Evidence for the Reaction of Nitrosocarbonyl Compounds as Heterodienes in the Diels-Alder Reaction

By DONALD MACKAY,* KENNETH N. WATSON, and LÊ H. DAO

(*Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada* N2L 3G1)

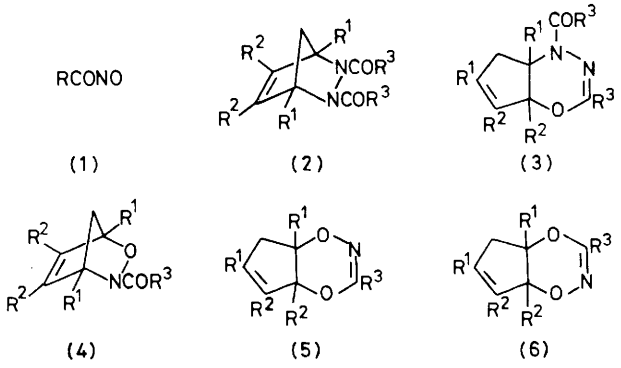
Summary Evidence is given that a nitrosocarbonyl compound can react with a cyclic diene to give a 5,6-dihydro-1,4,2-dioxazine, not only by isomerisation of an initially formed 2-acyl-3,6-dihydro-1,2-oxazine, but also by reacting as a heterodiene directly with a π-bond in the cyclic diene; the role of the ring oxygen in retarding the isomerisation of an oxazine to a dioxazine is discussed.

THE existence of nitrosocarbonyl compounds, (**1**), proposed as intermediates in the oxidation of hydroxamic acids,[1] has now been clearly demonstrated.[2,3] They react with both acyclic[2] and cyclic dienes[2-4] in the Diels–Alder reaction to give 3,6-dihydro-1,2-oxazines. In at least one example the initially formed oxazine has been shown to be thermally isomerisable to the 5,6-dihydro-1,4,2-dioxazine.[4]

This isomerisation exactly parallels that of the Diels–Alder adduct (**2**) of azodicarbonyl compounds to the 5,6-dihydro-1,3,4-oxadiazines (**3**) which we have studied extensively.[5] We report now that dioxazine formation may occur directly from (**1**) in a reaction competitive with, as well as consequent on, oxazine formation, and that when dioxazines are formed by isomerisation, the latter is very much slower than that of the analogous azodicarbonyl adducts.

Oxidation of hydroxamic acids with *N*-bromosuccinimide and pyridine in the presence of cyclopentadiene gave good to excellent yields of the expected adducts (**4**) ($R^1 = R^2 = H$). These were easily recognizable from their spectra, especially the presence of a tertiary amide CO and absence of C=N in the i.r. spectra, and the great similarity in the ^1H n.m.r. spectra of the cyclopentadiene-derived protons to those in (**2**) ($R^1 = R^2 = H$). Thus (**4a**), m.p. 73—75·5 °C (this compound is elsewhere described as an unstable oil[3]) had: $\nu(CCl_4)$ 1658 cm^{-1} (C=O); λ_{max} (EtOH) sh, 270 nm; $\tau(CCl_4)$ included 3·30, 3·68 (2 vinyl H), 4·63, 4·78 (2 tertiary H), 7·91, 8·22 (2 methylene H, AB q, J 8 Hz). The adducts (**4b**) and (**4c**) had m.p. 119·5—121 °C and m.p. 36—37·5 °C, respectively, and spectra in accord with those of (**4a**).

In the purification of (**4c**) (silica gel chromatography) a small amount of an oily isomer was isolated (*ca.* 10% of the total isomeric yield) to which we assign one of the regioisomeric structures (**5c**) (the formal product of a 3,3-sigmatropic rearrangement) or (**6c**), a distinction between these not being possible from the i.r. or ^1H n.m.r. spectra. These included $\nu(CCl_4)$ 1621m cm^{-1} (C=N); $\tau(CCl_4)$ 4·05 (2 vinyl H), 4·92, 5·85 (2 tertiary H), 7·40 (2 methylene H), and 8·87 (9 Bu^tH); of particular diagnostic significance is the upfield shift of a tertiary absorption to 5·85 (β to double bond) and the downfield shift of the methylene absorption, compared with (**4c**). It is likely that (**5c**) is, in part at least, a primary reaction product of (**1c**), rather than a product of isomerisation of (**4c**) under the reaction or work-up conditions. It is present in the final reaction mixture before chromatography, and its formation in low yield seems to be quite general, for example, when lead tetra-acetate in methylene chloride or silver oxide in ethyl acetate are used as alternatives to *N*-bromosuccinimide–pyridine.



a; $R^1 = R^2 = H$; $R^3 = Ph$
b; $R^1 = R^2 = H$; $R^3 = p\text{-}NO_2C_6H_4$
c; $R^1 = R^2 = H$; $R^3 = Bu^t$
d; $R^1 = Me$; $R^2 = Ph$; $R^3 = p\text{-}NO_2C_6H_4$

Compounds (**4a**), (**4b**), and (**4c**), which might be expected to show an increasing tendency to isomerisation by analogy with their azodicarbonyl counterparts,[5] were heated at their b.p.'s in a variety of solvents (chloroform, benzene, toluene, or tetrachloroethylene). In all cases, there was slow decomposition with formation of tar, but ^1H n.m.r. analysis gave no conclusive evidence for the formation of (**5a**), (**5b**), or (**5c**). Specifically when (**4c**) was heated in C_6D_6 at 80 °C decomposition was two-thirds complete in 80 h, with a first-order rate constant of *ca.* 3×10^{-6} s^{-1}. Though a control experiment showed that the dioxazine (**5c**) or (**6c**), described above, was completely stable at this temperature (no detectable decomposition after 80 h in C_6D_6), peaks attributable to it could not be recognized with certainty in the spectrum.† By contrast, at 80 °C (iso-octane) the (quantitative) isomerisation of (**2c**) to (**3c**) is over 3000 fold faster[6] with a rate constant of 1×10^{-2} s^{-1}. The ring oxygen in (**4c**) therefore, inhibits isomerisation *vis à vis* the $NCOBu^t$ group in (**2c**) to the extent of at least 5·7 kcal mol^{-1} in free energy of activation ($\Delta\Delta G^{\ddagger}$, 80 °C). Whether this is solely the result of steric factors (the group $NCOR^3$ is presumably better able to force the reacting $NCOR^3$ group into the pyramidal geometry necessary for bond formation than is the oxygen atom), or involves electronegativity effects as well, is at this point not known.

Oxidation of *p*-nitrobenzohydroxamic acid in the presence of 1,4-dimethyl-2,3-diphenylcyclopentadiene gave an excellent yield of a product, m.p. 164·5—166 °C, whose spectra fully supported the dioxazine structure (**5d**) [or

† The spectrum of the solution was complex. Peaks coinciding with those expected for (**5c**) accounted for < 10% of the total reaction product. This sets an upper limit for the rate constant for the formation of (**5c**) of 3×10^{-7} s^{-1}.

(**6d**)] rather than the oxazine (**4d**): $\nu(CCl_4)$ 1620 cm^{-1} (C=N); $\tau(CDCl_3)$ included Me singlets at 7·92 and 8·98, much too widely separated for the structure (**4d**). Efforts to determine whether (**4d**) was initially formed, as the precursor of (**5d**), have so far been unsuccessful.

As in the case of the azodicarbonyl adducts of dimethyldiphenylcyclopentadiene the methyl and phenyl substituents were expected to have a significant accelerating effect on the isomerisation of (**4**) to (**5**), but not to the extent that the isomerisation would be complete at room temperature, given the large inhibitory effect of the ring oxygen atom just discussed.

The isolation of the dioxazine (**5c**) as a co-product in the synthesis of (**4c**), the great difficulty in general in isomerising the oxazines (**4a**—**c**), coupled with the failure to observe any of the oxazine (**4d**) accompanying the formation of (**5d**), all point to one conclusion. That is, that as well as the demonstrated[2—4] reaction of dienes with (**1**) in a 4 + 2 mode, the direct 2 + 4 mode (heterodiene reaction) may be possible. The choice of pathways is clearly very dependent on the diene substituents.

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