Synthesis of Nitroso- and Dinitroso Compounds by Reaction of Nitrosyl Benzoate and Dinitrosylterephthalate with Tetrasubstituted Alkenes

Thomas R. Sharpe,[a,c] Brian G. Gowenlock*[b]

[a] P. O. Box 7288, Wilmington, Delaware, DE 19803, USA
[b] Riccarton, 5 Roselands, Sidmouth, Devon EX10 8PB, UK
E-mail: Brian.gowenlock@btinternet.com
[c] Explosives Department, E. I. Du Pont de Nemours & Company, Du Pont Experimental Station, Wilmington, Delaware, DE 19898, USA

Received 12 December 2005; revised 12 January 2006

Abstract: The reaction of nitrosyl benzoate with tetrasubstituted alkenes at 0 °C produces monomeric *C*-nitroso compounds in high yields. Similarly, the reaction of dinitrosyl terephthalate with 2,3-dimethylbut-2-ene affords a monomeric dinitroso compound. Extension to other nitrosyl esters gives similar high yields.

Key words: nitrosyl esters, tetrasubstituted alkenes, cycloalkenes, nitroso compounds, dinitroso compounds

During the past fifteen years many synthetic routes for the preparation of *C*-nitroso compounds have been reported and the recent publication of two reviews[1,2] prompts this further detailed synthetic approach first explored some thirty eight years ago. A study on the addition of nitrosyl formate to various olefins was first reported by Hamann and Stern[3] in 1968, at the same time as this work was in progress. A conference paper[4] resulted in a study[5] of the ^{14}N NMR spectra of two of the compounds reported below. The present interest[6,7] in the coordination chemistry of *C*-nitroso compounds suggests that detailed information on the synthetic procedures could lead to the use of these compounds as ligands.

The synthetic routes, employed to produce monomeric nitroso compounds and dinitroso compounds, are shown in Scheme 1.

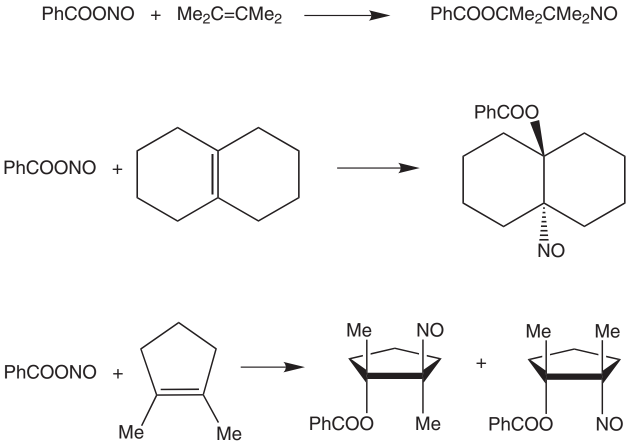
$$\mathrm{RCOONO} + \mathrm{R'_2C{=}CR'_2} \longrightarrow \mathrm{RCOOCR'_2CR'_2NO}$$

$$\mathrm{R''(COONO)_2} + 2\,\mathrm{R'_2C{=}CR'_2} \longrightarrow \mathrm{R''(COOCR'_2CR'_2NO)_2}$$

Scheme 1

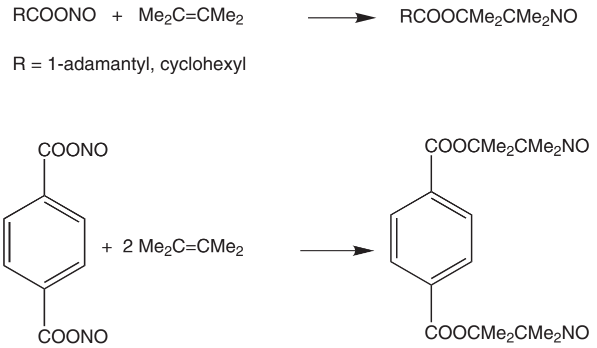
The reaction of nitrosyl benzoate was carried out using three different tetrasubstituted alkenes, namely 2,3-dimethylbut-2-ene, Δ^9-octalin and 1,2-dimethylcyclopentene (Scheme 2).

Further nitrosyl esters were reacted with 2,3-dimethylbut-2-ene, namely nitrosyl 1-adamantane carboxylate, nitrosyl cyclohexanecarboxylate (Scheme 3) and dinitrosyl terephthaloate. Yields of the nitroso compounds were greater than 65%.



Scheme 2

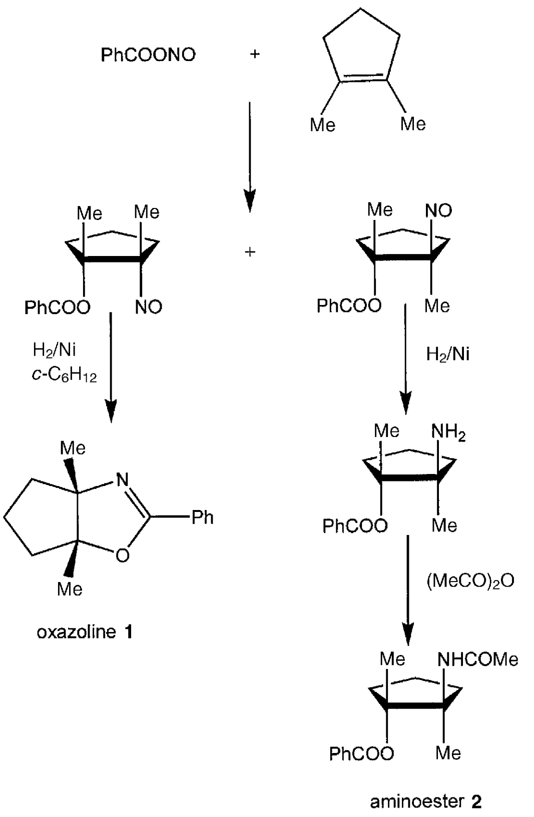
Information concerning the stereochemistry of the nitrosyl ester–tetrasubstituted alkene addition reaction was obtained by carrying out the reaction of nitrosyl benzoate with 1,2-dimethylcyclopentene in different solvents and by interpretation of the NMR spectra of the adducts. The dinitrosyl terephthaloate–tetramethylethylene adduct has two sharp methyl signals at 1.0 and 2.2 ppm which arise from CH_3CNO and CH_3COCO groups, respectively. The NMR spectrum of the adduct of the nitrosylbenzoate–1,2-dimethylcyclopentene reaction shows two signals in the 1 ppm region. The relative amounts of the two adducts as given by integration show that these are markedly depen-



Scheme 3

SYNTHESIS 2006, No. 12, pp 1991–1994
Advanced online publication: 11.05.2006
DOI: 10.1055/s-2006-942392; Art ID: P19205SS

dent upon the solvent employed for the reaction. There is no *a priori* way of knowing which of the two signals arises from the *cis*-adduct and which from the *trans*-adduct. The question was resolved by the application of catalytic hydrogenation to the products obtained from the addition reaction that was carried out using cyclohexane as the reaction medium (the ratio of the two products was 95:5). The product of this reaction was oxazoline **1** (Scheme 4) indicating that the major product was the *cis*-isomer. Confirmation is obtained by the observation that reduction of the 18:82 mixture (with nitromethane as solvent) gave aminoester **2** with only trace amounts of the oxazoline.



Scheme 4

Products **1** and **2** were identified by elemental analyses as well as IR and NMR spectroscopy in full accord with the indicated structures. At the time at which this work was carried out preparative HPLC was not available for the separation of the two geometric isomers, which were obtained as viscous oils.

The results are shown in Table 1 and suggest that the nitrosyl benzoate transfers the nitrosyl cation to the alkene to give a tight ion pair, which rapidly collapses in a low dielectric medium to give the *cis*-adduct, whereas in a high dielectric medium it may lead to a bridged nitrosonium intermediate.

IR, UV-Vis and ^{1}H NMR (recorded at 60 MHz) spectra as well as microanalyses were carried out in the analytical laboratories of Du Pont Experimental Station. Melting points are uncorrected.

Table 1 Isomer Proportions from Reaction of Nitrosyl Benzoate with 1,2-Dimethylcyclopentene

Solvent	% *cis*	% *trans*
Cyclohexane	95	5
CH_2Cl_2	73	27
Nitromethane	18	82

Because all nitrosyl acylates are highly sensitive to moisture, rapidly yielding the parent carboxylic acid and nitrous acid, all moisture must be excluded from the system during their preparation and in all subsequent reactions. The most convenient method for the preparation of nitrosyl benzoate is to react sodium benzoate with dinitrogen tetraoxide.

Preparation of Nitrosyl Benzoate

Sodium benzoate (72.0 g, 0.50 mol) and CH_2Cl_2 (300 mL) were placed in a 1 L three-necked flask equipped with a dropping funnel, thermometer and magnetic stirring bar. The mixture was cooled to 0 °C in an ice bath. Dinitrogen tetraoxide (48.0 g, 0.52 mol) in CH_2Cl_2 (25 mL) was then added dropwise over 2 h. The reaction was not noticeably exothermic, and the temperature did not exceed 2 °C. After the addition, the mixture was stirred for 15 min at 0 °C and for 1.5 h at r.t. The reaction mixture was then filtered through a filtration apparatus under nitrogen and was rinsed with CH_2Cl_2 (2 × 50 mL). The solvent and excess dinitrogen tetraoxide were distilled at aspirator pressure into a –80 °C trap yielding nitrosyl benzoate (71.6 g, 95%).

Reaction of Nitrosyl Benzoate with 2,3-Dimethylbut-2-ene

A solution of nitrosyl benzoate (9.7 g, 64 mmol) in CH_2Cl_2 (80 mL) was cooled to 0 °C under nitrogen and 2,3-dimethylbut-2-ene (6.4 g, 76 mmol) was added dropwise over 35 min. The solution immediately acquired a blue color and the temperature rose to 5 °C. Stirring was continued for 40 min at 0 °C, followed for 35 min at r.t. Solvent and excess alkene were removed initially at aspirator pressure and finally at 0.1 mm yielding 2-benzoyloxy-2,3-dimethyl-3-nitrosobutane (13.9 g, 92%). Analytical and spectroscopic data are in good agreement with the literature.[3]

IR (CCl_4): 1720 (C=O), 1570 (N=O), 1280 (ester) cm^{-1}.

^{1}H NMR (CCl_4): δ = 1.0 (s, 6 H), 2.15 (s, 6 H), 7.5 (m, 3 H), 7.8 (m, 2 H).

UV–Vis (EtOH): λ_{max} (ε) = 678 (8.6) nm.

Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.12; H, 7.32; N, 5.93.

Reaction of Nitrosyl Benzoate with Δ^9-Octalin

A solution of nitrosyl benzoate (10.0 g, 66.2 mmol) in anhyd $MeNO_2$ (100 mL) was cooled to 0 °C and Δ^9-octalin (9.0 g, 66 mmol) was added dropwise over 30 min. After the addition, stirring was continued at 0 °C for 1 h, followed by r.t. for 2 h. Solvent was removed in vacuo to give a green crystalline solid (18.6 g). Recrystallization from 73% EtOH (300 mL) gave *trans*-9-benzoyloxy-10-nitrosodecalin (12.2 g, 64%) as light blue platelets; mp 75–78 °C.

IR (KBr): 1710 (C=O), 1555 (N=O), 1275 (ester) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.1 (m, 2 H), 7.6 (m, 3 H), 0.2–3.7 (m, 16 H).

Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.05; H, 7.37; N, 4.87. Found: C, 70.95; H, 7.29; N, 4.91.

Reaction of Dinitrosyl Terephthalate with 2,3-Dimethylbut-2-ene

Disodium terephthalate (23.2 g, 0.11 mol), dinitrogen tetraoxide (20.2 g, 0.22 mol) and anhyd CH_2Cl_2 (200 mL) were stirred under nitrogen for 5 d at r.t. IR measurements of aliquots of the reaction mixture indicated that formation of the nitrosyl compound was complete after 2 d. Any unreacted dinitrogen tetraoxide was removed by stripping off 50 mL of solvent from the reaction mixture at aspirator pressure. The mixture was cooled to 0 °C under nitrogen and 2,3-dimethylbut-2-ene (18.5 g, 0.22 mol) was added dropwise over 90 min. The ice bath was removed and stirring was continued at r.t. overnight. The mixture was filtered, and the solid product was washed with CH_2Cl_2. Removal of solvent from the filtrate gave a crystalline blue solid (35.3 g). Recrystallization from EtOH (750 mL) gave blue plates of di-(2,3-dimethyl-3-nitrosobutyl) terephthalate (25.8 g, 60%); mp 143–143.5 °C (dec).

IR (CCl_4): $\delta = 1720$ (C=O), 1565 (N=O), 1280 (ester) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 1.0$ (3 × s, 12 H), 2.1 (12 H), 7.8 (4 H).

UV–Vis (cyclohexane): λ_{max} (ε) = 241 (17500) nm.

UV–Vis ($CHCl_3$): $\lambda_{max} = 675$ nm.

Anal. Calcd for $C_{20}H_{28}N_2O_6$: C, 61.21; H, 7.19; N, 7.14. Found: C, 61.19; H, 7.24; N, 7.05.

Reaction of Nitrosyl Benzoate with 1,2-Dimethylcyclopentene

(a) CH_2Cl_2 Solvent

1,2-Dimethylcyclopentene (7.0 g, 73 mmol) was added dropwise over 75 min to nitrosyl benzoate (10.0 g, 66 mmol) in CH_2Cl_2 (75 mL) at 0 °C. The resultant green liquid was stirred under nitrogen at 0 °C for a further 75 min followed by stirring for a further 60 min at r.t. Solvent and excess olefin were removed at aspirator pressure and finally at 1 mm giving a dark green liquid (15.1 g). TLC (silica gel, benzene) showed two blue components with R_f values of 0.56 and 0.54.

IR (CCl_4): 1725 (C=O), 1565 (N=O), 1280 (ester) cm^{-1}.

^1H NMR of the mixture gives two overlapping methyl signals at δ = 1.88 ($OCCH_3$) and two methyl signals at 0.90 and 0.97 ($O{=}NCCH_3$), which were well separated at a 50 cps sweep width with relative areas shown by integration to be 73% and 27% respectively. In accordance with the catalytic reduction described above the major component was assigned the *cis*-structure.

(b) Cyclohexane Solvent

With similar quantities and workup as for CH_2Cl_2 solvent a similar yield of a dark blue-green liquid was obtained the NMR of which showed that *cis*- and *trans*-addition occurred to the extent of 95% and 5%, respectively.

(c) Nitromethane Solvent

With similar quantities using freshly purified[8] $MeNO_2$ the following variation was adopted in the workup following removal of most of the solvent at aspirator pressure. The blue-green residue was dissolved in CH_2Cl_2 and washed with sat. $NaHCO_3$ (3 × 75 mL) and H_2O (100 mL). After drying over $MgSO_4$ removal of the solvent gave a green liquid in similar yield to the use of the other solvents. NMR showed the product composition to be 18% *cis* and 82% *trans*.

Reaction of Nitrosyl Cyclohexanecarboxylate with 2,3-Dimethylbut-2-ene

Nitrosyl cyclohexanecarboxylate was prepared from reaction of silver cyclohexanecarboxylate with nitrosyl chloride. The silver salt (27.7 g, 0.118 mol) was placed in a 500 mL flask fitted with a gas inlet tube, thermometer and magnetic stirrer and the system was flushed with nitrogen and cooled to –20 °C. Nitrosyl chloride (7 mL, 0.15 mol) was condensed into a calibrated trap and added to the reaction flask as a gas diluted with nitrogen over a period of 90 min, the temperature being maintained at –15 °C. After the addition the mixture was stirred for 60 min at 0 °C and then for 60 min at r.t. The mixture was than filtered under nitrogen into a 500 mL flask using CH_2Cl_2 (50 mL) as a rinse. The excess nitrosyl chloride and solvent were then distilled at aspirator pressure into a –80 °C trap, yielding nitrosyl cyclohexanecarboxylate (15.3 g, 83% yield) as an amber liquid.

Reaction with 2,3-dimethylbut-2-ene was carried out using the nitrosyl compound (13.8 g, 87.8 mmol) in CH_2Cl_2 (150 mL) at 0 °C with dropwise addition of the alkene (10.0 g, 119 mmol) over 15 min followed by stirring under nitrogen at 0 °C and at r.t. for 16 h. Solvent and excess alkene were removed as before to give a dark blue liquid which was fractionally distilled through a column giving 2-cyclohexylcarbonyloxy-2,3-dimethyl-3-nitrosobutane (16.1 g, 76%) as a blue liquid; bp 70–71 °C/0.15 mm.

IR (CCl_4): $\delta = 1735$ (C=O), 1575 (N=O) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 0.9$, 2.0 (CH_3), 1.5 (cyclohexyl-H).

Anal. Calcd for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.81. Found: C, 64.53; H, 9.74; N, 5.84.

Reaction of Nitrosyl 1-Adamantanecarboxylate with 2,3-Dimethylbut-2-ene

Silver 1-adamantane carboxylate (10.0 g, 34.9 mmol) was suspended in anhyd CH_2Cl_2 (70 mL) and the mixture was cooled to –10 °C. Nitrosyl chloride (3 mL, 64 mmol) was added as a gas diluted with nitrogen over 30 min and stirring at 0 °C was continued for 30 min. The cold reaction mixture was filtered under nitrogen into a three-necked flask containing a magnetic stirring bar. CH_2Cl_2 (30 mL) was used to rinse the filtration apparatus and the excess nitrosyl chloride was removed from the filtrate by distilling solvent (30 mL) at aspirator pressure. The resulting orange solution showed characteristic IR bands at 1790 (N=O) and 1715 (C=O) cm^{-1}. The solution was then cooled to 0 °C and 2,3-dimethylbut-2-ene (8.4 g, 0.10 mol) was added dropwise over 20 min. The mixture was stirred under nitrogen for 2.5 h at 0 °C followed by stirring overnight at r.t. The blue solution was filtered, solvent and excess alkene were removed in vacuo to give a blue crystalline solid (8.8 g). Recrystallization from 70% EtOH (100 mL) gave 2-(1-adamantanecarbonyloxy)-2,3-dimethyl-3-nitrosobutane (6.9 g, 68% yield) as blue platelets; mp 64.5–66 °C.

IR (CCl_4): 1725 (C=O), 1565 (N=O) cm^{-1}.

^1H NMR (benzene): 0.7(6 H, CH_3), 9 (6 H, CH_3), 1.8 (9 H, adamantine-H), 1.5 (6 H, adamantine-H).

UV–Vis (cyclohexane): λ_{max} (ε) = 685 (9.8) nm.

Anal. Calcd for $C_{17}H_{27}NO_3$: C, 69.59; H, 9.28; N, 4.77. Found: C, 69.63; H, 9.35; N, 5.06.

Acknowledgment

One of the authors (TRS) thanks the DuPont Company for the support of this research, to Drs Herbert S. Eleuterio and Allan E. Nader for their many helpful discussions, to Mr. William F. Herd for skilful technical assistance. We gratefully acknowledge the assistance of Dr Allan E. Nader in producing the reaction schemes.

References

(1) Gowenlock, B. G.; Richter-Addo, G. B. *Chem. Rev.* **2004**, *104*, 3315.

(2) Gowenlock, B. G.; Richter-Addo, G. B. *Chem. Soc. Rev.* **2005**, *34*, 797.

(3) Hamann, H. C.; Swern, D. *J. Am. Chem. Soc.* **1968**, *90*, 6481.

(4) Sharpe, T. R. Euchem Conference on *C*-Nitrosocompounds; Newbattle: Scotland, September 1969.

(5) Mason, J.; van Bronswijk, W.; Winter, J. G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 469.

(6) Cameron, M.; Gowenlock, B. G.; Vasapollo, G. *Chem. Soc. Rev.* **1990**, *19*, 355.

(7) Lee, J.; Chen, L.; West, A. H.; Richter-Addo, G. B. *Chem. Rev.* **2002**, *102*, 1019.

(8) Olah, G. A.; Kuhn, S. J.; Flood, S. H.; Hardin, B. A. *J. Am. Chem. Soc.* **1964**, *86*, 1043.