mixture was stirred at room temperature for 6 days to give the 3-methyl-2-pentanone in 61% yield. A similar reaction in which molecular sieves (3Å; to absorb any water present) and lithium bromide were added produced the ketone in 73% yield.

Registry No. 1, 80532-57-6; 2, 80532-58-7; 3, 80532-59-8; acetophenone, 98-86-2; (*E,Z*)-2,3-dimethyl-3-phenyl-2-oxiranecarboxylic acid, 80532-60-1; methyl (*E*)-2,3-dimethyl-3-phenyl-2-oxiranecarboxylate, 14366-95-1; methyl (*Z*)-2,3-dimethyl-3-phenyl-2-oxiranecarboxylate, 14664-76-7; methyl 3-hydroxy-2-chloro-2-methyl-3-phenylbutanoate, 80532-61-2; benzophenone, 119-61-9; 2-methyl-3,3-diphenyl-2-oxiranecarboxylic acid, 24834-34-2; methyl 2-methyl-3,3-diphenyl-2-oxiranecarboxylate, 15309-40-7; 2-butanone, 78-93-3; (*E,Z*)-methyl 3-ethyl-2,3-dimethyl-2-oxiranecarboxylate, 80532-62-3; methyl 2-chloro-3-hydroxy-2,3-dimethylpentanoate, 80532-63-4; 2,4-dimethyl-3-pentanone, 565-80-0; 2-methyl-3,3-diisopropyl-2-oxiranecarboxylic acid, 80532-64-5; methyl 2-methyl-3,3-diisopropyl-2-oxiranecarboxylate, 80532-65-6; benzaldehyde, 100-52-7; 2-methyl-3-phenyl-2-oxiranecarboxylic acid, 25547-51-7; (*E,Z*)-methyl 2-methyl-3-phenyl-2-oxiranecarboxylate, 80532-66-7; methyl 2-chloro-3-hydroxy-2-methyl-3-phenylpropanoate, 80532-67-8; propanal, 123-38-6; (*E,Z*)-2-methyl-3-ethyl-2-oxiranecarboxylic acid, 80532-68-9; 2-chloropropanoic acid, 598-78-7; 2-chloro-2-methyl-3-hydroxypentanoic acid, 80532-69-0; (*E,Z*)-methyl 2-methyl-3-ethyl-2-oxiranecarboxylate, 80532-70-3; cyclohexanone, 108-94-1; methyl 2-methyl-1-oxaspiro[2,5]octane-2-carboxylate, 73039-91-5; methyl 2-chloro-2-(1-hydroxycyclohexyl)propanoate, 80532-71-4; cyclopentanone, 120-92-3; methyl 2-methyl-1-oxaspiro[2,4]heptane-2-carboxylate, 73039-89-1; methyl 2-chloro-2-(1-hydroxycyclopentyl)propanoate, 80532-72-5; (*Z*)-2-isopropyl-3-methyl-3-phenyl-2-oxiranecarboxylic acid, 80532-73-6; (*E*)-2-isopropyl-3-methyl-3-phenyl-2-oxiranecarboxylic acid, 80532-74-7; (*E,Z*)-methyl 2-isopropyl-3-methyl-3-phenyl-2-oxiranecarboxylate, 80532-75-8; (*E*)-methyl 2-isopropyl-3-methyl-3-phenyl-2-oxiranecarboxylate, 80532-76-9; 2-isopropyl-3,3-diphenyl-2-oxiranecarboxylic acid, 80532-77-0; methyl 2-isopropyl-3,3-diphenyl-2-oxiranecarboxylate, 80532-78-1; methyl 2-bromo-3-hydroxy-2-isopropyl-3,3-diphenylpropanoate, 80532-79-2; (*E,Z*)-methyl 2-isopropyl-3-phenyl-2-oxiranecarboxylate, 80532-80-5; (*E,Z*)-methyl 2-isopropyl-3-ethyl-3-methyl-2-oxiranecarboxylate, 80532-81-6; (*E,Z*)-methyl 3-methyl-3-phenyl-2-oxiranecarboxylate, 5441-04-3; methyl 3-hydroxy-2-chloro-3-phenylbutanoate, 80532-82-7; (*E,Z*)-methyl 3-ethyl-3-methyl-2-oxiranecarboxylate, 65492-41-3; methyl 2-chloro-3-hydroxy-3-methylpentanoate, 80532-83-8; methyl 3,3-diphenyl-2-oxiranecarboxylate, 76527-25-8; methyl 2-chloro-3-hydroxy-3,3-diphenylpropanoate, 80532-84-9; (*E,Z*)-methyl 3-ethyl-2-oxiranecarboxylate, 80581-35-7; methyl 2-chloro-3-hydroxypentanoate, 80532-85-0; di-*tert*-butyl ketone, 815-24-7; methyl 2-isopropyl-3-ethyl-2-oxiranecarboxylate, 80532-86-1; 3-phenyl-2-butanone, 769-59-5; 2-methyl-4,4-diphenyl-3-butanone, 7495-04-7; 1,1-diphenyl-2-propanone, 781-35-1; 2-methyl-4-phenyl-3-pentanone, 20474-49-1; 3-methyl-2-pentanone, 565-61-7; 2-phenylpropanal, 93-53-8.

Synthesis of Simple Derivatives of (2*Z*,4*Z*)-3-Methyl-2,4-hexadienedioic Acid

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Methanolysis of 4-methyl-2,7-oxepindione yields a mixture of both monomethyl esters of (2*Z*,4*Z*)-3-methyl-2,4-hexadienedioic acid. 4-Methyl-1,2-benzoquinone is oxidized by lead(IV) acetate in methanol–benzene to give dimethyl (2*Z*,4*Z*)-3-methyl-2,4-hexadienedioate. The 6-monomethyl ester, but not the 1-monomethyl ester or dimethyl ester, spontaneously stereomutates to the 2*Z*,4*E* isomer. The monoesters also cyclize to lactone esters. The disodium salt of (2*Z*,4*Z*)-3-methyl-2,4-hexadienedioic acid, prepared by saponification of the corresponding dimethyl ester or cyclic anhydride, is stable in the presence of excess base but immediately gives (2*Z*,4*E*)-3-methyl-2,4-hexadienedioic acid upon acidification. The results fit the general mechanism of stereomutation of 3-substituted (2*Z*,4*Z*)-2,4-hexadienedioic acids and derivatives.

The 3-methyl-2,4-hexadienedioic (β-methylmuconic) acids, a classical object of stereochemical investigation, were the subject of much past argument because hydrolysis of the cyclic anhydride 1 (Chart I), obtained by Baeyer–Villiger oxidation of 4-methyl-1,2-benzoquinone, unexpectedly yielded the 2*Z*,4*E* isomer **2a** rather than the 2*Z*,4*Z* isomer **3a**.[2-8] Similarly, enzymatic oxidation of 4-methylcatechol at pH 7–8 furnished what appeared to be the dianion of **3a** in solution,[9,10] but the product isolated after acidification was **2a**.[9,11]

The phenomenon that a 3-monosubstituted (2*Z*,4*Z*)-2,4-hexadienedioic acid is stable in base, but very rapidly stereomutates to the 4*E* isomer in acid, was first recognized in the 3-carboxy series.[12] That the isomerization requires a free 1-carboxy group was discovered by Ainsworth and Kirby, who accounted for their observations by a mechanism involving nucleophilic attack of the 1-carboxy group at the 4-position and rotation about the C4–C5 bond before reversion to a 2,4-hexadienedioate.[13] It should follow from this mechanism that not only the dianion but also the 1-esters of **3a** will be capable of retaining the 4*Z* configu-

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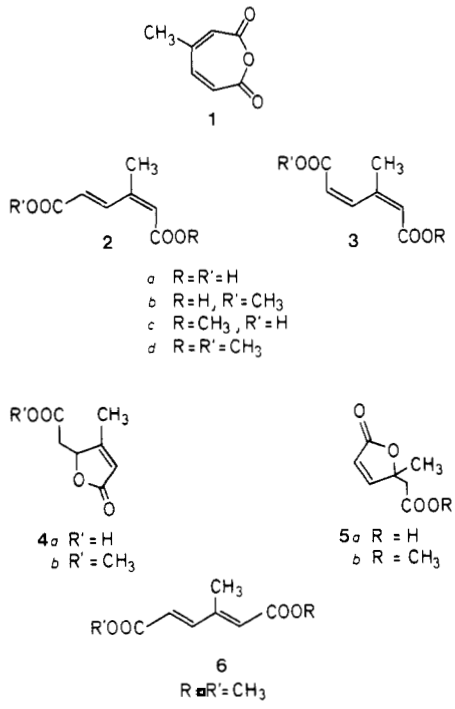
Table I. ^{1}H NMR Spectral Data (270 MHz) of 3-Methyl-2,4-hexadienedioic Acids and Derivatives

	chemical shift, δ					coupling constant,[b] Hz			
compd[a]	H2	H4	H5	CH_3	$COOCH_3$	$^3J_{H4,H5}$	$^4J_{H2,H4}$	$^5J_{H2,H5}$	$^4J_{H2,CH_3}$
1	6.36	6.61	6.45	2.15		12.1	1.8	0.7	1.4
2a	5.93	8.61	6.13	2.02		16.0	0.8	0.6	1.3
2d	5.95	8.64	6.18	2.05	3.75, 3.80	16.0	0.9	0.7	1.3
3a[c]	5.79	6.69	5.96	1.95		13.0	1.2	1.2	1.4
3b	5.80	7.11	5.87	2.10	3.70	12.2			
3c	5.77	7.18	5.90	2.10	3.66	12.2			
3d	5.83	7.17	5.92	2.10	3.67, 3.71	12.2	2.1	0.8	1.4
6	6.05	7.29	6.22	2.29	3.75, 3.79	15.8	0.7	0.5	1.3

[a] In $CDCl_3$, unless otherwise stated. [b] Absolute values of the long-range coupling constants were obtained by appropriate decoupling experiments. When necessary, the observed splittings were corrected for imperfect resolution. $^4J_{H4,CH_3}$ and $^5J_{H5,CH_3}$ were ca. 0 Hz in all cases except for **3d**, where $^4J_{H4,CH_3}$ was 0.8 Hz. For **3b** and **3c** the long-range couplings were not measured. [c] Disodium salt, in D_2O/NaOD, prepared in situ from **1** or **3d**.

Chart I



ration. Indeed, although methanolysis of **1** was earlier reported[5] to give monoesters **2b** and **2c**, we find that of the two initially formed monoesters **3b** and **3c** only the former undergoes stereomutation. We have also obtained and characterized the dimethyl ester **3d**[14] and, in solution, the dianion of the elusive acid **3a**, neither of which stereomutates spontaneously.

Solvolysis of **1** in neat methanol, evaporation of the solvent, and examination of the product by ^{1}H NMR spectroscopy (270 MHz) showed that no species with a 4*E* configuration (i.e., with ^3J ca. 16 Hz) was initially present in the mixture, which consisted of two 2*Z*,4*Z* monoesters (^3J = 12.2 Hz; Table I) in a ratio of 2:3. When the mixture was allowed to stand in methanolic solution for a few hours, gradual 4*Z* → 4*E* isomerization of the major but not of the minor monoester was observed, concurrently with formation of lactones **4b** and **5b**. Methylation of the initially formed 2*Z*,4*Z* monoesters with diazomethane afforded **3d**, while a brief heating to about 200 °C brought about their quantitative lactonization. Of the two lactones that resulted, **4b** predominated, and hence the major methanolysis product was **3b**. The formation of **3b** and **3c**, isomerization of the former, and gradual appearance of **4b** and **5b** was also observed when the methanolysis of **1** was carried out with methanol-d_4 and followed directly by ^{1}H NMR spectroscopy. On the other hand, hydrolysis of **1** in a 1:1 mixture of deuterium oxide and dimethyl sulfoxide-d_6[15] gave **2a** as the first observable product, the isomerization of **3a** being apparently faster than ring opening of **1**. Formation of **2a** or **2b** in the deuterated solvents occurred without deuterium incorporation, in accord with the proposed mechanism[13] for the stereomutation.

The diester **3d** could be conveniently obtained by oxidation of 4-methyl-1,2-benzoquinone with lead(IV) acetate in the presence of methanol, a method already used[16,17] for ring cleavage of some more stable 1,2-benzoquinones. Direct treatment[17] of 4-methylcatechol with lead(IV) acetate gave a poor yield of **3d**. Irradiation of the diester in acetonitrile containing catalytic amounts of iodine caused its rapid isomerization, giving after prolonged irradiation a photostationary equilibrium mixture of **2d** and **6** in a 1:2 ratio. Hydrolysis of **1** or **3d** with aqueous sodium hydroxide furnished solutions of the disodium salt of **3a**, which were stable for days in the presence of excess base but immediately gave **2a** upon acidification with dilute hydrochloric acid. Similarly, titration to neutrality with acetic acid-d_4 or phosphoric acid-d_3 of solutions of the salt of **3a** in a 1:1 mixture of deuterium oxide and dimethyl sulfoxide-d_6[15] furnished solutions of **2a**, which gradually lactonized, giving **4a** at an apparently much higher rate than when the solution was acidified with hydrochloric acid (followed by ^{1}H NMR spectroscopy). Since lactonization of **2a** and other 2,4-hexadienedioates possessing a free carboxy group requires protonation on carbon, the reaction may well be subject to general-acid catalysis.

The striking instability of the diacid **3a** toward stereomutation, as compared for example with the 2*Z*,4*Z* 2-methyl-1,4-hexadienedioic[18] and 2,4-hexadienedioic[19] acids, clearly reflects repulsive interactions between the 3-methyl and 6-carboxy groups. As a result of these interactions the

(14) The diester **3d** was earlier reported to be a product of ozonolysis of 1,2-dimethoxy-4-methylbenzene, but no characterization was given: Kratzl, K.; Claus, P.; Reichel, G. *Tappi* **1976**, *59*, 86.

(15) Dimethyl sulfoxide was used to avoid precipitation of **2a**.
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molecule adopts a nonplanar conformation with a geometry possibly close to that required in the transition state for nucleophilic attack of the 1-carboxy group at C4, i.e., the first step of the stereomutation. The steric hindrance to conjugation in **3d** is evident from its ultraviolet spectrum.[20] Furthermore, the magnitudes of the long-range interproton coupling constants in **3d** (Table I) differ markedly from those known in the unsubstituted diester, also indicating the presence of a nonplanar diene system in the former.[13,21-23] In order to estimate the conformational difference between the diene system of **3d** and dimethyl (2*Z*,4*Z*)-2,4-hexadienedioate, we optimized the molecular structures of the diesters using force-field calculations.[24] The lowest energy structure of the unsubstituted diester is fairly close to planar (C2–C3–C4–C5 torsion angle less than 10°), in agreement with available experimental data,[21,25] whereas that of **3d** shows the 6-methoxycarbonyl group rotated out of the plane of the C4–C5 double bond and a twist around the C3–C4 bond of about 40°.[26] A similar value of the C2–C3–C4–C5 torsion angle can also be derived[23] from the magnitude of the $^4J_{H2,H4}$ coupling constant (Table I). The optimized structures correspond to very flat energy minima, and considerable conformational flexibility is to be expected in solution.

The stereomutation of (2*Z*,4*Z*)-3-methyl-2,4-hexadienedioates is clearly predicated on an unesterified 1-carboxy group and an un-ionized or esterified 6-carboxy group, thus pointing up the general significance of the Ainsworth–Kirby stereomutation mechanism.[13,27] Several other examples of such sterically enforced[28] stereomutations of 3-substituted derivatives of (2*Z*,4*Z*)-2,4-hexadienedioic acid have passed unrecognized in the literature.[29] All these reactions are intramolecular analogues of the familiar stereoisomerization of α,β-unsaturated acids[30] catalyzed by external nucleophiles.

Recently it has been reported[31] that the dianion of **3a**, prepared enzymatically from 4-methylcatechol at pH 8, cyclized rapidly and exclusively to **5a** on acidification to pH 6.5, as concluded from analysis by liquid chromatography in 0.01 M phosphoric acid, apparently without comparison between the product and **4a**. Although **5a**, which cannot arise from **2a**, is in the form of one enantiomer the product of enzymatic lactonization of **3a**,[32] it has only once been reported to be produced on nonenzymatic cleavage of 4-methylcatechol or related compounds,[33] and then in much smaller amounts than the accompanying **4a**. Although the putative conversion of **3a** to **5a** might be thought analogous to cyclization of (2*E*,4*Z*)-3-chloro-2,4-hexadienedioic acid to (*E*)- and (*Z*)-5-oxo-2,5-dihydro-2-furanylideneacetic acids at pH 2.5–6,[31] the latter process, like stereomutation,[13] does not require protonation at carbon. In our experiments **5a** was not generated in amounts detectable by ^{1}H NMR spectroscopy when solutions of the dianion of **3a** were acidified. The conditions under which lactonization of **3a** to **5a** might be achieved in preference to stereomutation to **2a** as well as formation of **4a** thus require further study.

Experimental Section

Dimethyl (2*Z*,4*Z*)-3-Methyl-2,4-hexadienedioate (3d). To a solution of 4.2 g (34.4 mmol) of 4-methyl-1,2-benzoquinone[34] in 300 mL of a 1:1 benzene–methanol mixture (prechilled to 0 °C) was added 17 g (38.3 mmol) of lead(IV) acetate, and the solution was left in ice for 1 h in the dark. The solution was evaporated, the residue washed repeatedly with ether, the extract evaporated, and the product purified by column chromatography on silica gel with ether–pentane (2:3) as the eluant. This yielded 3.6 g (57%) of a mobile, colorless liquid. Slow addition at 0 °C of 2.5 g (20.1 mmol) of 4-methylcatechol to 20 g (45.1 mmol) of lead(IV) acetate in 150 mL of benzene–methanol (1:1) similarly yielded 0.3 g (8%) of the product: IR (film) 1725 (s), 1655 (w), 1605 (m) cm^{-1}; UV (CH_3OH) 245 nm (inflection; ε 7400); ^{13}C NMR ($CDCl_3$) δ 23.5, 51.1, 51.4, 117.8, 119.6, 145.2, 153.2, 165.9, 166.1; mass spectrum (70 eV), *m/e* (relative intensity) 184 (1.8), 169 (1.2), 152 (9), 137 (4), 125 (100) (m* for the $C_2O_2H_3$ loss observed).[35]

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.80; H, 6.74.

Irradiation of **3d** (Pyrex-filtered radiation from a mercury source) in acetonitrile (ca. 3%) containing 0.1% of iodine for 3–4 h gave **2d** and **6** in a 1:2 ratio (^{1}H NMR). The mixture was resolved by preparative TLC (silica gel, dichloromethane, developed four times) to give pure **2d** as an oil (lit.[4] mp 38 °C) and **6** as crystals, mp 54–56 °C (from methanol–water; lit.[4] mp 56 °C).

(20) (a) The 2*Z*,4*Z* isomers of 2,4-hexadienedioic[19,20b] and 2-methyl-2,4-hexadienedioic[18] acids and esters have intense absorption maxima (ε >20 000) around 260 and 270 nm, respectively, in contrast to **3d** (see Experimental Section). The dianion of **3a** (λ_{max} 257 nm), because of repulsion between the charges, may be more nearly planar than **3d** (Table I). (b) Sistrom, W. R.; Stanier, R. Y. *J. Biol. Chem.* **1954**, *210*, 821.

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(27) (a) Cf. also the stereochemical behavior of (2*E*,4*Z*)-3-chloro-2,4-hexadienedioic acid.[9,10,27b] (b) Evans, W. C.; Smith, B. S. W.; Moss, P.; Fernley, H. N. *Biochem. J.* **1971**, *122*, 509. Schmidt, E.; Knackmuss, H.-J. *Biochem. J.* **1980**, *192*, 339. (c) Diesters of 3-substituted (2*Z*,4*Z*)-2,4-hexadienedioic acids with even quite bulky 3-substituents do not stereomutate spontaneously, e.g.: Woodward, R. B.; Cava, M. P.; Ollis, W. D.; Hunger, A.; Daeniker, H. U.; Schenker, K. *Tetrahedron* **1963**, *19*, 247. Landesberg, J. M.; Kellner, D. *J. Org. Chem.* **1968**, *33*, 3374. Pines, S. H. *Ibid.* **1973**, *38*, 3854. Ettlinger, M. G.; Jaroszewski, J. W. *Tetrahedron Lett.* **1980**, *21*, 3503. See also ref 16.

(28) (2*E*,4*Z*)-3-Fluoro-2,4-hexadienedioic acid appears not to stereomutate rapidly, presumably because of the small size of fluorine: Schreiber, A.; Hellwig, M.; Dorn, E.; Reineke, W.; Knackmuss, H.-J. *Appl. Environ. Microbiol.* **1980**, *39*, 58. Although the authors believed the dimethyl (2*E*)-3-fluoro-2,4-hexadienedioate obtained from the diacid, a bacterial metabolite of 4-fluorobenzoate, to possess the 4*E* configuration because $^3J_{H4,H5}$ was 13 Hz, the coupling constant as well as the chemical shift of H4 (δ 7.28) strongly indicates the 4*Z* configuration (cf. Table I). We remark also that a metabolite of 4-fluorobenzoate (mp ca. 220 °C), tentatively called 3-fluoropropenoic acid, would appear to have been (2*Z*,4*Z*)-2-fluoro-5-hydroxy-2,4-hexadienedioic acid, resulting from an extradiol cleavage of 4-fluorocatechol: Harper, D. B.; Blakley, E. R. *Can. J. Microbiol.* **1971**, *17*, 1015.

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(35) Cf.: Mandelbaum, A.; Weinstein, S.; Gil-Av, E.; Leftin, J. H. *Org. Mass Spectrom.* **1975**, *10*, 842.

Addition of methanolic solutions of 1[2] or **3d** to 0.5–2 M aqueous sodium hydroxide gave solutions of the dianion of **3a**: UV λ_{max} 257 nm [lit.[9,10] λ_{max} 258 or 255 nm (ϵ 13 300 or 14 300)]; ^{13}C NMR (D_2O/NaOD) δ 21.9, 127.7, 128.9, 129.9, 142.6, 176.7, 178.3. After acidification of such solutions with hydrochloric acid at 0 °C, concentration and filtration gave **2a** in practically quantitative yield: mp 177–179 °C (lit.[4] mp 178 °C); IR spectrum as reported.[33]

Methanolysis of 4-Methyl-2,7-oxepindione (1). The cyclic anhydride[2] was dissolved in 100–200 parts by weight of methanol at room temperature. At various stages of the reaction (e.g. after 0.5, 1, 2, 5 h) a sample was evaporated and the residue examined by ^1H NMR spectroscopy ($CDCl_3$). After 1–2 h the product consisted largely of **3b** and **3c** together with an initially negligible but increasing amount of **2b** [δ 3.77 (methyl ester), 6.18 (H5), 8.53 (H4); ^3J_E = 16 Hz;[36] the remaining signals were overlapped by signals of major components], **4b**, and **5b**. Heating the mixture consisting of **3b** and **3c** in an oil bath (ca. 200 °C) for a few minutes and separation by column chromatography on silica gel with ether as the eluant gave the oily lactones **4b** and **5b**, which showed IR and ^1H NMR spectroscopic properties in close agreement with the literature.[33] Methylation of the mixture of **3b** and **3c** with ethereal diazomethane yielded **3d**.

(36) Cf.: Pattenden, G.; Weedon, B. C. L. *J. Chem. Soc. C* **1968**, 1984.

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Registry No. 1, 80533-00-2; **2a**, 31659-59-3; **2b**, 3555-79-1; **2d**, 80533-03-5; **3a**·2Na, 80533-04-6; **3b**, 80533-05-7; **3c**, 80533-06-8; **3d**, 61413-56-7; **4b**, 31656-70-9; **5b**, 31656-71-0; **6**, 80533-07-9; 4-methyl-1,2-benzoquinone, 3131-54-2; 4-methylcatechol, 452-86-8.

Acylative Cleavage of Ethers Catalyzed by Triorganotin Halides and Palladium(II) Complexes

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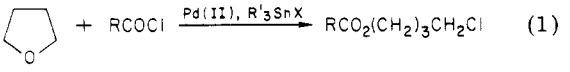
Benzylic, allylic, and cyclic ethers react with acyl halides under mild conditions in the presence of triorganotin halide and palladium(II) catalysts to give the corresponding esters in good yields. In the case of benzyl ether the other product is the benzyl halide, while in the reaction of allylic ethers the other products are various olefins resulting from the cleavage of the allyl group and an organotin moiety. The reaction is selective to these ethers, while acyclic aliphatic and phenolic ethers are unreactive. By control of the reaction conditions, benzylic and cyclic ethers could be cleaved in the presence of allylic ethers. The utility of the reaction as a deprotective method is demonstrated by the cleavage of a benzylic ether containing olefinic unsaturation. The mechanism of the benzylic and allylic ethers cleavage was studied by carrying out the corresponding stoichiometric reactions with the various palladium(II) complexes proposed in the catalytic cycle.

Introduction

Ethers are commonly used as blocking groups for the protection of hydroxylic functions; aliphatic, benzylic, and allylic ethers are used, among others, for this purpose.[2] The utility of ethers as protective groups depends on the susceptibility of the ether to facile removal by a specific reagent (that will not react with other functional groups present in the molecule). Some new reagents for selective ether cleavage have been reported recently[3a-f] (e.g., boron trifluoride etherate/mercaptoethanol,[3a] selenium dioxide/acetic acid,[3b] 1,2-bis[(trimethylsilyl)thio]ethane/zinc iodide/tetra-*n*-butylammonium iodide,[3c] and trimethylsilyl iodide[3d]). We here report a novel palladium-catalyzed cleavage of cyclic, allylic, and benzylic ethers is useful as a deprotection reaction for ethers but has no effect on other types of ethers (e.g., aliphatic, phenolic). A variety of other functional groups (including olefins, ketones, benzyl halides, and esters) that are sensitive to reductive or acidic cleavage procedures can be present in the reaction mixture.

Results and Discussion

Five-membered ring ethers can be cleaved and acylated in the presence of acyl halide, a catalytic amount of palladium(II) complex, and trialkyltin halide (eq 1) under mild conditions (Table I, entries 6, 8, 9), while almost no cleavage was detected with aliphatic and phenolic ethers (Table I, entries 1–4). The presence of a catalytic amount



(1)

of trialkyltin halide enhances the acylation although a slow reaction is detected even in the absence of the tin compound (Table I, entry 10). This selectivity is in contrast to that reported[4] for the acylation of aliphatic ethers catalyzed by acidic metal carbonyls of group 6 transition metals; in this case aliphatic ethers are readily cleaved. The interaction of the palladium catalyst with cyclic ethers is of interest since tetrahydrofuran is often used as a solvent in stoichiometric and catalytic reactions of palladium on the assumption that it is unreactive.

Strained cyclic ethers, including tetrahydrofuran, are known to be cleaved[5a-c] and to undergo cationic polym-

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