CONVERSION OF ARYLHYDRAZONES OF BROMONITROFORMALDEHYDE AND ARYLAZATRINITROMETHANES TO 3-ARYL-1,2,3,4-OXATRIAZOLIUM-5-ONES

M. N. Martynova, M. S. Pevzner,
N. A. Smorygo, and N. M. Serebryakova

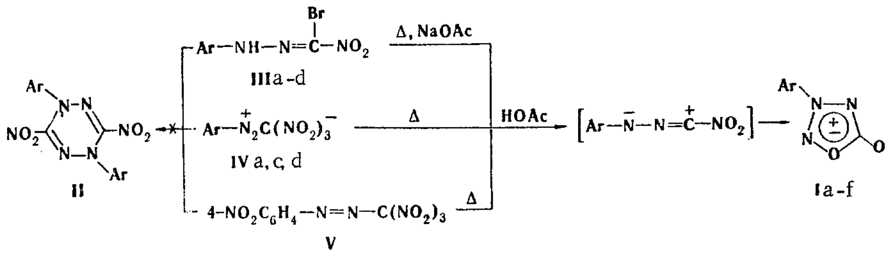
UDC 547.796.5

Mesoionic 3-aryl-1,2,3,4-oxatriazolium-5-ones rather than 1,4-diaryl-dihydro-3,6-dinitro-1,2,4,5-tetrazines, as previously assumed, are formed when arylhydrazones of bromonitroformaldehyde and arylazotrinitromethanes are heated in acetic acid.

When dinitroformaldehyde arylhydrazones, arylhydrazonomethanedisulfonates, arenediazonium salts of trinitromethane, and arylazotrinitromethanes are heated or treated with bases, they split out the elements of nitrous (or sulfurous) acid and are converted to cyclic compounds, to which a mesoionic 3-aryl-1,2,3,4-oxatriazolium-5-one structure (I) is assigned [1-4]. At the same time, according to the data in [5], 1,4-diaryl-1,4-dihydro-3,6-dinitro-1,2,4,5-tetrazines (II) are formed from bromonitroformaldehyde arylhydrazones.

It seemed strange that the similarly constructed arylhydrazones of dinitro- and bromonitroformaldehyde give different reaction products under similar conditions, although, according to [1, 5], both reactions proceed through the same intermediate. Unfortunately, detailed spectral data and the molecular masses are not presented in [5], and this makes it impossible to be completely convinced of the correctness of the structural conclusions.

To clarify this, we carried out the reaction of bromonitroformaldehyde arylhydrazones (IIIa-d) with sodium acetate by the method in [5] and investigated the structures of the products obtained by IR and UV spectroscopy and measurement of the dipole moments.



I a Ar=C_6H_5, b Ar=4-BrC_6H_4, c Ar=4-ClC_6H_4, d Ar=4-$NO_2C_6H_4$, e Ar=2-NO_2, 4-ClC_6H_3, f Ar=2,4-$(NO_2)_2C_6H_3$

Their elementary compositions (Table 1) correspond to structures I or III, but the molecular masses correspond to formula I (half the mass of II).

The IR spectra of the compounds (Table 2) that do not have nitro groups in the aryl substituent do not contain absorption bands that correspond to vibrations of the NO_2 group. Intense bands at 1750-1800 cm^{-1}, which correspond to C=O vibrations in mesoionic five-membered heterorings [6, 7] and most often appear in the form of a doublet, are observed in the spectra of all of the compounds. The same unusually high frequencies of C=O vibrations are also observed in the IR spectra of 3-alkyl-1,2,3,4-oxatriazolium-5-ones [8, 9]. Bands that can be assigned to the stretching vibrations of ring C—N and N—N bonds are present at 1000-1600 cm^{-1}. They are found in the same range of frequencies as the stretching vibrations of the C—N and N—N bonds in tetrazoles and other five-membered rings with four heteroatoms [10]. Absorption bands corresponding to phenyl C—H bonds are present in

---

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1682-1684, December, 1981. Original article submitted December 26, 1980.

0009-3122/81/1712- 1238$07.50

TABLE 1. 3-Aryl-1,2,3,4-oxatriazolium-5-ones

Compound	mp, °C	Found				Empirical formula	Calculated				Yield, % method
		C, %	H, %	N, %	M		C, %	H, %	N, %	M	
Ia	86 (98—100 [5])	52,3	3,3	26,3	163	$C_7H_5N_3O_2$	51,5	3,1	25,8	163	60 (A) 20 (B)
Ib	147 (158—160 [5])	34,7	1,6	17,1	246	$C_7H_4BrN_3O_2$*	34,7	1,7	17,4	242	35 (A)
Ic	132—133 (145—146 [5])	42,7	2,0	21,5	198	$C_7H_4ClN_3O_2$†	42,5	2,0	21,3	198	61 (A) 38 (B)
Id	168	39,0	2,2	27,6	208	$C_7H_4N_4O_4$	40,3	1,9	26,9	208	42 (A) 36 (B)
Ie	172—174	34,8	1,4	22,8	248	$C_7H_3ClN_4O_4$	34,7	1,2	23,1	243	11 (B)
If	125 (dec)	37,3	1,5	27,9	240	$C_7H_3N_5O_6$	33,2	1,2	27,7	253	23 (B) 17 (C)

---

*Found: Br 33.4%. Calculated: Br 33.0%.

†Found: Cl 18.8%. Calculated: Cl 17.9%.

TABLE 2. Physicochemical Properties of 3-Aryl-1,2,3,4-oxatriazolium-5-ones

Compound	IR spectrum, cm^{-1}					UV spectrum, λ_{max}, nm (log ε)	Dipole moment (solvent)
	C=O	C=N	$NO_{2\,as}$	$NO_{2\,s}$	C—N, N—N		
Ia	1790 v.s 1775 v.s	1540 w	—	—	1290 m; 1075 m	203 (4,06) 268 (4,07)	6,19±0,02 (benzene)
Ib	1802 v.s 1790 v.s	1530 w	—	—	1295 m; 1095 m	—	—
Ic	1810 v.s 1792 v.s	1530 w	—	—	1298, 1298 d; 1077 m	203 (4,06)	4,98±0,02
Id	1820 v.s 1782 v.s	1515 sh	1545 s	1325 m	1294 m —	203 (4,15)	2,77±0,2
Ie	1792 v.s	1515 sh	1535 s	1332 m	1294 cp; 1075 w	—	—
If	1840 v.s 1795 v.s	1500 m	1550 s	1340 m	1298 cp; 1082	—	—

the region of the stretching vibrations of C—N and N—H bonds, but no bands that could be ascribed to the NH group are present.

The UV spectra of the colorless compounds (Table 2) contain absorption maxima at 203, 218, and 266-276 nm, which correspond to the literature data for oxatriazoles I [3], but do not contain the maximum of bright-yellow tetrazines [5].

The compounds that we obtained have significant dipole moments (Table 2) that are in agreement with the data in [11] and the values calculated [12] for mesoionic oxatriazoles I; tetrazines II should have slight dipole moments. As expected, the introduction of an acceptor group (Cl, NO_2) in the para position of the phenyl substituent decreases the dipole moment in conformity with the vector contribution of these groups (compare Ia, c, d in Table 2).

Thus on the basis of the analytical and spectral data and the dipole moments, the compounds formed from bromonitroformaldehyde arylhydrazones are 3-aryl-1,2,3,4-oxatriazolium-5-ones (Ia-f) rather than dihydro-s-tetrazine derivatives (II).

To confirm this we carried out the thermolysis of benzene-, 4-chlorobenzene-, and 4-nitrobenzenediazonium salts of trinitromethane (IVa, c, d) and 4-nitrophenylazotrinitromethane (V) [13] in glacial acetic acid by a modified method [14, 15] and obtained identical compounds.

In the case of the thermolysis of 4-chloro- and 4-nitrobenzenediazonium derivatives we observed migration of one of the nitro groups of the trinitromethyl fragment to the ortho position of the phenyl ring to give 2,4-disubstituted phenyl derivatives of oxatriazole (Ie, f).

Similar migration of the nitro group was previously observed [16, 17] in the case of transformations of arenediazonium salts of phenyldinitromethane and phenylcyanonitromethane in ether.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral and fluorinated oils were recorded with an IKS-29 spectrometer. The UV spectra of solutions of the compounds in alcohol were recorded with a Perkin-Elmer 402 spectrophotometer. The dipole moments were determined on the basis of data on the dielectric permeabilities of solutions measured with a Tangens-214 apparatus and the refractive indexes in benzene and dioxane. The solvents were purified by the method in [18].

3-Aryl-1,2,3,4-oxatriazolium-5-ones (Ia-d). A) A mixture of 0.01 mole of the corresponding bromonitroformaldehyde arylhydrazone (IIIa-d) [19], 2.46 g (0.03 mole) of finely ground anhydrous sodium acetate, and 35 ml of glacial acetic acid was heated at 120°C for 3 h, after which it was cooled and poured into ice water. The resulting precipitate was washed with water, purified by means of column chromatography on silica gel [elution with ether—hexane (1:1)], and crystallized from ethanol (Table 1).

B) A 0.012-mole sample of the freshly prepared arenediazonium salt of trinitromethane (IVa, c, d) [13] was heated in 15 ml of glacial acetic acid at 65°C until the evolution of nitrogen oxides was complete (14 h). Compound Ia was isolated after evaporation of the solvent and was purified by method A. 1,2,3,4-Oxatriazolium-5-ones Ic–e were obtained as follows. The reaction mixture was cooled, and the precipitated Ie was removed by filtration and crystallized from ethanol [0.3 g (11%)]. Dilution of the filtrate with water gave 4-(p-chlorophenyl) derivative Ic [1.65 g (38%)]. The following procedure was used in the case of Id, f. Cooling of the reaction mixture precipitated Id [1.30 g (36%)], while dilution of the filtrate with water gave If [0.54 g (23%), crystallization from ethanol].

C) From 4-Nitrophenylazotrinitromethane (V) [13]. The reaction (carried out for 7 h) and the isolation of Id, f were carried out by method B.

LITERATURE CITED

1. Houben-Weyl, Methoden der Organischen Chemie, Bd. X/3, Stickstoffverbindungen I, Th. 3 (1965), pp. 507, 611.
2. S. Hünig and O. Boes, Liebigs Ann., 579, 28 (1953).
3. W. V. Farrar, J. Chem. Soc., 906 (1964).
4. G. Ponzio, Gazz. Chim. Ital., 63, 471 (1933).
5. L. C. Pupko, A. I. Dychenko, and P. S. Pel'kis, Khim. Geterotsikl. Soedin., No. 4, 759 (1969).
6. A. J. Paine and N. H. Werstiuk, Can. J. Chem., 56, 1319 (1978).
7. F. H. C. Stewart, Chem. Rev., 64, 129 (1964).
8. J. H. Boyer and F. C. Canter, J. Am. Chem. Soc., 77, 1280 (1955).
9. M. Hashimoto and M. Ohta, Bull. Chem. Soc. Jpn., 35, 766 (1962).
10. M. M. Sokolova, V. V. Mel'nikova, V. A. Ostrovskii, G. I. Koldobskii, and B. V. Gidaspov, Zh. Org. Khim., 11, 1744 (1975).
11. R. N. Hanley, W. D. Ollis, and C. A. Ramsden, J. Chem. Soc., Perkin Trans. I, 600 (1978).
12. K. Sundaram and W. P. Pursell, Internat. J. Quantum Chem., 2, 145 (1968).
13. M. S. Pevzner, A. K. Pan'kov, I. N. Shokhor, A. G. Gal'kovskaya, and L. I. Bagal, Zh. Org. Khim., 6, 1944 (1970).
14. A. Quilico, Gazz. Chim. Ital., 62, 912 (1932).
15. J. H. Boyer and J. A. Hernandez, J. Am. Chem. Soc., 78, 5124 (1956).
16. G. Ponzio and G. Charrier, Gazz. Chim. Ital., 39, I, 625 (1911).
17. G. Ponzio, Gazz. Chim. Ital., 39, II, 535 (1911).
18. A. Gordon and R. Ford, The Chemist's Companion, Wiley (1973).
19. L. S. Pupko, G. A. Lanchuk, and A. I. Dychenko, Ukr. Khim. Zh., 29, 610 (1963).