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CHARACTERISTICS OF THE DISSOCIATIVE IONIZATION OF 9-ARYL(HETARYL)-3,3,6,6-TETRAMETHYLDECAHYDROACRIDINE-1,8-DIONES UNDER THE INFLUENCE OF ELECTRON IMPACT

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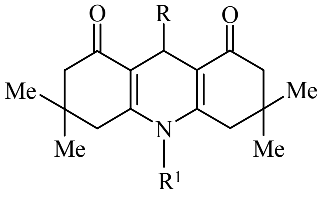
The mass spectra of 9-aryl(hetaryl)-3,3,6,6-tetramethyldecahydroacridine-1,8-diones have been studied and the basic directions of their dissociative ionization under the influence of electron impact have been elucidated. It has been shown that the decomposition pathways of decahydroacridine-1,8-diones depend on the nature of the substituents at position 10 and is connected with the preferential formation of a pyridinium structure with subsequent retrodiene decomposition of the molecules.

Keywords: 3,3,6,6-tetramethyl-9-R-decahydroacridine-1,8-diones, dissociative ionization, retrodiene decomposition.

Beside the wide use of mass spectrometry in contemporary organic chemistry to obtain information on the structure of materials, this method has received relatively limited use for the structural investigation of such classes of organic compounds as decahydroacridine-1,8-diones [1, 2]. In a continuation of the study of the regularities of the synthesis and properties of the latter [3-7] we have undertaken the investigation of the mass spectral behavior of a large series of 9-aryl(hetaryl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-diones (**1a-n**). The wide variation in the substances studied allowed the elucidation of the basic rules of the dissociative ionization of compounds **1** under the influence of electron impact depending on their structures. Structural assignments were carried out using literature data on the mass spectrometric investigation of 1,8-dioxo-*sym*-octahydroxanthenes [8], 6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindoles [9], 7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinolines [10], and 3,5-diacyl-1,4-dihydropyridines [11]. The structures of the substituted decahydroacridine-1,8-diones **1a-n** were established by IR and ^{1}H NMR spectroscopy [3-5].



1a–n

1 a,**b** R^1 = H, **c-g** R^1 = Me, **h-j** R^1 = Ph, **k-n** R^1 = $PhCH_2$; **a**, **f**, **i**, **m** R = 5-O_2N-2-C_4H_2O (5-nitro-2-furyl), **b**, **g**, **j**, **n** R = 2-C_4H_3S (2-thienyl), **c**, **k** R = Ph, **d**, **h**, **l** R = 4-$MeOC_6H_4$, **e** R = 2-C_4H_3O (2-furyl)

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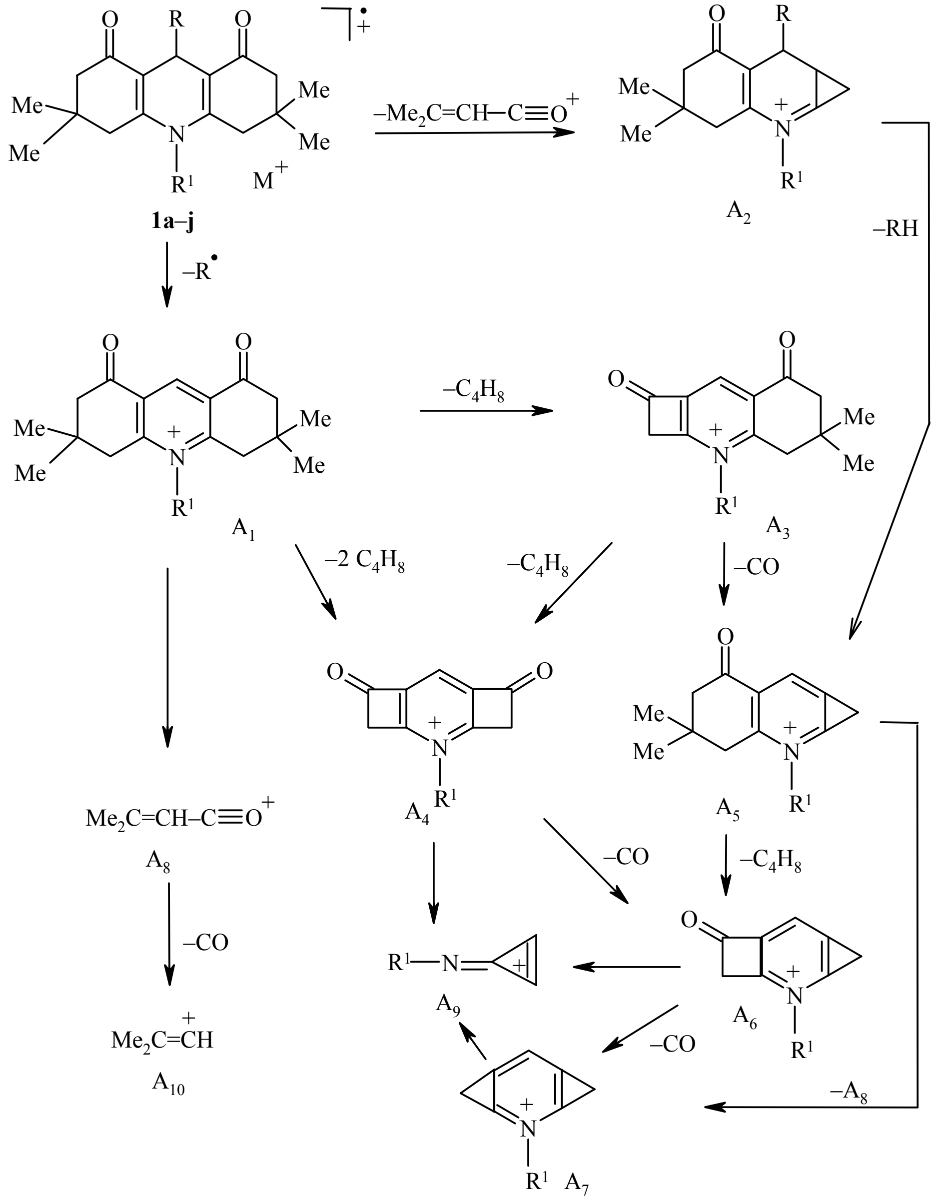
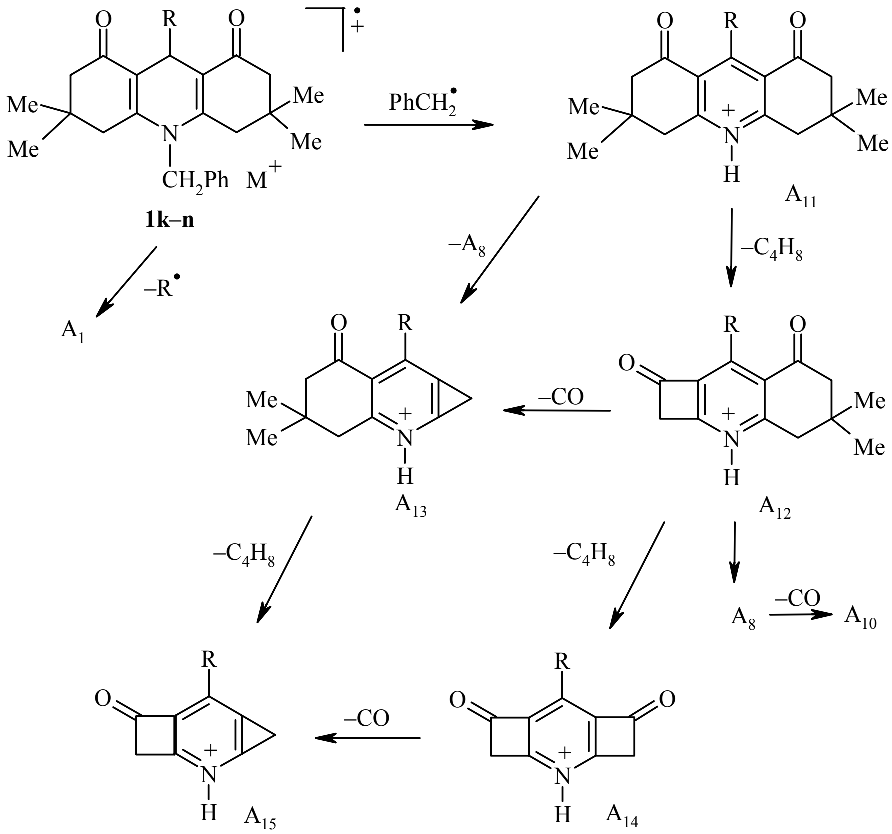


In the spectra of NH-decahydroacridine-1,8-diones **1a,b**, and also of the hydroacridines **1c-j**, which contain methyl or phenyl substituents on the nitrogen atom, the molecular ion peaks M^+ are quite intense, and this peak is the most intense for 10-phenyl-9-thienyldecahydroacridinedione **1j** (Table 1). On the other hand, the N-benzyldecahydroacridine-1,8-diones **1k-n** are characterized by M^+ peaks of low intensity. The presence of a *para*-methoxyphenyl radical in position 9 (compounds **1d,h,l**) decreased the relative intensity of the molecular ion peak. The presence of the MeO group in these compounds causes the formation of the ion $[M^+ - CH_2O]^+$ which is characteristic for the dissociative ionization of anisoles [12]. The stability of the M^+ ions (W_M) changes in dependence of the nature of the substituent groups at positions 9 and 10: the largest value of W_M was observed for the acridinediones **1b,g,j** which have a thienyl group in position 9, and the smallest value was for the N-benzyl-substituted 1,8-dioxodecahydroacridines **1k-n**. Compounds **1a,f,i** have moderate values of W_M which is normal for nitroaromatic compounds [13]. In their spectra peaks for the ions $[A - NO]^+$ are present which indicates the elimination of the fragment NO from the species formed by decomposition of the molecular ion.



In the case of the 1,8-dioxodecahydroacridines **1a-j**, decomposition of the molecular ion may follow two different pathways. The dominant direction of dissociative ionization is scission of the radical R from position 9 of the molecular ions leading to the formation of stable pyridinium cations A_1, which is in agreement with the fragmentation of 4-R-1,4-dihydropyridnes [10-11, 14]. This process is accompanied by the appearance of intense peaks, which, for compounds **1a-i**, are the most intense peaks present. The other pathway is *via* loss of the ion $C_5H_7O^+$ ($m/z = 83$), however the peaks arising in this way (A_2) have low intensity.

Further fragmentation of the A_1 ions occurs *via* retrodiene decomposition with successive elimination of two C_4H_8 molecules to form the cations A_3 and A_4. The mass numbers of fragments A_1-A_4 indicate that the substituent on the nitrogen atom is retained.

In the mass spectra of the decahydroacridin-1,8-diones **1a-j** peaks of the ions A_5, A_6, and A_7 are observed which arise from loss of the molecule CO from the cations A_3, A_4, and A_6. Fragment A_5 may also be formed directly from A_2 and A_6 from A_5 from a retro-Diels–Alder reaction with loss of an alkene molecule, and A_7 from A_5 by elimination of the ion $C_5H_7O^+$ (A_8). There are also the ions A_9, which evidently have a cyclopropenylium structure, and cations A_8 and A_{10} which are characteristic for derivatives of 5,5-dimethyl-2-cylohexenone [8, 10, 15].

In contrast to the 9-R-10-R^1-decahydroacridine-1,8-diones **1a-j** (R^1 = H, Me, Ph), the effect of the structure of the substituent on the nitrogen atom in the 10-benzyldecahydroacridine-1,8-diones **1k-n** on the direction of decomposition under the influence of electron impact can be traced. A feature of the dissociative ionization of 1,8-dioxodecahydroacridines **1k-n** is associated with the appearance in their spectra of very intense fragments A_{11} which arise from scission of the C-N bond and loss of the radical $PhCH_2\cdot$ from M^+ ion. This route is confirmed by the presence of the signal for the ion $C_7H_7^+$ (evidently with the tropylium structure), which is characteristic of the electron impact mass spectra of alkylbenzenes [16]. The peak A_1 has low intensity for the acridindiones **1k-n** and the peaks for the cations A_2-A_7 are absent. In the high and medium mass number

TABLE 1. Mass-spectra of Decahydroacridine-1,8-diones **1a-n**

Compound	m/z (I_{rel}, %)	W_M
1a	386 (5), 385 (12), 384 [M$^+$] (52), 367 (14), 301 (23), 272 (100), 216 (57), 188 (32), 160 (19), 132 (12), 104 (10), 83 (19), 55 (15), 52 (6)	22.5
1b	357 (10), 356 (19.5), 355 [M$^+$] (84), 272 (100), 216 (29), 188 (18), 160 (11), 132 (8), 104 (5), 83 (10), 55 (8), 52 (7)	57.9
1c	365 (9), 364 (20), 363 [M$^+$] (76), 286 (100), 280 (19), 230 (49), 202 (36), 174 (25), 146 (17), 118 (12), 83 (11), 66 (9), 55 (5)	37.1
1d	395 (4), 394 (7), 393 [M$^+$] (26), 363 (17), 310 (11), 286 (100), 230 (53), 202 (39), 174 (27), 146 (20), 118 (13), 83 (14), 66 (12), 55 (14)	24.7
1e	355 (8), 354 (17), 353 [M$^+$] (70), 286 (100), 270 (20), 230 (48), 202 (33), 174 (24), 146 (17), 118 (9), 83 (16), 66 (7), 55 (12)	33.2
1f	400 (7), 399 (14), 398 [M$^+$] (58), 381 (32), 315 (27), 286 (100), 230 (53), 202 (36), 174 (28), 146 (19), 118 (12), 83 (20), 66 (9), 55 (16)	22.4
1g	371 (11), 370 (22.5), 369 [M$^+$] (92), 286 (100), 230 (31), 202 (21), 174 (14), 146 (9),118 (5), 83 (10), 66 (5), 55 (7)	62.1
1h	457 (8), 456 (16), 455 [M$^+$] (48), 425 (16), 372 (9), 348 (100), 292 (45), 274 (32), 236 (23), 208 (14), 180 (8), 128 (10), 83 (16), 55 (12)	25.3
1i	462 (8), 461 (17), 460 [M$^+$] (58), 443 (12), 377 (16), 348 (100), 292 (64), 274 (41), 236 (31), 208 (22), 180 (15), 128 (12), 83 (27), 55 (18)	23.2
1j	433 (16), 432 (30), 431 [M$^+$] (100), 348 (92), 292 (44), 274 (31), 236 (23), 208 (15), 180 (10), 128 (6), 83 (11), 55 (6)	61.3
1k	441 (3), 440 (6), 439 [M$^+$] (18), 368 (23), 348 (100), 292 (54), 264 (36), 236 (19), 208 (8), 91 (32), 83 (17), 55 (10)	9.0
1l	471 (2), 470 (4), 469 [M$^+$] (12), 439 (10), 378 (100), 368 (29), 322 (57), 294 (34), 266 (18), 264 (8), 238 (11), 236 (7), 91 (36), 83 (20), 55 (12)	5.3
1m	476 (2), 475 (5), 474 [M$^+$] (17), 383 (100), 368 (19), 327 (61), 299 (49), 297 (26), 271 (32), 243 (9), 241 (11), 213 (5), 91 (42), 83 (24), 55 (17)	6.1
1n	447 (3), 446 (7), 445 [M$^+$] (23), 368 (19), 354 (100), 298 (47), 270 (36), 242 (29), 214 (13), 91 (27), 83 (16), 55 (9)	9.1

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* Found, %: S 10.40. Calculated , %: S 10.33

range splintering peaks A_{12}-A_{15} are most characteristic, which arise from a decomposition scheme similar to the fragmentation of the 1,8-dioxodecahydroacridines **1a,b** which are not substituted on the nitrogen atom. The peaks of the cations A_8 and A_{10} observed in the spectra of compounds **1k-n** have considerably greater intensity than in their NH-, N-methyl, and N-phenyl analogs **1a-j**.

It should be noted that in all cases the nature of the substituent at position 9 has no effect on the decomposition pathways for the decahydroacridin-1,8-diones under the influence of electron impact.

Thus we have investigated the mass spectra of 9-aryl(hetaryl)-3,3,6,6-tetramethyldecahydroacridine-1,8-diones and discovered the basic directions of their dissociative ionization under the influence of electron impact. The factor which determines the decomposition pathways of the decahydroacridine-1,8-diones studied is the structure of the substituent at position 10. Fragmentation of these compounds is predominantly connected with the formation of pyridinium structures and subsequent retrodiene decomposition of the molecules. The results obtained can be used to determine the structures of decahydroacridine-1,8-diones and related compounds.

EXPERIMENTAL

Chromato-mass spectra were obtained with a Hewlett-Packard HP-5972A with an HP-5890 mass selective detector, using a capillary column packed with 5% methylphenylsilicone (30 m × 0.25 mm). The column temperature was 250°C, the carrier gas was nitrogen, and the ionization energy of the electrons was 70 eV.

The decahydroacridine-1,8-diones **1a-n** were synthesized by the known methods [3-5].

REFERENCES

1. P. Shanmugasundaram, K. J. Prabahar, and V. T. Ramakrishnan, *J. Heterocycl. Chem.,* **30**, 1003 (1993).
2. A. A. Bakibaev and V. D. Filimonov, *Zh. Org. Khim.,* **25**, 1579 (1989).
3. T. G. Nikolaeva, Yu. M. Shchekotikhin, A. S. Ponomarev, and A. P. Kriven'ko, *Khim. Geterotsikl. Soed.,* 475 (2000).
4. Yu. M. Shchekotikhin, T. G. Nikolaeva, G. M. Shub, and A. P. Kriven'ko, *Khim.-farm. Zhur.,* No. 4, 29 (2001).
5. Yu. M. Shchekotikhin, Yu. A. Getmanenko, T. G. Nikolaeva, and A. P. Kriven'ko, *Khim. Geterotsikl. Soed.,* 1344 (2001).
6. T. G. Nikolaeva, Yu. M. Shchekotikhin, Yu. A. Getmanenko, and A. P. Kriven'ko, *Khim. Geterotsikl. Soed.,* 416 (2000).
7. T. G. Nikolaeva, and Yu. M. Shchekotikhin, *Khim. Geterotsikl. Soed.,* 693 (2004).
8. J. Baldas and Q. N. Porter, *Tetrahedron Lett.,* 1351 (1968).
9. C. Dagher, R. Hanna, P. B. Terentiev, Y. G. Boundel, A. N. Kost, and B. I. Maksimov, *J. Heterocycl. Chem.,* **19**, 645 (1982).
10. P. Gupka, J. Bella, and A. Martvon, *Coll. Czech. Chem. Commun.,* **52**, 742 (1987).
11. U. Eisner and J. Kuthan, *Chem. Rev.,* **72**, 1 (1972).
12. C. S. Barnes and J. H. Occolowitz, *Austral. J. Chem.,* **16**, 219 (1963).
13. R. A. Khmel'nitskii, Yu. A. Efremov, and N. V. Fedyainov, *Izv TSKhA*, No. 3, 199 (1978).
14. J. Kuthan and A. Kurfurst, *Ind. Eng. Chem, Prod. Res. Dev.,* **21**, 191 (1982).
15. A. Maquestiau and P. Lejeune, *Bull. Soc. Chim. Belg.,***76**, 133 (1967).
16. F. W. McLafferty, *Mass Spectrometry of Organic Ions.* Academic Press, New York (1963), p. 10.