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ISOMERIC META-BRIDGING OF ELECTRON DEFICIENT AROMATICS. THE REACTION OF TRINITROANISOLE WITH 1,3-DICARBOMETHOXYACETONE: AN X-RAY STRUCTURAL ANALYSIS OF THE PRODUCT.

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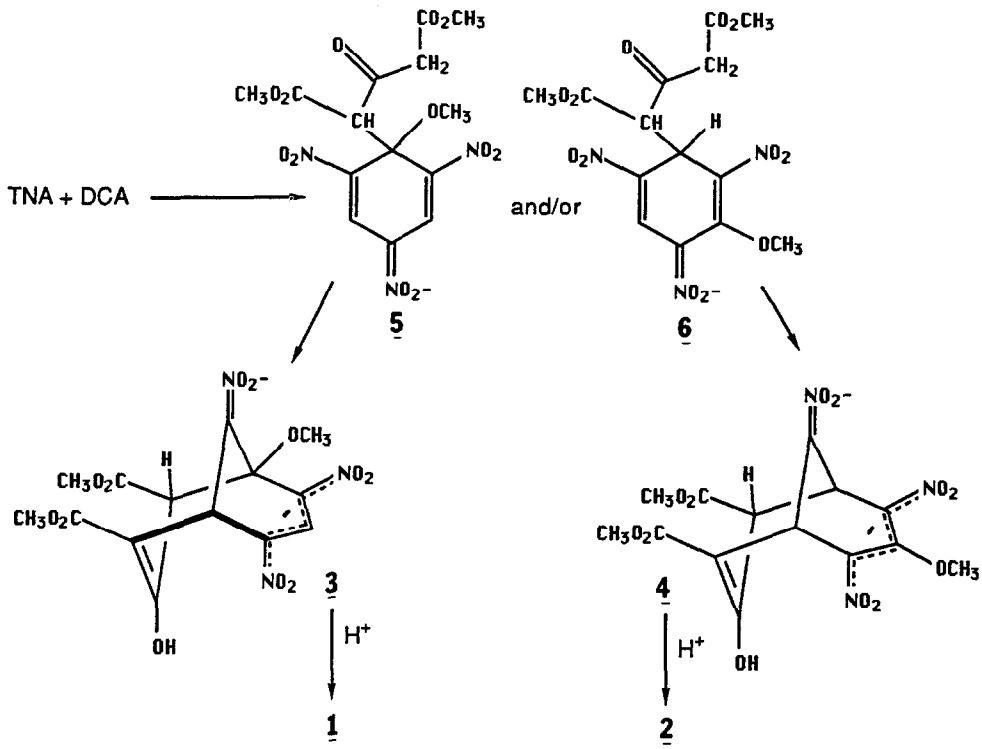
Abstract: The reaction of 1,3-dicarbomethoxyacetone with trinitroanisole in the presence of triethylamine yields two isomeric bridged anions. The structural features of these products have been studied by both pmr and single crystal x-ray analysis, and the mechanisms by which they are formed are discussed.

The one step bridging of an aromatic ring to yield the bicyclo [3.3.1] nonane skeleton was discovered 20 years ago.[1] Since then meta-bridging reactions of trinitro-substituted electron deficient aromatics have been investigated by a number of researchers.[2] Nevertheless, there has been no published x-ray confirmation of the bicyclic structures formed and the stereochemistry at several key centers (e.g., at the $CHNO_2$ bridge and at positions alpha to the carbonyl of the bridging fragment) has not been substantiated in many cases. Since these stereochemical features importantly relate to mechanistic steps by which such anions are formed, we were prompted to examine meta-bridging of a substrate which could yield several regiospecific products, and to examine the products by both pmr and single crystal x-ray analysis. We report here the first example of meta-bridging on a 1-X-substituted-2,4,6-trinitrobenzene in which both isomeric bridgehead and nitropropane nitronate substituted products are obtained. One of these formed crystals suitable for x-ray analysis.

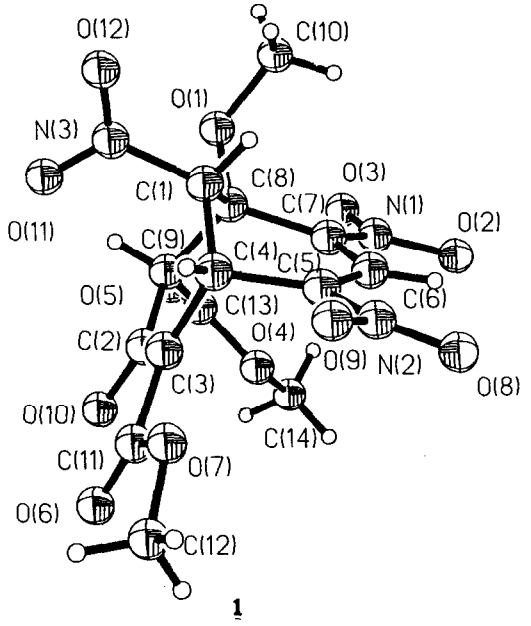
One of the most reactive reagents in meta-bridging reactions is 1,3-dicarbomethoxyacetone (DCA). We have found that this compound bridges 2,4,6-trinitroanisole (TNA) rapidly in the presence of triethylamine to give two isomeric products. Addition of triethylamine to a concentrated solution of TNA and DCA yields, after precipitation with ether, a red-brown powder. When recrystallized from ether/ethanol, a mixture of yellow and orange crystals is formed. Elemental analysis of the mixture shows the product to be a 1:1:1 adduct of amine, aromatic and ketone. The visible spectra of the mixture as



well as the colors and spectra of the individual products (separated by hand under a 3-D binocular microscope), are consistent with structures containing both unsubstituted and 2-substituted nitropropene nitronate functions respectively[3] (λ_{max} = 460nm and λ_{max} = 492nm). Pmr spectra of the isolated products are consistent with enolic bridged structures. The orange crystals show a one proton singlet downfield at δ 8.6 ppm consistent with a proton on the central carbon of the delocalized anionic portion of 1. This absorption is absent in the yellow crystals indicating methoxy substitution on the central carbon of the delocalized nitronate function in 2[3]. Decoupling experiments on 1 are also consistent with methoxy substitution at the bridgehead. Irradiation of the signal at δ 8.6 ppm collapses the doublet of doublets at δ 5.06 ppm (bridgehead proton) into a clean doublet.

X-ray analysis confirms the structure of 1. It shows bridgehead (C-8) substitution on the opposite side of the molecule from the enol. It is likely that enolization occurs in this direction because the carbomethoxy group lies quite near the C-4 bridgehead. Methoxy substitution at C-4 would hinder coplanarity of the enolic system. Interestingly, the C-1 NO_2 group is anti to the delocalized nitropropene nitronate function. This stereochemistry is determined by a final protonation of 3, the direct precursor to 1.[4] The formation of intermediates like 3 has been confirmed by mechanistic studies of

meta-bridging in related systems, where the final product arises as shown in the conversion of 3 to 1.[4]

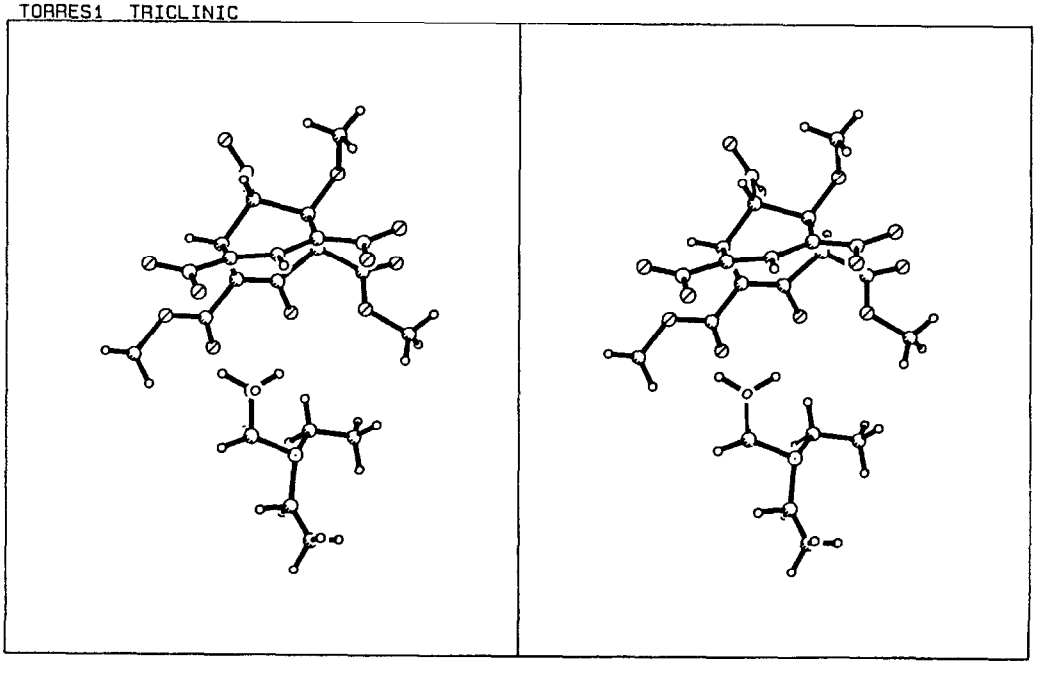


1

STRUCTURE DETERMINATION SUMMARY

Crystal Data

Empirical Formula	$C_{20}H_{30}N_4O_{12}$
Color; Habit	Orange Needles
Size	0.10mm x 0.15mm x 0.35 mm
Space Group	Triclinic, P $\bar{1}$
Unit Cell Dimensions	a = 9.890(5) Å
	b = 11.089(6) Å
	c = 11.427 (4) Å
	α = 91.68(3)°
	β = 99.62(3)°
	γ = 92.99(4)°
Volume	1233.0(9) $Å^3$
Molecules/cell	2
Molecular weight	518.4 AMU
Density(calc.)	1.40g/cm^3
Density(obs.)	1.38 g/cm^3
F(000)	548 e^-



Pmr studies in dilute solution (relative to the preparative procedure where a very concentrated solution is used) show distinct absorptions for the thermodynamically most stable addition complex[2b] 6, where the enolate adds to C-3 of TNA. This is a direct precursor of 4. Cyclization of 6 by intramolecular attack at the one remaining unsubstituted meta position yields 4, which is protonated to give the final product, 2. Crystals of 2 were not suitable for x-ray analysis. While it is difficult to detect by pmr, it is likely that at higher concentrations involved in the preparative procedure, the kinetically preferred complex 5 is also formed, and this can only cyclize to 3. While 1 could also arise by intramolecular cyclization of 6, such a process is not detected in more dilute solution.

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