FLUORINE-CONTAINING HETEROCUMULENES.

XVI.* REACTION OF NITRONES WITH KETENIMINES AND ACYLKETIMINES AND CRYSTALLINE STRUCTURE OF 2,3-DIPHENYL-4-TRIFLUOROMETHYL-4-DIETHYLAMINOCARBONYL-5,5-DIFLUOROISOXAZOLIDINE

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We have already found [2, 3] that nitrones oxidize N-aryl-bis(trifluoromethyl)ketenimines into oxindoles. We have now shown that ketenimine (II) also reacts with the participation of its aromatic ring with nitrone (I) to form oxindole (III)



The presence of one o-CH, group in ketenimine (IV) does not hinder the oxygen transfer reaction. The cycloadduct (V), which probably forms as an intermediate product, converts so readily into oxindole(VII) that it cannot be recorded even by spectral methods



Betaine (VI) is stabilized due to cyclization in the unsubstituted o position of the aromatic ring of the ketenimine. Nitrone (I) reacts with N-mesityl-bis(trifluoromethyl)ketenimine (VIII) in a different way. In this case, cycloadduct (IX) does not split benzalanilide, but isomerizes into the corresponding amidine (X), as in the reaction of nitrones with acetylenes [4]

*For communication XV, see [1].

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As the result of the retarded rotation around the amide bond, two rotamers of amidine (X) are observed in the ¹⁹F NMR spectra, whose ratio is very dependent on the nature of the solvent. The temperature of overlapping of the signals cannot be recorded, since on heating, amidine (X) undergoes complex and irreversible transformations.

In the reaction of nitrones with N-benzenesulfonyl-bis(trifluoromethyl)ketenimine (XI) no splitting of the corresponding anils occurs, but in this case the intermediately formed cycloadducts (XII) or betaines (XIII) are stabilized by the reaction with N-phenyl ring of the nitrone with the formation of amide (XIV), i.e., ketenimine (XI) reacts with nitrones in the same way as ketenes [3, 5]:



When heated with aqueous alcohol, amide (XIVa) converts into oxindole (XV) with splitting of benzenesulfonamide and benzaldehyde, while treatment with an alcoholic solution of HCl leads to indolenine (XVI). During the hydration of amide (XIVa), N-benzyloxindole (XVII) is formed, whose structure was confirmed by an alternative synthesis



| Temperature Factors | |
|---------------------|---------------------------------|
| Anisotropic | |
|) and Their | · + …)] |
| oms (.10 | $B_{12}hka^{*}b^{*}$ |
| on Nonhydrogen At | $_{11}h^2a^{*2} + \ldots + 2$ |
| 1. Coordinates | exp(-1/4 · 10 ⁻²)(B |
| 3LE | n |

| X | A | | 2 | Bu | B2 | B_{33} | B ₁₂ | B ₁₃ | B ₂₃ |
|--|---|---------------|-----|--------------------|-----------|--|------------------|-----------------|-----------------|
| | | | | | | | 71 | | |
| 67043 (15) 4218 (13) 2677 (8) | 4218(13) 2677(8) | 2677 (8) | | 587 (8) | 443(8) | 419(7) | -26(6) | 57(6) | -151(7) |
| 53521 (15) 4591 (13) 11175 (8) | 4591(13) 11175(8) | 11175 (8) | | 442(7) | 427 (8) | 622(9) | -147(6) | 140(6) | -84(7) |
| 75924(15) 4093(13) 13298(8) | 4093(13) 13298(8) | 13298(8) | | 515(8) | 366(7) | 492(8) | 09 (Q) 00 (Q) | -41(6) | (9)6- |
| 47604(16) 21374(15) -97(8) | 21374(15) -97(8) | -97 (8) | | 470(8) | 710(10) | 438(7) | 40(7) | -182(6) | -119(8) |
| 58281(17) 38218(16) 1184(9) | 38218(16) $1484(9)$ | 1184(9) | _ | 597 (9) | 556(10) | 1144(11) | 95(7) | -31(8) | 249(9) |
| 44423(19) 32790(23) 9040(9) | 32790(23) 9040(9) | (6) 0506 | | 437 (10) | 1239(18) | 323(9) | 336(11) | -66 (7) | -41(10) |
| 89657(16) 29056(17) 12479(9) | 29056(17) 12479(9) | 12479(9) | | 290(7) | 635(11) | 381(9) | -74(7) | 43(6) | -118(8) |
| 86139(21) 26081(21) 850(11) | 26081(21) 850(11) | 850(11) | - | 861(10) | 556(13) | 330(10) | -32(9) | 78 (8) | -3(10) |
| 48137 (18) 28255 (19) 16276 (10) | 28255(19) 16276(10) | 16276(10) | - | 219(8) | 441(11) | 323(9) | 31(8) | -25(7) | -26(9) |
| 65616(26) $8876(24)$ $9065(13)$ | 8876(24) 9065(13) | 9065(13) | | 343(12) | 389(13) | 337 (12) | -19(10) | 15(10) | -62(11) |
| 81684(24) 26414(22) 7393(13) | 26414 (22) 7393 (13) | 7393(13) | | 294(11) | 343(12) | 340(12) | 11(9) | 47 (9) | -19(10) |
| 63559 (22) 28136 (22) 16597 (12) | 28136(22) 16597(12) | 16597 (12) | | 224(9) | 283(11) | $\begin{bmatrix} 298(11) \\ 298(11) \\ 200(10) \\ 20$ | -15(9) | 13(8) | -2(9) |
| 66408 (22) 22/15(21) 9199 (12) | 22/13(21) 9199(12) | A199(12) | - | (A) 292 | 310(11) | 269(10) | -8(8) | -5(8) | -20(9) |
| 53973 (25) 28667 (27) 4827 (13) | 28667 (27) 4827 (13) | 4827 (13) | | 338(11) | 532(16) | 306(11) | 46(11) | -23(10) | -19(12) |
| 78308 (36) 23296 (36) -5898 (15) | | -5898(15) | | 514(17) 079/200 | 1/9(23) | 334(14) | -35(16) | 83(12) | -68(15) |
| (07/206) (05/63/86) (60) F00// | (07) 200 (10) 07000 (07) 07000 (10) 07000 | (67) 27011- | | 202(11) | (06) 682 | 400(13) 554(47) | (10)017 | -0(20) | (07)027 |
| 101001 (33) 20402 (33) 200 (19) 101001 (40) 100 (19) | 17352 (56) 636 (40) | 636 (40) | | 481 (21) | 1299(41) | 1544 (48) | 139(25) | 978(97) | 193 (37) |
| 41370(22) 36504(22) 20786(12) | 36504(22) 20786(12) | 20786 (12) | | 243(9) | 322 (12) | 350(11) | 43(9) | 27(8) | 28(10) |
| 26941(26) 35179(26) 21041(17) | 35179(26) 21041(17) | 21041 (17) | | 279(11) | 343(13) | 717(18) | 0(10) | 81(11) | 77 (14) |
| 19775 (31) 42498 (28) 25381 (20) | 42498(28) 25381(20) | 25381 (20) | | 289(12) | 420(16) | 980(24) | 16 (12) | 220(14) | -56(16) |
| 26637 (30) 51068 (28) 29540 (17) | 51068(28) 29540(17) | 29540(17) | _ | 406(14) | 441(16) | 636(18) | 95(12) | 192 (13) | -42(14) |
| 40859(29) 52390(29) 28256(16) | 52390(29) 28256(16) | 28256(16) | ~~~ | 374(13) | 544(17) | 505(15) | 28(12) | 59(12) | -164(14) |
| 48240(27) 45157(26) 24891(14) | 45157 (26) 24891 (14) | 24891 (14) | | 269(11) | 497 (15) | 446 (14) | 6(11) | 62(10) | -104(12) |
| 69051(22) 22304(21) 23454(11) | 22304(21) 23454(11) | 23454(11) | | 258(9) | 292(11) | 275(10) | 24(9) | 35(8) | -32(9) |
| 81021(26) 26901(27) 27108(14) | 26901 (27) 27108 (14) | 27108(14) | | 327(11) | 455(15) | 336(12) | -36(11) | -23(10) | -2(11) |
| 85645 (32) 22323 (33) 33599 (15) | 22323 (33) 33599 (15) | 33599(15) | | 404(14) | 717(19) | 345(13) | 0(14) | -86(11) | -24(14) |
| 78444(35) [13199(30)] 36619(16) | 13199 (30) 36619 (16) | 36619(16) | | 589 (17) | 543(17) | 314(14) | 164(15) | -19(13) | 36(13) |
| 66485 (34) 8665 (27) 33133 (15) | 8665 (27) 33133 (15) | 33133 (15) | _ | 571 (16) | 349(14) | 366 (14) | 49(13) | 134(12) | 37 (12) |
| 61785(27) 13262(24) 26601(13) | 1 13262(24) 1 26601(13) 1 | 1 20001(13) 1 | - | 340 (12) | 1 34/(13) | 1 352(12) | -30(10) | 18(10) | -15(11) |

Thus, nitrones play the role of oxygen donors only in the case of N-aryl-bis(trifluoromethyl)ketenimines with at least one unsubstituted o position in the aromatic ring. In other cases isomerization products are formed with or without the participation of the aromatic ring of the nitrone.

These differences in the reactions of nitrones with ketenimines (compare [6]) led us to study the reactions of nitrones also with certain other classes of organofluorine compounds. We found that hexafluoroacetone benzoylimine with nitrone (I) forms a stable product of 1,3-dipolar cycloaddition, the oxadiazolidine (XVIII), which shows no change at $\sim 20^{\circ}$ C during a year, and when heated *in vacuo* at 140°C, decomposes into the starting benzoylimine and nitrone, and not into benzalaniline and oxaziridine (XIX):



With nitrone (I), N,N-dialkyl perfluoromethacrylamides also give stable cycloadducts (XX), which do not change on prolonged storage



In the ¹⁹F NMR spectra, the value of Δv AB of the geminal fluorine atoms is usually high, and in the ¹H NMR spectra, no division of signals from two nonequivalent alkyl groups, characteristic of dialkylamides [7], is observed.

The structure of the cycloadduct (XXa) has been unequivocally established by x-ray diffraction analysis.

The coordinates of atoms and their temperature factors are given in Tables 1 and 2. Figure 1 shows the structure of the molecule and the valence angles, while Table 3 lists the principal bond lengths.

The five-membered ring has an envelope conformation: The N², O¹, C⁵ and C⁴ atoms are present in one plane (deviations from the mean plane do not exceed 0.07 Å, the N²O¹C⁵C⁴ torsion angle is 9.5°), while the C³ atom projects from this plane by 0.65 Å (the inflection angle over the C⁴-N² line is 42°). The angle between the planes of the benzene rings is 100.5°, and the C¹⁰N²C³C¹⁶ torsion angle is 107.6°. The configuration of the C atoms in the five-membered ring is distorted tetrahedral, and of the N² atom pyramidal (sum of the valence angles 325°). This nitrogen atom projects from the C³C¹⁰O¹ plane by 0.51 Å. The N¹C²O²C⁴ fragment of the molecule is planar (deviations no more than 0.02 Å), and the N¹ atom has a planar configuration. Most of the bond lengths and valence angles in the molecule have the usual values.

EXPERIMENTAL

Crystals of (XXa) are fairly large, and therefore unsuitable for direct exposure on diffractometer. By spinning one of them, a small sphere was obtained with a diameter of 0.3 mm. This was etched with a solvent (CH₃CN) to remove the defective surface layer. The experimental material was obtained on a four-circuit diffractometer Syntex P2₁ (5332 reflections, of which 3059 were with I > $2\delta(I)$, $\theta/2\theta$ scanning, Mo radiation, graphite monochromator). The crystals of (XXa) are monoclinic: $\alpha = 9.5309(20)$, b = 11.0835(20), c = 19.0086(36) Å, $\beta =$ 94.004(16) Å, V = 2003.1(5) Å³. $\rho_{calc} = 1.34$ g/cm³, Z = 4, steric group $2P_1/n$.

| | zoouropic | remperature | | , |
|---|--|--|---|--|
| Atom | X | Ŷ | Z | ^B iso ^{Å2} |
| H ³ H ⁶ , H ⁷ , H ⁷ , H ⁷ , H ⁹ , H ⁹ , H ⁹ , H ⁹ , H ⁹ , H ¹¹ H ¹² H ¹³ H ¹⁴ H ¹⁵ H ¹⁸ H ¹⁹ H ¹⁹ H ¹⁹ H ¹⁰ H ¹¹ H ¹² H ¹² | $\begin{array}{c c} & 675 (2) \\ & 687 (3) \\ & 832 (3) \\ & 877 (5) \\ & 734 (4) \\ & 718 (4) \\ & 984 \\ & 1080 \\ & 1189 (4) \\ & 1055 \\ & 1082 \\ & 226 (3) \\ & 103 (3) \\ & 216 (2) \\ & 458 (2) \\ & 578 (2) \\ & 859 (2) \\ & 938 (3) \\ & 818 (3) \\ & 814 (2) \\ \end{array}$ | $\begin{array}{c c} & 362 (2) \\ 204 (2) \\ 165 (2) \\ 354 (4) \\ 407 (4) \\ 317 (3) \\ 304 \\ 355 \\ 192 (4) \\ 115 \\ 129 \\ 290 (2) \\ 413 (3) \\ 560 (2) \\ 579 (2) \\ 464 (2) \\ 333 (2) \\ 256 (2) \\ 101 (2) \\ 26 (2) \end{array}$ | $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$ | $\begin{array}{c} 19 (4) \\ 45 (6) \\ 53 (7) \\ 140 (20) \\ 120 (20) \\ 90 (10) \\ 70 \\ 70 \\ 107 (12) \\ 70 \\ 107 (12) \\ 70 \\ 48 (6) \\ 63 (8) \\ 51 (6) \\ 49 (7) \\ 45 (6) \\ 51 (7) \\ 61 (7) \\ 53 (7) \\ 43 (6) \end{array}$ |
| H ²⁰ H ²¹ | 535(2) | 106 (2) | 244(1) | 32(5) |

TABLE 2. Coordinates of Hydrogen Atoms* $(\cdot 10^3)$ and Their Isotropic Temperature Factors $(\cdot 10^1)$

*The numeration of the hydrogen atoms corresponds to the carbon atoms to which they are attached.

TABLE 3. Bond Lengths

| Bond | d, Å | Bond | d, Å |
|---|---|---|--|
| $\begin{array}{c} C^{1}-C^{4}\\ C^{4}-C^{5}\\ C^{5}-O^{1}\\ 0^{1}-N^{2}\\ N^{2}-C^{3}\\ N^{2}-C^{3}\\ C^{3}-C^{4}\\ C^{3}-C^{16}\\ C^{4}-C^{2}\\ C^{2}-O^{2}\\ C^{2}-N^{1}\\ N^{1}-C^{6}\\ N^{1}-C^{8}\\ C^{6}-C^{7}\\ C^{3}-C^{11}\\ C^{6}-C^{11}\\ C^{1}-C^{11}\\ C^{1}-C^{1}\\ C^{1}-C^{1}\\ C^{1}-C^{11}\\ C^{1}-C^{1}\\ C^{1}-C^{1}\\ C^{1}-C^{1}\\ C^{1}-C^{1}\\ C^{1}-C^{1}\\ C^{1}-C^{1}\\ C^$ | $\begin{array}{c} 1,535(4)\\ 1,547(3)\\ 1,334(3)\\ 1,484(3)\\ 1,467(3)\\ 1,570(3)\\ 1,570(3)\\ 1,573(3)\\ 1,573(3)\\ 1,523(3)\\ 1,223(3)\\ 1,343(3)\\ 1,471(4)\\ 1,481(4)\\ 1,519(7)\\ 1,447(7)\\ 1,487(2)\\ 287(2)\\ 287(3)$ | $\begin{array}{c} C^{11}-C^{12}\\ C^{12}-C^{13}\\ C^{13}-C^{14}\\ C^{14}-C^{15}\\ C^{10}-C^{15}\\ C^{10}-C^{15}\\ C^{17}-C^{18}\\ C^{18}-C^{19}\\ C^{19}-C^{20}\\ C^{20}-C^{21}\\ C^{16}-C^{21}\\ C^{1}-F^{11}\\ C^{1}-F^{12}\\ C^{1}-F^{13}\\ C^{5}-F^{51}\\ C^{5}-F^{52} \end{array}$ | $\begin{array}{c} 1,372 (3) \\ 1,372 (3) \\ 1,368 (3) \\ 1,381 (3) \\ 1,373 (4) \\ 1,373 (4) \\ 1,378 (4) \\ 1,371 (5) \\ 1,373 (4) \\ 1,371 (5) \\ 1,373 (4) \\ 1,387 (4) \\ 1,387 (4) \\ 1,387 (4) \\ 1,335 (3) \\ 1,335 (3) \\ 1,334 (3) \\ 1,335 (3) \\ 1,349 (3) \\$ |
| u | 1 1.001(0) 1 | u -r | 1.010(0) |

The structure was interpreted by direct method according to the MULTAN program. According to the better phase variant, the E synthesis revealed 15 nonhydrogen atoms; in the subsequent F synthesis the whole molecule was found. The structure has been more precisely specified by the method of least squares in a complete-matrix anisotropic approximation up to R = 0.047 ($R_w = 0.040$) with respect to 2585 reflections with $F_{min} > 4.5$. In a differential synthesis, all the H atoms were identified; their coordinates and isotopic temperature factors were also accurately specified. However, the specification led to much too high temperature factors for the H atoms of the CH₂ and CH₃ groups (the H⁹², H⁹³, H⁹¹ and H⁹²), and therefore, the coordinates of all these four atoms are given geometrically. All the calculations were carried out on the Eclipse S/200 computer according to the XTL program.

The IR spectra were run on the UR-20 spectrometer. The PMR spectra were recorded on the Perkin-Elmer R-12 apparatus (60 MHz), with tetramethylsilane (TMS) as external standard. The ¹⁹F NMR spectra were recorded on the Hitachi H-60 apparatus (56.46 MHz), with CF₃COOH as external standard. The chemical shifts are given on the δ scale, ppm with reference to TMS or CF₃COOH, respectively.

<u>3-Trifluoromethyl-3-carbomethoxyoxindole (III)</u>. A 2-g portion of anil (II) was added gradually to a suspension of 1.64 g of nitrone (I) in 10 ml of absolute ether. At the end of the exothermal reaction, the ether was distilled off, and the residue crystallized. Yield, 1.7 g (80%) of oxindole (III), mp 144-145°C (from a C₆H₅-CCl₄ mixture). Found (%): C 50.24, H 3.05, F 21.74, N 5.33. $C_{11}H_8F_3NO_3$. Calculated (%): C 50.96, H 3.01, F 22.01, N 5.45.





IR spectrum (ν , cm⁻¹): 1625, 1715, 1760 (arom., C=0); 3130-3310 (NH). PMR spectrum (in CH₃CN): 3.3 s (CH₃), 5.95-6.6 m (arom.), 7.5-8.1 (NH). F NMR spectrum (in CH₃CN): -8.4 s (CF₃). Mol. wt. 259 (mass spectrometrically).

3,3-Bis(trifluoromethyl)-7-methyloxindole (VII). A 1.44-g portion of ketenimine (IV) was gradually added to a suspension of 1.06 g of nitrone (I) in 2.5 ml of absolute ether. At the end of the exothermal reaction, ether was distilled off, and the residue crystallized. Yield, 0.92 g (60%) of oxindole (VII), mp 148.5-150° (from hexane). Found (%): C 46.66, H 2.49, F 40.35, N 5.01. $C_{11}H_7F_6NO$. Calculated (%): C 46.65, H 2.47, F 40.30, N 4.95. IR spectrum (ν , cm⁻¹): 1605, 1630, 1740 (arom., C=O), 3130-3310 (NH). ¹⁹F NMR spectrum (in acetone): -8.7 s (CF₃).

<u>N-Hexafluoroisobutyryl-N-mesityl-N'-phenyl Benzoic Acid Amidine (X).</u> A mixture of 1.22 g of nitrone (I) and 1.88 g of ketenimine (VIII) in 10 ml of absolute ether was stirred for 6 h at $\sim 20^{\circ}$ C to dissolution of the nitrone. Then the mixture, whose ¹⁹F NMR spectrum showed the presence of oxadiazolidine (IX) only [3], was left to stand at $\sim 20^{\circ}$ C. After 5 days ether was distilled off, and the residue washed with hexane. Yield, 1.15 g (37%) of amidine (X), mp 112-114°C (from hexane). Found (%): C 63.03, H 4.52, F 22.81. C₂₆H₂₂F₆H₂O. Calculated (%): C 63.41, H 4.47, F 23.17. IR spectrum (ν , cm⁻¹): 1650 (C=N), 1705 (C=O), PMR spectrum [in C₆F₆, hexamethyldisiloxane (HMDS) _ inner standard]: 1.12 s (CH₃), 1.85 s (CH₃), 1.93 s (CH₃), 3.87 g [(CF₃)₂CH, J_{H=F} = 8 Hz], 6.15-8.1 m (arom.). ¹⁹F NMR spectrum (in C₆H₆): -15.1 d, 14.7 d [(CF₃)₂CH, J_{H=F} = 8 Hz]. Mol. wt. 492 (mass spectrometrically).

<u>N-Benzenesulfonyl o-(N'-Benzylideneamino)phenylhexafluoroisobutyramide (XIVa).</u> A solution of 1.6 g of ketenimine (XI) in 5 ml of absolute ether was added with ice cooling to a suspension of 1 g of nitrone (I) in 5 ml of absolute ether. The mixture was left to stand for 4 h at $\sim 20^{\circ}$ C, and the precipitate was filtered. Yield, 1.6 g (61.5%) of amide (XIVa), mp 183-185°C (reprecipitation from CH₂Cl₂ with hexane). Found (%): C 53.65, H 3.21, F 22.12, N 5.54. C₂₃H₁₆F₆N₂O₃S. Calculated (%): C 53.69, H 3.11, F 22.17, N 5.44. IR spectrum (v, cm⁻¹): 1630 (C=N), 1745 (C=O), 3245 (NH). ¹⁹F NMR spectrum (in CH₃CN): -14.5 unresolved m (CF₃).

Under similar conditions, from 1.79 g of triphenylnitrone and 2 g of ketenimine (XI) in 15 ml of absolute ether, 2.2 g (59%) of N-benzenesulfonyl o-(N'-diphenylmethyleneamino)phenylhexafluoroisobutyramide (XIVb), mp 196-198°C (reprecipitation from CH_2Cl_2 with hexane), were obtained. Found (%): C 58.77, H 3.31, F 18.99, N 4.89. $C_{29}H_{20}F_6H_2O_3S$. Calculated (%): C 58.98, H 3.38, F 19.32, N 4.74. IR spectrum (v, cm⁻¹): 1620 (C=N), 1750 (C=O), 3230 (NH). ¹⁹F NMR spectrum (in acetone): -15.5 unresolved m (CF₃).

Hydrolysis of Amide (XIVa). a) A 0.3-g portion of amide (XIVa) was boiled for 4 h in a mixture of 4 ml of $C_{2}H_{5}OH$ and 1 ml of $H_{2}O$. The mixture was diluted with water and the precipitate filtered. Yield, 0.15 g (95%) of 3,3-bis-(trifluoromethyl)oxindole (XV), mp 165-169°C [2]. From the filtrate, 0.1 g of benzaldehyde 2,4-dinitrophenylhydrazone, mp 225-229°C, was obtained. b) A 0.5-g portion of amide (XIVa) was dissolved at $\sim 20°$ C in 10 ml of absolute

 C_2H_5OH saturated with HC1. The mixture was left to stand for 16 h at $\sim 20^{\circ}C$, and the precipitate was filtered. Yield, 0.35 g (87.5%) of 2-N-(benzenesulfonamido-3,3-bis(trifluoromethy1)-indolenine (XVI), mp 162-164°C (from C_2H_5OH , C_6H_6). Found (%): C 47.16, H 2.40, N 6.92. $C_{16}H_{10}F_6N_2O_2S$. Calculated (%): C 47.05, H 2.45, N 6.86. IR spectrum (ν , cm⁻¹): 1645 (C=N), 3330 (NH). ¹⁹F NMR spectrum (in acetone): -8.45 s (CF₃). Benzaldehyde 2,4-dinitrophenylhydrazone, mp 226-230°C, was obtained from the filtrate.

Hydration of Amide (XIVa). Hydrogen was passed at $\sim 20^{\circ}$ C through a suspension of 1 g of amide (XIVa) and 0.3 g of Raney Ni in 20 ml of absolute alcohol until no more was absorbed. The catalyst was filtered. Hexane was added to the solid residue after distillation of the alcohol, and the insoluble residue was filtered. Thus, 0.25 g of benzenesulfonamide, mp 148-151°C, was obtained. From the hexane filtrate, 0.4 g (55%) of N-benzyl-3,3-bis(trifluoro-methyl)oxindole (XVII), mp 87-89°C (from hexane), was obtained. Found (%): C 56.92, H 3.17, F 31.30, N 4.09. C₁₇H₁₁F₆NO₂. Calculated (%): C 56.82, H 3.06, F 31.75, N 3.89. IR spectrum (ν , cm⁻¹): 1740 (C=0). PMR spectrum (in CCl₄, HMDS - internal standard): 4.9 s (CH₂), 6.7-7.8 m (arom.). ¹⁹F NMR (in CCl₄):-10 s (CF₃).

<u>N-Benzy1-3,3-bis(trifluoromethyl)oxindole (XVII).</u> A mixture of 0.5 g of oxindole (XV), 0.7 g of benzyl bromide, 0.5 g of K₂CO₃ and a catalytic amount of KI in 5 ml of absolute dimethylformamide (DMFA) was boiled for 8 h, and then filtered. The filtrate was diluted with water, and the precipitate was filtered. Thus, 0.4 g (57.5%) of oxindole (XVII), mp 83-85°C (from hexane), was obtained, which was identical with the product obtained during the hydration of amide (XIVa).

2,3-Diphenyl-4-benzoyl-5,5-bis(trifluoromethyl)-1,2,4-oxadiazolidine (XVIII). A 1.35-g portion of hexafluoroacetone benzoylimine was added to a suspension of 1 g of nitrone (I) in 7 ml of absolute ether. The mixture was left to stand for 16 h at $\sim 20^{\circ}$ C, and the precipitate was filtered. Yield, 1.8 g (78%) of oxadiazolidine (XVIII), mp 115-116°C (from a mixture of CCl4 and hexane). Found (%): C 59.27, H 3.35, F 24.24. N 6.21. C₂₃H₁₆F₆O₂. Calculated (%): C 59.23, H 3.64, F 24.46, N 6.01. IR spectrum (ν , cm⁻¹): 1685 (C=O). PMR spectrum (in CH₃CN): 5.5 s (CH), 6.5-6.0 m (arom.). ¹⁹F NMR spectrum (in CH₃CN): -4.6 q (CF₃), -8.3 q (CF₃). J_{F-F} = 7.4 Hz.

When 0.75 g of oxadiazolidine (XVIII) was heated *in vacuo* (2 mm Hg) at 140°C for 3.5 h, 0.25 g (58%) of hexafluoroacetone benzoylimine distilled off. From the residue, 0.16 g (50%) of nitrole (I) was isolated.

2,3-Diphenyl-4-trifluoromethyl-4-diethylaminocarbonyl-5,5-difluoroisoxazolidine (XXa). A 1.67-g portion of N,N-diethyl perfluoromethacrylamide was added to a suspension of 1.42 g of nitrone (I) in 7 ml of absolute ether. The mixture was left to stand for 6 days at 20°C, and the precipitate was filtered. Yield, 1.95 g (58%) of isooxazolidine (XXa), mp 127-128.5°C (from a mixture of CC14 and hexane). Found (%): C 58.25, H 4.83, F 22.16, N 6.73. $C_{21}H_{21}F_{3}N_{2}O_{2}$ Calculated (%): C 58.89, H 4.90, F 22.20, N 6.53. IR spectrum (v, cm⁻¹): 1640(C=O), PMR, spectrum (in C₆F₆): 0.75 m (CH₃), 3.1 q (CH₂), 5.4 s (CH), 6.1-7.4 m (arom.). ¹⁹F NMR spectrum (in ethyl acetate): -16.5 d.d (CF₃), -17.2 d.m (F^A), +1.85 d.q (F^B), J_{CF₃-F^A = 4.2, J_{CF₃-F^B = 11.7, J_FA-F^B = 148 Hz.}}

Under similar conditions, from 0.9 g of nitrone (I) and 1 g of N,N-dimethyl perfluoromethacrylamide, 1.1 g (58%) of 2,3-diphenyl-4-trifluoromethyl-4-dimethylaminocarbonyl-5,5difluoroisoxazolidine (XXb), mp 114-115°C (for a mixture of CCl₄ and hexane), was obtained. Found (%): C 57.22, H 4.29, F 24.68, N 7.32. $C_{19}H_{17}F_5N_2O_2$. Calculated (%): C 57.00, H 4.25, F 23.75, N 7.0. IR spectrum (ν , cm⁻¹);1660 (C=O). PMR spectrum (in acetone): 2.7 s (CH₃), 5.8 s (CH), 6.7-8.0 m (arom.). ¹⁹F NMR spectrum (in acetone): -16.9 d.m (CF₃), -17.2 d.m (F^A), +0.4 d.q (F^B), J_{CF₃-F^B} = 19.2 Hz, J_FA-F^B = 147 Hz. Mol. wt. 400 (mass spectrometrically).

CONCLUSIONS

1. The reactions of nitrones with fluorine-containing ketenimines and acylketimines were found to differ greatly.

2. The structure of 2,3-diphenyl-4-trifluoromethyl-4-diethylaminocarbonyl-5,5-difluoroisoxazolidine was determined by x-ray diffraction analysis.

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FLUORINE-CONTAINING HETEROCUMULENES. XVII.* EPIMINATION OF BIS(TRIFLUOROMETHYL)KETENE ANIL

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Fluoroolefins are successfully epiminated with N anions carrying readily removable groups [2]. In the application to bis(trifluoromethyl)ketenimines, this reaction led to the synthesis of a new type of fluorine-containing three-membered metrocycles, the iminaziridines. Iminoaziridines which do not contain fluorine are obtained by dehydrohalogenation of α -bromoamidines [3, 4]. The article on the synthesis of iminoaziridine from diisopropylcarbodiimide and carbethoxycarbene [5] is inaccurate, since the IR spectra of the compound obtained (1665, 1725 cm⁻¹) correspond to a five-membered ring, and not to a three-membered structure. Attempts to obtain iminoaziridines by cycloaddition of carbethoxynitrene to dialkylketenimines also led to five-membered iminooxazolines only [6].

We found that under the action of N-(p-nitrobenzenesulfonyloxy)urethane (II) and Et₃N, the anil of bis(trifluoromethyl)ketene (I) gives a triethylammonium salt of p-nitrobenzenesulfonic acid and N-carbethoxy-bis(trifluoromethyl)phenyliminoaziridine (III)[†], as confirmed by spectra methods. In the IR spectrum of the reaction mixture, the cumulene absorption band (2080 cm⁻¹) disappears, and the absorption bands at 1770 and 1825 cm⁻¹, corresponding to the C=O and C=N groups, and expected for iminoaziridine (compare [3]), appear, while in the ^{1°}F NMR spectrum, the singlet due to ketenimine (I) at -22 ppm is replaced by a singlet at -9.2 ppm from the CF₃ groups in the iminoaziridine (III). At 0°C, the reaction mixture remains unchanged for a long time, but at 20°C iminoaziridine (III) isomerizes in the course of three days into iminooxazoline (IV). When an attempt was made to isolate (III) by distillation or by chromatography on silica gel, the compound also was almost completely converted into (IV).[‡] Due to the presence of phenylisocyanide in the reaction mixture, which we succeeded in "intercepting" by hexafluoroacetone [thus iminodioxolane (VI) was isolated together with (IV)], we can conclude that this isomerization is related to the decomposition of three-membered ring** to isocyanide and acylamine (V), which then form the 1,4-cycloadduct:

*For communication XVI, see [1].

**Perfluorinated iminoaziridines [3] and iminooxirans [7] undergo a similar decomposition.

[†]During the reaction of ketenimine (I) with N-(p-nitrobenzenesulfonyloxy)benzenesulfonamide, a product is formed which in its composition corresponds to N-benzenesulfonyl-bis(trifluoromethyl)phenyliminoaziridine. However, the spectral characteristics of this compound do not correspond to this structure.

[‡]In one of the numerous experiments on the distribution of the reaction mixture in a high vacuum, we succeeded in isolating a mixture of nearly equal amounts of (III) and (IV). The composition of the mixture did not change on heating (10 h, 100°C), which indicates the stability of iminoaziridine (III) in the absence of impurities.

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