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1,3-DIARYL-2,2-DIHALOAZIRIDINES IN NITRATION AND BROMINATION REACTIONS

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In the nitration of 3-(4-nitrophenyl)-1-phenyl-2,2-dichloroaziridine in acetic acid, 1-(o- and p-nitrophenyl)-derivatives are formed in a 35:65 ratio. 1,3-Diphenyl-2,2-dichloroaziridine undergoes opening of the three-membered ring under the same conditions, forming a mixture of o- and p-nitroanilides and 2-nitro-4chloroanilides of 2-acetoxy (or 2-chloro)-2-phenylacetic acids. The bromination of 3-(4-nitrophenyl)-1-phenyl-2,2-dichloroaziridine in aqueous acetic acid leads to 1-(4-bromophenyl)-3-(4-nitrophenyl)-2,2-dichloroaziridine, while in a mixture of acetic acid and acetic anhydride it leads to the anilide of 2-bromo-2-phenylacetic acid and 2-bromo-N-(2,4-dibromophenyl)-1-(4-nitrophenyl)-2,2-dichloroethylamine.

1,3-Diary1-2,2-dihaloaziridines, formed in the interaction of dihalocarbenes with benzylidenanilines, can be used in the synthesis of amidines [1, 2], imidoesters [2, 3], heterocycles [4-6], and other compounds [2, 7-9].

We studied the reactions of nitration and bromination of the aziridines Ia and b. In the nitration of the aziridine Ia a mixture of aziridines Ic and Id is formed in a 65:35 ratio; their structure was confirmed by the PMR spectra (Table 1) and by hydrolysis in 20% sulfuric acid to o- and p-nitroanilines. Nitration of the aziridine Ib leads to a complex mixture of anilides IIa-f in the amounts indicated on the scheme. The structure of compounds IIa-f is confirmed by the data of the PMR and IR spectra (Table 1). In the IR spectra of the anilides, the bands of the amide group are observed at 1658-1715 (C=O) and 3295-3395 cm⁻¹ (NH); in the spectra of anilides of 2-acetoxy-2-arylacetic acids, in addition, there is the band of the C=O

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of the acetoxy group (1757-1775 cm^{-1}). The PMR spectra of the anilides contain signals of the methine proton in the region of 5.39-6.20 ppm, the protons of substituted aromatic rings, the broad signal of the proton of the amide group in the region of 9.4-11.4 ppm, as well as the methyl group at 2.10-2.16 ppm in acetoxy derivatives. The weak-field 0.8-1.2 ppm shift of the signal of the NH proton and the $60-80 \text{ cm}^{-1}$ decrease in the frequency of the vibrations of the NH bond in ortho-nitro-substituted N-arylamides in comparison with the para-isomers may be caused by the formation of an intramolecular hydrogen bond between the NH and NO₂ group. The anilides IIa-f, in hydrolysis in alkali medium, give the corresponding substituted anilines. Since 1-(4-nitrophenyl)-3-phenyl-2,2-dichloroaziridine is not converted to the anilides IIa, b under the conditions of the nitration reaction, we should assume that compounds IIa-f are formed as a result of an initial opening of the aziridine ring, followed by conversions. Actually, under the action of conc. H_2SO_4 on a solution of the aziridine Ib in a mixture of acetic acid and acetic anhydride, a mixture of the anilides IIk and l is formed. When a nitrating agent is added to this mixture, a mixture of the analides Ia-f is obtained. Treatment of a solution of the analide IIk in acetic acid and acetic anhydride with a nitrating mixture with an addition of HCl leads to the formation of the anilides IIa, c, e; the anilide IIc is not chlorinated under these conditions. This permits us to conclude that the formation of the anilides IIe, f occurs with the participation of chloride ions liberated in the isomerization of the aziridine Ib; the chlorination process precedes nitration.

Bromination of the aziridine Ia in aqueous acetic acid leads to the aziridine Ie and to products of its subsequent conversions — the anilides IIg-i. The structure of the aziridine Ie is confirmed by spectral data (Table 1) and by the formation of the anilides IIg, h when it is heated with water.



I a $R^1 = NO_2$, $R^2 = R^3 = H$; b $R^1 = R^2 = R^3 = H$; c $R^1 = R^2 = NO_2$, $R^3 = H$; d $R^1 = R^3 = NO_2$, $R^2 = H$; e $R^1 = NO_2$, $R^2 = Br$, $R^3 = H$; II a $R^1 = R^3 = H$, $R^2 = NO_2$, $R^4 = CI$; b $R^1 = R^3 = H$, $R^2 = NO_2$, $R^4 = OAc$; c $R^1 = R^2 = H$, $R^3 = NO_2$, $R^4 = OI$; d $R^1 = R^2 = H$, $R^3 = NO_2$, $R^4 = OAc$; e $R^1 = H$, $R^2 = R^4 = CI$, $R^3 = NO_2$; f $R^1 = H$, $R^2 = CI$, $R^3 = NO_2$, $R^4 = OAc$; g $R^1 = NO_2$, $R^2 = Br$, $R^3 = H$, $R^4 = CI$; h $R^1 = NO_2$, $R^2 = Br$, $R^3 = H$, $R^4 = OH$; i $R^1 = NO_2$, $R^2 = Br$, $R^3 = H$, $R^4 = OAc$; j $R^1 = NO_2$, $R^2 = R^3 = H$, $R^4 = Br$; k $R^1 = R^2 = R^3 = H$, $R^4 = CI$; J $R^1 = R^2 = R^3 = H$, $R^4 = OAc$

In the bromination of the aziridine Ia in a mixture of acetic acid and acetic anhydride, a mixture of the anilide IIk and the amine III is obtained. The anilide IIj is identical in physical and spectral chracteristics with the preparation obtained from 2,2-dibromo-3-(4-nitrophenyl)-1-phenylaziridine (If). The structure of the amine III was confirmed by spectral data. The mass spectrum of compound III contains a peak of the molecular ion (5%), two intense peaks of the ions $[M - HCBrCl_2]^{+\bullet}$ (100%) and $[M - 2HBr]^{+\bullet}$ (85%). In the IR spectrum of compound III, absorption is observed at 3395 cm⁻¹, characteristic of secondary amines. The PMR spectrum of the amine III contains a singlet signal of the methine proton, which becomes a triplet when CF₃COOH is added, a group of lines of the protons of the p-nitrophenyl substituent, and a group of lines of the protons of the 2,4-disubstituted aniline aromatic ring. Under the action of t-BuOK in t-BuOH on the amine III, 2,4-dibromoaniline is isolated.

TABLE 1. Spectral Data for 1,3-Diary1-2,2-dihaloaziridines (Icf), N-arylamides, and 2-Bromo-N-(2,4-dibromopheny1)-1-(4-nitropheny1)-2,2-dichloroethylamine (III)

Com-		PMR s	pectrur	n, δ, p	pm (J,	Hz)
pound	Frequencies in the IR spectrum, cm ⁻¹	CH₃CO	-сн	N—Ar	CAr	NH
Ic	859 \$, 902, 1094, 1118, 1170, 1180, 1284, 1311, 1330, 1352 \$, 1395, 1433, 1500 \$, 1539 \$, 1600 \$,1615, 3044, 3088		4,47	7,40, 8,28 (9)	7,86, 8,31 (9)	
Id	850, 904, 1104, 1179, 1278, 1303, 1326, 1355 s, 1392, 1488, 1540 s, 1588, 1615 s, 3045, 3085	—	4,47	7,34, 7,46, 7,69, 8,19 (2,8)	7,84, 8,29 (9)	
ke.	834 s, 845, 864, 897 s, 1013, 1074 s, 1091, 1111, 1164, 1274, 1297, 1324, 1350 s, 1393, 1433, 1490 s, 1534 s, 1593, 1608, 3054 w, 3090 w		3,66	6,89, 7,45 (9)	7,63, 8,21 (9)	
Ħ	861, 883, 1074, 1114, 1277, 1310, 1322, 1360 s, 1394, 1431, 1498 s, 1534 s, 1603, 2860 s, 3020, 3055, 3077		3,75	7,08, 7,45	7,72, 8,33 (9)	
Ila	854, 1115, 1254, 1307, 1345 s, 1412, 1520 s, 1548 s, 1603, 1616, 1705 s, 3015 s, 3075 w, 3397		5,76	7,91, 8,19 (9)	7,31, 7,71	10,20
IID	860, 934, 1031, 1048, 1174, 1254, 1305, 1345 s, 1374, 1415, 1518 s, 1544 s, 1600, 1617, 1715 s, 1765 s, 3015, 3055, 3075, 3423	2,10	6,06	7,81, 8,07 (9)	7,21, 7,64	10,18
lic	858, 934, 1150, 1167, 1278 s 1343 s, 1444 s, 1460, 1504 s, 1591s, 1622, 1702 s, 3015, 3055, 3075, 3096, 3315	-	5,39	8,76, 8,17, 7,59, 7,15 (2,9)	7,25— 7,53	11,36
IIG	860, 933, 1033, 1043, 1083, 1111, 1167, 1248, 1281 s, 1316, 1344 s, 1376, 1443 s, 1460, 1506 s, 1592 c, 1613 s, 1710 s, 1760 s, 3014, 3048, 3074, 3336	2,23	6,20	8,60 (9), 8,18 (9,2), 7,22, 7,72	7;29— 7,63	11,07
He	838, 864, 894, 1138, 1274 s, 1344 s, 1400, 1457 s, 1505 s, 1552, 1584 s, 1705 s, 3013, 3050, 3095, 3320	—	5,82	7,64 (3,9), 8,16 (3), 8,58 (9)	7,29— 7,63	10,99
IIf	840, 890, 933, 1032, 1050, 1084, 1156, 1274 s, 1333s, 1374, 1458, 1505, 1585 s, 1613, 1715s, 1760 s, 3024 w, 3075 w, 3105 w, 3340	2,23	6,20	(3,9), (3,9), 8,18 (3), 8,67 (9)	7,29— 7,61	11,12
I Ig	726, 773, 825 s, 866, 1010, 1073, 1110, 1179, 1247, 1311, 1350 s, 1400, 1493 s, 1533 s, 1613, 1673 s, 3084, 3124, 3200, 3265		5,64	7,36, 7,54	7,84, 8,21 (9)	
Ιħ	811, 830, 857, 1010, 1070, 1081 s, 1109, 1188, 1231, 1281, 1314, 1344 s, 1403 s, 1493 s, 1520 s, 1534 s, 1593, 1608, 1658 s, 3250 s, 3370 s	5,36 (5) (OH)	5,99 (5)	(10) 7,39, 7,67 (9)	(3) 7,81, 8,17 (9)	9,44
111	834, 854, 1013, 1053, 1078, 1256, 1354 s, 1374, 1400, 1442 w, 1495, 1536 s, 1595, 1613, 1704, 1774, 2960 w, 3040, 3425	2,16	6,14	7,38, 7,56 (9)	7,83, 8,23 (9)	9,65
IIj	832, 857, 1114, 1164, 1184, 1250, 1321, 1351 s, 1448 s, 1505, 1537, 1603 s, 1687 s, 3020, 3046, 3080, 3084, 3395	-	5,83	6,97 7,69	7,93, 8,21 (9)	9,68
III	934, 964, 1032, 1047, 1254, 1313, 1374, 1448 s, 1504, 1540 s, 1603, 1700 s, 3015, 3055, 3075, 3430	2,11	6,02	6,91	7,68	9,47
III	860, 874, 1020, 1037, 1248, 1264, 1317, 1354 s, 1390, 1425 w, 1455 w, 1506 s, 1535 s, 1592, 1613, 3050 w, 3075 w, 3085 w, 3395		5,83	6,84 (9), 7,24 (9, 2), 7,60	8,05, 8,25 (9)	
				$(2)^{(1)}$		

The formation of compounds IIj and III in the reaction of bromine with the aziridine Ia in a mixture of acetic acid and acetic anhydride may proceed through a complex of the aziridine with bromine of the type of IV. The latter can be detected as a result of nucleophilic attack of bromine with the formation of $p-O_2NC_6H_4CH(CCl_2Br)NBrPh$, which is then brominated in the aromatic ring to the amine III, or with the formation of $p-O_2NC_6H_4CBrCCl=NPh$, which is

then hydrolyzed to the anilide IIj. The use of aqueous acetic acid as the solvent in the bromination of the aziridine Ia leads to a substantial increase in the rate of electrophilic bromination in the aromatic ring (cf. [10]), leading to the aziridine Ie, which then undergoes a partial opening of the three-membered ring, forming the anilide IIg-i.

EXPERIMENTAL

The physical constants and data of elementary analysis of the substances obtained are cited in Table 2, the spectral data in Table 1. The IR spectra of compounds IIj and h were recorded in KBr tablets, and of the remaining compounds in 2% solutions in CHCl₃ (cuvette 400 μ) on a UR-20 instrument. The PMR spectra were recorded on Varian HA-100D-15 (100 MHz) and Varian EM-360 (60 MHz) instruments for 15% solutions in acetone-D₆, with the exception of compounds Ie, f, and IIc, the spectra of which were recorded in 15% solutions in CCl₄. The aziridine Ia, b, and f were produced from the corresponding azomethines and dihalocarbenes, generated under the conditions of interfacial catalysis [11].

<u>Nitration of the Aziridine Ia</u>. To a solution of 1 g(3.2 mmoles) of the aziridine Ia in 30 ml of acetic acid and 3 ml of acetic anhydride, cooled with ice, a solution of 0.55 g (5.4 mmoles) KNO₃ in 2 ml conc. H₂SO₄ was added dropwise with mixing, mixed for 15 min, and poured out into 200 ml of water. The precipitate was removed and dried. Yield 1.11 g. A mixture of the aziridines Ic, d (1 g) was separated by the method of thin-layer chromatography on SiO₂ (ether-hexane), yielding 0.57 g of compound Ic and 0.31 g of compound Id.

<u>Hydrolysis of a Mixture of Aziridine Ic, d.</u> A mixture of aziridines Ic, d (0.076 g) was heated with a reflux condenser at 140°C in 20% aqueous N₂SO₄ for 24 h, then adjusted to an alkaline pH by the addition of NaOH, extracted carefully with ether, and analyzed by the method of gas-liquid chromatography. The ratio of p- and o-nitroanilines was 65:35.

<u>Nitration of the Aziridine Ib</u>. To a solution of 2.62 g (9.9 mmoles) of the aziridine Ib in 35 ml of acetic acid and 35 ml acetic anhydride, a solution of 3 g (30 mmoles) KNO₃ in 9 ml H_2SO_4 was added dropwise with cooling (-10°C) and mixing, and mixed for another 1 h. The reaction mixture was poured out into 300 ml of water and treated with ether. The solution in ether was washed with water, with a solution of NaHCO₃, and dried with CaCl₂. The residue after removal of the solvent was separated by column chromatography on SiO₂. The anilides IIa (0.30 g, 10%) (mp 147-148°C (from aqueous ethanol) [12]), IIb (0.32 g, 10%) (oil), IIc (0.24 g, 8%), IId (0.29 g, 9%), IId (0.16 g, 5%), and IIf (0.20 g, 6%) were obtained.

<u>Alkaline Hydrolysis of the Anilides IIa-f.</u> A solution of 0.05 g of the anilide was mixed in 5 ml of 5% solution of NaOH in 80% ethanol until the reaction ended (monitored by the method of thin-layer chromatography), the solvent was evaporated under vacuum, the residue extracted with ether, and the substituted aniline isolated by thin-layer chromatography. The anilines were identified according to their melting points (mixed melting point test) and according to their IR spectra (comparison with the spectra of authentic preparations).

<u>Hydrolysis of the Aziridine Ib.</u> To a solution of 2.26 g (8.6 mmoles) of the aziridine Ib in 30 ml of acetic acid and 30 ml of acetic anhydride at 0°C, 8 ml of conc. H_2SO_4 was added dropwise with mixing, mixed for another 1 h, and poured out into 0.5 liters of water, then extracted with ether. The extract was washed with water and with a NaHCO₃ solution and dried with MgSO₄. The solvent was evaporated and 0.75 g of the anilide II1 mp 118-119°C (from ethanol); according to the data of [13] mp 117.5°C, and 0.59 g of the anilide IIk [mp 148-149°C (from ethanol); according to the data of [12], mp 146°C] were isolated from the residue by thin-layer chromatography.

Nitration of the Products of Hydrolysis of the Aziridine Ib. To a solution of 0.262 g (0.99 mole) of the aziridine Ib in 3.5 ml of acetic acid and 3.5 ml acetic anhydride, 0.9 ml of conc. H₂SO₄ was added with mixing, and after complete conversion of Ib (monitored by thin-layer chromatography), a solution of 0.3 g KNO₃ in 0.8 ml of conc. H₂SO₄ was added to the reaction mixture. After 15 min the mixture was treated as described for the nitration of Ib, and the anilides IIa-f were identified by the method of thin-layer chromatography.

<u>Nitration of the Anilide IIk in the Presence of HC1.</u> To a solution of 0.153 g (0.6 mmole) of the anilide IIk in 2 ml acetic acid and 2.4 ml acetic anhydride, 0.2 ml conc. HC1 was added, and then, while cooling with ice, a solution of 0.185 g (1.8 mmoles) KNO₃ in 0.6 ml of conc. H_2SO_4 was added with mixing, and mixed for another 30 min. After treatment analogous to that described for the nitration of the aziridine Ib, the anilides IIa (0.013 g, 7%), IIc (0.054 g, 30%), and IIe (0.049 g, 24%) were isolated by the method of thin-layer chromatography on SiO₂.

TABLE 2. Melting Points and Data of Elementary Analysis of Compounds Ic-f, IIc-i, and III

Com- pound	mp, °C	Found, %				Gross formula	Calculated, %			
		с	н	Hal	N	Gloss Iolinula	с	н	Hal	N
k Id Ie If Ic Id Ile Ilf Ilf Ilf Ilf	170—171 ^a 165—166 ^a 138—140 ^b 125—127 ^c 78—80 ^d 105—107 ^d 118—119 ^e 122—123 ^e 131—132 ^f 179—181 ^f 195—196 ^g 135—137 ^b	47,3 47,2 43,3 41,9 58,1 61,2 51,7 54,9 45,7 47,6 48,8 30,8	2,7 2,4 2,4 2,3 3,9 4,7 2,9 3,9 2,9 2,9 3,6 1,9	19,8 20,3 38,5 39,8 12,5 21,5 10,2 21,2 22,6 20,1 56,2	11,5 11,6 7,1 6,8 9,5 8,8 7,8 7,8 7,4 7,6 6,8 5,0	$\begin{array}{c} C_{14}H_9Cl_2N_3O_4\\ C_{14}H_9Cl_2N_3O_4\\ C_{14}H_9BrCl_2N_2O_2\\ C_{14}H_1BrCl_2N_2O_2\\ C_{14}H_{10}Br_2N_2O_3\\ C_{16}H_{14}N_2O_5\\ C_{14}H_{10}Cl_2N_2O_3\\ C_{16}H_{13}ClN_2O_5\\ C_{14}H_{10}BrClN_2O_3\\ C_{14}H_{10}BrN_2O_4\\ C_{16}H_{13}BrN_2O_5\\ C_{16}H_{13}BrN_2O_5\\ C_{16}H_{19}Br_3Cl_2N_2O_2\\ \end{array}$	47,5 47,5 43,3 42,2 57,8 61,1 51,7 55,1 45,5 47,9 48,9 30,7	2,6 2,3 2,5 3,8 4,5 3,1 3,8 2,7 3,2 3,3 1,7	20,0 20,0 38,9 40,2 12,2 21,8 10,2 21,6 22,8 20,3 56,7	11,9 11,9 7,2 7,0 9,6 8,9 8,6 8,0 7,6 8,0 7,1 5,1

^aFrom diethyl ether. ^bFrom dipropyl ether. ^cFrom a mixture of diethyl ether with hexane. ^dFrom hexane. ^eFrom a mixture of CCl₄ with hexane. ^fFrom a mixture of acetone with CCl₄. ^gFrom acetone.

Bromination of the Aziridine Ia in Aqueous Acetic Acid. To a solution of 2.47 g (8.0 mmoles) of the aziridine Ia in 100 ml of acetic acid and 25 ml of water, 1.28 g (8.0 mmoles) of bromine in 20 ml of acetic acid was added dropwise with mixing at room temperature over a period of 1 h 30 min and left overnight, then poured out into 200 ml of water, the precipitate removed, washed with water, dried, and 1.95 g (63%) of the aziridine Ie, 0.19 g (6.4%) of the anilide IIg, and 0.17 g (6.1%) of the anilide IIi were isolated by column chromatography on SiO₂.

Hydrolysis of the Aziridine Ie. A suspension of 0.1 g (0.25 mmole) of the aziridine Ie was boiled in 4 ml of water for 30 h, the precipitate removed, and 0.064 g (67%) of the anilide IIg and 0.017 g (19%) of the anilide IIh were isolated by thin-layer chromatography on SiO_2 .

Bromination of the Aziridine Ia in Anhydrous Acetic Acid. To a solution of 2.47 g (8.0 mmoles) of the aziridine Ia in 100 ml of glacial acetic acid and 10 ml of acetic anhydride, 1.28 g (8.0 mmoles) of bromine in 20 ml of acetic acid was added dropwise with mixing at room temperature over a period of 2 h; in this case a green color was observed, the intensity of which was decreased with time. After 12 h the reaction mixture was poured out into 0.5 liter of water, the precipitate removed, the filtrate extracted with a mixture of ether and hexane (5:1), the organic layer removed, washed with water, with a solution of NaHCO₃, and with water, dried with MgSO₄, the solvent evaporated under vacuum, the residue combined with the precipitate, and 1.72 g (64%) of the anilide IIj [mp 146-147°C (from a mixture of acetone-CCl₄) [14]] and 0.99 g (23%) of the amine III were isolated by column chromatography on SiO₂. The anilide IIj was also produced by countersynthesis — by hydrolysis of the aziridine If in boiling water for 24 h.

Reaction of the Amine III with t-BuOK. A mixture of 0.07 h (0.13 mmole) of the amine III and 0.072 g (0.64 mmole) t-BuOK in 20 ml t-BuOH was mixed for 24 h at ~20°C, diluted with water, and extracted with ether; after removal of the solvent the residue was recrystallized from aqueous ethanol. Yield of 2,4-dibromoaniline 0.025 g (78%) (mp 78°C; according to the data of [15], mp 79-90°C).

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INVESTIGATION OF METHODS FOR THE SYNTHESIS OF AZIRIDINES AND

AZIRINES ON THE BASIS OF ETHYL- β , β -BIS (TRIFLUOROMETHYL) ACRYLATE

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Various methods for the preparation of aziridines and azirines on the basis of ethyl β , β -bis(trifluoromethyl) acrylate were studied. Alkaline treatment of the products of addition of nucleophilic reagents to ethyl β , β -bis(trifluoromethyl) acrylate leads to the preparation of compounds of various classes that contain a hexafluoroisopropyl fragment.

In the present research we attempted to synthesize 2-carbalkoxy-3,3-bis(trifluoromethy1)aziridines and 2-carbalkoxy-3,3-bis(trifluoromethy1)azirines on the basis of ethy1 β , β -bis-(trifluoromethy1) acrylate.

It is known that nucleophilic reagents attack the α position of ester I [1], where N-(2-carboxyethyl)-N',N'-dialkylhydrazine derivatives form the corresponding aziridines upon treatment with bases [2].

The reaction of ester I with N,N-dimethylhydrazine leads to addition product II, which forms hydrazinium salt III; the latter was assumed to undergo cyclization under the influence of tert-BuOK. However, instead of the expected aziridine IV, we obtained a mixture of imine V and enamine VI, which was separated by preparative liquid chromatography (Tables 1-3).



A similar transformation is observed in an attempt to cyclize hydroxylamine O-mesitylensulfonate (VII), which we obtained from ester I and hydroxylamine:



Mixtures of the imine and enamine in a ratio of VI:V = 9:1 (according to PMR data) are obtained in both cases after precipitation of the resulting salts and evaporation. After

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