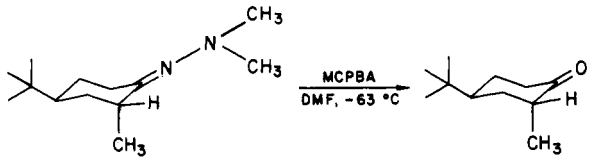
their parent carbonyl compounds, exhibit marked differences in reactivity due largely to the lower acidity of protons on the α-carbons and their greater tolerance to self-condensation. Stereospecific generation of α-lithio imines,[2] oxime ethers,[3] and hydrazones[4] and their subsequent reaction with electrophiles have produced, in good yields and with high regio- and stereoselectivity, alkylated carbonyl compounds which are otherwise difficult to obtain in pure form. Corey's hydrazone alkylation[4,5] is one such example.

During our syntheses of chiral dienes[6] to study their chiroptical properties, we were in need of a cyclohexanone in which a 2-methyl substituent is oriented in an axial position. Following Corey's procedure,[4] we obtained the *N,N*-dimethylhydrazone of *trans*-4-*tert*-butyl-2-methylcyclohexanone (1). The cleavage of 1 to obtain 2 could



1 2

be achieved by $NaIO_4$.[4] The limitations of this reagent are that it is expensive and very large reaction volumes were necessary even for a 0.1-mol scale. Since we needed the ketone 2 in preparative scales an alternate method of hydrazone cleavage was necessary. *m*-Chloroperbenzoic acid seemed to be the reagent of choice only if we could prevent epimerization of the product by *m*-chlorobenzoic acid. First we noted, by cleaving the *N,N*-dimethylhydrazone of 4-*tert*-butylcyclohexanone, that the reaction was very facile in many solvents, giving 4-*tert*-butylcyclohexanone in quantitative yields. Of various conditions employed for the target molecule 1, the one using 2 equiv of MCPBA in DMF at −63 °C was found to give ketone 2 in quantitative yield and without isomerizing the axial methyl group to the more stable equatorial position. Moreover, the reaction could be carried out in a very short time, using a relatively inexpensive reagent (MCPBA), and it was amenable to very small as well as large quantities of substrate.

An alternative method of hydrolysis of 1 is by quarternization of the hydrazone with CH_3I followed by aqueous hydrolysis.[4b,7] This procedure also yields unisomerized ketone 2 but, in our hands, the yield was quite low (≃20%).

Experimental Section

The hydrazone 1 (60.0 g, 0.285 mol) was dissolved in 1.0 L of dry DMF and the solution was cooled to −63 °C (dry ice/$CHCl_3$). *m*-Chloroperbenzoic acid (80–90%; 90.0 g, 0.57 mol) was slowly added while the solution was being stirred and the temperature maintained. After 0.5 h, *the cold solution* was poured into $NaHCO_3$ (~60 g) solution and diluted with more ice-cold water to completely dissolve the DMF. The cold mixture was immediately extracted twice with hexane. The hexane extract was washed with cold sodium bisulfite, $NaHCO_3$, and water. The solution was filtered through Na_2SO_4 and evaporated and the residue was distilled under vacuum, bp 75 °C (1.25 mm) to yield 45.5 g (95%) of *trans*-4-*tert*-butyl-2-methylcyclohexanone (2): ^1H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 1.15 (d, J = 7 Hz, 3 H), 1.15–2.8 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 16.84 (q), 26.18 (t), 27.40 (q), 32.44 (s), 32.99 (t), 38.03 (t), 41.35 (d), 42.96 (d), 216.11 (s).

Acknowledgment. This work was supported by a grant from the National Science Foundation for which we are grateful.

Registry No. 1, 58911-80-1; 2, 3211-26-5; MCPBA, 937-14-4.

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Mercury in Organic Chemistry. 29.[1] An Improved, Stereospecific Approach to Vinylmercurials via Hydroboration–Mercuration of Alkynes

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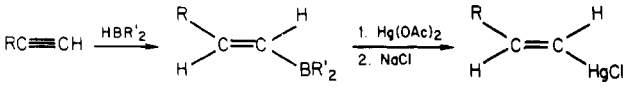
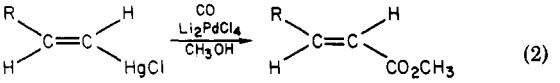
In recent years vinylmercurials have proven to be valuable intermediates in the synthesis of symmetrical[2,3] and unsymmetrical[4] 1,3-dienes, 1,4-dienes,[5] α,β-unsaturated ketones,[6] carboxylic acids and esters,[7] enol esters,[8] butenolides,[9] and (π-allyl)palladium compounds.[10,11] Some years ago we reported a convenient approach to vinylmercurials via hydroboration of alkynes with either dicyclohexylborane[12] or catecholborane[13] and subsequent transmetalation by mercuric acetate (eq 1). In that work,



(1)

alkynes of low molecular weight, usually containing eight of less carbons, were employed and the overall hydroboration–mercuration procedure was observed to be highly stereospecific. In the intervening years, carbonylation of these organomercurials (eq 2) has established that the



(2)

mercuration step is not stereospecific for alkynes of higher

(1) For "Mercury in Organic Chemistry. 28..." see: R. C. Larock and K. Takagi, *J. Org. Chem.* **1984**, *49*, 2701.

(2) Larock, R. C. *J. Org. Chem.* **1976**, *41*, 2241.

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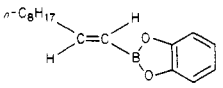
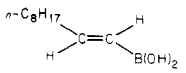
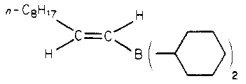
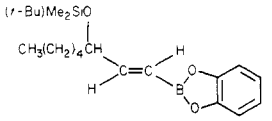
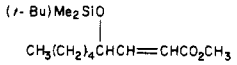
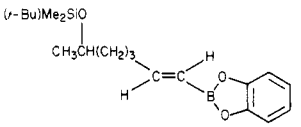
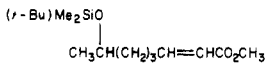
0022-3263/84/1949-3411$01.50/0

Table I. Mercuration and Subsequent Carbonylation of Vinylboranes

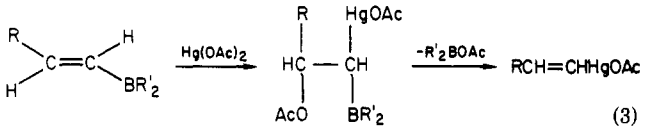
entry	vinylborane	mercuration solvent	mercuration temp, °C	additional reagents	mercuric salt	methyl ester	trans:cis ratio
1		CH_3CN	0 → 25		$Hg(O_2CCH_3)_2$	n-$C_8H_{17}CH{=}CHCO_2CH_3$	50:50
2		HMPA					77:23
3		CH_2Cl_2	−78 → 25				50:50
4			25				75:25
5					$Hg(O_2CCF_3)_2$		84:16
6		THF	−78 → 25		$Hg(O_2CCH_3)_2$		43:57
7				NaO_2CCH_3			98:2
8					$Hg[O_2C(CH_2)_2CH_3]_2$		52:48
9					$HgCl_2$		99:1
10				$NaOCH_3$			99:1
11			−78 → 0		$Hg(O_2CCH_3)_2$		98:2
12			−78 → 25		$HgCl_2$		90:10
13			−78 → 0	2NaOH (−40 → 0)			97:3
14			0		$Hg(O_2CCH_3)_2$		67:33
15			−78 → 25				90:10
16				NaO_2CCH_3			86:14
17			−78 → 0	NaOAc			98:2
18							95:5

molecular weight.[7] The low stereospecificity of this reaction has proven to be a serious problem in our more recent efforts to utilize vinylmercurials in the synthesis of natural products, particularly prostaglandins. To overcome these difficulties, we have recently reexamined this approach to vinylmercurials. We now report an improved, stereospecific approach to these compounds.

Our initial work focused on the mercuration of vinylboranes derived from 1-decyne, since it is with that alkyne that the lack of stereospecificity was originally observed.[7] It was first established by NMR and IR spectral analyses that the vinylboranes derived from dicyclohexylborane and catecholborane were the expected pure trans isomers. A variety of mercuration conditions were then examined. The results are summarized in Table I. Yields of vinylmercurials varied from 60–90%. Stereochemical analysis was most easily carried out by carbonylation of the vinylmercurials, followed by NMR and/or gas chromatographic analysis of the resulting methyl esters. The esters were obtained in 70–80% isolated yields.

Best results were obtained by using the catecholborane-derived mercurial (entries 1–10). The corresponding boronic acid (entries 11–13) is more difficult to prepare and no more stereospecific in its reactions. The dicyclohexylborane products (entries 14–16) lacked stereospecificity. The best reagents for mercuration of the *trans*-1-decenylcatecholborane were either $Hg(OAc)_2$ plus NaOAc (entry 7) or $HgCl_2$ (entries 9 and 10). Unfortunately, in attempting to extend the latter procedure to the siloxy-substituted vinylborane of entry 17, we observed unreacted borane and an absence of vinyl peaks corresponding to the vinylmercurial in the NMR spectrum. However, the $Hg(OAc)_2$/NaOAc procedure worked nicely on this vinylborane as well as that of entry 18. Applications of these latter two vinylmercurials in the synthesis of prostaglandins and brefeldin A are currently under study.

Mechanistically, we believe that these reactions proceed by an addition–elimination sequence (eq 3). A trans (cis)



(3)

addition, followed by a cis (trans) elimination results in overall retention. The stereospecificity is apparently lost during one or both of the two steps. Addition of sodium acetate promotes a more stereospecific reaction.

Experimental Section

Equipment. Gas chromatographic analyses were carried out on a Varian Model 3700 gas chromatograph with a flame ionization detector. In addition, a Finnegan 4023 gas chromatograph–mass spectrometer was employed to identify the products. ^1H NMR spectra were obtained on a Varian EM-360 spectrometer using tetramethylsilane as an internal standard.

Reagents. All reagents were used as obtained commercially unless otherwise noted. All solvents were distilled prior to use. 3-(*tert*-Butyldimethylsiloxy)-1-octyne was prepared from commercially available 1-octyn-3-ol (Aldrich). 6-(*tert*-Butyldimethylsiloxy)-1-heptyne was synthesized according to the published procedure starting from 3-methylcyclohexen-1-one (Aldrich).[14]

The vinylcatecholboranes were prepared from the corresponding acetylenes by using the standard hydroboration procedure.[15] The *trans*-1-decenylboronic acid was prepared by

(14) Greene, A. E.; Le Drian, C. *J. Am. Chem. Soc.* **1982**, *104*, 5473.
(15) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370.

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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Received March 9, 1984

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

(1) van Lier, P. M.; Meulendijks, G. H. W. M.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 337.
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