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MASS SPECTRA OF 1,3-DIPOLAR CYCLOADDUCTS OF BENZO[h]NAPHTHYRIDINIUM N-ETHOXYCARBONYLMETHYLIDES

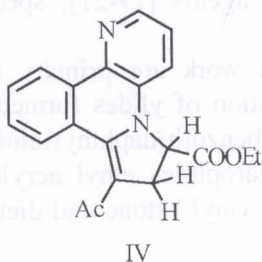
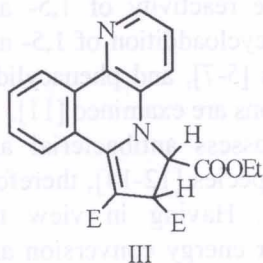
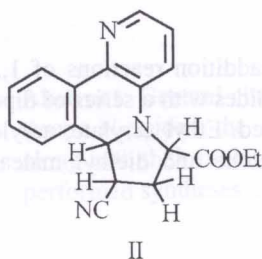
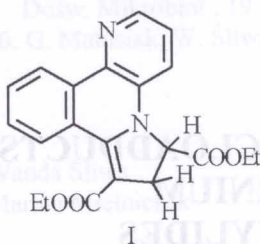
Abstract: Mass spectra of products of 1,3-dipolar cycloaddition reactions of 1,5- and 1,6-benzo[h]naphthyridinium N-ethoxycarbonylmethylides with a series of dipolarophiles are described and fragmentation modes proposed. Ethyl acrylate, acrylonitrile, dimethyl acetylenedicarboxylate, methyl vinyl ketone and diethyl maleate were used as dipolarophiles.

In a continuation of our research concerning the reactivity of 1,5- and 1,6-benzo[h]naphthyridines [1-4], especially 1,3-dipolar cycloaddition of 1,5- and 1,6-benzo[h]naphthyridinium ethoxycarbonylmethylides [5-7], and phenacylides [8-10], mass spectra of products obtained in these reactions are examined [11].

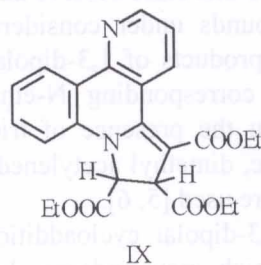
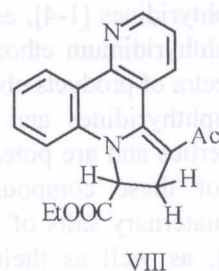
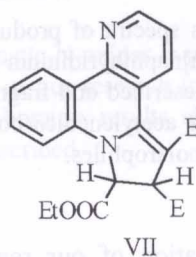
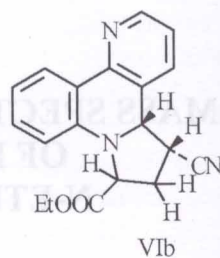
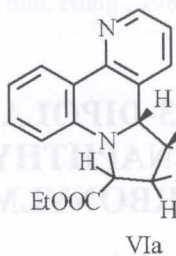
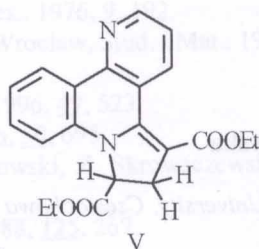
Benzo[h]naphthyridines and their derivatives possess antibacterial and antifungal properties and are potential antineoplastic species [12-14], therefore investigations of these compounds are of interest. Having in view the usefulness of quaternary salts of azaaromatics in solar energy conversion and storage [15-18], as well as their use as biological agents [19-21], species belonging to this class deserve an attention [23, 24].

Compounds under consideration in the present work are primary and secondary products of 1,3-dipolar cycloaddition reaction of ylides formed in situ from corresponding N-ethoxycarbonylmethyl benzo[h]naphthyridinium bromides in the presence of triethylamine; as dipolarophiles ethyl acrylate, acrylonitrile, dimethyl acetylenedicarboxylate, methyl vinyl ketone and diethyl maleate were used [5, 6].

The 1,3-dipolar cycloaddition results at the first step in primary cycloadducts which may undergo dehydrogenation and rearrangement involving H shift [6-9].



E = COOMe



If the primary cycloadducts are stable enough they are isolated as the main products, as it was in the case of II and VI, however, if they are unstable and readily susceptible to dehydrogenation, the dehydrogenated species are isolated; this was observed for I, IV, V, VIII and IX. Also the rearrangement of primary products involving the H shift is possible, as in case of III and VII.

Formulae of considered compounds I-IV (1,5-benzo[h]naphthyridine series) and V-IX (1,6-benzo[h]naphthyridine series) are given. The examples of 1,3-dipolar cycloaddition reactions of 1,6-benzo[h]naphthyridinium ylide isomer are shown in Scheme 1.

The m/z and relative intensity values of I-IX are presented in Table 1 and chosen example of fragmentation (II, III, V and VIII) in Schemes 2-4.

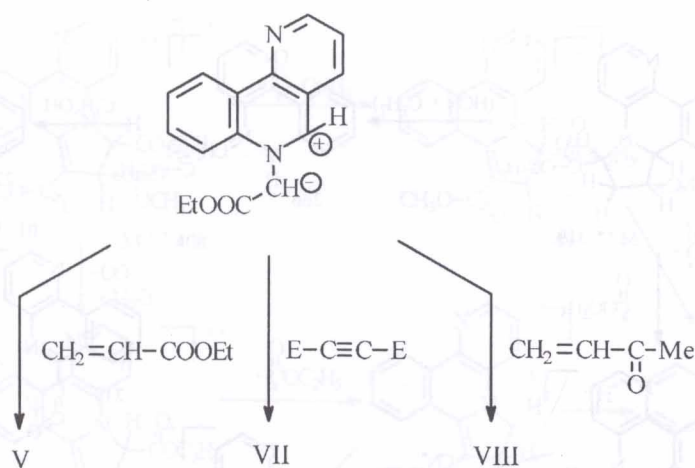
For considered compounds the common feature is the formation of four-ring species m/z 218 or 219.

Experimental

The low-resolution mass spectra were recorded on an LKB-2901 instrument at a nominal energy 70 eV and 15 eV. The temperature of the ion source was 255 °C and samples were introduced via the direct probe. Accelerating voltage was 3,5 kV, trap current 50 μ A.

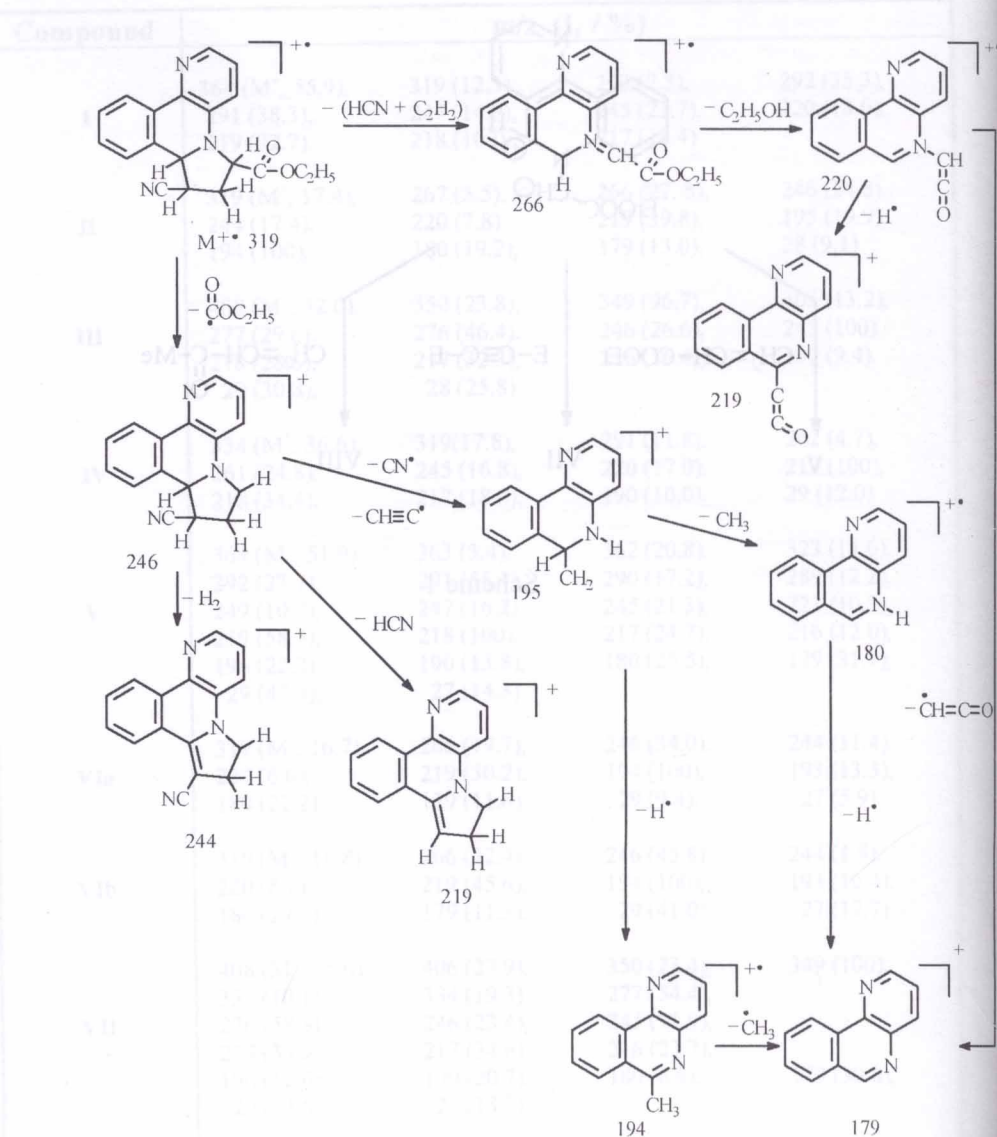
Table 1. Mass spectral data of the prepared compounds

Compound	m/z (I_r / %)			
I	364 (M^+ , 55.9),	319 (12.3),	293 (7.5),	292 (35.3),
	291 (38.3),	247 (14.9),	245 (23.7),	220 (13.0),
	219 (72.7),	218 (100),	217 (18.4)	
II	319 (M^+ , 17.4),	267 (5.5),	266 (27.8),	246 (24.8),
	244 (17.4),	220 (7.8),	219 (39.8),	195 (19.9),
	194 (100),	180 (19.2),	179 (13.0),	28 (9.1)
III	408 (M^+ , 32.0),	350 (23.8),	349 (96.7),	303 (13.2),
	277 (29.6),	276 (46.4),	246 (26.6),	245 (100),
	218 (28.6),	217 (32.3),	216 (16.4),	190 (9.4),
	29 (30.8),	28 (25.8)		
IV	334 (M^+ , 36.6),	319 (17.8),	291 (11.8),	262 (4.7),
	261 (24.8),	245 (16.8),	220 (17.0),	219 (100),
	218 (34.4),	217 (18.0),	190 (10.0),	29 (12.0)
V	364 (M^+ , 51.0),	363 (3.4),	362 (20.8),	323 (14.6),
	292 (23.7),	291 (55.1),	290 (17.2),	289 (12.2),
	249 (10.7),	247 (16.2),	245 (21.3),	221 (10.3),
	219 (58.5),	218 (100),	217 (24.7),	216 (12.0),
	196 (22.2),	190 (13.8),	180 (25.5),	179 (31.7),
	29 (47.4),	27 (14.3)		
VIa	319 (M^+ , 16.7),	266 (19.7),	246 (34.0),	244 (11.4),
	220 (6.0),	219 (30.2),	194 (100),	193 (13.3),
	180 (22.2),	179 (11.6),	29 (9.4),	27 (5.9)
VIb	319 (M^+ , 18.8),	266 (22.4),	246 (45.8),	244 (1.8),
	220 (8.2),	219 (45.6),	194 (100),	193 (10.4),
	180 (19.6),	179 (11.3),	29 (41.0),	27 (17.7)
VII	408 (M^+ , 35.6),	406 (27.9),	350 (23.4),	349 (100),
	335 (10.1),	334 (19.3),	277 (54.4),	
	276 (58.8),	246 (23.4),	245 (91.9),	
	218 (39.9),	217 (34.6),	216 (23.7),	
	196 (12.0),	190 (20.7),	180 (6.9),	179 (30.8),
	29 (63.6),	27 (13.7)		
VIII	334 (M^+ , 53.6),	319 (13.0),	291 (9.3),	262 (5.8),
	261 (25.0),	245 (13.3),	220 (18.8),	219 (100),
	218 (26.3),	217 (11.7),	190 (6.4),	43 (26.7)
IX	436 (M^+ , 2.2),	363 (7.1),	282 (67.7),	237 (14.1),
	236 (31.6),	210 (20.53),	209 (92.9),	
	180 (25.3),	179 (100),	153 (10.9),	127 (14.8),
	78 (10.5),	29 (16.6),	28 (16.6)	



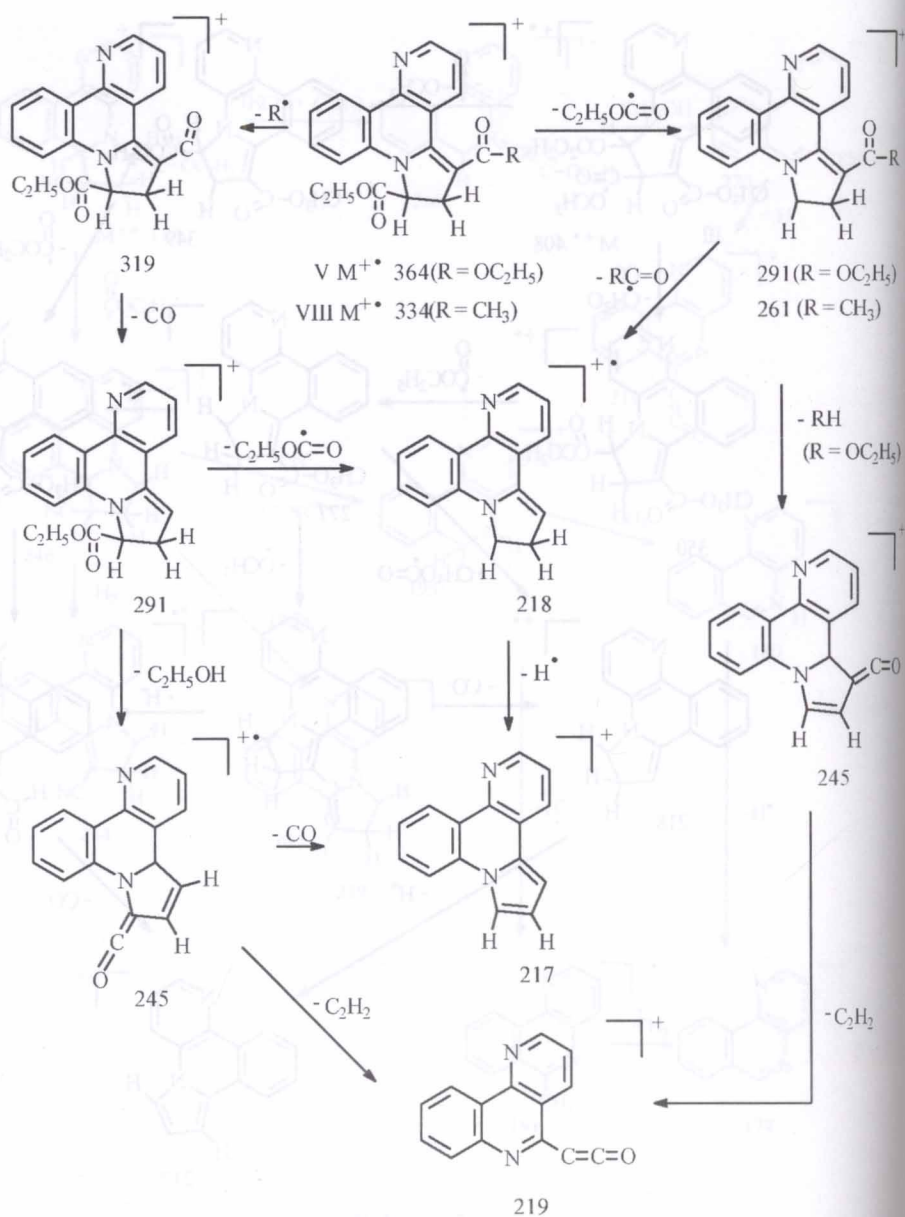
Scheme 1

Table 1. Mass spectral data of the prepared compounds



Scheme 2

Scheme 3



Scheme 4

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**Widma masowe 1,3-dipolarnych cykloadduktów
N-etoksykarbonylo metylidów benzo[h]naftyrydyniowych**

Streszczenie: Opisano widma masowe produktów reakcji 1,3-dipolarnej cykload-dycji N-etoksykarbonylo metylidów benzo[h]naftyrydyniowych z serią dipolarofili i zaproponowano sposób fragmentacji. Jako dipolarofili użyto akrylan etylu, akrylo-nitryl, acetylenodikarboksylan dimetylu, keton metylowo-winyłowy i meleinian dietylu.