

dissolved in 5 ml of acetic acid, and 0.1 g of 58% perchloric acid was added. The precipitated salt was removed by filtration and crystallized from acetic acid. The yield was 0.08 g.

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#### ALLYLIC MIGRATION OF THE AZIRIDINE RING

#### IN 2-AZIRIDINO-3-TRIFLUOROMETHYL-4,4-DIFLUORO-3-BUTENOATES

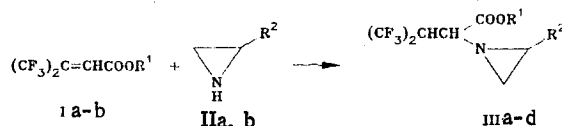
I. V. Solodin, A. V. Eremeev,  
É. É. Liepin'sh, and R. G. Kostyanovskii

UDC 547.717'722.3'413.5

Products of allylic rearrangement of 2-aziridino-3-trifluoromethyl-4,4-difluoro-3-butenates, viz., 4-aziridino-3-trifluoromethyl-4,4-difluoro-2-butenates, were obtained in the dehydrofluorination of 2-aziridino-3-trifluoromethyl-4,4,4-trifluorobutenates.

Numerous examples of allylic rearrangements and reactions involving allylic substitution are known [1-4], whereas such reactions in N-allyl-substituted nitrogen heterocycles have been described only in [5, 6]. It was shown that 6-aryl-3-ethoxycarbonyl-4-pyrrolidino(piperidino)-4H-thiopyran readily undergoes rearrangement to 6-aryl-3-ethoxycarbonyl-2-pyrrolidino(piperidino)-2H-thiopyran [5] and that N-( $\alpha$ -methallyl)pyridinium tetrafluoroborates undergo thermal isomerization to N-( $\gamma$ -methallyl) derivatives [6].

Reactions of this type are unknown for N-allyl-substituted aziridines. In the course of studies of the nucleophilic addition of amines to  $\beta$ , $\beta$ -bis(trifluoromethyl)acrylates (Ib) [7] we obtained 2-aziridino-3-trifluoromethyl-4,4,4-trifluorobutenates (IIIa-d) in high yields in the reaction of esters Ia,b with aziridine (IIa) and 2-methylaziridine (IIb) in ether:

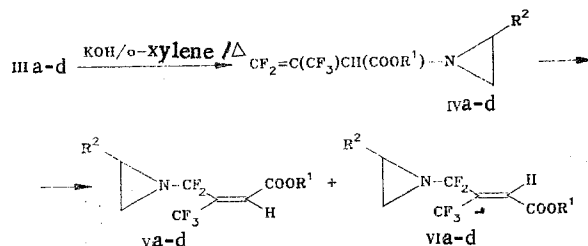


Ia, IIIa,b R<sup>1</sup>=Me; Ib, IIIc,d R<sup>1</sup>=Et; IIa, IIIa,c R<sup>2</sup>=H; IIb, IIIb,d R<sup>2</sup>=Me

In the dehydrofluorination of IIIa-d with powdered KOH by refluxing in o-xylene, instead of the expected 2-aziridine-3-butenates (IVa-d), we isolated 4-aziridino-2-butenates in 50% yield in the form of mixtures of E and Z isomers (Va-d and VIa-d, respectively) in a ratio of 3:1.

Isomers V and VI were separated by high-performance liquid chromatography (HPLC) and were identified from their <sup>1</sup>H and <sup>19</sup>F NMR spectra (Tables 1 and 2). Their formation can be explained by allylic rearrangement of esters of the IV type. In fact, ester IVa was isolated in 55% yield and identified in the dehydrofluorination of IIIa under mild interphase-catalysis conditions in the CCl<sub>4</sub>-solid KOH-Bu<sub>3</sub>N<sup>+</sup>CH<sub>2</sub>Ph<sup>-</sup>Cl<sup>-</sup> system at 0°C. Ester IVa undergoes quantitative isomerization to ester Va when it is heated (100°C). Allylic rearrangement of IVa takes place not only when it is heated, but also under the influence of catalytic amounts of

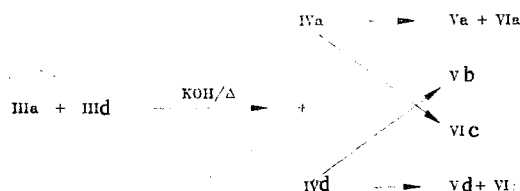
Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow 117334. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 4, pp. 505-508, April, 1985. Original article submitted March 28, 1984.



aziridine at  $-30^{\circ}\text{C}$ ; as in the case of thermal rearrangement, only isomer Va is formed in this case.

In the reaction of ester IVa with an equimolar amount of 2-methylaziridine, in addition to Va, a product of allylic substitution (Vb) is also formed (according to PMR data, the ratio of Va to Vb is 1:4).

To ascertain the character of the observed rearrangement of esters IV, we subjected a mixture of IIIa to IIIId to thermal treatment with alkali. In this case, in addition to two pairs of E and Z isomers of the products of "normal" rearrangement (IVa and IVd), in the reaction mixture we also detected substances that can be formed only as a result of exchange of aziridine residues between esters IVa and IVd:



Thus the  $\text{IV} \rightarrow \text{V} + \text{VI}$  arrangement is, at least partially, the result of a bimolecular process, and it may be assumed that it is realized via an  $\text{S}_{\text{N}}2'$  mechanism; the aziridine molecule is the leaving group and the attacking nucleophile in this case.

The clearly expressed catalytic action of aziridine that we observed provides a basis for the assumption that the rearrangement of esters of the IV type without the addition of aziridine is realized as a result of its generation after the addition to ester IV of some proton-containing nucleophile from the medium (for example, traces of  $\text{H}_2\text{O}$ ). In the case of the reaction of secondary amines with 2-methylallyl chloride it has been shown [8] that  $\text{S}_{\text{N}}2'$  reactions are syn stereospecific, i.e., the attacking nucleophile and the leaving group are located on only one side of the allylic system. Let us note that syn-nucleophilic attack by

TABLE 1. Parameters of the  $^1\text{H}$  NMR Spectra of I and III-VI

| Compound | Solvent                | $\delta$ , ppm  |      |   |       |                            | $J$ , Hz  |
|----------|------------------------|-----------------|------|---|-------|----------------------------|---|
|          |                        | COOR            | =CH  | aziridine ring protons                    | NCHCO | $\text{CH}(\text{CF}_3)_2$ |   |
| IIIa     | $\text{CDCl}_3$        | 3,80            | 6,87 | —   | —     | —                          | 1,1 ( $^4J_{\text{HF}}$ )                               |
| IIIa     | $d_8$ -Toluene         | 3,28            | —    | 1,00, 1,62                                | 2,32  | 3,72                       | 3,8 ( $^3J_{\text{HH}}$ ),<br>8,2 ( $^3J_{\text{HF}}$ ) |
| IIIb     | $\text{C}_6\text{H}_6$ | 3,40            | —    | 1,0—1,7 ( $\text{CHCH}_2$ ),<br>1,06 (Me) | 2,53  | 3,82                       | 2,0 ( $^3J_{\text{HH}}$ ),<br>8,2 ( $^3J_{\text{HF}}$ ) |
| IIIc     | $\text{CDCl}_3$        | 4,28, 1,33 (Et) | —    | 1,46, 2,08                                | 2,71  | 3,84                       | 3,6 ( $^3J_{\text{HH}}$ ),<br>9,0 ( $^3J_{\text{HF}}$ ) |
| IIId     | $\text{CDCl}_3$        | 4,31, 1,35 (Et) | —    | 1,5—2,0 ( $\text{CHCH}_2$ ),<br>1,22 (Me) | 2,80  | 3,87                       | 3,0 ( $^3J_{\text{HH}}$ ),<br>8,1 ( $^3J_{\text{HF}}$ ) |
| IVa      | $d_8$ -Toluene         | 3,28            | —    | 0,6—1,9                                   | 2,44  | —                          | —   |
| Va       | $d_8$ -Toluene         | 3,37            | 6,42 | 1,67                                      | —     | —                          | 1,5 ( $^4J_{\text{HF}}$ )                               |
| Vb       | $\text{CDCl}_3$        | 3,73            | 6,73 | 2,44, 2,17, 1,64,<br>1,20 (Me)            | —     | —                          | 1,4 ( $^4J_{\text{HF}}$ )                               |
| Vc       | $\text{CDCl}_3$        | 4,24, 1,28 (Et) | 6,75 | 2,02                                      | —     | —                          | 1,6 ( $^4J_{\text{HF}}$ )                               |
| Vd       | $\text{CDCl}_3$        | 4,24, 1,29 (Et) | 6,73 | 2,44, 2,20, 1,67,<br>1,20 (Me)            | —     | —                          | 1,6 ( $^4J_{\text{HF}}$ )                               |
| VIa      | $d_8$ -Toluene         | 3,30            | 6,62 | 1,47                                      | —     | —                          | 1,8 ( $^4J_{\text{HF}}$ )                               |
| VIb      | $\text{CDCl}_3$        | 3,82            | 6,95 | 2,44, 2,24 and 1,64,<br>1,24 (Me)         | —     | —                          | 1,6 ( $^4J_{\text{HF}}$ )                               |
| VIC      | $\text{CDCl}_3$        | 4,31, 1,31 (Et) | 6,95 | 2,04                                      | —     | —                          | 1,6 ( $^4J_{\text{HF}}$ )                               |
| VID      | $\text{CDCl}_3$        | 4,31, 1,33 (Et) | 6,92 | 2,40, 2,22 and 1,75,<br>1,24 (Me)         | —     | —                          | 1,6 ( $^4J_{\text{HF}}$ )                               |

TABLE 2. Parameters of the  $^{19}\text{F}$  NMR Spectra of Ia-VIa

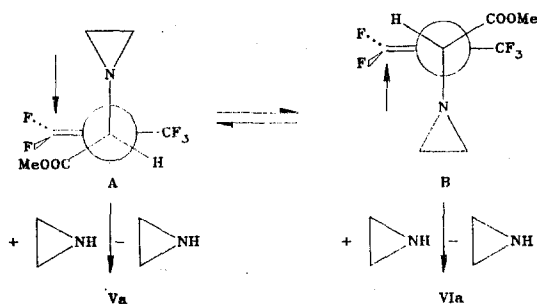
| Compound | Solvent         | $\delta$ , ppm        |                     | J, Hz   |
|----------|-----------------|-----------------------|---------------------|---|
|          |                 | $\text{CF}_3$         | $\text{CF}_2$       |   |
| Ia       | $\text{CDCl}_3$ | 12,8 (E),<br>17,1 (Z) |                     | 7,5 ( $\text{CF}_3\text{---CF}_3$ ),<br>1,1 (E--- $\text{CF}_3\text{---C---CH}$ )                               |
| IIIa     | $d_8$ -Toluene  | 14,9                  |                     | 9,4 ( $\text{CF}_3\text{---CF}_3$ ),<br>8,2 ( $\text{CF}_3\text{---C---H}$ )                                    |
| IVa      | $d_8$ -Toluene  | 21,0                  | 4,3 (Z),<br>0,1 (E) | 12,4 ( $\text{F}_2\text{F}_2$ ),<br>10,0 ( $\text{CF}_3\text{---F}_E$ ),<br>19,6 ( $\text{CF}_3\text{---F}_Z$ ) |
| Va       | $d_8$ -Toluene  | 18,9                  | -12,0               | 8,6 ( $\text{CF}_3\text{---CF}_2$ ),<br>1,8 ( $\text{CF}_2\text{---C---CH}$ )                                   |
| VIa      | $d_8$ -Toluene  | 14,6                  | -8,3                | 8,6 ( $\text{CF}_3\text{---CF}_2$ ),<br>1,5 ( $\text{CF}_3\text{---C---CH}$ )                                   |

TABLE 3. Characteristics of I and III-VI

| Compound | bp, °C<br>(mm) | IR spectrum,<br>$\nu$ , $\text{cm}^{-1}$ |      | Found, % |     |     | Empirical<br>formula                              | Calc., % |     |     | Yield,<br>% |
|----------|----------------|--|------|----------|-----|-----|---|----------|-----|-----|-------------|
|          |                | C=O                                      | C=C  | C        | H   | N   |   | C        | H   | N   |             |
| Ia       | 112 (760)      | 1760                                     | 1680 | 32,1     | 1,9 | —   | $\text{C}_8\text{H}_4\text{F}_6\text{O}_2$        | 32,1     | 1,8 | —   | 85          |
| IIIa     | 40 (5)         | 1750                                     | —    | 36,5     | 3,3 | 5,0 | $\text{C}_8\text{H}_9\text{F}_6\text{NO}_2$       | 36,2     | 3,4 | 5,2 | 90          |
| IIIb     | 45 (5)         | 1755                                     | —    | 38,8     | 3,8 | 5,3 | $\text{C}_9\text{H}_{11}\text{F}_6\text{NO}_2$    | 38,7     | 3,9 | 5,0 | 91          |
| IIIc     | 50 (5)         | 1750                                     | —    | 38,3     | 3,7 | 5,1 | $\text{C}_9\text{H}_{11}\text{F}_6\text{NO}_2$    | 38,7     | 3,9 | 5,0 | 92          |
| IIId     | 60 (5)         | 1750                                     | —    | 40,5     | 4,2 | 4,5 | $\text{C}_{10}\text{H}_{13}\text{F}_6\text{NO}_2$ | 40,9     | 4,4 | 4,7 | 91          |
| IVa      |                | 1755                                     | 1680 | 39,6     | 3,1 | 5,4 | $\text{C}_8\text{H}_8\text{F}_5\text{NO}_2$       | 39,2     | 3,3 | 5,7 | 55          |
| Va       |                | 1750                                     | 1680 | 38,8     | 3,5 | 5,5 | $\text{C}_8\text{H}_8\text{F}_5\text{NO}_2$       | 39,2     | 3,3 | 5,7 | 36          |
| Vb       |                | 1750                                     | 1680 | 42,0     | 3,8 | 5,1 | $\text{C}_9\text{H}_{10}\text{F}_5\text{NO}_2$    | 41,7     | 3,9 | 5,4 | 45          |
| Vc       |                | 1745                                     | 1680 | 41,5     | 3,8 | 5,3 | $\text{C}_9\text{H}_{10}\text{F}_5\text{NO}_2$    | 41,7     | 3,9 | 5,4 | 40          |
| Vd       |                | 1745                                     | 1679 | 43,7     | 4,5 | 5,0 | $\text{C}_{10}\text{H}_{12}\text{F}_5\text{NO}_2$ | 43,9     | 4,4 | 5,1 | 47          |
| VIa      |                | 1750                                     | 1680 | 39,0     | 3,2 | 5,8 | $\text{C}_8\text{H}_8\text{F}_5\text{NO}_2$       | 39,2     | 3,3 | 5,7 | 12          |
| VIb      |                | 1750                                     | 1680 | 41,5     | 4,0 | 5,2 | $\text{C}_9\text{H}_{10}\text{F}_5\text{NO}_2$    | 41,7     | 3,9 | 5,4 | 15          |
| VIc      |                | 1748                                     | 1675 | 41,9     | 4,0 | 5,1 | $\text{C}_9\text{H}_{10}\text{F}_5\text{NO}_2$    | 41,7     | 3,9 | 5,4 | 15          |
| VIId     |                | 1748                                     | 1680 | 43,5     | 4,3 | 4,8 | $\text{C}_{10}\text{H}_{12}\text{F}_5\text{NO}_2$ | 43,9     | 4,4 | 5,1 | 17          |

\*The boiling points were not determined for IVa, Va-d, and VIa-d because of the small amounts (10-20 mg) of the products.

aziridine on ester IV is possible in two conformations of the latter (A and B in the case of IVa):



The primary or exclusive formation of one of the products of the rearrangement that we observed is apparently explained by the higher rate of the  $\text{S}_{\text{N}}2^{\ddagger}$  reaction for conformer A than for conformer B.

#### EXPERIMENTAL

The PMR spectra of 10% solutions of samples of the compounds in  $\text{CDCl}_3$  or  $d_8$ -toluene were recorded with a Bruker WH-90 spectrometer (90 MHz) with tetramethylsilane (TMS) as the internal standard; the  $^{19}\text{F}$  NMR spectra were recorded with JNM-C60-HL (56 MHz) and R-12 (56.4 MHz) spectrometers with  $\text{CF}_3\text{COOH}$  as the external standard. The IR spectra of thin films of the compounds were recorded with a Specord IR-75 spectrometer. Chromatographic separation was accomplished with an EAK MP-4 liquid chromatograph with a Lichrosorb-60 column (250  $\times$  22.6 mm)

and a refractometric Waters Prep. 500 A detector by elution with hexane-ether (7:3), as well as with a Pye-Unicam 105 preparative gas chromatograph. Chromatographic mass-spectrometric data were obtained with a Kratos GS/MS-25 apparatus with a 1.5-m-long column packed with OV-17 at 100°C and an ionic voltage of 70 eV.

The characteristics of I and III-VI are presented in Table 3.

2-Aziridino-3-trifluoromethyl-4,4,4-trifluorobutanoates (IIIa-d). A 0.1-mole sample of aziridine IIa,b was added dropwise at 0°C to a solution of 0.1 mole of ester Ia,b [9] (the characteristics of ester Ia are presented in Table 3) in 100 ml of absolute ether, and the mixture was maintained at this temperature for 0.5 h. After evaporation of the solutions, the residues were distilled *in vacuo*.

4-Aziridino-3-trifluoromethyl-4,4-difluoro-2-butenates (Va-d, VIa-d). A 2.8-g (0.05 mole) sample of ground KOH was added to a solution of 0.01 mole of adduct IIIa-d in 20 ml of o-xylene, and the mixture was refluxed for 10 min. It was then filtered, the o-xylene was evaporated, and the residue, which was a mixture of butenoates Va-d and VIa-d, was separated by means of high-performance liquid chromatography (HPLC).

"Cross Rearrangement." A 5.6-g (0.1 mole) sample of ground KOH was added to a solution of 2.65 g (0.01 mole) of adduct IIIa and 2.93 g (0.01 mole) of adduct IIIId in 40 ml of o-xylene, and the mixture was refluxed for 10 min. The solution was then filtered and analyzed by means of chromatographic mass spectrometry.

Methyl 2-Aziridino-3-trifluoromethyl-4,4-difluoro-3-butenate (IVa). A 5.6-g (0.1 mole) sample of ground KOH and 0.15 g (0.5 mmole) of tributylbenzylammonium chloride were added at 0°C to a solution of 2.65 g (0.01 mole) of adduct IIIa in 50 ml of CCl<sub>4</sub>, after which the mixture was stirred for 1.5 h. It was then filtered and evaporated, and the residue, which, according to TLC data, contained a residual amount of adduct IIIa in addition to ester IVa, was separated by means of preparative liquid chromatography; the eluent impurities were then removed by means of preparative gas chromatography.

Reaction of Butenoate IVa with 2-Methylaziridine. A 57-mg (1 mmole) sample of 2-methylaziridine was added at -30°C to a solution of 245 mg (1 mmole) of ester IVa in 5 ml of toluene, and the mixture was maintained at this temperature for 5 min. It was then filtered, and the filtrate was evaporated and analyzed by means of the PMR spectra. The ratio of Va and Vb was 1:4.

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