acetate: 0.6 g (70%); mp 176–177 °C (lit.[11] mp 174–175 °C for the racemate); ^{13}C NMR (D_2O) δ 177.00 (CO), 49.94 (CH), 41.76 (CH_2N), 30.23 (CH_2-2) 27.89 (CH_2-3); ^1H NMR (D_2O) δ 3.70 (m, 1 H, CH-4), 3.35 (m, 2 H, CH_2-5), 2.60 (m, 2 H, CH_2-2), 2.10 (m, 2 H, CH_2-3); mass spectrum, m/z (relative intensity) 114 (16, M^+ – 18, 5-(aminomethyl)-2-pyrrolidone), 98 (22, 5-methylene-2-pyrrolidone), 84 (40, 2-pyrrolidone); $[\alpha]^{20}_D$ +4.6° (c 2.5, water). On cellulose TLC it had R_f 0.18 (2-propanol/hydrochloric acid/water, 5/1/1).

Anal. Calcd for $C_5H_{14}Cl_2N_2O_2$: C, 29.3; H, 6.9; N, 13.7. Found: C, 29.2; H, 6.8; N, 13.6.

(*S*)-(–)-4,5-Diaminovaleric acid dihydrochloride (6b) was obtained following the procedure described for its enantiomer **6a**. From 1 g of **5b** was obtained 0.7 g (85%) of **6b**: mp 180–181 °C (methanol–ethyl acetate); $[\alpha]^{20}_D$ –4.6° (c 1.5, water). On cellulose TLC it had R_f 0.15 (solvent as for **6a**).

Anal. Calcd for $C_5H_{14}C_{12}N_2O_2$: C, 29.3; H, 6.9; N, 13.7. Found: C, 29.3; H, 6.8; N, 13.8.

(*R*)-5-(((Methylsulfonyl)oxy)methyl)-2-pyrrolidone (4). Mesyl chloride (2.5 mL) was added to a stirred solution of 0.4 g of **2a** in 5 mL of anhydrous pyridine kept at 5 °C. The mixture was stirred at 25 °C during 90 min, and it was then evaporated to dryness in vacuo. The residue was dissolved in a small volume of 10% methanol in chloroform, and the solution was applied to a TLC silica gel column (2 × 20 cm) packed and prewashed with the same solvent. The mesylate was eluted with the same eluant, the eluate was evaporated to dryness, and the residue was recrystallized from chloroform–hexane: 0.3 g (60%); mp 75–76 °C; ^{13}C NMR (D_2O) δ 178.00 (CO), 71.10 (CH), 52.30 (CH_2O), 36.81 (CH_3), 29.10 (CH_2-3), 22.10 (CH_2-4); ^1H NMR (Cl_3CD) δ 7.10 (s, 1 H, NH), 4.10 (m, 3 H, CH_2O, H-5), 3.10 (s, 3 H, CH_3), 2.10 (m, 4 H, CH_2).

Anal. Calcd for $C_6H_{11}NO_4S$: C, 37.3; H, 5.7; N, 7.2. Found: C, 37.2; H, 5.8; N, 7.1.

Acknowledgment. This work was made possible by a grant (GM-11973) from the National Institutes of Health (to B.F.) and the Louis Block Fund of the University of Chicago. Support from CONICET (Argentina) is also acknowledged.

Registry No. **1a**, 68766-96-1; **1b**, 7149-65-7; **2a**, 66673-40-3; **2b**, 17342-08-4; **3a**, 138541-53-4; **3b**, 72479-04-0; **4**, 138541-54-5; **5a**, 138541-55-6; **5b**, 138541-56-7; **6a**, 138661-27-5; **6b**, 130338-27-1; potassium phthalimide, 1074-82-4.

Chemoselective Synthesis of Functionalized Conjugated Nitroalkenes

Roberto Ballini,* Roberto Castagnani, and Marino Petrini

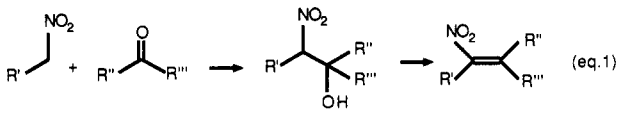
Dipartimento di Scienze Chimiche dell'Università, Via S.Agostino n.1, 62032 Camerino, Italy

Received September 25, 1991

Unsaturated nitro compounds have proved to be valuable precursors to a wide variety of target molecules. Historically, the nitroalkenes were of importance because of their biological activity such as insecticides,[1,2] fungicides,[1,3–5] and pharmacologically active substances.[6–9]

The utility of nitroalkenes in organic synthesis is largely due to their easy conversion into a variety of functionalities.[10] Alternatively they are powerful dienophiles in Diels–Alder reactions or readily undergo addition reactions with many different nucleophiles.

The classical preparation of nitroalkenes involves the Henry condensation reaction of aldehyde or ketone with a nitroalkane followed by dehydratation of the resultant β-nitro alcohol[11] (eq 1).



(eq.1)

Several methods, using reagents such as methanesulfonyl chloride,[12] phthalic anhydride,[13,14] dicyclohexylcarbodiimide (DCC),[15] and pivaloyl chloride[16,17] have been used for the dehydration step. However some of these are indirect methods or require high temperature and, moreover, they seem of little utility in the dehydration of functionalized β-nitro alcohols. The importance of functionalized nitroalkenes prompted us to search for a chemoselective and more convenient dehydrating agent for functionalized β-nitro alcohols.

In a previous paper we reported[18] a mild, simple heterogeneous method for synthesis of 2-nitroalkanols from nitroalkanes and aldehydes on an alumina surface at room temperature and in the absence of a solvent. Later we noted[19] that this solvent-free nitro-aldol reaction between functionalized nitroalkanes and aryl aldehydes such as 2-furaldehyde gave 1-(2-furyl)-2-nitroalk-1-enes in high yields.

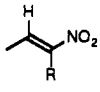
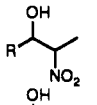
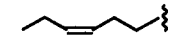
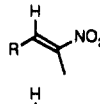
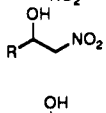
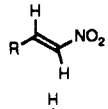
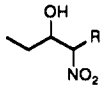
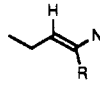
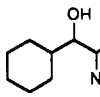
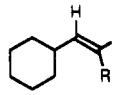
Based on these previous results we have found that basic alumina is a far superior catalyst for the chemoselective dehydration of the functionalized β-nitro alcohols.

Our method is carried out at 40 °C by simply dissolving the appropriate nitroalkanol in dichloromethane, with basic alumina (activity I according to Brockmann). After stirring at 40 °C for the right time (see Table I), the product is isolated, as the *E* isomer,[20] in good yields (60–85%) by filtration, evaporation, and purification by distillation or chromatography. In this procedure the formation of conjugated nitroalkenes is preferred even if the other isomer is expected by Saytzeff orientation (23

(1) Bousquet, E. W.; Kirby, J. E.; Searle, N. E. U.S. Patent 2,335,384, 1943; *Chem. Abstr.* **1944**, *38*, 2834.
(2) Brown, A. W. A.; Robinson, D. B. W.; Hurtig, H.; Wenner, B. J. *Can. J. Res.* **1948**, *26D*, 177.
(3) Brian, P. W.; Grove, J. F.; McGowan, J. C. *Nature* **1946**, *158*, 876.
(4) McGowan, J. C.; Brian, P. W.; Hemming, H. G. *Ann. Appl. Biol.* **1948**, *35*, 25.
(5) Bocobo, F. C.; Curtis, A. C.; Block, W. D.; Harrell, E. R.; Evans, E. E.; Haines, R. F. *Antibiol. Chemother.* **1956**, *6*, 385.
(6) Schales, O.; Graefe, H. A. *J. Am. Chem. Soc.* **1952**, *74*, 4486.
(7) Dann, O.; Moller, E. F. *Chem. Ber.* **1949**, *82*, 76.
(8) Harker, R. J. U.S. Patent 2,889,246, 1959; *Chem. Abstr.* **1959**, *53*, 17414i.
(9) Zee-Cheng, K.; Cheng, C. *J. Med. Chem.* **1969**, *12*, 157.
(10) (a) Barrett, A. G. W.; Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751. (b) Kabalka, G. W.; Varma, R. S. *Org. Prep. Proc. Int.* **1987**, *19*, 283. (c) Barrett, A. G. M. *Chem. Soc. Rev.* **1991**, *20*, 95.
(11) (a) Bauer, H. H.; Urbas, L. *The Chemistry of the Nitro and Nitroso Group*; Feuer, H., Ed.; Interscience: New York, 1970; Part 2, pp 75–200. (b) Seebach, D.; Colvin, E. W.; Leher, F.; Weller, T. *Chimia* **1979**, *31*, 1. (c) Schickh, O. V.; Apel, G.; Padeken, H. G.; Schwartz, H. H.; Segnitz, A. In *Houben-Weyl: Methoden der Organische Chemie*; Muller, E., Ed.; George Thieme Verlag: Stuttgart, 1971; Vol. 10/1, pp 9–462. (d) Rajappa, S. *Tetrahedron* **1981**, *37*, 1453. (e) Perekalin, V. V. *J. Org. Chem. USSR (Engl. Transl.)* **1985**, *21*, 1011.
(12) Melton, J.; Mc Murry, J. E. *J. Org. Chem.* **1975**, *40*, 2138.
(13) Buckley, G. D.; Caife, C. W. *J. Chem. Soc.* **1947**, 1471.
(14) Ranganathan, D.; Rao, C. B.; Ranganathan, S.; Mehrotra, R. *J. Org. Chem.* **1980**, *45*, 1185.
(15) Knochel, P.; Seebach, D. *Synthesis* **1982**, 1017.
(16) Knochel, P.; Seebach, D. *Tetrahedron Lett.* **1982**, *23*, 3897.
(17) Seebach, D.; Knochel, P. *Helv. Chim. Acta* **1984**, *67*, 261.
(18) Rosini, G.; Ballini, R.; Sorrenti, P. *Synthesis* **1983**, 1014.
(19) Rosini, G.; Ballini, R.; Petrini, M.; Sorrenti, P. *Synthesis* **1985**, 515.
(20) The *E* geometry was readily assigned on the basis of ^1H NMR spectra: (a) Ono, N.; Kamimura, A.; Kawai, T.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1550. (b) Hamayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Tetrahedron Lett.* **1982**, *23*, 4733. (c) Hamayama, T.; Somoda, S.; Takeuchi, Y.; Nomura, Y. *Chem. Lett.* **1982**, 1109.

0022-3263/92/1957-2160$03.00/0

Table I. Dehydration of 2-Nitro Alcohols to Conjugated Nitroalkenes

2-nitro alcohol	no.	R	conjugated nitroalkene	no.	reaction time (h)	yield (%)
	1	Me		2	8	75
	3	Et		4	7	77
	5	$(CH_2)_4COOMe$		6	7	76
	7	$CH_2CHOHCH_3$		8	7	73
	9			10	7	85
	11	$Ph(CH_2)_2$		12	9	68
	13	Et		14	48	60
	15	n-C_6H_{13}		16	50	61
	17	$(CH_2)_6OH$		18	7	68
	19	CH_2OH		20	9	64
	21	Me		22	7	64
	23	n-C_5H_{11}		24	24	72

to **24**). It is noteworthy that other functions such as ester, *Z* double bond, or hydroxy group are preserved. Moreover, in the nitro β,β'-diol it is possible to effect a chemoselective dehydration of the secondary hydroxy group (**19** to **20**) with respect to the primary one.

Furthermore, a one-pot synthesis of conjugated nitroalkenes **12**, **22**, and **24**, starting from aliphatic aldehydes, consisting of a solvent-free nitro-aldol reaction on alumina at room temperature, followed by in situ dehydration, with addition of dichloromethane and warming at 40 °C, has been developed.

Since the nitroalkenes are amenable to transformation into carbonyl compounds,[21] the present chemoselective synthesis of nitroalkenes will increase the use of β-nitroalkanols in the preparation of functionalized ketones.[22]

In summary, the present methodology to obtain conjugated nitroalkenes is mild, and highly selective, and proceeds in good yields also on a large scale.

Experimental Section

General. GC analyses were performed on a capillary column of Duran glass (0.32 mm × 25 m), stationary phase OV1 (film thickness 0.4–0.45 nm). All ^1H NMR spectra were recorded, in $CDCl_3$ as solvent, at 300 MHz. Boiling points are uncorrected. Basic alumina (activity I according to Brockmann) was purchased from Carlo Erba. The β-nitro alcohols were prepared by the Henry reaction[18] as a mixture of the diastereomeric forms erythro–threo. The β-nitro alcohols **7**, **17**, and **19** were prepared in the same way starting from 4-nitro-2-butanol, 7-nitro-1-heptanol,[23] and 2-nitroethanol, respectively. The crude conjugated nitroalkenes were purified by distillation or chromatography. Preparation of **4** is described here as a typical procedure.

(*E*)-3-Nitro-2-pentene (4). 3-Nitro-2-pentanol (**3**) (6.65 g, 0.05 mol), in CH_2Cl_2 (60 mL), was stirred mechanically at rt in a 250 mL, three-necked flask. Chromatographic alumina (Carlo Erba RS, activity I according to Brockmann, 10 g) was added, and stirring was continued at 40 °C for 7 h (the reaction progress was monitored by GC and TLC). The mixture was filtered, the alumina was washed with CH_2Cl_2 (3 × 30 mL), and the filtered extract was evaporated at reduced pressure to give the crude nitroalkene **4** which after distillation gave 4.43 g (77%) of pure product: bp_{10} 65 °C (lit.[24] bp_{12} 69–70 °C); IR (film) ν 1670 (C=C), 1520 cm^{-1} (NO_2); ^1H NMR δ 1.12 (t, 3 H, J = 7.4 Hz), 1.9 (d, 3 H, J = 7.4 Hz), 2.62 (q, 2 H, J = 7.4 Hz), 7.18 (q, 1 H, J = 7.4 Hz). Anal. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 51.95; H, 8.01; N, 11.98.

(*E*)-2-Nitro-2-butene (2): yield 3.78 g (75%); bp_{20} 80 °C (lit.[15] bp_{10} 40–42 °C); IR (film) ν 1675 (C=C), 1515 cm^{-1} (NO_2); ^1H NMR δ 1.89 (d, 3 H, J = 7.4 Hz), 2.18 (s, 3 H), 7.2 (q, 1 H, J = 7.4 Hz). Anal. Calcd for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.85. Found: C, 47.70; H, 7.1; N, 13.68.

(*E*)-Methyl 6-nitro-6-octenoate (6): yield 7.64 g (76%); oven $temp_{0.08}$ 165 °C (Kugelrohr); IR (film) ν 1735 (CO), 1665 (C=C), 1515 cm^{-1} (NO_2); ^1H NMR δ 1.45–1.75 (m, 4 H), 1.88 (d, 3 H, J = 7.3 Hz), 2.3 (t, 2 H, J = 7.2 Hz), 2.6 (t, 2 H, J = 7.8 Hz), 3.65 (s, 3 H), 7.18 (q, 1 H, J = 7.3 Hz). Anal. Calcd for $C_9H_{15}NO_4$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.90; H, 7.38; N, 7.10.

(*E*)-4-Nitro-4-hexen-2-ol (8): yield 5.3 g (73%); oil; IR (film) ν 3435 (OH), 1670 (CO), 1515 cm^{-1} (NO_2); ^1H NMR δ 1.38 (d, 3 H, J = 6.8 Hz), 1.65 (broad s, 1 H), 1.97 (d, 3 H, J = 7.6 Hz), 1.75–1.85 (m, 2 H), 4.00–4.15 (m, 1 H), 7.38 (q, 1 H, J = 7.6 Hz). Anal. Calcd for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65. Found: C, 49.82; H, 7.71; N, 9.49.

(2*E*,6*Z*)-2-Nitro-2,6-nonadiene (10): yield 7.18 g (85%); oven $temp_{0.55}$ 136 °C (Kugelrohr); IR (film) ν 1670 (C=C), 1520 cm^{-1} (NO_2); ^1H NMR δ 0.88 (t, 3 H, J = 7.6 Hz), 1.9–2.1 (m, 2 H), 2.18 (s, 3 H), 2.15–2.30 (m, 4 H), 5.22–5.32 (m, 1 H), 5.4–5.5 (m, 1 H), 7.12 (t, 1 H, J = 7.4 Hz). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found: C, 64.01; H, 9.05; N, 8.13.

(*E*)-1-Nitro-1-butene (14): yield 3.03 g (60%); bp_8 54 °C (lit.[24] bp_{12} 55 °C); IR (film) ν 1645 (C=C), 1520 cm^{-1} (NO_2); ^1H NMR δ 1.1 (t, 3 H, J = 6.9 Hz), 2.25–2.40 (m, 2 H), 6.95–7.03 (m, 1 H), 7.25–7.40 (m, 1 H). Anal. Calcd $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.85. Found: C, 47.70; H, 7.13; N, 13.69.

(*E*)-1-Nitro-1-octene (16): yield 4.79 g (61%); oven $temp_{0.7}$ 150 °C (Kugelrohr) (lit.[24] bp_9 112 °C); IR (film) ν 1645 (C=C), 1520 cm^{-1} (NO_2); ^1H NMR δ 0.9 (t, 3 H, J = 6.9 Hz), 1.2–1.6 (m, 8 H), 2.18–2.35 (m, 2 H), 6.97–7.00 (m, 1 H), 7.25–7.33 (m, 2 H). Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.00; H, 9.80; N, 9.02.

(*E*)-7-Nitro-7-decen-1-ol (18): yield 6.83 g (68%); oil; IR (film) ν 3340 (OH), 1615 (C=C), 1515 cm^{-1} (NO_2); ^1H NMR δ 1.12 (t, 3 H, J = 8.8 Hz), 1.3–1.65 (m, 8 H), 2.25 (m, 2 H, J = 7.6 Hz), 2.55–2.6 (dd, 2 H, J = 7.3, 7.7 Hz), 3.64 (t, 2 H, J = 6.5 Hz), 7.08 (t, 1 H, J = 7.9 Hz). Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.68, H, 9.52; N, 6.96. Found: C, 59.53; H, 9.66; N, 7.07.

(*E*)-2-Nitro-2-penten-1-ol (20): yield 4.2 g (64%); oven $temp_{0.5}$ 150 °C (Kugelrohr); IR (film) ν 3400 (OH), 1640 (C=C), 1513 cm^{-1} (NO_2); ^1H NMR δ 1.18 (t, 3 H, J = 7.1 Hz), 2.3–2.45 (m, 2 H, J = 7.9 Hz), 4.55 (d, 1 H, J = 7.4 Hz), 7.21–7.25 (m, 1 H). Anal. Calcd for $C_5H_9NO_3$: C, 45.8; H, 6.92; N, 10.68. Found: C, 45.98; H, 6.79; H, 10.80.

One-Pot Synthesis of Conjugated Nitroalkenes 12, 22, and 24. Typical Example: Preparation of (*E*)-2-Nitro-2-pentene

(21) (a) Varma, R. S.; Varma, M.; Kabalka, G. W. *Tetrahedron Lett.* **1985**, *26*, 3777. (b) Monti, D.; Grammatica, P.; Speranza, G.; Manitto, P. *Tetrahedron Lett.* **1983**, *24*, 417. (c) Torii, S.; Tanaka, H.; Katoch, T. *Chem. Lett.* **1983**, 607. (d) Mourad, M. S.; Varma, R. S.; Kabalka, G. W. *Synthesis* **1985**, 654. (e) Aizpurua, J. M.; Oiarbide, M.; Palomo, C. *Tetrahedron Lett.* **1987**, *28*, 5365. (f) Hwu, J. R.; Gilbert, B. A. *J. Am. Chem. Soc.* **1991**, *113*, 5917.

(22) Rosini, G.; Ballini, R. *Synthesis* **1988**, 833.

(23) Ballini, R.; Petrini, M.; Rosini, G. *Tetrahedron* **1990**, *46*, 7531.

(24) Schmidt, E.; Rutz, G. *Ber.* **1928**, *61B*, 2142.

(22). A solution of propionaldehyde (2.9 g, 0.05 mol) and nitroethane (3.75 g, 0.05 mol) was mechanically stirred for 5 min at 0 °C, while cooling with an ice bath. After the addition of chromatographic alumina (Carlo Erba RS, activity I, 10 g) and stirring for 30 min at 0 °C, the mixture was allowed to stand at rt for 20 h. CH_2Cl_2 (60 mL) was added, and the mixture was stirred and heated at 40 °C for 7 h. The mixture was then filtered, and the alumina was washed with CH_2Cl_2 (3 × 30 mL). The organic layer was evaporated and purified by distillation to give 3.68 g (64%) of **22**: bp_{10} 66 °C (lit.[12] bp_{20} 85 °C); IR (film) ν 1650 (C=C), 1510 cm^{-1} (NO_2); ^1H NMR δ 1.12 (t, 3 H, J = 7.6 Hz), 2.1–2.4 (m, 2 H), 2.17 (s, 3 H), 7.12 (t, 1 H, J = 7.5 Hz). Anal. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.02; H, 7.99; N, 12.05.

(*E*)-2-Nitro-5-phenyl-2-pentene (12): yield 6.5 g (68%); $bp_{0.07}$ 163 °C; IR (film) ν 1670, 1600 (C=C), 1515 cm^{-1} (NO_2); ^1H NMR δ 2.08 (s, 3 H), 2.55 (q, 2 H, J = 7.4 Hz), 7.1–7.4 (m, 5 H). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.93; H, 6.97; N, 7.45.

(*E*)-2-Nitro-1-cyclohexyl-1-heptene (24): yield 8.1 g (72%); oil; IR (film) ν 1665 (C=C), 1520 cm^{-1} (NO_2); ^1H NMR δ 0.9 (t, 3 H, J = 7 Hz), 1.2–1.6 (m, 19 H), 2.18–2.35 (m, 2 H), 6.97 (d, 1 H, J = 10.8 Hz). Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.41; H, 10.13; N, 6.38.

Acknowledgment. We are grateful to Professor G. Rosini for useful discussions. We thank the Ministero della Pubblica Istruzione of Italy for financial support of this work.

Registry No. (*R**,*S**)-**1**, 82978-02-7; (*R**,*R**)-**1**, 82978-01-6; **2**, 27748-48-7; (*R**,*S**)-**3**, 138751-71-0; (*R**,*R**)-**3**, 138751-72-1; **4**, 68837-74-1; (*R**,*S**)-**5**, 138668-08-3; (*R**,*R**)-**5**, 138668-21-0; **6**, 138668-09-4; **7**, 127811-20-5; **8**, 138668-10-7; (*R**,*S**)-**9**, 138668-11-8; (*R**,*R**)-**9**, 138668-22-1; **10**, 138668-12-9; (*R**,*S**)-**11**, 138668-13-0; (*R**,*R**)-**11**, 138668-23-2; **12**, 138668-14-1; **13**, 3156-74-9; **14**, 27675-37-2; **15**, 2224-39-7; **16**, 127143-69-5; (*R**,*S**)-**17**, 138668-15-2; (*R**,*R**)-**17**, 138668-24-3; **18**, 138668-16-3; (*R**,*S**)-**19**, 138668-17-4; (*R**,*R**)-**19**, 138668-25-4; **20**, 138668-18-5; (*R**,*S**)-**21**, 138668-19-6; (*R**,*R**)-**21**, 138668-26-5; **22**, 27748-50-1; (*R**,*S**)-**23**, 138693-75-1; (*R**,*R**)-**23**, 138668-27-6; **24**, 138668-20-9; propionaldehyde, 123-38-6; alumina, 1344-28-1; nitroethane, 79-24-3; 3-phenylpropanal, 104-53-0; cyclohexanecarboxaldehyde, 2043-61-0; 1-nitrohexane, 646-14-0.

Synthesis of Perfluorodiamantane by Aerosol Direct Fluorination

James L. Adcock* and Huimin Luo

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Received August 23, 1991

Syntheses of organic cage hydrocarbons with novel structural carbon frameworks are an interesting and active field of research in organic chemistry.[1] Many novel cage hydrocarbons such as adamantane,[2] cubane,[3] and dodecahedrane[4] have been successfully synthesized. However, far fewer perfluorinated cage hydrocarbons are known. The synthesis of perfluoroadamantane by aerosol direct fluorination was reported several years ago by our group.[5] We report the synthesis of perfluorodiamantane by aerosol direct fluorination.

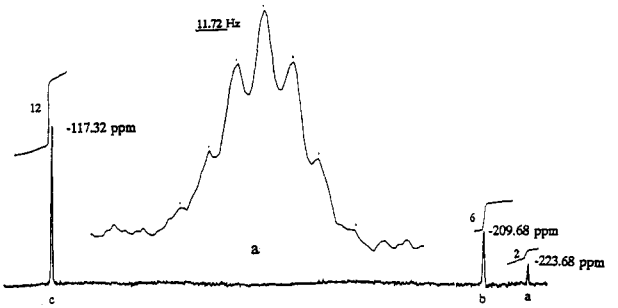


Figure 1. The ^{19}F NMR spectrum of perfluorodiamantane.

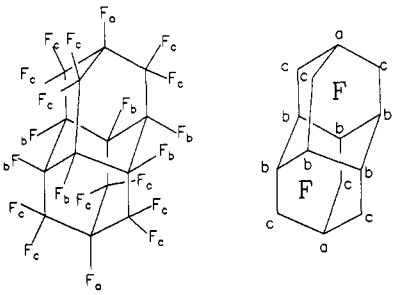


Figure 2. The structure and ^{19}F magnetic environments of perfluorodiamantane.

In 1965, Schleyer et al. first reported the synthesis of congressane,[6] which was later named diamantane. Although mono-, di-, and tetrafluorodiamantane have been prepared from the corresponding bromodiamantanes,[7,8] syntheses of higher fluorinated diamantanes have not to our knowledge been reported.

Results and Discussion

The perfluorination of diamantane was carried out in an improved aerosol reactor described elsewhere.[9] Briefly, this method involves the condensation of the starting material onto the surfaces of microscopic nucleating sodium fluoride preaerosol particles injected at a rate of 10–100 mg/h (0.4–4 mmol/h). The particulates so formed are fluorinated while traversing a concentration gradient of fluorine gas. The heat released during the fluorination is dissipated into the particulates and also efficiently removed by the external cooling system. As a result of the low temperature, condensed phase, and the relatively low acidity ($HF:F^-$, 25:1 to 2.5:1) produced by the injected fluoride ion, cationic rearrangements caused by super acidic endogenous hydrogen fluoride and fragmentation of the hydrocarbon frameworks can be all but eliminated during the fluorination. This is an especially important consideration in cage compounds. The low yield is most probably due to the difficulty in trapping the highly stable aerosol. Losses due to inefficient product capture are supported by the insufficient amounts of side products collected and the lack of residues deposited in the reactor.

The sole isolated product displayed the expected molecular ion, m/z 548, with accurate ^{13}C isotope peaks. The thermal electrons produced by negative chemical ionization (electron attachment) mass spectrometry produce anions by attachment to the fluorocarbon molecules with minimal fragmentation and excellent molecular ion intensities. The parent peak at m/z 548 not only was the base peak, but

(1) Olah, G. A., Ed. *Cage Hydrocarbons*; John Wiley & Sons, Inc.: New York, 1990.
(2) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1957**, *79*, 3292.
(3) Eaton, P. E.; Cole, T. W. *J. Am. Chem. Soc.* **1964**, *86*, 3157.
(4) Ternasky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4509.
(5) Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 3128.
(6) Cupas, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1965**, *87*, 917.
(7) Olah, G. A.; Shih, J. G.; Krishnamurthy, V. V.; Singh, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4492.
(8) Krishnamurthy, V. V.; Shih, J. G.; Singh, B. P.; Olah, G. A. *J. Org. Chem.* **1986**, *51*, 1354.
(9) Adcock, J. L.; Cherry, M. L. *Ind. Eng. Chem. Res.* **1987**, *26*, 208.

0022-3263/92/1957-2162$03.00/0