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BORON FLUORIDES OF cis- AND trans-2-ARYL-3-AROYLAZIRIDINES

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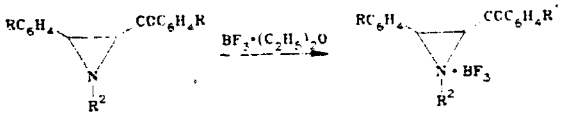
The reaction of boron trifluoride etherate with cis- and trans-2-aryl-3-aroylaziridines yields the respective complexes in high yield. According to PMR spectral data the methyl group of boron trifluoride trans-1-methyl-3-aroylaziridines is located in syn-position, and in the cis-aziridine complexes in anti-position, to the carbonyl group.

With certain acids ($HClO_4$, $HFSO_3$) aziridine derivatives form quite stable salts [1-3] that show increased reactivity toward nucleophiles [4, 5]. We have shown [6, 7] that complexes of 3-aroylaziridines with boron trifluoride also react quite easily with acetone and acetonitrile. But no data have been published on the synthesis and structure of these complexes.

In the present work we establish that the boron fluoride trans-2-aryl-3-aroylaziridines (I-XII) (Table 1) can be obtained in high yield (85-90%) by treatment of trans-2-aryl-3-aroylaziridines in methanol at −20° to −30° with an equimolar amount of boron trifluoride etherate.



I-XX

I, XI, XIV R=p-Cl, II, XII, XIII R=p-Br, III, XV R=m-NO_2, IV R=p-NO_2, V, X, XVI R=p-CH_3, VI—IX, XVII—XX R=H; I—VI, IX—XVII R^1=H, VII, XVIII R^1=p-Br, VIII, XIX R^1=p-Cl, XX R^1=OCH_3; I—VIII, XIII—XX R^2=CH_3, IX—XII R^2=H

When compounds I-XII are treated with aqueous salt solution the respective free aziridines separate; this confirms [2] the retention of the aziridine ring in the complex.

Similarly cis-1-methyl-2-aryl-3-aroylaziridines also react with boron trifluoride etherate to form complexes. The yield of complexes XIII-XX is also high, 85-90% (Table 1).

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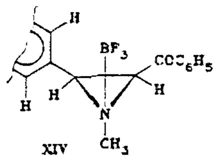
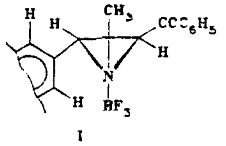
TABLE 1

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
I	175	56.3	4.3	4,0	$C_{16}H_{14}ClNO \cdot BF_3$	56.5	4.1	4.1	95
II	179	50.2	3.9	3,4	$C_{16}H_{14}BrNO \cdot BF_3$	50,0	3.6	3.6	95
III	181	55,2	4,1	7,8	$C_{15}H_{14}N_2O_3 \cdot BF_3$	54.9	4.0	8.0	93
IV	178	54.7	4.1	8,0	$C_{15}H_{14}N_2O_3 \cdot BF_3$	54.9	4.0	8.0	97
V	153	64.1	5.2	4.2	$C_{17}H_{17}NO \cdot BF_3$	63.9	5.3	4.4	92
VI	133	62.8	5.2	4.5	$C_{16}H_{15}NO \cdot BF_3$	62.9	4.9	4.5	90
VII	174	50,3	3.4	3,5	$C_{16}H_{14}BrNO \cdot BF_3$	50,0	3.6	3.5	93
VIII	169	56.3	4.4	4.0	$C_{16}H_{14}ClNO \cdot BF_3$	56.5	4.1	4.1	94
IX	142	59.3	4,1	4.2	$C_{15}H_{13}NO \cdot BF_3$	59.0	4.3	4.6	79
X	144	60.3	4.9	4.1	$C_{15}H_{15}NO \cdot BF_3$	60.2	4,7	4.4	87
XI	148	53.2	3.4	4.1	$C_{15}H_{12}ClNO \cdot BF_3$	53.0	3.5	4.1	85
XII	149	48.4	3.0	3.8	$C_{15}H_{12}BrNO \cdot BF_3$	48.6	3.2	3.7	83
XIII	171	50.3	3.9	3.4	$C_{16}H_{14}BrNO \cdot BF_3$	50,0	3.6	3.6	94
XIV	159	56,7	4.0	3.9	$C_{16}H_{14}ClNO \cdot BF_3$	56,5	4,1	4.1	92
XV	165	54.9	4,1	7,7	$C_{15}H_{14}N_2O_3 \cdot BF_3$	54,9	4.0	8,0	95
XVI	149	64.2	5,0	4,5	$C_{17}H_{17}NO \cdot BF_3$	63.9	5.3	4.4	94
XVII	145	62.9	5.0	4.3	$C_{16}H_{15}NO \cdot BF_3$	62,9	4,9	4.6	91
XVIII	147	50.3	3.3	3.3	$C_{16}H_{14}BrNO \cdot BF_3$	50.0	3.6	3.6	93
XIX	155	56.3	4,4	4.0	$C_{16}H_{14}ClNO \cdot BF_3$	56.5	4,1	4.1	91
XX	152	61,3	5,4	4,0	$C_{17}H_{17}NO_2 \cdot BF_3$	60,9	5,1	4,2	90

TABLE 2. Oberhauser Nuclear Effect

Compound	Group irradiated	Proton observed	ONE, %
 XIV	o-HAr (7,25 ppm)	3-H	0
	o-HAr (7,25 ppm)	2-H	25
	N—CH_3 (3,47 ppm)	3-H	12
	N—CH_3 (3,47 ppm)	2-H	13
 I	o-HAr (7,50 ppm)	3-H	21
	o-HAr (7,50 ppm)	2-H	24
	N—CH_3 (2,86 ppm)	3-H	0
	N—CH_3 (2,86 ppm)	2-H	11

The PMR spectra of boron trifluoride trans-2-aryl-3-aroyl-1-methylaziridines I-VIII show singlet signals of methyl protons in the 2.80-2.97 ppm region, doublets of the 3-H (5.70-6.00 ppm) and 2-H methine protons (4.73-5.07 ppm) (J = 6.2-6.4 Hz) (which are evidence for their trans-configuration), and a multiplet of aromatic protons at 7.50-8.67 ppm. The spectra of the boron fluoride trans-2-aryl-3-aroylaziridines IX-XII also have doublet signals for methyne protons (but more upfield than the signals of I-VIII), 3-H (5.58-5.63 ppm) and 2-H (4.50-4.53 ppm) with SSCC J = 5.8-6.0 Hz, and an aromatic proton multiplet at 7.27-8.17 ppm. The PMR spectra of boron trifluoride cis-2-aryl-3-aroyl-1-methylaziridines XIII-XX show methyl proton signals as signals downfield (relative to the trans-analogs I-VIII) at 3.17-3.50 ppm 3-H (5.10-5.47 ppm) and 2-H (4.77-5.10 ppm) methyne proton doublets, with SSCC J = 8.2-8.4 Hz (which are evidence for the cis-configuration of XIII-XX [3]), and an aromatic proton multiplet at 7.03-8.33 ppm.

The IR spectra of boron trifluorides I-XX show the typical aromatic ring bands (3090, 1605, and 1510 cm^{-1}), C=O bands at 1690-1695 cm^{-1}, and the intense broad band of B—F bond vibration (1060-1120 cm^{-1}). The increase in carbonyl vibrational band frequency in the salt form as compared with the 2-aryl-3-aroyl-1-methylaziridine bases is apparently due to the decreased conjugation between the carbonyl and the aziridine ring, because of the donor—acceptor nature of the N—BF_3 bond.

Additional confirmation was desired to confirm the relative configuration of the boron fluoride cis- (XIII-XX) and trans-2-aryl-3-aroylaziridines (I-XII) and to assign the 2-H and 3-H methyne proton signals in the PMR spectra. An experiment on the determination of the

Oberhauser nuclear effect (ONE) [8] was therefore performed with cis-1-methyl-2-p-chlorophenyl-3-benzoyl- (XIV) and trans-1-methyl-2-p-chlorophenyl-3-benzoylaziridine (I) as typical complexes (Table 2).

We compared the signal intensities of the 3-H and 2-H methyne proton signals of compounds I and XIV in PMR spectra that varied as a result of ONE when the ortho-phenyl protons in position 2 of the aziridine ring were irradiated. We confirmed the trans-configuration for compound I and the cis-configuration for XIV. On the basis of the ONE data, the methyne proton signals in the spectra of boron fluoride 3-aroylaziridines located downfield correspond to 3-H protons, while the upfield signals correspond to 2-H protons (Table 2). The change in intensity of the 2-H and 3-H methyne proton signals when the methyl protons of compound I are irradiated (Table 2) showed that in the trans-3-aroylaziridine complexes, I-VIII, methyl is cis with respect to carbonyl, just as in the 3-aroylaziridine bases [9]; i.e., the reaction of trans-1-methyl-2-aryl-3-aroylaziridines with boron trifluoride etherate is stereoselective, just as in the reaction with fluorosulfonic acid [2, 10]. The configuration of the nitrogen atom is also retained in the case of the boron trifluoride cis-2-aryl-3-aroyl-1-methylaziridines (Table 2).

EXPERIMENTAL

IR spectra in KBr tablets were recorded with UR-20 and IR-75 spectrometers. PMR spectra of 5-10% solutions of materials in deuteroacetone-D_6 were obtained with a Tesla BS-467 spectrometer, with HMDS internal standard. ONE was determined on 5-7% solutions in deuteroacetone-D_6, previously degassed.

Boron Trifluoride trans-2-Aryl-3-aroylaziridines (I-XII). A solution of 0.1 mole of trans-2-aryl-3-aroylaziridine in a minimal amount of acetone was quickly cooled to −20 to −30° to avoid crystallization of 3-aroylaziridine. Then 0.1 mole of freshly distilled boron trifluoride etherate was added with stirring, while the temperature of the reaction mixture was kept no higher than 10°. As the boron trifluoride solution precipitated, the mixture was diluted with 100-150 ml of dry ether. When precipitation was complete the complex was filtered off, washed with dry ether, and recrystallized from acetonitrile—ether mixture (Table 1).

Boron Trifluoride cis-2-Aryl-3-aroylaziridines (XIII-XX). A solution of 0.1 mole of cis-2-aryl-3-aroylaziridine in 50-70 ml of 1:4 methanol—dry ether was quickly cooled to −20 to −30° to avoid crystallization of 3-aroylaziridine. Then 0.1 mole of freshly distilled boron trifluoride etherate was added with stirring, while the temperature of the reaction mixture was kept no higher than −15°. As boron trifluoride solution precipitated, the mixture was diluted with 150-200 ml of dry ether and filtered. The crystals were washed with dry ether and recrystallized from acetonitrile—ether mixture (Table 1).

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