hydrolysis of the corresponding catecholborane.[15]

(*E*)-3-(*tert*-Butyldimethylsiloxy)-1-octenylcatecholborane: ^{1}H NMR ($DCCl_3$) δ 0.09 (6 H, s, $SiMe_2$), 0.93 (9 H, s, *t*-Bu), 0.7-1.8 (11 H, m, C_5H_{11}), 4.26 (1 H, m, CHO), 6.91 (1 H, dd, J = 18 and 2 Hz, vinyl), 6.76-7.30 (5 H, m, vinyl and aryl); MS, *m/e* 360.23053 (calcd for $C_{20}H_{33}O_3BSi$, 360.22921).

(*E*)-6-(*tert*-Butyldimethylsiloxy)-1-heptenylcatecholborane: ^{1}H NMR ($DCCl_3$) δ 0.06 (6 H, s, $SiMe_2$), 0.8 (9 H, s, *t*-Bu), 1.05 (3 H, d, J = 6 Hz, CH_3), 1.3-1.6 (4 H, m, CH_2's), 2.0-2.3 (2 H, m, $=CCH_2-$), 3.66-4.0 (1 H, m, CHO), 5.7 (1 H, dt, J = 1.5 and 16 Hz, $-BCH=$), 6.7-7.25 (6 H, m, $-BC=CH-$ and aryl); MS, *m/e* 345.20657 (calcd for $M^+ - H$, $C_{19}H_{30}BO_3Si$, 345.20573).

Representative Procedure for the Stereospecific Synthesis of Vinylmercurials. *trans*-1-Decenylcatecholborane (3 mmol) was dissolved in 3 mL of THF and cooled to -78 °C. One equivalent of sodium acetate was added and the mixture was stirred for 10-15 min. Mercuric acetate (0.954 g, 3 mmol) was added and the reaction mixture warmed up to 0 °C. The solution was poured into ice-cold water containing 3 mmol of sodium chloride, the THF layer was separated and dried, and the solvent was removed on a rotary evaporator. The *trans*-1-decenylmercuric chloride was collected on a filter funnel, washed with water, and dried to yield 1.0 g (89%) of white solid.[7]

In the case of the two siloxy mercurials which turned out to be oils at room temperature, after the evaporation of THF, the resulting oil was extracted with pentane and dried over $MgSO_4$. Evaporation of the solvent gave the colorless oil. Purification was effected by column chromatography using 1:1 hexane/ethyl acetate.

(*E*)-3-(*tert*-Butyldimethylsiloxy)-1-(chloromercurio)-1-octene: 72% yield; ^{1}H NMR (C_6D_6) δ 0.06 (6 H, bs, $SiMe_2$), 0.8-1.8 (20 H, m, alkyl), 3.96 (1 H, m, CHO), 5.37 (2 H, m, vinyl); ^{13}C NMR ($DCCl_3$) δ 152.30, 132.14, 74.65, 37.91, 31.73, 25.88, 24.65, 22.50, 18.14, 13.98, -4.29, -4.81; IR ($HCCl_3$) 3000, 2942, 2920, 2845, 1600 (w), 1460, 1350, 1248 cm^{-1}. Anal. Calcd for $C_{14}H_{29}ClHgOSi$: C, 35.21; H, 6.12; Hg, 42.01. Found: C, 35.37; H, 6.26; Hg, 41.72.

(*E*)-6-(*tert*-Butyldimethylsiloxy)-1-(chloromercurio)-1-heptene: 80-85% yield; ^{1}H NMR ($DCCl_3$) δ 0.06 (6 H, s, $SiMe_2$), 0.8 (9 H, s, *t*-Bu), 1.05 (3 H, d, J = 6 Hz, CH_3), 1.3-1.6 (4 H, m, CH_2's), 2.0-2.3 (2 H, m, $C=CCH_2$), 3.66-40 (1 H, m, CHO), 5.66 (2 H, m, vinyl); ^{13}C NMR ($DCCl_3$) δ 150.57, 133.24, 68.23, 36.27, 30.36, 26.73, 25.92, 23.80, 18.06, -4.30, -4.63; IR ($HCCl_3$) 3010, 2960, 2920, 2860, 1600 (w), 1460, 1370, 1245, 1200 cm^{-1}. Anal. Calcd for $C_{13}H_{27}ClHgOSi$: C, 33.76; H, 5.84; Hg, 43.29. Found: C, 34.32; H, 6.01; Hg, 41.08.

General Carbonylation Procedure. Palladium chloride (1 mmol) and lithium chloride (2 mmol) were stirred with 10 mL of methanol and cooled to -78 °C. Two millimoles of magnesium oxide or diisopropyl ethylamine and 1 mmol of the vinylmercurial were added at -78 °C. The flask was flushed with carbon monoxide, and a balloon of carbon monoxide was attached. The reaction mixture was allowed to warm to room temperature overnight and filtered through Celite. The Celite was washed with ether. The combined ether layers were washed with water and saturated NH_4Cl, dried over $MgSO_4$, and evaporated.

Methyl (*E*)-2-undecenoate:[7] ^{1}H NMR ($DCCl_3$) δ 0.7-1.0 (3 H, m, CH_3), 1.1-1.67 (10 H, m, CH_2's), 2.0-2.3 (2 H, m, $C=CCH_2$), 3.70 (3 H, s, CO_2CH_3), 5.75 (1 H, dt, J = 17 and 1.5 Hz, $=CHCO-$), 6.97 (1 H, td, J = 17 and 6 Hz, $=CHCH_2$).

Methyl (*E*)-4-(*tert*-butyldimethylsiloxy)-2-nonenoate: ^{1}H NMR ($DCCl_3$) δ 0.06 (6 H, s, $SiMe_2$), 0.8 (9 H, s, *t*-Bu), 2.0-2.57 (8 H, m, CH_2's), 3.66 (3 H, s, CO_2CH_3), 4.0-4.33 (1 H, m, CHO), 5.81 (1 H, dd, J = 16 and 1.5 Hz, $=CHCO-$), 6.83 (1 H, dd, J = 16 and 4 Hz, $=CHCH-$); MS, *m/e* 300, 285, 269, 242, 229, 211.

Methyl (*E*)-7-(*tert*-butyldimethylsiloxy)-2-octenoate: ^{1}H NMR ($DCCl_3$) δ 0.06 (6 H, s, $SiMe_2$), 0.8 (9 H, s, *t*-Bu), 1.05 (3 H, d, J = 6 Hz, CH_3), 1.3-1.6 (4 H, m, CH_2's), 2.0-2.3 (2 H, m, $C=CCH_2$), 3.66-4.0 (4 H, s and m, CO_2CH_3 and CHO), 5.78 (1 H, dt, J = 18 and 1.5 Hz, $=CHCO-$), 6.66-7.18 (1 H, dt, J = 18 and 6 Hz, $=CHCH_2$); MS, *m/e* 255 ($M^+ - 31$), 229 ($M^+ - 57$), 197, 159, 95, 89, 81, 75.

Acknowledgment. We gratefully acknowledge the National Institutes of Health, the Petroleum Research Fund, administered by the American Chemical Society, and the American Heart Association, Iowa Affiliate, for their generous financial support of this research. We also thank Mr. Harold Hsu for supplying the vinylborane used in entry 17 of the table. Johnson Matthey and Engelhard Industries kindly provided the palladium chloride.

Registry No. (*E*)-*n*-$C_8H_{17}CH=CHCO_2CH_3$, 56453-83-9; (*Z*)-*n*-$C_8H_{17}CH=CHCO_2CH_3$, 54299-03-5; *trans*-1-decenylcatecholborane, 91280-69-2; *trans*-1-decenylboronic acid, 86883-77-4; *trans*-1-decenyldicyclohexylborane, 91280-70-5; (*E*)-3-(*tert*-butyldimethylsiloxy)-1-octenylcatecholborane, 91280-71-6; (*E*)-6-(*tert*-butyldimethylsiloxy)-1-heptenylcatecholborane, 91280-72-7; methyl (*E*)-4-(*tert*-butyldimethylsiloxy)-2-nonenoate, 91280-73-8; methyl (*E*)-7-(*tert*-butyldimethylsiloxy)-2-octenoate, 91280-74-9; *trans*-1-decenylmercuric chloride, 56453-77-1; (*E*)-3-(*tert*-butyldimethylsiloxy)-1-(chloromercurio)-1-octene, 91280-75-0; (*E*)-6-(*tert*-butyldimethylsiloxy)-1-(chloromercurio)-1-heptene, 91280-76-1; 3-(*tert*-butyldimethylsiloxy)-1-octyne, 60134-93-2; 6-(*tert*-butyldimethylsiloxy)-1-heptyne, 62957-48-6.

A New Class of Chiral Detergents. The Formation of Single Micelles from *N,N*-Dimethyl-1-dodecyl-2,4-dimethyl-3-carbamoylpyridinium Bromide. A CD Study

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From racemic *N,N*-dimethyl-2,4-dimethyl-3-carbomoylpyridine (CPB)[1] a new class of optically active detergents is prepared via alkylation of the pyridine nitrogen with *n*-dodecyl bromide leading to *N,N*-dimethyl-1-dodecyl-2,4-dimethyl-3-carbamoylpyridinium bromide (C_{12}CPB). This chirality which is present in the carbamoylpyridinium moiety[2-4] is the result of an out-of-plane orientation of the carboxamide group by two adjacent methyl groups. With the method of circular dichroism (CD) we were able to determine the critical micelle concentration (cmc) for these optically active single-stranded model substrates. Varying the concentration of (±)-C_{12}CPB resulted in an abrupt change in the extinction coefficients ($\Delta\epsilon$) of the CD spectra for the two transitions at 240 nm and 278 nm. A pronounced deviation from Lambert-Beer is demonstrated for 240 nm (see Figure 1). The CD spectra are given in Figure 2. The concentration corresponding with the abrupt change in $\Delta\epsilon$ was interpreted as the cmc of the surfactant, since its value (~10 mM) is in good agreement with the cmc values for related substrates obtained by other physicochemical procedures.[5] No such spectral changes are observed in the UV spectra. The closely related optically active *N,N*-dimethyl-1-methyl-2,4-dimethyl-3-carbamoylpyridinium bromide[4] (C_1CPB) which is a nonmicelle-forming salt, displays similar CD and UV transitions as C_{12}CPB *without* discrepancies from Lambert-Beer. The change of the

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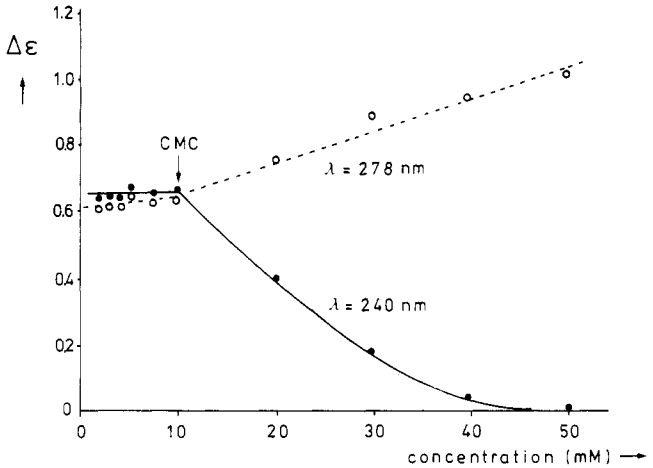


Figure 1. $\Delta\epsilon$ plot vs. the concentration of (−)-C_{12}CPB. A similar plot, although with negative $\Delta\epsilon$ values, was obtained for (+)-C_{12}CPB.

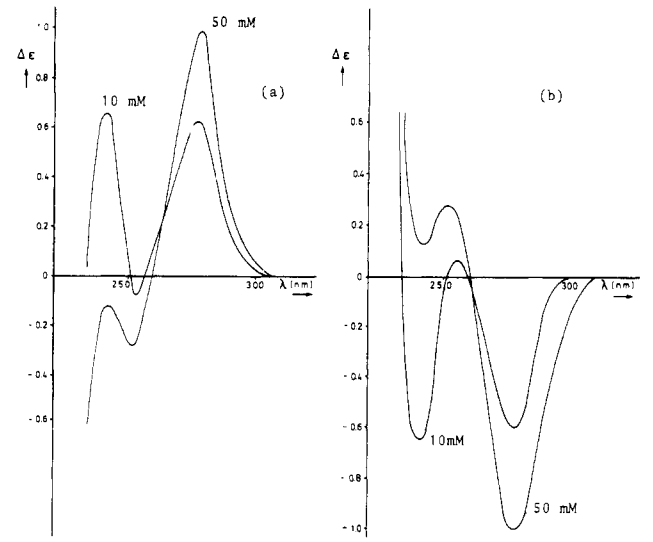
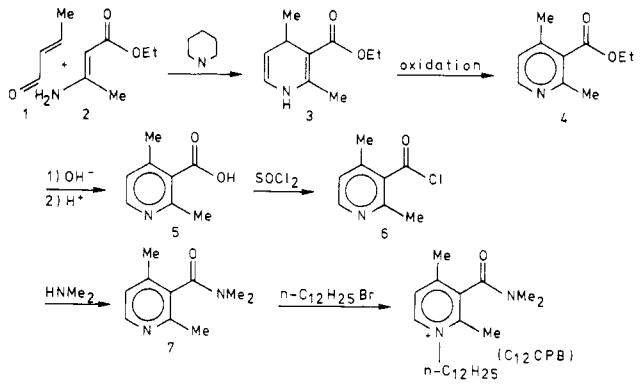


Figure 2. $\Delta\epsilon$ plot vs. the wavelength of (−)-C_{12}CPB for different concentrations (a). $\Delta\epsilon$ plot vs. the wavelength of (+)-C_{12}CPB for different concentrations (b).

240-nm band at concentrations above the cmc may be due to an increase of the very strong dichroic absorption at the short-wavelength side. However, the absolute intensity and position of this strong multiple band could not be detected properly due to an overload of the detection system. Explanation of the concentration effects on the absorption band at 240 nm in terms of other aspects, such as increasing particle sizes and microscopic changes in solvent effects, are unlikely because these would modulate all absorptions in a corresponding manner.[6,7] Spectra similar to the 50-mM spectrum of Figure 2 are obtained for C_1CPB in acetonitrile.[4] This may indicate that (partial) dehydration occurs upon aggregation which results in a less polar environment for the carboxamide group in C_{12}CPB. This effectuates deviations from planarity within the carboxamide group and/or deviations of the out-of-plane orientation of the carboxamide group with respect to the pyridinium moiety which is strongly reflected in the rotational strength of the absorption at 240 nm.

The synthetic steps involved in the preparation of C_{12}CPB are outlined in Scheme I. Refluxing croton-

Scheme I. Synthesis of the Chiral Substrate *N,N*-Dimethyl-1-dodecyl-2,4-dimethyl-3-carbamoylpyridinium Cation



aldehyde (1) and ethyl β-aminocrotonate (2) in the presence of piperidine according to Hantzsch[8] gave the dihydropyridine 3. Oxidation by means of *p*-chloranil yielded ethyl 2,4-dimethylnicotinate (4). The 2,4-dimethylpyridine-3-carboxylic acid (5) was obtained after hydrolysis and acidification of 4. Chlorination resulted in 2,4-dimethylpyridine-3-carbonyl chloride (6), which was converted to *N,N*-dimethyl-2,4-dimethyl-3-carbamoylpyridine (7). Alkylation with *n*-dodecyl bromide afforded the racemic C_{12}CPB. The separation of both enantiomers of C_{12}CPB was accomplished by complexation with optically pure silver α-bromocamphor-π-sulfonate monohydrate and repeated crystallization of the diastereoisomeric mixture. Full details are presented in the Experimental Section.

Experimental Section

General Remarks. The ^{1}H NMR spectra were recorded with a Varian EM-360 A NMR spectrometer using Me_4Si as internal standard (δ = 0.00). The optical rotations were measured on an Optical Activity AA-10 polarimeter. The CD spectra were recorded on a Jobin Yvon Dichrograph Mark III-S. The UV spectra were obtained from a Perkin-Elmer double beam grating spectrophotometer. Ethyl β-aminocrotonate (2) and crotonaldehyde (1) were purchased from Aldrich. Ethyl 2,4-dimethyl-1,4-dihydronicotinate (3),[8] ethyl 2,4-dimethylnicotinate (4),[8] 2,4-dimethyl-3-carboxylpyridine hydrochloride,[3,4] *N,N*-dimethyl-2,4-dimethyl-3-carbamoylpyridine,[4,9] and silver (+)-α-bromocamphor-π-sulfonate monohydrate[10] were prepared by using modified literature procedures.

(−)-*N,N*-Dimethyl-1-dodecyl-2,4-dimethyl-3-carbamoylpyridinium Bromide ((−)-C_{12}CPB). A stirred solution of dodecyl bromide (25 g, 100 mmol) and amide 7 were heated to 90–100 °C during 2 days. The excess dodecyl bromide was decanted. The precipitate was washed with Et_2O and dried, which resulted in 6.6 g (69%) of bromide C_{12}CPB: oil; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3, CH_2CH_3), 1.25 (m, 20, 10 CH_2), 2.50 (s, 3, CH_3), 2.77 (s, 3, CH_3), 3.00 (s, 3, CH_3), 3.17 (s, 3, CH_3), 4.73 (t, 2, NCH_2), 7.80 (d, 1, Pyr H), 9.06 (d, 1, pyr H). A diastereoisomeric pair of C_{12}CPB was obtained after complexation with silver (−)-α-bromocamphor-π-sulfonate monohydrate. Repeated crystallization from acetone/hexane resulted in the pure (−) diastereoisomer. Treatment of the (−) complex with Amberlite IRA-400 (Br^- form) resulted in (−)-C_{12}CPB: CD (H_2O) $\Delta\epsilon$ +0.6 (278 nm), +0.65 (240 nm); $[\alpha]^{20}_D$ −12.4° (H_2O, *c* 0.005).

(+)-*N,N*-Dimethyl-1-dodecyl-2,4-dimethyl-3-carbamoylpyridinium Bromide ((+)-C_{12}CPB). Prepared analogously to (−)-C_{12}CPB by using silver (+)-α-bromocamphor-π-sulfonate

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monohydrate: CD (H_2O) $\Delta\epsilon$ −0.6 (278 nm), −0.65 (240 nm); $[\alpha]^{20}_D$ +12.3° (H_2O, 0.005).

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 7, 55314-19-7; (−)-C_{12}CPB, 91238-47-0; (+)-C_{12}CPB, 91238-48-1; dodecyl bromide, 143-15-7.

Di-*tert*-butyl Peroxide: Can Its Photolysis Be Quenched by Carbon Tetrachloride and Why Is It Stable at Room Temperature?[1]

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It has been reported[3] that photolysis of acetonitrile solutions containing di-*tert*-butyl peroxide and carbon tetrachloride in the cavity of an EPR spectrometer yielded the spectra of methyl and trichloromethyl radicals, even when the carbon tetrachloride was screened from direct photolysis.

The methyl radical was presumed[3] to have been formed by β-scission of *tert*-butoxyl, which was accelerated by the polar solvent, eq 1 and 2.[4] However, literature data[5]

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}\cdot \quad (1)$$

$$t\text{-BuO}\cdot \rightarrow (CH_3)_2CO + \dot{C}H_3 \quad (2)$$

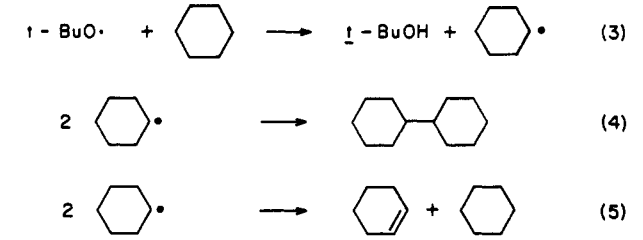
indicated that the rate of chlorine abstraction by methyl from carbon tetrachloride was too slow to have given rise to trichloromethyl under the reaction conditions. It was therefore concluded[3] that carbon tetrachloride was acting as a quencher of the peroxide photolysis to yield ·Cl and ·CCl_3.

These experimental results have been confirmed in our laboratory. However, their original interpretation[3] conflicts with gas-phase[6,7] and theoretical[8] work which suggest that the singlet excited states of dialkyl peroxides are dissociative and therefore ought not to be quenched by carbon tetrachloride. We now describe a number of experiments designed to resolve this problem.

The decomposition of carbon tetrachloride can be sensitized by ketones[9] whose triplet energy is greater than the carbon–chlorine bond dissociation energy of 73 kcal mol^{-1}.[10] Thus, photolysis of benzophenone (0.1 M) in carbon tetrachloride at 25 °C did not give rise to an EPR spectrum of trichloromethyl since the triplet energy of the ketone[11] is only 68.6 kcal mol^{-1}. However, trichloromethyl was observed when di-*tert*-butyl peroxide was added to the reaction mixture under conditions where the benzophenone absorbed essentially all of the light. Clearly the ketone could not have transferred enough energy to the peroxide for the latter to have *sensitized* the decomposition of the carbon tetrachloride. However, the ketone certainly provided sufficient energy to induce the decomposition of the peroxide.[12] Hence, trichloromethyl must have been formed in a chemical reaction between one of the products of the peroxide decomposition and carbon tetrachloride.

In a second set of experiments, the mixtures described in Table I were photolyzed in a merry-go-round apparatus at 35 °C. The compositions of the mixtures and the choice of photolysis wavelengths ensured that the light was being absorbed by the peroxide alone and that the same amount of light was absorbed by each sample. The samples were photolyzed to low conversions <1.0% so to avoid complications from secondary reactions. Products were identified by mass spectrometry and were quantified by GC using a 20 ft, 12% OV-101 column. *tert*-Butylbenzene was used as an internal standard, and pure samples of each of the products were used as sensitivity calibrants.

Sample I contained di-*tert*-butyl peroxide and cyclohexane and acted basically as an actinometer. Photolysis gave *tert*-butyl alcohol as the only peroxide-derived product. Bicyclohexyl was also detected but cyclohexene could not be resolved from cyclohexane at these low levels of conversion, thus making it impossible to quantify the radical combination–disproportionation yields, eq 3–5. The yield of *tert*-butyl alcohol divided by the photolysis time gave the rate of initiation, R_i, as 1.04×10^{-5} M s^{-1} under our experimental conditions.



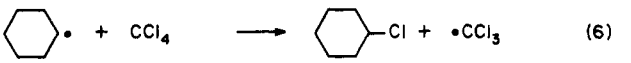
(3)

(4)

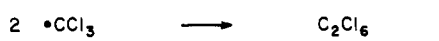
(5)

Sample II was similar to I except that it contained carbon tetrachloride. Nevertheless, the yiels of *tert*-butyl alcohol were the same, within experimental error, in both cases. This confirms that the photolysis of the peroxide was neither quenched physically nor chemically by carbon tetrachloride.

The yield of cyclohexyl chloride was greater than expected on the basis of reactions 6 and 7 alone and chloroform was also detected as a product. These results imply that there was significant hydrogen abstraction from cyclohexane by the trichloromethyl radical, eq 8. The



(6)



(7)

(8)

product yields are exactly consistent with the stoichiometry dictated by this additional process. Thus eq 6 and 8 represent the propagation steps of a chain reaction. Moreover, since no bicyclohexyl was detected, reaction 7 must have been the termination step, i.e., $k_6 \gg k_8$. Ap-

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