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REARRANGEMENT OF NITROCARBENES TO ACYL NITROSO COMPOUNDS

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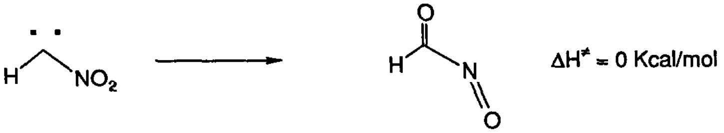
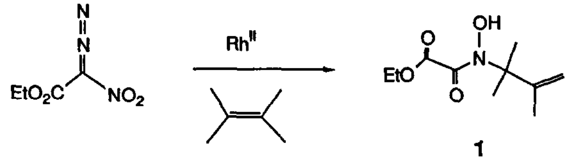
Summary: Acyl nitroso compounds may be trapped as eneophiles and Diels-Alder adducts under thermal and transition metal catalyst conditions using nitrodiazomethane, ethyl nitrodiazoacetate and trifluoromethylnitrodiazomethane.

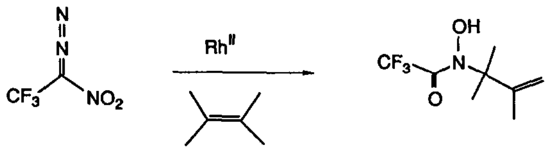
There are several reports of attempts to prepare and trap nitrocarbenes, but they have proven to be very elusive species.[1] While nitrocarbene may be transferred from nitrodiazomethane to electron rich alkenes using a transition metal catalyst, high level *ab initio* calculations predict that free singlet nitrocarbene will spontaneously rearrange to nitrosoformaldehyde.[2] We have obtained experimental evidence that confirms this prediction.



Attempted catalytic cyclopropanation of 2,3-dimethyl-2-butene with ethyl nitrodiazoacetate[3] or trifluoromethylnitrodiazomethane[3] yielded no cyclopropane derived products. Rather, good yields of rearrangement products **1**[1a] and **2** were obtained.[4]

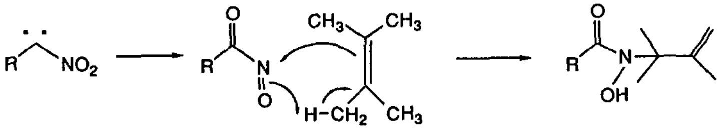


1



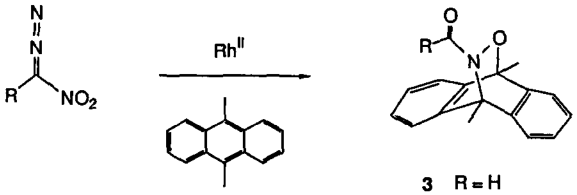
2

These products may arise from an ene reaction between an acyl nitroso compound and 2,3-dimethyl-2-butene. Surprisingly, the analogous ene product could not be detected with nitrodiazomethane.



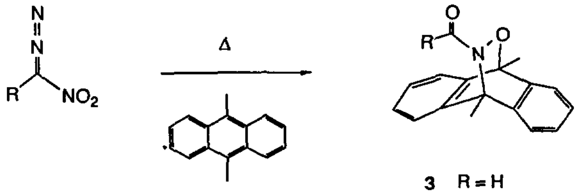
Previous workers isolated the corresponding ene products from the thermolysis and photolysis of ethyl nitrodiazoacetate and nitrodiazomethane in 2,3-dimethyl-2-butene. They, however, favored a free radical mechanism to account for the formation of products.[1a,1b]

While there is still no direct spectroscopic evidence for acyl nitroso compounds, their chemistry has been well studied by Kirby[6a,b] and exploited in synthesis by Keck.[6c] Traditionally, these highly reactive species are generated in solution by the periodate oxidation of hydroxamic acids and are trapped as eneophiles or dieneophiles. An excellent diene for the acyl nitroso Diels-Alder reaction is 9,10-dimethylanthracene. When nitrodiazomethane, ethyl nitrodiazoacetate and trifluoromethylnitrodiazomethane were treated with a catalytic amount of rhodium(II) acetate in the presence of 9,10-dimethylanthracene, Diels-Alder adducts **3**, **4**, and **5** were obtained in 25%, 67% and 65% yields respectively.



3 R = H
4 R = CO_2Et
5 R = CF_3

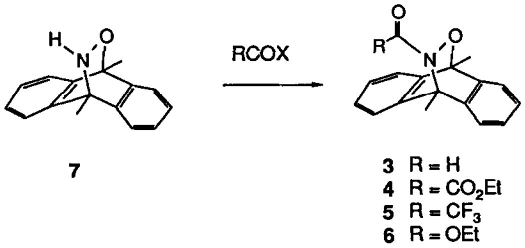
Moreover, **3** and **4** were obtained under mild thermal conditions in refluxing chloroform solution without a catalyst. The trifluoromethyl derivative **5** could not be detected, although control experiments revealed that **5** was stable under the reaction conditions. The decarbonylated adduct **6** was formed in an amount about equal to **4** during the reaction with ethyl nitrodiazoacetate.



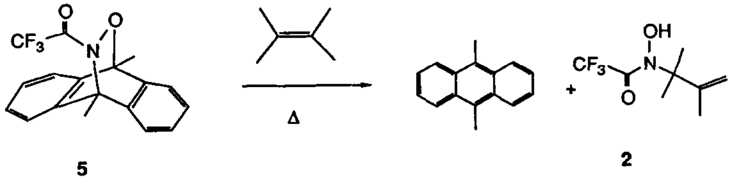
3 R = H
4 R = CO_2Et
6 R = OEt

We believe that this is convincing evidence that nitrocarbenes do undergo a facile [1,2] oxygen atom shift to yield acyl nitroso compounds. The oxygen atom shift from a nitro group to a carbene carbon may be a very general reaction. For instance, a [1,3] oxygen atom transfer from a nitro group to a carbene carbon to give a transient nitroso compound was observed by Franck-Neumann and Miesch.[1c] Experiments are underway to observe an intermolecular example of such an oxygen atom migration.

Acylation of the known amine **7**[6] with formic anhydride[7], trifluoroacetic anhydride, ethyl oxalyl chloride and ethyl chloroformate provided authentic Diels-Alder adducts **3** - **6** respectively.



As others have shown[5] the Diels-Alder adducts **3** - **6** may be used as convenient thermal sources of the corresponding acyl nitroso compound. For instance, refluxing a toluene solution of **5** with 2,3-dimethyl-2-butene yields the ene product **2** in 30% yield. The other Diels-Alder adducts behave similarly.



Attempts to spectroscopically observe the extremely unstable acyl nitroso compounds from the adducts **3** - **6** using a combination of flash vacuum pyrolysis and matrix isolation conditions have so far beeen unsuccessful. Matrix isolation studies using nitrodiazomethanes as precursors to nitrocarbenes or acyl nitroso compounds are in progress.

Thus, we have found that nitrodiazomethane may be a source of either nitrocarbene or nitrosoformaldehyde depending on the substrate and reaction conditions. In contrast, both ethyl nitrodiazoacetate and trifluoromethylnitrodiazomethane in the presence of 2,3-dimethyl-2-butene or 9,10-dimethylanthracene are sources of only the corresponding acyl nitroso compound. We are presently investigating other nitrodiazo compounds to determine whether this trend continues to hold.

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4 All new compounds were fully characterized by ir, nmr and mass spectral data or satisfactory elemental analyses.

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