nitrogen atmosphere. For the potentiometric titration we used a circuit consisting of a glass electrode and silver chloride electrode with potassium chloride saturated in methanol. The glass electrode was first immersed in 0.1 N aqueous hydrochloric acid over 24 h and then for about this duration in distilled water, while it was immersed prior to operation in DMF for about 1 h. Measurement of the electromotive force of the circuit in a buffer solution consisting of benzoic acid and sodium benzoate \( (c_{\text{acid}} = c_{\text{salt}} = 1 \text{ mM}) \) was used to follow the state of the glass electrode. A weighed sample of the compound studied was dissolved in 13 ml DMF. Then, 1 eq. 0.01 N sodium methylate solution was added. The mixture was thoroughly stirred using a magnetic stirrer and the pH was measured thrice on a 362 pH-meter. Benzoic acid, which was used as the standard, was titrated with sodium methylate under analogous conditions.

**LITERATURE CITED**


**CATALYTIC REDUCTION OF 4-(3-OXOQUINUCLIDYL-2-METHYLIDENE)-6-METHOXYQUINOLINE AND ITS ETHYLENEKETAL**


An examination was carried out on the catalytic reduction of 4-(3-oxoquinuclidyl-2-methylidene)-6-methoxyquinoline, its ethyleneketal, and the ethyl ester of 6-(3,4-dimethoxystyril)picolinic acid. Stepwise nature was shown for the hydrogenation of the pyridine and quinoline rings, side chains, and catalytic demethoxylation using PMR spectroscopy, mass spectrometry, and gas-liquid chromatography.

In a search for new cardiovascular drugs, we studied the catalytic reduction of possible intermediates in their synthesis, namely 4-(3-oxoquinuclidyl-2-methylidene)-6-methoxyquinoline (I) and its ethyleneketal (V). PMR spectroscopy, mass spectrometry, and gas-liquid chromatography were used to study the stepwise hydrogenation of the exocyclic double bond and the different fragments and the catalytic demethoxylation (see scheme at top of following page).

Quinoline (I) was obtained according to Bender [1] by the condensation of 3-quinuclidone with quinaldehyde and its structure was confirmed by PMR spectroscopy (Table 1). Similarly to analogously synthesized 2-arylidene- and 2-heteroarylidene-3-oxoquinuclidines [2-4], I is

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a Z isomer but undergoes Z-E isomerization in acid medium as indicated by the appearance of a second set of PMR peaks in a spectrum taken in CD$_3$OD. The mass spectrum of I (Table 2, scheme A) shows a strong molecular ion peak 294$^+$ and fragments of stepwise bond dissociation in the quinuclidine system: [M - CO]$^+$ 266, [M - HCO]$^+$ 265, [M - COCH$_3$]$^+$ 251, [M - CO-C$_2$H$_5$]$^+$ 238, [M - COC$_2$H$_5$]$^+$ 237, and also the 183 ion, whose formation is a consequence of the conjugation of the exocyclic double bond with the 6-methoxyquinoline ring. The catalytic reduction of I in the presence of palladium on activated charcoal at room temperature led to a 61.5% yield of (3'-oxoquinuclidyl-2')(6-methoxyquinolyl-4)methane (II). The PMR spectrum of (II) lacks the singlet for the proton at C(9), while multiplets arise at 2.8-3.8 ppm corresponding to 9-H and 2'-H with an integral intensity of three proton units. The oxo group at C(3') of the quinuclidine system as indicated by the chemical shift of the proton at C(9) (2.55 ppm) [5]. The mass spectrum shows a molecular ion peak at 296, corresponding to the addition of two hydrogen atoms to unsaturated ketone I and a strong peak for the 172 ion, indicating reduction of the exocyclic double bond with retention of the 6-methoxyquinoline ring (Table 2; scheme B).

Major pathways for the mass spectrometric decomposition of I-IX.

A (I; Va,b) 185
B (II, VI) 172
C (IV, VIII) 162 (IV, VIII)
D (VII) 256
E (IX) 146 (IV, VIII)

A, B, C I, II R$^1$ R$^2$ = O; III, IV R$^1$ = OH, R$^2$ = H; Va, b, VI, VIII R$^1$ R$^2$ = OCH$_3$, CH$_3$, O

The letters a and b in the scheme indicate structural isomers of the same compounds.

*Here and below, the m/z values are given.