

STABLE NITRIC ACID COMPLEXES OF ADAMANTANES

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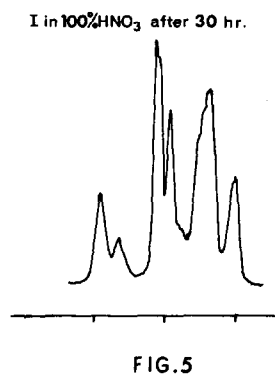
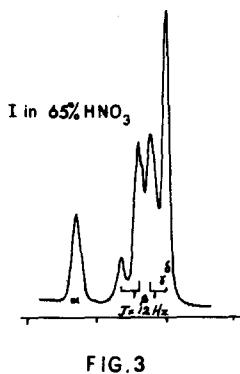
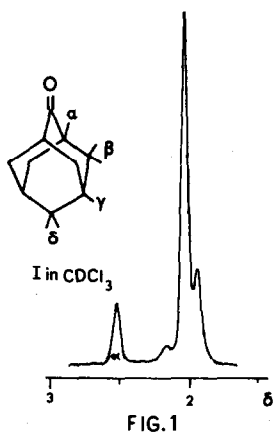
Several examples of crystalline adducts of aldehydes and ketones with Brönsted acids have been reported (1). The electron donating carbonyl compounds in these complexes generally possessed an aromatic structure or one stabilized otherwise by resonance. There are only a few instances of complexes of aliphatic carbonyl compounds with proton acids, due to their poor stability or poor crystallinity (2).

We found that adamantanone (I) formed an exceptionally stable crystalline complex with nitric acid. Other proton acids, e.g. sulphuric acid, perchloric acid, and picric acid, gave complexes also, but they were less stable and exhibited only poor crystallizing properties. The  $\text{HNO}_3$ -complex of I was obtained by dissolution of I in 65%  $\text{HNO}_3$  at  $60^\circ$ . Upon cooling, crystals separated which were filtered off and recrystallized from n-hexane (m.p.  $74-76^\circ$ ). The complex proved, by acidimetric titration, to be a 1:1 adduct of I with  $\text{HNO}_3$ . The substance was soluble in various organic solvents and was recovered unchanged upon evaporation of these solvents.

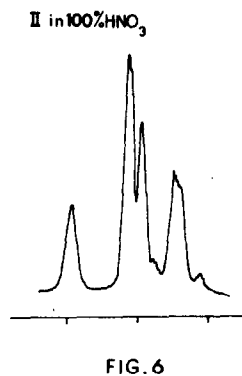
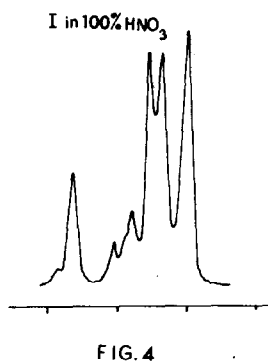
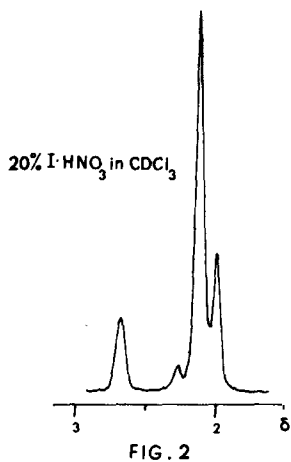
The IR spectrum of the Nujol mull (3) showed a broad, hydrogen-bonded OH stretching band at about  $2500\text{ cm}^{-1}$ . The carbonyl stretching band at  $1670\text{ cm}^{-1}$  proved to have been shifted to a lower frequency (by  $50\text{ cm}^{-1}$ ) compared with I, indicating a strong hydrogen bond to the carbonyl oxygen. Furthermore characteristic bands were found of hydrogen-bonded  $\text{HNO}_3$ , at  $1630(\text{s})(\text{asym. NO}_2)$ ,  $1290(\text{vs})(\text{sym. NO}_2)$ ,  $950(\text{s})(\text{HO-NO}_2)$ ,  $766(\text{m})(\delta\text{-NO}_2)$ ,  $687(\text{m})(\gamma\text{-NO}_2)$ , and  $1410(\text{s})\text{ cm}^{-1}$ , most of which are within the range quoted for alkyl nitrates (4). The IR spec-

trum of the complex in  $\text{CCl}_4$  ( $\text{CaF}_2$  cuvet) showed two OH bands, at 3080(w) and 2680(s), a carbonyl stretching band at 1695(s), and bands at 1670(s), 1390(m), and 1290(vs)  $\text{cm}^{-1}$ . The shift of the carbonyl band due to hydrogen bonding is comparable with the shifts found in other ketones with trifluoroacetic acid (5).

The  $^1\text{H}$  NMR spectrum of the complex in  $\text{CDCl}_3$  showed also hydrogen-bonded I, characterized by a downfield shift of the signals, which depended upon the concentration (Figures 1 and 2). For comparison,  $^1\text{H}$  NMR spectra of I in 65%  $\text{HNO}_3$  and 100%  $\text{HNO}_3$  were recorded (Figures 3 and 4). These spectra showed an appreciable resolution of the  $\beta$ -hydrogen signals, which could be attributed to a  $\text{HNO}_3$  solvent shift, because this resolution was not observed in other acids (TPA,

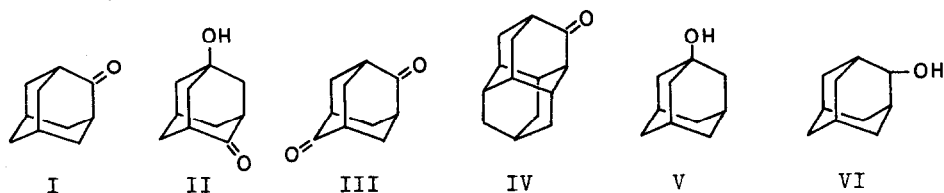


For note regarding the figures, cf. ref. 9.



or  $\text{H}_2\text{SO}_4$ ). Additional signals were found in the spectrum of I in 100%  $\text{HNO}_3$ . Further investigation revealed that this spectrum changed with time (Figure 5), due to oxidation of I to 5-hydroxy-2-adamantanone (II) (Figure 6). This led to a convenient synthesis of 1,4-substituted adamantanes (6).

X-ray diffraction analysis of the crystalline adamantanone- $\text{HNO}_3$  adduct revealed a carbonyl bond length of 1.23 Å, which may be considered quite normal for a cyclic ketone. Comparison with I itself, however, was not possible because adequate X-ray data could not be obtained from crystals of I (7). Furthermore from the X-ray data of the  $\text{HNO}_3$ -adduct two almost equal N-O bonds of 1.19 and 1.20 Å and a N-O bond of 1.32 Å were computed, indicating that the proton of the acid must still be located much closer to the  $\text{NO}_3^-$  site than to the carbonyl group. From a difference Fourier map the acidic hydrogen could be detected at distances of 1.6(8) Å from the carbonyl oxygen and 0.9(5) Å from that nitric acid oxygen exhibiting the longest N-O bond. Details of the X-ray analysis and further results concerning the determination of the crystal structure of this compound will be published elsewhere (8).



Besides I, also II formed a stable 1:1  $\text{HNO}_3$ -complex, m.p. 91-94° (from  $\text{CCl}_4$ ). 2,6-Adamantanedione (III) and diamantanone (IV) gave crystalline  $\text{HNO}_3$ -complexes, too. Furthermore 1-adamantanol (V) formed a crystalline compound with  $\text{HNO}_3$ , a rather curious behaviour for an alcohol. A 1:1 complex with  $\text{HNO}_3$  was obtained as an oil when V was added to 65%  $\text{HNO}_3$  at room temperature. After being heated at 80° in vacuo for a few minutes, the oily complex solidified upon cooling. Acidimetric titration of the solid revealed that the complex had lost half a mole of  $\text{HNO}_3$ , leaving a 2:1 complex of V with  $\text{HNO}_3$ . After addition of water, neutralisation of the acid with  $\text{NaHCO}_3$ , and extraction with  $\text{CH}_2\text{Cl}_2$  the alcohol was recovered unchanged almost completely. A small amount of the alcohol proved to have been esterified by the acid. Prolonged heating of the

complex resulted in extended esterification of V to 1-adamantyl nitrate (m.p. 98-100°, yield 70%).

2-Adamantanol (VI) did not give a stable  $\text{HNO}_3$ -adduct. This secondary alcohol was rapidly oxidized by  $\text{HNO}_3$  to adamantanone at room temperature. Thus when VI was added to 65%  $\text{HNO}_3$  the crystals liquified to an oily mass (intermediate  $\text{HNO}_3$ -complex) which dissolved after a few minutes under slight evolution of heat and formation of nitrous fumes; thereafter the  $\text{HNO}_3$ -complex of I crystallized out in almost quantitative yield.

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#### References.

1. A.Klages and P.Allendorff, *Chem.Ber.*, 31, 1298 (1898).  
J.Collil and Th.Thickle, *J.Chem.Soc.*, 75, 710 (1899).  
G.Reddelien, *J.Prakt.Chem.*, 91, 213 (1915).
2. A.Shukow and F.Kassatkin, *Chem.Zentr.* I, 1761 (1909).  
D.McIntosh, *J.Am.Chem.Soc.*, 27, 1013 (1905).  
V.A.Palm, Ü.L.Haldna, and A.J.Talvik, in "The Chemistry of the Carbonyl Group", Chapt. 9, Ed. S.Patai, Interscience Publishers, London, 1966.  
G.A.Olah and A.M.White, *Chem.Rev.*, 70, 561 (1970).
3. KBr or NaCl discs could not be used because the complex decomposed. The Nujol mull was measured between polished NaCl plates. KBr also reacted with the Nujol mull under formation of bromine.
4. IRSCOT-System (Infrared Structural Correlation Tables), Ed. R.G.J.Miller and H.Willis, Heyden and Son Ltd., London.  
R.D.Guthrie and H.Spedding, *J.Chem.Soc.*, 953 (1960).
5. C.Viel, E.Waegell, and P.Witz, *Bull.Soc.Chim.Fr.*, 1104 (1966).
6. H.W.Geluk, to be published.
7. Although the crystals of I (from  $\text{Et}_2\text{O}$  or  $\text{AcOEt}$ ) exhibited a perfectly regular shape macroscopically, with flat faces, the lattice proved to be disordered. The carbonyl group seemed to be orientated arbitrarily throughout the crystal.
8. P.B.Braun and J.Hornstra, Philips Research Laboratories, Eindhoven, The Netherlands.
9. The spectra were measured on a Varian HA 100 locked on the internal reference TMS (Figures 1 and 2) or on the solvent  $\text{HNO}_3$  without a reference (Figures 3 to 6).