(1 mmol) in DME (2 ml) with stirring usually at −15 °C (ice–salt bath) or as indicated in Table I. The reaction mixture was stirred at that temperature for a certain period of time (Table I) as required for completion (monitored by TLC) and quenched with careful dropwise addition of aqueous hydrochloric acid (0.5 N). The organic phase was separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic phase and ether extract was washed with water (2 × 10 mL), dried ($MgSO_4$), and evaporated to leave the product, which was identified by comparison with an authentic sample (TLC, IR, and ^1H NMR). In general, the yield was nearly quantitative, and the product did not need further purification.

Acknowledgment. Financial support from DST (Grant No. SP/S1/G-49/88) is gratefully acknowledged. A.R.D. thanks C.S.I.R. for awarding him a Junior Research Fellowship.

Registry No. Cyclopentanone, 120-92-3; 3-methylcyclopent-2-en-1-one, 2758-18-1; 3-methylcyclohexanone, 591-24-2; 3-methylcyclohex-2-en-1-one, 1193-18-6; cyclohexanone, 108-94-1; cyclohex-2-en-1-one, 930-68-7; cycloheptanone, 502-42-1; 7-methoxy-1-benzosuberone, 6500-65-8; 2-chlorocyclohexanone, 822-87-7; ethyl 2-oxacyclopentanecarboxylate, 611-10-9; ethyl acetoacetate, 141-97-9; 3,4,8,8a-tetrahydro-8a-methyl-1,6-(2*H*,7*H*)-naphthalenedione, 20007-72-1; 5,6-dibenzoyl-4-methoxybicyclo[2.2.2]oct-5-en-2-one, 93621-14-8; cyclopentenone, 96-41-3; zinc borohydride, 17611-70-0; 3-methylcyclohexanol, 591-23-1; cyclohexanol, 108-93-0; cyclohex-2-en-1-ol, 822-67-3; cycloheptanol, 502-41-0; 2-chlorocyclohexanol, 1561-86-0; ethyl 2-oxacyclopentanecarboxylate, 54972-10-0; ethyl 3-hydroxybutanoate, 5405-41-4; 4,4a,5,6,7,8-hexahydro-5-hydroxy-4a-methyl-2(3*H*)-naphthalenone, 4242-00-6; 5,6-dibenzoyl-4-methoxybicyclo[2.2.2]oct-5-en-2-ol, 129467-74-9; $PhCH{=}CHCHO$, 104-55-2; $PhCH{=}CHCOCH_3$, 122-57-6; $PhCHO$, 100-52-7; $PhCOCH_3$, 98-86-2; $Me_2C{=}CHCH_2C(Me){=}CHCHO$, 5392-40-5; $Me_2C{=}CHCH_2CH_2C(Me){=}CHCOCH_3$, 817-88-9; $PhCH{=}CHCH_2OH$, 104-54-1; $PhCH_2OH$, 100-51-6; $PhCH_2OHCH_3$, 98-85-1; $Me_2C{=}CHCH_2CH_2C(Me){=}CHCH_2OH$, 624-15-7.

---

(8) A stock solution of zinc borohydride in DME, prepared according to the reported procedure (ref 3c), can be stored in a refrigerator in a closed container for several weeks.

Facile Elimination of Nitrous Acid from Quaternary Nitroalkanes[1]

Claus D. Weis and George R. Newkome*

Center for Molecular Design and Recognition, Department of Chemistry, University of South Florida, Tampa, Florida 33620

Received May 10, 1990

The recent resurgence of the chemistry of nitroalkanes has largely dealt with their reactivity toward nucleophiles;[2] in particular, the new synthetic approaches have utilized the single-electron-transfer (SET) mechanism.[3] Attention has also been devoted to $S_{RN}1$ reactions of nucleophiles with α-substituted nitroalkanes; however, with excess base, nitroalkanes eliminated HNO_2 to afford the corresponding α,β-unsaturated derivatives. Recently, facile elimination of HNO_2 from an angular tertiary nitro group upon contact with silica gel or neutral alumina at ambient temperature has been reported.[4]

In our quest for functionalized methane derivatives suitable for the construction of all carbon unimolecular micelles,[5] convenient starting materials were the tertiary nitro triesters, obtained from the base-catalyzed addition of nitromethane to alkyl acrylates. Although syntheses of these triesters have generally been performed in modest yields, using sodium or potassium hydroxide[6] or sodium methoxide in *tert*-butyl alcohol,[7] and in improved yields using liquid ammonia[8] or ion exchange resins,[9] they have generally been plagued with eratic exothermicity. We herein report the preparation of these triesters in 95% yield when the reaction is conducted in the presence of 40% aqueous Triton-B using dimethoxyethane as solvent. The nitro triesters were isolated in >98% purity and were uncontaminated with either the mono- or diester precursors. Saponification of **1a** afforded $O_2NC(CH_2CH_2CO_2H)_3$, which represents an alternative method to using the tris nitrile.[1] These esters are also important starting materials in the preparation of oxo-2,2-pyrrolidinepropionates, as well as a series of novel polymers.[10]

$$O_2NCH_3 + 3CH_2{=}CHCO_2R \rightarrow \underset{\textbf{1}}{O_2NC(CH_2CH_2CO_2R)_3}$$

Attempts to distill these triesters **1**, as reported,[6] at 10^{-2} mmHg gave rise to partial decomposition with the slow evolution of a reddish gas; only **1a** could be purified by distillation (10^{-3} mmHg) without substantial decomposition. Analytically pure samples of **1** were obtained by flash chromatography on silica gel, without decomposition.

Esters **1** were subjected to thermolysis (305–310 °C) for 12–15 min under an inert atmosphere to probe this degradation, rapid extrusion of HNO_2, in the form of nitrous oxide(s) and water, was observed under these conditions. Although some resinification was observed, the β,γ-unsaturated esters **2** were obtained in 62–65% yield. The

$$\underset{\textbf{1}}{O_2NC(CH_2CH_2CO_2R)_3} \rightarrow \underset{\textbf{2}}{(RO_2CCH_2CH_2)_2C{=}CHCH_2CO_2R}$$

a (R = Me), **b** (R = Et), **c** (R = *n*-Bu)

elimination process could be monitored by the disappearance of the prominent absorption (1537 cm^{-1}) for the nitro group in the IR spectrum. The ^1H NMR data for **2** shows a doublet at δ ca. 3.1 for the α-CH_2 triplet at δ ca. 5.4 for the $=CH$ indicative of the β,γ-double bond; no evidence of double-bond migration was observed.

4-Nitro-4-(3-hydroxypropyl)-1,7-dihydroxyheptane[1] when treated with acetic anhydride in pyridine afforded (92%) the nitro triacetate **3**, which was confirmed (^1H NMR) by the singlet at δ 1.99 for the acetate methyl. Under similar thermolysis conditions, **3** extruded HNO_2 to generate (67%) the desired trisubtituted olefin **4**, which possessed three unique acetyl methyl groups.

The facile preparation of **1**, which circumvents the well-known detrimental exothermicity in this Michael

---

[1] Building blocks for Cascade Polymers. 3. For the previous paper in this series, see: Newkome, G. R.; Moorefield, C. N.; Theriot, K. J. *J. Org. Chem.* **1988**, *53*, 5552.

[2] Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 23.

[3] Ono, N.; Miyake, H.; Tanikaga, R.; Kaji, A. *J. Org. Chem.* **1982**, *47*, 5017.

[4] Marchand, A. P.; Suri, S. C. *J. Org. Chem.* **1984**, *49*, 670.

[5] Newkome, G. R, *Abstracts of Papers*; 199th National Meeting of American Chemical Society, Boston, MA, April 22–27, 1990, ORGN–317.

[6] Schickh, O. v. *Angew. Chem.* **1950**, *62*, 557. Hopf, H.; Schickh, O. v.; Wiest, G. Bad. Anilin and Sodafabriken Ger. Pat. 851,342 (Oct. 2, 1952); *Chem. Abstr.* **1958**, *52*, 10168c. Ger. Pat. 855,256 (Nov. 10, 1952); *Chem. Abstr.* **1956**, *50*, 5025d. Schickh, O. v. Bad. Anilin and Sodafabriken Ger. Pat. 857,362 (Nov. 27, 1952); *Chem. Abstr.* **1958**, *52*, 5455t.

[7] Allen, S. J.; Drewitt, J. G. N. Celanese Corp. U. S. Pat. 2,502,548 (Apr. 4, 1950); *Chem. Abstr.* **1950**, *44*, 7585b.

[8] Wakamatsu, S.; Shimo, K. *J. Org. Chem.* **1962**, *27*, 1609. Jpn. Pat. 3419 (64) (Dec. 29, 1961); *Chem. Abstr.* **1964**, *61*, 2978g.

[9] Schmidle, C. J.; Mansfield, R. C. Rohm and Haas Co. U.S. Pat. 2,658,070 (Nov. 3, 1953); *Chem. Abstr.* **1954**, *48*, 13715f.

[10] Butler, D. Warner Lambert Co. U.S. Pat. 4,454,327 (Jun. 12, 1984); *Chem. Abstr.* **1984**, *101*, 171,084.

0022-3263/90/1955-5801$02.50/0

$$\underset{\mathbf{3}}{O_2NC(CH_2CH_2CH_2OAc)_3} \rightarrow \underset{\mathbf{4}}{(AcOCH_2CH_2CH_2)_2C{=}CHCH_2CH_2OAc}$$

addition, provides convenient access to trisubstituted olefins possessing thermal functionalization.

Experimental Section

General Comments. Melting points were taken in capillary tubes and are uncorrected. The ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$, unless otherwise stated, with Me_4Si, as the internal standard ($\delta = 0$ ppm). Infrared spectra (IR) were recorded in a Perkin-Elmer 621 grating infrared spectrometer. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Diethyl 4-Nitro-4-[1-[2-(ethoxycarbonyl)ethyl]]heptanedioate (1b). General Procedure. To a stirred solution of $MeNO_2$ (15.25 g, 250 mmol), Triton B (benzyltrimethylammonium hydroxide, 40% in water; 1 mL), and dimethoxyethane (40 mL) was added dropwise ethyl acrylate (75 g, 750 mmol) over 30 min at a rate that the temperature of 72–78 °C was maintained. Additional Triton B was added twice when the temperature started to decrease; then stirring was continued for an additional 45 min. After concentration in vacuo, the residue was dissolved in $CHCl_3$ (250 mL), washed with dilute aqueous HCl (0.5 N, 100 mL), and then brine (3 × 80 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford the crude triester, which was column chromatographed on SiO_2 eluting with $EtOAc/C_6H_{14}$ (1:5) to give (85%) triester **1b** as a light yellow oil: 90 g; ^1H NMR δ 1.24 (t, $CH_2\mathit{CH}_3$, $J = 7.1$ Hz, 9 H), 2.26 (b, 8 H), 4.10 (q, CH_2CH_3, $J = 7.1$ Hz, 6 H); ^{13}C NMR δ 13.81 (CH_3), 28.43 (OCH_2), 30.02 ($\mathit{C}H_2CH_2CO$), 60.73 ($\mathit{C}H_2CO$), 91.07 ($\mathit{C}NO_2$), 171.80 (C=O); IR (neat) 1738 (CO_2Et), 1542 (NO_2) cm^{-1}. Anal. Calcd for $C_{16}H_{27}NO_8$: C, 53.17; H, 7.65; N, 3.88 Found: C, 53.63; H, 7.53; N, 4.09.

Dimethyl 4-nitro-4-[1-[2-(methoxycarbonyl)ethyl]]heptanedioate (1a): oil; 96%, ^1H NMR δ 2.20 (b, CH_2CH_2, 12 H), 3.59 (s, OCH_3, 9 H); ^{13}C NMR δ 28.19 ($CH_2\mathit{C}H_2CO$), 29.98 ($\mathit{C}H_2CH_2CO$), 51.70 ($O\mathit{C}H_3$), 91.79 (quaternary C), 171.80 (C=O); IR (neat) 1738 (CO_2CH_3), 1542 (NO_2) cm^{-1}. Anal. Calcd for $C_{13}H_{21}NO_8$: C, 48.89; H, 6.62; N, 4.38. Found: C, 49.07; H, 6.87; N, 4.52.

Dibutyl 4-nitro-4-[1-[2-(butoxycarbonyl)ethyl]]heptanedioate (1c): oil; 92%; ^1H NMR δ 0.93 (t, CH_3, $J = 6.2$ Hz, 9 H), 1.23–1.51 (m, CH_2CH_2, 12 H), 2.27 (CH_2CH_2CO, 12 H), 4.07 (t, OCH_2, $J = 6.4$ Hz, 6 H); ^{13}C NMR δ 13.3 (CH_3), 18.8 ($CH_3\mathit{C}H_2$), 30.4 ($CH_3CH_2\mathit{C}H_2$), 32.4 ($\mathit{C}H_2CH_2CO$), 41.1 ($\mathit{C}H_2CO$), 64.0 ($\mathit{C}H_2O$), 93.1 (quaternary C), 172.1 (C=O); IR (neat) 1738 (C=O), 1542 (NO_2) cm^{-1}. Anal. Calcd for $C_{22}H_{39}NO_8$: C, 59.30; H, 8.82; N, 3.14. Found: C, 59.54; H, 8.67; N, 3.27.

4-Nitro-4-[1-(2-carboxyethyl)]heptanedioic Acid. A suspension of the nitro trimethyl ester **1a** (16.0 g, 50 mmol), aqueous sodium hydroxide (80 mL), and CH_3OH (30 mL) was stirred at 25 °C for 24 h. The solution was concentrated in vacuo and then acidified with concentrated H_2SO_4 (12 g). The precipitate was filtered and washed with ice water (30 mL) to afford (98%) the triacid, as white crystals: 14 g; mp 184 °C (lit.[11] mp 186 °C).

Diethyl 4-[2-(Ethoxycarbonyl)ethyl]hept-3-enedioate (2b). General Procedure. The neat triester **1b** (7 g, 190 mmol) was heated to 305 °C under nitrogen for 15 min, during which time gases were extruded. After cooling to 25 °C, the crude residue was distilled (Kugelrohr) in vacuo to give (60%) the alkene, as a light yellow oil: 3.62 g; bp 170 °C (0.1 mm); ^1H NMR δ 1.25 (t, $J = 7.1$ Hz, CH_3, 9 H), 2.38 (b, CH_2, 8 H), 3.08 (d, $J = 7.2$ Hz, CH_2, 2 H), 4.08 (q, $J = 7.1$ Hz, 3 × CH_2, 6 H), 5.42 (t, $J = 7.2$ Hz, =CH—, 1 H); ^{13}C NMR δ 13.80 (CH_3) 32.10, 32.30, 32.83 (3 × CH_2), 25.4, 30.8 (2 × CH_2), 63.67 (OCH_2), 118.13 (=CH—), 139.20 (=C), 171.80 (C=O), 172.8, 172.9 (2 × C=O); IR (neat) 1175 (C—O), 1738 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_6$: C, 61.12; H, 8.34. Found: C, 61.28; H, 8.26.

Dimethyl 4-[2-(methoxycarbonyl)ethyl]hept-3-enedioate (2a) was prepared in similar manner from **1a**: oil; 62%; bp 155 °C (0.1 mm); ^1H NMR δ 2.39 (s, CH_3, 9 H), 3.09 (d, $J = 7.2$ Hz, 2 H), 3.67 (bs, CH_2CH_2, 8 H), 5.41 (t, $J = 7.2$ Hz, =CH—, 1 H); ^{13}C NMR δ 32.1, 32.3, 32.8 (3 × $COCH_2$), 25.4, 30.8 (2 × CH_2), 51.20 (OCH_3), 118.10 (=CH—), 139.24 (C=), 171.80, 172.83 (2 C=O); IR (neat) 1738 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.49; H, 7.09.

Dibutyl 4-[2-(butoxycarbonyl)ethyl]hept-3-enedioate (2c) was prepared from **1c**: oil; 64%; bp 200 °C (0.2 mm); ^1H NMR δ 0.93 (t, $J = 6.2$ Hz, CH_3, 9 H), 1.21–1.53 (m, CH_2CH_2, 12 H), 3.08 (d, $J = 7.2$ Hz, CH_2, 8 H), 4.07 (t, $J = 6.4$ Hz, OCH_2, 2 H), 5.42 (t, $J = 7.2$ Hz, =CH—, 1 H); ^{13}C NMR δ 13.3 (3 × CH_3), 18.8 (3 × CH_3CH_2), 25.4 ($CHCH_2CO$), 30.4 (3 × CH_2), 31.0, 32.4, 32.6, 33.1 (2 × CH_2CH_2), 63.9, 64.0, 64.1 (3 × CH_2O), 118.0 (=CH), 139.2 (C=), 171.48, 172.56 (2 C=O); IR (neat) 1738 (C=O) cm^{-1}. Anal. Calcd for $C_{32}H_{38}O_6$: C, 66.29; H, 9.61. Found: C, 66.27; H, 9.62.

4-Nitro-4-[1-(3-acetoxypropyl)]-1,7-diacetoxyheptane (3). A stirred solution of $O_2NC(CH_2CH_2CH_2OH)_3$[1] [bp > 150 °C (0.3 mm); 7.4 g, 31 mmol], Ac_2O (25 mL), and pyridine (5 drops) was heated to 70 °C for 12 h. After cooling, the mixture was poured into water, stirred for 3 h, then neutralized with $NaHCO_3$, and extracted with ether (3 × 50 mL). The combined extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a residue, which was column chromatographed (SiO_2) eluting with benzene to afford (92%) the triacetate **3**, as a light yellow oil: 10.5 g; ^1H NMR δ 1.86 (m, CH_2, 12 H), 1.99 (m, 3 × $C\mathit{H}_3$, 9 H), 4.00 (t, $C\mathit{H}_2O$, $J = 6.1$ Hz, 6 H); ^{13}C NMR δ 20.6 (CH_3), 22.93 ($CCH_2\mathit{C}H_2$), 31.77 ($C\mathit{C}H_2$), 63.34 (CH_2O), 93.09 (quaternary C), 170.61 (C=O); IR (neat) 1743 (ester), 1542, 1363 (NO_2) cm^{-1}. Anal. Calcd for $C_{16}H_{27}NO_8$: C, 53.17; H, 7.53; N, 3.88. Found: C, 53.59; H, 7.51; N, 3.82.

4-[1-(2-Acetoxypropyl)]-1,7-diacetoxyhept-3-ene (4) was prepared from **3**: 73%; bp 185 °C (0.1 mm); ^1H NMR δ 1.73–1.81 (m, CH_2CH_2, 8 H), 2.03 (s, CH_3, 3 H), 2.04 (s, CH_3, 3 H), 2.05 (s, CH_3, 3 H), 2.40 (d, $J = 7.2$ Hz, $=CHCH_2$, 2 H), 4.05 (t, 3 × OCH_2, $J = 6.7$ Hz, 6 H), 5.18 (t, $J = 7.2$ Hz, =CH, 1 H); ^{13}C NMR δ 20.58 (CH_3), 26.0, 26.70 (CH_2CH_2), 26.93, 27.03 ($CH_2C{=}CH$), 32.5 ($=CHCH_2$), 63.76 (OCH_2), 121.25 (=CH—), 139.86 (—C=), 171.01 (C=O); IR (neat) 1743 (ester) cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_6$: C, 61.12; H, 8.33. Found: C, 61.15; H, 8.27.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grants DMR-86-00929; 89-06792) for their support of this work.

---

(11) Sorm, F.; Beranek, J. *Collect. Czech. Chem. Commun.* **1954**, *19*, 298.