) Preparation of (Vb). To (III) at −55 to −25° was added 20 ml of abs. MeOH and the mixture was stirred at −25 to −18° for 20 min. Distillation gave 0.84 g (89%) of (Vb); n_D^{19} 1.5356. Found: C 69.84; H 9.03; S 14.19%. $C_{13}H_{20}OS$: Calculated: C 69.64; H 8.93; S 14.28%.

c) Preparation of (Vc). The treatment of (III) was run with 5 ml of Et_2NH in 5 ml of CH_2Cl_2 at −60 to −30° for 15 min. We isolated (Al_2O_3, petroleum ether: $CHCl_3$: AcOEt = 10 :5 :0.1) 0.66 g (60%) of (Vc), bp 155-160° (2 mm); $n_D^{20.5}$1.5252. Found: C 72.06; H 10.25; S 11.90%. $C_{16}H_{27}SN$. Calculated: C 72.45; H 10.19; S 12.07%.

d) Preparation of (Vd). To (III) was added 1 g of $NaBH_4$ in 5 ml of CH_2Cl_2 at −60 to −35° and the mixture was stirred for 20 min, gradually raising the temperature up to 20°. We isolated (Al_2O_3, hexane: $CHCl_3$: AcOEt = 13 :2 :1). 0.28 g (34%) of (Vd), bp 120-125° (2 mm); n_D^{20} 1.5381. Found: C 74.61; H 9.48; S 16.32%. $C_{12}H_{18}S$. Calculated: C 74.23; H 9.28; S 16.49%. We also isolated 0.3 g (34%) of the corresponding alcohol (Vh); $n_D^{20.5}$1.5515. Infrared spectrum: 3450 cm^{-1} (OH); NMR spectrum: 0.98 s (9H), 2.87 d.d. (1H, J_{AC} = 8.0, J_{BC} = 4.5 Hz), 3.56 m (2H, J_{AB} = 11.5), 2.3 s (OH), 7.24 m (5H); corresponds to the structure $(CH_3)_3CCH(SC_6H_5)CH_2OH$.

e) Preparation of (Ve). The treatment of (III) with sodium dimethylmalonate (from 1 g of Na and 15 ml of dimethylmalonic ester) was run at −30° for 15 min and at ~20° for 1 h. The excess dimethylmalonic ester was removed in vacuo. From the residue we isolated (Al_2O_3, hexane : AcOEt = 5 :1) 0.47 g (~50%) of (Ve); n_D^{20} 1.5092, which was identical with an authentic sample.

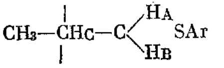
f) Preparation of (Vf). To (III) at −40 to −50° was added 10 ml of abs. CH_3CN and the mixture was kept at this temperature for 5 min, and then the temperature was raised up to 20° in 30 min, after which to the reaction mixture at −50° was added 25 ml of glacial AcOH and the mixture was stirred for 30 min (temperature up to −15°). We isolated (SiO_2, petroleum ether : AcOEt = 7 : 1) 0.28 g (27%) of (Va) and 0.65 g (62%) of (Vf). Infrared spectra: 1520, 1670, 3440 cm^{-1} (monosubstituted amide). Found: C 67. 16; H 8.66; S 12.29%. $C_{14}H_{21}ONS$. Calculated: C 66.93; H 8.37; S 12.75%.

g) Preparation of (Vg). The treatment of (III) with 10 ml of abs. C_6H_5CN was run at −50°, similar to the preparation of (Vf). We isolated (Al_2O_3, petroleum ether: $CHCl_3$ = 11 : 5) 0.58 g (44%) of (Vg), mp 69-71° (from petroleum ether). Found: C 72.58; H 7.40; S 10.92; N 4.30%. $C_{19}H_{23}ONS$. Calculated: C 72.84; H 7.35; S 10.22; N 4.47%. Infrared spectrum: 1510, 1660, 3420 cm^{-1} (C_6H_5CONH).

Preparation of 3,4,4-Trimethyl[5,6]benzothiochroman (VIII) (rearrangement of (III)). A solution of complex (III), obtained at −40°, was heated up to 18° and kept at this temperature for 1.5 h, after which it was cooled to −40 to −50°, 25 ml of glacial AcOH was added, and the mixture was worked up in the usual manner. We isolated (Al_2O_3, petroleum ether: $CHCl_3$ = 5 : 2) 0.62 g (76.5%) of (VIII); n_D^{20} 1.5781. Found: C 74.33; H 8.46; S 15.91%. $C_{12}H_{16}S$. Calculated: C 75.00; H 8.33; S 16. 67%. NMR spectrum: 0.85 d (3H, CH_3CH_X, J_{H,CH_3} = 7 Hz), 1.13 and 1.20 2c (6H, CH_3CCH_3); 1.75 m (1H, CH_XCH_3); 2.50 d.d. (1H, CH_B, J_{AB} = 12, J_{BX} = 5 Hz); 3.17 d.d. (1H, CH_A, J_{AX} = 4 Hz); 6.97 m (4H, C_6H_4). Mass spectrum: M^+ with m/e 192, and intense fragments with m/e 177, 150, 149, 135, 44.

Preparation of Adduct (XII) (path B + C). Step B (preparation of (XVI)). To a solution of 2.32 g of 2,4-$(O_2N)_2C_6H_3SBr$ in 15 ml of CH_2Cl_2 at 20° was added 0.53 g of (I) and the mixture was let stand for 12 h. After distilling off the solvent we isolated (Al_2O_3, petroleum ether: AcOEt = 5 : 1) 1.47 g (65%) of Br-adduct (XVI), mp 106-107° (from petroleum ether). Found: C 38.92; H 4.18; N 7.91%. $C_{12}H_{15}O_4N_2BrS$. Calculated: C 39.67; H 4.13; N 7.71%.

The corresponding Cl-adduct (XV) was obtained in a similar manner from 1.53 g of 2,4-$(O_2N)_2C_6H_3SCl$ in 15 ml of CH_2Cl_2 and 0.53 g of (I). Preparative TLC (Al_2O_3, petroleum ether : AcOEt = 5 : 1) gave 1.41 g (71%) of (XV), mp 97-98° (from petroleum ether). Found: C 45.38; H 4.69; N 8.45%. $C_{12}H_{15}O_4N_2ClS$. Calculated: C 45.21; H 4.71; N 8.79%.

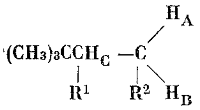
Step C (preparation of (XII)). To a solution of 0.13 g of (XVI) in 2 ml of CH_2Cl_2, cooled to −50°, was added in 1 min 0.07 g of $AgBF_4$ in 0.25 ml of abs. CH_3NO_2 and the mixture was kept at −50 to −30° for 10 min. Then 10 ml of glacial AcOH was added at −45 to −10° and the mixture was stirred at −10° to +18° for 30 min. After the usual workup we isolated 0.07 g (65%) of (XII), mp 96-97°. Found: C 47.55; H 5.11%. $C_{12}H_{15}O_4N_2FS$. Calculated: C 47.68; H 4.96%. NMR spectrum: 1.04 d (3H, CH_3CH_C; J_{H,CH_3} = 6 Hz); 1.22 and 1.58 2 d (6H, $(CH_3)_2CF$; $J_{CH_3,F}$ = 22.5 Hz); 1.82 m (1H, CH_CCH_3); 2.62 2 d (1H, CH_B, J_{AB} = 12, J_{BC} = 11.5 Hz); 3.55 2 d (1H, CH_A; J_{AC} = 3 Hz); protons A, B, and C belong to the  $CH_3{-}\overset{|}{\underset{|}{C}}H_C{-}C{<}^{H_A}_{H_B}SAr$ fragment; the aromatic protons form an XYZ system: 7.68 d (1 H, H_X; J_{XY} = 9; J_{XZ} = 1 Hz); 8.37 2 d (1H, H_Y; J_{YZ} = 2.5 Hz); 9.03 d (1 H, H_Z). Mass spectrum: M^+ with m/e 302, and intense fragments with m/e 183, 103, 83, 61. Adduct (XII) was obtained in a similar manner from Cl-adduct (XV) in 71% yield.

Adduct (XII) was also obtained by the direct reaction of (I) with 2,4-$(O_2N)_2C_6H_3SBF_4$ (path A). However, intense tarring was observed in these cases and the yield of (XII) did not exceed 22-23%. The formation of (XII) was not observed when (I) is reacted with 2,4-$(O_2N)_2C_6H_3SSbF_6$ (0.176 g of (I), 0.586 g of 2,4-$(O_2N)_2C_6H_3SBr$, and 0.859 g of $AgSbF_6$ in a 3 : 1 $CH_2Cl_2-CH_3NO_2$ medium, at −50 to −40°), and from the residue, obtained after the usual workup (nucleophile = AcOH), we isolated 0.1 g of product (XIIa), mp 103-105°. Mass spectrum: $(M-1)^+$ with m/e 365 (2,4-$(O_2N)_2C_6H_3S\cdot C_6H_{12}\cdot C_6H_{11}$).

Generation of Intermediate (XVII). Path A. To a solution of 0.117 g of Me_2S in 3 ml of CH_2Cl_2, cooled to −40 to −50° and protected from the light, was added in 3 min 0.2 g of Br_2 in 3 ml of CH_2Cl_2, after which the reaction mixture was kept at −20 to −30° for 8 min. To the obtained CH_3SBr solution were added in 0.5 min 0.487 g of $AgBF_4$ in 1.5 ml of CH_3NO_2 and 0.176 g of (I) in 2 ml of CH_2Cl_2, and to complete the reaction the mixture was kept for another 10 min at −40 to −25°. The intermediate (XVII) was obtained in a similar manner using CH_3SCl to generate the CH_3SBF_4.

Path (B + C). To the CH_3SBr solution, obtained by the preceding procedure, at −45 to −50°, in 0.5 min, was added 0.176 g of (I) in 2 ml of CH_2Cl_2, and the mixture was stirred at −20 to −30° for 20 min. Here the CH_3SBr color disappears and the corresponding CH_3SBr-adduct is formed, which without isolation was then

TABLE 1. NMR Spectrum of Adducts of General Formula



$(CH_3)_3CCH_C(R^1)-C(R^2)(H_A)H_B$

Compound	R^1	R^2	$(CH_3)_3C$	CH_C	CH_AH_B	R^1	R^2
(IV)	SC_6H_5	Cl	1,01 s	2,98 m ($J_{AC}=5,5$ *)	3,58 m ($J_{AB}=12$)	7,20 m	—
(Va)	SC_6H_5	$OCOCH_3$	1,03 s	3,00 d. d ($J_{AC}=J_{BC}=5,5$)	4,20 m ($J_{AB}=12$)	7,22 m	1,72 s
(Vb)	SC_6H_5	OCH_3	1,01 s	2,85 d. d ($J_{AC}=6$, $J_{BC}=4,8$)	3,48 m ($J_{AB}=10$)	7,2 m	3,14 s
(Vc)	SC_6H_5	$N(C_2H_5)_2$	0,98 s	2,15—2,88	$(-\underline{CH}_C-\underline{CH_2}-$, $(\underline{CH_2}-CH_3)_2)$	7,2 m	0,87 m (6H, $(\underline{CH_3}-CH_2)_2-$)
(Vd)	SC_6H_5	H	0,97 s	2,90 q ($J=7$)	1,17 d($\underline{CH_3}-CH_C-$)	7,15 m	
(Ve)	SC_6H_5	$CH_X(COOCH_3)_2$	1,05 s	2,83 m	1,76 m (H_A); 2,35 m (H_B)	7,22 m	3,55 s, 3,68 s (6H, $>C(COOCH_3)_2$); 3,83 d; 4,00 d (1H, H_X, $J_{BX}=12,5$; $J_{AX}=3$)
(Vf)	$NHCOCH_3$	SC_6H_5	1,03 s	4,0 m	3,0 m	6,1 m (NH), 1,76 (CH_3CO)	7,2 m
(Vg)	$NHCOC_6H_5$	SC_6H_5	1,03 s	4,13 m ($J_{AC}=J_{BC}=4,5$)	3,10 m ($J_{AB}=11$)	6,7 m (NH, $J_{NH, H_C}=8$)	7,18 m (C_6H_5S- and C_6H_5CO-)
(XVI)	2,4-$(O_2N)_2$-C_6H_3S	Br	1,15 s	3,15—4,05 (3H, H_C, H_A, H_B)		7,68—9,00 m	—
(XVIII)	SCH_3	$OCOCH_3$	1,03 s	2,42 t ($J_{AC}=J_{BC}=6$)	4,20 m ($J_{AB}=12$)	1,98 s	2,12 s

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*Values of the SSCC (J), Hz; the integral intensity of the signals corresponds to the indicated assignment (the assignment was also checked by the double-resonance data).

treated at −45 to −50° with a solution of 0.487 g of $AgBF_4$ in 1.5 ml of CH_3NO_2. To completely precipitate the AgBr the mixture was kept for another 5 min at −40 to −30°.

Intermediate (XVII) was also generated by path (B + C) via the Cl-adduct (see [12] for preparation), but more drastic conditions were required to precipitate the AgCl: 15 min at −10 to −5°.

Preparation of (XVIII). The treatment of (XVII) with 15 ml of glacial AcOH was run at −50°, after which the temperature was raised to 0° in 15 min. The obtained adduct contained (GLC) mainly (XVIII). Distillation gave 0.38 g (95%) of (XVIII); n_D^{22} 1.4640. Infrared spectrum: 1735 cm^{-1} ($OCOCH_3$). Found: C 56.22; H 9.84; S 17.49. $C_9H_{18}O_2S$. Calculated: C 56.84; H 9.47; S 16.84%.

CONCLUSIONS

1. It was shown that stable intermediate of the episulfonium-ion type can be generated from tert-butylethylene, and their reactions with various nucleophiles were studied.

2. It was discovered that skeletal rearrangements are possible in the discussed complexes.

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FLUORINE-CONTAINING ALLENES

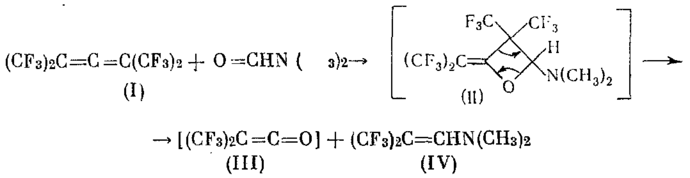
COMMUNICATION 6*. REACTION OF TETRAKIS(TRIFLUOROMETHYL)ALLENE WITH DIMETHYLFORMAMIDE

M. D. Bargamova, N. S. Mirzabekyants,
Yu. A. Cheburkov, and I. L. Knunyants

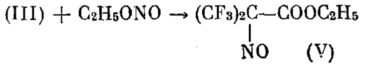
UDC 542.91:547.315.1'161:547.298.1

Heterocumulenes, for example isocyanates [2-4] or fluorine-containing ketenes [5, 6], react with a weak nucleophile like DMF to respectively give formamidines or enamines and CO_2.

In the present paper it was shown that a cumulene like tetrakis(trifluoromethyl)allene (I) reacts with DMF at 20° C to give hexafluoroisobutenyldimethylamine (IV) [5] and CO_2. The same as in the case of other heterocumulenes, the process apparently proceeds via the cyclic adduct (II), which is unstable and decomposes to give bis(trifluoromethyl)ketene (III) and enamine (IV). However, ketene (III) cannot be isolated in the pure form since, as was already mentioned, it reacts with DMF under the reaction conditions to give (IV) and CO_2.



To prove the proposed reaction scheme it was necessary to isolate bis(trifluoromethyl)ketene as the adduct with such a third component as could compete with DMF in the reaction with ketene (III). Such a component proved to be ethyl nitrite. According to the data in [7], it reacts with (III) at −60° to give the ethyl ester of α-nitrosohexafluoroisobutyric acid (V), whereas allene (I) does not react with ethyl nitrite even at 100°. The addition of equimolar amounts of ethyl nitrite to a mixture of allene (I) and DMF made it possible to isolate ketene (III) as ester (V) and thus confirm the proposed reaction scheme.



$$\text{(III)} + C_2H_5ONO \rightarrow \underset{\displaystyle NO}{(CF_3)_2\overset{}{C}}\text{—}COOC_2H_5 \quad \text{(V)}$$

The studied reaction again indicates the substantial electrophilicity of the cumulene system of bonds in tetrakis(trifluoromethyl)allene (cf. [8]), which makes it exceedingly reactive even toward a weak nucleophile like DMF.

EXPERIMENTAL METHOD

Reaction of Tetrakis(trifluoromethyl)allene (I) with DMF. A mixture of 2.8 g (0.009 mole) of allene (I) and 1.4 g (0.02 mole) of abs. DMF, sealed at −78° in a glass ampul, was kept at 20° for 30 h until homogenization was complete. After distillation we obtained 2.6 g (71%) of 1-H-hexafluoroisobutenyldimethylamine (IV), which was identical (GLC) with an authentic specimen, and 0.2 g (61%) of CO_2.

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*See [1] for Communication 5.

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