

Mass spectra of 1,3-dipolar cycloadducts of benzo[*h*]naphthyridinium *N*-phenacylides

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

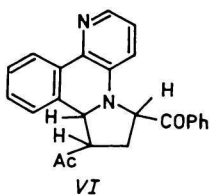
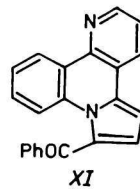
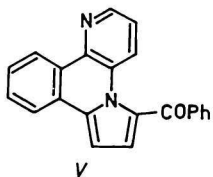
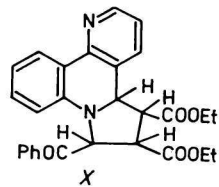
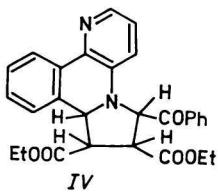
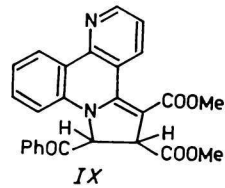
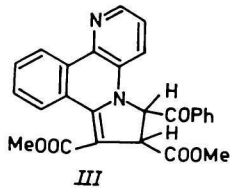
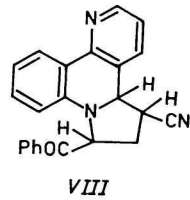
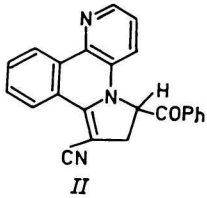
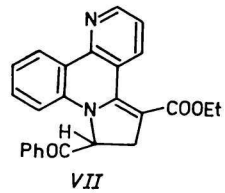
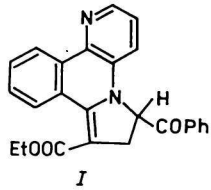
The present paper is a continuation of our research concerning synthesis and properties of benzo[*h*]naphthyridines [1, 2]. These compounds are interesting for their reactivity, for instance substitution and quaternization [3, 4], as well as complexation reactions with transition metal ions [5—7].

The complexing properties of benzo[*h*]naphthyridines are due to the presence of nitrogen atoms in the molecule, as in analogous azaaromatics [8, 9]. Benzo[*h*]naphthyridines and their derivatives deserve an attention for their biological properties, they exhibit antibacterial and antifungal activities [1, 4] and some among them are potential antineoplastic agents [10].

Quaternary salts of azaaromatics are intensively studied from the theoretical and practical points of view [11, 12], *e.g.* they are useful in the solar energy conversion and storage [13—18], therefore the chemistry of *N*-substituted benzo[*h*]naphthyridines is of interest.

Studying the reactivity of quaternary benzo[*h*]naphthyridinium salts, we investigated 1,3-dipolar cycloaddition reactions of 1,5- and 1,6-benzo[*h*]naphthyridinium *N*-phenacylides [19, 20] and *N*-carboethoxymethylides [21, 22]. Mass spectra of primary and secondary products of these reactions are determined and presented. Ylides playing the role of 1,3-dipoles were generated *in situ* by treatment of 5- or 6-phenacylbenzo[*h*]naphthyridinium bromides with triethylamine; as dipolarophiles ethyl acrylate, acrylonitrile, dimethyl acetylenedicarboxylate, diethyl maleate, maleic anhydride, and methyl vinyl ketone were used [19, 20].

In general, reactions of ylides with dipolarophiles afford primary cycloadducts, which may undergo the subsequent dehydrogenation to give the secondary products. For instance, the cycloaddition of 1,5- and 1,6-benzo[*h*]naphthyridinium *N*-phenacylides with diethyl maleate afforded the primary products *IV*

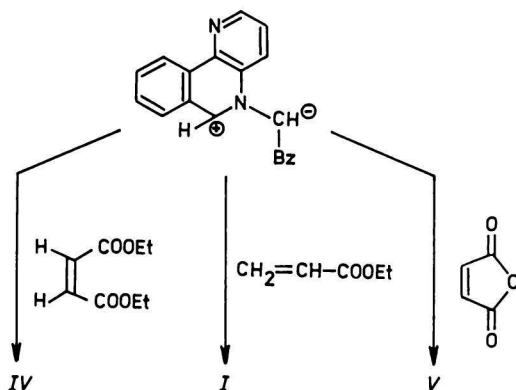


Formulae of products of 1,3-dipolar cycloaddition reactions of 1,5- and 1,6-benzo[*h*]naphthyridinium *N*-phenacylides

Table 1

Mass spectral data of the prepared compounds

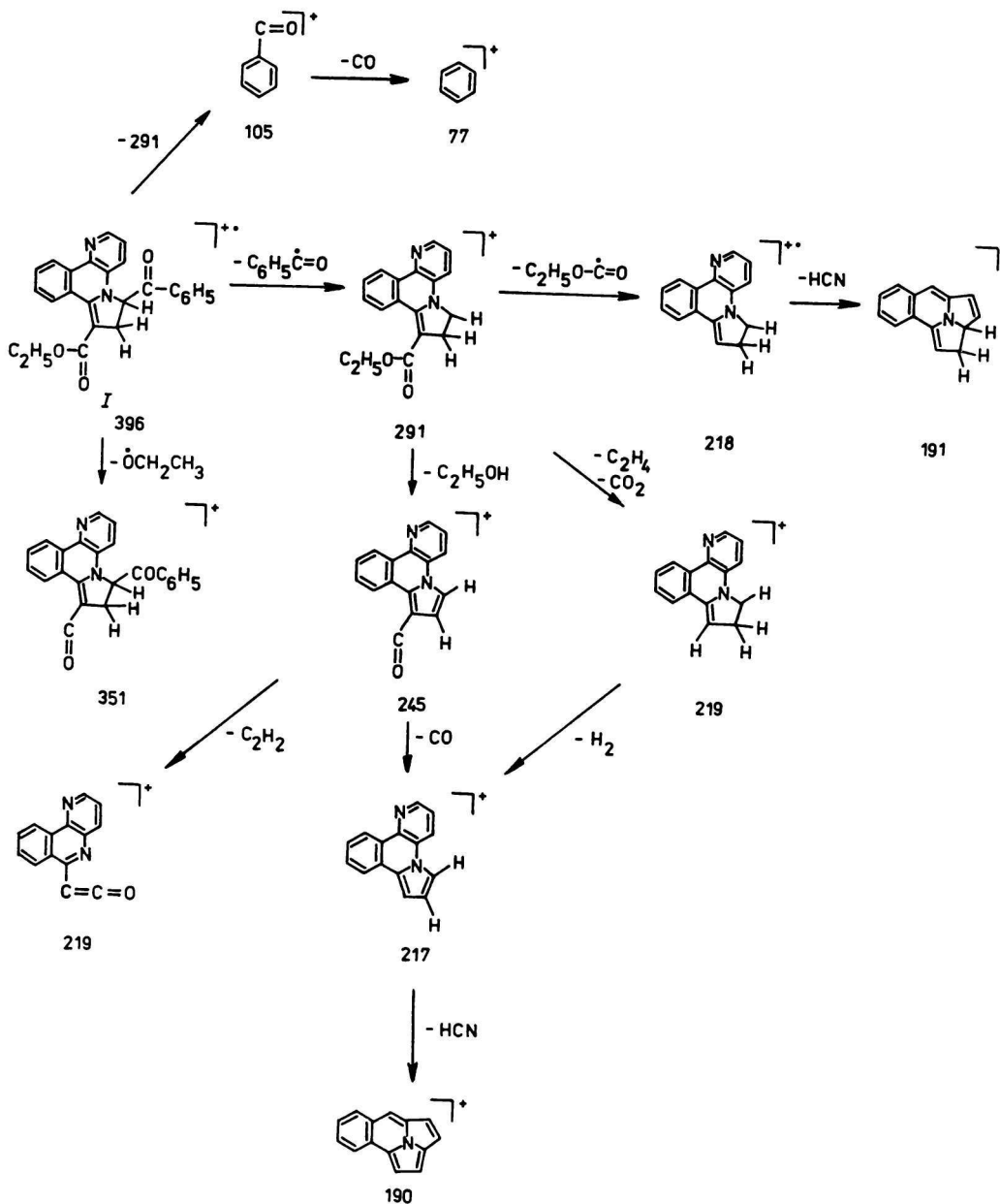
Compound	m/z ($I_r/\%$)
I	397 (10), 396 (M^+ , 28.4), 351 (9.5), 291 (83.0), 245 (21.4), 219 (44.8), 218 (100), 217 (17.8), 190 (6.2), 191 (5.52)
II	350 (4.4), 349 (M^+ , 17.0), 244 (100), 243 (28.5), 242 (5.7), 217 (5.0), 216 (6.4), 190 (3.6), 189 (2.7)
III	441 (4.1), 440 (M^+ , 11.5), 382 (2.2), 381 (6.5), 335 (9.7), 303 (12.1), 277 (1.7), 276 (7.4), 246 (5.1), 245 (21.3), 218 (4.4), 217 (7.1), 216 (3.2), 190 (2.1), 105 (100)
IV	471 (2.7), 470 (M^+ , 7.3), 425 (8.7), 397 (3.4), 366 (20.8), 365 (84.9), 351 (5.3), 319 (18.6), 292 (5.7), 291 (22.7), 266 (100), 220 (30.5), 219 (54.5), 218 (31.1), 217 (8.1), 196 (26.3), 194 (18.9), 193 (5.3), 181 (20.3), 180 (9.2), 179 (14.6), 105 (62.9)
V	323 (4.6), 322 (M^+ , 18.6), 294 (7.5), 293 (15.9), 292 (4.8), 245 (14.7), 217 (49.2), 216 (38.7), 190 (44.6), 189 (17.6), 164 (15.9), 163 (14.2), 105 (34.9), 77 (100)
VI	369 (0.4), 368 (M^+ , 1.4), 326 (4.3), 325 (10.3), 263 (2.6), 236 (21.9), 221 (9.1), 220 (1.6), 219 (5.9), 218 (3.2), 207 (27.7), 196 (17.3), 194 (9.1), 180 (24.9), 179 (11.8), 105 (22.4), 86 (100), 77 (21.7), 42 (14.1)
VII	396 (M^+ , 25.6), 394 (8.5), 351 (7.3), 291 (81.7), 289 (2.2), 245 (17.4), 219 (47.6), 218 (100), 217 (17.4), 216 (6.9), 190 (9.1), 105 (21.7), 77 (26.2)
VIII	352 (2), 351 (M^+ , 7.0), 298 (5.7), 297 (13.6), 247 (18.9), 246 (100), 220 (7.9), 219 (47.6), 180 (13.8), 179 (6.7), 153 (2.1), 127 (1.9), 105 (4.2), 77 (8.7)
IX	440 (M^+ , 8.7), 381 (5.9), 335 (12.3), 303 (1.3), 276 (9.0), 245 (19.2), 217 (10.3), 216 (4.2), 196 (14.7), 190 (4.6), 105 (100), 78 (97.7), 77 (55.8)
X	471 (2), 470 (M^+ , 6.7), 425 (7), 397 (4.5), 395 (3.0), 368 (0.9), 366 (21.4), 365 (100), 351 (8.0), 319 (12.0), 292 (5.4), 291 (15.7), 266 (88.4), 219 (66.1), 218 (33.8), 217 (7.3), 194 (15.5), 193 (4.8), 181 (16.0), 180 (6.4), 179 (6.2), 105 (59.0), 77 (30.3)
XI	322 (M^+ , 100), 294 (19.0), 293 (32.1), 292 (14.3), 246 (10.9), 245 (40.1), 218 (9.2), 217 (32.3), 216 (15.0), 190 (7.9), 105 (11.1), 77 (29.4)



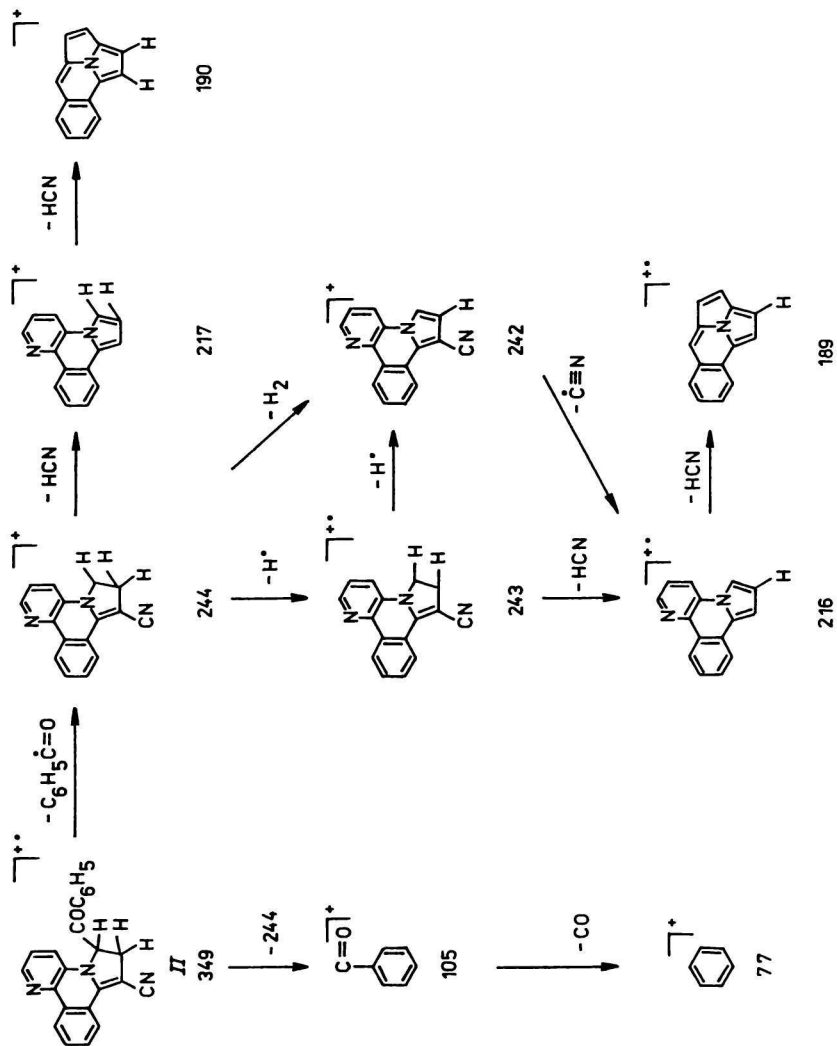
Scheme 1

and *X*, whereas in the case of ethyl acrylate used as dipolarophile, dehydrogenated compounds *I* and *VII* were formed.

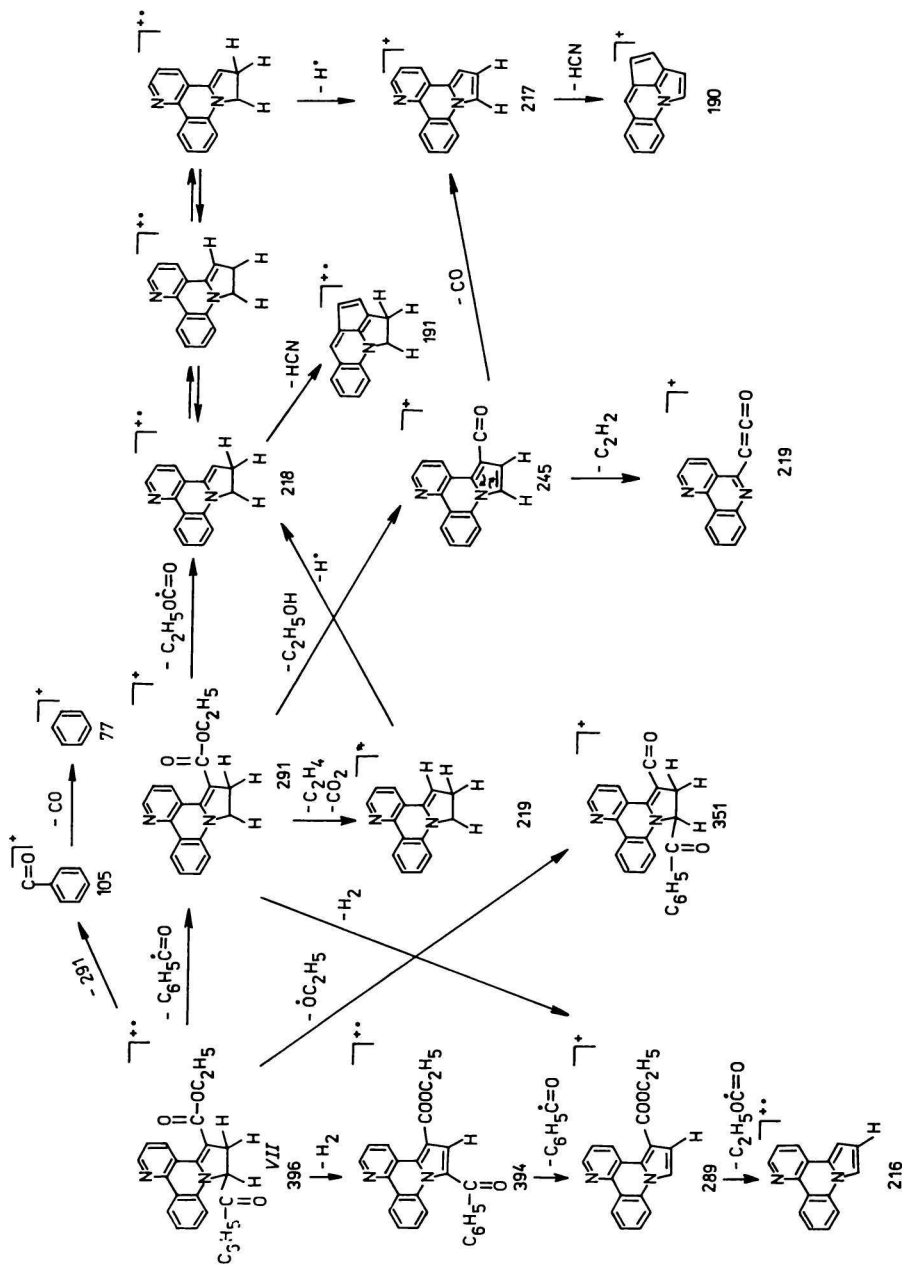
Also other rearrangements of primary cycloadducts are possible, *e.g.* when



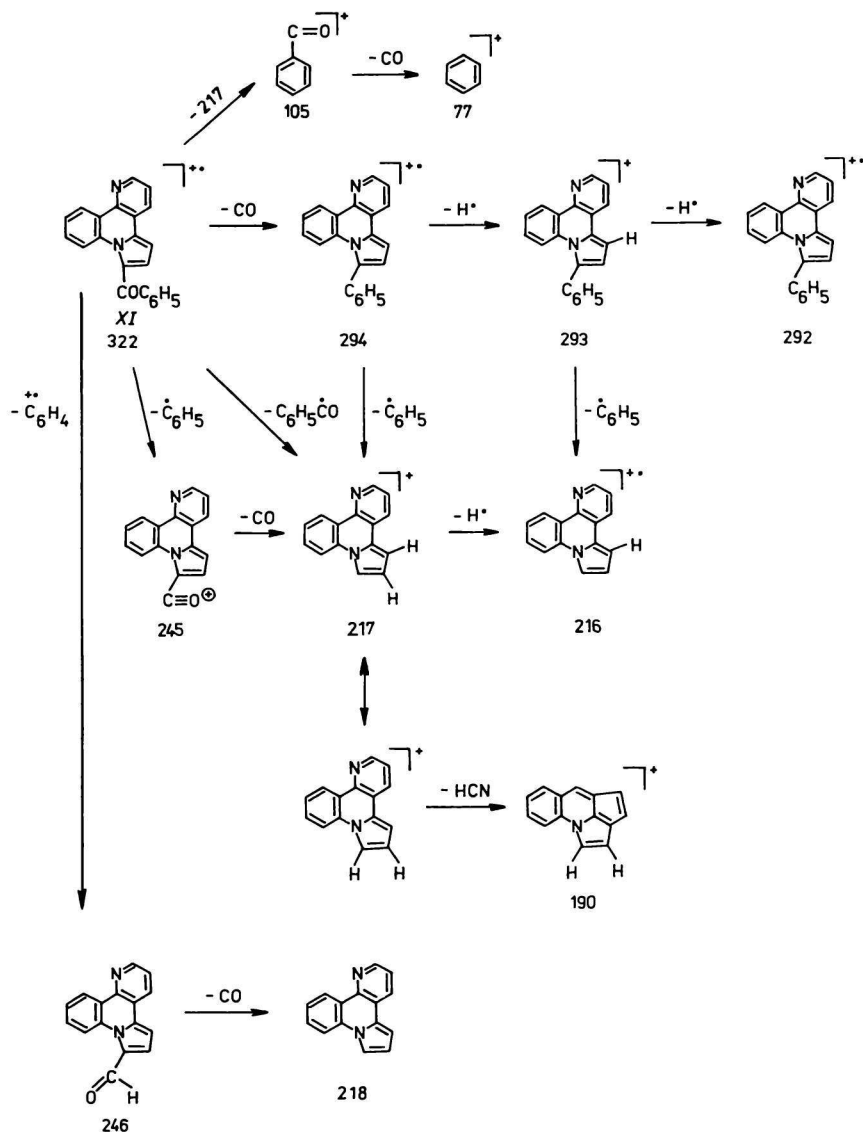
Scheme 2



Scheme 3



Scheme 4



Scheme 5

maleic anhydride served as dipolarophile, primary cycloadducts underwent hydrolysis and subsequent decarboxylation along with dehydrogenation to give *V* and *XI* [19, 20].

Formulae of considered compounds *I*—*VI* (1,5-benzo[*h*]naphthyridine series) and *VII*—*XI* (1,6-benzo[*h*]naphthyridine series) are given. The examples of 1,3-dipolar cycloaddition reactions of 1,5-benzo[*h*]naphthyridinium *N*-phenacylide isomer are shown in Scheme 1.

The m/z and relative intensity values of I — XI are presented in Table 1, and chosen examples of fragmentation (I , II , VII , and XI) in Schemes 2—5.

In all cases the characteristic feature is the formation of $C_6H_5CO^{+\bullet}$ and $C_6H_5^+$ species.

Experimental

The low-resolution mass spectra for each compound 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.

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