EXPERIMENTAL

The mass spectra were measured on an MKh-1303 spectrometer, modified for chemical ionization studies [8], with direct insertion of the sample into the ion source. The energy of the ionizing electrons was 400 eV, and the potential of the ejection electrode was 6 V relative to the ionization chamber, which corresponds to a field strength of 18.5 V/cm; the temperature of the ion source was 100°C, and that of the admission system was 25°; the reagent gas was isobutane, and the pressure was 0.3 torr. The samples were chromatographically pure.

CONCLUSIONS

1. The cleavage of the second and third molecules of CH_3OH from β-methyl-2,3,4,6-tetra-O-methyl-D-galactopyranoside under chemical ionization conditions occurs predominantly as the result of 1,2-elimination.

2. The formation of the fragments $[M + H - 2CH_3OH]^+$ is accompanied by the cleavage of H from C^2 (by 84%), while the formation of the ions $[M + H - 3CH_3OH]^+$ is accompanied by the cleavage of H from C^2 and C^5 (respectively by 86 and 90%).

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REACTION OF BIS(β-AMINOETHYLATO)ETHANOLAMINEAQUOCHROMIUM CHLORIDE $[(NH_2CH_2CH_2O)_2Cr \cdot (NH_2CH_2CH_2OH) \cdot H_2O]Cl$ WITH ALDEHYDES

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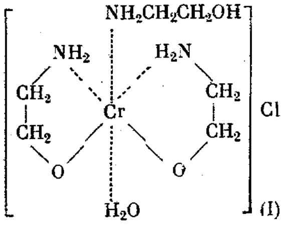
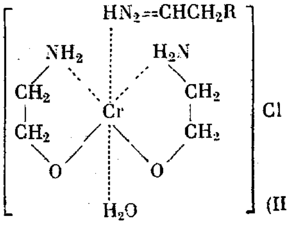
UDC 541.49:547.435:546.76'131:547.28

The complex $[(NH_2CH_2CH_2O)_2Cr \cdot (NH_2CH_2CH_2OH) \cdot H_2O]Cl$ (I) contains (I) in the inner sphere of the ethanolamine (EA) molecule, which is attached to the Cr^{3+} ion via the unshared pair of the NH_2 group [1].

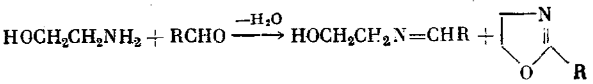


(I)



(II)

The reaction of (I) with aliphatic and aromatic aldehydes was studied in the present paper. It is known that amino compounds readily form azomethines N=CHR with RCHO, while EA gives an equivalent mixture of the azomethine and oxazoline.



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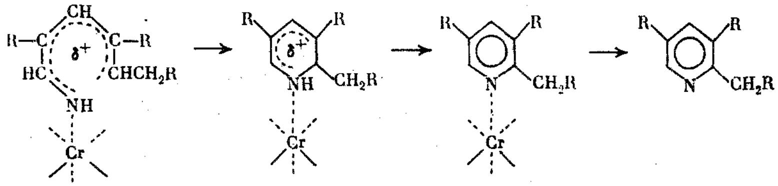
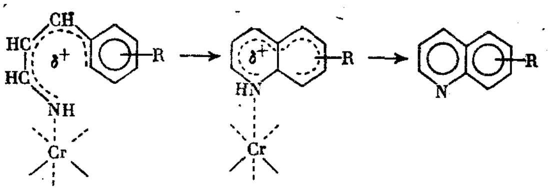
0568-5230/78/2705-1050$07.50

It was found that when (I) is reacted with aldehydes the EA contained in the complex actively condense with RCH_2CHO, but not as actively as the free EA molecule. The addition of an equimolar (relative to EA) amount of the aldehyde to (I) gave new complexes of composition $[(NH_2CH_2CH_2O)_2Cr \cdot (NH{=}CHCH_2R) \cdot H_2O]Cl$ (II). The same complexes are formed when (I) is treated with a large excess of the aldehyde. Only when (II) is stored (20°C, > 10 h) does the amount of carbon in the complexes gradually increase, while the amount of the metal decreases. As a result, the reaction of (I) with an aldehyde has two characteristics: Only one of the three NH_2 groups present in (I) enters into the reaction, while the formation of the azomethine is accompanied by the elimination of the 2-hydroxyethyl group as acetaldehyde (GLC data). Due to the coordination $C = \overset{+}{N}H \rightarrow Cr$ the protons adjacent to the methylene group of the imine $RCH_2CH{=}NH$ have a high lability and the imine molecule enters with unusual ease into the crotonic type of condensation with the excess aldehyde present in the mixture. Here, from compound (II) are evidently formed in succession $[(NH_2CH_2CH_2O)_2Cr \cdot (NH = CHCR = CHCH_2R) \cdot H_2O]Cl$, $[(NH_2CH_2CH_2O)_2Cr \cdot (HN = CHCR = CHCR = CHCH_2R) \cdot H_2O]Cl$, etc. Due to the delocalization of the positive charge of the N atom along the system of conjugated bonds an electrophilic center appears at the end of the polyene chainlet and the possibility arises of electrophilic attack by the terminal C atom on the coordinated N atom.



The building up of the unsaturated chainlet and the cyclization of the polyunsaturated ligand inside the complex itself proceeds slowly even when (II) is stored or when solutions of $CrCl_3$—EA—aldehyde are let stand. The corresponding pyridine bases are rinsed from the surface of the long stored (II) with ether, or are extracted from solutions of $CrCl_3$ in EA and the aldehyde. The amount of thus isolated pyridines is small, and their main portion is bound in the complexes. The intermediate complexes or pyridine sources are rapidly cleaved at 200-250°. When heated at this temperature the pure alkyl-substituted pyridine is distilled from the reaction mass. The 3,5-dimethyl-2-ethyl-, 3,5-diethyl-2-propyl-, and 3,5-dipropyl-2-butylpyridines were respectively obtained in this manner by the reaction of (I) with propionaldehyde, butyraldehyde, and valeraldehyde. When reacted with (I), both acetaldehyde and crotonaldehyde 2-propylpyridine. The corresponding quinolines were isolated from the reaction mixture after (I) was heated with cinnamaldehyde and the substituted cinnamaldehydes. In this case the C atom of the aromatic ring takes part in the closure of the six-membered ring, and additional building up of the polyene chainlet is not required.



The yields of the alkylpyridines are 20-40 mole %, and that of the unsubstituted quinoline is 23%, when based on one of the three EA molecules of the starting (I). The 6-methoxy- and 6,7-dimethyoxyquinolines were isolated in smaller amount: Due to the low heat stability of these compounds they undergo substantial decomposition under our adopted conditions of working up the reaction mixtures.

EXPERIMENTAL

Complex $[(NH_2CH_2CH_2O)_2Cr \cdot (NH = CHCH_2CH_3) \cdot H_2O]Cl \cdot H_2O$. To a solution of 10 g of $CrCl_3 \cdot H_2O$ (green chloride) in 5 ml of methanol at 5-10° was added 12 ml (0.2 mole) of EA. To the obtained violet solution of (I) was added in drops 21.6 ml (0.6 mole) of propionaldehyde, and after 20-30 min the mixture was filtered, and the blue needle crystals were washed with ether and dried in vacuo, mp 150°; the compound is easily hydrolyzed. Found: C 28.32; H 7.51; N 13.94; Cl 12.30; Cr 17.32%. $C_7H_{23}N_3O_4ClCr$. Calculated: C 27.96; H 7.63; N 14.03; Cl 11.79; Cr 17.29%.

Complex $[(NH_2CH_2CH_2O)_2Cr \cdot (HN = CH(CH_2)_3CH_3) \cdot H_2O]Cl \cdot H_2O$. Obtained by treating a solution of (I) with valeraldehyde, mp 191°. Found: C 32.78; H 8.32; N 13.40; Cl 10.41; Cr 15.54%. $C_9H_{27}N_3O_4ClCr$. Calculated: C 32.89; H 8.22; N 12.80; Cl 10.79; Cr 15.82%.

3,5-Dimethyl-2-ethylpyridine. A mixture of (I) and propionaldehyde was heated in an oil bath, with gradual elevation of the temperature to 250°. The fraction with bp >120° was dried over K_2CO_3 and distilled. Yield 40%, bp 85-90° (13 mm); picrate, mp 152°; cf. [2].

3,5-Dipropyl-2-butylpyridine. Obtained from (I) and valeraldehyde in 20% yield, bp 127-130° (4-5 mm); picrate, mp 96°. Found: C 81.86; H 11.18; N 6.58%. $C_{15}H_{25}N$. Calculated: C 82.13; H 11.49; N 6.38%.

3,5-Diethyl-2-propylpyridine. Obtained from (I) and butyraldehyde in 33% yield, bp 96-100° (5 mm); picrate, mp 122°; cf. [3].

2-Propylpyridine. The yield from the reaction of (I) with crotonaldehyde was 30%, and 25% when reaction was with acetaldehyde, bp 165-169°; picrate, mp 78°, which coincides with the data given in [4].

6,7-Dimethoxyquinoline. The yield from the reaction of (I) with m,p-dimethoxycinnamaldehyde was 12%, mp 30-33°; picrate, mp 252-254°, which corresponds with the data given in [5].

6-Methoxyquinoline. The yield from m-methoxycinnamaldehyde was 3%, mp 26-29°; cf. [6].

CONCLUSIONS

1. In bis(β-aminoethylato)ethanolamineaquochromium chloride only one of the three amino groups reacts with aldehydes. The condensation is accompanied by the elimination of acetaldehyde and rupture of the C−N bond, and leads to the aldimine.

2. The formed coordinated aldimine exhibits a high activity in the crotonic type of condensation and is quickly converted to a polyunsaturated ligand, which then is cyclized to either the pyridine or quinoline base.

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WOLFF REARRANGEMENT OF ALKOXYCARBONYLCARBENES DURING THERMAL DECOMPOSITION OF ALKYL DIAZOACETATES IN PRESENCE OF GASEOUS UNSATURATED COMPOUNDS*

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and E. A. Shapiro

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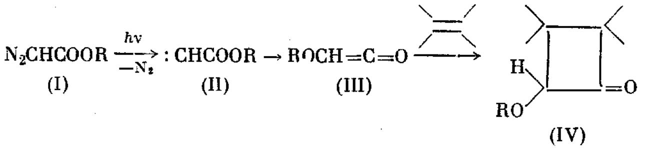
It is known that in the photolysis of ethyl diazoacetate (Ib) in liquid olefins as the medium the initially formed ethoxycarbonylcarbene (IIb) partially undergoes the Wolff rearrangement to ethoxyketene (IIIb), which reacts with olefins to give 2-ethoxycyclobutanones (IV) as the end products [3].



R=CH_3(a); C_2H_5 (b)

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*See [1] for preliminary communications; a part of the work was presented at the Second All-Union Convention on the Chemistry of Carbenes and Their Analogs [2].

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