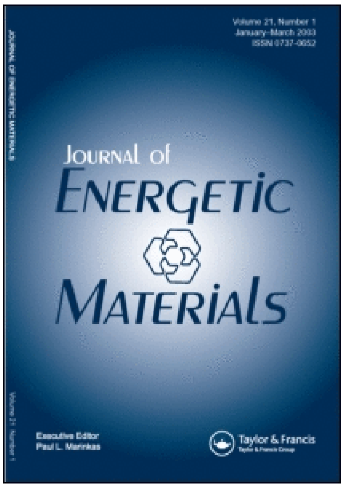

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Studies on energetic compounds: Part 6 synthesis of ring-substituted arylammonium salts of 3-nitro-1,2,4-triazole-5-one(NTO)

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To cite this Article Singh, Gurdip , Kapoor, Inder Pal Singh , Mannan, S. Muddi and Tiwari, Sunil Kumar(1998) 'Studies on energetic compounds: Part 6 synthesis of ring-substituted arylammonium salts of 3-nitro-1,2,4-triazole-5-one(NTO)', Journal of Energetic Materials, 16: 1, 31 — 43

To link to this Article: DOI: 10.1080/07370659808216092

URL: http://dx.doi.org/10.1080/07370659808216092

STUDIES ON ENERGETIC COMPOUNDS

PART 6# SYNTHESIS OF RING-SUBSTITUTED ARYLAMMONIUM SALTS OF 3-NITRO-1,2,4-TRIAZOLE-5-ONE(NTO)

Gurdip Singh*, Inder Pal Singh Kapoor
S. Mudi Mannan and Sunil Kumar Tiwari

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Gorakhpur - 273009, India

ABSTRACT

In continuation of our programme of preparing new energetic materials, fifteen arylammonium (having electron donating or attracting substituents) salts of 3-Nitro-1,2,4-triazole-5-one (NTO) have been synthesised and characterised. These compounds have been found to be ionic in nature.

Preceeding paper : Ref. 16

* Author to whom correspondence should be addressed.

Journal of Energetic Materials Vol. 16, 031-043 (1998)
Published in 1998 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

3-Nitro-1,2,4-triazole-5-one (NTO) has been reported to be a potential member of a class of high energetic explosives[1-4] and offers attractive explosive performance with a high degree of insensitivity[5,6]. A number of stable salts of NTO (acidic) with basic compounds have been reported by many workers, which are moderately sensitive to impact and are used as ingredients of gun propellants[7,8] and explosives[9-11]. However, these are reported to be more useful as compared to ammonium nitrate and ammonium perchlorate.

Although, a number of aliphatic amine salts of NTO are known but studies on ring-substituted arylamine salts of NTO are not yet reported in literature. Very recently, we have undertaken extensive investigations on nitrate[12-14], perchlorate[15-17] and sulphate[18-20] salts of aromatic amines. In continuation of our programmes of preparing new energetic compounds[21-23], we report here the synthesis and characterization of ring-substituted arylammonium (having electron donating/withdrawing substituents) salts of NTO. Further, TG, DTA and explosion delay data on these compounds have been presented in the proceeding paper (part 7) of the series.

EXPERIMENTAL

Materials :

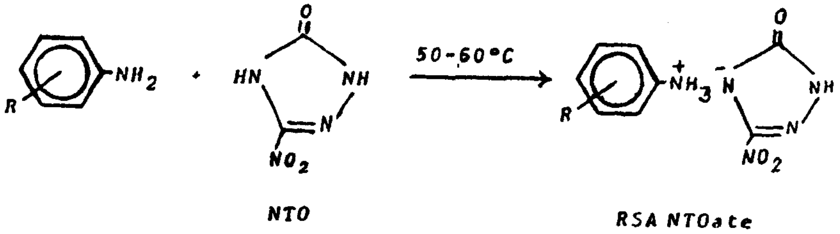
The following chemicals (obtained from the sources given in parentheses) were purified according to usual methods : aniline (Qualigens); 2-and 3-chloroanilines, 3-toluidine, 2-, 3- and 4-nitroanilines (Robert Johnson); 4-toluidine (BDH); 2-toluidine, 4-aminobenzoic acid, 3-anisidine (Merck); 4-anisidine (Burgoyne); 2-anisidine (Ranbaxy); 2-Phenetidine (Riedel-de Hain); 4-Phenetidine (Wilson). Semicarbazide hydrochloride (S.D. Fine Chemicals); formic acid, silica-gel (TLC, Merck) and nitric acid (AR,Qualigens) were used as received.

Synthesis of NTO :

NTO was prepared in gram batches in our laboratory by the method reported earlier[1,24,25] and characterised by gravimetric estimation, TLC and I.R. spectroscopy[2,26].

Synthesis of Ring-substituted Arylammonium Salts of NTO (RSA NTOates)

Aromatic amine salts of NTO were prepared by adding dropwise hot aqueous solution of NTO to the solution of corresponding arylamine in 1:1 molar ratio. The reaction is given below :



Where R = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-Cl, 3-Cl, 4-CO_2H, 2-NO_2, 3-NO_2, 4-NO_2, 2-OCH_3, 3-OCH_3, 4-OCH_3, 2-OC_2H_5 or 4-OC_2H_5.

The mixture was then heated at 50-60°C for 10-15 minutes with constant stirring. It has been found that aniline salt and salts having 3-CH_3, 3-Cl substituents were crystallised out on keeping the reaction mixture under vacuum (90 mm Hg) over night, whereas remaining salts appeared after 2-3 hours when kept in ice bath. All the salts were recrystallised from doubly distilled hot water to get amorphous/crystalline solids and these were dried under vacuum. The yield of all the salts having different colours was greater than 90%.

Characterisation of RSA NTOates :

All the salts were characterised by gravimetric estimation, TLC, conductivity and pH measurements. Their I.U.P.A.C. names, colour, crystal shape and melting point are reported in Table 1.

The purity of these salts was checked by TLC using different mobile phases and iodine was used as locating reagent. Brown coloured spots were obtained for most of the salts. However, yellow spot were obtained for salts having 3-CH_3, 3-Cl, 2-NO_2 groups. The R_f values for each salts are reported in Table 2.

Conductivity and pH Measurements on RSA NTOates :

The conductivity of RSA NTOates and NTO was measured in 0.005M aqueous solution at 18°C using digital conductivity meter (Chemito-CL01) with a conductivity cell (Cell constant = 0.748) and data are given in Table 2. pH of these salts was also measured in 0.005M aqueous solution at 18°C by digital pH meter (Century CP901) and data are reported in Table 2.

I.R. Studies on RSA NTOates :

I.R. on NTO, A NTOate, 3-CH_3A NTOate, 2-ClA NTOate and 3-ClA NTOate was taken in KBr pellet using Perkin-Elmer spectrometer. The important peaks are given below :

NTO :	ν_{max}; 3190-3210b, 2900s, 1710-1690b, 1530b, 1460s, 1340s, 1170s, 1000vs, 990vs, 810vs, 770s, 740s, 715vs, 670b, 590vs.
A NTOate :	1700s, 1630b, 1490s, 1360s, 1290vs, 1030s, 1000s, 765s, 725vs, 460s.

3-CH_3A NTOate: 1610-1585b, 1490b, 1360s, 1285s, 1140b, 1040vs, 995s, 765-755b, 730vs, 765vs, 600-590b, 420vs.

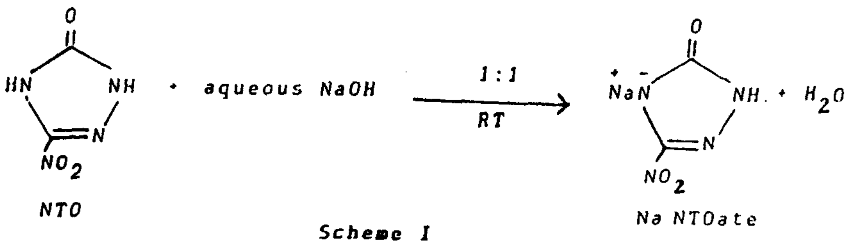
2-ClA NTOate : 3480-60b, 1610-1600b, 1500-1490b, 1365s, 1390vs, 1040vs, 1000vs, 770s, 730vs.

3-ClA NTOate : 3560s, 3180b, 1700b, 1530-20b, 1490-80b, 1365s, 1285vs, 1000s, 810vs, 765b, 710vs, 655s.

Gravimetric estimation

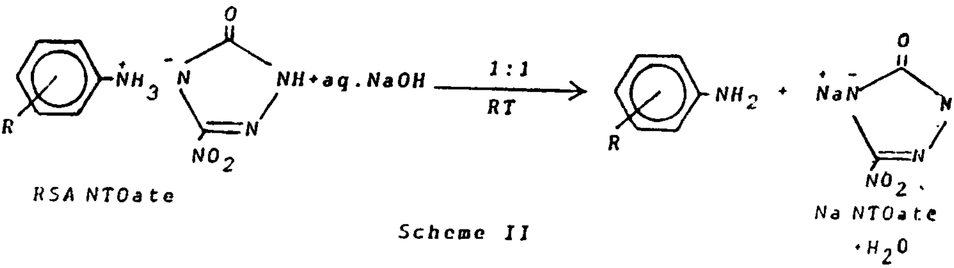
RSA NTOates have been found to dissociate in aqueous sodium hydroxide solution to form Na NTOates and free amines. Only Na NTOate was obtained in case of NTO. The amines were separated and Na NTOates were recovered from their respective solutions as described below

NTO (100 mg) was treated with aqueous sodium hydroxide in 1:1 molar ratio at room temperature (RT) and the mixture then concentrated on water bath at 50-60°C for 10-15 miuntes to get yellow crystalline Na NTOate (Scheme I). The later was then recrystallised from double distilled (DD) water and its purity was checked by TLC (R_f = 0.70; n-BuOH : Dioxane : water (7:6:1)) using authentic sample[24,25]. The experimental and theoretical weights of Na NTOates are given in Table 2.



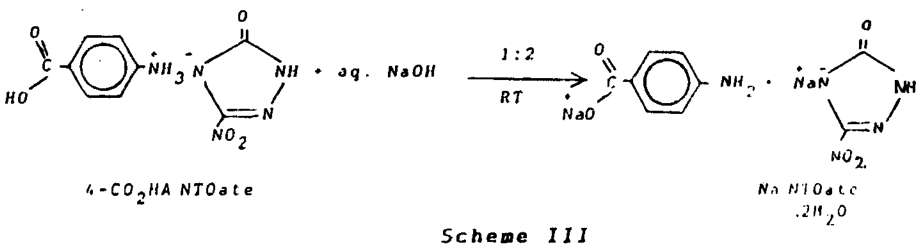
Scheme I

On treating 100 mg of RSA NTOate with aqueous NaOH in 1:1 molar ratio at RT, the former was found to dissociate to gave Na NTOate and corresponding arylamine (Scheme II). The solid amines were filtered out, whereas liquid amines separated by solvent extraction. Yellow crystalline Na NTOate was crystallised out on concentrating the aqueous layer. The experimental and theoretical weights of Na NTOate are reported in Table 2.



Scheme II

In case of 4-CO_2HA NTOate (Scheme III), both sodium (4-amino)-benzoate and Na NTOate were found to be soluble in aqueous NaOH and hence the later was separated by preparative TLC.



Scheme III

RESULTS AND DISCUSSION

pH, gravimetric, conductivity, TLC (Table 2) and I.R. spectra suggest beyond doubt that the interaction of NTO and arylamines leads to the formation of ionic salts (structures are presented in Table 3). It is inferred that their salt formation may be due to the transfer of more acidic proton of NTO (pka =

3.67)[26] to the basic nitrogen of amine. Moreover, the salt having meta substituents recrystallised out with difficulty. This may be due to the decrease of electron density at nitrogen of amine by -I effect of the substituent. The abnormal behaviour (-I effect) of 3-CH_3 has already been reported[12,15,27,28] earlier. Inspite of having chromophoric (-NO_2) and auxochromic (>NH) groups, colourless salts such as 2-CH_3 A NTOate and 2-ClA NTOate were obtained which may be due to the steric inhibition of resonance[29].

It is very clear from the conductivity data (Table 2) that all the salts are electrolytes. 3-NO_2 is a strong electron withdrawing group in 3-NO_2A NTOate which may cause the salt to dissociate to a greater extent and hence, highest value of conductance was observed for their salt. Moreover, lowest value for 4-CH_3A NTOate may be due to the strong +I effect of 4-CH_3 group. However, gravimetric estimation also suggest the ionic nature (salts) of RSA NTOates.

pH values reported in Table 2 suggest that all the salts are less acidic than NTO. Among the series, very low value of 2-NO_2A NTOate is undoubtedly due to -I and ortho effects. Moreover, high value of 4-OCH_3A NTOate, 4-OC_2H_5A NTOate and 4-CH_3A NTOate is due to strong inductive (+I), resonance and hyperconjugative effects, which cause the strengthening of N-H bond of arylamines.

ACKNOWLEDGEMENTS

Thanks are due to DRDO, Ministry of Defence and DST, New Delhi for financial assistance; DRDE, Gwalior for IR spectra and Head of Chemistry Department, Gorakhpur University, Gorakhpur for laboratory facilities.

REFERENCES

1. K.Y. Lee, L.B. Chapman and M.D. Coburn, J. Energ. Mat., 5, 27 (1987).
2. K.V. Prabhakaran, S.R. Naidu and E.M. Kurian, Thermochim. Acta, 241, 199 (1994).
3. H. Ostmark, H. Bergman and G. Aqvist, Thermochim. Acta, 213, 165 (1993).
4. B.C. Beard and J. Sharma, J. Energ. Mat., 11, 325 (1993).
5. K.Y. Lee and M.D. Coburn, Los Almos National Laboratory Report LA-10302, Los Almos, NM, 1985.
6. X.Yi, H. Rongzu, Y. Chaoging, F. Guofu and Z. Tihua, Propell., Explos., Pyrotech., 17, 298 (1992).
7. K.Y. Lee and M.D., Coburn, "3-Nitro-1,2,4-triazole-5-one, a Less Sensitive Explosive". U.S. Patent 4, 733, 610, 1988.
8. K.Y. Lee and N.M. Stinecipher, Propell., Explos., Pyrotech., 14, 241 (1989).
9. L. Jiarong, C. Boren, B. Yuxiang and Z. Neijue, Propell., Explos., Pyrotech., 16, 145 (1991).
10. T.P. Korkman, Zh. Organich Khimii, 16, 420 (1979).
11. K.Y. Lee, Report LA-UR-84-2038 (1984), Los Almos National Laboratory, Los Almos, NM, USA.
12. G.Singh and I.P.S. Kapoor, Combust. Flame, 92, 283 (1993).
13. G.Singh, I.P.S. Kapoor, S.M. Mannan and J.P. Agrawal, Combust. Flame, 97, 355 (1994).
14. G.Singh, I.P.S.Kapoor and S.M. Mannan, Thermochim. Acta, 262, 117 (1995).

15. G.Singh and I.P.S. Kapoor, J. Phys. Chem., 96, 1215 (1992).
16. G.Singh, I.P.S. Kapoor and S.M. Mannan, J. Energ. Mat., 13, 141 (1995).
17. G. Singh, I.P.S. Kapoor and S.M. Mannan, J. Therm. Anal., 46, 1751 (1996).
18. G. Singh and I.P.S. Kapoor, J.C.S. Perkin 2, 2155 (1989).
19. G. Singh, I.P.S. Kapoor and M. Jain, J.C.S., Perkin 2, 1521 (1993).
20. G. Singh, I.P.S. Kapoor and M. Jain, Indian J. Chem., 35B, 369 (1996).
21. G. Singh, M. Yunus and P. Srivastava, J. Therm. Anal., 30, 133 (1993).
22. G. Singh, I.P.S. Kapoor and S.M. Mannan, J. Energ. Mat., 12, 113 (1994).
24. A. Becuwe (Soc. Nat. des Poudres at Explo.), Fr. Denade FR. 2584066 (C1C06B 25/34) issued Jan. 2, 1987.
25. G. Cipens, R. Bokalders and V. Grinsteins, Khim, Geterotsikl Soedin, A. Kard, Nauk Latv. SSR, 2, 110 (1966).
26. T.P. Kafman, M.S. Pevzner, L.N. Zhukova, T.A. Kravchenko and G.M. Fralova, Zh. Org. Khim., 16, 375 (1980).
27. P.V.R. Schleyer and C.W. Woodworth, J. Am. Chem. Soc., 90, 6530 (1968).
28. T.H. Lowry and K.S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 1976, p.226, 229, 230.
29. I.L. Finar, "Organic Chemistry", Vol.1, 5th ed., 1970, pp823-826.

TABLE - 1

Physical Parameters for NTO and RSA NTOates

Compound No.	IUPAC Name	Acronym	Molecular formula	Colour	Crystal shape	Melting point (°C)
1.	3-Nitro-1,2,4-triazole-5-one	NTO	$C_2H_2N_4O_3$	White	Crystalline	d268
2.	Anilinium 3-nitro-1,2,4-triazole-5-onate	A NTOate	$C_8H_9N_5O_3$	Yellow	Crystalline	166
3.	2-Methylanilinum 3-nitro-1,2,4-triazole-5-onate	2-CH_3A NTOate	$C_9H_{11}N_5O_3$	White	Amorphous	188
4.	3-Methylanilinum 3-nitro-1,2,4-triazole-5-onate	3-CH_3 A NTOate	$C_9H_{11}N_5O_3$	Pink	Amorphous	d165
5.	4-Methylanilinum 3-nitro-1,2,4-triazole-5-onate	4-CH_3 A NTOate	$C_9H_{11}N_5O_3$	Yellow	Amorphous	d195
6.	2-Chloroanilinium 3-nitro-1,2,4-triazole-5-onate	2-Cl A NTOate	$C_8H_8N_5O_3Cl$	White	Crystalline	d265
7.	3-Chloroanilinium 3-nitro-1,2,4-triazole-5-onate	3-Cl A NTOate	$C_8H_8N_5O_3Cl$	Yellow	Crystalline	180
8.	2-Nitroanilinium 3-nitro-1,2,4-triazole-5-onate	2-NO_2 A NTOate	$C_8H_8N_6O_5$	Yellowish Orange	Amorphous	200
9.	3-Nitroanilinium 3-nitro-1,2,4-triazole-5-onate	3-NO_2 A NTOate	$C_8H_8N_6O_5$	Yellow	Amorphous	205
10.	4-Nitroanilinium 3-nitro-1,2,4-triazole-5-onate	4-NO_2 A NTOate	$C_8H_8N_6O_5$	Yellow	Crystalline	d233
11.	4-Carboxylanilinium 3-nitro-1,2,4-triazole-5-onate	4-CO_2H A NTOate	$C_9H_9N_5O_5$	Orange	Amorphous	197-199
12.	2-Methoxyanilinium 3-nitro-1,2,4-triazole-5-onate	2-OCH_3 A NTOate	$C_9H_{11}N_5O_4$	Yellowish white	Amorphous	169-171
13.	3-Methoxyanilinium 3-nitro-1,2,4-triazole-5-onate	3-OCH_3 A NTOate	$C_9H_{11}N_5O_4$	Yellowish brown	Amorphous	d159-161
14.	4-Methoxyanilinium 3-nitro-1,2,4-triazole-5-onate	4-OCH_3 A NTOate	$C_9H_{11}N_5O_4$	Yellow	Amorphous	d212-214
15.	2-Ethoxyanilinium 3-nitro-1,2,4-triazole-5-onate	2-OC_2H_5 A NTOate	$C_{10}H_{13}N_5O_4$	Greenish yellow	Amorphous	d187-190
16.	4-Ethoxyanilinium 3-nitro-1,2,4-triazole-5-onate	4-OC_2H_5 A NTOate	$C_{10}H_{13}N_5O_4$	Light yellow	Amorphous	d194-196

TABLE - 2

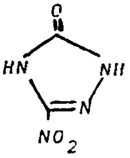
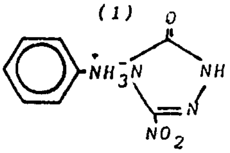
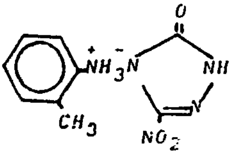
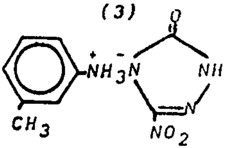
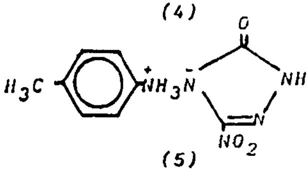
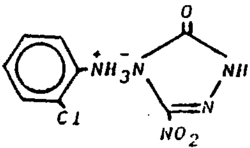
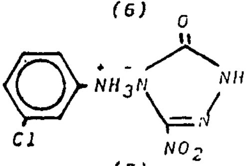
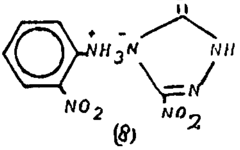
Analytical data, TLC, pH and conductivity measurements on NTO and RSA NTOates

Compd. No.	Wt. of Na NTOate (mg)		TLC		pH	Conductance $\mu\,\Omega^{-1}$ cm-1 at 291°K
	Theoretical	Experimental	Mobile phase	Rf		
1.	116.9	117.1	a:b:e:f:h (1:3:3:4:3)	0.84	2.96	10.2
2.	68.2	68.5	a:b:c:d:e (1:3:5:5:1.5)	0.87	3.83	9.1
3.	64.1	63.9	a:b:c:d:e (1:3:7:10:3)	0.67	4.21	18.0
4.	64.1	63.9	a:b:e:f:h (1:2:4:3:4)	0.93	4.35	13.3
5.	64.1	64.9	a:b:c:d:e (1:2:3:5:2)	0.82	4.49	9.4
6.	58.0	57.7	a:b:c:d:e (0.5:2:3:5:2)	0.90	3.03	17.1
7.	58.0	58.3	a:e:f:g:h (1:4:1.5:2.5:5)	0.90	3.65	17.0
8.	56.7	56.6	a:b:c:d:e (1:2:3:5:2)	0.94	2.98	10.0
9.	56.7	57.2	"	0.86	3.10	33.0
10.	56.7	57.1	"	0.91	3.02	18.6
11.	56.9	56.6	a:b:c:d:e (1:5:7:10:4)	0.99	3.38	18.3
12.	60.1	59.9	a:b:c:d:e (0.5:4:7:11:4)	0.86	4.21	19.2
13.	60.1	90.8	a:b:c:d:e (1:5:7:10:4)	0.91	4.04	10.1
14.	60.1	60.4	"	0.85	4.64	11.0
15.	56.9	57.2	a:b:c:d:e (0.5:4:7:11:4)	0.66	4.02	15.2
16.	56.9	56.5	"	0.77	4.60	11.3

where, a = water, b = Glacial acetic acid, c = Chloroform, d = Carbon tetrachloride, e = Dioxane, f = Ethyl methyl ketone , g = n-Hexane, h = Benzene.

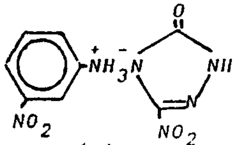
TABLE- 3

I.U.P.A.C. Names and Structures of NTO and RSA NTOateS

3-Nitro-1,2,4-triazole-5-One	 (1)
Anilinium 3-Nitro-1,2,4-triazole-5-Onate	 (2)
2-Methylanilinium 3-Nitro-1,2,4-triazole-5-Onate	 (3)
3-Methylanilinium 3-Nitro-1,2,4-triazole-5-Onate	 (4)
4-Methylanilinium 3-Nitro-1,2,4-triazole-5-Onate	 (5)
2-Chloroanilinium 3-Nitro-1,2,4-triazole-5-Onate	 (6)
3-Chloroanilinium 3-Nitro-1,2,4-triazole-5-Onate	 (7)
2-Nitroanilinium 3-Nitro-1,2,4-triazole-5-Onate	 (8)

Contd.

3-Nitroanilinium 3-Nitro-1,2,4-triazole-5-Onate



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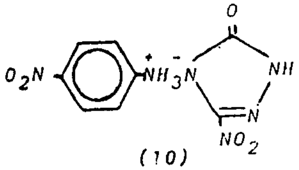
4-Nitroanilinium 3-Nitro-1,2,4-triazole-5-Onate



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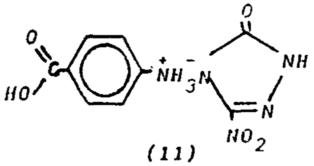
4-Carboxylanilinium 3-Nitro-1,2,4-triazole-5-Onate



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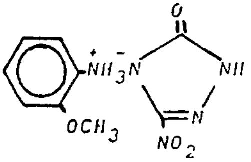
2-Methoxyanilinium 3-Nitro-1,2,4-triazole-5-Onate



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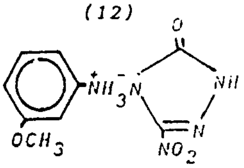
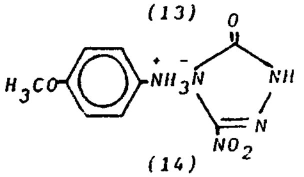
3-Methoxyanilinium 3-Nitro-1,2,4-triazole-5-Onate



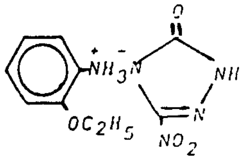
(13)

4-Methoxyanilinium 3-Nitro-1,2,4-triazole-5-Onate



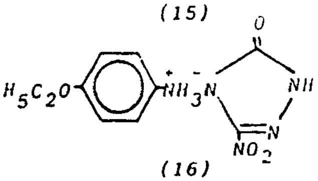
(14)

2-Ethoxyanilinium 3-Nitro-1,2,4-triazole-5-Onate



(15)

4-Ethoxyanilinium 3-Nitro-1,2,4-triazole-5-Onate



(16)