(5 mL) was added, and stirring was continued for 10 min, whereupon the organic solvent was decanted from the oily brown sludge present in the reaction mixture. Ether (2 × 5 mL) was used to wash the brown residue, and the combined organic solutions were then filtered through a Florisil/$MgSO_4$ pad. Evaporation of the filtrate gave pure **10** (78 mg, 80%): retention time (130 °C–2 min, 32 °C/min to 250 °C–6 min), 1.40 min; IR ν_{max} 1710 cm^{-1} (s, C=O); NMR δ 0.95 (s, 3 H), 1.08 (s, 3 H), 1.65–2.15 (m, 3 H), 2.65 (d, 1 H), 3.19 (d, 1 H), 3.46 (t, 1 H); MS *m/e* 140.

Preparation of the *trans*-Epoxy Alcohol 11. To a solution of **10** (100 mg, 0.72 mmol) in toluene (2 mL) at 0 °C was added over a period of 5 min triisobutylaluminum (Texas Alkyls; 1.23 M in toluene, 0.60 mL, 1 equiv). The solution was stirred for 15 min and then quenched by the successive addition of methanol (0.3 mL), saturated NH_4Cl (0.3 mL), ether (6 mL), and Celite (0.5 g). This mixture was stirred for 1 h and then filtered through a $MgSO_4$ pad, and the filtrate was evaporated to give **11** (98% pure by GC and NMR; 101 mg, 99%): retention time (130 °C–2 min, 32 °C/min to 250 °C–6 min), 2.0 min; IR ν_{max} 3460 cm^{-1} (broad, OH); NMR δ 0.90 (s, 3 H), 0.98 (s, 3 H), 1.00–1.82 (m, 4 H), 2.75 (OH), 3.07 (d, 1 H), 3.20 (t, 1 H), 4.09 (m, 1 H); MS *m/e* 142.

Preparation of the Allylic Alcohol 13. To a stirred suspension of lithium aluminum hydride (320 mg, 8.0 mmol) in ether (14 mL) was slowly added at room temperature a solution of the enone **12** (2.0 g, 16.1 mmol) in ether (16 mL). After the addition was complete, the reaction mixture was stirred for 1 h and then cooled to 0 °C and quenched with saturated sodium sulfate. The resulting mixture was filtered through $MgSO_4$ and the solvent evaporated to give **13** (1.64 g, 82%): IR ν_{max} 3600 (s, OH), 3450 (broad, OH) cm^{-1}; NMR δ 1.20–1.80 (m, 4 H), 1.95 (s, 3 H), 1.95 (OH), 2.05 (s, 3 H), 5.60 (m, 2 H); MS *m/e* 126.

Preparation of the *cis*-Epoxy Alcohol 14. To a solution of **13** (785 mg, 6.23 mmol) in methylene chloride (7 mL) at 0 °C was added dropwise a solution of *m*-chloroperbenzoic acid (1.60 g, 9.35 mmol, 85%) in methylene chloride (15 mL) and ethyl acetate (3.5 mL). The resulting mixture was stirred at 0 °C for 8 h and then quenched with 5% sodium hydroxide (28 mL) and extracted with methylene chloride (4 × 15 mL). The combined extracts were filtered through $MgSO_4$ and evaporated to an oil. Chromatography of this oil on silica eluting with 2:1 ether/hexane gave pure **14** (565 mg, 64%): retention time (120 °C–2 min, 32 °C/min to 250 °C–6 min), 1.52 min; R_f (2:1 hexane/ether) 0.175; IR ν_{max} 3350 cm^{-1} (broad, OH); NMR δ 1.00 (s, 3 H), 1.05 (s, 3 H), 1.20–1.42 (m, 4 H), 2.60 (m, 1 H), 2.90 (d, 1 H), 3.30 (t, 1 H), 3.92 (OH); MS *m/e* 142.

Preparation of the Keto Epoxide 15. Pyridinium chlorochromate (378 mg, 1.75 mmol), alcohol **14** (100 mg, 0.877 mmol), sodium acetate (143 mg, 1.74 mmol), and methylene chloride (1.8 mL) were stirred at room temperature for 6 h. The organic solution was decanted, and the remaining brown residue was washed with methylene chloride (3 × 5 mL). The combined organic washes were filtered through Florisil and then evaporated to give pure **15** (88 mg, 88%): retention time (120 °C–2 min, 32 °C/min to 250 °C–6 min), 1.92 min; R_f (hexane/ether, 2:1) 0.55; IR ν_{max} 1710 cm^{-1} (s, C=O); NMR δ 1.04 (s, 3 H), 1.25 (s, 3 H), 1.80–2.60 (m, 4 H), 3.30 (s, 2 H); MS *m/e* 140.

Preparation of the *trans*-Epoxy Alcohol 16. To **15** (100 mg, 0.714 mmol) in toluene (1.5 mL) at 0 °C was slowly added triisobutylaluminum (0.638 mL, 1.23 M in toluene), and the resulting mixture was stirred at 0 °C for 40 min. The reaction mixture was diluted with ether (4 mL) and then quenched by the addition of methanol (0.5 mL), saturated NH_4Cl (1 mL), and Celite. After stirring for 1 h, the mixture was filtered through $MgSO_4$ and the filtrate was evaporated to dryness, giving **16** (93 mg; 93% pure by GC and NMR analysis): retention time (120 °C–2 min, 32 °C/min to 250 °C–2 min), 1.52 min; R_f (hexane/ether, 2:1) 0.175; IR ν_{max} 3460 cm^{-1} (broad, OH); NMR δ 1.00 (two overlapping singlets, 6 H), 1.15–1.70 (m, 4 H), 2.65, (d, 1 H), 2.95 (d, 1 H), 3.30 (OH), 3.85 (t, 1 H); MS *m/e* 142.

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Registry No.—**7**, 4694-17-1; **8**, 25866-56-2; **9**, 38309-46-5; **10**, 17421-93-1; **11**, 66036-65-5; **12**, 1073-13-8; **13**, 5020-09-7; **14**, 38309-45-4; **15**, 1074-26-6; **16**, 66036-66-6.

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Reaction of *tert*-Butyldimethylsilyl Esters with Oxalyl Chloride–Dimethylformamide: Preparation of Carboxylic Acid Chlorides under Neutral Conditions

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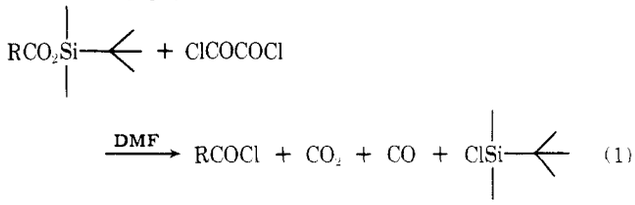
One of the more common transformations encountered in organic synthesis is the conversion of a carboxylic acid to the corresponding carboxylic acid chloride. Most current methods[1] which accomplish this conversion involve acidic conditions and consequently, if a carboxylic acid contains an acid sensitive functionality, it is likely that the desired carboxylic acid chloride may be obtained in low yield or not at all. In this communication we describe a new method for forming carboxylic acid chlorides under neutral conditions.

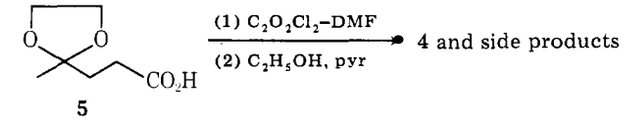
The *tert*-butyldimethylsilyl group has recently been reported to be of value as a protecting group for alcohols and carboxylic acids.[2] Furthermore, the report of the conversion of trimethylsilyl pyruvate to its corresponding acid chloride[3] encouraged us to investigate the reaction of *tert*-butyldimethylsilyl esters with oxalyl chloride in the presence of a catalytic amount of dimethylformamide (DMF) as a potential method of forming carboxylic acid chlorides under neutral conditions (eq 1).



(1)

Treatment of *tert*-butyldimethylsilyl heptanoate (**1**) with 1.2 equiv of oxalyl chloride in methylene chloride in the presence of a catalytic quantity of DMF resulted in slow gas evolution over a period of 2 h. Removal of the solvent and exposure of the resulting acid chloride to ethanol in pyridine gave ethyl heptanoate (**2**) in 92% yield. In a similar manner, treatment of the various *tert*-butyldimethylsilyl esters listed in Table I with oxalyl chloride–DMF gave, after treatment of the resulting acid chlorides with ethanol–pyridine, the respective ethyl esters in the indicated isolated yields.

The results presented in Table I indicate that this reaction will tolerate an acid sensitive functionality quite well. For example, while the conversion of the *tert*-butyldimethylsilyl ester **3** which contains an acid sensitive ketal moiety to the ethyl ester **4** proceeds in excellent yield, the reaction of the corresponding carboxylic acid **5**[4] with oxalyl chloride–DMF



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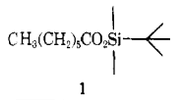
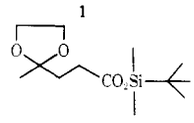
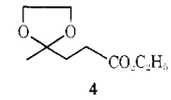
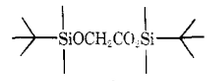
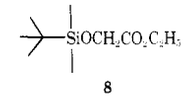
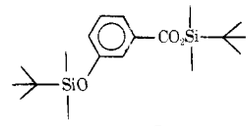
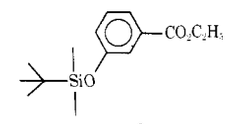
under identical conditions followed by the reaction with ethanol–pyridine gives **4** in much lower yield; moreover the product is accompanied by at least three additional less volatile side products (see Experimental Section).

0022-3263/78/1943-3972$01.00/0

Table I. Ethyl Esters Prepared [a]

tert-butyldimethylsilyl ester	registry no.	ethyl ester	reigstry no.	% yield [b]
 1	54251-63-7	$CH_3(CH_2)_5CO_2C_2H_5$ 2	106-30-9	92
 3	67226-75-9	 4	941-43-5	95
 6	67226-76-0	 8	67226-78-2	87
 7	67226-77-1	 9	67226-79-3	98

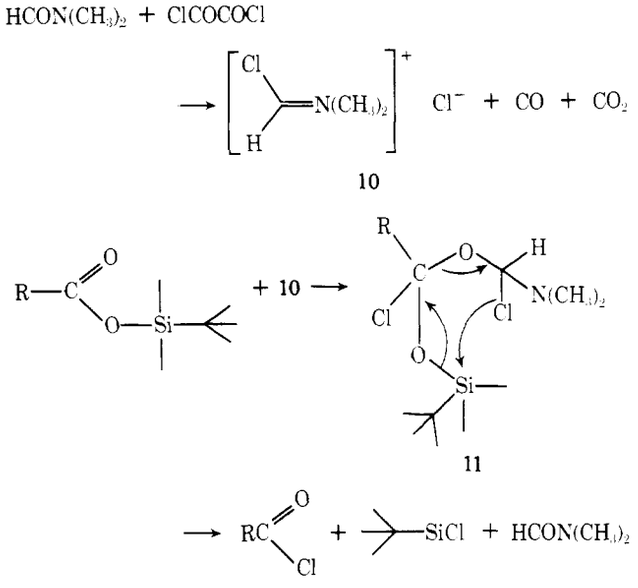
[a] See Experimental Section for conditions. [b] Yields are for distilled products.

Since we have found that *tert*-butyldimethylsilyl ethers are usually stable to oxalyl chloride–DMF under reaction conditions which lead to acid chloride formation and since both the hydroxyl and carboxylate moieties of a hydroxy acid can be silylated in a single step, this method is particularly useful for the preparation of carboxylic acid chlorides which are derived from hydroxy substituted carboxylic acids as illustrated with the bissilylated hydroxy acids **6** and **7** which were converted via the corresponding acid chlorides to the ethyl esters **8** and **9**, respectively, in excellent yields.

Control experiments employing **7** have demonstrated that acid chloride formation proceeds extremely slowly in the absence of DMF; this implicates dimethylformiminium chloride[5] (**10**) as the reactive species. Conceivably, the mechanism for the transformation of a *tert*-butyldimethylsilyl ester to a carboxylic acid chloride could involve addition of dimethylformiminium chloride to the carboxyl group of the silyl ester to give intermediate **11** or a formal equivalent which undergoes fragmentation as postulated to generate *tert*-butyldimethylchlorosilane, DMF, and the carboxylic acid chloride (Scheme I).

Thus, the reaction of a *tert*-butyldimethylsilyl ester with oxalyl chloride in the presence of a catalytic amount of DMF is an effective method for the preparation of carboxylic acid chlorides under neutral conditions. Furthermore, particularly for the preparation of less volatile acid chlorides, this method has a distinct advantage over the triphenylphosphine–carbon tetrachloride procedure[6] which is commonly employed for this purpose since unlike the latter method, which results in the formation of an equivalent of triphenylphosphine oxide, the side products (*tert*-butyldimethylchlorosilane, CO, and CO_2) in this case are volatile and can be removed with ease. Of equal importance, this procedure provides a facile method of preparing carboxylic acid chlorides derived from hydroxy substituted carboxylic acids. In this respect, this reaction is likely to show advantages over the carboxylic acid sodium salt–oxalyl chloride method[7] since activation of the carboxylate group for acid chloride formation and protection of the hydroxy moiety can be accomplished in a single silylation step whereas the latter procedure as applied to hydroxy acids would require separate protection and sodium salt formation steps. Furthermore, it is likely that for many situations, the preparation of an easily purified (distillation or recrystallization) silyl ester would be more convenient then the preparation of a carboxylic sodium salt which in some cases might be hydroscopic, difficult to dry, or have low solubility in reaction media.

Scheme I



Experimental Section

General Procedure for the Preparation of *tert*-Butyldimethylsilyl Esters: *tert*-Butyldimethylsilyl Heptanoate (1). To a solution of 13.0 g (100 mmol) of heptanoic acid and 15.82 g (105 mmol) of *tert*-butyldimethylchlorosilane in 20 mL of dry DMF was added 13.96 g (205 mmol) of imidazole. The solution was stirred overnight, poured into H_2O, and extracted with petroleum ether. The organic solution was washed with a saturated solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed and the residue was distilled (95–100 °C (1.5 mm)) giving 21.0 g (86%) of **1**: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 2.30 (t, 2 H, CH_2CO), 1.30 (m, 8 H, $-(CH_2)_4-$), 0.97 (s, 12 H, $SiC(CH_3)_3$, terminal CH_3), 0.27 (s, 6 H, $Si(CH_3)_2$); IR (neat) 1730 cm^{-1}.

Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.87; H, 11.54. Found: C, 64.10; H, 11.46.

***tert*-Butyldimethylsilyl 2-Methyl-1,3-dioxolan-2-propionate (3).** This was prepared from 7.0 g (44 mmol) of **5**,[4] 7.2 g (48 mmol) of *tert*-butyldimethylchlorosilane, and 5.95 g (87 mmol) of imidazole in 19 mL of DMF (60 °C, 4 h) which gave after molecular distillation (bath temperature 125 °C (0.3 mm)) 10.2 g (85%) of **3** as a colorless liquid: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 3.86 (s, 4 H, OCH_2CH_2O), 2.13 (m, 4 H, $(CH_2)_2CO$), 1.26 (s, 3 H, CH_3), 0.86 (s, 9 H, $SiC(CH_3)_3$), 0.19 (s, 6

H, $Si(CH_3)_2$); IR (neat) 1724 cm^{-1}; MS calcd for $C_{12}H_{23}O_4Si$ (m-H_2O), 259.1365 (found, 259.1355).

Anal. Calcd for $C_{13}H_{26}O_4Si$: C, 56.89; H, 9.55. Found: C, 56.73; H, 10.06.

***tert*-Butyldimethylsilyl *tert*-Butyldimethylsilyloxyacetate (6).** This was prepared from 10.0 g (130 mmol) of glycolic acid, 40.6 g (270 mmol) of *tert*-butyldimethylchlorosilane, and 36.3 g (530 mmol) of imidazole in 80 mL of DMF (25 °C, 18 h) to give after removal of solvent and drying under vacuum 39.2 g (98%) of **6** as a white solid: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 4.14 (s, 2 H, OCH_2), 0.87 (s, 18 H, $C(CH_3)_3$), 0.22 (s, 6 H, Si $(CH_3)_2$), 0.04 (s, 6 H, Si $(CH_3)_2$); IR (KBr) 1748 cm^{-1}.

Anal. Calcd for $C_{14}H_{32}O_3Si_2$: C, 55.21; H, 10.59.

***tert*-Butyldimethylsilyl *m*-(*tert*-Butyldimethylsilyloxybenzoate) (7).** This was prepared from 10.0 g (72 mmol) of m-hydroxybenzoic acid, 22.9 g (152 mmol) of *tert*-butyldimethylchlorosilane, and 19.7 g (290 mmol) of imidazole (50–60°, 5 hr) to give after molecular distillation (bath temperature 170 °C (1.0 mm)) 25.5 g (98%)) of **7**: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 7.44, 7.22, 7.00 (m's, 4 H, aromatic), 0.96 (s, 9 H, $C(CH_3)_3$), 0.93 (s, 9 H, $C(CH_3)_3$), 0.32 (s, 6 H, $Si(CH_3)_2$), 0.16 (s, 6 H, $Si(CH_3)_2$); IR (neat) 1703 cm^{-1}.

Anal. Calcd for $C_{19}H_{34}O_3Si_2$: C, 62.24; H, 9.35. Found: C, 62.11; H, 9.28.

General Procedure for the Reaction of *tert*-Butyldimethylsilyl Esters with Oxalyl Chloride–DMF: Ethyl Heptanoate (2). To a solution of 10.0 g (41 mmol) of **1** in 40 mL of CH_2Cl_2 containing 4 drops of DMF was added dropwise 4.5 mL (51 mmol) of oxalyl chloride at 0 °C. After stirring 1.5 h at 0 °C and 0.5 h at room temperature, the solvent was removed. To the residue was slowly added a mixture of 10 mL of ether, 10 mL of pyridine, and 10 mL of ethanol. After stirring 1 h, the mixture was diluted with ether and filtered. The solvents were removed and the residue was distilled twice to give 5.98 g (92%) of **2**: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 4.12 (q, 2 H, OCH_2CH_3), 2.28 (t, 2 H, CH_2CO), 2.70–2.10 (m, 8 H, $-(CH_2)_4-$), 1.22 (t, 3 H, OCH_2CH_3), 0.87 (m, 3 H, terminal CH_3).

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.46. Found: C, 68.00; H, 11.82.

Heptanoyl Chloride. The above reaction was repeated without the addition of ethanol–pyridine. The CH_2Cl_2 was removed and the residue was distilled under aspirator pressure giving a low-boiling fraction (40–43 °C) consisting of *tert*-butyldimethylchlorosilane and a higher boiling fraction (70–73 °C) consisting of 5.2 g (86%) of heptanoyl chloride. Both compounds were identified by comparison of their ^1H NMR spectrum with that of authentic samples.

Ethyl 2-Methyl-1,3-dioxolan-2-propionate (4). This was prepared from 5.1 g (19 mmol) of **3** and 2.72 g (21 mmol) of oxalyl chloride in 19 mL of CH_2Cl_2 containing 3 drops of DMF. After a 1.25-h reaction time, ethanol–pyridine quenching, and molecular distillation (bath temperature 90–110 °C (0.5 mm)), 3.3 g (95%) of **4** was obtained: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 4.10 (q, 2 H, CH_2CH_3), 3.90 (s, 4 H, OCH_2CH_2O), 2.17 (m, 4 H, $(CH_2)_2CO$), 1.28 (s, 3 H, CH_3), 1.22 (t, 3 H, CH_2CH_3); IR (neat) 1740 cm^{-1}.

Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.68; H, 8.49.

Ethyl *tert*-Butyldimethylsilyloxyacetate (8). This was obtained from 15.0 g (49 mmol) of **6** and 7.2 g (57 mmol) of oxalyl chloride in 60 mL of CH_2Cl_2 containing 10 drops of DMF. After a reaction time of 3 h, ethanol–pyridine quenching, and molecular distillation (bath temperature 110–120 °C (25 mm)), 9.24 g (87%) of **8** was obtained: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 4.17 (s, 2 H, OCH_2), 4.16 (q, 2 H, CH_2CH_3), 1.20 (t, 3 H, CH_2CH_3), 0.84 (s, 9 H, $SiC(CH_3)_3$), 0.03 (s, 6 H, $Si(CH_3)_2$); IR (neat) 1760 cm^{-1}.

Anal. Calcd for $C_{10}H_{22}O_3Si$: C, 55.00; H, 10.15. Found: C, 54.63; H, 10.42.

Ethyl *m*-(*tert*-Butyldimethylsilyloxy)benzoate (9). This was prepared from 6.0 g (16 mmol) of **8** and 2.0 mL (23 mmol) of oxalyl chloride in 13 mL of CH_2Cl_2 containing 6 drops of DMF. After a 40 h reaction time, quenching with ethanol–pyridine, and molecular distillation (bath temperature 115 °C (0.4 mm)), 4.51 g (98%) of **9** was obtained: ^1H NMR δ_{Me_4Si} ($CDCl_3$) 7.40, 7.16, 6.88 (m's, 4 H, aromatic), 4.26 (q, 2 H, CH_2CH_3), 1.28 (t, 3 H, CH_2CH_3), 0.90 (s, 9 H, $C(CH_3)_3$), 0.12 (s, 6 H, $Si(CH_3)_2$); IR (neat) 1724 cm^{-1}; MS calcd for $C_{15}H_{24}O_3Si$, 280.1494 (found, 280.1485).

Anal. Calcd for $C_{15}H_{24}O_3Si$: C, 64.24; H, 8.63. Found: C, 63.83; H, 8.54.

Reaction of 2-Methyl-1,3-dioxolan-2-propionic Acid (5) with Oxalyl Chloride–DMF. To a solution of 1.0 g (6.3 mmol) of **5**[4] in 4 mL of CH_2Cl_2 containing 2 drops of DMF was added 0.61 mL (7.0 mmol) of oxalyl chloride. The solution was stirred at room temperature for 1 h. The solvent was removed and a mixture of 1.3 mL of ethanol and 2.6 mL of pyridine was added. After stirring 15 min, the solution was poured into a saturated solution of $NaHCO_3$ and extracted with ether. The ether solution was dried over Na_2SO_4. The solvent was removed. The residue was distilled (bath temperature 90–110 °C (0.5 mm)) to give 0.28 g of distillate and 0.28 g of pot residue.

TLC ($CHCl_3$–ether, 19:1) of the distillate indicated that it consisted of **4** and three additional more polar components; the pot residue consists only of the more polar side products.

Acknowledgments. We wish to thank Mr. L. Brancone and staff for microanalyses and Messrs. W. Fulmor and G. Morton and Dr. R. T. Hargreaves and staff for spectral data.

Registry No.—5, 4388-57-2; heptanoic acid, 111-14-8; *tert*-butyldimethylchlorosilane, 18162-48-6; glycolic acid, 79-14-1; m-hydroxybenzoic acid, 99-06-9; oxalyl chloride, 79-37-8; dimethylformamide, 68-12-2; heptanoyl chloride, 2528-61-2.

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Synthesis of 2-Methyl-1-cyclopentene-1-carboxylate Esters. Reaction of Cuprates with β-Substituted Cyclopentenecarboxylates

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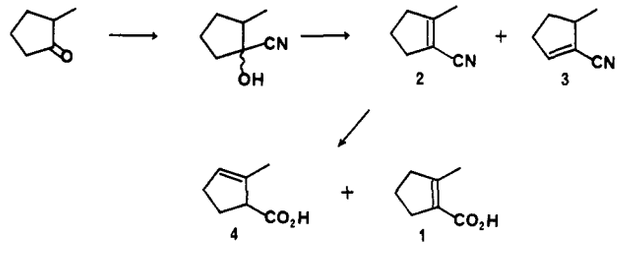
In connection with other synthetic work we had need for an efficient synthesis of 2-methyl-1-cyclopentene-1-carboxylic acid (**1**). The classical procedure[1] for preparation of this material (Scheme I) involves addition of cyanide to 2-methylcyclopentanone, dehydration of the resulting cyanohydrin, and hydrolysis to the acid. Recent studies[2] have shown that this procedure gives a mixture of acids, since dehydration of the cyanohydrin gives both unsaturated nitriles **2** and **3.** We found[3] that even after separation of pure nitrile **2,** hydrolysis gave a mixture of acid **1** and the nonconjugated isomer **4,**[4] from which acid **1** could be isolated by crystallization.[5]

The inefficiency of the above procedure, which requires a somewhat expensive starting material, led us to investigate new methods for synthesis of acid **1.** Subsequent to the development of the methodology described below, another method for synthesis of the ethyl-2-methyl-1-cyclopentene-1-carboxylate (**6**) was described[6] (Scheme II) based upon methodology reported by Büchi. By this method, ester **6** can be prepared from keto ester **5** in 46% yield. Keto ester **5** was prepared from 2-methycyclohexanone in two steps in unreported yield.[8] The reports by Casey[9] that acyclic β-acyloxy

Scheme I



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