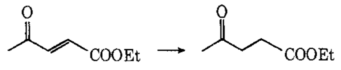
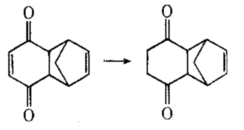
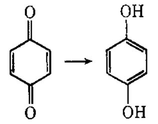
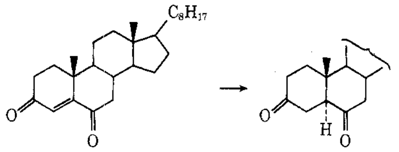
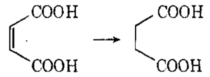
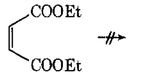
Table I
Reduction of Enedicarbonyl Compounds with $TiCl_3$

Reaction	Yield, %
 2 3	84
 4 5	95
 6 7	98
 8 9	86
 10 11	45
 12	

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.

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(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.
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(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

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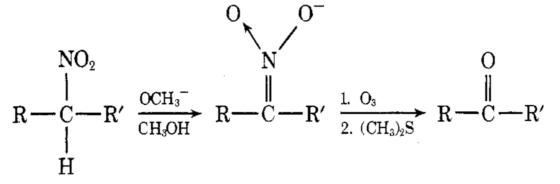
The nitro group is a function of considerable importance in synthetic chemistry because of the variety of reactions it can undergo. One of the more useful of these reactions is the transformation nitro → carbonyl, and a number of methods have been devised for accomplishing this goal, including the Nef 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.

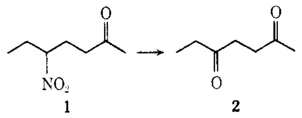
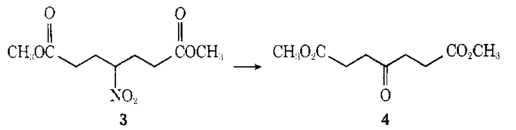
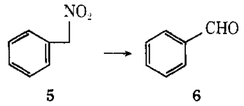
It has been known for some time[6] that a C═N (such as a 2,4-DNP) will react with ozone to generate the corresponding ketone or aldehyde, and we therefore examined ozonolysis of nitronate salts as a possible synthetic method.

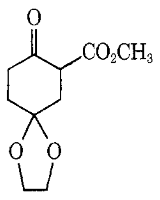


The desired reaction does in fact proceed rapidly and cleanly. Some examples we have run are listed in Table I.

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.

Table I
Ozonolysis of Nitronate Salts

Reaction	Yield, %
 1 → 2	83
 3 → 4	88
 5 → 6	68
$CH_3(CH_2)_6CH_2NO_2 \longrightarrow CH_3(CH_2)_6CHO$ 7 → 8	65



9

Experimental Section

General Reaction Procedure. The nitro compound (0.020 mol) in 50 ml of anhydrous methanol was treated with 1 equiv of sodium methoxide (1.08 g, 0.020 mol) and stirred for 10 min to form the nitronate salt. This methanolic solution was then cooled to −78°, and a stream of ozone-oxygen was passed through.[9] For secondary nitro compounds, ozonolysis was continued until the reaction mixture was light blue (excess O_3). For primary nitro compounds, however, it was found necessary to meter in only 1 equiv of O_3 since an excess led to further reaction and consequent lower yields of aldehyde product.

After 30 min, the reaction mixture was purged with a nitrogen stream to remove excess ozone, and was then treated with 5 ml of dimethyl sulfide at −78° and slowly allowed to come to room temperature. After standing for 16 hr, volatile material was removed at the rotary evaporator. The residue was taken up in ether and washed with water and brine, then dried (Na_2SO_4), concentrated, and purified either by distillation or crystallization.

In this manner, the following compounds were prepared.

Heptane-2,5-dione (2) was prepared from 5-nitroheptan-2-one,[5] and identified by spectral comparison with an authentic sample,[5] 83% yield.

Dimethyl 4-oxopimelate (4) was prepared from dimethyl 4-nitropimelate,[7] and purified by crystallization from hexane, mp 49–50° (lit.[8] mp 49–50°), 88% yield.

Benzaldehyde (6) was prepared from α-nitrotoluene,[10] purified by distillation, and identified by spectral comparison with an authentic sample, 68% yield, bp 70–75° (20 mm).

Octanal (8) was prepared from 1-nitrooctane,[11] purified by distillation, and identified by spectral comparison with an authentic sample, 65% yield, bp 80° (30 mm).

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

Registry No. 1, 42397-25-1; **2,** 1703-51-1; **3,** 7766-83-8; **4,** 22634-92-0; **5,** 622-42-4; **6,** 100-52-7; **7,** 629-37-8; **8,** 124-13-0.

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(4) N. Kornblum and P. A. Wade, *J. Org. Chem.*, **38**, 1418 (1973).
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(6) *Cf.* G. A. Fleisher and E. C. Kendall, *J. Org. Chem.*, **16**, 556 (1951).
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(10) W. Emmons, *J. Amer. Chem. Soc.*, **77**, 4558 (1955).
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Ruthenium-Catalyzed Hydrogen–Deuterium Exchange in Alcohols. A Convenient Method for Deuterium Labeling of Primary Alcohols

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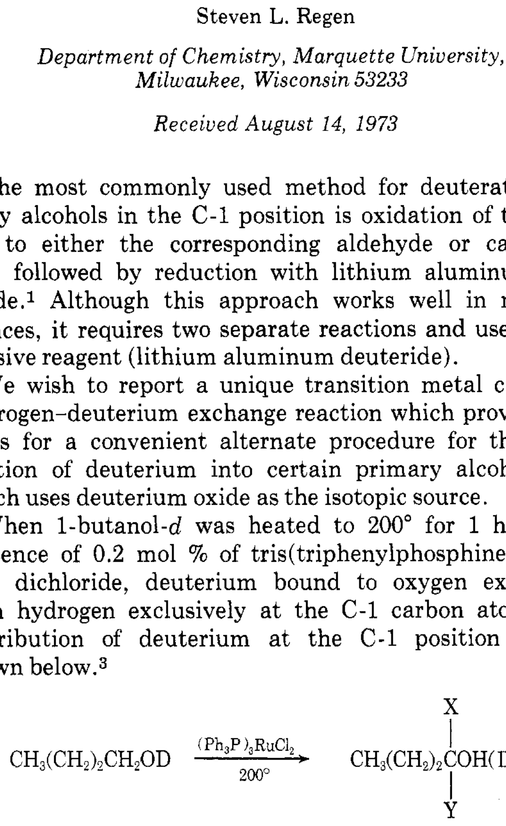
The most commonly used method for deuterating primary alcohols in the C-1 position is oxidation of the alcohol to either the corresponding aldehyde or carboxylic acid followed by reduction with lithium aluminum deuteride.[1] Although this approach works well in most instances, it requires two separate reactions and uses an expensive reagent (lithium aluminum deuteride).

We wish to report a unique transition metal catalyzed hydrogen–deuterium exchange reaction which provides the basis for a convenient alternate procedure for the introduction of deuterium into certain primary alcohols and which uses deuterium oxide as the isotopic source.

When 1-butanol-*d* was heated to 200° for 1 hr in the presence of 0.2 mol % of tris(triphenylphosphine)ruthenium dichloride, deuterium bound to oxygen exchanged with hydrogen exclusively at the C-1 carbon atom;[2] the distribution of deuterium at the C-1 position is that shown below.[3]



$$CH_3(CH_2)_2CH_2OD \xrightarrow[200^\circ]{(Ph_3P)_3RuCl_2} CH_3(CH_2)_2\overset{X}{\underset{Y}{C}}OH(D)$$

1a, X = Y = H (55%)
b, X = H; Y = D (35%)
c, X = Y = D (10%)

In an effort to determine whether the ruthenium complex is a unique catalyst for exchanging hydrogen with deuterium in 1-butanol-*d*, we have tried the same procedure, substituting each of the following metallic catalysts for the ruthenium complex: $(Ph_3P)_3RhCl$, $(Ph_3P)_2PtCl_2$, Pd/C, $(Ph_3P)_2IrCOCl$, Raney nickel, and K_2PtCl_4. While the ruthenium complex proved most effective for this conversion, all of the other metals exhibited no detectable catalytic activity.

Although we have found that primary alcohols readily undergo hydrogen exchange, those secondary alcohols investigated gave poor results (Table I). Little exchange was detected in the case of 2-propanol and cyclododecanol, and prolonged heating resulted in considerable dehydration. For primary alcohols, we detected no decomposition (<0.1%) under the reaction conditions described.[4]

We have found that, by adding deuterium oxide to a mixture of the ruthenium catalyst and any one of the primary alcohols tested, this exchange reaction becomes a synthetically useful method for deuterium labeling. For example, when 1-decanol and deuterium oxide were heated in the presence of the ruthenium catalyst, the recovered alcohol contained a significant amount of deuterium incorporated in the C-1 position. The amount of deuteri-