3,3-Dimethyllevulinic Acid N-(p-Cyanophenyl)amide (IIg). The method used to prepare Ia was used to synthesize this compound from 2.4 g (20 mmole) of p-aminobenzonitrile. Workup gave 2.0 g of an oily product, which was dissolved in 20 ml of methanol—water—chloroform saturated with HCl (15:2:1), and the resulting solution was heated at 80° for 3 h. It was then evaporated with a rotary evaporator at 20°, and the residue was dissolved in 15 ml of chloroform and reprecipitate by the addition of hexane to give 1.5 g (31%) of anilide IIg with mp 150-151°. PMR spectrum (in $CDCl_3$): 3-$(CH_3)_2C$ 1.29 (s, 6H); CH_3CO 2.21 (s, 3H); 2-CH_2 2.60 (s, 2H); C_6H_4 7.58 (m, 4H) ppm. IR spectrum: 1695-1705 (amide and ketone CO), 2220 (CN), and 3325 cm^{-1} (NH). Found, %: C 68.8; H 6.4; N 11.3. $C_{14}H_{16}N_2O_2$. Calculated, %: C 68.8; H 6.6; N 11.4.

3,3-Dimethyllevulinic Acid N-Methyl-N-phenylamide. This compound was obtained by the method in [2] from 1.52 g (15 mmole) of N-methylaniline anilide, which was removed by vacuum distillation. Workup gave 2.1 g (90.3%) of a product with bp 105-107° (0.08 mm). PMR spectrum (in $CDCl_3$) : 3-$(CH_3)_2C$ 1.10 (s, 6H); CH_3CO 2.20 (s, 3H); 2-CH_2 2.40 (s, 2H), N-CH_3 3.21 (s, 3H); C_6H_5 7.01-7.40 (m, 5H) ppm. IR spectrum (in a thin layer): 1710 (ketone CO) and 1660 cm^{-1} (amide CO). Found, %: C 71.8; H 7.8; N 5.8. $C_{14}H_{19}NO_2$. Calculated, %: C 72.0; H 8.2; N 6.0.

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MASS SPECTROMETRIC STUDY OF ISATINS.

II.* N-PROPYL(ALLYL, PROPARGYL)ISATINS

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The mass spectra of N-propyl- (I), N-allyl- (IV), and N-propargylisatin (VII) and their 5-methyl (II, V, VIII) and 7-methyl (III, VI, and IX) derivatives were recorded. It is shown that a portion of the $[M-2CO]^+$ ions in the mass spectra of N-propargylisatins undergo rearrangement to give ions with a quinoline structure. A scheme for the fragmentation of the investigated compounds is presented. The mass spectra of the 5- and 7-methyl derivatives are compared.

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*See [1] for communication I.

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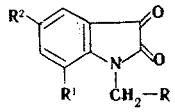
The mechanism of the fragmentation of N-alkylisatins with a normal chain of carbon atoms (C_1-C_{10}) has previously been reported [1]. Continuing these studies, we investigated the dependence of the dissociative ionization of isatins on the degree of unsaturation of the grouping attached to the nitrogen atom and on the presence of a methyl group in the 5 or 7 position of the aromatic ring, since it is known [2] that the mass spectrum of 7-methylisatin differs considerably with respect to the intensities of the peaks from the spectra of 4(5,6)-methylisatins.

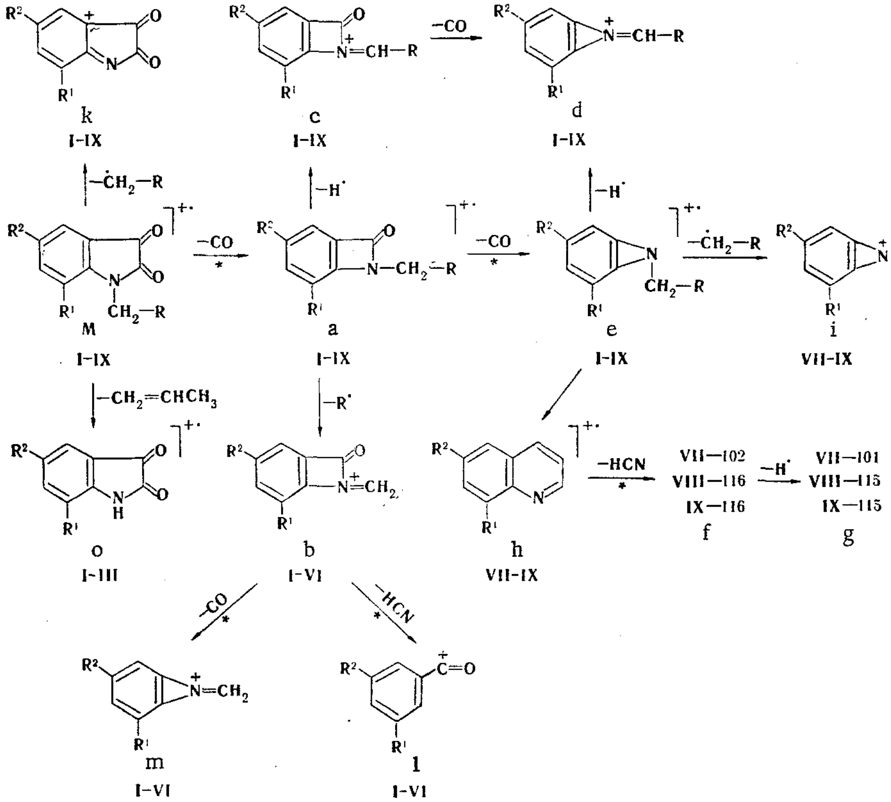
The following compounds of general formula A were synthesized and investigated by mass spectrometry:



A

I $R=C_2H_5$, $R^1=R^2=H$; II $R=C_2H_5$, $R^1=H$, $R^2=CH_3$; III $R=C_2H_5$, $R^1=CH_3$, $R^2=H$; IV $R=CH{=}CH_2$, $R^1=R^2=H$; V $R=CH{=}CH_2$, $R^1=H$, $R^2=CH_3$; VI $R=CH{=}CH_2$, $R^1=CH_3$, $R^2=H$; VII $R=C{\equiv}CH$, $R^1=R^2=H$; VIII $R=C{\equiv}CH$, $R^1=H$, $R^2=CH_3$; IX $R=C{\equiv}CH$, $R^1=CH_3$, $R^2=H$

As seen from the scheme below, the molecular ions ($\overset{+}{M}$) may undergo fragmentation via three pathways. Fragmentation via the $\overset{+}{M} \rightarrow o$ pathway is characteristic only for compounds containing a saturated hydrocarbon substituent in the 1 position. The resulting isatin pseudomolecular ion subsequently undergoes fragmentation via a previously described scheme [3].



The fragmentation of $\overset{+}{M}$ to give ion k was recorded for all of the investigated compounds. The principal pathway of dissociative ionization involves the ejection of a CO molecule from M^+ to give ion a, the relative intensity of which in the mass spectra of I, IV, and VII increases in the order I < VII < IV. A similar regularity is also retained in the stability values* of ion k; this is probably connected with the increase in the stabilities of the detached radicals in the order propyl < propargyl < allyl.

Ion a undergoes fragmentation mainly via three pathways: a → c → d, a → e → d, and a → e → i. The α cleavage of the C-C bond of ion a (fragmentation via the a → b pathway), which is extremely characteristic for N-alkylisatins [1], is energically less favorable in the presence of a double bond (IV-VI) and is not observed at all in the case of VII-IX, which

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*In fractions of the total ion current.

TABLE 1. Mass Spectra of I-IX

Compound	m/e values (relative intensity, %)
I	189 (98), 161 (3), 160 (2), 147 (4), 146 (7), 133 (28), 132 (100), 119 (17), 118 (17), 105 (12), 104 (31), 92 (6), 91 (7), 90 (14), 78 (11), 77 (32), 76 (8), 64 (6), 63 (7), 51 (12), 50 (7)
II	203 (83), 175 (7), 174 (3), 161 (5), 160 (7), 147 (40), 146 (100), 132 (32), 119 (15), 118 (53), 104 (14), 92 (8), 91 (39), 90 (8), 89 (11), 78 (8), 77 (20), 65 (23), 64 (5), 63 (11), 51 (15), 50 (6)
III	203 (75), 175 (3), 174 (2), 161 (12), 160 (15), 147 (19), 146 (85), 132 (16), 119 (12), 118 (100), 104 (18), 92 (5), 91 (40), 90 (7), 89 (1), 78 (5), 77 (23), 65 (23), 64 (3), 63 (7), 51 (15), 50 (3)
IV	187 (62), 159 (28), 158 (4), 146 (30), 132 (13), 131 (20), 130 (100), 118 (3), 105 (7), 104 (20), 103 (7), 91 (6), 90 (45), 78 (16), 77 (35), 65 (9), 64 (8), 63 (17), 51 (25), 50 (11)
V	201 (70), 173 (30), 172 (6), 160 (20), 146 (10), 145 (20), 144 (100), 130 (29), 119 (6), 118 (18), 117 (7), 105 (3), 104 (26), 103 (5), 91 (4), 90 (8), 89 (12), 78 (10), 77 (29), 65 (16), 64 (6), 63 (11), 51 (20), 50 (8)
VI	201 (85), 173 (21), 172 (5), 160 (75), 146 (8), 145 (16), 144 (100), 130 (21), 119 (9), 118 (34), 117 (16), 105 (6), 104 (46), 103 (10), 91 (28), 90 (12), 89 (20), 78 (16), 77 (44), 65 (23), 64 (11), 63 (23), 51 (33), 50 (15)
VII	185 (76), 157 (24), 156 (18), 146 (19), 130 (20), 129 (100), 128 (32), 103 (12), 102 (52), 101 (10), 90 (52), 77 (11), 76 (28), 64 (20), 63 (24), 51 (19), 50 (24)
VIII	199 (82), 171 (24), 170 (8), 160 (13), 144 (15), 143 (100), 142 (60), 128 (4), 117 (13); 116 (28), 115 (44), 104 (28), 103 (9), 91 (14), 90 (10), 89 (20), 77 (38), 76 (14), 65 (12), 64 (8), 63 (23), 51 (37), 50 (17)
IX	199 (100), 171 (31), 170 (6), 160 (38), 144 (11), 143 (87), 142 (46), 128 (4), 117 (6), 116 (19), 115 (44), 104 (35), 103 (10)., 91 (15), 90 (14), 89 (21), 77 (48), 76 (16), 65 (14), 64 (11), 63 (21), 51 (40), 50 (17)

contain a triple bond. The peaks of the b, l, and m ions, which are intense in the mass spectra of propyl derivatives I-III, are therefore considerably less intense in the case of IV-VI and are completely absent in the mass spectra of VII-IX.

Characteristic differences in the mass spectra of I-IX are observed for ions e ([M — 2CO/$^{+\cdot}$) and d ([M — 2CO — H]$^{+\cdot}$). The ratios of the intensities of the peaks of these ions (I_e/I_d) are 2.5-4 (for N-propylisatins I-III), 5-6 (for N-allylisatins IV-VI), and 0.3-0.6 (for N-propargylisatins VII-IX). The particularly appreciable difference in the latter case is explained by the fact that a rearranged ion with the structure of the molecular ion of quinoline (fragmentation via the a → h pathway), which has high stability, is formed after ejection of two CO groups and migration of a hydrogen atom from the methylene group to the adjacent carbon atom. The above is additionally confirmed by the fact that characteristic (for the quinoline ion) ejections by ion h of an HCN molecule with subsequent loss of a hydrogen atom (fragmentation pathway h → f → g) are observed in the mass spectra of VII-IX. A similar acetylenic rearrangement to give a quinoline ion has also been described for other compounds that form intermediate fragment ions of the N-propargylisatin type [4, 5].

The peak of ion d ([M — 2CO — H]$^{+}$) has, as a rule, the maximum intensity in the mass spectra of N-propyl- and N-allylisatins. The same peak (although of considerably lower intensity) is also present in the mass spectra of N-propargylisatins and, consequently, only a portion of the e ions ([M — 2CO]$^{+\cdot}$) are isomerized to quinoline ions. The low mass number range in the mass spectra of I-IX is less characteristic and does not appreciably reflect the effect of the character of the substituent attached to the nitrogen atom.

The mass spectra of isomeric methylisatins are compared in [2], and it is shown that the mass spectra of 4-, 5-, and 6-methylisatins are almost identical and differ markedly from the mass spectrum of 7-methylisatin. The introduction of a methyl group in the aromatic ring of N-propylisatin leads to a decrease in the stability (W_M) of the molecular ion from 0.19 for I to 0.12 for II and III, whereas in N-allyl- (IV-VI) and N-propargylisatins (VII-IX) it does not have an appreciable effect on the stabilities (W_M ranges from 0.09 to 0.11 for these compounds). The most characteristic differences between the corresponding 5- and 7-methylderivatives that can be used as a basis for their mass spectrometric identification, consist in the fact that the I_k/I_a values for the 5-methyl derivatives are always lower than unity, whereas they are always much larger than unity for the 7 isomers.

Peaks with m/e 132 (II-III), 130 (V-VI), and 128 (VII-IX), the relative intensities of which decrease on passing from the propyl to propargyl derivatives, are present in the mass spectra of the methyl derivatives. Considering that these peaks differ by 2 amu, it may be supposed that the substituent attached to the nitrogen atom (CH@-R) is retained in the fragments. Consequently, these fragments are formed as a result of detachment of a methyl group from ion e ($[M - 2CO]^{+\cdot}$).

EXPERIMENTAL

Compounds I-IX were obtained by a known method [6] and were purified as described in [1].

The mass spectra were recorded with an MKh-1303 spectrometer equipped with a glass system for direct introduction of the samples. The vaporization temperature in the inlet tube was 95-120°, the ionization chamber temperature was 150°, the ionizing voltage was 70 V, and the emission current was 1.0 mA. The reproducibility of the mass spectra during recording over a long time (14-60 days) was 8-10 rel.%.

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MASS SPECTROMETRIC STUDY OF ISATINS.

III.* ISATIN AND N-METHYLISATIN KETALS

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In contrast to isatin and N-methylisatin, their ethylene-, propylene-, and 2,3-butyleneketals undergo fragmentation via several pathways. In addition to the principal fragmentation pathway – successive loss by the molecular ion (M^+) of a CO group and a dioxolane ring or its fragment, the M^+ ions of the ketals are also fragmented with elimination of a dioxolane fragment or the substituent attached to the nitrogen atom and, subsequently, a fragment of the dioxolane ring. The fragmentations of some of the fragment ions were investigated by means of the mass spectra of N-trideuteromethyl analogs.

In the course of a systematic study of the mechanism of the dissociative ionization of various isatin derivatives [1, 2], we studied the mass spectrometric behavior of ethylene-, propylene-, and 2,3-butyleneketals of isatin and N-methylisatin (A).

The selectivities ($S_{1/2}$) of the fragmentation of isatin β-ketals II and II and N-methylisatin β-ketals III-V differ considerably. The $S_{1/2}$ values in the mass spectra of I and II range from two to three and those of III-V range from six to seven, whereas $S_{1/2}$ is two in the mass spectrum of isatin and three in the mass spectrum of N-methylisatin [1]. Consequently, replacement of the β-keto group by a dioxolane ring has a considerably greater effect on the character of the fragmentation of N-methylisatin derivatives than on that of isatin derivatives.

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*See [2] for communication II.

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