OXIDATIVE ELIMINATION OF PHENYL GROUP FROM α POSITION OF QUATERNARY QUINOLINIUM SALTS

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Action of alkaline solution of potassium ferricyanide on the quaternary quinolinium salts *IIIa* to *IIIc* results in splitting off of 2-phenyl substituent and formation of the quinolones *IVa*–*IVc*. A possible mechanism of this transformation is discussed.

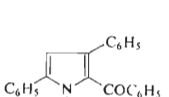
In our recent communications[1,2] we have shown that oxidation of quaternary 2,4,6-triphenylpyridinium salts with alkaline solution of potassium ferricyanide gives high yields of pyrrole derivatives type *I*. On the contrary, quaternary 2,3,4,5,6-pentaphenylpyridinium salts gave[3] tetraphenylpyrroles *II* under the same conditions. It was interesting to find whether also the quinolinium salts *IIIa*–*IIIc* would undergo a ring contraction to give indole derivatives. The results obtained are dealt with in the present communication.

The starting quinolinium salts *IIIa*–*IIIc* were prepared by quaternization of the respective bases with triethyloxonium tetrafluoroborate. The products of their ferricyanide oxidation were isolated by crystallization and preparative column chromatography and identified by spectral methods (Table I).

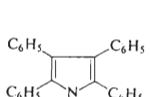
From the reaction mixture after oxidation of the salts *IIIa*–*IIIc* we could isolated high yields of the 2-quinolone derivatives *IVa*–*IVc*. On the contrary, we could not isolate the indole derivatives expected on the basis of the above-mentioned findings on oxidation of pyridinium salts. Hence, it can be concluded that the contraction of heteroaromatic ring does not take place due to steric and electronic effects of the adjacent benzene ring. In our previous communication[4], however, we observed a smooth formation of pyridone *V* in ferricyanide oxidation of the salt *VI*.

The ferricyanide oxidation is supposed[5] to be initiated by addition of OH^- ion to α position of the quaternary cation. According to the mechanism given in Scheme 1 it is possible to consider oxidation of the tautomeric forms *VIII* and *IX* of the 1,2-dihydroderivative *VII* formed by addition of OH^- ion. In the semi-quinone structures *VIII* and *IX* the bond between the heterocycle and the original 2-phenyl substituent can be expected to be destabilized towards alkaline oxidation medium. Thus the

oxidation of *VIII* and *IX* should produce, besides the isolated quinolone *IVa*, also 1,2- and 1,4-benzoquinones, respectively, which, however, undergo further transformations due to their instability to alkaline oxidation medium[6].



I



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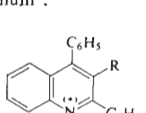
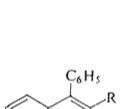
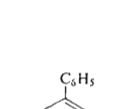


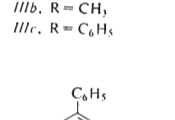
IIIa, R = H
IIIb, R = CH_3
IIIc, R = C_6H_5



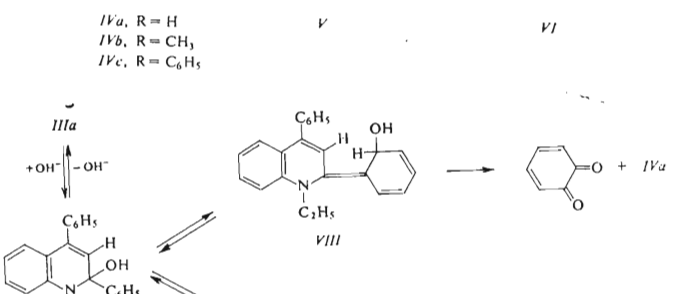
IVa, R = H
IVb, R = CH_3
IVc, R = C_6H_5



V



VI



VII

VIII

IX

The results given in the present and the previous[4] communications show that the known method[5] of preparation of pyridones and quinolones by ferricyanide oxidation of quaternary salts with non-substituted α positions can be extended, in the cases

TABLE I
Properties of the compounds prepared

Compound	M.p., °C yield, %	Formula (mol.mass)	Calculated/Found %C	 % H	 % N	ν(C=O), cm^{-1}	δ ppm, 100 MHz
IIIa	160—162 62	$C_{23}H_{20}BF_4N$ (397·2)	69·55 69·59	5·07 5·11	3·53 3·52	—	1·56 t (CH_3), 4·95 q (CH_2), 7·5—8·6 m (15 H)
IIIb	187—189 80	$C_{24}H_{22}BF_4N$ (411·2)	70·96 70·83	5·39 5·21	3·41 3·14	—	1·50 t (CH_3), 1·90 s (CH_3), 4·80 q (CH_2), 7·3—8·5 m (14 H)
IIIc	257—258 82	$C_{29}H_{24}BF_4N$ (473·3)	73·59 73·58	5·11 4·94	2·96 2·97	—	1·63 t (CH_3), 4·92 q (CH_2), 6·8—8·6 m (19 H)
IVa	— 82	$C_{17}H_{15}NO$ (249·1)	249·1154[a] 249·1149[b]		— —	1 650	1·41 t (CH_3), 4·40 q (CH_2), 6·64 s (1 H), 7·0—7·7 m (9 H)
IVb	107—109 81	$C_{18}H_{17}NO$ (263·1)	263·1310[a] 263·1329[b]		— —	1 630	1·41 t (CH_3), 2·00 s (CH_3) 4·40 q (CH), 7·0—7·7 m (9 H)
IVc	161—163 87	$C_{23}H_{19}NO$ (325·1)	324·1388[a,c] 324·1390[b,c]		— —	1 630	1·46 t (CH_3), 4·46 q (CH_2), 6·8—7·6 m (14 H)

[a] The found *m/e* value of the molecular ion; [b] the relative molecular mass calculated for the respective molecular formula; [c] the values for the ion $M^+ - 1$.

of suitably chosen derivatives, also to the quaternary salts with substituted α positions. As far as we know, the splitting off of phenyl substituent in the ferricyanide oxidation of quaternary salts has not yet been observed.

EXPERIMENTAL

The temperature data are not corrected. The ^{1}H NMR spectra were measured with a Varian XL-100 apparatus in deuteriochloroform against tetramethylsilane. The IR spectra were measured with a Perkin–Elmer 325 spectrometer in chloroform. The mass spectra were measured with an AEI MS 902 apparatus at 70 eV.

1-*Ethyl*-2,4-*diphenylquinolinium tetrafluoroborate* (IIIa): 20·0 g triethyloxonium tetrafluoroborate[2] in 50 ml dichloromethane was treated with solution of 8·0 g 2,4-diphenylquinoline[8] in 30 ml dichloromethane. After 7 h boiling and standing overnight, 30 ml methanol was added, the solvents were evaporated in vacuum, and the residue was dissolved in 200 ml chloroform. The solution was washed with water, the solvent was evaporated in vacuum, and the residue was recrystallized from ethanol to give compound *IIIa*.

1-*Ethyl*-2,4-*diphenyl*-3-*methylquinolinium tetrafluoroborate* (IIIb): The starting 2,4-diphenyl--3-methylquinoline[9] was quaternized in the same way as the compound *IIIa*.

1-*Ethyl*-2,3,4-*triphenylquinolinium tetrafluoroborate* (IIIc): The starting 2,3,4-triphenylquinoline[9] was quaternized in the same way as compound *IIIa*.

Oxidation of IIIa: Solution of 3·0 g salt *IIIa* in 180 ml ethanol was boiled and treated with solution of 6·0 g potassium ferricyanide and 3·0 g potassium hydroxide in 60 ml water. After 2 h boiling and stirring, the mixture was diluted with 1 l water and extracted with 3 × 100 ml chloroform. Chloroform was evaporated, and the residue was submitted to column chromatography (silica gel, chloroform) to give oily quinolone *IVa*.

Oxidation of IIIb: The same procedure as in oxidation of *IIIa* gave the quinolone *IVb* from 2·0 g salt *IIIb*, 4·0 g potassium ferricyanide, and 2·0 g potassium hydroxide with subsequent chromatographic separation and crystallization from methanol.

Oxidation of IIIc: In the same way as the compound *IIIa*, the salt *IIIc* (2·5 g) was oxidized with 5·0 g potassium ferricyanide and 2·5 g potassium hydroxide. Evaporation of the chloroform extract and crystallization from methanol gave the quinoline *IVc*.

Mass spectra, m/e (% r.i.): *IVa*: 249 (83), 248 (72), 222 (28), 221 (100), 220 (42), 205 (39), 193 (33), 178 (20), 165 (42), 77 (19). *IVb*: 263 (86), 262 (100), 235 (14), 234 (52), 218 (10), 217 (7), 216 (12), 203 (7). *IVc*: 325 (70), 324 (100), 297 (12), 296 (42), 280 (16), 278 (18).

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