SYNTHESIS OF 1,3-DIARYL-2,2-DICHLOROETHYLENEIMINES

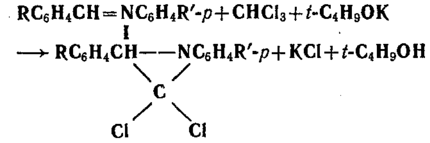
N. S. Kozlov, V. D. Pak,
and V. V. Mashevskii

UDC 547.574'71.07

1,3-Diaryl-2-dichloroethyleneimines were synthesized by the reaction of aromatic Schiff bases with chloroform in the presence of potassium tert-butoxide. Several properties of these compounds were studied.

Over a number of years we have made a systematic study of the reactivities of Schiff bases [1]. In the present paper, it seemed of interest to investigate the reaction of azomethines with chloroform in the presence of potassium tert-butoxide. According to the literature, this reaction has received very little study. Thus only benzylideneaniline [2], benzylidene-p-chloroaniline, and benzylidene-p-ethoxyaniline [3] have been introduced into the reaction with chloroform.

We have found that the major direction of the reaction of aromatic azomethines with chloroform in the presence of potassium tert-butoxide is the formation of 1,3-diaryl-2,2-dichloroethyleneimines (II), (Table 1).



II

A dichlorocarbine is apparently initially formed in the reaction of chloroform with potassium tert-butoxide, and the carbine then, as an electrophilic reagent, adds to azomethine I to form substituted aziridine II.

It was found that aliphatic-aromatic Schiff bases undergo complete resinification when they are introduced into the reaction [4]. The activity of I depends on the nature of the substituents in the benzene

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

R	R′	Mp, °C	Empirical formula	Found, %		Calc., %		Yield, %
				Cl	N	Cl	N	
H	H	97—98,5[2]	$C_{14}H_{11}Cl_2N$	27,1; 27,3	—	26,9	—	60
H	CH_3	55	$C_{15}H_{13}Cl_2N$	25,9; 26,1	5,2; 5,4	25,5	5,1	45
H	OCH_3	88—90	$C_{15}H_{13}Cl_2NO$	23,7; 23,7	4,6; 4,7	24,2	4,8	50
H	Cl	71—72[3]	$C_{14}H_{10}Cl_3N$	35,5; 35,6	—	35,7	—	68
H	Br	92—93	$C_{14}H_{10}BrCl_2N$	—	4,3; 4,3	—	4,1	49
p-Cl	H	83—85	$C_{14}H_{10}Cl_3N$	35,6; 35,7	4,9; 5,0	35,7	4,7	44
p-Br	H	76—78	$C_{14}H_{10}BrCl_2N$	—	4,3; 4,3	—	4,1	51
p-OCH_3	H	93—95	$C_{15}H_{13}Cl_2NO$	23,6; 23,9	5,0; 5,1	24,2	4,8	55
3,4-$(OCH_3)_2$	H	85—86	$C_{16}H_{15}Cl_2NO_2$	22,3; 22,3	4,3; 4,3	21,9	4,3	50
p-Cl	OCH_3	90—91	$C_{15}H_{12}Cl_3NO$	31,9; 32,0	4,1; 4,2	32,4	4,3	48
p-Cl	Cl	93—95	$C_{14}H_9Cl_4N$	42,8; 43,0	4,4; 4,5	42,6	4,2	46

D. N. Pryanishnikov Permsk Agricultural Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 180-181, February, 1972. Original article submitted February 12, 1971.

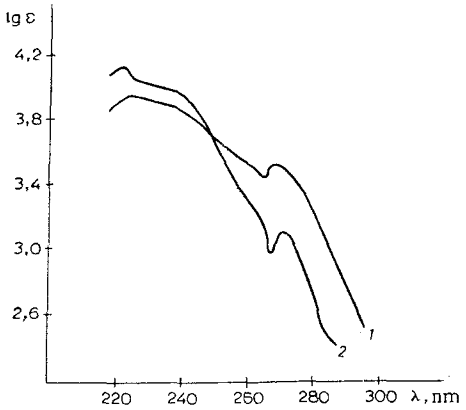
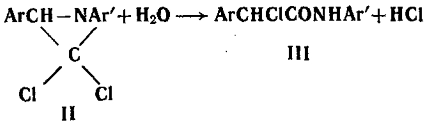


Fig. 1. UV spectra: 1) 1-phenyl-3-(p-methoxyphenyl)-2,2-dichloroethyleneimine; 2) 1-phenyl-3-(p-chlorophenyl)-2,2-dichloroethyleneimine.

ring in both the imine and aldehyde portions. Thus Schiff bases I with strong electron-acceptor substituents (NO_2, COOH, and $COOCH_3$) are passive, while electron-donor substituents (CH_3, OCH_3, and OC_2H_5) and halogens promote the formation of ethyleneimines II.

The structures of the compounds obtained were proved by spectral and chemical methods. The UV spectra of the 1,3-diaryl-2,2-dichloroaziridines have two absorption maxima at 222 and 270 nm (Fig. 1). These data are in good agreement with the spectra of diaryl-substituted three-membered heterocycles, for example, oxaziridines and epoxides [5].

The IR spectra of ethyleneimines II do not contain absorption bands corresponding to the vibrations of the C = N bond. The hydrolysis of reaction product II gives α-chloro-α-arylacetanilides III.



$$\underset{\text{II}}{\mathrm{ArCH{-}\underset{\underset{Cl\quad Cl}{C}}{}NAr'}} + H_2O \longrightarrow \underset{\text{III}}{\mathrm{ArCHClCONHAr'}} + HCl$$

EXPERIMENTAL

1,3-Diaryl-2,2-dichloroethyleneimines (II). A three-necked flask was charged with 0.1 mole of I, 0.4 mole of potassium tert-butoxide, and 25 ml of hexane. A total of 0.4 mole of chloroform was added dropwise with stirring and cooling under nitrogen, and the mixture was stirred at 16-18°C for 13 h. The hexane layer was separated by filtration. The solvent was partially removed by distillation. On standing in the cold, the mixture gave a precipitate, which was recrystallized from hexane. The dichloroaziridines (II) are colorless, crystalline substances that are quite soluble in alcohol, ether, dioxane, and hydrocarbons and unstable at room temperature. Hydrolysis of II ($Ar = Ar' = C_6H_5$) was carried out via the method in [2].

The UV spectra of 10^{-4} M solutions were measured with an SF-4A spectrophotometer at a layer thickness of 1 mm. Mineral oil pastes were used to obtain the IR spectra.

LITERATURE CITED

1. N. S. Kozlov, V. D. Pak, and N. A. Ivanov, Zh. Organ. Khim., 6, 1867 (1970).
2. E. Fields and I. Sandri, Chem. Ind., 1216 (1959).
3. A. Cook and E. Fields, J. Org. Chem., 27, 3686 (1962).
4. R. W. Layer, Chem. Rev., 63, 489 (1963).
5. E. Schmitz, Three-Membered Heterocycles with Two Heteroatoms [Russian translation], Mir, Moscow (1970), p. 61.