17094-21-2; **4a**, 64165-15-7; **4b**, 771-12-0; **4c**, 135147-54-5; **6a**, 132723-19-4; **6b**, 132723-22-9; **6c**, 57558-70-0; **6d**, 132723-21-8; **6e**, 691-45-2; **6f**, 135147-55-6; **6g**, 36277-50-6; **6h**, 135147-56-7; **6i**, 36832-93-6; **9a**, 609-02-9; **9b**, 6065-52-7; **9c**, 609-08-5; diethyl oxalate, 95-92-1; dimethyl oxalate, 553-90-2; pinacolone, 75-97-8; cyclohexanone, 108-94-1; tetrahydronaphthalen-1-one, 529-34-0; ethyl propionate, 105-37-3; methyl propionate, 554-12-1.

Supplementary Material Available: Experimental procedures for preparation of **1a–c**, **3d**, **3j**, and **3k**; ^{1}H NMR (60-MHz) spectra of **1d–f**, **3g**, **3h**, **3j**, **3k**, **4c**, and **9a**; ^{1}H NMR (300-MHz) and ^{13}C spectral data for **1a–c** and **3a–d**; mass spectral data for keto and enol forms of **3g**; FTIR spectral data (neat) for authentic samples of **1a**, **1b**, **1d**, **1e**, **3d**, **3g**, **3h**, **3j**, **3k**, **9a**, and **9b** (7 pages). Ordering information is given on any current masthead page.

Novel Template Effects of Distannoxane Catalysts in Highly Efficient Transesterification and Esterification

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The transesterification of carboxylic esters and the esterification of carboxylic acids are effected under mild conditions under catalysis by 1,3-disubstituted tetraalkyldistannoxanes **1**. Various functional groups remain unaffected and otherwise difficult to obtain esters are accessible. An ester bearing a tertiary butyl group in the carboxylic acid moiety remained unchanged in competition experiments with a less bulky ester, which undergoes transesterification quantitatively. The unique features of the reactions are attributable to the template effects of the dimeric structure of **1**. The facility with which compounds **1** can be converted into alkoxydistannoxanes **2** and the synergistic effect of the proximate tin atoms of **2** play key roles in permitting smooth reactions and high selectivity. Another notable feature of compounds **1** is their unusually high solubility in organic solvents, even though the compounds have a metaloxane core as a major skeletal part. The double-layered structure of **1**, in which the inorganic moiety is surrounded by eight alkyl groups, permits esterification to be driven to completion simply by heating a mixture of the carboxylic acid and the alcohol. The distannoxane-catalyzed esterification is irreversible, and thus, no hydrolysis of the product esters occurs when compounds **1** are used as catalysts.

Introduction

The partial hydrolysis of diorganotin dihalides under alkaline conditions gives 1,3-disubstituted tetraorganodistannoxanes **1**.[1] In striking contrast, hydrolysis of the analogous diorganodihalosilanes gives polydiorganosiloxanes, even in the presence of only a catalytic amount of base. What differentiates the two hydrolyses is that the hydrolysis of the organotin compounds leads to the formation of a stable rigid ladder structure.[2] This unusual structure, which exists both in the solid state[3] and in solution,[4] gives rise to various properties. Two kinds of pentacoordinate tin atoms exist in compounds **1**. Sn(1) is bonded to two alkyl groups, two oxygen atoms, and one Y group, whereas Sn(2) is bonded to two alkyl groups, one oxygen atom, and one X and one Y group. Because the two types of tin atom are in close proximity, it is possible that a chemical transformation occurring in the vicinity of one tin atom can be influenced by the presence of the other tin atom or that substrates that are bonded to, or coordinated with, the tin atoms can interact with each other. Such synergistic effects exerted by proximate metal centers are extremely interesting and are one of the features of metal cluster chemistry. Another unique property of compounds **1** is their high solubility in organic solvents. Although they possess a metaloxane core as a major component of their molecular skeleton, distannoxanes are soluble in most organic solvents, including aliphatic hydrocarbons. The exceptions are the tetramethyldistannoxanes, which are soluble in such solvents only under reflux. This unusual solubility arises from the double-layered structure of compounds **1**, in which surface

1a: R = Bu, X = Y = -NCS; **1b**: R = Bu, X = -NCS, Y = OH, **1c**: R = Bu, X = Y = Cl

1d: R = Bu, X = Cl, Y = OH; **1e**: R = Me, X = Y = -NCS

Table I. Effects of the Structure and Concentration of the Distannoxane Catalyst 1 on Transesterification[a]

$$n\text{-}C_3H_7COOMe + PhCH_2OH \xrightarrow{1} n\text{-}C_3H_7COOCH_2Ph + MeOH$$

1 (concn)[b]	reactn time (h)	yield of n-$C_3H_7COOCH_2Ph$[c] (%)
1a (0.005)	3	100
1b (0.005)	4	100
1c (0.005)	3	100
1e (0.005)	10	100
1b (0.0005)	20	77
1c (0.0005)	20	100
1d (0.0005)	20	100
1e (0.0005)	20	83

[a] Reaction conditions: n-C_3H_7COOMe:$PhCH_2OH$ = 1:2, toluene reflux. [b] Molar ratio catalyst to n-C_3H_7COOMe. [c] Determined by GLC analysis.

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[1] Okawara, R.; Wada, M. *Adv. Organomet. Chem.* **1967**, *5*, 137.

[2] Okawara, R. *Proc. Chem. Soc.* **1961**, 383. Alleston, D. L.; Davies, A. G.; Figgis, B. N. *Ibid.* **1961**, 457. More practically, these compounds can be prepared from diorganotin oxides and dihalides. See the Experimental Section.

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[4] (a) Okawara, R.; Wada, M. *J. Organomet. Chem.* **1963**, *1*, 81. (b) Alleston, D. L.; Davies, A. G.; Hancock, M. *J. Chem. Soc.* **1964**, 5744. (c) Considine, W. J.; Baum, G. A. *J. Organomet. Chem.* **1965**, *3*, 308. (d) Wada, M.; Okawara, R. *Ibid.* **1967**, *8*, 261. (e) Davies, A. G.; Smith, L.; Smith, P. J. *Ibid.* **1971**, *29*, 245. (f) Mitchell, T. N. *Org. Magn. Reson.* **1976**, *8*, 34. (g) Yano, T.; Nakashima, K.; Otera, J.; Okawara, R. *Organometallics* **1985**, *4*, 1501.

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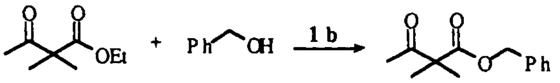
alkyl groups surround the metaloxane core and thereby shield it from exposure to the ambient organic solvent phase. Solutions of 1 in organic solvents therefore consist of highly polar stannoxane "islands" dispersed in less polar "ocean"-like reverse micelles.[5]

We expected that the unusual structural features of compounds 1 would be reflected in unusual catalytic activity. In fact, we suggested earlier[6] that the high catalytic activity displayed by compounds 1 in the reaction of alcohols and isocyanates to yield urethanes could be explained by the following sequence: (1) facile formation of an alkoxydistannoxane upon mixing 1 and an alcohol, (2) coordination of the carbonyl group of the isocyanate with the alkoxydistannoxane, and (3) nucleophilic attack of the alkoxy group on the carbonyl group. We have found that such carbonyl activation also apparently plays a part in transesterification and esterification and is responsible for unprecedented reactions of considerable synthetic utility.[7]

Results and Discussion

Transesterification. Distannoxane-catalyzed transesterification is readily achieved by heating a mixture of an ester and an alcohol in the presence of a catalytic amount of 1 in a hydrocarbon or halocarbon solvent.[8] First, the effect of the substituents of 1 on the reaction of methyl butyrate and benzyl alcohol was investigated (Table I). At a catalyst concentration of 0.5 mol %, the natures of the alkyl groups and the substituents X and Y had little influence on the catalytic activity. Accordingly, the butyl derivatives were used in most of the experiments described in this study because of their excellent solubility. The high catalytic activity of 1 was made evident by the fact that the reaction could be driven to completion in the presence of 0.05 mol % of the catalyst. However, a longer reaction time was required.

The synthetic importance of distannoxane-catalyzed transesterification was alluded to in an earlier paper.[7] Yields are uniformly high. Various labile functional groups present in the reactants are unaffected because the reaction conditions are essentially neutral. Ethyl acetoacetate can be converted into useful esters. Although the difficulty in transesterifying β-keto esters has recently been overcome by the use of (*N*,*N*-dimethylamino)pyridine as a catalyst,[9] that method cannot be applied to nonenolizable esters. However, distannoxanes are effective transesterification catalysts for use with such compounds (eq 1). The optical purity of chiral alcohols does not decrease during transesterification. For example, (1*R*,2*S*,5*R*)-(−)-menthol and [(1*S*)-*endo*]-(−)-borneol were recovered without loss of optical purity by the alkaline hydrolysis of the transesterification products menthyl and bornyl acetoacetate, respectively.



(1)

Scheme I

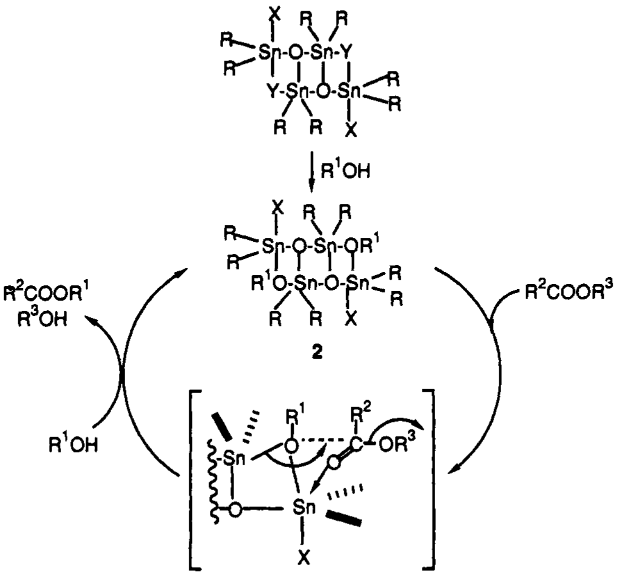


Table II. Effect of the Bulkiness of the Ester and Alcohol on Transesterification[a]

$$\mathrm{RCOOR' + R''OH \xrightarrow{1b} RCOOR'' + R'OH}$$

entry	RCOOR′	R″OH	yield of RCOOR″[b] (%)
1	n-C_3H_7COOMe	$PhCH_2OH$	95
2	$(CH_3)_2CHCOOMe$	$PhCH_2OH$	77
3	c-$C_6H_{11}COOMe$	$PhCH_2OH$	82
4	$(CH_3)_3CCH_2COOMe$	$PhCH_2OH$	12
5	$(CH_3)_3COOMe$	$PhCH_2OH$	10
6	$CH_3COOCH_2C(CH_3)_3$	$PhCH_2OH$	31
7	$CH_3COOC(CH_3)_3$	$PhCH_2OH$	17
8	n-C_3H_7COOMe	n-C_4H_9OH	99
9	n-C_3H_7COOMe	$(CH_3)_3CCH_2OH$	89

[a] Reaction conditions: RCOOR′:R″OH:1b = 1:2:0.1, benzene, reflux. [b] Determined by GLC analysis.

The most probable mechanism for the transesterification is depicted in Scheme I. The initial step is formation of the alkoxydistannoxane 2.[6] Then, the carbonyl oxygen atom of the ester coordinates with Sn(2). The ability of the tin atom to accommodate an additional donor atom would be enhanced to some extent by loss of halide or isothiocyanate ion coincident with coordination.[6] Such coordination would aid the substrate's approach to the reaction field and would also activate the carbonyl group toward nucleophilic attack by the alkoxy group. The mechanism does not involve enolization of the ester. Thus, it explains why β-keto esters, which are unable to form enolates, can be transesterified.

If the proposed mechanism is valid, the approach of an ester to the reaction field should be hampered by steric hindrance. This proved indeed to be the case, as Table II shows. Esters and alcohols of varying bulk were subjected to the reaction (10 mol % 1b, refluxing benzene). Esters bearing a tertiary butyl group in either the acid or alcohol moiety reacted sluggishly (entries 4–7), in contrast to the smooth reaction of other esters (entries 1–3). However, the approach of the alcohol reactant apparently suffers no steric hindrance because 2,2-dimethylpropanol (entry 8) reacts as smoothly as other, less bulky, alcohols (entries 1 and 9). These results emphasize the importance

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(6) Otera, J.; Yano, T.; Okawara, R. *Chem. Lett.* **1985**, 901. Otera, J.; Yano, T.; Okawara, R. *Organometallics* **1986**, *5*, 1167.

(7) For a preliminary report, see: Otera, J.; Yano, T.; Kawabata, A.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 2383.

(8) For examples of transesterifications mediated by other organotin compounds, see: Pereyre, M.; Colin, G.; Delvigne, J.-P. *Bull. Soc. Chim. Fr.* **1969**, 262. Poller, R. C.; Retout, S. P. *J. Organomet. Chem.* **1979**, *173*, C7. Pilati, F.; Munari, A.; Manaresi, P. *Polymer Commun.* **1984**, *25*, 187. Titanium alkoxides have also proved to be effective catalysts. See: Seebach, D.; Hungerbuehler, E.; Naef, R.; Schnurrenberger, P.; Weidmann, B.; Zueger, M. *Synthesis* **1982**, 138. Rehwinkel, H.; Steglich, W. *Ibid.* **1982**, 826.

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Table III. Distannoxane-Catalyzed Esterification[a]

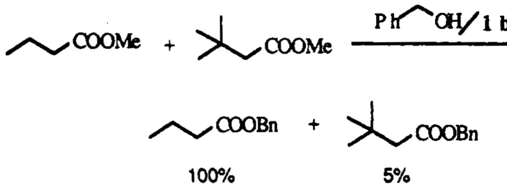
$$RCOOH + R'OH \xrightarrow{1} RCOOR'$$

entry	RCOOH	R'OH	1	solvent[b]	yield of RCOOR'[c] (%)
1	n-C_3H_7COOH	n-C_4H_9OH	**1a**	N	95
2	n-C_3H_7COOH	n-C_4H_9OH	**1b**	N	100
3	n-C_3H_7COOH	n-C_4H_9OH	**1b**	H	90
4	n-C_3H_7COOH	n-C_4H_9OH	**1b**	B	92
5	n-C_3H_7COOH	n-C_4H_9OH	**1b**	T	91
6	n-C_3H_7COOH	n-C_4H_9OH	**1b**	D	43
7	n-C_3H_7COOH	n-C_4H_9OH	**1c**	N	95
8	n-C_3H_7COOH	n-C_4H_9OH	**1d**	N	88
9	n-C_3H_7COOH	n-C_4H_9OH	**1e**	N	91
10	n-C_3H_7COOH	C_2H_5OH	**1b**	N	92
11	n-C_3H_7COOH	$(CH_3)_2CHCH_2OH$	**1b**	N	100
12	n-C_3H_7COOH	$(CH_3)_3CCH_2OH$[d]	**1b**	N	95
13	n-C_3H_7COOH	$C_2H_5CH(CH_3)OH$	**1b**	N	20
14	n-C_3H_7COOH	$(CH_3)_3COH$	**1b**	N	0
15	$(CH_3)_2CHCOOH$	n-C_4H_9OH	**1b**	N	97
16	c-$C_6H_{11}COOH$	n-C_4H_9OH	**1b**	N	88
17	$(CH_3)_3COOH$	n-C_4H_9OH	**1b**	N	33
18	PhCOOH	n-C_4H_9OH	**1b**	N	38
10	$(CH_3)_3CCH_2COOH$	n-C_4H_9OH	**1b**	N	20

[a] RCOOH:R'OH:1 = 1:30:0.1. [b] N: no solvent, 80 °C. H: hexane, reflux. B: benzene, reflux. T: THF, reflux. D: DMF, 100 °C. [c] Determined by GLC analysis. [d] RCOOH:R'OH:1 = 1:10:0.1.

of the carbonyl-group coordination step proposed above and, furthermore, suggest that the alcohol approaches the tin atom Sn(1) from the less crowded side of the stannoxane "ladder" (Figure 1a), whereas the ester approaches Sn(2) from the more crowded bottom of the "ladder" (Figure 1b). Approach from those directions is necessary for subsequent effective interaction between the ester and the alkoxy group.

The template effect described above enabled the differentiation of esters in terms of bulkiness in a competition experiment (eq 2). In the reaction of methyl butyrate and



(2)

methyl *tert*-butylacetate (each 1 mmol) with benzyl alcohol (2 mmol) catalyzed by **1b** (0.03 mmol) in refluxing benzene, the former was converted to benzyl butyrate in 100% yield, whereas the latter was converted to benzyl *tert*-butyl acetate in only 5% yield after 20 h.

Esterification of Carboxylic Acids. Exposure of a carboxylic acid to a large excess of an alcohol in the presence of a catalytic amount of **1** provided the corresponding ester in excellent yield (Table III).[10] Excess alcohol can conveniently serve as the solvent, although the reaction proceeds just as well in other solvents (entries 3–5). The reaction in DMF (entry 6) is an exception. Employment of a 20–30-fold excess of the alcohol is generally required because the use of lesser amounts of this reactant led to an unsatisfactory yield of the ester. The reaction proceeded equally well with various catalysts (entries 1, 2, and 7–9). Good yields of esters were obtained from α-alkyl and α,α-dialkyl carboxylic acids (entries 2, 15, and 16). However, pivalic acid and benzoic acid afforded esters in only low yield (entries 17 and 18). In contrast to primary alcohols, secondary and tertiary alcohols reacted sluggishly (entries 13 and 14). As was also observed in transesterification, the presence of a tertiary butyl group in the carboxylic acid diminished the reactivity of the acid (entry 19), whereas the bulkiness of the alcohol hardly influenced the rate of reaction (entry 12). Accordingly, a mechanism analogous to that proposed for transesterification is apparently operating. However, it is likely that **1** initially reacts with the more acidic carboxylic acid rather than with the alcohol (Scheme II). The alkoxydistannoxane **2** would be produced by ligand exchange with carboxydistannoxane **3**. However, the equilibrium is biased thermodynamically in favor of **3**. It is not probable, however, that the product ester is formed via the reaction of **3** with the alcohol because the reactivity of the carboxy group of **3** toward nucleophilic attack by the alcohol would be decreased by the presence of the tin atom and also because the ability of the alcohol to coordinate with Sn(2) is less than that of a carbonyl group.[11] On the other hand, the nucleophilicity of the alkoxy group of **2** would be sufficiently enhanced by bonding to the electropositive tin to enable it to attack the carbonyl group. Thus, the reaction of the distannoxane with a carboxylic acid would shift the equilibrium in favor of **2**. The most interesting aspect of the distannoxane-catalyzed esterification, which is quite different from "ordinary" esterification, is that the reverse reaction (hydrolysis) cannot

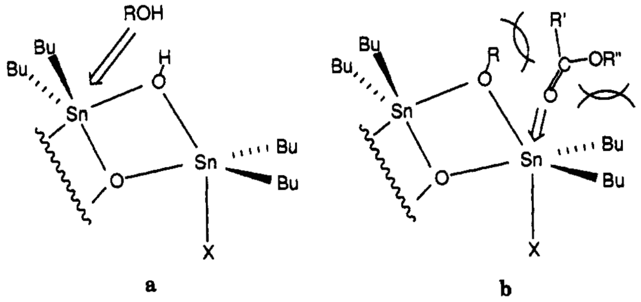


Figure 1. (a) Approach of the alcohol reactant to the distannoxane template. (b) Approach of the ester reactant to the distannoxane template.

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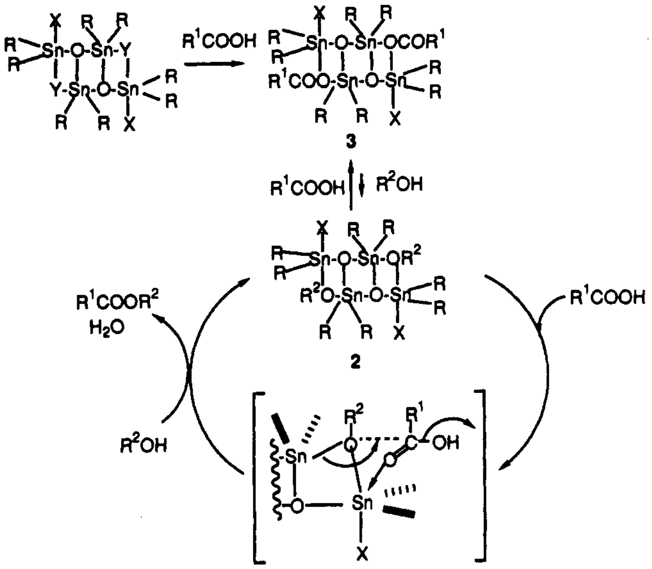
[10] Diorganotin dihalide mediated esterification has been reported. See: Kumar, A. K.; Chattopadhyay, T. K. *Tetrahedron Lett.* 1987, 28, 3713.

[11] Organotin halide–carbonyl compound complexes are well-documented, whereas little is known about the analogous organotin halide–alcohol complexes. For example, see: Petrosyan, V. S.; Yashina, N. S.; Bakhmutov, V. I.; Permin, A. B.; Reutov, O. A. *J. Organomet. Chem.* 1974, 72, 71.

Scheme II



occur. Therefore, simply heating the two reactants completes the reaction. Removal of the water that is formed is unnecessary. The irreversibility of the esterification was confirmed by the following experiment. A mixture of butyl butyrate, a 30-fold excess of water, 1 mol % of a distannoxane catalyst (**1a**, **1b**, or **1e**), and a solvent like benzene, THF, 1,4-dioxane, or diglyme was refluxed. After 20 h, butyl butyrate was recovered quantitatively in all cases. The absence of hydrolysis is a consequence of the double-layered structure of **1**, the surface alkyl groups of which prevent water from approaching the catalytically important core sites, i.e., the tin atoms.

It has already been reported that compounds **1** are also effective catalysts for the lactonization of ω-hydroxy carboxylic acids.[12] Distannoxane-catalyzed lactonization proceeds smoothly without recourse to azeotropic removal of water and provides macrolides in higher yields than does $\mathrm{Bu_2SnO}$-promoted lactonization, which requires the use of a Dean-Stark apparatus.[13] The superiority of compounds **1** as catalysts lies in the fact that, in their presence, lactonization is irreversible. For example, the attempted hydrolysis of hexadecanolide in the presence of **1** failed, and the starting lactone was recovered quantitatively.[12] On the other hand, under similar conditions, in the presence of $\mathrm{Bu_2SnO}$, cleavage of the lactone occurred to a considerable extent.[13]

In conclusion, the catalysis displayed by compounds **1** in the transesterifications and esterification described here arises from the unique structural features of **1**. Bridging by group Y activates the Sn–Y bond, which both facilitates formation of the alkoxydistannoxanes **2** and enhances the reactivity of the resulting alkoxy group. The presence of the electron-withdrawing group X allows the coordination of the tin atom with the carbonyl group, and the proximity of the two types of tin atom, Sn(1) and Sn(2), enables direct interaction between the alkoxy group and the coordinated carbonyl group.

Experimental Section

Column chromatography was performed with Kieselgel 60 (70–230 mesh, E. Merck). Melting points are uncorrected. All solvents were purified by standard methods before use. Authentic samples of the product esters (except benzyl 2,2-dimethylacetoacetate) were commercially available or were prepared by standard esterification or by Taber's method.[9] The organotin precursors of the catalysts were products of Nitto Kasei Co. Ltd. Distannoxanes, **1a**[14] and **1c**,[4a,15] were prepared by literature methods. Improved methods for the preparation of the other compounds are described below.

1-Hydroxy-3-(isothiocyanato)tetrabutyldistannoxane (1b). A mixture of $\mathrm{Bu_2SnO}$ (14.9 g, 60.0 mmol), $\mathrm{Bu_2Sn(NCS)_2}$ (6.97 g, 20.0 mmol), and 95% EtOH (200 mL) was refluxed. After 6 h, the transparent solution that resulted was concentrated to give a white powder. This was pulverized then was exposed to the ambient atmosphere overnight in order to convert the partially formed ethoxydistannoxane to the corresponding hydroxydistannoxane. Recrystallization (hexane, 0 °C) of the crude product afforded **1b** (15.1 g, 69%): mp dec 120–130 °C (lit.[14] mp 123–134 °C).

The chloro derivative **1d** was obtained in a similar manner from $\mathrm{Bu_2SnCl_2}$: mp 107–115 °C (lit.[4a] 109–121 °C).

1,3-Bis(isothiocyanato)tetramethyldistannoxane (1e): A mixture of $\mathrm{Me_2SnO}$ (16.5 g, 100 mmol) and $\mathrm{Me_2SnCl_2}$ (22.0 g, 100 mmol), and benzene (500 mL) was refluxed for 17 h, during which time most of the $\mathrm{Me_2SnO}$ dissolved. The hot mixture was filtered to remove a small amount of solid material. The filtrate was concentrated and the residue was recrystallized (benzene) to give 1,3-dichlorotetramethyldistannoxane (35.2 g, 92%):[16] mp >250 °C; NMR ($\mathrm{CDCl_3}$) δ 1.25 (s, 6 H), 1.32 (s, 6 H).

A mixture of 1,3-dichlorotetramethyldistannoxane (3.84 g, 10.0 mmol), NaSCN (1.70 g, 21.0 mmol), and EtOH (200 mL) was refluxed for 5 min, during which time a transparent solution formed. The EtOH was evaporated, and $\mathrm{CH_2Cl_2}$ was added to the residue. Solid NaCl was removed by filtration. The filtrate was concentrated. The residue was recrystallized ($\mathrm{CH_2Cl_2}$/hexane) to give **1e** as white crystals (3.80 g, 88%): mp 207–210 °C (lit.[3b] mp 205–207 °C); IR (Nujol mull) 2050, 2010 $\mathrm{cm^{-1}}$.

Distannoxane-Catalyzed Transesterification: Typical Procedure. A toluene solution (25 mL) of ethyl 2,2-dimethylacetoacetate (791 mg, 5.00 mmol), BnOH (5.40 g, 50.0 mmol), and **1b** (278 mg, 0.500 mmol) was refluxed for 24 h. The toluene and excess BnOH were evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc (95:5)) to give benzyl 2,2-dimethylacetoacetate (968 mg, 88%): ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.20 (s, 6 H), 1.80 (s, 3 H), 4.90 (s, 2 H), 7.03 (br s, 5 H); MS *m/z* 220 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{13}H_{16}O_3}$: C, 70.89; H, 7.32. Found: C, 70.96; H, 7.28.

The other transesterifications were performed in a similar manner. A hydrocarbon GLC internal standard was added to the reaction mixture before GLC analysis.

Recovery of Optically Active Alcohols. A mixture of (1*R*,2*S*,5*R*)-menthyl acetoacetate (970 mg, 4.00 mmol), MeOH (10 mL), and 1 N aqueous NaOH (1 mL) was stirred at room temperature overnight. The mixture was then extracted with $\mathrm{CH_2Cl_2}$. The extract was washed with 1 N aqueous HCl and water, dried ($\mathrm{Na_2SO_4}$), and concentrated. Column chromatography of the residue on silica gel (hexane/EtOAc (97:3)) afforded (1*R*,2*S*,5*R*)-(−)-menthol (192 mg, 82%): $[\alpha]_D$ −48.5 (EtOH, *c* 10). The specific rotation of the menthol employed in the transesterification was −48.9.

In a similar manner, from the hydrolysis of bornyl acetoacetate, (*S*)-(−)-borneol was recovered in 85% yield: $[\alpha]_D$ −35.5 (EtOH, *c* 5). The specific rotation of the borneol employed in the transesterification was −35.8.

Competitive Transesterification. A benzene solution (5 mL) of methyl butyrate (102 mg, 1.00 mmol), methyl *tert*-butylacetate (130 mg, 1.00 mmol), BnOH (216 mg, 2.00 mmol), **1b** (16.7 mg, 0.03 mmol), and undecane (GLC internal standard, 156 mg, 1.00 mmol) was refluxed for 20 h. GLC analysis of the reaction mixture showed that benzyl butyrate and benzyl *tert*-butylacetate were

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produced in yields of 100% and 5%, respectively.

Esterification of Carboxylic Acids. A mixture of carboxylic acid (1 mmol), alcohol (20–30 mmol), 1 (0.1 mmol), and an alkane (a GLC internal standard) was heated, with stirring, at 80 °C for 24 h. The yield of the ester was determined by GLC analysis. Similar results were obtained when an inert solvent (2 mL) was used. However, the use of a larger amount of inert solvent led to a decrease in the rate of reaction.

Attempted Hydrolysis of Butyl Butyrate. A mixture of butyl butyrate (360 mg, 2.50 mmol), water (0.5 mL), 1 (0.025 mmol), decane (GLC internal standard, 1.00 mmol), and solvent (benzene, THF, 1,4-dioxane, and diglyme; 5 mL) was refluxed for 20 h. GLC analysis showed that the butyl butyrate remained intact (99–100% yield).

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Spectroscopy and Photochemistry of 2-Quinolones and Their Lewis Acid Complexes[1]

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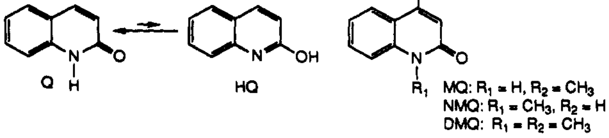
The spectroscopic properties, photodimerization, and cross-cycloaddition reactions of 2-quinolone and three of its methylated derivatives have been investigated in the absence and presence of the strong Lewis acid BF_3. Comparison of quinolone, which forms a hydrogen-bonded dimer, and its N-methylated derivatives establishes that hydrogen bonding has little effect on these properties. Methylation at C-4 also has little effect on spectroscopic properties, but does retard photodimerization and result in the formation of photoene products in competition with cycloadduct formation with alkenes. All of the quinolones form strong complexes with BF_3. Complex formation results in changes in the NMR, absorption, and fluorescence spectra of the quinolones and in their photochemical behavior. Complexation is proposed to occur on oxygen for all of the quinolones resulting in changes in electron populations that have been probed using GAUSSIAN 86 calculations. A decrease in the energy of the oxygen nonbonding orbitals upon complexation results in a change in the configuration of the lowest singlet state from n,π^* to π,π^* upon complexation. This change results in an increase in singlet lifetime and a change in cycloaddition mechanism from triplet (stepwise) to singlet (concerted) upon complexation.

Introduction

The spectroscopy and structure of 2-quinolone (Q) are of continuing interest because of the possible existence of its tautomer, 2-hydroxyquinoline (HQ), the observation of fluorescence from the neutral and its conjugate base and acid,[2-5] and the utility of some of its derivatives as laser dyes.[6] In nonaqueous solution and in the solid state[7] Q exists in the form of the hydrogen-bonded dimer. A very large free energy of association (−8.8 kcal/mol) accounts for its limited solubility in most solvents.[8] HQ has been identified as a minor tautomer in the vapor phase, but there is no evidence for its formation upon irradiation of Q in the vapor phase or in solution.[2,3] Protonation of Q occurs on the carbonyl oxygen, resulting in a significant increase in the fluorescence quantum yield and lifetime.[4] The ground state and lowest singlet are of roughly comparable basicity.[4,5]



Q HQ

MQ: $R_1 = H$, $R_2 = CH_3$
NMQ: $R_1 = CH_3$, $R_2 = H$
DMQ: $R_1 = R_2 = CH_3$

The photochemical behavior of Q and some of its derivatives has also been investigated. Photodimerization occurs via a triplet-state mechanism[9] to yield the anti head-to-head dimer.[10] Irradiation in the presence of both electron-rich and electron-deficient alkenes is reported to yield [2 + 2] cycloadducts, often in high preparative yield.[11-13] The absence of quenching of Q fluorescence by

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