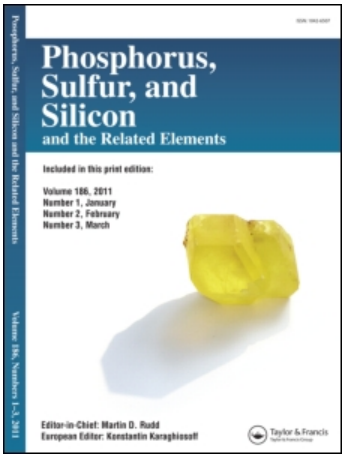

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AMINOLYSIS, HYDROLYSIS STUDIES AND X-RAY STRUCTURE OF 1,2,4-TRIAZOLE AND 1,2,4 -OXADIAZOLE FROM THE REACTION OF 1-AZA-2-AZONIAALLENE SALTS WITH ISOTHIOCYANATE*

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From the Hydrolysis of the 1,2,4-thiodiazolium salt of **(1)** in acetonitrile/sodium hydroxide solution the expected 1,2,4-oxadiazole adducts **3** could be isolated, and in addition, the 1,2,4-triazole adduct **4** was obtained from the aminolysis process. This is evidenced by spectroscopic and x-ray studies.

Keywords: Hydrolyses; X-ray structure; aminolysis; isothiocyanate

INTRODUCTION

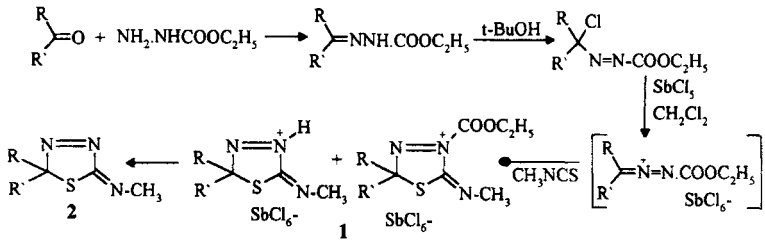
Like many azo alkane derivatives[1] 1-hydroxyl/or 1-amino 1,2-(1-adamantyl) diazine (**1′** or **1″**) has aroused some interest as a free radical source[2–4]. Apart from the investigation of the thermal stability[3–4] an attempt has been reported[3] to functionalize the hydroxyl and amino groups of **1′** and **1″**. Water or ammonia solution were anticipated to add to the azo functions. Notably, from the reaction of **1** in acetonitrile/sodium hydroxide the expected adduct, namely the 1,2,4-thiodiazole **2** could be isolated, and conformed by spectroscopic evidence. Instead, merely the 1,2,4-oxadiazole or 1,2,4-triazole has been isolated when acetonitrile/water or ammonia solution were used for hydrolysis or aminoly-

* Dedicated to Professor Ahmad Saleh Aly on the occasion of his 58th birhday.

† Correspondence Author.

sis. These compounds have been regarded to be the fragmentation products of the presumed intermediate diazenes **1′**. However, no complementing fragments containing the isothiocyanate moiety or the azo nitrogen atoms of the educt **1′** have been found. This lack of stoichiometry led to the reinvestigation of this reaction.

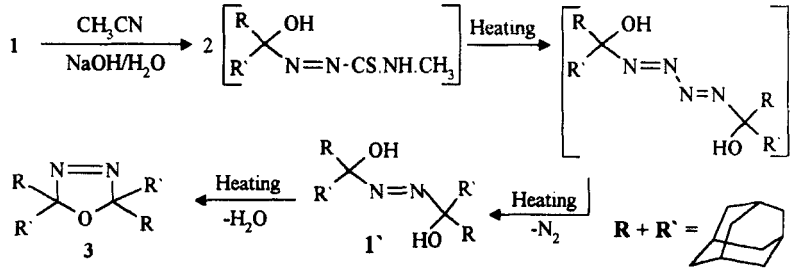
As against the notoriously high reactivity of organic diazocompounds toward protic nuclophiles, the high reactivity of bis (hyhydoxyalkyl)diazene **1′** is striking. Compound **1** has been noted for its activeness toward water, thus not permitting the formation of **2** (and its homologues) in aqueous solution. The hydrolysis of **1** with water or ammonia solution and prolonged heating at elevated temperature is requried to convert **1** into several products (Schemes 1, 2).



SCHEME 1

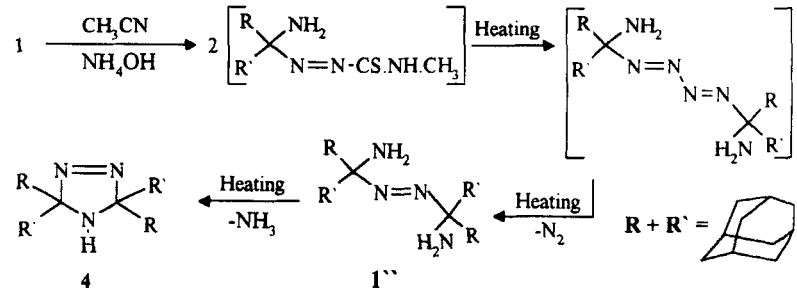
Adamantyl- and ethylhydrazone of adamantanone and hydrazinocarboxylic acid ethyl ester are transformed to the 1-chloroadamantylazo-derivative compound with t-butyl hypochlorite. The latter compound reacts with methylisothiocyanate in presence of antimony (V) chloride in methylene chloride to give 1-aza-2-azoniaallene salts as reactive intermediates, which are intercepted as a mixture of 3*H*-1,2,3-thiadiazo-lium salts **1** with isothiocyanate[5] (Scheme 1).

The solution of **1** (6.43g, 10 mmol) in acetonitrile (50 ml) and water (5 ml) was boiled under reflux for 10 hrs. After cooling the adduct was extracted by chloroform (100 ml) followed by evaporation of the solvent under reduced pressure. The solid residue upon addition of diethyl ether furnished colorless crystals of 1,2,4-oxadiazole-3,3–5,5-bisadamantane (**3**) in a good yield 2.33 g, (71%), (Scheme 2).



SCHEME 2

To a solution of 1 (6.43g, 10 mmol) in acetonitrile (50 ml) and ammonium hydroxide solution (20 ml, 40%) was added and the reaction mixture boiled under reflux for 14 hrs. After cooling, the adduct was extracted by chloroform (100 ml), and the solvent was evaporated under reduced pressure. The solid residue upon addition of diethyl ether furnished colorless crystals of **1**,2,4-triazole-3,3–5,5-bisadamantane (**4**) (1.99 g, 64%), (Scheme 3) .



SCHEME 3

^{1}H-, ^{13}CNMR and IR spectra of the new compounds are collected in Tables III and IV. We found it difficult to decide the cofiguration of the substituents on the adamantyl moiety. Therefore, an x-ray diffraction analysis of adducts **3** and **4** was carried out confirming the substitution at C3 and C5. The structure was solved using programs SHELXS-86[33] and SHELX-76[34] by the Patterson method with subsequent difference-Fou-

rier synthesis. The anisotropic refinement led to agreement factors $R_1 = 9.0\%$, $wR_2 = 13.8\%$. A molecular plot[6] for the adducts **3** and **4** is shown in figures 1, 2. Selected bond lenghts, bond angles and torsional angles are presented in Table I, II.

TABLE I Selected Bond Lengths (pm), Bond angles and Torsional Angles (deq) of the aduct **3**. (Monoclinic/p21/c, temp. 244(2)K, Wave lenght 0.71073)

N1-N2	1.243 (2)	N2-N1-C1	110.9 (2)
N2-C11	1.489 (3)	C1-O-C11	108.55 (14)
O-11	1.428 (2)	O-C1-C8	110.8 (2)
C1-C2	1.532 (3)	O-C1-C2	111.4 (2)
C11-C18	1,533 (3)	C8-C1-C2	109.6 (2)
N1-C1	1.495 (2)	O-C11-C12	110.5 (2)
O-C 1	1.425 (2)	O-C 11-C18	111.2 (2)
C1-C8	1.528 (3)	C12-C11-C18	109.8(2)
C11-C12	1.524 (3)	N1-N2-C11	111.2 (2)
O-C 1-C8-C7	177.6 (2)	N1-N2-C11-C12	-121.2 (2)
O-C11-C18-C17	-60.9 (2)	N1-N2-C11-O	-2.4 (2)

TABLE II Selected Bond Lengths (pm), Bond angles and Torsional Angles (deq) of the aduct **4**. (Monoclinic/p21/c, temp. 236(2)K, Wave lenght 0.70089)

N1-N2	1.248 (2)	N2-N1-C1	111.4 (2)
N2-C11	1.483 (3)	C1-N3-C11	119.21(14)
N3-C1	1.478 (2)	N3-C1-C8	109.8 (2)
C1-C2	1.542 (3)	N3-C1-C2	113.1 (2)
C11-C18	1,521 (3)	C8-C1-C2	109.4 (2)
N1-C1	1.473 (2)	N3-C11-C12	111.2(2)
N3-C1	1.485 (2)	N3-C11-C18	111.3 (2)
C1-C8	1.538 (3)	C12-C11-C18	109.9 (2)
C11-C12	1.519 (3)	N1-N2-C1 1	112.3 (2)
N3-C1-C8-C7	174.5 (2)	N1-N2-C11-C12	-122.2 (2)
N3-C11-C18-C17	-58.9 (2)	N1-N2-C11-N3	-2.2 (2)

TABLE III Physical, analytical and IR Spectral data of compounds **3** and **4**

Comp No.	*Yield (%)*	*m.p. °C*	*Mol. Form (Mol. wt)*	*Anal (Calcd./Found)*			*IR Spectral data Cm^{-1}*	
				C	*H*	*N*	*-NH*	*-N=N-*
3	71	155	$C_{20}H_{28}N_2O$ (3 12.4)	76.88 76.61	9.03 8.97	8.97 9.01	----	1560
4	64	123	$C_{20}H_{29}N_3$ (311.5)	77.12 77.09	9.38 9.44	13.49 13.57	3180	1548

TABLE IV ^{1}H-, ^{13}C-NMR Spectral data of compounds **3** and **4**

Comp. No.	*^{1}H-NMR, (δ), ppm ($CDCl_3$)*	*^{13}C-NMR, (δ), ppm ($CDCl_3$)*
3	1.56, 1.66, 1.71, 1.80, 1.86, 2.04, 2.05, 2.07, 2.12, 2.17, 2.54 and 2.59 (as multiplet signals for 28 protons)	26.87, 27.56, 34.43, 35.15, 37.39, 39.44, 123.29 for 20 sp^3 carbon atoms
4	1.53, 1.158, 1.68, 1.81, 1.88, 2.08, 2.15, 2.17, 2.19, 2.27, 2.58, 2.67 (as multiplet signals for 28 protons) and 4.69 broad band for NH	26.81, 27.44, 34.38, 35.19, 37.48, 39.56, 124.69 for 20 sp^3 carbon atoms

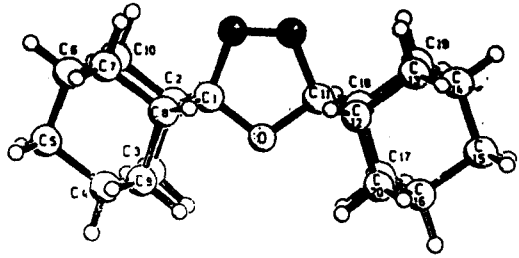


FIGURE 1

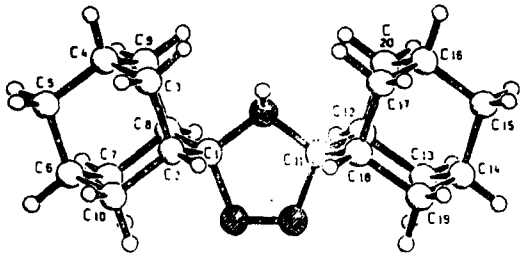


FIGURE 2

CONCLUSION

The present study offers a new method for the preparation of 1,2,4-oxadiazole and 1,2,4-triazole derivatives from triazolium salts. Also, the solving of the cofiguration around C3 and C5 by x-ray studies for the produced compounds.

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References

[1] J. G. Schantl, H. Gastach, P. Hebeisen, and N. Lanznaster, *Tetrahedron*, **41,** 5525 (1985).
[2] H. C. Lang and R. E. Macleay, US Pat. 4,028, 344 (1977); *Chem. Abstr.*, **87,** 103033p (1978).
[3] J. Akers, M. F. Dube, L. M. Trefonas, J. W. Timberlake, and R. Majeste, *Tetrahedron Lett.*, 5083 (1978).
[4] M. F. Dube, and, J. W. Timberlake, *Tetrahedron*, 1753 (1980).
[5] A. B. El-Gazzar and J.C. Jochims, **(Published results).**
[6] K.E. Schakal, a FORTRAN program for the grahpic representation of molecular models, Freiburg, 1980.