Synthesis of 1,2,2-Trinitroadamantane

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Introduction

Although several polynitropolycyclic compounds have been synthesized, very few examples of vicinal dinitro groups are known. Without exception, these are derived with concomitant carbon–carbon bond formation resulting from coupling of dioximes,[1] or C-nitro compounds,[2] and in one case by a novel rearrangement.[3] Oxidation of vicinal diamino groups in polycyclic systems has not been successful, owing to carbon–carbon bond cleavage by a mechanism believed to be akin to that of Grob fragmentation.[4] An extreme case in point is that of 1,2-diaminocubane, where unstoppable cage cleavage upon its attempted oxidation has been reported.[5] As the oxidation proceeds, electron pair donation from the nitrogen atom in a lower oxidation state and electron withdrawal by the nitrogen in higher oxidation state results in a "push–pull" effect, weakening the C–C σ bond.[6] We present here the synthesis of 1,2,2-trinitroadamantane, **1**, from a suitably 1,2-functionalized adamantane as an example of the first synthesis of vicinal dinitro compound of this type. This approach should prove useful for the synthesis of elusive polynitroadamantanes which have been pursued in these laboratories[7] and elsewhere.[8]

Results and Discussion

In view of the difficulties associated with the oxidation of vicinal diamino groups, we opted for a route that does not require the intermediacy of a vicinal amino nitro grouping. The best method for the introduction of a nitro group at a tertiary carbon requires oxidation of an amino functionality, and a geminal dinitro functionality at the secondary position can be introduced from the corresponding oxime, without the intermediacy of amine. Strategically, introduction of the nitro group at the tertiary position followed by simultaneous introduction of the geminal dinitro group would circumvent having an amino nitro adamantane as an intermediate.

The starting material of choice for the synthesis of the title compound is 2-oxoadamantane-1-carbonyl chloride, **3**, which was synthesized by thionyl chloride-mediated cyclization of bicyclo[3.3.1]nonane-3,7-dicarboxylic acid, **2**, prepared from adamantanone as described by Peters et al.[9] Conversion of the carbonyl chloride group of **3** to the corresponding amine hydrochloride, **4**, was achieved via Curtius reaction as described by Sasaki et al.[10]

Oxidation of the amine function of **4** was achieved using an acetone solution of dimethyldioxirane to give nitroadamantan-2-one in 80% yield. The IR spectrum of **5** showed absorptions typical of carbonyl and nitro groups at 1730 and 1540 cm^{-1}, respectively. Other spectral characteristics fully supported the structure (vide infra). α-Nitro ketones are important intermediates of considerable synthetic utility and therefore have been the subject of considerable current interest.[11] Oxidation of α-amino ketones offers an interesting method for the synthesis of the corresponding α-nitro ketones, which are most commonly synthesized by nitration of enolates,[12] enol ethers,[13] or enol acetates[14] and by intramolecular cyclizations to a lesser extent.[15]

The keto group of **5** was converted to the corresponding oxime by treatment with hydroxylamine hydrochloride and sodium acetate in ethanol. Treatment of the oxime in refluxing methylene chloride with 100% nitric acid gave 1,2,2-trinitroadamantane, **1**, which was obtained in 22% yield after chromatographic separation. Another fraction contained 25% of the starting nitro ketone, **5**, which could be recycled. The IR spectrum of **1** showed characteristic absorption for a nitro group at 1575 cm^{-1} and the absence of carbonyl absorption.

The structure of 1,2,2-trinitroadamantane obtained from this reaction sequence is further reinforced by the observation of the requisite number of resonance signals, the DEPT multiplicity determinations shown in Table 1, and the characteristic signals for CNO_2 and $C(NO_2)_2$ at δ 85.6 and 122.3, respectively. This structure is further confirmed by a combination of homonuclear and heteronuclear correlation spectra. NOESY spectra were ambiguous because of the almost identical chemical shifts of the two protons attached to C-6, but the COSY spectrum showed spin coupling between protons of chemical shifts δ 1.98 and 2.56 in addition to the other expected two- and three-bond couplings. Since these protons are attached to C-4/C-9 and C-8/C-10, respectively, and are four bonds removed from each other the observed coupling may be attributed to a coplanar "W"

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Scheme 1

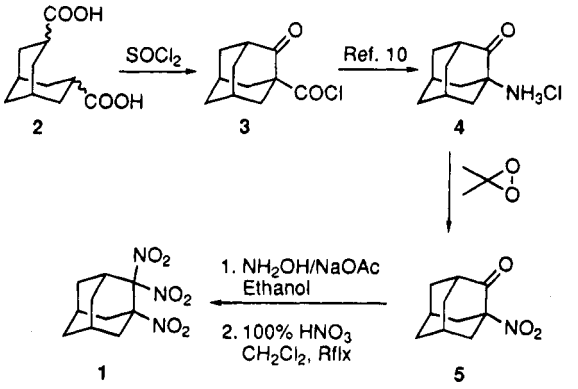
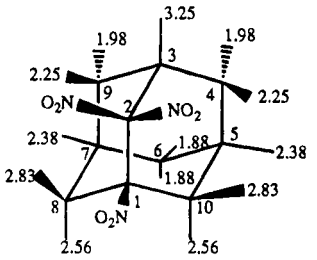


Table 1. ^1H and ^{13}C Chemical Shift Correlations for 1,2,2-Trinitroadamantane in Chloroform-d_1



carbon/proton	$\delta^{13}C$ (ppm)	multiplicity	δ^1H (ppm)
C-1	85.6	Cq	
C-2	122.3	Cq	
C-3/H-3	38.90	CH	3.25
C-4/H-4	34.03	CH_2	1.98, 2.25
C-5/H-5	28.14	CH	2.38
C-6/H-6	36.12	CH_2	1.88, 1.88
C-7/H-7	28.14	CH	2.38
C-8/H-8	40.72	CH_2	2.83, 2.56
C-9/H-0	34.03	CH_2	1.98, 2.25
C-10/H-10	40.72	CH_2	2.83, 2.56

arrangement.[7c] Thus, these experiments permit the complete structural assignment of the spatial configuration of all of the spin-coupled and dipolar-coupled protons in the molecule.

In conclusion, the above approach demonstrates a successful method for obtaining cyclic α-nitro ketones and the conversion of suitable functional groups on vicinal secondary and tertiary carbons to nitro groups.

Experimental Section

Dimethyldioxirane was prepared from oxone and sodium bicarbonate by a modification of the procedure described by Murray and Jeyaraman.[16] Nitric acid (100%) was prepared by distillation of 98% nitric acid from an equal volume of sulfuric acid, immediately prior to use. CAUTION: Nitric acid is highly corrosive and should be handled with appropriate precautions in a well-ventilated fume hood. Urea and ammonium nitrate should be added carefully in small portions to the nitric acid/methylene chloride solution since a slight exotherm occurs and nitrogen oxide fumes are evolved.

Nitroadamantan-2-one, 5. To 2-oxoadamantaneamine hydrochloride (0.27 g, 1.34 mmol) was added an acetone solution of dimethyldioxirane, (~0.1 molar, 250 mL), and the mixture was stirred overnight at room temperature. The reaction mixture was then concentrated under reduced pressure, and the residue was chromatographed on silica gel eluting with 10% acetone in hexanes. The relevant fractions were combined and concentrated in vacuo, and the residue was recrystallized from methylene chloride/hexanes to give **5** as a colorless crystalline solid (0.20 g, 80%): mp 170–71 °C; IR (KBr) 1730 (s), 1540 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.88 (m, 1H), 2.84 (m, 2H), 1.80–2.43 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 19.0, 34.3, 37.9, 42.2, 46.9, 93.7, 203.2. Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.57; H, 6.71; N, 7.17. Found: C, 61.48; H, 6.54; N, 7.05.

1,2,2-Trinitroadamantane, 1. To nitroadamantan-2-one (0.1 g, 0.51 mmol) in absolute ethanol (50 mL) were added hydroxylamine hydrochloride (0.05 g, 0.77 mmol) and sodium acetate trihydrate (0.31 g, 2.31 mmol). The resulting mixture was stirred overnight at room temperature. The mixture was then concentrated in vacuo, and the residue was partitioned between methylene chloride (50 mL) and water (50 mL). The organic layer was separated, dried using magnesium sulfate, filtered, and concentrated to give the oxime as a mixture of isomers. This mixture was taken up in the next step without further purification.

To a refluxing solution of the oxime in methylene chloride (25 mL) was added dropwise, under nitrogen atmosphere, a solution of 100% nitric acid (2 mL), urea (0.05 g), and ammonium nitrate (0.05 g) in methylene chloride (5 mL). The initial blue-green color faded as more nitric acid was added. After the addition, the mixture was stirred at reflux for a further 30 min. The reaction mixture was then cooled to room temperature and poured over ice. The layers were separated, the organic layer was successively washed with saturated sodium bicarbonate solution (50 mL) and water (50 mL), dried over magnesium sulfate, and filtered, and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel eluting with 40% methylene chloride/hexanes. The relevant fractions were combined and concentrated, and the residue was recrystallized from acetone/hexanes to give pure 1,2,2-trinitroadamantane (0.03 g, 22%): mp 248–9 °C; IR (KBr) 1575 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25 (m, 1H), 2.81 (m, 2H), 2.55 (m, 2H), 1.87–2.36 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 28.0, 33.9, 36.0, 38.7, 40.6, 85.6, 122.3; HRMS (FAB) calcd M + 1 272.0882, found 272.0879.

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Supplementary Material Available: A copy of the ^{13}C NMR spectrum of 1,2,2-trinitroadamantane, **1** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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