3. D. P. Del'tsova and N. P. Gambaryan, Izv. Akad. Nauk SSSR, Ser. Khim., 2566 (1973).
4. S. Takahashi and H. Kano, Tetrahedron Lett., 1687 (1963).
5. S. St. Black, R. F. Crozier, and V. C. Davis, Synthesis, 205 (1975).
6. N. Murai, M. Komatsu, Y. Ohshiro, and T. Agawa, J. Org. Chem., 42, 448 (1977).
7. W. E. Stewart and T. H. Siddall, Chem. Rev., 70, 517 (1970).

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 Et_3N, 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 ^{19}F NMR spectrum, the singlet due to ketenimine (I) at −22 ppm is replaced by a singlet at −9.2 ppm from the CF_3 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].

†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.

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

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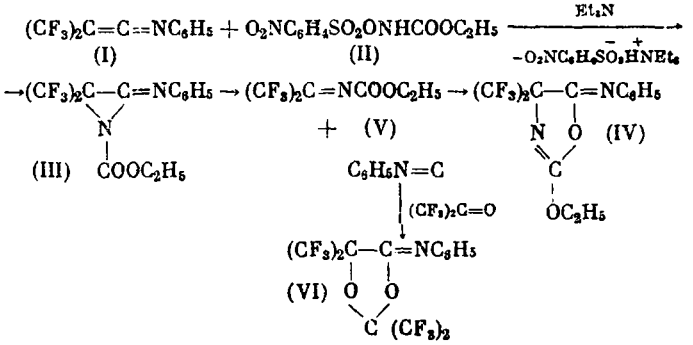
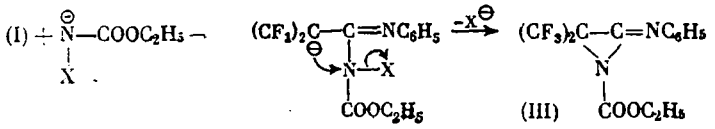


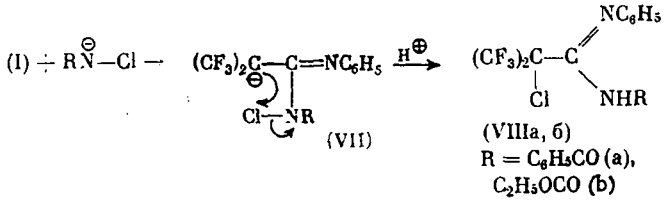
Compounds (IV) and (VI) were obtained by an alternative synthesis, i.e., by the reactions of hexafluoroacetone and acylamine (V) with phenyl isocyanide (compare [8-10]). The structure of (IV) was also confirmed by the IR spectrum (1680, 1765 cm^{-1}) and ^{19}F NMR spectrum (singlet at −3.9 ppm).

Iminoaziridine (III) could not be obtained by the cycloaddition of carbethoxynitrene, formed by thermolysis of carbethoxyazide, to ketenimine (I); of the fluorine-containing products, only a dimer of ketenimine (I), 1-phenyl-2-hexafluoroisopropylidene-3,3-bis(trifluoromethyl)-4-phenyliminoazetidine, was identified [11]. Therefore, we can assume that the epimination of ketenimine (I), and other compounds with activated C=C bonds, with sulfonyloxyurethane (II) [2] takes place by a nucleophillic mechanism

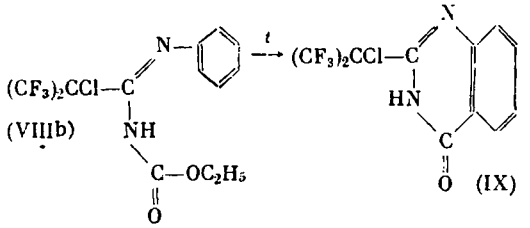


$X = O_2NC_6H_4SO_3^{\ominus}$

It is interesting to note that the direction of the reaction of ketenimine (I) with N anions changes completely when the readily removable p-nitrobenzenesulfonyloxy group is replaced by the difficulty removable chlorine atom (compare [2]). This in the reactions of ketenimine (I) with N-chlorobenzamide and N-chlorourethane in the presence of bases, the epimination products are not produced, but N-phenyl-N'-acyl α-chlorohexafluoroisobutyric acid amidines (VIII) are exclusively formed; i.e., in this case, the intermediate anion (VII) becomes stabilized by the transfer of the chlorine atom to the anionic center, and not by its intramolecular nucleophillic substitution



At 165°C, compound (VIIIb) completely cyclizes into quinazolone (IX):



This reaction represents a convenient method for the synthesis of fluorine-containing quinazolones.

EXPERIMENTAL

The NMR spectra were run on the Perkin-Elmer R-12 (^1H, 60 MHz) and Hitachi (^{19}F, 56.46 MHz) spectrometers. The chemical shifts were measured in ppm with reference to tetramethyl-

silane (^1H, δ scale) and CF_3COOH (^{19}F) as external standards, the IR spectra were recorded on the UR-20 spectrometer.

2-Ethoxy-4-phenylimino-5,5-bis(trifluoromethyl)-2-oxazoline (IV). A 1.8-g portion of hexafluoracetone carbethoxyimine was added dropwise with ice cooling to a solution of 0.9 g of phenyl isocyanide in 7 ml of cyclohexane, and the mixture was left to stand for 2 h at ~20°C. By distillation, 1.5 g (58%) of oxazoline (IV), bp 70-72°C (10^{-2} mm), mp 57-58°C (from hexane), was isolated. Found (%): C 45.97, H 2.96, F 33.24. $C_{13}H_{10}F_6N_2O_2$. Calculated (%): C 45.89. H 2.94, F 33.53. PMR spectrum (in CCl_4): 0.8 t (CH_3), 3.9 q (CH_2), 6.7 s (C_6H_5).

2,2,4,4-Tetrakis(trifluoromethyl)-5-phenyliminodioxolane (VI). A 2.5-ml portion of hexafluoroacetone (−78°C) was passed through an ice-cooled solution of 0.6 g of phenyl isocyanide in 5 ml of cyclohexane. By distillation, 2 g (81%) of dioxolane (VI), bp 52-53°C (2 mm), were isolated. Found (%): C 35.85, H 1.13, F 52.43, N 3.38. $C_{13}H_5F_{12}NO_2$. Calculated (%): C 35.86, H 1.15, F 52.41, N 3.22. IR spectrum (ν, cm^{-1}): 1755 (C=N). PMR spectrum: 6.8 s (C_6H_5). ^{19}F NMR spectrum: multiplets at −3.7 and +2.1 ppm.

Reaction of Bis(trifluoromethyl)ketene Anil with N-(p-Nitrobenzenesulfonyloxy)urethane. A 2.5-g portion of ketenimine (I), and then 1.1 g of Et_3N were added with stirring and ice cooling to a suspension of 3.1 g of the sulfonyloxyurethane (II) in 25 ml of absolute ether. The mixture was heft to stand for 3 h at 20°C, and the precipitate was filtered and washed with ether. Bu distillation of the filtrate, 2.2 g (65%) of a fraction, bp 70-72°C (10^{-2} mm), were isolated, which according to the IR and NMR spectral data contained oxazoline (IV) with an admixture of iminoaziridine (III). After treatment with hexane, pure(IV) was isolated, mp 57-58°C.

An excess of hexafluoroacetone was added to the reaction mixture obtained in an analogous experiment. The mixture was left to stand for a few days in a sealed tube. By distillation, iminodioxolane (VI) and oxazoline (IV) were isolated in a yield of 17% and 31%, respectively.

Reaction of Bis(trifluoromethyl)ketene Anil with N-(p-Nitrobenzenesulfonyloxy)benzenesulfonamide. A 1.5-g portion of ketenimine (I) was added to a suspension of 2.9 g of sulfonyloxybenzenesulfonamide in 10 ml of absolute CH_3CN, and then, 0.6 g of Et_3N in 5 ml of CH_3CN was added dropwise during cooling with ice. For 3h CH_3CN was evaporated *in vacuo*, absolute ether was added to the residue, and the precipitate of the triethylammonium salts of p-nitrobenzenesulfonic acid was filtered. The filtrate was evaporated, and the residue was recrystallized from hexane. Yield, 1.2 g (49%) of crystals, mp 124-128°C. Found (%): C 46.95, H 2.68, F 27.48, N 7.04. $C_{16}H_{10}F_6N_2O_2S$. Calculated (%): C 47.05, H 2.45, F 27.94, N 6.86. IR spectrum (ν, cm^{-1}): 1760. ^{19}F NMR spectrum (in nitrobenzene): −4.6 q (CF_3), −6.2 q (CF_3), $J_{CF_3-CF_3}$ - 4.5 Hz.

N-Phenyl-N'-benzoyl α-chlorohexafluoroisobutyric Acid Amidine (VIIIa). A 2.5-g portion of ketenimine (I) was added with cooling to 1.6 g of N-chlorobenzamide and 0.8 ml of pyridine in 10 ml of absolute CH_3CN. After ~15 h, the reaction mixture was poured into water. From the precipitate, 3 g (74.5%) of amidine (VIIIa), mp 118-119°C (from aqueous alcohol), were obtained. Found (%): C 50.39, H 3.05, F 28.03, N 6.84. $C_{17}H_{11}F_6ClN_2O$. Calculated (%): C 49.94, H 2.70, F 27.91, N 6.85. IR spectrum (ν, cm^{-1}): 1650, 1690. ^{19}F NMR spectrum (in acetone): −9.1 s (CF_3). In a similar reaction, when pyridine was replaced by potassium tert-butylate, the amidine (VIIIa) was obtained in a yield of 79%.

N-Phenyl-N'-carbethoxy α-chlorohexafluoroisobutyric Acid Amidine (VIIIb). A 1.9-g portion of ketenimine (I) was added with stirring and cooling to −30°C to 1.1 g of the sodium salt of N-chlorourethane in 10 ml of absolute CH_3CN. After ~15 h, the mixture was poured into dilute HCl. From the precipitate 2.6 g (93%) of amidine (VIIIb), mp 68-70°C (from hexane), was obtained. Found (%): C 41.17, H 2.89, F 30.36, N 7.08. $C_{13}H_{11}F_6ClN_2O_2$. Calculated (%): C 41.43, H 2.92, F 30.28, N 7.43. IR spectrum (ν, cm^{-1}): 1665, 1725. ^{19}F NMR spectrum (in CH_3CN): −9.5 s (CF_3).

2-α-Chlorohexafluoroisopropyl-4-quinazolone (IX). A 1.95-g portion of amidine (XIIIb) was heated for 4 h at 165-170°C. After recrystallization from acetone 1,5 g (88%) of quinazolone (IX), mp 184-186°C, was obtained. Found (%): C 40.01, H 1.90, F 34.58, N 8.5. $C_{11}H_5F_6ClN_2O$. Calculated (%): C 39.93, H 1.51, F 34.39, N 8.47. IR spectrum (ν, cm^{-1}): 1615, 1690). ^{19}F NMR spectrum (in hexametapol): −9.3 s (CF_3).

CONCLUSIONS

1. It was shown that N-carbethoxy-bis(trifluoromethyl)phenyliminoaziridine is formed during nucleophilic epimination of the anil of bis(trifluoromethyl)ketene with p-nitrobenzenesulfonyloxyurethane. A scheme of its isomerization to 2-ethoxy-4-phenylimino-5,5-bis(trifluoromethyl)-2-oxazoline was established.

2. The reaction of bis(trifluoromethyl)ketene anil with N-chloroamides yielded N-phenyl-N'-acyl α-chlorohexafluoroisobutyric acid amidines.

LITERATURE CITED

1. D. P. Del'tsova, Z. V. Safronova, N. P. Gambaryan, M. Yu. Antipin, and Yu. T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1881 (1978).
2. Yu. V. Zeifman, E. M. Rokhlin, U. Utebaev, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 226, 1337 (1976).
3. H. Quast and E. Schmitt, Angew. Chem., 82, 395 (1970).
4. H. Quast and P. Schafer, Tetrahedron Lett., 1057 (1977).
5. A. J. Hubert, A. Feron, R. Warin, and P. Teyssie, Tetrahedron Lett., 1317 (1976).
6. W. J. Kauffman, J. Org. Chem., 35, 4244 (1970).
7. H. Kagen and I. Lillien, J. Org. Chem., 31, 3728 (1966).
8. N. O. Gambaryan, E. M. Rokhlin, Yu. V. Zeifman, L. A. Simonyan, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 166, 864 (1966).
9. W. J. Middleton, D. C. England, and C. G. Krespan, J. Org. Chem., 32, 948 (1967).
10. Yu. V. Zeifman, N. P. Gambaryan, L. A. Simonyan, R. B. Minasyan, and I. L. Knunyants, Zh. Obshch. Khim., 37, 2476 (1967).
11. D. P. Del'tsova, Yu. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, Zh. Organ. Khim., 8, 856 (1972).

ORGANOBORON COMPOUNDS.

346. ADDITION OF ALLYL(ALKYL)BORANES TO CARBONYL COMPOUNDS

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After we have developed the preparative methods for the preparation of mixed allyl(alkyl)-boranes [1-4], we started a systematic study of the chemical properties of this class of compounds and their possible utilization in organic synthesis. In [3], we described the irreversible allyl rearrangement and the splitting of the boron–allyl bonds under the action of water and alcohols.

In the present work, we studied the reactions of allyl(dialkyl)boranes or triallylborane with carbonyl compounds, leading to unsaturated esters of organoboric acids and allyl carbinols.

The direction of the reactions of the organic boron derivatives with aldehydes and ketones is determined by the nature of the radical attached tothe boron atom, structure of the carbonyl compound, and the conditions of the process. Alkyl- and arylboranes do not add to the double bond of the C=O group, except in the reaction of trialkylboranes R_3B with monomeric CH_2O, which in the presence of atmospheric oxygen leads to compounds R_2BOCH_2R [5]. When heated above 100°C, aromatic aldehydes are quantitatively reduced by trialkylboranes to the corresponding alcohols [6-8]. The reaction is accompanied by the elimination of the olefinic hydrocarbon, and had been used for the synthesis of pure α-olefins [6, 7] and counterthermodynamic isomerization of methylcyclenes into methylenecyclanes [6].

Aliphatic aldehydes and ketones react with triphenyl- and tribenzylboranes at 145-170°C, mainly with the formation of ethers of type $RCH{=}CR'{-}OBR_2''$ (I) [9]. In the presence of pivalic acid as catalyst, vinyloxyboranes (I) are readily obtained at 80-100°C from trialkylboranes also [10], while triethylborane converts many cycloalkanones and acyclic ketones into dimeric and trimeric products of crotonic condensation [11]. Triallylborane [12] and other allylboranes [12-15] react with aldehydes and ketones, including ketones of the steroids class

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