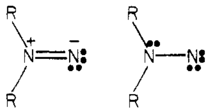
this reaction, which is exothermic by 2.3 kcal/mol. The apparent reason for this high activation energy becomes evident upon inspection of the π orbitals. The formal (p_z) π bond is not completely formed in the 1,1-diazene (bond order = 0.90). This phenomenon is surely due to the unsymmetrical nature of the molecule. The substituted nitrogen tends to have more than half of the p_z π electrons as suggested by the resonance structures, in which the π-bonding electrons are sometimes localized on that nitrogen. To compensate, the terminal nitrogen has an almost completely filled p_y orbital (population 1.87). In the transition state the p_y–π bond is virtually completely formed. The three-electron p_y–π bond involves the p_y–π^* orbital. This orbital has a node near the substituted nitrogen so the bonding interaction between this orbital and the departing ethyl group must not contribute very much to the stabilization of the transition state.



Conclusion

The MNDO reaction paths reported agree remarkably well with the observed and best theoretical estimates of the relative energies of the stable species and transition states for stepwise thermolyses of **1**–**3**. Concerted paths are much higher in energy. The preferred reaction sequence for most *trans*-azoalkanes should involve the cis transition state.

Acknowledgment. This work was supported by PSC–BHE Grant 13361.

Registry No. 1, 15463-99-7; 2, 58911-62-9; 3, 38534-43-9.

Supplementary Material Available: The complete geometries of all the optimized species (4 pages). Ordering information is given on any current masthead page.

Conversion of Nitro Paraffins into Aldehydes and Ketones[1]

Nathan Kornblum,* Allen S. Erickson, William J. Kelly, and Barbara Henggeler

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received April 13, 1982

The use of potassium permanganate provides a simple and effective means for converting nitro paraffin salts to pure aldehydes and ketones in 81–96% yields. Even the carbon–carbon double bond is less readily attacked by permanganate than a nitro paraffin anion. Thus, the salt of ω-nitroundecylene is converted to undecylenic aldehyde in 59% yield.

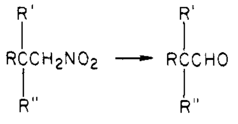
Many years ago Nef found that the salt of primary nitro paraffins are transformed into aldehydes, and those of secondary nitro compounds into ketones, when they are treated with aqueous mineral acid (eq 1 and 2).[2] Although

$$RC^{-}HNO_2 \xrightarrow{H_3O^+} RCHO + N_2O \qquad (1)$$

$$R_2C^{-}NO_2 \xrightarrow{H_3O^+} R_2C{=}O + N_2O \qquad (2)$$

the Nef reaction has repeatedly been employed to advantage, reports exist of its inadequacy and, indeed, downright failure. This, coupled with a heightened awareness of the utility in synthesis of aliphatic nitro compounds, has led a number of investigators to devise alternate procedures for converting nitro paraffins into aldehydes and ketones.[3]

In 1981 we described a general synthesis of quaternary carbon compounds (**1**) in which a CH_2NO_2 group is bonded to the quaternary carbon.[1] Conversion of these compounds into quaternary aldehydes (**2**), i.e., the reaction of eq 3, would make these difficultly accessible aldehydes readily available. Efforts to achieve the transformation of eq 3 by the Nef reaction, and by procedures employing $TiCl_3$, were unpromising, and attention was then directed to the use of potassium permanganate. We were encouraged to do so because Shechter and Williams,[3] following the early work of Nametkin,[3] had shown that aqueous potassium permanganate oxidizes nitro paraffin salts almost instantaneously and had reported that it is an effective reagent for converting the salts of primary nitro compounds to aldehydes. However, even though 20 years have elapsed since potassium permanganate was proposed as a reagent for converting the salts of primary nitro paraffins into aldehydes, its use has not achieved the status of a synthetically useful procedure. Indeed, the numerous alternatives to the Nef reaction have all been published since the Shechter–Williams paper appeared.[3a]



$$R\overset{R'}{\underset{R''}{C}}CH_2NO_2 \longrightarrow R\overset{R'}{\underset{R''}{C}}CHO \qquad (3)$$

1 **2**

The original permanganate procedure[3a] has some less than satisfactory aspects and, in our hands, it gave erratic

---

[1] A preliminary report of a portion of this work has been published: Kornblum, N.; Erickson, A. S. *J. Org. Chem.* **1981**, *46*, 1037.

[2] Nef, J. U. *Justus Liebigs Ann. Chem.* **1894**, *280*, 264.

[3] (a) $KMnO_4$: Shechter, H.; Williams, F. T. *J. Org. Chem.* **1962**, *27*, 3699. Nametkin, S. S.; Zabrodina, A. S. *Ber. Dtsch. Chem. Ges.* **1936**, *69*, 1789. (b) Modified Nef reactions: Black, D. St. C. *Tetrahedron Lett.* **1972**, 1331. Jacobson, R. M. *Ibid.* **1974**, 3215. Keinan, E.; Mazur, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3862. (c) Ozonolysis: McMurry, J. E.; Melton, J.; Padgett, H. *J. Org. Chem.* **1974**, *39*, 259. (d) $TiCl_3$: McMurry, J. E.; Melton, J. *J. Am. Chem. Soc.* **1971**, *93*, 5309; *J. Org. Chem.* **1973**, *38*, 4367. (e) VCl_2: Kirchhoff, R. *Tetrahedron Lett.* **1976**, 2533. (f) *t*-BuOOH: Bartlett, P. A.; Green, F. R., III; Webb, T. R. *Ibid.* **1977**, 331. (g) $Ce(NH_4)_2(NO_3)_6$: Olah, G. A.; Gupta, B. G. B. *Synthesis* **1980**, 44. (h) H_2O_2: Olah, G. A.; Arvanaghi, M.; Vankar, Y. D.; Prakash, G. K. S. *Synthesis* **1980**, 662. (i) $NaNO_2$ + RONO: Kornblum, N.; Wade, P. A. *J. Org. Chem.* **1973**, *38*, 1418. (j) MoO_5: Galobardes, M. R.; Pinnick, H. W. *Tetrahedron Lett.* **1981**, 5235.

0022-3263/82/1947-4534$01.25/0

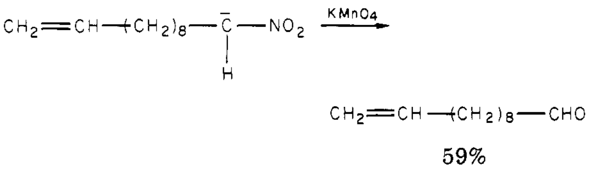
results. However, the modified procedure described herein enables one routinely to carry out the transformation of eq 3; excellent yields of pure quaternary aldehydes are obtained even when other functional groups are present (Table I).[4]

Attention was then turned to the somewhat more difficult problem of converting straight-chain primary nitro compounds into aldehydes, e.g., the conversion of 1-nitrodecane into decanal (eq 4). Here again aldehydes are

$$CH_3(CH_2)_8CH_2NO_2 \rightarrow CH_3(CH_2)_8CHO \qquad (4)$$

isolated in a high state of purity and in excellent yields (Table I). And, not surprisingly, secondary nitro compounds readily give ketones (Table I).

In view of these results the possibility that carbon–carbon double bonds might be less rapidly attacked by permanganate than nitro paraffin anions seemed worthy of consideration. A stringent test[5] of this possibility was provided by treating the olefinic nitro salt of eq 5 with potassium permanganate. This resulted in a 59% yield of the pure unsaturated aldehyde and, in addition, 17% of the pure starting nitroolefin was recovered.



$$CH_2{=}CH{-}(CH_2)_8{-}\underset{H}{\overset{-}{C}}{-}NO_2 \xrightarrow{KMnO_4} CH_2{=}CH{-}(CH_2)_8{-}CHO \qquad (5)$$

59%

It is clear, then, that the extraordinary ease with which potassium permanganate oxidizes nitro paraffin salts provides a simple and effective means for converting these salts to aldehydes and ketones with little, if any, destruction of other functional groups.[6]

Experimental Section

Infrared spectra (IR) were recorded on a Beckman IR-33 spectrometer. Nuclear magnetic resonance spectra (NMR) were obtained on a Perkin-Elmer R-32 90 MHz spectrometer.

Quaternary Aldehydes. The nitro compounds **1**–**6** from which these aldehydes are prepared were obtained as described earlier.[1] Quaternary aldehydes are rapidly attacked by oxygen at 25 °C; destruction is apparent after a few hours and is complete in less than 24 h. However, under nitrogen at −78 °C, quaternary aldehydes are stable. Highly preliminary evidence suggests that acyl radicals are formed and that they lose carbon monoxide readily, even at room temperature.[7] Except for the salt of nitroundecene (**9**), conversion of nitro salts to aldehydes and ketones is relatively insensitive to the amount of permanganate employed and to the time of reaction. The conversion of 1-nitro-2-methyl-2-(1-cyanocyclohexyl)propane (**3**) to the aldehyde is illustrative of the procedure employed with the quaternary carbon compounds.

Conversion of 1-Nitro-2-methyl-2-(1-cyanocyclohexyl)-propane (3) to the Aldehyde. A 60% oil dispersion of sodium hydride (0.200 g, 5 mmol) was washed with pentane and the oil-free hydride was transferred to a nitrogen-filled 1-L flask with the aid of 20 mL of *tert*-butyl alcohol. The mixture was stirred for 10 min under N_2 and to the resulting solution a solution of nitro compound **3** (0.420 g, 2 mmol) in 20 mL of *tert*-butyl alcohol was added. Stirring was continued for 20 min and to the white suspension was added 400 mL of ice-cold pentane and this was followed at once by 50 g of ice and an ice-cold solution of $KMnO_4$ (0.237 g, 1.5 mmol) in 80 mL of water. The mixture was stirred vigorously for 10 min and then 2 mL of 1 M sodium metabisulfite ($Na_2S_2O_5$) was introduced and this was followed at once by 4 mL of 1 M H_2SO_4. The two phases were separated, and the aqueous layer was extracted with more pentane. The combined pentane solutions were washed with ice-cold water and brine and then dried ($MgSO_4$) under N_2 for ca. 30 min. Removal of the pentane gave a white solid (0.310 g), which was purified by flash column chromatography[8] on silica gel (E. Merck, 230–400 mesh), using benzene–pentane (1:1). This gave 0.293 g (82% yield) of pure 2-(1-cyanocyclohexyl)-2-methylpropanal: white crystals, mp 61.5–62 °C; NMR ($CDCl_3$) δ 1.22 (s, 6 H), 1.3–2.2 (m, 10 H), 9.72 (s, 1 H); IR (KBr) 2720 (O=CH), 2220 (C≡N), 1710 (C=O) cm^{-1}.

Anal. Calcd for $C_{11}H_{17}ON$: C, 73.74; H, 9.49; N, 7.83. Found: C, 73.78; H, 9.59; N, 8.00.

Conversion of 2,2-Dimethyl-1-nitrotridecane (1) to the Aldehyde. The nitro compound (0.257 g, 1 mmol) was treated with more $KMnO_4$ than in the preceding case (0.158 g, 1 mmol) and for 20 min rather than 10 min. After the usual workup, 0.217 g (96% yield) of the VPC-pure aldehyde was obtained as a colorless liquid merely on removal of the pentane: NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.03 (s, 6 H), 1.26 (s, 20 H), 9.42 (s, 1 H); IR (neat) 2680 (O=CH), 1710 (C=O) cm^{-1}.

Anal. Calcd for $C_{15}H_{30}O$: C, 79.64;, H, 13.27. Found: C, 79.53; H, 13.48.

Conversion of *tert*-Butyl 2,2,3,3-Tetramethyl-4-nitrobutyrate (2) to the Aldehyde. The nitro ester (0.245 g, 1 mmol) was treated as described for nitro compound **3** with the exception that the nitro compound **2** was in contact with the sodium *tert*-butoxide solution for only 1 min before the pentane, ice, and $KMnO_4$ were added.[1] Removal of the pentane under N_2 gave 0.195 g (91% yield) of the pure aldehyde as a colorless oil: NMR ($CDCl_3$) δ 1.04 (s, 6 H), 1.20 (s, 6 H), 1.42 (s, 9 H), 9.77 (s, 1 H); IR (neat) 2730 (O=CH), 1710 (C=O) cm^{-1}.

Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.29; H, 10.28. Found: C, 67.27; H, 10.45.

Conversion of 2-Methyl-2-[3,5-bis(trifluoromethyl)-phenyl]-1-nitropropane (4) to the Aldehyde. This nitro compound (0.351 g, 1 mmol) was treated in the same way as the nitro ester **2**. Removal of the pentane under N_2 gave 0.275 g (88% yield) of the pure aldehyde as a colorless oil: NMR ($CDCl_3$) δ 1.57 (s, 6 H), 7.7–8.0 (m, 3 H), 9.6 (s, 1 H); IR (neat) 2710 (O=CH), 1710 (C=O) cm^{-1}.

Anal. Calcd for $C_{12}H_{10}F_6O$: C, 50.70; H, 3.52; F, 40.14. Found: C, 50.53; H, 3.80; F, 39.90.

Conversion of 2-[(*p*-Phenylsulfonyl)phenyl]-2-methyl-1-nitropropane (5) to the Aldehyde. The nitro sulfone (0.319 g, 1 mmol) was dissolved in 30 mL of *tert*-butyl alcohol by warming to 60 °C and the warm solution was added to 2.5 mmol of oil-free sodium hydride. The mixture was stirred under N_2 for 20 min while cooling to room temperature and then 200 mL of ethyl acetate was added. This was immediately followed by an ice-cold solution of $KMnO_4$ (0.158 g, 1 mmol) in 40 mL of water. The mixture was stirred vigorously for 20 min and then worked up as described for **3** except that ethyl acetate was used for extracting the aqueous phase. After being washed and dried the combined ethyl acetate solutions yielded 0.280 g of white crystals, mp 107–108 °C. A solution of these crystals in methylene chloride–pentane (1:1) was chromatographed on a short silica gel column.

---

[4] Since it appears that oxidation of the nitro paraffin anion and the aldehyde become competitive in the later stages of the reaction, it is desirable to remove the aldehyde from the reaction zone as soon as it is formed. This is accomplished by layering the reaction mixture with an organic solvent. The solvents of choice are good solvents for aldehydes, are insoluble in water, are poor solvents for the nitro paraffin and permanganate anions, are resistant to permanganate, and, preferably, are low boiling. Three solvents that meet these specifications are pentane, benzene, and ethyl acetate. Pentane is preferred because of its lower boiling point, but aldehyde solubility considerations sometimes create a preference for benzene or ethyl acetate. As a consequence of this use of an immiscible solvent, the yield of aldehyde is rather insensitive to the use of excess $KMnO_4$.

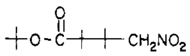
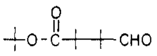
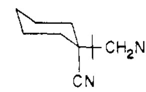
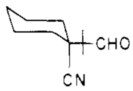
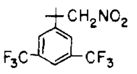
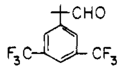
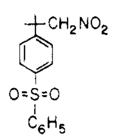
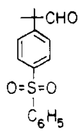
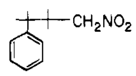
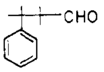
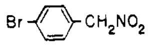
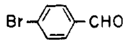
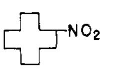
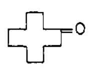
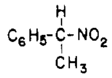
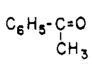
[5] The salt of 4-methyl-6-nitrocamphene has been converted to 4-methyl-6-oxocamphene by the action of potassium permanganate, but the yield of purified ketone was not reported [Nametkin, S. S.; Zabrodina, A. S. *Ber. Dtsch. Chem. Ges.* **1936**, *69*, 1789]. It is noteworthy that this unsaturated ketone only slowly decolorizes permanganate.

[6] In this connection, the recent paper by N. A. Noureldin and D. G. Lee (*Tetrahedron Lett.* **1981**, 4889) is of considerable interest.

[7] Decarbonylation of acyl radicals is not without precedent, but the previous examples required higher temperatures; cf. Winstein, S.; Seubold, F. *J. Am. Chem. Soc.* **1947**, *69*, 2916; Cramer, R. *Ibid.* **1957**, *79*, 6215; Urry, W. H.; Nishihara, A.; Niu, J. H. Y. *J. Org. Chem.* **1967**, *32*, 347.

[8] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Table I. Conversion of Nitro Compounds to Aldehydes and Ketones

1			96
2			91
3			81
4			88
5			91
6			88
7	$CH_3(CH_2)_6-CH_2NO_2$	$CH_3(CH_2)_6-CHO$	85
8	$CH_3(CH_2)_8-CH_2NO_2$	$CH_3(CH_2)_8-CHO$	92
9	$H_2C{=}CH-(CH_2)_8-CH_2NO_2$	$H_2C{=}CH-(CH_2)_8-CHO$	59
10	$CH_3(CH_2)_{14}-CH_2NO_2$	$CH_3(CH_2)_{14}-CHO$	87
11	$C_6H_5CH_2CH_2CH_2NO_2$	$C_6H_5CH_2CH_2CHO$	82
12			90
13			91
14	 $C_6H_5-\underset{CH_3}{\overset{H}{C}}-NO_2$	 $C_6H_5-\underset{CH_3}{C}{=}O$	90

[a] Pure, isolated aldehyde or ketone.

This gave 0.263 g (91% yield) of the pure aldehyde: mp 110–111 °C; NMR ($CDCl_3$) δ 1.45 (s, 6 H), 7.3–8.1 (m, 9 H), 9.47 (s, 1 H); IR (KBr) 2710 (O=CH), 1710 (C=O) cm^{-1}.

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.67; H, 5.55; S, 11.11. Found: C, 66.43; H, 5.47; S, 11.01.

Conversion of 2,2,3-Trimethyl-3-phenyl-1-nitrobutane (6) to the Aldehyde. The nitro compound (0.221 g, 1 mmol) was treated with 0.158 g (1 mmol) of $KMnO_4$ as described for 3. On workup the pentane layer was isolated and the aqueous phase was extracted with methylene chloride. The combined pentane and methylene chloride solutions were washed with cold water and dried ($MgSO_4$), and then the solvent was removed. When the resulting 0.186 g of oil was Kugelrohr distilled at 65 °C (0.05 mm), 0.167 g (88% yield) of the pure aldehyde was obtained as a colorless oil: NMR ($CDCl_3$) δ 0.97 (s, 6 H), 1.40 (s, 6 H), 7.27 (br s, 5 H), 9.52 (s, 1 H); IR (neat) 2720 (O=CH), 1712 (C=O) cm^{-1}.

Anal. Calcd for $C_{13}H_{12}O$: C, 82.10; H, 9.47. Found: C, 82.26; H, 9.55.

Conversion of 1-Nitrooctane[9] to Octanal. The procedure employed here, and in the remaining reactions of this paper, differs to some extent from the procedures employed with compounds 1–6. A 60% oil dispersion of sodium hydride (160 mg, 4 mmol) was washed free of oil with pentane and transferred to a nitrogen-filled flask with the aid of 20 mL of *tert*-butyl alcohol. After this was stirred for 10 min, a solution of 1-nitrooctane (318 mg, 2 mmol) in 40 mL of *tert*-butyl alcohol was added all at once; a heavy white precipitate formed immediately. The mixture was stirred for 20 min and then 600 mL of ice-cold pentane was added; this was followed at once by 50 g of ice and an ice-cold solution of 316 mg (2 mmol) of potassium permanganate and 248 mg (4 mmol) of boric acid in 80 mL of water. The mixture was stirred vigorously under nitrogen for 10 min and then 2 mL of 1 M aqueous sodium metabisulfite ($Na_2S_2O_5$) and 4 mL of 1 M sulfuric acid were added.

The pentane phase was isolated and the aqueous layer was extracted twice with 60-mL portions of pentane. The combined pentane solutions were washed three times with 400-mL portions of ice-cold water and then dried ($MgSO_4$) under N_2. Removal of the pentane under the vacuum of a water pump gave 249 mg (97% yield) of crude aldehyde; 240 mg of this oil was dissolved in ca. 2 mL of pentane, the solution was filtered through a 3 cm × 2.5 cm column of deactivated silica gel,[10] and then the column was washed with pentane. Removal of the pentane gave 215 mg (89% yield) of a very pale yellow oil, which by VPC, NMR, and IR was pure octanal.

Anal. Calcd for $C_8H_{16}O$: C, 75.00; H, 12.5. Found: C, 75.18; H, 12.49. Three duplicate experiments in which 3 mmol of NaH and 3 mmol of H_3BO_3 were employed gave 83%, 84%, and 85% yields of pure octanal. Last and not least, four duplicate experiments in which no H_3BO_3 was present, and in which 2.5–4 mmol of NaH were employed, gave 81–83% yields of pure octanal.

Conversion of 1-Nitrodecane[9] to Decanal. This was carried out exactly as for octanal except that 124 mg (2 mmol) of boric acid was employed. In three experiments the yield of colorless decanal averaged 92%. The products were pure by VPC, NMR, and IR.

Anal. Calcd for $C_{10}H_{20}O$: C, 76.92; H, 12.82. Found: C, 76.89; H, 13.05.

Preparation of ω-Nitroundecylene (9). To 500 mL of dry CH_2Cl_2 were added ω-undecylenyl alcohol (17.03 g, 0.100 mol) and triethylamine (15.26 g, 0.152 mol). The solution was cooled in an ice-salt bath and while stirring methanesulfonyl chloride (12.63 g, 0.112 mol) was added dropwise over 15 min. The solution was then stirred for an additional 15 min at 0 °C after which it was washed twice with 100 mL of ice-cold H_2O, twice with 200 mL of ice-cold 3 M HCl, 200 mL of saturated Na_2CO_3 solution, and 200 mL of brine. The organic solution was dried ($MgSO_4$) and the solvent removed under vacuum to afford 19.42 g of a yellow liquid. Fractional distillation under reduced pressure through a column packed with glass helicies gave 18.22 g (73%) of VPC-pure ω-undecylenyl mesylate as a colorless liquid: bp 154–156 °C (0.80 mm); IR (neat) 1625 (CH_2=CH), 1340 (SO_3Me) cm^{-1}.

The mesylate (15.50 g, 0.062 mol) was added to a solution of NaI (15.00 g, 0.100 mol) in 300 mL of dry acetone. The system was protected from light and the mixture was stirred for 2 h. The reaction mixture was then filtered and the solvent was removed in vacuo to give a pale-yellow solid. The ω-undecylenic iodide was leached out by repeatedly washing this solid with anhydrous

---

(9) Kornblum, N.; Ungnade, H. E. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 724.

(10) E. Merck silica gel 60, no. 9385 (40–63 μm) was stirred with acetone for 30 min, filtered, air-dried, and then oven-dried at 120 °C for 12 h. We are indebted to Professor D. W. Brooks for these directions.

(11) This corresponds to the spectrum recorded in the Aldrich Library of NMR Spectra: **1974**, *2*, 100A.

ether (~400 mL). Removal of the ether gave 19.20 g of a yellow oil. The pure iodide was obtained by column chromatography on silica gel using hexane–ether (3:1): 16.74 g (93% yield) of a VPC-pure pale-yellow oil; IR (neat) 1640 (CH$_2$=CH) cm^{-1}.

To a 500-mL flask were added dry AgNO$_2$[9] (10.0 g, 0.065 mol) and 100 mL of anhydrous ether. The mixture was cooled in an ice bath and a solution of ω-iodoundecylene (15.34 g, 0.055 mol) in 150 mL of anhydrous ether was added dropwise with vigorous stirring over 2 h. The system was protected from light and stirred for an additional 15 h at 0 °C and then for 8 h at room temperature. The mixture was filtered and the filtrate was concentrated in vacuo to a colorless oil. Fractional distillation under reduced pressure through a column packed with glass helicies afforded 7.82 g (72%) of VPC-pure ω-nitroundecylene as a colorless liquid: bp 114–115 °C (1.5 mm); NMR (CDCl$_3$) δ 1.28 (s, 10 H), 2.00 (m, 4 H), 4.32 (t, 2 H), 5.00 (t, 2 H), 6.75 (m, 1 H); IR (neat) 1640 (CH$_2$=CH), 1540 (NO$_2$) cm^{-1}.

Anal. Calcd for C$_{11}$H$_{21}$NO$_2$: N, 7.09. Found: N, 7.18.

Conversion of ω-Nitroundecylene (9) to ω-Undecenyl Aldehyde. With 0.400 g (2 mmol) of the nitro olefin **9**, the reaction was effected exactly as with 1-nitrodecane except for the following: (1) instead of 600 mL of pentane, 600 mL of benzene (precooled to incipient freezing) was employed; (2) the reaction mixture was cooled by means of an ice bath; (3) less KMnO$_4$ was used here, i.e., 0.237 g (1.5 mmol) instead of the usual 2 mmol of KMnO$_4$; and (4) the ice-cold aqueous solution of KMnO$_4$ + H$_3$BO$_3$ was added dropwise over the course of 10 min after which the vigorous stirring was continued for another 2 min. Then, in the usual way, the reaction mixture was treated with 2 mL of 1 M Na$_2$S$_2$O$_5$ and 4 mL of 1 M H$_2$SO$_4$. The aqueous phase was then extracted with more benzene, and the combined benzene solutions were washed with cold water and brine and dried (MgSO$_4$) under N$_2$. Removal of the benzene under reduced pressure gave 0.263 g of a green-yellow oil. This was dissolved in 2 mL of hexane and subjected to flash column chromatography[8] on a 15 × 2 cm silica gel column (E. Merck, 230–400 mesh) eluted with hexane–benzene (4:1). Two major components were obtained: first, 0.060 g (16% recovery) of the nitro olefin **9**, which by VPC and IR was pure. This was followed by 0.197 g (59% yield) of VPC-pure ω-undecylenic aldehyde, a pale-yellow oil: NMR (CDCl$_3$) δ 1.30 (s, 10 H), 1.65 (m, 2 H), 2.05 (m, 2 H), 2.42 (t, 2 H), 5.00 (m, 2 H), 5.81 (m, 1 H), 9.78 (t, 1 H),[11] IR (neat) 2695 (O=CH), 1715 (C=O) cm^{-1}.[12]

Preparation of 1-Nitrohexadecane (10). 1-Hexadecanol was converted to the mesylate as described above for ω-undecenol; recrystallization of the crude from hexane gave white plates of the mesylate: mp 53–54 °C; IR (KBr) 1350 (SO$_3$Me) cm^{-1}. Conversion of the mesylate to 1-iodohexadecane was effected as in the ω-undecylenyl case. The crude iodide was chromatographed on silica gel with hexane–ether (3:1) to give a pale-yellow oil, which was VPC pure. This 1-iodohexadecane (15.25 g, 0.043 mol) was treated with AgNO$_2$ (10 g, 0.065 mol) as described for ω-undecenyl iodide except that the crude product (an oil) was not distilled but, rather, was crystallized several times from pentane. This gave 8.33 g (71% yield) of 1-nitrohexadecane: white plates, mp 33–34 °C; NMR (CDCl$_3$) δ 0.72 (m, 2 H), 1.22 (s, 26 H), 1.92 (m, 2 H), 4.30 (t, 2 H), IR (CHCl$_3$) 1535 (NO$_2$) cm^{-1}.

Anal. Calcd for C$_{16}$H$_{33}$NO$_2$: C, 70.85; H, 12.18; N, 5.17. Found: C, 71.04; H, 12.08; N, 5.43.

Conversion of 1-Nitrohexadecane (10) to Hexadecanal. This was carried out exactly as for octanal except that (a) 124 mg (2 mmol) of boric acid was used and (b) 600 mL of ethyl acetate was employed instead of 600 mL of pentane. The usual workup was followed except that ethyl acetate was used to extract the aqueous phase. Removal of the ethyl acetate gave a crude product that contained 1-nitrohexadecane. The pure aldehyde was obtained by flash column chromatography[8] on a 16 × 2 cm silica gel (E. Merck, 230–400 mesh) column, eluting with hexane–benzene (2:1). This gave two major components: 0.028 g (5% recovery) of pure starting nitro compound and 0.445 g (92% yield) of pure hexadecanal as a white solid of mp 35–36 °C: NMR (CDCl$_3$) δ 0.85 (t, 3 H), 1.22 (s, 24 H), 1.55 (m, 2 H), 2.40 (t, 2 H), 9.72 (s, 1 H); IR (CHCl$_3$) 2690 (O=CH), 1700 (C=O) cm^{-1}. In two additional duplicate runs the yields of pure aldehyde were 82% and 87%.

Anal. Calcd for C$_{16}$H$_{32}$O: C, 80.00; H, 13.33. Found: C, 80.02; H, 13.50.

Conversion of 3-Phenyl-1-nitropropane (11) to 3-Phenylpropanal. The procedure was the same as in the case of 1-nitrooctane except that (a) 600 mL of cold benzene was used in place of 600 mL of cold pentane, (b) only 0.237 g (1.5 mmol) of KMnO$_4$ was employed, and (c) only 0.124 g (2 mmol) of H$_3$BO$_3$ was used.

After workup the aqueous phase was extracted with benzene, and the combined benzene solutions were washed with cold water and brine and then dried (MgSO$_4$) under N$_2$. Removal of the benzene gave 0.258 g of a yellow liquid, which was subjected to flash chromatography[8] on an 18 × 2 cm silica gel column (E. Merck, 230–400 mesh); hexane–benzene (3:1) was employed as the eluent. In this way 0.013 g (4%) of the pure nitro compound **11** was recovered and this was followed by 0.231 g (84% yield) of the pure aldehyde as a very pale yellow liquid. In a duplicate run the yield was 80%. NMR (CDCl$_3$) δ 2.82 (m, 4 H), 7.22 (s, 5 H), 9.80 (s, 1 H); IR (neat) 2600 (O=CH), 1720 (C=O) cm^{-1}.

Anal. Calcd for C$_9$H$_{10}$O: C, 80.60, H, 7.46. Found: C, 80.81; H, 7.70.

This aldehyde was unusually sensitive to air, and, therefore, during its isolation, efforts were made to keep it under nitrogen as much as possible. On exposure to air an impurity having broad absorption in the region 3500 cm^{-1} was soon formed. By maintaining the aldehyde under N$_2$ at 0 °C this process was minimized.

Conversion of (*p*-Bromophenyl)nitromethane (12) to *p*-Bromobenzaldehyde. The nitro compound (0.432 g, 2 mmol) was converted to the aldehyde by following the procedure described for 1-nitrohexadecane (**10**). The 0.363 g of crude product, mp 51–54 °C, was purified by flash column chromatography[8] on E. Merck silica gel (230–400 mesh), using hexane–benzene (3:1) followed by sublimation at 30–45 °C (0.1 mm of pressure). This gave 0.334 g (90% yield) of the pure aldehyde, mp 55.5–56.5 °C; a mixture melting point with authentic *p*-bromobenzaldehyde was undepressed. The NMR and IR spectra are the same as the spectra reported for *p*-bromobenzaldehyde. In two duplicate experiments 87% and 95% yields of pure aldehyde were obtained. When pentane was substituted for ethyl acetate, the yields were slightly lower (80% and 84%).

Conversion of Nitrocyclododecane (13) to Cyclododecanone. Two millimoles (0.426 g) of the nitro compound was treated as described for 1-nitrooctane except for the following: (a) 0.120 g of 60% NaH (3 mmol) was employed and (b) MgSO$_4$ (8 g) was used in place of boric acid. The crude ketone (0.352 g, mp 54–55 °C) was sublimed at 45 °C and 0.3 mm of pressure; this gave 0.331 g (91% yield) of white crystals: mp 57–58 °C (lit.[13] mp 59 °C); NMR (CDCl$_3$) δ 1.25 (s, 12 H), 1.68 (m, 4 H), 2.42 (m, 4 H); IR (KBr) 1700 (C=O) cm^{-1}.

Whether the MgSO$_4$ is really necessary was not established. In this connection it should be noted that for the conversion of α-phenyl-α-nitroethane (14) to acetophenone, H$_3$BO$_3$ was employed.

Conversion of α-Phenyl-α-nitroethane (14) to Acetophenone. The nitro compound (0.310 g, 2 mmol) was treated exactly as described for 1-nitrooctane except that (a) 0.124 g (2 mmol) of boric acid was used and (b) ethyl acetate was employed instead of pentane. On removal of the ethyl acetate, 0.230 g of a colorless liquid remained. This, on short-path evaporation (25 °C and 0.1 mm), afforded 0.210 g (90% yield) of VPC-pure acetophenone, the NMR and IR of which were identical with that of authentic acetophenone.

Acknowledgment. We thank the National Science Foundation and Merck & Co. for their support. We also are indebted to Dr. C. S. Yeh for her cooperation in promptly carrying out the elemental analyses of these rather unstable aldehydes.

Registry No. 1, 76173-43-8; **2**, 76173-36-9; **3**, 76173-47-2; **4**, 76173-51-8; **5**, 76173-53-0; **6**, 76173-54-1; **7**, 629-37-8; **8**, 4609-87-4; **9**,

---

(12) This is identical with the spectrum recorded in the Aldrich Library of IR Spectra: **1975**, 2nd ed., 251C.

(13) Ruzicka, L.; Stoll, M.; Schinz, H. *Helv. Chim. Acta* **1926**, *9*, 256.

40244-98-2; **10**, 66271-50-9; **11**, 22818-69-5; **12**, 29559-25-9; **13**, 1781-70-0; **14**, 7214-61-1; 2,2-dimethyl-1-tridecanal, 76173-57-4; *tert*-butyl 2,2,3,3-tetramethyl-4-oxobutanoate, 76173-37-0; 2-methyl-2-(1-cyanocyclohex-1-yl)propanal, 76173-58-5; 3,5-bis(trifluoromethyl)-α,α-dimethylbenzeneacetaldehyde, 76173-59-6; α,α-dimethyl-4-(phenylsulfonyl)benzeneacetaldehyde, 76173-61-0; 3-phenyl-2,2,3-trimethylbutanal, 76173-62-1; 1-octanal, 124-13-0; 1-decanal, 112-31-2; 10-undecenal, 112-45-8; 1-hexadecanal, 629-80-1; benzenepropanal, 104-53-0; *p*-bromobenzaldehyde, 1122-91-4; cyclododecanone, 830-13-7; acetophenone, 98-86-2; KMnO$_4$, 7722-64-7.

Alkylaluminum Halide Induced Cyclization of Unsaturated Carbonyl Compounds

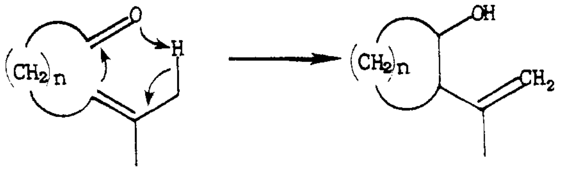
Barry B. Snider,*[1] Michael Karras, Robert T. Price, and David J. Rodini

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received March 4, 1982

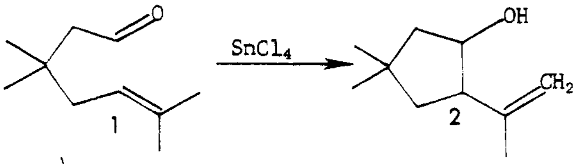
2,6-Dimethyl-5-heptenal (**3**) and 5-octenal (**24**) undergo concerted ene reactions with 1 equiv of Me$_2$AlCl and cation-olefin cyclizations with 2 equiv of Me$_2$AlCl, MeAlCl$_2$, or EtAlCl$_2$ to give a zwitterion which reacts to give several products including an ene adduct. 3,7-Dimethyl-6-octenal (**12**) and (*Z*)- and (*E*)-6-nonenal (**18** and **19**) undergo only ene reactions with all catalysts. The enones **31** and **32** formed by reaction of **3** and **12** with acetonylidenetriphenylphosphorane react analogously to **3** and **12** in the presence of Lewis acid. The effect of ring size on the nature of these cyclizations is explained on the basis of thermodynamic and kinetic data.

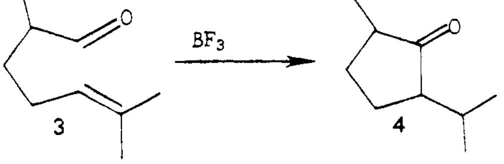
Lewis acid induced cyclization of unsaturated carbonyl compounds is an attractive method for the synthesis of highly functionalized cyclic compounds.[2,3] Type I intramolecular ene reactions[4] to give cyclohexanols (eq 1, *n* = 4) are well-known. These reactions proceed at 150–300 °C



(1)

or with Lewis acid catalysis[3] at room temperature. In a detailed study of the scope of this reaction, Andersen reported the first example of the synthesis of a cyclopentanol via this type of ene reaction (eq 1, *n* = 3).[5] Treatment of **1** with 0.1 equiv of SnCl$_4$ for <15 min at 0 °C gives an 85% yield of **2** as an 80:20 cis–trans mixture. This reaction may not be general, since treatment of the closely related aldehyde **3** with 2.9 equiv of BF$_3$·Et$_2$O for 1 h at 25 °C gives the cyclopentanone **4**.[6]





We set out to determine the reasons for the differing behavior of **1** and **3** under apparently similar conditions and to try to develop procedures which would allow us to control the course of the reaction. The use of alkylaluminum halides as the Lewis acid catalysts has provided a tool to study this problem. We have recently exploited these reagents as unique Lewis acids which are also Brønsted bases.[7] Proton-catalyzed side reactions are minimized by the use of these reagents. Furthermore, RAlCl$_2$, R$_3$Al$_2$Cl$_3$, R$_2$AlCl, and R$_3$Al constitute a series with perdictably decreasing Lewis acidity.

Results and Discussion

Reactions of 3 and 12. The reactions of 2,6-dimethyl-5-heptenal (**3**) indicate that the nature of the reaction can be controlled by variation of the strength and amount of Lewis acid.[8] Most remarkably, we have found that both concerted and stepwise ene reactions of **3** occur, giving adducts with different stereochemistry.

Treatment of **3** with 1.0 equiv of Me$_2$AlCl at −78 °C gives primarily **5a** and **5b** in a 4:1 ratio. The detailed results are shown in Table I. (In the text **3**–**11** refer to the alcohol or carbonyl compound obtained after workup from the structures shown in Scheme I). At 0 °C, no starting material is recovered, but the reaction is less selective. We believe that **5** is formed by a concerted process since concerted thermal ene reactions of 1,6-dienes have been shown to give mainly cis-substituted cyclopentanes.[2,9]

Treatment of **3** with 2 equiv of Me$_2$AlCl gives the more electrophilic aldehyde, (Me$_2$AlCl)$_2$ complex, or a species stoichiometrically equivalent to it.[10] This complex reacts

---

(1) Address correspondence to this author at the Department of Chemistry, Brandeis University, Waltham, MA 02254.

(2) For a review of intramolecular ene reactions see: Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.

(3) For a review of Lewis acid catalyzed ene reactions see: Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.

(4) This very useful terminology for classifying intramolecular ene reactions according to the connectivity of the ene and enophile components is discussed in ref 2.

(5) Andersen, N. H.; Ladner, D. W. *Synth. Commun.* **1978**, *8*, 449 and references cited therein. See also: Paquette, L. A.; Han, Y.-K. *J. Am. Chem. Soc.* **1981**, *103*, 1835.

(6) Kulkarni, B. S.; Rao, A. S. *Org. Prep. Proc. Int.* **1978**, *10*, 73. Related reactions are known: Sakai, K.; Ide, J.; Oda, O.; Nakamura, N. *Tetrahedron Lett.* **1972**, 1287. Baldwin, J. E.; Lusch, M. J. *J. Org. Chem.* **1979**, *44*, 1923. Cookson, R. C.; Smith, S. A. *J. Chem. Soc., Chem. Commun.* **1979**, 145.

(7) Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, T. C.; Deutsch, E. A.; Cordova, R.; Price, R. T. *Tetrahedron* **1981**, *37*, 3927.

(8) For a preliminary report see: Karras, M.; Snider, B. B. *J. Am. Chem. Soc.* **1980**, *102*, 7951.

(9) McQuillin, F. J.; Parker, D. G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 809.

(10) Alkylaluminum halides often disproportionate in the presence of a deficit of base. Disproportionation is more favored for RAlCl$_2$ than for R$_2$AlCl.[11,12] Analysis in this case is complicated by lack of data on the relative rates of cyclization and disproportionation.

(11) Mole, T.; Jeffery, E. A. "Organoaluminum Compounds"; Elsevier: Amsterdam, 1972; p 32.

0022-3263/82/1947-4538$01.25/0 © 1982 American Chemical Society