Acknowledgment. We are grateful for financial support from the Council for Scientific and Industrial Research, Pretoria.

Registry No. 1, 280-64-8; 2, 62197-73-3; (*n*-BuC≡C)(Me)CuLi, 41799-09-1; (*n*-BuC≡C)(*n*-Pr)CuMgBr, 95765-20-1; (PhO)(*n*-Bu)CuLi, 95765-21-2; (PhO)(*t*-Bu)CuLi, 50281-68-0; (PhO)(*n*-Pr)CuMgBr, 95765-23-4; (*t*-BuO)(*n*-Bu)CuLi, 41655-89-4; MeOH, 67-56-1; *n*-BuOH, 71-36-3; *n*-PrOH, 71-23-8; *t*-BuOH, 75-65-0; $C_5H_{11}COOH$, 142-62-1; (PhS)(Me)CuLi, 56831-21-1; (PhS)(Ph)CuMgBr, 95765-25-6; (PhS)($PhCH_2$)CuMgBr, 95765-27-8; (PhS)(*n*-Bu)CuLi, 53128-68-0; (PhS)(*t*-Bu)CuLi, 50281-66-8; (PhS)(*n*-Pr)CuMgBr, 95765-29-0; PhOH, 108-95-2; $PhCH_2OH$, 100-51-6; *n*-BuC≡CH, 693-02-7; *n*-BuC≡CCu, 33589-44-5; PhSH, 108-98-5; PhSLi, 2973-86-6; PhOLi, 555-24-8; *t*-BuOLi, 1907-33-1; *cis*-1,5-cyclooctanediol, 23418-82-8.

A Simple Procedure for Stereospecific Vicinal Dicarboxylation of Olefins

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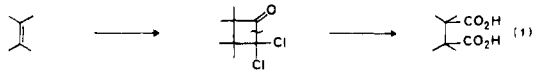
Received November 15, 1984

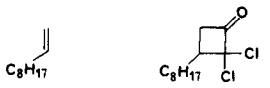
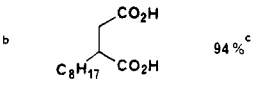
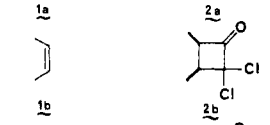
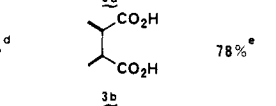
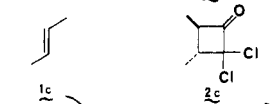
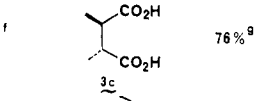
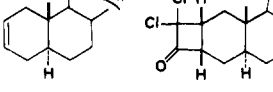
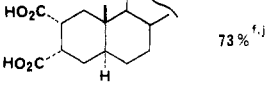
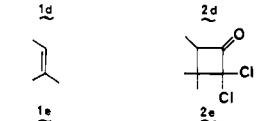
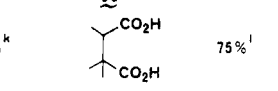
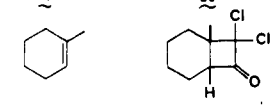
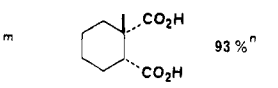
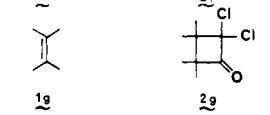
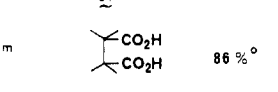
Recently, we required a method for effecting vicinal dicarboxylation or dicarbalkoxylation of a trisubstituted olefin and were unable to find any suitable procedures in the literature. The best known method for effecting this kind of transformation is the palladium-catalyzed carbonylation reaction; however, this is very limited in scope, being applicable only to certain types of mono- and disubstituted olefins.[1]

Our interest in the chemistry of α,α-dichlorocyclobutanones[2] led us to consider the possibility of effecting dicarboxylation through the intermediacy of the dichloroketene–olefin cycloadducts[3] (eq 1). In this note we offer a straightforward procedure based on such an approach.



In a few cases, cleavage of the $-CCl_2CO-$bond of these cycloadducts to give potentially useful intermediates has been possible through reaction with alkoxides or amines;[3a,d,4] most often, though, the products from these and similar treatments are those resulting from cleavage of the other carbon–carbonyl bond, ring contraction, and ring expansion (processes involving cine displacement).[3d,5]

Table I. Vicinal Dicarboxylation of Olefins

olefin	dichlorocyclobutanone	yield[a]	succinic acid	yield
 1a	2a	88%[b]	 3a	94%[c]
 1b	2b	79%[d]	 3b	78%[e]
 1c	2c	80%[f]	 3c	76%[g]
 1d	2d	73%[h,i]	 3d	73%[h,i]
 1e	2e	87%[k]	 3e	75%[l]
 1f	2f	83%[m]	 3f	93%[n]
 1g	2g	61%[m]	 3g	86%[o]

[a] Yield of distilled product based on olefin (**2a,f**) or reagent (**2b,c,e,g**). [b] Reference **2a**. [c] mp 87 °C (lit.[1d,15] mp 90 °C). Lithium dimethylcopper was used.[12] [d] Reference 10. [e] mp 199 °C dec [lit.[16] mp 209 °C (198 °C dec)]. [f] See Experimental Section. [g] mp 128 °C (lit.[16] mp 129 °C). [h] 5α-Cholest-2-ene.[9] [i] Reference 11. Crude product used in next step. [j] Yield based on **1d**. [k] Reference 3c. [l] mp 146 °C (lit.[17] mp 152 °C). [m] References 3b,c. [n] mp 156–157 °C (lit.[18] mp 159.5–161 °C). [o] mp 196 °C (lit.[19] mp 200 °C).

Instead of searching for other nucleophiles that might more generally attack the carbonyl, we sought to profit from an earlier observation that the α,α-dichlorocyclobutanones, in most cases, can be cleanly converted to the corresponding α-chloro enolates merely through treatment with *n*-butyllithium.[6] While we were unsuccessful in finding a high-yield method for directly oxidizing the enolates to succinic acids, an efficient, normally one-pot procedure was found for carrying out the desired cleavage via these enolates, viz., through successive treatment of the α,α-dichlorocyclobutanones with *n*-butyllithium, acetic anhydride, and sodium metaperiodate–ruthenium dioxide.[7] Examples of the vicinal dicarboxylation are given in Table I.

The *overall* yields for the dicarboxylation range from 52% to 83% and average 68%. Not unexpectedly,[8] the conversion is totally stereospecific: **1b** yields only **3b** and **1c** gives only **3c**. Finally, in that lithium dimethylcopper can be used in place of *n*-butyllithium,[2b,c] the procedure can accommodate certain additional functional groups, as illustrated in eq 2.

We expect that this dicarboxylation method will prove useful due to its simplicity, generality, and high yields.

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(2) (a) Greene, A. E.; Deprês, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 4003–4005. (b) Deprês, J. P.; Greene, A. E. *J. Org. Chem.* **1980**, *45*, 2036–2037. (c) Greene, A. E.; Luche, M. J.; Deprês, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2435–2439.

(3) (a) Ghosez, L.; Montaigne, R.; Roussel, A.; Vanlierde, H.; Mollet, P. *Tetrahedron* **1971**, *27*, 615–633. (b) Krepski, L. R.; Hassner, A. *J. Org. Chem.* **1978**, *43*, 2879–2882. (c) Bak, D. A.; Brady, W. T. *Ibid.* **1979**, *44*, 107–110. (d) Brady, W. T. *Tetrahedron* **1981**, *37*, 2949–2966, and references therein.

(4) Potts, T. R.; Harmon, R. E. *J. Org. Chem.* **1969**, *34*, 2792–2793. See also: Conia, J. M.; Ripoll, J. L. *Bull. Soc. Chim. Fr.* **1963**, 763–767.

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(6) Greene, A. E.; Luche, M. J., unpublished results. Lithium dimethylcopper can also be used. See ref 2b,c and 12.

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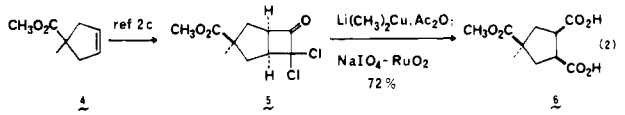

4 5 6

Experimental Section

Solvents were generally distilled prior to use. Tetrahydrofuran and ether were distilled from sodium hydride–lithium aluminum hydride. Phosphorus oxychloride was distilled from potassium carbonate. Reaction mixtures were generally stirred under a nitrogen or argon atmosphere. Thin-layer chromatography was performed on Merck $60F_{254}$ (0.25 mm) sheets, which were visualized with molybdophosphoric acid in ethanol. Merck 70–230-mesh silica gel 60 and Florisil (60–100 mesh) were employed for column chromatography. A Perkin-Elmer Model 397 spectrophotometer was used to record the IR spectra. A Bruker WP 80 SY spectrometer was employed for the ^1H NMR spectra (Me_4Si as the internal reference). Mass spectra were obtained on a VG Micromass 70 70F instrument. Melting points were obtained with a Büchi-Tottoli apparatus and are not corrected. Microanalyses were performed by the Central Service of the CNRS.

Dichlorocyclobutanones. The cycloadducts **2a–g** and **5** were obtained from the commercially available olefins **1a–c** and **1e–g** and the known olefins **1d**[9] and **4**,[2c] by using the procedure of Krepski and Hassner.[3b] The cycloadducts **2a**,[2a] **2b**,[10] **2d**,[11] **2e**,[3c] **2f**,[3b,c] **2g**,[3b,c] and **5**[2c] have been reported previously.

***trans*-2,2-Dichloro-3,4-dimethylcyclobutanone (2c)**: bp 30 °C (0.5 torr); ^1H NMR (CCl_4) δ 1.30 (d, J = 7.1 Hz, 3 H), 1.44 (d, J = 6.3 Hz, 3 H), 2.30–2.70 (m, 1 H), 2.95–3.25 (m, 1 H); IR (film) 1802 cm^{-1}; mass spectrum, m/e 168 (M^+ + 1), 167 (M^+), 166, 140, 139, 138, 109 (100%).

Succinic Acids. General Procedure. To a stirred solution of 4 mmol of the α,α-dichlorocyclobutanone in 16 mL of dry tetrahydrofuran at −78 °C was added over 1 min 2.84 mL (4.4 mmol) of 1.55 M n-butyllithium[12] in hexane. After 15 min, 2.8 mL (29.7 mmol) of acetic anhydride were added and the solution was allowed to come to room temperature. After being stirred for 1.5 h, the reaction mixture was concentrated under reduced pressure[13] and the resulting solid residue was dissolved in 28 mL of acetonitrile–carbon tetrachloride–water (8:8:12) and treated with 4.8 g (22.4 mmol) of sodium metaperiodate and 100 mg (0.75 mmol) of ruthenium dioxide.[7] After being efficiently stirred for 14 h, the mixture was treated with 24 mL of 10% aqueous sodium hydroxide and stirring was continued for an additional 6 h in order to hydrolyze any anhydride present.[14] The mixture was extracted with ether and the aqueous phase was acidified to pH 2–3 with 10% aqueous hydrochloric acid and then thoroughly extracted with ether or ethyl acetate. After being washed with 2% aqueous sodium thiosulfate, the organic phase was dried over sodium sulfate and concentrated under reduced pressure to yield the diacid, which generally crystallized spontaneously. Diacids **3a**,[1d,15] **3b**,[16] **3c**,[16] **3e**,[17] **3f**,[18] and **3g**[19] have been described previously.

5α-Cholestane-2α,3α-dicarboxylic acid (3d): mp 207–208 °C (dichloromethane–pentane); ^1H NMR ($CDCl_3$) δ 0.65 (s), 0.82 (s), 0.90 (s), 2.50–2.85 (m), 3.20–3.40 (m), 8.60 (br, s); IR (Nujol) 3080, 2660, 1710 cm^{-1}. Anal. Calcd for $C_{29}H_{48}O_4 \cdot {}^1/_2H_2O$: C, 74.16; H, 10.52. Found: C, 74.18; H, 10.44.

(1*R*,2*S*,4*r*)-4-(Methoxycarbonyl)-4-methylcyclopentane-1,2-dicarboxylic acid (6): mp 132 °C (dichloromethane–hexane); ^1H NMR ($CDCl_3$) δ 1.31 (s, 3 H), 1.78–2.13 (m, 2 H), 2.54–2.87 (m, 2 H), 3.05–3.45 (m, 2 H), 3.68 (s, 3 H), 10.70 (br s, 2 H); IR (Nujol) 3030, 2700, 1730, 1700 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.03; H, 6.02.

Acknowledgment. We thank Professor A. Rassat, Dr. J. L. Luche, and Dr. C. Morat for their interest in this work, the CNRS (LA 332) for financial support, and the C.N.Pq. for a fellowship award to F.C.

Registry No. **1a**, 872-05-9; **1b**, 590-18-1; **1c**, 624-64-6; **1d**, 570-73-0; **1e**, 513-35-9; **1f**, 591-49-1; **1g**, 563-79-1; **2a**, 71221-64-2; **2b**, 64512-26-1; **2c**, 95864-67-8; **2d**, 28415-02-3; **2e**, 68212-49-7; **2f**, 32166-29-3; **2g**, 66239-90-5; **3a**, 2530-32-7; **3b**, 608-40-2; **3c**, 57694-62-9; **3d**, 95864-68-9; **3e**, 2103-16-4; **3f**, 76704-91-1; **3g**, 630-51-3; **4**, 95864-69-0; **5**, 95864-70-3; **6**, 95864-71-4; $Cl_2C{=}C{=}O$, 4591-28-0; n-BuLi, 109-72-8; Ac_2O, 108-24-7; RuO_2, 12036-10-1; $NaIO_4$, 7790-28-5.

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(11) Fletcher, V. R.; Hassner, A. *Tetrahedron Lett.* **1970**, 1071–1074. Cragg, G. M. L. *J. Chem. Soc. C* **1970**, 1829–1832.
(12) Treatment of **2a** and **5** with lithium dimethylcopper[2b,c] in lieu of n-butyllithium led to considerably higher yields of the diacids **3a** and **6**, respectively. (In these cases, the enol acetates were isolated by extraction prior to oxidative cleavage.) Generally, however, the greater simplicity of the n-butyllithium procedure more than compensates for any lower yield.
(13) With volatile substrates, the reaction mixture was instead treated with aqueous sodium bicarbonate and the crude enol acetate was then isolated with 1:1 ether–hexane [IR (film) 1770, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ ~2.15 (s, 3 H)].
(14) This step was omitted in the conversion of **5** to **6**.
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A Synthesis of β-Methylene-γ-butyrolactones

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Received November 15, 1984

In contrast to the many procedures that exist for obtaining α-methylene-γ-butyrolactones,[1] there are relatively few methods available for the synthesis of β-methylene-γ-butyrolactones.[2] Not unexpectedly, a direct approach to α,α-disubstituted lactones of this type by successive alkylation of 3-methylbut-2-enolide fails due to preferential proton abstraction at C-4.[3] While in principle this problem could be overcome through the use of β-methylene-γ-butyrolactone, in practice the instability to conjugation of this molecule[2a,4] (and its α-monoalkyl derivatives[4a]) renders its use in synthesis impractical at best.

It seemed quite likely that a suitably protected γ-hydroxy dimethylacrylate derivative would, in contrast, undergo selective deprotonation at the methyl position[5] and

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