ml). The reaction mixture was stirred for 2 hr at −20° and then for 2 hr at 0°. The reaction was quenched at 0° by addition of a saturated sodium thiosulfate solution (20 ml) followed by extraction of the product with three 20-ml portions of ether. The combined ether extracts were washed with water (2 × 30 ml) and 5% hydrochloric acid (2 × 25 ml). The organic layer was then dried over magnesium sulfate and evaporated, giving the (+) olefin **10** (515 mg, 2.05 mmol, 100%) as a yellow oil which was homogeneous by tlc: nmr ($CDCl_3$) δ 7.33 (5 H, s, aromatic H), 5.80–6.15 (2 H, m, =CH), 5.40–5.60 (1 H, m, HCOCO), 4.52 (2 H, s, CH_2 phenyl), 3.40 (2 H, d of d, J = 6, 3 Hz, CH_2O), and 2.2–3.0 (4 H, m); ir (neat) 1770, 1165, 1100, 1020, 740, and 690 cm^{-1}; tlc R_f 0.48 (1:1 benzene–ether); $[\alpha]^{27}D$ +205.7° (*c* 0.7, $CHCl_3$).

Anal. Calcd for $C_{15}H_{16}O_3$: mol wt, 244.1100. Found: mol wt, 244.1106.

Preparation of the (+) Acetoxy Lactone 11.[8] The (+) benzyl ether lactone **10** (500 mg, 2.05 mmol) was dissolved in acetic anhydride (10 ml) and cooled to 0° under an argon atmosphere. Boron trifluoride etherate (0.05 ml) was added dropwise with stirring at 0°. After stirring for 15 min at 0° the reaction was quenched with water (1.5 ml). The solvent was then evaporated. The crude product was passed through a column of silica gel (Woelm, activity III, 25 g) to remove benzyl acetate. Elution was carried out with benzene (200 ml), 99:1 benzene–ether (200 ml), 97:3 benzene–ether (200 ml), and 95:5 benzene–ether (500 ml), giving the acetoxy lactone **11** 380 mg, 94%): nmr ($CDCl_3$) δ 6.03 (2 H, br s, =CH), 5.45–5.68 (1, H, m, HCOCO), 4.08 (2 H, d, J = 6 Hz, CH_2OAc), 2.1–3.2 (4 H, m), and 2.02 (3 H, s, CH_3CO_2); ir (neat) 1770, 1730, 1240, 1165, 1020, and 755 cm^{-1}; tlc R_f 0.30 (1:1 benzene–ether), 0.50 (17:3 benzene–methanol); $[\alpha]^{27}D$ +226.7° (*c* 1.73, $CHCl_3$).

Anal. Calcd for $C_{10}H_{12}O_4$: mol wt, 196.0736. Found: mol wt, 196.0723.

Preparation of the Acetoxy Lactone 8. The (+) acetoxy lactone **11** (210 mg, 1.07 mmol) and 5% rhodium on alumina (150 mg) were placed in 10 ml of tetrahydrofuran and stirred for 4 hr at 27° under hydrogen (1 atm). The solution was then filtered and the residue was washed with several portions of ether. The combined filtrates were evaporated, giving the saturated acetoxy lactone **8** (205 mg, 1.03 mmol, 96%): nmr ($CDCl_3$) δ 4.98 (1 H, m, CHOCO), 4.03 (2 H, d J = 6 Hz, CH_2OAc), 2.05 (3 H, s, CH_3CO_2), and 1.2–3.0 (8 H, m); ir (neat) 1770, 1740, 1230, 1165, and 1035 cm^{-1}; tlc R_f 0.30 (1:1 benzene–ether); $[\alpha]^{27}D$ −1.2° (*c* 0.81, $CHCl_3$); mass spectrum *m/e* 198 (M, w), 156 (M − CH_2CO, s), and 138 (M − CH_3CO_2H, vs).

Anal. Calcd for $C_{10}H_{14}O_4$: mol wt, 198.0892. Found: mol wt, 198.0890.

Preparation of Alcohol 9. The acetoxy lactone **8** (200 mg, 1.01 mmol) and freshly powdered potassium carbonate (138 mg, 1.0 mmol) were dissolved in methanol (4 ml) under argon. The solution was stirred for 30 min at 25° and neutralized with 10 *N* hydrochloric acid (0.2 ml). The solvent was evaporated and the resulting slurry was washed exhaustively with ethyl acetate. The combined organic extracts were dried over magnesium sulfate and concentrated to afford the alcohol **9** (154 mg, 0.98 mmol, 97%) which was homogeneous by tlc: nmr ($CDCl_3$) δ 5.00 (1 H, br, CHOOC), 3.92 (1 H, br, OH), 3.54 (2, H, d, J = 6 Hz, CH_2OH), 1.3–3.0 (8 H, m); ir (neat) 3400, 1770, 1170, 1035 cm^{-1}; tlc R_f 0.30 (17:3 benzene–methanol); $[\alpha]^{27}D$ −20.4° (*c* 0.66, $CHCl_3$); mass spectrum *m/e* 156 (M, s), 139 (M − OH, m), and 138 (M − H_2O, vs).

Anal. Calcd for $C_8H_{12}O_3$: mol wt, 156.0786. Found: mol wt, 156.0789.

Oxidation of Alcohol 9. Collins reagent (2.34 g, 9 mmol) and dry Celite (4.3 g) were dissolved in 23 ml of dry methylene chloride under argon and cooled to 0°. A solution of alcohol **9** (154 mg, 0.98 mmol) in 5 ml of methylene chloride was added. The solution was stirred for 1 hr at 0° and sodium bisulfate (5.0 g) was added. The solution was stirred for 10 min at 25° and filtered through a pad of anhydrous magnesium sulfate. The residue was washed with several portions of methylene chloride. The combined filtrate was evaporated, giving aldehyde **7** (125 mg, 0.81 mmol, 83%) which was homogeneous by tlc: nmr ($CDCl_3$) δ 9.71 (1 H, s, CHO), 5.05 (1 H, m, CHOCO), 1.4–3.6 (8 H, m); ir (neat) 2720, 1765, 1715, and 1165 cm^{-1}; tlc R_f 0.55 (17:3 benzene–methanol); $[\alpha]^{27}D$ − 41° (*c* 0.61, $CHCl_3$); mass spectrum *m/e* 154 (M), 126 (M − CO), and 110 (M − CO_2).

Preparation of Enone 5. The aldehyde **7** (105 mg, 0.68 mmol) was treated as described above giving the enone **5** (110 mg, 0.44 mmol, 65%) which was homogeneous by tlc. This material was identical with an authentic sample by tlc and ir and nmr spectral comparison, $[\alpha]^{27}D$ +39.6° (*c* 1.59, $CHCl_3$).

Acknowledgment. This work was assisted financially by the National Institutes of Health and the National Science Foundation.

Registry No. (±)-**1**, 43119-22-8; (−)-**1**, 43119-23-9; (−)-**1** (+)-1-(1-naphthyl)ethylamine salt, 43119-24-0; **1a**, 43119-25-1; **1a** (−)-1-(1-naphthyl)ethylamine salt, 43119-26-2; **2b**, 43119-27-3; **3**, 43119-28-4; **4**, 43119-29-5; **5**, 43119-30-8; **6**, 31767-37-0; **7**, 43119-32-0; **8**, 43119-33-1; **9**, 43119-34-2; **10**, 35761-79-6; **11**, 35761-78-5; (−)-1-(1-naphthyl)ethylamine, 10420-89-0; (+)-1-(1-naphthyl)-ethylamine, 3886-70-2.

References and Notes

(1) E. J. Corey and T. Ravindranathan, *Tetrahedron Lett.*, 4753 (1971).
(2) E. J. Corey and B. B. Snider, *Tetrahedron Lett.*, 3091 (1973).
(3) Available from Norse Laboratories, Inc., Santa Barbara, Calif.
(4) J. P. Jennings, W. Klyne, and P. M. Scopes, *J. Chem. Soc.*, 7211 (1965).
(5) E. J. Corey and J. Mann, *J. Amer. Chem. Soc.*, in press.
(6) P. Crabbe and A. Guzman, *Tetrahedron Lett.*, 115 (1972).
(7) E. J. Corey, T. K. Schaaf, W. Huber, W. Koelliker, and N. M. Weinshenker, *J. Amer. Chem. Soc.*, **92**, 397 (1970); E. J. Corey, S. M. Albonico, U. Koelliker, T. K. Schaaf, and R. K. Varma, *J. Amer. Chem. Soc.*, **93**, 1491 (1971).
(8) E. J. Corey and P. A. Grieco, *Tetrahedron Lett.*, 107 (1972).
(9) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

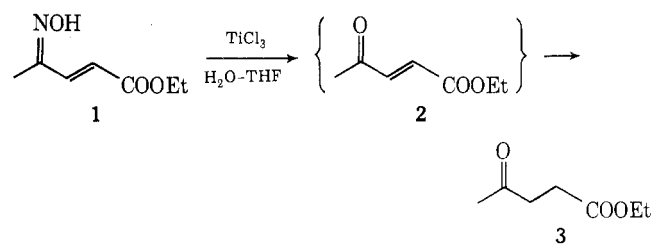
Reduction of Enedicarbonyl Compounds with Titanous Ion

Larry C. Blaszczak and John E. McMurry*

Thimann Laboratories, University of California, Santa Cruz, California 95064

Received July 27, 1973

We recently had occasion to treat ethyl 4-oximino-2-pentenoate (**1**) (obtained from ethyl 3-bromolevulinate by Mattox–Kendall reaction with hydroxylamine[1]) with aqueous $TiCl_3$ according to the deoximation procedure of Timms and Wildsmith.[2] Although we expected that ethyl 4-oxo-2-pentenoate (**2**) would result, the sole product of the reaction was the saturated keto ester, ethyl levulinate (**3**).



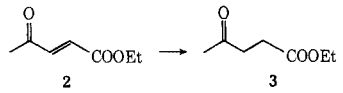
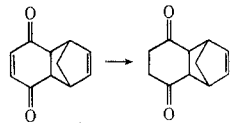
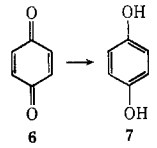
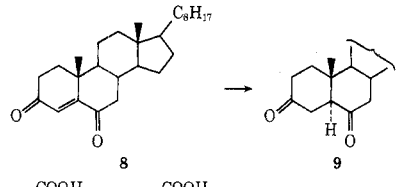
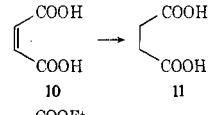
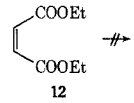
1 2 3

The simplest rationalization of this result is to assume that **2** is in fact formed initially, and that $TiCl_3$ is capable of effecting rapid further reduction of enedicarbonyl compounds to their saturated analogs. This has indeed proved to be the case, and we have carried out a short study of the reaction which suggests that it is a gentle, effective, and remarkably simple method to use. Our results are given in Table I.

As can be seen from Table I, the reaction, which is usually complete within 15 min at room temperature, works quite well for diketones (examples **4**, **6**, **8**), for keto esters (example **2**), and for diacids (example **10**). The reaction fails completely for diesters, however, even when a prolonged reflux is employed. This presumably reflects the undoubted higher reduction potential of **12** *vs.* the other substrates.[3]

Similar methods of reduction of enedicarbonyl compounds have been reported using chromous ion,[4-6] al-

Table I
Reduction of Enedicarbonyl Compounds with $TiCl_3$

Reaction	Yield, %
	84
	95
	98
	86
	45
	

though only moderate yields were obtained, and the well-known zinc–acetic acid reagent is also effective.[7] Because of the high yields obtained and mild conditions required by this new $TiCl_3$ method, however, we believe that it will be a useful procedure.

Experimental Section

The titanium(III) chloride was obtained as a 20% aqueous solution (~1.6 *M*) from Matheson Coleman and Bell and was found to be stable for long periods when stored under nitrogen.

Representative Reaction Procedure. Reduction of Cholest-4-ene-3,6-dione (8). A 50-ml, three-neck flask, fitted with a nitrogen inlet, magnetic stirrer, and rubber septum, was charged with cholest-4-ene-3,6-dione[8] (**8**, 200 mg, 0.5 mmol) and 10 ml of acetone. Cold $TiCl_3$ solution (0.62 ml, 1.0 mmol) was then injected and the reaction mixture was stirred for 7 min at room temperature. The solution was then poured into 50 ml of brine, and the aqueous phase was extracted with ether. The combined extracts were dried (Na_2SO_4), filtered, and concentrated to give 197 mg (98%) of crude solid product. Two recrystallizations from isopropyl ether gave 173 mg (86%) of pure 5α-cholestane-3,6-dione (**9**): ir ($CHCl_3$) 1702 cm^{-1}; nmr ($CDCl_3$) no vinyl protons; mp 168–169° (lit.[9] mp 168–170°).

The following reductions were carried out in a similar manner.

Ethyl 4-oxo-2-pentenoate (2) gave ethyl levulinate (84%) identified by comparison with an authentic sample.

Benzoquinone gave hydroquinone identified by comparison with an authentic sample.

Benzoquinone–cyclopentadiene adduct (4) gave the saturated diketone **5**: ir (neat) 1705 cm^{-1}; nmr (CCl_4) δ 6.14 (t, 2 H, J = 1.6 Hz), 3.40 (m, 2 H), 3.12 (m, 2 H), 2.38 (m, 4 H), 1.35 (m, 2 H).

Maleic acid gave succinic acid (45%), identified as the dimethyl ester, after a reaction time of 24 hr.

Acknowledgment. We thank the National Science Foundation for their support of this work through Grant GP 28173.

Registry No. **2**, 6742-53-6; **4**, 1200-89-1; **5**, 21428-54-6; **6**, 106-51-4; **8**, 984-84-9; **9**, 2243-09-6; **10**, 110-16-7; $TiCl_3$, 7705-07-9.

References and Notes

(1) V. R. Mattox and E. C. Kendall, *J. Amer. Chem. Soc.*, **70**, 882 (1948).
(2) G. H. Timms and E. Wildsmith, *Tetrahedron Lett.*, 195 (1971).
(3) Although the reduction potentials of our substrates are not known, we presume that, in accordance with the recent results of House [H. O. House and M. J. Umen, *J. Amer. Chem. Soc.*, **94**, 5495 (1972)], an unsaturated ester would have a reduction potential higher (more negative) than would an unsaturated ketone.
(4) W. Traube and W. Passarge, *Chem. Ber.*, **49**, 1692 (1916).
(5) C. E. Castro, R. D. Stephens, and S. Moje, *J. Amer. Chem. Soc.*, **88**, 4964 (1966).
(6) J. R. Hanson and E. Premuzic, *J. Chem. Soc. C*, 1201 (1969).
(7) *Cf.* A. Windaus, *Chem. Ber.*, **39**, 2249 (1906).
(8) L. F. Fieser, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., p 189.
(9) J. S. Moffatt, *J. Chem. Soc.*, 872 (1947).

A New Method for Converting Nitro Compounds into Carbonyls. Ozonolysis of Nitronates

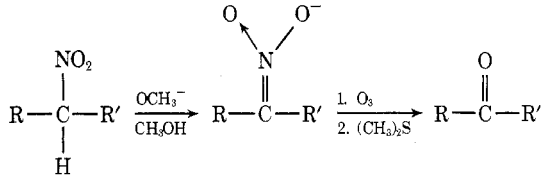
John E. McMurry,* Jack Melton, and Henry Padgett

Thimann Laboratories, University of California, Santa Cruz, California 95064

Received August 10, 1973

The nitro group is a function of considerable importance in synthetic chemistry because of the variety of reactions it can undergo. One of the more useful of these reactions is the transformation nitro → carbonyl, and a number of methods have been devised for accomplishing this goal, including the Nef reaction[1] (strongly acidic); permanganate oxidation of nitronate salts[2] (basic, oxidative); persulfate oxidation of nitronates[3] (basic, oxidative); treatment with a mixture of organic and inorganic nitrite[4] (neutral, oxidative); and our own recently introduced method involving treatment of free nitro compounds with $TiCl_3$[5] (neutral, reductive). Of these possibilities, only the $TiCl_3$ method can be considered truly general in that a wide variety of functional groups survive and that both ketones and aldehydes can be produced in good yields. The major drawback to the use of $TiCl_3$ is that a large amount (4 equiv per nitro group) must be used, making the method inconvenient for large-scale use. We therefore sought yet another method for transforming a nitro group into a carbonyl.

It has been known for some time[6] that a C=N (such as a 2,4-DNP) will react with ozone to generate the corresponding ketone or aldehyde, and we therefore examined ozonolysis of nitronate salts as a possible synthetic method.



The desired reaction does in fact proceed rapidly and cleanly. Some examples we have run are listed in Table I.

Both aldehydes and ketones can be produced in good yields, and of course a wide variety of functional groups are stable to ozone. One of the more useful examples in Table I is the preparation of dimethyl 4-oxopimelate (4) from the readily available[7] nitro diester **3**, in 88% yield. Diester **4** can be ketalized and Dieckmann cyclized to diketone **9**, a compound much used in natural product synthesis, but heretofore obtained only by a tedious route from furfural.[8] This new method should therefore prove of considerable use in synthetic chemistry.