DUAL TYPE OF REACTIVITY OF 1,2-DISUBSTITUTED DIHYDRO-N-HETEROAROMATIC SYSTEMS.

11.* AROMATIZATION OF N-SULFONYL-1,2-DIHYDROQUINOLINES AND ISOQUINOLINES CONTAINING AN α-INDOLYL OR PYRROLYL SUBSTITUENT

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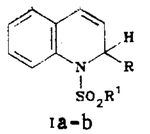
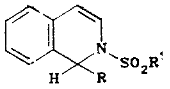
When N-sulfonyl-1,2-dihydroquinolines and isoquinolines, containing an indolyl or pyrrolyl substituent at the α-position, react with trityl perchlorate, this substituent is split off, and N-sulfonyl quinolinium and isoquinolinium cations and tritylindole or tritylpyrrole are formed. A similar reaction with 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate proceeds with splitting of hydrogen or retention of the α-substituent, which leads to the corresponding α-substituted N-sulfonylquinolinium and isoquinolinium cations.

N-Alkyl(acyl)-α-substituted dihydroheteroaromatic compounds have dual activity [2, 3], as their aromatization proceeds with loss or retention of the α-substituent, depending on the ratio between the oxidizing and electrophilic power of the aromatizing agent. Stronger oxidizing agents with weaker electrophilic properties, for example, 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate, split a hydride ion according to a SET mechanism [4], while triphenylmethylcarbenium perchlorate with stronger electrophilic properties and lower oxidizing power splits off α-substituents. This regularity is usually observed when the substituents are different CH-acids or indole. When these split off, aniono-stabilized particles are formed [3, 5].


Ia-b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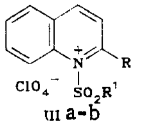
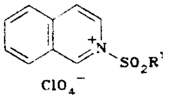
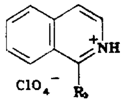

III a-b

;


IV a-j

; Ph_3CR ;

Va-c


VI

I a,b, II c,d, IV i,j, Va, VI R = 3-indolyl; II a,b, V b, IV e,g R = 1-methyl-2-pyrrolyl; II e, IV h, V c R = 1-methyl-3-indolyl; III a,b, IV a-e R = H; I a, II a, IV a,f R = β-naphthyl; I b, II b, IV b,g R = p-$C_6H_5NO_2$; II c, IV c,i R = C_3H_7; II d, IV d,j R = C_6H_{11}; II e, IV e R = C_6H_5.

In the present work, we studied the action of these reagents on N-sulfonyl derivatives, containing α-indolyl and pyrrolyl substituents. The characteristic feature of these compounds is the presence of sulfonyl residues at the nitrogen hetero atom, with electronic properties different from those of the acyl residues. This should cause a change in their activity in both aromatization with splitting of the substituent, and in dehydroaromatization. However, the pyrrole residue is a more mobile leaving group than indole, since pyrrole is a stronger CH-acid, and it can therefore be assumed that in all cases splitting of a substituent, and not dehydroaromatization, will take place.

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*For Part 10, see [1].

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TABLE 1. Physicochemical Characteristics of Salts IIIa,n, IVa-h

Compound	mp, °C (CH_3CN)	IR spectrum, cm^{-1}			Found, %				Empirical formula	Calculated, %				Yield, %
		$\nu_{as(SO_2)}$	$\nu_{s(SO_2)}$	ν_{ClO_4}	C	H	N	S		C	H	N	S	
IIIa	.126—127	1395, 1380	1160	1095	54,1	3,5	3,5	7,7	$C_{19}H_{14}ClNO_6S$	54,4	3,3	3,3	7,6	50
IIIb	123—124	1395, 1375	1145	1095	43,0	2,6	6,8	7,8	$C_{15}H_{11}ClN_2O_8S$	43,4	2,7	6,8	7,7	55
IVa	173—174*	1395, 1370	1160	1100	54,4	3,3	3,2	7,7	$C_{19}H_{14}ClNO_6S$	54,4	3,3	3,3	7,6	52
IVb	166—167*	1395, 1370	1140	1100	43,2	2,6	6,8	7,7	$C_{15}H_{11}ClN_2O_8S$	43,4	2,7	6,8	7,7	55
IVc	149—150	1395, 1370	1150	1100	43,0	4,5	4,0	9,5	$C_{12}H_{14}ClNO_6S$	42,9	4,2	4,2	9,5	50
IVd	158—160	1395, 1380	1190	1095	48,0	4,9	3,5	8,6	$C_{15}H_{18}ClNO_6S$	47,9	4,8	3,7	8,5	89
IVe	172—174**	1390, 1365	1130	1100	48,7	3,5	3,9	9,0	$C_{15}H_{12}ClNO_6S$	48,7	3,3	3,8	8,7	67
IVf	151—152	1370, 1350	1170	1095	57,4	3,8	5,9	6,0	$C_{24}H_{19}ClN_2O_6S$	57,8	3,8	5,6	6,4	92
IVg	161—162	1380, 1350	1170	1095	48,9	3,7	8,5	6,8	$C_{20}H_{16}ClN_3O_8S$	48,6	3,2	8,5	6,5	64
IVh	198—199	1380, 1360	1170	1100	57,5	4,0	5,6	6,7	$C_{24}H_{19}ClN_2O_6S$	57,8	3,8	5,6	6,4	85

*Triphenyl(1-methyl-2-pyrrolyl)methane was isolated from the reaction mixture in a yield of 100%, mp 213-214°C (from butanol). Found, %: C 89.0, H 6.6, N 4.4. $C_{24}H_{21}N$. Calculated, %: C 89.2, H 6.5, N 4.3.

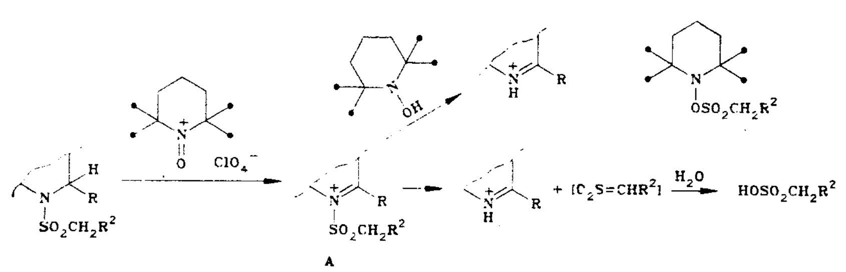
**Triphenyl(1-methyl-3-indolyl)methane was isolated from the reaction mixture in a yield of 98%, mp 183-185°C [6].

In fact, dihydrobenzopyridines Ia,b, IIa-e are readily aromatized by trityl perchlorate with splitting of a substituent and formation of sulfonyl salts IIIa,b and IVa-e. The corresponding triphenyl-R-methanes (Va-c) were isolated from the reaction mixture in yields up to 100% and sulfonyl salts in yields varying from 50 to 90%. The sulfonyl salts IIIa,b, IVa-e obtained are stable.

In the IR spectra of salts IIIa,b, IVa-e, absorption bands are observed due to the stretching vibrations of the sulfonyl group $\nu_{as}(SO_2)$ 1365-1380 and 1390-1395, $\nu_s(SO_2)$ 1140-1160, of the double bonds $\nu_{C=C}$ 1620-1650 and 1595-1605, and of the perchlorate anion ν_{ClO_4} 1100-1095 cm^{-1}.

In the reactions of dihydrobenzopyridines I, II with 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate, we obtained salts IVe-h, in which the pyrrole and indole substituents were retained. However, in some cases, the sulfonyl substituent is split off, for example in the formation of salt VI. In the IR spectra of salts IVf-h, there are absorption bands due to the stretching vibrations of the sulfonyl group: $\nu_{as}(SO_2)$ 1340-1360 and 1370-1380 and $\nu_s(SO_2)$ 1165-1170 cm^{-1}. Splitting of the sulfonyl band is observed for all the salts.

Aromatization of the sulfonyl dihydro derivatives IIc,d, containing an active α-methylene grouping in the sulfonyl substituent, proceeds somewhat differently. In these cases a mixture of sulfonyl derivatives (IVi,j) and hydroperchlorates (VI) is formed, and irrespective of the ratio of the oxoammonium salt and dihydrobenzopyridine (1:1-3:2), a mixture of salts is formed with a preferential hydroperchlorate content. According to the data of elemental analysis, the ratio of salts IVi,j and VI is 2:3.



Due to the presence of two types of salts in the reaction mixture, we can assume the following scheme for the reaction with the oxoammonium salt.

First, dehydroaromatization takes place with loss of a hydride ion, probably by the SET-mechanism [4] with the formation of sulfonyl salts (A) and hydroxopiperidine. There follows partial dissociation of these salts with the formation of sulfenes and migration of a proton, or sulfonylation of hydroxopiperidine.

EXPERIMENTAL

The IR spectra were run on a Specord IR-75 spectrophotometer in KBr tablets.

N-β-Naphthylsulfonylquinolinium Perchlorate (IIIa). N-β-Naphthylsulfonyl-2-(3-indolyl)-1,2-dihydroquinoline (Ia) (0.22 g, 0.5 mmole) is added at 20°C in portions to a solution of 0.17 g (0.5 mmole) of triphenylmethyl perchlorate in 5 ml of dry acetonitrile. After the reaction has been completed (1 h), 50 ml of dry ether are added to the reaction mixture, the salt that separates is filtered and recrystallized from acetonitrile. Yield, 0.11 g (50%).

After separation of salt IIIa, the filtrate is evaporated, the residue is washed with 5 ml of methanol and recrystallized from butanol. The yield is 0.13 g (70%) of triphenyl(3-indolyl)methane (Va), mp 209-210°C [7].

Salts IIIb, IVa-e, whose principal characteristics are given in Table 1, were obtained in a similar way.

N-β-Naphthylsulfonyl-1-(1-methyl-2-pyrrolyl)isoquinolinium Perchlorate (IVf). N-β-Naphthylsulfonyl-1-(1-methyl-2-pyrrolyl)-1,2-dihydroisoquinoline (IIa) (0.2 g, 0.5 mmole) is added in portions in the course of 10 min to a solution of 0.13 g (0.5 mmole) of 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate in 5 ml of dry acetonitrile. The reaction mixture is held for 2 h at 20°C and 50 ml of dry ether are added. The salt that separates is filtered and recrystallized from acetonitrile. Yield, 0.23 g (92%).

Salts IVg,h were obtained in a similar way (Table 1).

In the aromatization of compounds IIc,d by the oxoammonium salt, mixtures of salts IVi and VI, IVj and VI, respectively were obtained, which could not be separated.

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