SYNTHESIS AND SOME PROPERTIES OF 1,3-DIARYL-2,2-DIBROMOAZIRIDINES

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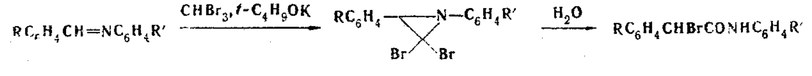
1,3-Aryl-2,2-dibromoaziridines have been synthesized and their hydrolytic cleavage in an aqueous medium has been performed.

The reaction of azomethines with dichlorocarbene is well known [1, 2], but the reaction of dibromocarbene with Schiff's bases has not been studied. We have established that the main direction of the reaction of aromatic Schiff's bases (I) with bromoform in the presence of potassium tert-butoxide is the formation of 1,3-diaryl-2,2-dibromoaziridines (II):


II

Apparently, the dibromocarbene formed by the reaction of the bromoform with the potassium tert-butoxide, as an electrophilic reagent, adds to the azomethine bond of compound (I) with the formation of the substituted aziridines (II) (Table 1). Schiff's bases with a high basicity react considerably more rapidly with dibromocarbene than azomethines with a lower basicity. Thus, while the reaction of p-methoxybenzylideneaniline (pK_a 11.16) with dibromocarbene takes place in from 2 h 30 min to 3 h, the reaction of benzylidene-m-nitroaniline (pK_a 7.88) with dibromocarbene is complete only after 8 h. Benzylidene-p-nitroaniline (pK_a 7.47) and p-nitrobenzylidene-p-nitroaniline (pK_a 6.08) are completely inert. Halogen-substituted Schiff's bases, such as p-chlorobenzylideneaniline (pK_a 9.10) and benzylidene-p-bromoaniline (pK_a 9.00) [3], the basicity of which is fairly high, also form the aziridines (II) very readily.

The structure of compounds (II) were confirmed by their conversion into α-aryl-α-bromoacetanilides (III) (Table 2).

TABLE 1. 1,3-Diaryl-2,2-dibromoaziridines (II)

R	R'	Mp, °C	Empirical formula	N, %		Yield, %
				found	calculated	
H	*p*-Cl	89—91	$C_{14}H_{10}Br_2ClN$	3,7; 3,8	3,6	55
H	*o*-Cl	111—112	$C_{14}H_{10}Br_2ClN$	3,6; 3,7	3,6	74
p-F	H	75—77	$C_{14}H_{10}Br_2FN$	3,7; 3,7	3,8	63
p-F	*p*-Cl	88—90	$C_{14}H_9Br_2ClFN$	3,5; 3,6	3,4	66
p-F	*p*-CH_3	74—75	$C_{15}H_{12}Br_2FN$	3,7; 3,8	3,6	73
o-F	*m*-Br	90	$C_{14}H_9Br_3FN$	2,9; 3,0	3,1	56
o-F	*p*-I	109—110	$C_{14}H_9Br_2FIN$	2,9; 3,0	2,8	54
p-Br	*m*-Cl	98—100	$C_{14}H_9Br_2ClN$	2,8; 2,9	3,0	63
p-Cl	*o*-Cl	102—104	$C_{14}H_9Br_2Cl_2N$	3,4; 3,4	3,3	69
p-I	*o*-Br	120—122	$C_{14}H_9Br_3IN$	2,4; 2,5	2,5	52
p-I	*o*-Cl	110—111	$C_{14}H_9Br_2ClIN$	2,8; 2,9	2,7	71
p-I	*m*-Br	121—123	$C_{14}H_9Br_3IN$	2,3; 2,4	2,5	60
p-Cl	H	96—98	$C_{14}H_{10}Br_2ClN$	3,5; 3,6	3,6	75
H	*m*-NO_2	117—119	$C_{14}H_{10}Br_2N_2O_2$	6,8; 6,9	7,0	67
p-OCH_3	H	97—98	$C_{15}H_{13}Br_2NO$	3,5; 3,6	3,6	61

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TABLE 2. α-Aryl-α-bromoacetanilides (III)

R	R'	Mp, °C	Empirical formula	N, %		Yield, %
				found	calculated	
H	*p*-Cl	154—156	$C_{14}H_{11}BrClNO$	4,4; 4,5	4,3	
p-F	H	137—139	$C_{14}H_{11}BrFNO$	4,6; 4,6	4,5	79
p-F	*p*-Cl	145—147	$C_{14}H_{10}BrClFNO$	4,1; 4,2	4,1	67
p-F	*p*-CH_3	162—163	$C_{15}H_{13}BrFNO$	4,2; 4,3	4,3	71
o-F	*p*-I	130—131	$C_{14}H_{10}BrFINO$	3,2; 3,3	3,2	73
H	*m*-NO_2	154—156	$C_{14}H_{11}BrN_2O_3$	8,3; 8,4	8,4	66
p-Br	*m*-Cl	151—153	$C_{14}H_{10}Br_2ClNO$	3,4; 3,5	3,5	80
p-I	*o*-Cl	141—142	$C_{14}H_{10}BrClINO$	3,2; 3,3	3,1	78
p-I	*o*-Br	152—154	$C_{14}H_{10}Br_2INO$	2,9; 3,0	2,8	82
p-I	*m*-Br	170—172	$C_{14}H_{10}Br_2INO$	2,8; 2,9	2,8	76

The PMR spectra of (II) have signals at 3.5-3.6 ppm (proton of a three-membered ring), and signals at 7.1-7.2 ppm (protons of benzene rings), which is in good agreement with information for substituted aziridines [4]. The IR spectra of the amides (III) have the bands of C=O stretching vibrations (1650-1648 cm^{-1}) and the band of NH stretching vibrations (3260 cm^{-1}) [5, 6].

EXPERIMENTAL

The PMR spectra were taken on a YaMR-5535 (40 MHz) spectrometer in CCl_4 with HMDS as internal standard. The IR spectra were taken in paraffin oil.

1,3-Diaryl-2,2-dibromoaziridines (II) (Table 1). With stirring and cooling in an atmosphere of nitrogen, 0.4 mole of bromoform was added dropwise over 1 h 30 min to a mixture of 0.01 mole of an azomethine (I), 0.04 mole of potassium tert-butoxide, and 40 ml of hexane. The mixture was stirred at 16-18°C for another 4-7 h. The hexane layer was filtered off and the solvent was partially distilled off. The precipitate that deposited was filtered off and was crystallized from hexane. The dibromoaziridines form colorless crystalline substances readily soluble in ethanol, ether, and dioxane. They are unstable at room temperature; thus, 2,2-dibromo-3-(p-methoxyphenyl)-1-phenylaziridine resinifies after 20-30 min, while 2,2-dibromo-1-(m-nitrophenyl)-3-phenylaziridine is stable for three days. The dibromoaziridines can be stored for several weeks in vacuum at 0°C.

α-Aryl-α-bromoacetanilides (III) (Table 2). An aziridine (II) (0.005 mole) was boiled in 20 ml of water until the oil formed had been converted into a crystalline mass. The reaction product was crystallized from ethanol.

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