3 exists totally as the hydrate even in the solid state. Thus, the elemental analysis of 3 corresponds to the hydrate solvated by $^1/_2H_2O$. The ^{13}C NMR spectrum in $CDCl_3$ shows a hydrate carbon at 84 ppm, while ^1H NMR spectra have a methine proton at 4.5 ppm in $CDCl_3$ and 5.7 ppm in D_2O but no aldehyde proton in either solvent.

Catalysis of *p*-nitrophenyl diphenyl phosphate hydrolysis by 3.0 mM 3 in a pH 9.0 M borate buffer at 25.0 °C leads to a $k_{obsd} = 8.2 \times 10^{-3}$ s^{-1} (750 times faster than hydrolysis in the same buffer without 3). Although this micellar rate is large relative to many published in the literature,[2] it does not match that associated with 1. Packing problems, manifest in the high critical concentration of 3, may also be affecting the catalytic efficiency. Thus, the struggle to achieve enzyme-like efficiencies within the confines of a turnover mechanism must continue. Compounds 2 and 3 are, however, unusual dicationic surfactants, and hence we are now reporting their synthesis and properties.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton magnetic resonance spectra were recorded on a Nicolet FT-360 high-resolution spectrometer at 360 MHz. The carbon-13 nuclear magnetic resonance spectra were obtained from a Bruker AP-200-SY NMR spectrometer at 50 MHz or a Varian CFT-20 NMR spectrometer at 20 MHz. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Ultraviolet absorption spectra were measured on a Hewlett-Packard 8451A diode Array spectrophotometer with a H-P 7470A plotter. Elemental analyses were performed by Atlantic Microlabs Inc., Atlanta, GA.

Chemicals. 1-Bromohexadecane, 1,4-diazabicyclo[2.2.2]octane, 1,4-dibromobutene, 1,3-dichloroacetone, and lithium bromide were purchased from Aldrich Chemical Co. *N,N*-Dimethyl-*N*-dodecylamine was purchased from Kodak.

1,3-Dibromo-2-propanone.[14] 1,3-Dichloro-2-propanone was washed with cold diethyl ether until no brown color remained and then was dried under reduced pressure, mp 39–41.5 °C. To a stirred solution of dichloro-2-propanone (3.20 g, 25.2 mmol) in 100 mL of acetone at 0 °C was added LiBr (22.0 g, 253 mmol). The solution was allowed to warm to room temperature where it was stirred 48 h. An additional 10.0 g of LiBr and 50 mL of acetone were added to the reaction mixture, and stirring was continued 24 h more. Removing the solvent gave an off-white solid, which was dissolved in water and extracted twice with dichloromethane. The combined dichloromethane solutions were washed with cold water, cooled to 0 °C, filtered, dried over anhydrous $MgSO_4$, and stripped of solvent to afford 4.5 g (83%) of a yellow oil: IR (neat) 2940, 1730, 1390, 1275–1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (s).

Compound 2. *N,N*-Dimethyl-*N*-dodecylamine (6.78 g, 31.8 mmol) was slowly added with magnetic stirring to a solution of 1,3-dibromo-2-propanone (3.43 g, 15.8 mmol) in 50 mL of anhydrous ether at room temperature under a N_2 atmosphere. The solution turned from clear to dull yellow and then to dark brown as the amine was added. After 2 h the viscosity of the mixture prevented stirring. A yellow liquid was decanted, leaving a solid, which was washed with diethyl ether to remove excess starting amine. The ether was evaporated to yield 9.8 g of crude product (97%). Several recrystallizations from hot acetone afforded pure product: 4.2 g (41%); mp 80 °C dec; IR (KBr) 2920, 2850, 1749, 1465, 1375, 890, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.67 (s, 4 H), 3.55 (m, 4 H), 3.45 (s, 12 H), 1.84 (br s, 4 H), 1.35 (4 H), 1.25 (32 H), 0.87 (t, J = 6.9 Hz, 6 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 193.90, 67.99, 67.27, 57.51, 51.65, 31.82, 29.50, 29.31, 28.98, 26.18, 22.61, 16.01, 14.00. Anal. Calcd for $C_{31}H_{66}Br_2N_2O$: C, 57.92; H, 10.35; N, 4.28. Found: C, 57.68; H, 10.36; N, 4.20.

1-Hexadecyl-1,4-diazabicyclo[2.2.2]octane, Bromide Salt. In a 50-mL, round-bottom flask, 1,4-diazabicyclo[2.2.2]octane (2.24 g, 20.0 mmol) was stirred with 15 mL of anhydrous ethyl ether and cooled to −78 °C. 1-Bromohexadecane (6.10 g, 6.10 mL, 20.0 mmol) was added dropwise to this solution while stirring. The reaction mixture was allowed to warm to room temperature and stirred an additional 8 h. The resulting white precipitate was filtered, rinsed with ethyl ether, and recrystallized with hot CCl_4–toluene with filtration. After two recrystallizations 3.7 g (44%) of pure product was recovered: mp 108–109 °C; IR (KBr) 2920, 2851, 1469, 1377, 1101, 1058, 851, 796, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (t, 2 H, J = 7.2 Hz), 3.49 (m, 2 H), 3.24 (t, 2 H, J = 7.2 Hz), 2.00 (br s, 2 H), 1.73 (2 H), 1.32 (2 H), 1.22 (22 H), 0.85 (t, 3 H, J = 6.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 64.3, 52.2, 45.1, 31.5, 29.3, 29.1, 29.0, 28.9, 26.1, 21.8, 14.0.

Compound 3. In a dry, 50-mL, round-bottom flask fitted with a reflux condenser and flushed with N_2, a solution of 1-hexadecyl-1,4-diazabicyclo[2.2.2]octane, bromide salt (3.00 g, 7.18 mmol), in 20 mL of CH_3CN (previously dried over CaH_2 and distilled from P_2O_5) was stirred and warmed slightly to ensure complete solubility. To this solution was added bromoacetaldehyde (3.00 g, 24.4 mmol in CH_2Cl_2) via syringe while stirring. A white precipitate immediately fell out of solution. The mixture was heated to reflux and stirred overnight. The off-white solid was filtered under reduced pressure and washed first with CH_3CN and then several times with anhydrous ethyl ether. The off-white powder quickly hydrated when exposed to the air leaving 3.90 g of a tan, gummy solid. The solid was dissolved in H_2O, heated, and filtered twice. A white, fluffy solid remained after freeze-drying the filtrate: 3.4 g (85%); mp 167–168 °C; IR (D_2O, ZnBr cells) 3541–2845, 1202 cm^{-1}; ^1H NMR (D_2O) δ 5.70 (t, 1 H), 4.32 (m, 6 H), 4.24 (m, 6 H), 3.76 (m, 2 H), 3.35 (s, 2 H), 1.93 (2 H), 1.42 (2 H), 1.30 (24 H), 0.88 (t, 3 H, J = 6.5 Hz); ^{13}C NMR (50 MHz, D_2O) δ 84.45, 65.40, 52.49, 51.31, 32.01, 30.00, 29.88, 29.73, 29.67, 26.10, 22.68, 22.16, 13.93. Anal. Calcd for $C_{24}H_{50}N_2O_2 \cdot {}^1/_2H_2O$: C, 50.78; H, 9.06; N, 4.96. Found: C, 50.64; H, 9.07; N, 5.00.

Kinetic Studies. All kinetic measurements were performed at 25 °C on a Hewlett-Packard 8451A diode array spectrophotometer. Stock solutions of esters were prepared in acetonitrile (0.005 M). Reactions were initiated by injecting 25 μL of the ester solution into 3 mL of micellar solution preequilibrated at 25 °C and were monitored at 400 nm for the absorbance of 4-nitrophenol. All buffers were prepared from doubly distilled water. Borate buffer was used for solutions of 2 at pH 10 and adjusted with 0.4 N NaOH. Solutions of 2 at pH 8 were prepared in phosphate buffer and adjusted with 0.1 N NaOH. Ethyl morpholine buffer was used for all solutions of 3 to avoid problems of precipitation encountered with borate solutions. Rate constants were obtained from computer-generated values of the log of the absorbance with time. Correlation coefficients were >0.999.

Acknowledgment. This work was supported by the Army Research Office.

Registry No. 2, 108868-22-0; 3, 108868-23-1; $CH_3(CH_2)_4C(O)O$-*p*-$C_6H_4NO_2$, 956-75-2; *p*-$NO_2C_6H_4PPh_2$, 10359-36-1; $ClCH_2C(O)CH_2Cl$, 534-07-6; $BrCH_2C(O)CH_2Br$, 816-39-7; $CH_3(CH_2)_{11}NMe_2$, 112-18-5; $CH_3(CH_2)_{15}Br$, 112-82-3; 1,4-diazabicyclo[2.2.2]octane, 280-57-9; 1-hexadecyl-1,4-diazabicyclo[2.2.2]octane bromide salt, 62634-16-6.

(14) Kim, K. S.; Szarek, W. A. *Can. J. Chem.* **1981**, *59*, 878.

Acid Chloride to Ester Formation: Mechanism of SO_2–Amine Interference

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Introduction

Acid chlorides have been reported to be effectively converted to their esters in a reaction which uses a base to both neutralize the liberated hydrogen chloride and also to catalyze the reaction (Schotten–Baumann procedure).[1]

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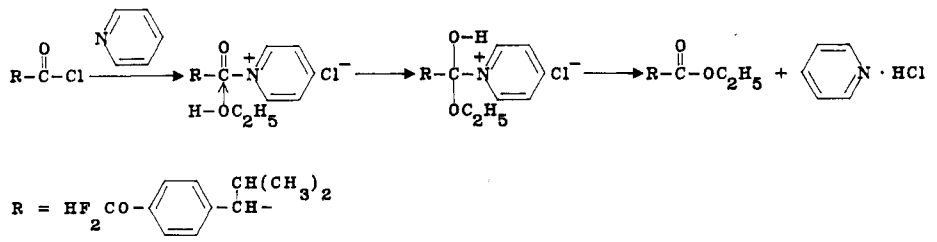
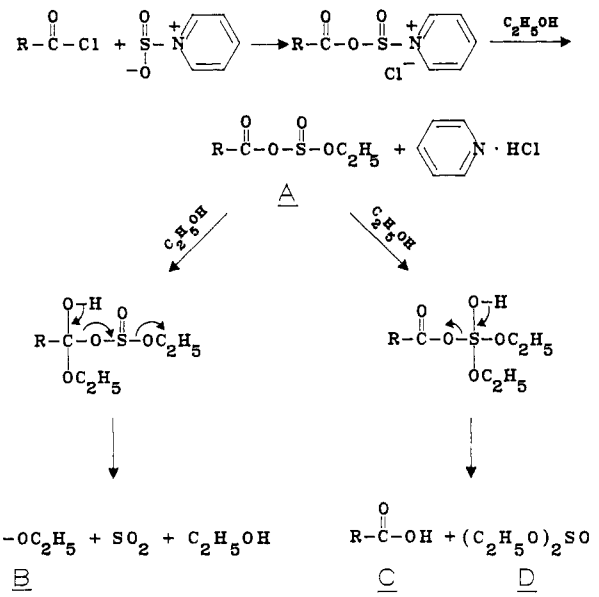
Scheme I



Scheme II



In our laboratory, this technique was used as part of a gas chromatographic–flame ionization detection (GC–FID) method to assay for an acid chloride in a toluene process stream by converting it to its ethyl ester derivative. Pyridine was used as the catalyst[2] and HCl scavenger (Scheme I).

An incomplete conversion of the acid chloride to ester was observed when sulfur dioxide (SO_2) was present in the sample as a gaseous byproduct of the thionyl chloride reaction that was used to produce the acid chloride.[3] Samples that were sparged of SO_2 produced a nearly quantitative amount of ester while samples entrained with SO_2 generated low acid chloride assay values. The decrease in ester formation was accompanied by the formation of the corresponding acid.

In this paper, a mechanism is proposed to show how SO_2 and pyridine react to inhibit the quantitative conversion of the acid chloride to its ethyl ester. The mechanism involves the formation of a nucleophilic complex between SO_2 and pyridine[4,5] which reacts with the acid chloride to produce an acylated sulfite intermediate (Scheme II). Attack of ethanol can take place at either the carbonyl or the sulfonyl group. The former addition produces the ester derivative of the acid chloride, while the latter gives rise to the carboxylic acid and dialkyl sulfite. To confirm the mechanism, a labeling experiment was carried out by using SO_2 enriched with oxygen-18. The reaction products were identified by using gas chromatography/mass spectrometry (GC/MS) and quantitated by using GC–FID.

Table I. The Effect of SO_2 on the Conversion of Acid Chloride to Its Ethyl Ester with and without the Use of Base in the Reaction

expt	SO_2	pyridine	other	% conversn rel to control smple
1	–	+	–	100.0
2	+	–	–	99.6
3	+	+	–	56.9
4	+	–	*a*	60.3
5	+	–	*b*	99.3

[a] Triethylamine. [b] Sodium carbonate, anhydrous.

Results and Discussion

To study the action of SO_2 on the quantitative conversion of the acid chloride to its ethyl ester in the presence of an amine base, five experiments were carried out. The results are shown in Table I.

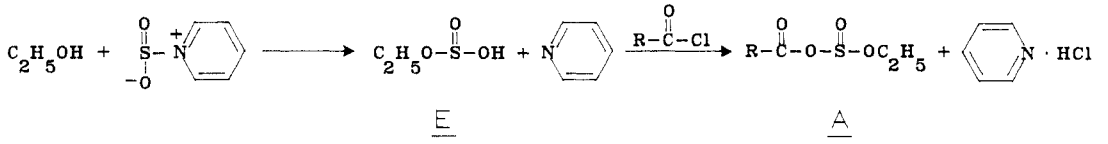
A control sample of the acid chloride was prepared which contained no SO_2. The sample assayed 23.9% acid chloride when pyridine was used in the esterification reaction (experiment 1). This conversion of the acid chloride to ester was nearly quantitative (>98%), based on the known quality of the starting acid.

In a second experiment, SO_2 was added to the control sample at a 25 wt % level relative to the acid chloride to simulate a typical process stream before sparging. When the esterification was carried out *without* pyridine, this sample assayed the same as experiment 1. However, the yield of ester was reduced by a factor of 2 when the same experiment was repeated *with* pyridine present (experiment 3). The lower acid chloride level also correlated with the formation of the corresponding carboxylic acid. Similar results were produced when a different amine base, triethylamine, was substituted for pyridine in the reaction (experiment 4). Hydrolysis of the acid chloride was eliminated as a cause for low ester yields, considering the quantitative esterifications observed in experiments 1 and 2. These data showed a trend in which both SO_2 and amine base had to be present to interfere in the complete conversion of the acid chloride to its ester derivative. This correlation was further supported when the SO_2-spiked sample was esterified in the presence of a weak inorganic base, anhydrous sodium carbonate, and a nearly quantitative conversion to ester was observed (experiment 5).

The commonly accepted role of pyridine as a catalyst in derivatizing acid chlorides to esters is based on its effectiveness as both a nucleophile and an excellent leaving group.[2] Pyridine reacts with the acid chloride to form an acyl pyridinium salt. The ester is produced by nucleophilic attack of the alcohol at the carbonyl and displacement of pyridine. The conversion was nearly quantitative (>98%) under these conditions in the case of our acid chloride.

(1) Buehler, C. A.; Pearson, D. E. *Survey of Organic Synthesis*; Wiley: New York, 1970; p 807.
(2) Human, J. P. E.; Mills, J. A. *Nature (London)* **1946**, *158*, 877.
(3) Morrison, R. T.; Boyd, N. R. *Organic Chemistry*, 3rd ed.; Allyn and Bacon: Boston, 1974; p 601.
(4) Moede, J. A.; Curran, C. *J. Am. Chem. Soc.* **1949**, *71*, 852.
(5) Bateman, L. C.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1944**, 243.
(6) Bartlett, P. D.; Herbrandson, H. F. *J. Am. Chem. Soc.* **1952**, *74*, 5971.

Scheme III



E A

Table II. GC–MS Data for Products Formed in Experiment 3: Conversion of Acid Chloride to Its Ethyl Ester in the Presence of Pyridine and SO_2

component ID	2-methylpropane CI ions,[a] m/z
Diethyl Sulfite	139 (100) [$(M+H)^+$]
Ethyl ester	273 (100) [$(M+H)^+$]
Acid	245 (100) [$(M+H)^+$]

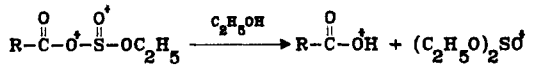
[a] Relative ion intensities are given in parentheses.

However, in the presence of sulfur dioxide (SO_2), the production of ester was reduced by approximately 40%. In addition to the low yield of ester, the formation of the corresponding carboxylic acid was observed. As discussed above, water was eliminated as the source of oxygen for acid formation. To explain the results observed, the mechanism depicted in Scheme II was proposed in which SO_2 is the source of oxygen. The reaction proceeds through a common intermediate, the acylated sulfite, A, which forms from the well-known pyridine–SO_2 complex.[4,5]

Alternatively, A can be produced by a route which proceeds through ethyl hydrogen sulfite, E, as shown in Scheme III.[7]

The acylated sulfite contains two available sites for attack by ethanol. Addition at the carboxyl carbon yields the desired ester derivative of the acid chloride B, while reaction at sulfur results in the formation of the carboxylic acid C and diethyl sulfite, D.

To investigate the proposed mechanism of Scheme II, a sample of the acid chloride was spiked with oxygen-18 enriched SO_2 and esterified with ethanol in the presence of pyridine. The mechanism would be supported by incorporation of the labeled SO_2 in the acylated sulfite. Attack of ethanol at the sulfur should yield the carboxylic acid with oxygen-18 incorporated in the hydroxyl group and diethyl sulfite isotopically enriched with one oxygen-18 atom at the sulfonyl bond.



A

An alternative source of diethyl sulfite could be a reaction between ethanol and unreacted thionyl chloride.[6] However, the diethyl sulfite produced in this way would not contain the oxygen-18 label.

The reaction products formed in experiment 3 and the isotope enriched SO_2 experiment were analyzed by GC–MS using 2-methylpropane chemical ionization (CI) as the mode of ionization. Table II summarizes the mass spectral data for experiment 3.

The GC–MS results for the labeled experiment confirmed that SO_2 was the source of oxygen in the carboxylic acid. Its mass spectrum showed oxygen-18 incorporation. This was evidenced by $(M + H)^+$ ions at m/z 245, 247, and 249 with intensity ratios of 38:54:7. Deviation from theory (30:70:0) was probably due to label scrambling in the ion source since enhancement of the unlabeled (245^+) and doubly labeled (249^+) ions was balanced by depletion of the singly labeled ion (247^+). The diethyl sulfite produced peaks at m/z 141 and 139 in a ratio of 80:20, within experimental error for one oxygen-18 label. The ethyl ester derivative, however, contained no label.

These results support the proposed mechanism (Scheme II) in which the formation of the pyridine–SO_2 complex is crucial. Also, this overall reaction must take place faster than the expected reaction of the acid chloride with ethanol.

Conclusions

The nearly quantitative conversion of an acid chloride to its ester derivative using the Schotten–Baumann technique was shown to be impeded when sulfur dioxide (SO_2) was present. The SO_2 can be entrained in the acid chloride as a byproduct of the formation of the acid chloride from its acid precursor by using the thionyl chloride reaction. A mechanism was proposed, tested, and supported to show the interaction between SO_2 and amine base and how they are involved in inhibiting the normal esterification reaction. Although a single acid chloride was used in these experiments, it seems reasonable that these results could have wider implications in the esterification of acid chlorides as a general class of compounds.

Experimental Section

Preparation of Acid Chloride. Technical acid chloride was prepared in toluene by reacting thionyl chloride with the corresponding acid. Entrained acidic gases were removed by purging the sample with nitrogen and trapping the gases with a basic scrubber. Unreacted thionyl chloride was removed by distillation.

The acid chloride control sample was prepared by rotary evaporating the acid chloride at 45 °C under a 1–2 mmHg vacuum for 15 min to remove entrained gases.

The SO_2-spiked samples were prepared by bubbling the gas (after passage through anhydrous $CaSO_4$) through a toluene solution of the acid chloride until a 5% increase in absolute weight was obtained.

Analytical Sample Preparation. Analytical solutions for the GC–FID and GC–MS analyses were prepared by charging 150 mg of the acid chloride toluene sample to a 100-mL volumetric flask. Anhydrous ethanol (5 mL) and 0.1 mL of dry pyridine (where applicable) were added to convert the acid chloride to its ethyl ester. A biphenyl solution in chloroform (10 mL, approximately 850 mg/100 mL) were pipetted into each sample solution as an internal standard for the GC–FID analysis. The solutions were diluted to volume with methylene chloride.

Gas Chromatography–Flame Ionization Detection (GC–FID). The assay for the acid chloride as its ethyl ester derivative was carried out on a Hewlett-Packard Model 5840 gas chromatograph equipped with a flame ionization detector. The components were resolved at 155 °C on a 10 ft by 2 mm i.d. glass column packed with 10% OV 17 on Gas ChromQ (100–120 mesh). The injection port and detector temperature were set at 200 and 300 °C, respectively. Helium was used as the carrier gas at a flow rate of 60 mL/min. Each sample solution (3 μL) was injected in duplicate.

Gas Chromatography–Mass Spectrometry (GC–MS). The GC–MS analyses were carried out on a Varian Aerograph Series 1400 gas chromatograph interfaced to a Finnigan 1015C quadrupole mass spectrometer operated in the chemical ionization (CI) mode. The components were resolved on a 6 ft by 2 mm i.d. glass column packed with 10% OV 17 on Gas ChromQ (80–100 mesh). The GC oven was held at 95 °C for 3 min and then programmed to 280 °C at a rate of 10 °C/min. The injection port temperature was set at 240 °C. 2-Methylpropane (Matheson) was used both

(7) Jung, M., private communication.

as the carrier and CI reagent gas. The GC flow rate was adjusted to provide a source pressure of 500 μm. The mass spectrometer was scanned from 75 to 375 amu at a rate of 6 s per scan.

Chemicals. GC materials were purchased from Supelco. Pure ethyl alcohol (dehydrated U.S.P.) from U.S. Industrial Chemicals Co. and "Baker Analyzed Reagent" grade pyridine were dried over Type 4A molecular sieves. Anhydrous sulfur dioxide was purchased from Matheson with a minimum purity of 99.98%. Sulfur dioxide, enriched with 70 atom % of oxygen-18, was special ordered from U.S. Services, Inc. Biphenyl internal standard was obtained from Eastman Kodak Co. Solvents were purchased from J. T. Baker Co.

Acknowledgment. We thank Dr. D. J. Thoennes for invaluable discussions and critical review of this manuscript. We also acknowledge Dr. P. C. Mowery for his contributions in the early stages of this work. Appreciation is owed to Dr. T. J. Francl for his proofreading of this paper and to Jessie Selzer for typing this manuscript.

Registry No. A, 108834-99-7; B, 88149-99-9; C, 70124-99-1; D, 623-81-4; E, 42761-68-2; F_2CHO-*p*-$C_6H_4CH(CH(CH_3)_2)C(O)Cl$, 70125-00-7; SO_2, 7446-09-5; EtOH, 64-17-5; thionyl chloride, 7719-09-7; pyridine, 110-86-1; *N*-sulfinopyridinium hydroxide inner salt, 42824-17-9.

Lewis Acid Promoter Reaction of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione with Ethyl Diazoacetate: A Synthetic Entry into the Pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]tridecane Ring System

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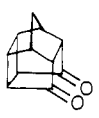
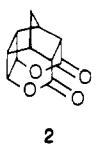
It has recently been reported[1] that pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**1**) undergoes Baeyer-Villiger oxidation to afford a single, symmetrical dilactone, **2**. As part of a program designed to explore the



1



2

synthesis and chemistry of novel, functionalized pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes,[2] we have examined the corresponding reaction of **1** with ethyl diazoacetate in the presence of boron trifluoride etherate as catalyst (Scheme I).

In our hands, the boron trifluoride etherate catalyzed reaction of **1** with ethyl diazoacetate (2 equiv) afforded a

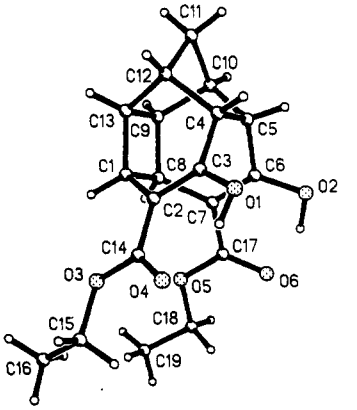
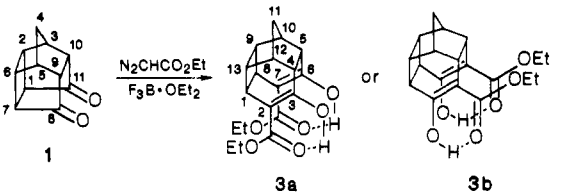


Figure 1. Diagram of **3a** as determined by X-ray diffraction. Only one of the two molecules in the asymmetric unit is shown.

Scheme I



1 **3a** **3b**

single 2:1 adduct (**3**, 45% yield). The ^{13}C NMR spectrum of **3** displayed only ten signals, a result which suggests that **3** possesses twofold symmetry. Of the three possible 2:1 adducts, only two (**3a** and **3b**, Scheme I) possess the required symmetry. The fact that the material which we isolated possesses structure **3a** rather than **3b** was confirmed unambiguously via single-crystal X-ray structural analysis. Interestingly, analysis of the infrared spectrum and of the ^1H and ^{13}C NMR spectra of **3a** suggests that this material exists virtually exclusively in its (hydrogen-bonded) enol form (see Experimental Section). The exclusive migration of the C(1)-C(11) and C(7)-C(8) bonds accompanying Baeyer-Villiger oxidation of **1** (that leads to the formation of a single dilactone, **2**)[1] is mirrored in the boron trifluoride catalyzed reaction of **1** with 2 equiv of ethyl diazoacetate.

Compound **3a**, diethyl 3,6-dioxopentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]tridecane-2,7-dicarboxylate ($C_{19}H_{22}O_6$, Figure 1) crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a = 11.028 (4) Å, b ; 20.429 (6) Å, c = 16.015 (5) Å, β = 105.28 (3)°, and Z = 8 (two molecules per asymmetric unit). The volume of the cell is 3480.5 (2) Å^3, the molecular formula weight is 346.38, and the calculated crystal density is 1.32 g cm^{-3}.

Bond lengths and angles for the two molecules in the asymmetric unit are in good mutual agreement, and both molecules display the same conformation. All bond lengths fall into normal ranges except for the C(1)-C(8) [1.575 (5), 1.572 (5) Å] and C(4)-C(5) [1.582 (5), 1.586 (5) Å] bonds, which are longer than normal, unstrained sp^3-sp^3 carbon-carbon σ-bonds. Bond angles in **3a** also fall into normal ranges with the exception of the C(10)-C(11)-C(12) angle (94.7 (3)°, 94.8 (3)°] which is much smaller than a normal tetrahedral C-C-C bond angle (109.4°). These deviations result from internal strain in the cage and from the effects of nonbonded interactions between groups in each ketoester moiety. The six-membered rings defined by C(1)-C(2)-C(3)-C(4)-C(12)-C(13) and by C(5)-C(6)-C(7)-C(8)-C(9)-C(10) bend away from one another wherever they are not constrained by cross-cage bonds [i.e., C(1)-C(8), C(4)-C(5), and C(9)-C(13)]. The nonbonded C(3)···C(6) contact is only 2.87 Å, which is much less than

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