

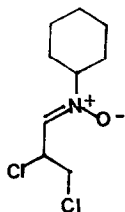
UNUSUAL CYCLOADDITION OF AN UNSATURATED NITRONE TO A VINYLOGOUS ESTER

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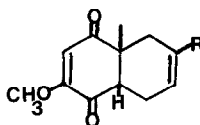
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Abstract: The anomalous addition of α -dichloro-N-cyclohexylpropanaldonitrone (1) to the carbonyl of quinoidal, vinylogous ester 2 is reported.

Chemical investigations of nitrones and unsaturated nitrones¹ has led to important synthetic advances in recent years.² A number of studies of α,β -dichloro-N-cyclohexyl-propanaldonitrone (1) have given rise to a reasonably predictable chemo-, regio- and stereoselective pattern of adducts with olefins.³ We report herein an exception to this pattern when quinoidal system 2⁴ reacts with nitrone 1.



1

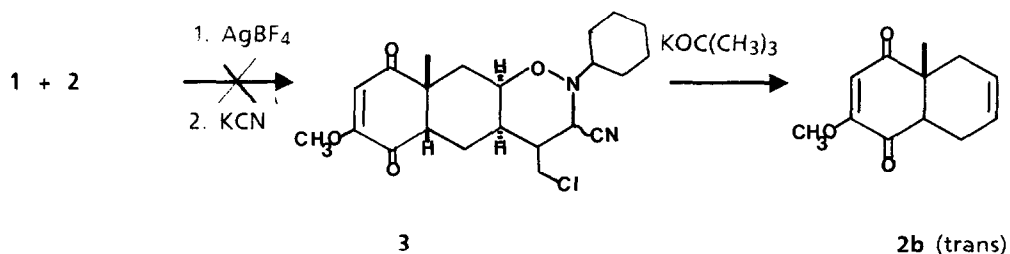


2, R = H

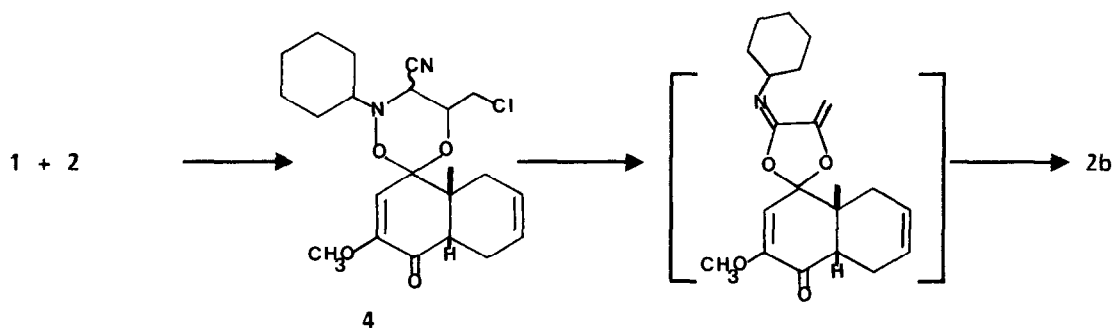
5, R = CH₃

6, R = CH₂OAc

The reaction of 1 with substrate 2 gave results inconsistent with the expected³ cyanide trapped addition products 3. Examination of the epimeric nitrile adducts obtained showed nitrone addition to 2 had undoubtedly occurred.⁵ However, spectral analysis⁶ did not coincide with that expected for the olefin adduct 3. Attempted base catalyzed rearrangement and hydrolysis of the adduct 3 gave, instead of an α -methylene- γ -butyrolactone, a rather complex mixture of products from which *trans*-quinoidal system 2⁹ was isolated.



Single crystal X-ray analysis⁷ shows that for quinoidal system 2, nitron addition occurs at the C-1 carbonyl (Figure 1, below). Thus, an unusual 1,3,4-dioxazine system, 4, is the actual product of addition. It would follow that attempted "base catalyzed rearrangement" of 4 was, in fact, 1,3,5-dioxazine cleavage¹¹ and base catalyzed epimerization of the quinoidal system (2b)⁴.



This addition to the hindered, but electron rich vinylogous ester carbonyl of quinoidal systems appears to be general in that 5 and 6 give adducts with spectral characteristics of 4.¹⁰ These ketal systems represent unusual "protected" α,β -unsaturated vinylogous esters and are the current topic of additional efforts in our labs.

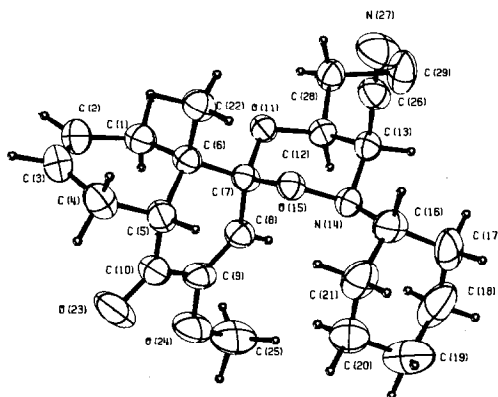


Single-Crystal X-ray Analysis of 4.

A representative crystal was surveyed and a 1-A data set (maximum $\sin \theta/\lambda = 0.5$) was collected on a Syntex P1 diffractometer. A trial structure was obtained by direct methods using the MULTAN program.⁷ The refined structure was plotted using the ORTEP computer program of Johnson.³

Coordinates, anisotropic temperature factors, distances and angles are available as supplementary material.

FIGURE 1

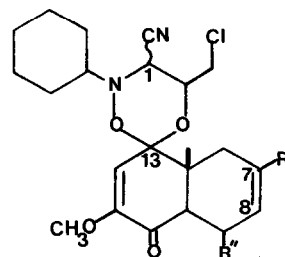


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5. The infrared spectra shows strong carbonyl and vinyl ether absorbance; *elemental analysis* and mass spectroscopy show nitron addition had occurred.
6. The PMR spectrum shows the C-7, C-8 olefinic protons unchanged while the C-2 vinyl proton is split and shifted downfield.
7. G. Germain, P. Main, M. M. Woolfson *Acta Crystallogr.* (1971), **A27**, 368.
8. C. K. Johnson ORETP. Report ORNL-3794, Oak Ridge National Laboratory, Tennessee.
9. The *cis*-quinoidal system, **2**, epimerizes with base to *trans*-**2**, see reference 4.
10. 6-acetoxy **2** also adds nitron **1** at the C-1 carbonyl, but is complicated by elimination of acetic acid on treatment with base.

C-1 Adduct	δ C2-H*	δ C7(8)H	δ C13-H	λ cm ⁻¹ (HCCl ₃)
4	6.45, 6.18	5.6m	4.0	1700, 1630†
5	6.45, 6.10	5.65	3.75	1740, 1710, 1660
6	6.45, 6.10	5.6	4.0	1700, 1630
(6-OAc)-4	6.44, 6.15	5.95(5.5)	3.75	1740, 1710, 1660



*combined integration = 1H, epimeric "aza-ketal adduct"; †mpt of epimers 131-135°, 58-60°.

11. Adduct **4** forms an isolatable, but hydrolytically unstable, product, [λ cm⁻¹ (HCCl₃): 1710, 1670, 1600; δ (DCCl₃): 5.7(m), 5.8(d); m/e 357, 207 (~loss of imine ketal), consistent with structures identified by Eschenmoser, *et al.*, reference 1.

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