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Trinitromethanide and Tricyanomethanide Salts Restricted to C, H, N, and O Atoms

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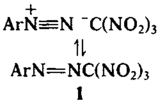
ABSTRACT

Trinitromethane combined with oximes of cyclopentanone, cyclohexanone, and diphenylcyclopropenone and with melamine and two 1,3-dialkyl-2,4-dialkylimino-1,3-diazetidines to give simple trinitromethanide salt adducts. Tricyanomethane added to diphenylcyclopropenone oxime to give hydroxylamino-2,3-diphenylcyclopropenylium tricyanomethanide.

INTRODUCTION

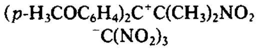
Utilization of the energy-rich trinitromethyl group in energetic molecules composed of C, H, N, and O atoms has been limited to a few ammonium trinitromethanide salts $RNH_3^+\ ^-C(NO_2)_3$ [1] and to molecules with covalent attachment of trinitromethyl to a carbon atom [2–5]. Examples of trinitromethyl attachment to an oxygen atom are unknown, and examples of the rarely encountered covalent attachment to a nitrogen atom are found in tetranitromethane and in arylazotrinitromethanes **1** in equilibrium mixtures with aryldiazonium trinitromethanides [6,7].

In a recent report on 2-nitropropan-2-ylbis-(*p*-methoxyphenyl)methylium trinitromethanide **2**, a steric inhibition toward the C–C covalent isomer was proposed [8]. A predominance of ionic over covalent C–C bonding to the trinitromethyl group in an organic molecule was also shown in our elucidation of the ionic structure of guanidinium trinitromethanide **3** without detection of a C–C covalent isomer [9–11].



$$\begin{array}{c} Ar\overset{+}{N}\equiv N\ ^-C(NO_2)_3 \\ \upharpoonleft\downharpoonright \\ ArN{=}NC(NO_2)_3 \end{array}$$

1



$$\begin{array}{c} (p\text{-}H_3COC_6H_4)_2C^+C(CH_3)_2NO_2 \\ ^-C(NO_2)_3 \end{array}$$

2

$(H_2N)_3C^+\ ^-C(NO_2)_3$

3

An interest in the discovery of additional molecules restricted to C, H, N, and O atoms with suppression of a covalent attachment of the trinitromethyl group to a carbon atom in favor of the dissociated isomeric trinitromethanide salt led to the present investigation. With recognition of the claim [2] that it does not yield isolable adducts with aldehydes and ketones other than formaldehyde, the addition of trinitromethane [$HC(NO_2)_3$, nitroform], pK_a 0 [2], to ketones, ketoximes, and amidines was selected for initial investigations. In contrast with a scarceness of literature on the 1,2-addition of trinitromethane to carbonyl and azomethine linkages, Michael additions to give β-trinitromethyl derivatives are well established [2].

RESULTS AND DISCUSSION

Molecules structurally related to trinitromethylcyclopropene **4** and/or cyclopropenylium trinitromethanide **5** and their derivatives were sought for the energy to be derived from both trinitromethyl and the strained ring [12–14]. When an adduct from cyclopropenone and nitroform, obtained as an impure unstable yellow viscous oil tentatively identified as hydroxycyclopropenylium trinitromethanide **6** on the basis of its absorption at λ_{max}(ethanol) 350 nm (see below), decomposed on storage and warming, our attention shifted to similar adducts from ketoximes.

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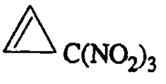

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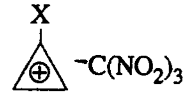
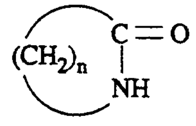


5 X = H

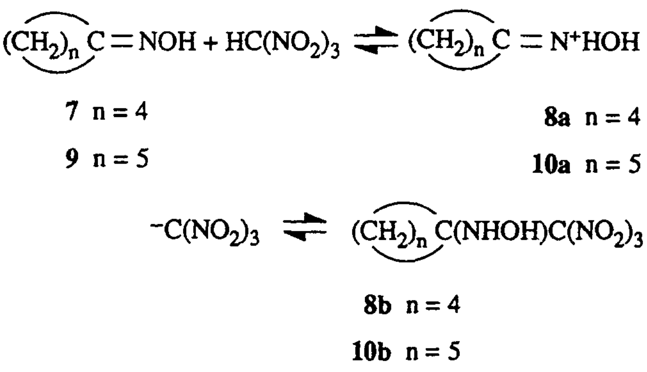
6 X = OH



11 n = 4

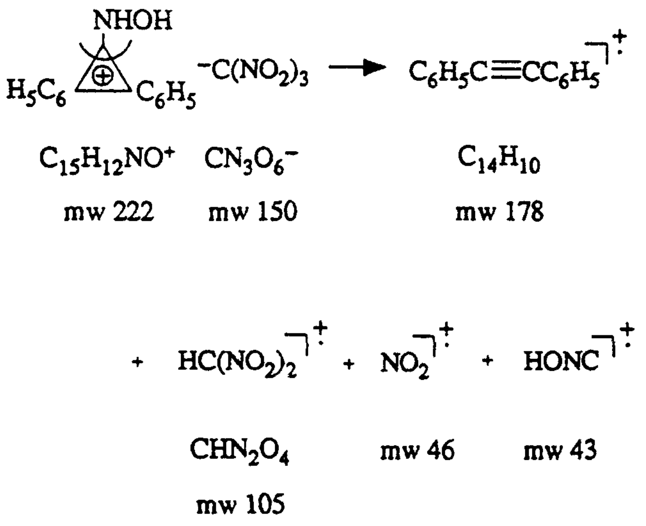
12 n = 5

Simple adducts from nitroform and ketoximes **7**, **9** were readily obtained as cyclopentanone and cyclohexanone oxime trinitromethanides **8a**, **10a** (Equation 1) isolated as viscous yellow oils. In each, the trinitromethanide anion was shown by UV absorption to be present: **8a** (ethanol), λ_{max} 350 nm, log ϵ 4.20; **10a** (ethanol), λ_{max} 350 nm, log ϵ 4.30; for comparison, potassium trinitromethanide gave absorption for the anionic chromophore at λ_{max} (ethanol) 350 nm, log ϵ 4.31 (Ref. [15] λ_{max} (water) 350 nm, log ϵ 4.16). Insofar as covalent trinitromethane derivatives including nitroform were transparent in this spectral region, the absence (or minimal presence) of the covalent isomers **8b**, **10b** was revealed by both the absorption and the molar absorption coefficient values. Facile thermal and hydrolytic dissociations of the adducts **8a**, **10a** regenerated nitroform and the oximes **7**, **9**. The absence of Beckmann rearrangements of oximes **7**, **9** to lactams **11**, **12** attested to noninteraction between the oxime hydroxyl function and nitroform or the trinitromethanide anion.



(1)

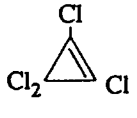
Somewhat more stable adducts from both nitroform and cyanoform [HC(CN)$_3$, tricyanomethane], pK_a −5 [2], with the oxime of diphenylcyclopropenone were readily obtained as amorphous yellow solids identified as hydroxylaminodiphenylcyclopropenylium trinitromethanide **13** and tricyanomethanide **14** on the basis of elemental and spectroscopic analysis. The hydroxylaminodiphenylcyclopropenylium cation was detected by (a) absorption at λ_{max} 310 nm, log ϵ 4.07 for compound **13** (ethanol) and at λ_{max} 312 nm, log ϵ 4.13 for compound **14** (ethanol) in close agreement with absorption at λ_{max} 312 nm, log ϵ 4.12 for the known hydroxylaminodiphenylcyclopropenylium chloride **15** (ethanol) and (b) IR absorption at v 1908 for compound **13** and v 1912 for compound **14** in agreement with absorption at v 1920 reported for the salt **15** [16]. The trinitromethanide anion was detected in compound **13** (ethanol) by absorption at λ_{max} 350 nm, log ϵ 4.15 (compare values above for potassium trinitromethanide). The tricyanomethanide anion was detected in compound **14** by IR absorption at v 2160 [17]. Further confirmation of the structure for the salt **13** was found in its EI-MS fragmentation pattern, Equation 2 (see the Experimental section).



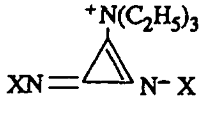
(2)

An attempt to obtain the trinitromethanide salt **13** from the corresponding chloride **15** [16] in an ion exchange reaction with potassium trinitromethanide was unsuccessful. Similar attempts to obtain diethylaminodiphenylcyclopropenylium and trisdiethylaminocyclopropenylium trinitromethanides **16**, **17** by treating the respective tetrafluoroborate **18** [18] and perchlorate **19** [19] with potassium trinitromethanide were also unsuccessful.

Although tetrachlorocyclopropene **20** reacted with a mixture of cyanamide and triethylamine at −30°C to give the zwitterionic product **21** [20], a replacement of cyanamide with nitramine [21] failed to give the zwitterion **22** and led instead to an intractable mixture, a result also obtained in reactions between tetrachlorocyclopropene **20** and either ethyl carbamate or hydrazine. An independent treatment with triethylamine brought about a dissociation of nitramine [22].

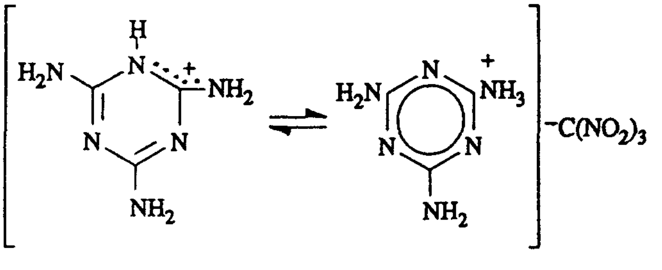


20



21 X = CN

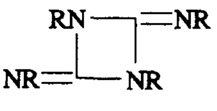
22 X = NO$_2$



23

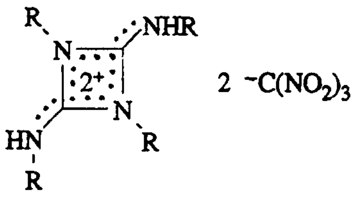
and equivalent structures

An extension of the investigation of guanidinium trinitromethanide **3** [9] led to the discovery of similar amidinium trinitromethanides. Melamine and nitroform readily gave a 1:1 yellow solid ionic adduct identified as melaminium trinitromethanide **23** by elemental analysis and absorption at λ_{max} (ethanol) 350 nm, log ϵ 4.15. Although di- and triprotonation of melamine were known [23], attempts to obtain 1:2 and 1:3 adducts between melamine and nitroform were unsuccessful. In a similar manner, unstable ionic yellow viscous oil adducts (1:2) **26** (*R* = isopropyl) and **27** (*R* = cyclohexyl), λ_{max} (ethanol) 350 nm, log ϵ 4.15 and 4.24, respectively, were obtained from the 1,3-dialkyl-2,4-dialkylimino-1,3-diazetidines **24**, **25** and nitroform.



24 R = (CH$_3$)$_2$CH

25 R = *c*-C$_6$H$_{11}$



26 R = (CH$_3$)$_2$CH

27 R = *c*-C$_6$H$_{11}$

The thermal instability of all trinitromethanide salts reported here precludes their practical application as energetic materials.

EXPERIMENTAL

Melting and decomposition points were determined on a Mel-Temp II apparatus and are uncorrected. Elemental analyses were obtained from Midwest Microlab, Indianapolis, IN. Instruments included the following: Perkin-Elmer 1600 series FT-IR, HP5985 (70 eV) GC/MS, and Cary 17 UV spectrometer. The preparation of potassium trinitromethanide from tetranitromethane [24], its conversion to nitroform [24], and reactions of nitroform were carried out in a hood. Potassium trinitromethanide was stored at 0°C; it should be handled as an unstable compound capable of decomposition on extended storage or warming [4]. Diphenylcyclopropenone was commercially available; its oxime was prepared as reported [16]. Melamine was commercially available. 1,3-Diisopropyl-2,4-bis(isopropylimino)-1,3-diazetidine **24** and 1,3-dicyclohexyl-2,4-bis(cyclohexylimino)-1,3-diazetidine **25** were prepared as reported [25]. Solvents were removed by rotary evaporation under reduced pressure. Analyses for nitrogen content were generally unsatisfactory and not reproducible. Similar results from attempted analysis for elemental nitrogen content in trinitromethyl derivatives were reported [4].

Nitroform

A suspension of potassium trinitromethanide (0.19 g, 1.0 mmol) and anhydrous ether (15 ml) in a three-necked RB flask equipped with a calcium chloride guard tube and a nitrogen inlet was held at 0–5°C. A solution of hydrogen chloride in ether was added in drops with stirring until the yellow color disappeared. Nitrogen was bubbled through the suspension for 15 minutes to remove hydrogen chloride. The colorless nitroform solution at 0–5°C was transferred to another three-necked flask by filtration.

Hydroxycyclopropenylium Trinitromethanide **6**

Cyclopropenone [26] (0.16 g, 3.0 mmol) was added to a solution of nitroform (0.45 g, 3.0 mmol) in ether (25 ml) and stirred for 2 hours at 0–5°C. Removal of ether left the salt **10** as a yellow viscous oil (0.15 g, 75%). IR (neat): ν 3028, 2984, 2900, 1590, 1305, 1097, 1073, 941, 837, 777, 626; UV (C$_2$H$_5$OH) λ_{max} 350 nm, log ϵ 4.14. Instability precluded its further purification.

Cyclopentanone Oxime Trinitromethanide **8a**

Cyclopentanone oxime (0.1 g, 1.0 mmol) was added to a solution of nitroform (0.15 g, 1.0 mmol) in ether (15 ml) at 0–5°C and stirred for 2 hours. Evaporation of the solvent left the salt **8a** as a viscous yellow liquid (0.22 g, 88%). IR (neat): ν 3441, 2890, 1592, 1487, 1404, 1272, 1158, 1066, 940, 787; UV (C$_2$H$_5$OH) λ_{max} 350 nm, log ϵ 4.20. Attempts at further purification were unsuccessful.

Cyclohexanone Oxime Trinitromethanide **10a**

Treatment of cyclohexanone oxime (0.11 g, 1.0 mmol) with a solution of nitroform (0.15 g, 1.0

mmol) in ether (15 ml) at 0–5°C for 2 hours gave the salt **7** as a yellow viscous liquid (0.24 g, 90%) after solvent was removed under vacuum at 20°C. IR (neat): ν 3421, 2945, 1591, 1545, 1484, 1282, 1158, 1061, 941, 787; UV (C_2H_5OH) λ_{max} 350 nm, log ϵ 4.30. Anal. calcd. for $C_7H_{12}N_4O_7$: C, 31.82; H, 4.55. Found: C, 32.55; H, 4.57.

Water (20 ml) was added to the salt **10a** (2.0 g, 7.5 mmol), and the mixture was stirred for 20 hours at room temperature. It was extracted with dichloromethane (3 × 20 ml), and the combined extracts were washed with water (1 × 10 ml) and dried over anhydrous magnesium sulfate. Evaporation left cyclohexanone oxime (0.11 g, 13%) which melted at 89°C (Ref. [27] 87–88°C). A similar hydrolysis of the salt **8a** gave cyclopentanone oxime.

Hydroxylamino-2,3-diphenylcyclopropenylium Trinitromethanide **13**

2,3-Diphenylcyclopropenone oxime (0.22 g, 1.0 mmol) was added at 0–5°C to a solution of nitroform (0.15 g, 1.0 mmol) in ether (15 ml) and stirred for 6 hours. After isolation, washing with cold pentane, and drying under a vacuum, the salt **13** was obtained as a yellow solid (0.32 g, 85%), mp 75–76°C (dec). IR (KBr): ν 3221, 2976, 2814, 1908, 1597, 1542, 1277, 787, 734; UV (C_2H_5OH): λ_{max} 350 nm, log ϵ 4.15. Anal. calcd. for $C_{16}H_{12}N_4O_7$: C, 51.61; H, 3.23. Found: C, 51.23; H, 3.36. EI-MS, *m/z* (%): 178 (88), 105 (96), 77 (100), 51 (77), 50 (44), 46 (42), 43 (56). Diphenylacetylene, mw 178, was known to give the fragments *m/z* 77, 51, and 50 [28].

Hydroxylamino-2,3-diphenylcyclopropenylium Tricyanomethanide **14**

Diphenylcyclopropenone oxime (0.11 g, 0.5 mmol) was added to a moist ether solution of cyanoform [29] obtained without isolation from potassium tricyanomethanide (0.07 g, 0.5 mmol) [30]. The mixture was stirred for 1 hour at room temperature, filtered, washed several times with cold water, and dried in vacuum to give the salt **14** as a pale yellow solid (0.1 g, 65%), mp 132°C (dec). IR (KBr): ν 3086, 2852, 2160 ($^-C(CN)_3$) [17], 1912 (hydroxylaminocyclopropenylium cation) [16], 1597, 1569, 1448, 1406, 1083, 946, 763, 681, and 567. Anal. calcd. for $C_{19}H_{12}N_4O$: C, 73.08; H, 3.85. Found: C, 72.97; H, 4.05.

Melaminium Trinitromethanide **23**

Melamine (0.13 g, 1.0 mmol) was added to a stirred solution of nitroform (0.15 g, 1.0 mmol) in ether at 0–5°C. After stirring for 2 hours, a yellow solid was isolated, washed with cold pentane, and dried in vacuum to give the salt **23** (0.22 g, 78%), mp 155°C (dec). IR (KBr): ν 3124, 1683, 1489, 1421, 1275, 1177, 793, 733; UV (C_2H_5OH) λ_{max} 350 nm, log ϵ 4.15. Anal. calcd. for $C_4H_7N_9O_6$: C, 17.33; H, 2.53; N, 45.49. Found: C, 17.80; H, 2.65; N, 45.10.

1,3-Dialkyl-2,4-bis(alkylimino)-1,3-diazetetidinium Bistrinitromethanides **26, 27**

1,3-Diisopropyl-2,4-bis(isopropylimino)-1,3-diazetidine **24** (0.26 g, 1.0 mmol) was added at 0–5°C to a solution of nitroform (0.30 g, 2.0 mmol) in ether (20 ml) and stirred for 6 hours. Evaporation of the solvent afforded the salt **26** as a yellow viscous oil (0.5 g, 90%). IR (neat): ν 1676, 1542, 1288, 742; UV (C_2H_5OH) λ_{max} 350 nm, log ϵ 4.15. A similar treatment of 1,3-dicyclohexyl-2,4-bis(cyclohexylimino)-1,3-diazetidine **25** (0.41 g, 1.0 mmol) with nitroform (0.30 g, 2.0 mmol) gave the salt **27** as a yellow viscous oil (0.6 g, 85%). IR (neat): ν 1651, 1540, 1262, 733; UV (C_2H_5OH) λ_{max} 350 nm, log ϵ 4.24. Instability precluded further purification.

ACKNOWLEDGMENT

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