Tetrahedron Letters,Vol.29,No.7,pp 769-772,1988
Printed in Great Britain

0040-4039/88 $3.00 + .00
Pergamon Journals Ltd.

OXIDATIVE BISDECARBOXYLATION OF α -ALKOXYMALONIC ACIDS WITH CERIUM(IV)

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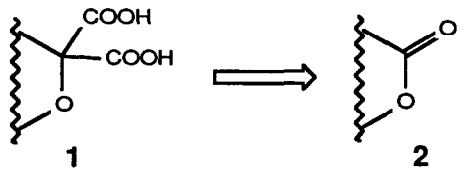
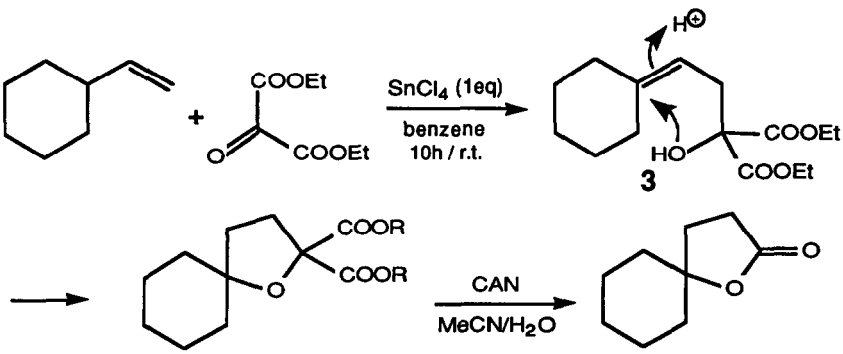
Summary: Ceric ammonium nitrate is an excellent reagent for preparing carboxylic esters from α-alkoxymalonic acids by oxidative bisdecarboxylation.

Previously we discovered that ceric ammonium nitrate (CAN) provides good to excellent yields of carboxylic acids by oxidative bisdecarboxylation of α-hydroxymalonic acids in many cases for which the previously known reagent, sodium periodate, is unsatisfactory.[1] We now find that CAN converts α-alkoxymalonic acids **1** into carboxylic esters **2**. The utility of this new reaction is demonstrated by several C-C connective syntheses of γ-butyro and δ-valerolactones.



1 **2**

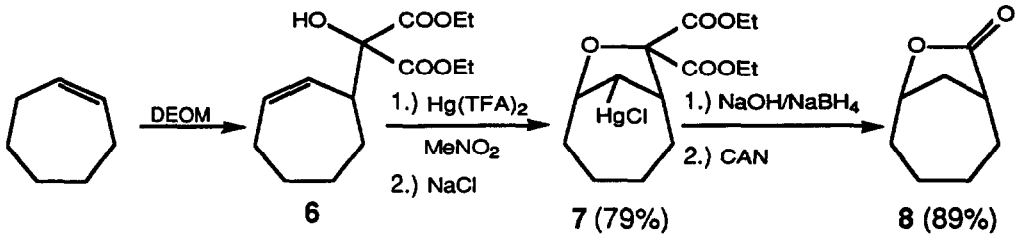
Spirolactonization. Reaction of diethyl oxomalonate (DEOM)[2] with vinylcyclohexene in the presence of $SnCl_4$ at room temperature produces furan **4**[3] instead of the expected[1] Lewis acid-catalyzed ene reaction product **3**. Presumably, **3** is produced but undergoes acid-catalyzed cyclization to **4** (R = Et). Oxidative bisdecarboxylation of the corresponding diacid **4** (R = H) with CAN delivers spiro-γ-butyrolactone **5**.[4]



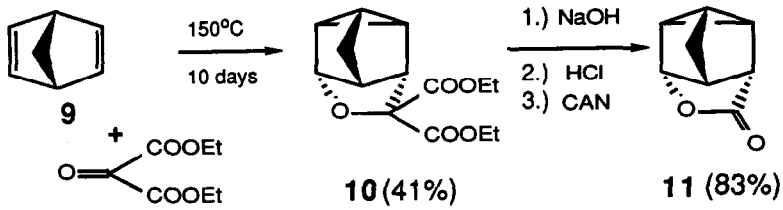
3

4 (80%) **5 (91%)**

Bicyclolactonization. Not all ene adducts of DEOM undergo acid-catalyzed cyclization analogous to that observed with **3**. For the ene adduct **6**[3] of cycloheptene, cyclization was achieved by intramolecular oxymercuration. Reductive demercuration-saponification of the resulting chloromercurial **7** followed by oxidative bisdecarboxylation of the crude intermediate α-alkoxymalonic acid delivered the bicyclic butyrolactone **8**.[3]

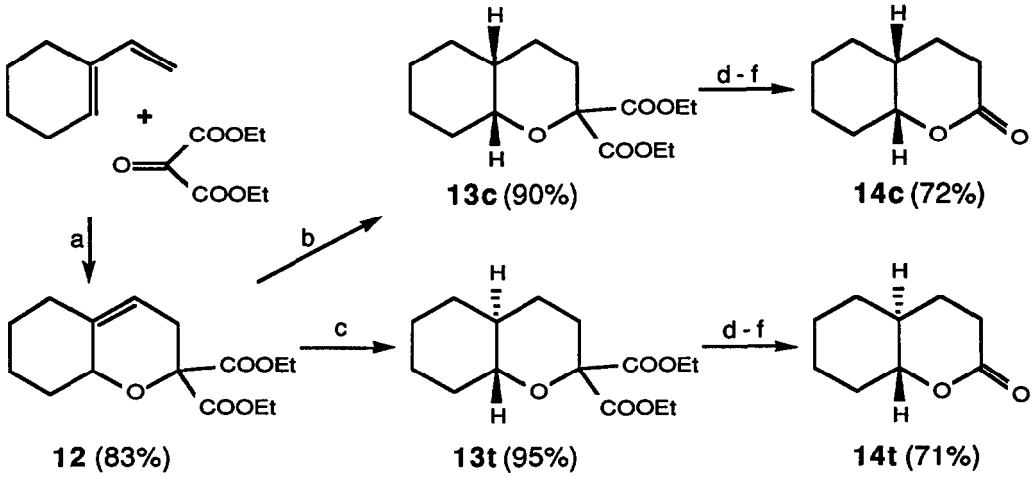


A Homodienophilic Equivalent of Carbon Dioxide. Numerous dienophiles participate in thermal $2\pi + 2\pi + 2\pi$ cycloadditions with 1,4-dienes.[5] While carbon dioxide is unreactive toward bicyclo[2.2.1]hepta-2,7-diene (**9**), DEOM reacts with **9** to provide cycloadduct **10** (R = Et).[3] Oxidative bisdecarboxylation of the derived α-alkoxymalonic acid with CAN delivered γ-butyrolactone **11**[6] in excellent yield. The overall process, conversion of **9** to **11** corresponds to a homo Diels-Alder addition of carbon dioxide.



A Synthesis of δ-Valerolactones. Another route to α-alkoxymalonic esters is Diels-Alder reaction of DEOM with 1,3-dienes. The resulting 2,2-dicarboethoxy-3,5-dihydro-2H-pyrans have been exploited previously for synthesis of 3,5-dihydro-2H-pyran-2-ones.[7] Oxidative bisdecarboxylation of intermediate α-alkoxymalonic acids was achieved in 40-60% yields by reaction with lead tetraacetate. Better yields (up to 72%) were obtained by a multistep process involving Curtius rearrangement of the corresponding acyl azides. We now find that catalytic hydrogenation of 2,2-dicarboethoxy-3,5-dihydro-2H-pyrans can be achieved with a remarkable degree of stereoselectivity. In conjunction with oxidative bisdecarboxylation by CAN, this finding provides a highly stereoselective new synthesis of δ-valerolactones from 1,3-dienes. This is exemplified with the preparation of either *cis* or *trans*-fused lactones **14c** or **14t** from the $4\pi + 2\pi$ cycloadduct **12**[3] from DEOM and vinylcyclohexene (Scheme 1). Thus, hydrogenation of **12** in the presence of Adams catalyst (i.e. PtO_2) delivers the *cis*-fused isomer **13c**[3] exclusively, while hydrogenation of **12** in the presence of Wilkinson's catalyst (i.e. $(Ph_3P)_3RhCl$) delivers the *trans*-fused isomer **13t**.[3] The isomerically pure lactones **14c**[8] or **14t**[8] were obtained from the corresponding α-alkoxymalonic acids by oxidative bisdecarboxylation with CAN.

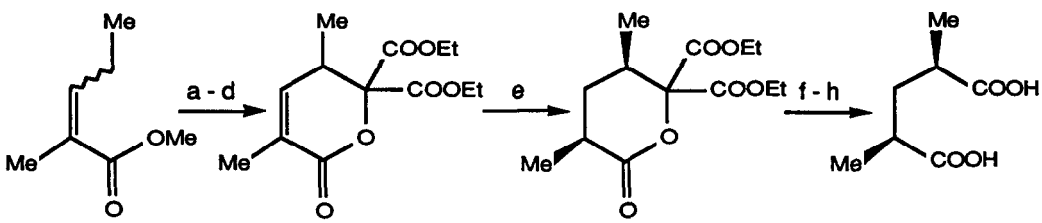
Scheme 1



(a) 160° C/16h, (b) $H_2/PtO_2/EtOH$, (c) $H_2/(Ph_3P)_3RhCl/EtOH$, (d) $KOH/H_2O/MeOH$, (e) HCl, (f) $Ce(NH_4)_2(NO_3)_6/H_2O/MeCN$

A Glutaric Acid Synthesis. Stereoselective catalytic hydrogenation can also be exploited in conjunction with oxidative bisdecarboxylation by cerium (IV) to achieve stereocontrolled C-C connective syntheses of glutaric acids. The synthesis of *meso*-2,4-dimethylglutaric acid (**17**) outlined in scheme 2 is illustrative. Diels-Alder reaction of DEOM with a silyl ketene acetal derived from methyl 2-methylpent-2-enoate delivered lactone **15** after hydrolysis of an intermediate orthoester. Stereoselective catalytic hydrogenation then afforded **16** which was converted to the glutaric acid **17** by hydrolysis and subsequent oxidative bisdecarboxylation with CAN.

Scheme 2



(a) LDA/HMPA/THF, (b) TBDMSCl, (c) DEOM, (d) 10% $HF/H_2O/MeCN$, (e) $H_2/PtO_2/EtOH$, (f) 3N NaOH, (g) HCl, (h) $CAN/H_2O/MeCN$

TYPICAL EXPERIMENTAL PROCEDURES

Ene-Spirocyclization Reaction with DEOM. To a solution of vinylcyclohexene (3.3 g) and DEOM (5.2 g) in dry benzene (50 mL) was added $SnCl_4$ (7.8 g) dropwise with ice-water bath cooling and magnetic stirring under a blanket of dry nitrogen. After 10 h at room temperature, the resulting mixture was poured into ice cold 10% aqueous HCl and diethyl ether (80 mL). The

organic extract was washed with saturated aqueous NaCl followed by saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and solvent removed by rotary evaporation. Distillation under reduced pressure afforded ester **4** (R = Et, 6.8 g); bp 112-125°C/0.25 Torr; ^1H NMR δ 1.27(3H, t, J = 7Hz), 1.0-1.8(10H), 1.84(2H, t, J = 7Hz), 2.52(2H, t, J = 7Hz), 4.23(2H, q, J = 7Hz).

Oxidative Bisdecarboxylation of an α-Alkoxymalonic Acid. Malonic ester **4** (R = Et) was stirred vigorously with 20% aqueous KOH at room temperature for 30 h. After washing the resulting solution with ether, and cooling to 0° C, acidification to pH 2 with ice cold 20% HCl and extraction with ether provided malonic acid **4** (R = H) which was oxidatively decarboxylated without further purification. The malonic acid (2.3 g) in acetonitrile (150 mL) was added to a solution of ceric ammonium nitrate (28 g) in water (50 mL) and the mixture was magnetically stirred vigorously for 1 h at room temperature. The reaction product solution was poured into saturated aqueous NaCl (1 L) and the resulting mixture was extracted with chloroform (4 x 500 mL). The combined extracts were washed with saturated brine (2 x 500 mL), then saturated aqueous $NaHCO_3$ (500 mL), dried ($MgSO_4$), and filtered. Removal of solvents afforded lactone **5** (1.4 g). Analysis of this product by ^1H NMR showed it to be pure 1-oxaspiro[4.5]decan-2-one by comparison with a spectrum reported previously.[4]

ACKNOWLEDGMENT. This research was assisted financially by a grant from the National Science Foundation. We thank Eileen Easler Kummant, Howard S. Oster , and Theodore Illiadis for technical assistance.

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3. All new compounds gave satisfactory ^1H NMR spectra and elemental analyses or high resolution mass spectra. Yields are for products of >96% purity (^1H NMR analysis). Samples for elemental analysis were purified, if necessary, by gas liquid partition or silica gel thin layer chromatography. Details of these characterizations will be presented in a full account of this research.

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(Received in USA 18 November 1987)