QUATERNARY SALTS OF SOME HETEROCYCLES CONTAINING NITROGEN

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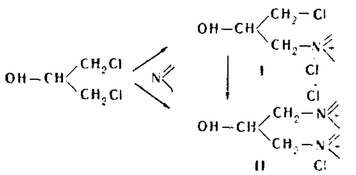
A series of mono- and biquaternary salts were synthesized from 1,3-dichloropropane-2-ol and the nitrogen-containing heterocycles quinoline, isoquinoline, quinaldine, pyridine, 2-picoline, and lepidine. The UV-spectra of the compounds obtained were investigated.

The molecule of glycerol dichlorohydrin (DCLG) contains two reactive halogens that are activated by the hydroxyl group. We may therefore assume that it is possible to synthesise two series of quaternary ammonium salts (I and III) from reactions of DCLG with heterocyclic bases containing nitrogen:



Special interest is attached to the monoderivatives I. As alkylating agents, they introduce quaternary ammonium groups into various compounds, some of high molecular weight, e.g., ionites [1], by means of the free chloromethyl group. The hydroxyl group attached to the alkyl residue participates at the same time in the formation of the macromolecular chain.

The production of quaternary salts from glycerol dichlorohydrin and heterocycles containing nitrogen has received little attention in the literature. There is a recent patent [2] that describes the preparation of betaines from similar salts, but which omits the separation stage of the quaternary salts.

An investigation of such salts is interesting insofar as it elucidates the chemical processes through which some ionites of AB-16 type are obtained (as is known, it has not been possible to separate individual products from the reactions of tertiary amines with epichlorohydrin [3]).

This paper discusses the conditions for preparing mono- and biquaternary salts of glycerol dichlorohydrin and some of their properties. The quaternary salts were prepared at 130°–140°; below 100° the reaction proceed very slowly. Glycerol dichlorohydrin and the bases are mutually soluble, so the reaction may be carried out with or without high-boiling solvents. Quaternary salts I and II are both colored and clear crystalline products (Table 1), soluble in polar solvents and often hygroscopic. The mono- and bis-compounds were obtained using a 2–4 fold excess in the ratio of glycerol to base of glycerol and base respectively. Upon completion of the

Table 1

Characteristics of the Quaternary Salts Obtained

Initial base	Type of compound	Mp, °C (solvent)	Color of crystals	Empirical formula	Found %				Calculated, %				Yield, %
					C	H	Cl′ (Cl)*	N	C	H	Cl′ (Cl)*	N	
Quinoline	I	218—220 (ethanol-ether)	Pink	$C_{12}H_{13}Cl_2NO$	55.85	5.07	(27.86)	5.55	56.00	5.07	(27.20)	5.43	88
	II	240—242 (ethanol)	Red	$C_{21}H_{20}Cl_2N_2O$	65.61	5.20	—	6.98	65.12	5.18	—	7.25	26
Quinaldine	I	235—237 (ethanol-petroleum ether)	Pink	$C_{13}H_{15}Cl_2NO$	—	—	13.20	5.13	—	—	13.10	5.17	29
	II	210—212 (decomp., chlorobenzol)	Pink	$C_{23}H_{24}Cl_2N_2O$	66.61	5.62	—	6.93	66.60	5.82	—	6.76	64
Isoquinoline	I	184—186 (ethanol)	Yellow	$C_{12}H_{13}Cl_2NO$	55.67	5.03	13.67	—	56.00	5.07	13.75	—	80
	II	118—120 (decomp., ethanol-ether)	Yellow	$C_{21}H_{20}Cl_2N_2O$	—	—	—	7.01	—	—	—	7.25	72
Lepidine	I	218—219 (ethanol)	Yellow	$C_{13}H_{15}Cl_2NO$	57.50	5.55	—	5.03	57.50	5.53	—	5.17	5
	II	166—167 (decomp., ethanol-ether)	Violet	$C_{23}H_{24}Cl_2N_2O$	—	—	(17.52)	6.93	—	—	(16.90)	6.76	12
Pyridine	I	94—96 (ethanol-petroleum ether)	Colorless	$C_8H_{11}Cl_2NO$	46.09	5.43	16.13	6.66	46.30	5.31	15.96	6.73	85
	II	210—212 (chlorobenzol)	Colorless	$C_{13}H_{16}Cl_2N_2O$	—	—	—	9.65	—	—	—	9.75	35
2-Picoline	I	171—172 (ethanol)	Greenish	$C_9H_{13}Cl_2NO$	48.64	5.81	—	6.54	48.90	5.89	—	6.34	50

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*Cl′—chlorine contents entering into the organic molecule; (Cl)—total chlorine contents of the quaternary salt.

Table 2

UV Spectra of the Bases and Their Mono- and Biquaternary Salts with Glycerol Dichlorohydrin

Compound*		250–270 nm band		270–320 nm band		Reference
		λ_{max}, nm	lg ε	λ_{max}, nm	lg ε	
Quinoline	b	276	3.59	300 313	3.13 3.41	4
	m	236	4.78	315	4.04	
	bis	238	5.04	315	4.08	
Quinaldine	b	273	3.54	300 320	3.00 3.08	4
	m	240	4.55	320	3.08	
	bis	234	4.72	310	4.17	
Isoquinoline	b	267	3.28	305 320	3.16 3.19	5
	m	234	4.73	330	3.79	
	bis	236	5.02	330	4.06	
Lepidine	b	263	3.48	300 313	2.90 2.93	
	m	235	3.60	315	3.08	
	bis	235	3.85	315	3.10	
Pyridine	b	251	2.37	256 262	2.61 2.60	4
	m	260	2.76	—	—	
	bis	260	3.04	—	—	
2-Picoline	b	256	2.32	262 269	2.59 2.60	
	m	224	3.73	—	—	

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*b–base: m–monosalt; bis–bis-salt.

reaction, the excess reactant was vacuumed off or removed by washing. The products were purified by recrystallization from dry solvents or by reprecipitation. The biquaternary isoquinoline salt was obtained by the previously described method from the corresponding monosalt.

Table 3

Ratios of the Extinction Coefficients for Mono- and Bis-Salts

Base	Salt*	Extinction coefficients	$\frac{\varepsilon_m^*}{\varepsilon_b}$
Quinoline	m	60 260	0.55
	bis	109 600	
Quinaldine	m	34 500	0.66
	bis	52 480	
Isoquinoline	m	53 700	0.52
	bis	104 700	
Pyridine	m	575	0.52
	bis	1 096	
Lepidine	m	3 981	0.56
	bis	7 100	

*m—monosalt; bis—bis-salt.

Table 2 presents UV spectra of the bases and their quaternary salts. As a rule, the spectra of the bases exhibit two absorption bands : one in the 250–270mμ region, probably due to $\pi \rightarrow \pi^*$ transitions; and a second in the 270–320 mμ interval, associated with the $p \rightarrow \pi^*$ transitions, which exhibits a fine vibratory structure.

During salt formation, the free electron pair of the nitrogen atom of the base participates in forming the C—N bond, and the nitrogen atom gains a positive charge. As a result, the fine vibratory structure disappears from the spectra of the salts, and the intensity of the 270–320 mμ band increases. In general, this band disappears from the pyridine spectrum. The free electron pair acts as a supplementary chromophore. The disappearance of this electron pair from the quaternary salts produces an appreciable hypsochromic effect at the 250–270 mμ band, thus increasing its intensity.

Biquaternary salts exhibit a more intensive absorption than the corresponding monocompounds. The ratio of the extinction coefficients for the mono- and bis-salts (Table 3) shows that the introduction of a second chromophore leads to an almost additive increase in intensity, and also that there is insignificant electronic interaction between the two nuclear chromophores.

EXPERIMENTAL

N-(2-hydroxy-3-chloropropyl)quinoline hydrochloride. Heat to 145° 31.1 g (0.33 mole) of glycerol dichlorohydrin and add 38.7 g (0.3 mole) of quinoline drop by drop in the course of one hour. After adding all the quinoline, heat the reaction mixture for an additional half hour at 145°, cool and add 50–70 ml of ethanol. Then slowly add ether. Filter off the purple colored precipitate, and wash it on the filter with ether. Weight 40.9 g (88%) mp 218–220° (pink platelets) after recrystallization from a mixture of benzene and ethanol.

The remaining compounds are obtained in a similar way.

The UV-spectra were recorded in ethanolic solutions at concentrations 10^{-3} M on an SF-4 apparatus.

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