FORMYLATION AND VINYLFORMYLATION OF 2,3-CYCLOALKENOBENZOPYRYLIUM SALTS

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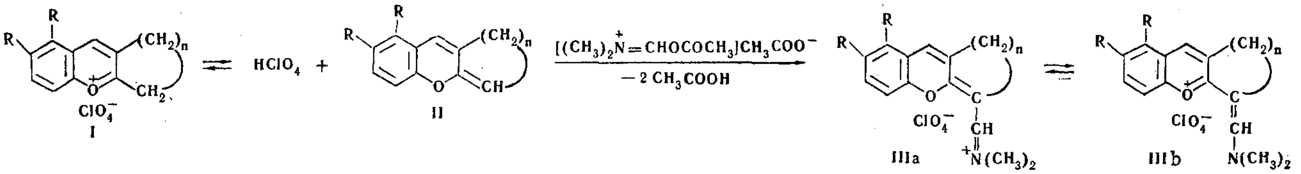
Heating of 2,3-cycloalkenobenzopyrylium salts in acetic anhydride with excess formylating agent (dimethylformamide, formanilide, N-formylmorpholine, and N-phenyl-N-methylaminoacrolein) gives monoiminium salts, the hydrolysis of which yields aldehydes or, in the presence of hydrosulfide, thioaldehydes. On treatment with the Vilsmeier complex, 1-methylquinaldinium salts give diiminium salts, which are hydrolyzed to the corresponding aldehydes.

Among the diverse ramifications of the Vilsmeier reaction [1], an important place belongs to reactions involving the formylation of compounds with active methylene groups [2]. Recently it was possible to also extend the reaction to compounds with strongly activated methyl or methylene groups within the heterocyclic or carbocyclic cation [3,4]. The diformylation of 2,4,6-trinitrotoluene is a reaction of this sort [5].

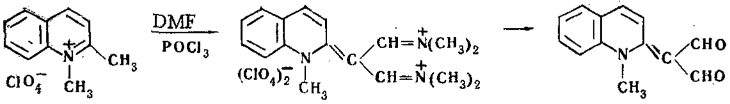
In this paper we report the possibility of the introduction of an aminomethylene grouping and its vinylogs into the α-methylene group of 2,3-cycloalkenobenzopyrylium salts (I) under mild conditions with subsequent hydrolysis of the monoiminium salts to aldehydes.* The aminomethylation proceeds with rather high yields during brief heating of the pyrylium salt with excess dimethylformamide (DMF) in acetic anhydride (compare with [3]).

The necessary intermediate is probably cyclomethine base II:



The participation of II in the reaction is indirectly confirmed by the known ability of methylene bases and olefins to be acylated at the methylene group [1,6].

Attempts to monoformylate nitrogen heterocycles with activated methyl groups (quaternary lepidine and quinaldine salts) did not give the expected results which, in accordance with the reaction scheme presented, may be explained by the lower (than that of I) acidity of the nitrogen quaternary salts and the low equilibrium concentration of base II. However, we were able to diformylate a quinaldine salt under the conditions of the Vilsmeier reaction



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*In the course of this investigation there appeared a communication [4] by Reynolds and Van Allan, who accomplished the mono- and diformylation of α- and γ-methyl-substituted diphenylpyrylium and benzopyrylium salts under similar conditions.

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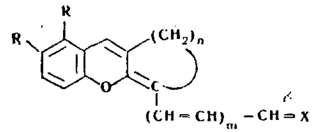
TABLE 1. Products of the Formylation of 2,3-Cycloalkenobenzopyrylium Salts



R	n	m	X	mp, °C	Empirical formula	Found %				Calculated %				Yield, %
						C	H	N	Cl	C	H	N	Cl	
H	3	0	$(CH_3)_2\overset{+}{N}\ ClO_4^-$	244—245	$C_{16}H_{18}ClNO_5$	56,7	5,2	4,0	10,9	56,5	5,3	4,1	10,6	55
H	3	0	$\underline{\overset{+}{N}(CH_2)_2O(CH_2)_2}\ ClO_4^-$	248—249	$C_{18}H_{20}ClNO_6$	56,6	5,2	3,7	9,3	56,5	5,2	3,7	9,4	50
C_4H_4	3	0	$(CH_3)_2\overset{+}{N}\ ClO_4^-$	265—266	$C_{20}H_{20}ClNO_5$	61,7	5,1	3,7	9,2	61,5	5,1	3,6	9,2	40
C_4H_4	3	0	O	179—180	$C_{18}H_{14}O_2$	82,5	5,3	—	—	82,4	5,3	—	—	35
C_4H_4	3	1	$C_6H_5\overset{+}{N}CH_3\ ClO_4^-$	223—224	$C_{27}H_{24}ClNO_5$	67,7	4,9	3,1	7,4	67,7	5,0	2,9	7,5	35
C_4H_4	3	1	O	133—134	$C_{20}H_{16}O_2$	83,5	5,4	—	—	83,3	5,6	—	—	36
H	4	0	$(CH_3)_2\overset{+}{N}\ ClO_4^-$	159—160 (разл.)	$C_{17}H_{20}ClNO_5$	57,4	5,5	4,0	10,3	57,6	5,7	4,0	10,2	60
H	4	0	$C_6H_5N(CH_3)N$	99—100	$C_{22}H_{22}N_2O$	80,1	6,7	8,7	—	80,0	6,7	8,5	—	—
H	4	0	$C_6H_5\overset{+}{N}H\ ClO_4^-$	209—210	$C_{21}H_{20}ClNO_5$	62,6	4,8	3,6	9,0	62,7	5,0	3,5	9,0	70
H	4	0	$\underline{\overset{+}{N}(CH_2)_2O(CH_2)_2}\ ClO_4^-$	235—236	$C_{19}H_{22}ClNO_6$	57,7	5,5	3,6	9,0	57,5	5,6	3,5	9,1	65
H	4	1	$C_6H_5\overset{+}{N}CH_3\ ClO_4^-$	207—208	$C_{24}H_{24}ClNO_5$	65,2	5,5	3,2	8,2	65,1	5,4	3,2	8,1	40
H	4	1	O	110—111	$C_{17}H_{16}O_2$	80,0	6,4	—	—	80,9	6,4	—	—	60
C_4H_4	4	1	$C_6H_5\overset{+}{N}CH_3\ ClO_4^-$	223—224	$C_{28}H_{26}ClNO_5$	68,4	5,4	3,0	7,4	68,3	5,3	2,8	7,3	45
C_4H_4	4	1	O	128—130	$C_{21}H_{18}O_2$	83,3	5,9	—	—	83,4	6,0	—	—	60
C_4H_4	4	0	$(CH_3)_2\overset{+}{N}\ ClO_4^-$	233—234	$C_{21}H_{22}ClNO_5$	62,2	5,6	3,5	9,1	62,4	5,5	3,5	8,9	75
C_4H_4	4	0	O	154—155	$C_{19}H_{16}O_2$	82,4	6,0	—	—	82,5	5,8	—	—	80
C_4H_4	4	0	S	251—252	$C_{19}H_{16}OS$*	78,1	5,6	—	—	78,0	5,5	—	—	70
C_4H_4	4	0	$\overset{+}{O}CH_3\ ClO_4^-$	174—175	$C_{20}H_{19}ClO_6$	61,6	4,9	—	9,2	61,5	4,9	—	9,1	65
C_4H_4	3	0	$\overset{+}{O}CH_3\ ClO_4^-$	202—203	$C_{19}H_{17}ClO_6$	60,8	4,9	—	9,4	60,7	5,1	—	9,3	80

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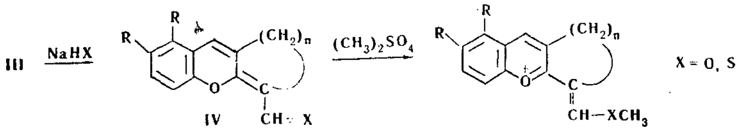
* Found %: S 11.0. Calculated %: S 10.9.

Iminium salts III are hydrolyzed to aldehydes IV, the carbonyl groups of which are strongly polarized and readily alkylated by means of dimethyl sulfate. The hydrolysis of salts III in the presence of sodium hydrosulfide leads to thioaldehydes.



Vinylogs of iminium salts of the III type and aldehydes of the IV type are obtained when N-phenyl-N-methylaminoacrolein – an analog of DMF – is used.

EXPERIMENTAL

The starting pyrylium salts were obtained by the methods in [7, 8].

Iminium Salts of the III Type (Table 1). These were obtained by heating a mixture of 0.01 mole of the appropriate pyrylium salt with a large excess of formylating agent at 100° for 5-10 min. The mixture was cooled and diluted with ether until complete precipitation of the salt, which was crystallized from acetic acid.

2-(2,6-Dimethyl-2,6-diaza-2,4-heptadienyl)quinaldinium Diperchlorate. A mixture of 0.006 mole of α-methylquinaldine perchlorate, 0.02 mole of $POCl_3$, and 0.11 mole of DMF was prepared at room temperature and heated at 90° (bath temperature) for 6 h. The reaction mass was cooled, and 40 g of ice was added. The resulting precipitate was filtered, treated with 20 ml of 52% $HClO_4$, and allowed to stand overnight. The mixture was then filtered, and the solid was washed with 50% aqueous alcohol to give 47% of a product with mp 268-270° (from nitroethane). Found %: C 44.9; H 5.1; Cl 16.0; N 6.3. $C_{17}H_{23}Cl_2N_3O_8$. Calculated %: C 44.8; H 5.0; Cl 15.8; N 6.2.

Hydrolysis of this salt with excess 2 N NaOH gave 35% of a dialdehyde with mp 199-200° (from acetonitrile). Found %: C 73.2; H 5.2; N 6.7. $C_{13}H_{11}NO_2$. Calculated %: C 73.2; H 5.2; N 6.6.

Hydrolysis of the Iminium Salts. This was accomplished in acetonitrile with excess 2 N NaOH (or 10% NaHS at pH 9). The mixture was stirred at room temperature for about 1.5 h, diluted with water, extracted with benzene (two 50-ml portions), and dried with K_2CO_3. The extract was evaporated until vigorous crystallization commenced. The precipitate was recrystallized from propanol (Table 1).

Methoxymethylene Derivatives of the Pyrylium Salts. These were obtained by heating a mixture of an aldehyde of the IV type with a twofold excess of dimethyl sulfate in dry benzene for about 1.5 h and allowing the mixture to stand for 2-3 days. The mixture was then filtered, and the solid was washed with ether, dissolved in acetic acid, and a twofold excess of 72% $HClO_4$ was added. During the night, the perchlorate precipitated and was crystallized from acetic acid (see Table 1).

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