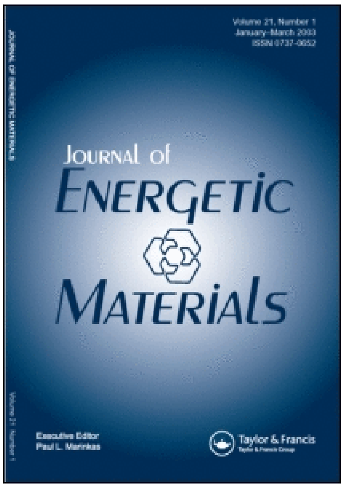

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THE REACTION OF TNT, AND RELATED COMPOUNDS, WITH FORMALDEHYDE

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ABSTRACT

An improved procedure was developed for preparing 1-(2-hydroxyethyl)-2,4,6-trinitrobenzene (I-A) from TNT and one mole of formaldehyde. The trinitro derivatives of ethylbenzene, 1,3-xylene, and mesitylene react similarly. Two of the compounds can also react with more than one mole of formaldehyde. Five related compounds are unreactive, probably because of steric hindrance. Several derivatives were prepared.

BACKGROUND

1-(2-Hydroxyethyl)-2,4,6-trinitrobenzene (I-A) was first prepared many years ago by Vender[1] by heating TNT (I) with aqueous formaldehyde in the presence of a weak base:

$$\underset{\text{(I)}}{\mathrm{PiCH_3}} + \mathrm{CH_2O} \longrightarrow \underset{\text{(I-A)}}{\mathrm{PiCH_2CH_2OH}}$$

(Pi = 2,4,6-trinitrophenyl)

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Although I-A has since then proved a convenient starting material for making 2,4,6-trinitrostyrene[2,3,4] and several other TNT derivatives,[5,6] only two brief attempts to improve the method of preparation have been reported[2,3] and there have been no efforts to extend the reaction to analogues of TNT. Accordingly, as part of our program on the chemistry of TNT and related compounds [7,8,9,10,11] we report herein our observations regarding this useful reaction, and the results of our efforts to extend it to similar materials. The compounds studied, and a summary of the results obtained, are given in Table 1.

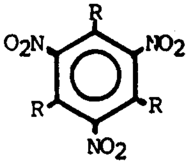
PREPARATION OF I-A

I-A was prepared by Vender by heating I with 37% formaldehyde and potassium bicarbonate or sodium hydroxide[12]. In our hands, this procedure with the former gave a light brown product containing 83.2% I-A; sodium hydroxide gave either excessive tar formation, or no reaction, depending upon the strength used. Our best result with this method yielded a crude product containing 93.0% I-A; this was obtained with sodium carbonate. Details are given in the Experimental Section.

The only effort to improve the Vender procedure is that reported by Bonecki and Urbanski[3]. They maintained an unstated alkaline pH by the incremental addition of potassium carbonate; the reaction mixture was neutral at the end of reaction. In our hands, this approach gave only partial conversion of I to I-A, and did not appear promising.

TABLE 1.

Structures of Compounds Studied and Summary of Results



Values of R	Designation	Extent of Reaction[a]
H, H, CH_3	I	1 (I-A),2[b] (I-B)
H,CH_3,CH_3	II	1 (II-A), 2 (II-B),3[b]
CH_3,CH_3,CH_3	III	1 (III-A)
CH_3,CH_3,$-C(CH_3)_3$	IV	0
H, H, $-CH_2CH_3$	V	1 (V-A)
H, H, $-CH(CH_3)_2$	VI	0
H, $-CH(CH_3)_2$, $-CH(CH_3)_2$	VII	0
H, H, $-CH_2Pi$	VIII	0
H, H, $-CH_2CH_2Pi$	IX	0

[a] Moles formaldehyde reacting per mole substrate; product designation in parenthesis

[b] Possible: See discussion in the text.

The use of an organic reaction solvent in the preparation of I-A was first mentioned in the literature only recently[2]. An earlier unpublished report[13], citing acetone as giving good results, was confirmed in the present study, and several other solvents were then screened by us for comparison. Tetrahydrofuran (THF) was expecially promising, since it gave 88-95% yields of light-colored crude product containing 97-99% I-A, and less than 2% unreacted I. It was adopted for our preferred procedure for preparing I-A and other compounds; details are given in the Experimental Section. Acetone gave somewhat darker products in 82-87% yield containing 96-98% of I-A. Comparatively low yields of dark I-A were obtained using N,N-dimethylformamide, dimethyl sulfoxide, sulfolane, 2-methoxyethanol or methanol; no reaction occurred in repeated tests with dioxane. We also obtained a dark product by a recent procedure[2] comprising refluxing I in methanol with paraformaldehyde and sodium acetate.

The only reaction product noted in past work from the reaction of I with formaldehyde was I-A. In our studies, the use of a substantial excess of formaldehyde also gave a viscous oil by evaporation of the solvent used to recrystallize the crude I-A. This material could also be prepared by further reacting pure I-A with formaldehyde by the same procedure used to make I-A from I. Attempts to crystallize the oil, or to obtain solid derivatives, were unsuccessful. However, the IR spectrum and analytical data tentatively suggest the structure $PiCH(CH_2OH)_2$ (I-B), resulting from the overall reaction of I with two moles of formaldehyde. It was converted to an oily diacetate of correct elemental analysis and IR spectrum. That I-A could be easily converted to I-B seems likely by analogy to the facile reaction of V to form V-A, as noted below. As discussed later, II also formed oily products by reaction with excess formaldehyde. Further study of these materials is required to make definite structural assignments.

REACTION WITH TNT ANALOGUES

We next undertook a brief study of the reaction of formaldehyde with other derivatives of 1,3,5-trinitrobenzene, since there was no mention of such in the literature. The results obtained are summarized in Table 1.

1,3-Dimethyl-2,4,6-trinitrobenzene (II) reacted easily with one mole of formaldehyde to give the monohydric alcohol II-A, and with two moles to form a diol, show by NMR analysis of two of its derivatives to be 1,3-bis(2-hydroxyethyl)-2,4,6-trintrobenzene (II-B). It was converted to a diacetate, a dinitrate, and a disulfate; with excess formaldehyde, II - like I - gave a viscous oil which could not be crystallized and was not studied further.

1,3,5-Trimethyl-2,4,6-trinitrobenzene (III), on the other hand, gave only a low yield of a 1:1 product even under forcing conditions (excess formaldehyde and base, long reaction time). Also, unlike the other trinitro compounds which reacted with formaldehyde, no reaction of III occurred with THF as solvent, although reaction did take place in acetone. These remarkable differences in reactivity between II and III are apparently symptomatic of steric crowding arising from the introduction of the third methyl group; that such can be a problem with alkyl derivatives of 1,3,5-trinitrobenzene has been discussed by Liss and Lohmann[14]. It was therefore not surprising that 1,3-dimethyl-5-tert.-butyl-2,4,6-trinitrobenzene (IV) did not react at all.

Ethyl-2,4,6-trinitrobenzene (V) reacted normally with one mole of formaldehyde, but the isopropyl analogue (VI) did not react, even with a greatly extended time. The diisopropyl compound (VII) also did not react. It is evident that the addition of a methyl group to the side chain in going from V to VI is sufficient to completely prevent reaction. On the other hand, addition of a methyl group to the ring in going from II to III, greatly inhibits reaction, but does permit a low yield of product.

In compounds VIII and IX, the high inductive effective resulting from the presence of two trinitrophenyl groups should result in potentially very easy reactivity with formaldehyde, but again reaction appears sterically impossible.

EXPERIMENTAL SECTION

Melting points were taken on a Thomas Hoover apparatus and are uncorrected. Infrared spectra were determined in KBr pellets with a Model 457A Perkin Elmer spectrophotometer. NMR spectra were obtained with a Varian T-60 spectrometer using tetramethylsilane as internal reference. Military Grade TNT (ca. 99% pure) was used. Compound IV is commercially available. Published procedures were used to make compounds II[15], III[16], V[17], VI[18], VII[18], VIII[19] and IX[9]. Product samples were analyzed by high performance liquid chromatography using a reverse-phase C-8 10 micron column (25 cm.x 0.46 mm.) at 40°. The mobile phase was 12% acetonitrile, 30% methanol, and 50% water at 2 ml./min. flow rate with a UV detector at 217 nannometers, and injection of 25 microliter samples. Sample weights were 11-18 mg. in 50 ml. acetonitrile. The procedure was calibrated using pure compounds as external standards.

<u>1-(2-Hydroxyethyl)-2,4,6-trinitrobenzene (I-A):</u>

1) By the modified Vender procedure.

I (5.0 g - 22 mmole) and a solution of anhydrous sodium carbonate (0.05 g - 0.47 mmole) in 2.5 ml (31 mmole) 37% formaldehyde were mixed and heated under reflux with vigorous magnetic stirring in a water bath at 90-95° for 2 hrs. The reaction mixture was poured into 50 ml water, the flask was rinsed with a small quantity of acetone, and the solution was acidified with 5 ml 10% hydrochloric acid. The oily product solidified on standing over night. It was filtered and dried; the yield was 4.9 g (88%); mp 100-4°. chromatographic analysis showed 93% I-A, 3.0% I, and 4.0% unknown. Recrystallization from toluene gave mp 108-10°; a second recrystallization from isopropanol gave mp 110-12° (lit.112° [1,2,3]).

Variations in the above procedure gave inferior results. Tests with potassium bicarbonate and with sodium hydroxide are mentioned above; potassium carbonate gave a product containing 88.6% I-A. Dark products resulted from using larger amounts of sodium or potassium carbonate. The use of excess 37% formaldehyde gave oily products, as mentioned above, probably from the reaction of two moles of formaldehyde per mole of I. Dilution of the usual quantity of 37% formaldehyde with an equal volume of water resulted in partial reaction. A reaction time of 1-2 hrs is satisfactory, but the reaction was incomplete in 0.5 hr. No advantage was noted in the use of recrystallized TNT compared to the Military Grade.

2) By the solvent procedure.

A solution of anhydrous potassium carbonate (0.6 g - 4.3 mmole) in 37% formaldehyde (12.0 ml - 147 mmole) was added all at once with stirring to a hot solution of I (13.5 g - 59 mmole) in THF (75 ml). The mixture was refluxed with stirring for 1 hr, poured into 400 ml water, and acidified with a small amount of hydrochloric acid. The crystals, which formed upon standing over night, were filtered and dried. The yield was 14.0 g (92%), mp 105-7°; chromatographic analysis showed 99.6% I-A and 0.3% I. Recrystallization from isopropanol gave mp 110-2°; IR: 3560 (OH), 3090, 1600, 1530 (NO_2),1350 (NO_2), 1040 (CH_2OH), 910,740,720 cm^{-1}.

The ammonium sulfate derivative of I-A, $\underline{\mathrm{PiCH_2CH_2OSO_3NH_4}}$, was prepared by adding chlorosulfuric acid (7.0 g) dissolved in dichloromethane (50 ml), dropwise with stirring at room temperature, to I-A (13.0 g) suspended in the same solvent (50 ml). After stirring for 0.5 hr, the solvent was decanted from the solid, and the latter was washed with a portion of fresh solvent. The solid was dissolved in isopropanol (400 ml) and a slight excess of 15% ammonium hydroxide was added with stirring to precipitate the product as a thick slurry. It was filtered and dried; yield 16.8 g (95% of theory); mp 235° (dec.) (ex isopropanol-water). IR: 3170(NH_4^+), 3080, 1600, 1530(NO_2), 1425 (SO_4), 1340(NO_2), 1240 (SO_4), 1210(SO_4), 1050, 1025, 970, 910, 750, 600 cm^{-1}.

Anal.: Calc'd: C,27.1; H,2.8;S,9.0; found: 27.1; 2.9; 8.9%.

The reaction of I-A with more formaldehyde to form what may be $PiCH(CH_2OH)_2$ (I-B), was effected by refluxing a mixture of I-A (2.6 g-10 mmole), 37% formaldehyde (4 ml - 49 mmole), anhydrous potassium carbonate (0.2 g - 1.5 mmole), and THF (25 ml) for 3.0 hrs. Workup as usual gave a viscous purple oil which did not crystallize; it was extracted with boiling water. Extraction of the cold water solution with dichloromethane gave I-B as a yellow oil which also did not crystallize. IR: 3360(broad-OH), 3090, 1600, 1530(NO_2), 1350(NO_2), 1040(CH_2OH), 910, 720 cm^{-1}. Anal.: Calc'd: C,37.6;H,3.1;N,14.7; found: 38.5; 3.0; 14.6%. The diacetate of I-B was prepared by refluxing it (1.5 g) with acetic anhydride (5 ml) for 5 hrs. The product was poured into water and extracted with dichloromethane; evaporation gave the oily diacetate. IR: 3080, 2960, 2880, 1730(acetate), 1600, 1540(NO_2), 1350 (NO_2), 1225 (acetate), 1040, 910, 810, 720 cm^{-1}. Anal.: Calc'd: C,42.1; H,3.5; N,11.3; found: 42.4; 3.7; 11.6%.

1-(2-Hydroxyethyl)-3-methyl-2,4,6-trinitrobenzene (II-A):

II (1.0 g -4 mmole), 37% formaldehyde (0.3 ml - 4 mmole), anhydrous potassium carbonate (0.1 g - 0.7 mmole), and THF (15 ml) were refluxed for 1 hr and worked up as above. The solid product (0.9 g) was extracted with boiling 15% nitric acid. The insoluble portion (0.5 g) was identified as unreacted II. Cooling the solution gave II-A,(0.3 g), a white solid, mp 117-9°, IR: 3320 (OH), 3100, 1520 (NO_2), 1340 (NO_2), 1040(CH_2OH), 900, 740 cm^{-1} Anal.: Calc'd: C,39.8; H,3.3;N, 15.5; found: 39.8; 3.4; 15.6%.

1,3-Bis-(2-hydroxyethyl)-2,4,6-trinitrobenzene (II-B):

II (10.0 g - 40 mmole), 37% formaldehyde (16 ml - 200 mmole - 100% excess), anhydrous potassium carbonate (0.8 g - 5.8 mmole), and THF (100 ml) were refluxed for 0.5 hr and worked up as above. The yield was 11.6 g (94%), mp 170-2°; recrystallization from butanol gave mp 171-3°; IR: 3200 (OH), 1530 (NO_2), 1350 (NO_2), 1040 (CH_2OH), 910,740 CM^{-1}. Anal.: Calc'd: C,40.0; H, 3.7 ; N, 14.0; found: 40.0; 3.6; 14.0. Incomplete reaction resulted from using the above conditions with only a 50% excess of formaldehyde at a reaction time of 0.25 hr.

The diacetate of II-B was prepared by refluxing it (0.5 g) with acetic anhydride (5 ml) for 1 hr. The cooled solution gave a solid (0.6 g- 93%) upon trituration with ice water, filtering and drying; mp 84° (ex methanol); IR: 3100, 1740 (acetate), 1040, 740 cm^{-1}; NMR (acetone d_6): δ1.9(s,6,$OCOCH_3$), δ3.1-3.5(t,4,$ArCH_2$), δ4.1-4.5(t,4,CH_2OAc), δ8.8(s,1,ArH). Anal.: Calc'd: C,43.6; H,3.9; N,10.9; found: 43.9; 4.0; 10.7%.

The dinitrate of II-B was prepared by stirring it (4.0g) with 90% nitric acid (12 ml) and dichloromethane (35 ml) in a test tube at 10° for 1 hr. The solution was washed with ice water, dried, and the solvent was removed, giving a viscous oil which soon solidified. It had mp 85-7° (ex-butanol); IR: 1625 (ONO$_2$), 1550 (NO$_2$), 1340(NO$_2$), 1280 (ONO$_2$), 860 (ONO$_2$) cm^{-1}; NMR (acetone d$_6$): δ3.3-3.6(t,4,ArCH$_2$), δ4.7-5.0 (t,4,CH$_2$O(NO$_2$), δ9.0(s,1,ArH). Anal.: Calc'd: C,30.8; H,2.3; found: 30.6; 2.4%.

The di(ammonium sulfate) of II-B was made as described above for the ammonium sulfate of I-A, using II-B (6.0 g), and chlorosulfuric acid (6.0 g). The yield was 8.7 g (87%), mp 287° (dec.) ex aqueous isopropanol); IR: 3160 (NH$_4^+$), 1520 (NO$_2$), 1390 (SO$_4$), 1340(NO$_2$), 1210(SO$_4$), 1060, 990, 910, 740 cm^{-1}. Anal.: Calc'd: C,24.2; H,3.4; found: 24.1, 3.6%.

1-(2-Hydroxyethyl)-3,5-dimethyl-2,4,6-trinitrobenzene (III-A):

III (6.5 g - 25 mmole), 37% formaldehyde (15 ml - 185 mmole), potassium carbonate (0.75 g - 5.4 mmole), and acetone (125 ml) were refluxed with stirring for 7 hrs. Workup as usual gave 6.4 g solid. Refluxing with methanol and filtering gave 3.0 g insoluble III; evaporation of the filtrate gave 2.9 g sticky brown solid. Recrystallization from butanol gave 0.3 g insoluble III, and 0.9 crude III-A. Recrystallization from methylcyclohexane gave light yellow III-A, mp 132-5°; IR: 3380 (OH), 2880, 1530(NO$_2$), 1350 (NO$_2$), 1040 (CH$_2$OH), 870, 740, 620 cm^{-1}; NMR (acetone d$_6$): δ2.3(s,6,CH$_3$), δ3.0-2.7(t,3, ArCH$_2$ and OH), δ3.8-3.5(t,2,CH$_2$OH). Anal.: Calc'd: C, 42.2; H,3.9; found: 42.4; 4.1%.

The acetate of III-A was prepared by refluxing it (0.6 g) with acetic anhydride (5 ml) for 1 hr. The oily product solidified on trituration with cold water, yielding 0.7 g; mp 102-4° (ex methanol); IR: 2900, 1740 (acetate), 1530 (NO_2), 1350 (NO_2), 1230 (acetate) 1050, 880, 740, 620 cm^{-1}.Anal.: Calc'd: C,44.1; H,4.0; N, 12.8; found: 43.8; 4.1; 12.9%.

1-(1-Methyl-2-hydroxyethyl)-2,4,6-trinitrobenzene (V-A):

V (2.4 g - mmole), 37% formaldehyde (4.0 ml - 49 mmole), anhydrous potassium carbonate (0.2 g - 1.5 mmole). and THF (25 ml) were refluxed for 4 hrs and worked up as usual, giving a viscous red oil (2.5 g), which did not crystallize. Extraction with boiling water gave a solid, mp 113-6° (ex isopropanol-water); IR: 3560 (OH), 3090, 1530 (NO_2), 1350 (NO_2), 1100, 1010 (CH_2OH), 915, 720 cm^{-1}. Anal.: Calc'd: C,40.0; ;H,3.3; N,15.5; found: 39.9; 3.4; 15.4%. The acetate, a viscous oil, which could not be crystallized, was obtained by refluxing V-A for 1 hr with acetic anhydride. IR: 3090, 1730 (acetate), 1530 (NO_2), 1350 (NO_2), 1225 (acetate), 1040, 910, 720 cm^{-1}.

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