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SYNTHESIS AND CHARACTERIZATION OF GLYCEROL TRIPICRATE AND ITS SIGMA COMPLEXES WITH METHOXIDE. REPLACING THE ONO_2 OF NITROGLYCERINE WITH $-OC_6H_2(NO_2)_3$.

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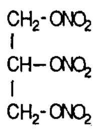
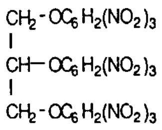
Abstract: The first synthesis of glycerol tripicrate is reported. It is a relatively stable compound which forms pi and sigma complexes.

We have recently been interested in the properties of nitrate esters in which the nitrate moiety is partially or completely replaced by picrate ($-ONO_2 \rightarrow -OC_6H_2(NO_2)_3$). The chemical and physical properties of such materials are, not surprisingly, quite different from the more shock sensitive nitrates. Our recently reported preparation of picryl nitrocellulose is illustrative of such a compound.[1] We report here the preparation and characterization of glycerol tripicrate, 2, the picryl analogue of nitroglycerine, 1, as well as some interesting chemical properties of 2. Previous attempts to prepare 2 by reaction of glycerol with picryl fluoride in the presence of a basic catalyst failed.[2] It appeared to us that a possible reason for this failure was the formation of the spirocyclic sigma complex, 3, through intramolecular addition in a monopicrylated glycerol as depicted in equation 1.



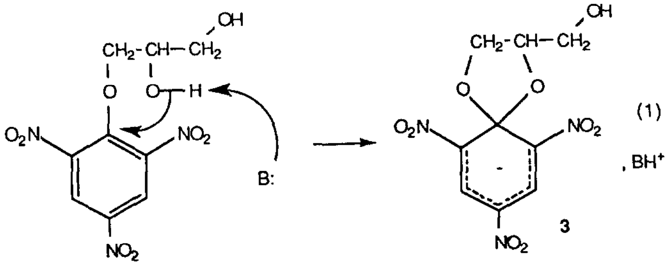
$$\begin{array}{l} CH_2{-}ONO_2 \\ | \\ CH{-}ONO_2 \\ | \\ CH_2{-}ONO_2 \end{array}$$

1



$$\begin{array}{l} CH_2{-}OC_6H_2(NO_2)_3 \\ | \\ CH{-}OC_6H_2(NO_2)_3 \\ | \\ CH_2{-}OC_6H_2(NO_2)_3 \end{array}$$

2

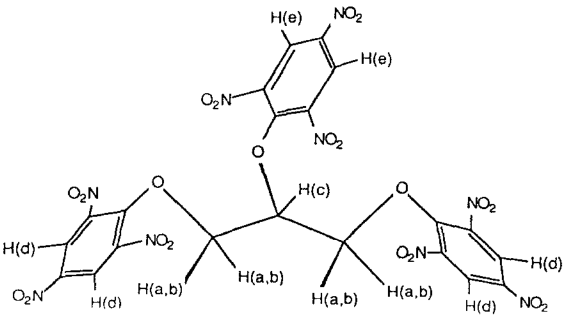


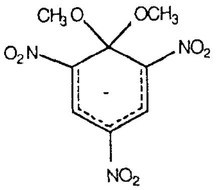
To avoid this problem, we prepared the previously reported tris-(2,4-dinitrophenyl)-glycerol[2] and nitrated this with a mixture of nitric and sulfuric acids. This nitration proceeds in good yield to give, upon workup, a white powder, m.p. 94-96°C. Recrystallization from toluene gives long white needles with an analysis (C,H,N) consistent with 2 and occluded toluene (confirmed by nmr). The latter is bound tenaciously and cannot be removed by heating at 60 °C at 3 mm for several days. Soxhlet extraction with diethyl ether for two days results in a 1:1 adduct of 2 and $C_6H_5CH_3$. This stoichiometry is not changed and remains constant even with further heating in vacuum or on additional ether extraction.

The nmr spectrum of 2 (Figure 1) clearly shows the diastereotopic protons H_a and H_b, a complex multiplet for H_c, and two low field singlets in a ratio of 2:1 for the aromatic ring protons H_d and H_e. In addition, there is a highly symmetrical multiplet for the normally narrow aromatic band of toluene, indicating strong pi complexation even in acetone solution. The center of the multiplet for toluene is 0.033 ppm downfield from that of the aromatic multiplet of toluene in acetone. The toluene methyl is also shifted downfield 0.034 ppm.

Attempts were made to examine rotational barriers by DNMR but 2 precipitated out at 190°K, even at a concentration of 1 mg/ml in a variety of useful polar solvents. Adequate solubility could only be obtained in more polar solvents with relatively high freezing points.

Glycerol tripicrate reacts with methanolic methoxide in DMSO to yield a dark red solution with absorption maxima at 422 and 495 nm characteristic of anionic sigma complexes like 4 or 5.[3] In an attempt to structurally characterize the species, the reaction was followed by nmr. Addition of one equivalent of methoxide in MeOH to a DMSO solution of one equivalent of 2 shows





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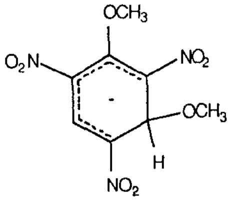
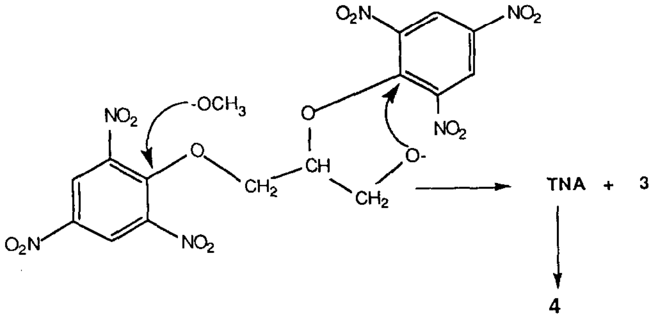


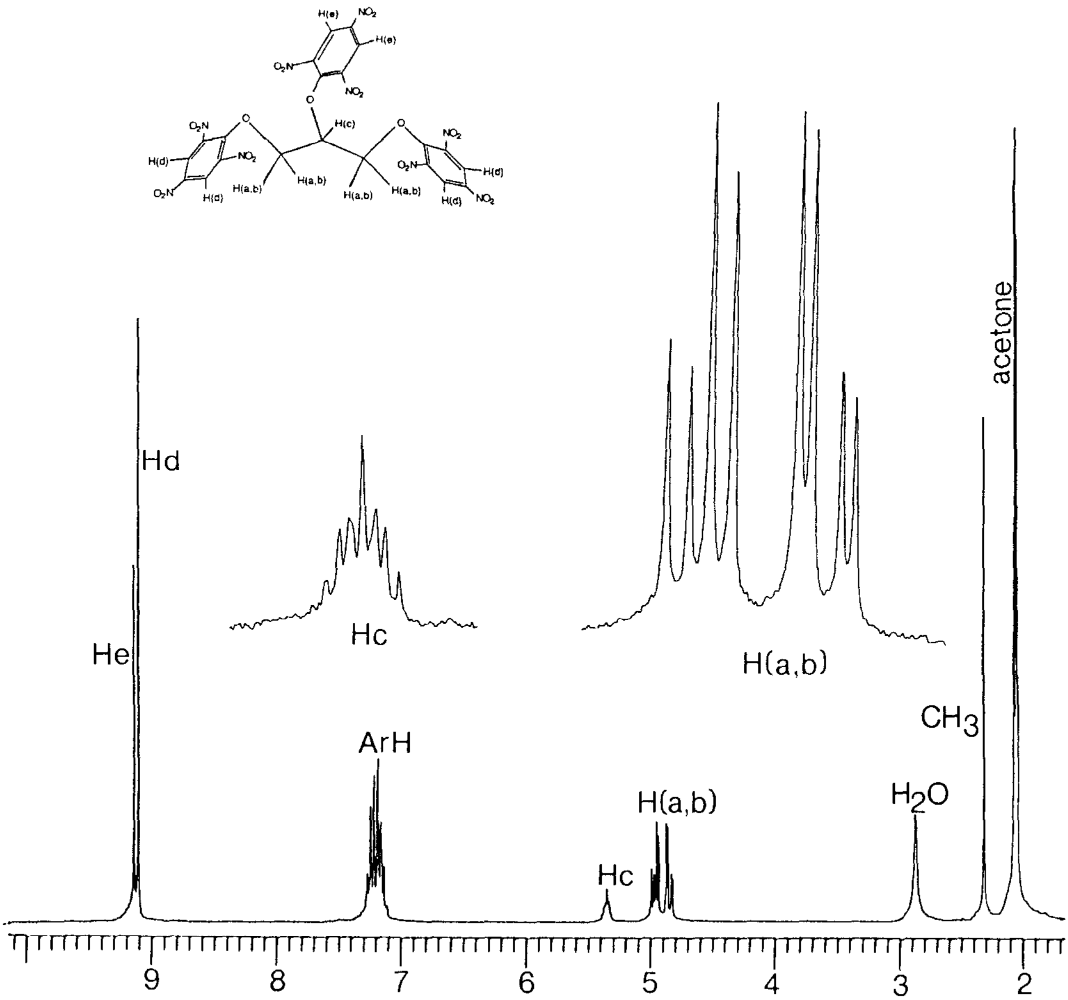
5

a rapidly formed absorption at 6.1 ppm, indicative of the sp^3 hybridized ring hydrogen in a 1,3-adduct like 5. These absorptions soon disappear and the spectrum becomes very complex and undergoes continuous change. To better understand what might be happening three equivalents of methoxide were added to one equivalent of 2. After initial formation and then disappearance of absorptions for species like 5, the spectrum evolved to a clean set of unchanging absorptions consistent with formation of one equivalent of 3 and two equivalents of 4. This could readily occur by initial displacement of dipicryl glycerol from 2 with concomitant formation of 2,4,6-trinitroanisole (TNA). The latter will rapidly form 4, whereas the dipicryl glycerol can undergo intramolecular cyclization and further S_NAr displacement by methoxide. The probable sequence leading to 3 and 4 is shown below.



To provide more evidence for this sequence a preparative scale reaction of 2 with three equivalents of methoxide was run in methanol and the red products were isolated. Thin layer chromatography showed the mixture to be composed of two orange colored complexes, one of which had an R_f value identical with that of 4 prepared independently from methoxide and TNA. The other complex had a smaller R_f value. The nmr spectrum of the mixture in DMSO had all of the absorptions previously reported[4] for 3, with additional absorptions for 4. To further corroborate the sequence, 3 was prepared independently from picryl chloride and glycerol. The nmr spectrum of the mixture of 3 and 4 obtained from the reaction of methoxide and 2 could then be duplicated by mixing the correct amounts of pure 3 and 4 in DMSO.

We have found glycerol tripicrate to be a relatively stable compound which forms stable pi and sigma complexes with a variety of pi and n donors. Details of this work will be reported elsewhere.



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