Table II. Pertinent Proton Magnetic Resonance Data for the Olefin–Mercuric Trifluoroacetate Adducts

Olefin adduct	K_{obsd} (δ)[a]	H_{irrad}	Pattern[b]	J_{H-H}, Hz	$J_{H-^{199}Hg}$ (*vic*), Hz
Cyclohexene (**1**)	H_1 (2.24)	None	m	$w_{h/2}$ = 23.5	
		H_2	m	$w_{h/2}$ = 15	
	H_2 (4.80)	None	m	$w_{h/2}$ = 22.5	*Ca.* 100
		H_1	m	$w_{h/2}$ = 14	
Norbornene (**2**)	H_2 (1.91)	None	dd	7; 2.5	
		H_3	d	2.5	
	H_3 (4.45)	None	d	7	92
Apobornylene (**3**)	H_2 (2.0)	None	d	8	
		H_3	s		
	H_3 (4.55)	None	d	8	110
		H_2	s		

[a] In perdeuteriobenzene solution with TMS as internal reference. [b] m, multiplet; dd, doublet of doublet; s, singlet; d, doublet.

Both α-methine protons in **1** appear as complex multiplets with peak width at half-height ($w_{h/2}$) of about 23 Hz. The one for H_1 is an apparent triplet of doublet, similar to that observed for *trans*-2-methoxycyclohexylmercuric chloride (**4**).[8] Irradiation of the multiplet due to H_1 reduces $w_{h/2}$ for H_2 by about 8.5 Hz, and the same value is also observed for H_1 when H_2 is irradiated. This indicates the two protons have a coupling constant of 8.5 Hz and accordingly are in a *trans*-axial,axial relationship.[9] The vicinal H–^{199}Hg coupling constant for **1**, *ca.* 100 Hz, also agrees with the observed value, 99 Hz, for *trans*-**4**, while the *cis* isomer exhibits a J value of 425 Hz.[10]

The distinct doublet for proton H_3 with J of 7 Hz in **2** and with J of 8 Hz in **3** reveals that it arises from H_{endo}–H_{endo} coupling.[11,12] The presence of a second coupling constant for H_2 in **2** is in line with what has been observed in other stable *cis-exo*-norbornyloxymercurials.[5,8,13,14] On the other hand, the adduct **3**, similar to 3-*exo*-acetoxyapoisobornylmercuric chloride[5] (**5**), shows only a doublet for H_3. Moreover, the vicinal H–^{199}Hg coupling constants in Table II correspond to the observed data for 3-*exo*-acetoxy-*exo*-norbornylmercuric chloride (93.2 Hz[10]) and **5** (114 Hz). Consequently, in both **2** and **3** the addition must be *cis-exo*, with the minor modification in the spectrum of the H_3 proton apparently arising from some as yet unknown effect of the 7,7-dimethyl substituents.

The lifetime of such 1,2-addition compounds must be longer than the pmr time scale since the resonances of the ^{199}Hg satellites are measurable. Although the reaction reaches its equilibrium position in about 1 min, the system is stable over a period of 24 hr without any significant change in pmr spectrum. Therefore, the observed steric course of the addition is the most favored one. More remarkably, in this typical nonpolar medium the reaction of mercuric trifluoroacetate with the three olefins under discussion exhibits the same stereochemistry as is observed for typical stepwise electrophilic additions.[15]

This facile addition of mercuric trifluoroacetate to olefins and the ready examination of the adducts in solution by pmr appear to provide a powerful new technique for exploring the nature of electrophilic additions to olefins of widely different structures. Further studies are in progress.

Acknowledgment. We are grateful to Professor John B. Grutzner for helpful discussions in the interpretation of the spectra.

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(16) Postdoctorate research associate, 1966–1968, on a research program supported by the Esso Research and Engineering Co.
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Reaction of Organoboranes with Ethyl 4-Bromocrotonate under the Influence of Potassium 2,6-Di-*t*-butylphenoxide. A Convenient Procedure for a Four-Carbon-Atom Homologation

Sir:

We wish to report that trialkylboranes readily react with ethyl 4-bromocrotonate under the influence of potassium 2,6-di-*t*-butylphenoxide in tetrahydrofuran to give the corresponding unsaturated esters in excellent yields. This provides a new convenient synthetic route to achieve a C-4 homologation.

The reaction of organoboranes with carbon monoxide in the presence of lithium trialkoxyaluminohydride provides a convenient method for a one-carbon-atom homologation[1] (eq 1). Similarly, C-2 homologations can be realized by the reaction of organoboranes with ethyl bromoacetate under the influence of potassium *t*-butoxide[2] (eq 2), by reaction with ethyl diazoacetate,[3] or with other acetic acid derivatives.[4] Moreover, the reaction of organoboranes with acrolein provides a simple C-3 homologation[5] (eq 3). Con-

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Table I. The Reaction of Trialkylboranes with Ethyl 4-Bromocrotonate under the Influence of Potassium 2,6-Di-*t*-butylphenoxide

Trialkylborane from olefin	Product[a]	Yield,[b] %	Physical properties	
			Bp, °C (mm)	n^{20}D
Ethylene	Ethyl 3-hexenoate	78	62–63 (10)	1.4260
1-Butene	Ethyl 3-octenoate	72	93–95 (10)	1.4362
Isobutylene	Ethyl 6-methyl-3-heptenoate	82	84–86 (8)	1.4346
2-Butene	Ethyl 5-methyl-3-heptenoate	89	85–87 (9)	1.4325
Cyclopentene[c]	Ethyl 4-cyclopentyl-3-butenoate	81	125–126 (15)	1.4645
Cyclohexene[c]	Ethyl 4-cyclohexyl-3-butenoate	73	123–125 (8)	1.4647

[a] All products appeared to be the *trans* derivatives. Their structures were confirmed by ir and nmr spectra. [b] By glpc analysis. [c] In these cases potassium 2,4,6-tri-*t*-butylphenoxide was used as the base to faciliate glpc analysis and isolation. In preliminary experiments the two bases exhibited the same activity.

sequently, the present extension of organoborane chemistry to a simple C-4 homologation (eq 4) adds to the versatility of synthetic procedures based on organoborane chemistry.

$$R_3B + CO \xrightarrow{LiAlH(OR)_3} \xrightarrow{[O]} RCHO \quad (1)$$

$$R_3B + CH_2BrCO_2C_2H_5 \xrightarrow{t\text{-BuOK}} RCH_2CO_2C_2H_5 \quad (2)$$

$$R_3B + CH_2{=}CHCHO \xrightarrow{H_2O} RCH_2CH_2CHO \quad (3)$$

$$R_3B + CH_2BrCH{=}CHCO_2C_2H_5 \xrightarrow{KO\text{-}C_6H_2(t\text{-Bu})_2} RCH{=}CHCH_2CO_2C_2H_5 \quad (4)$$

Previously we had attempted to extend the alkylation of ethyl bromoacetate with trialkylboranes under the influence of potassium *t*-butoxide[2] to the vinylog, ethyl 4-bromocrotonate. However, this procedure was not successful.

We recently described a new base, potassium 2,6-di-*t*-butylphenoxide.[6] This base not only achieved successful reaction in cases where potassium *t*-butoxide had previously been successful, but it permitted extension of the reaction to systems such as bromoacetone[6] and chloroacetonitrile,[6] where potassium *t*-butoxide had previously failed. Consequently, we were encouraged to reopen the study of the alkylation of ethyl 4-bromocrotonate. Indeed, it was observed that the addition of ethyl 4-bromocrotonate to an equimolar mixture of triethylborane and potassium 2,6-di-*t*-butylphenoxide in tetrahydrofuran gave the desired hexenoate ester in a yield of 78%.

We had originally anticipated that the ester produced would be ethyl 2-hexenoate. However, the observed properties clearly establish the structure to be the isomeric ethyl 3-hexenoate (79% *trans*), resulting from an allylic migration of the double bond: bp 62–63° (10 mm); n^{20}D 1.4260 (lit.[7] n^{20}D 1.4255); ν_{max} 1735, 967 cm^{-1} (no absorption in the 1600-cm^{-1} region); $\delta_{TMS}^{CCl_4}$ 5.5 ppm (vinyl proton, 2 H), 2.9 ppm (=C—CH$_2$—CO—, 2 H).

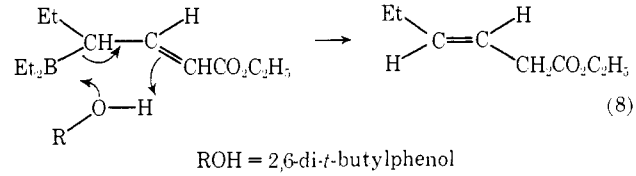
The unusual migration of the double bond observed in this reaction presumably takes place during the protonolysis of this intermediate organoborane, as indicated in the following mechanism (eq 5–8).

$$\text{O}^-\text{K}^+ + CH_2BrCH{=}CHCO_2C_2H_5 \longrightarrow$$

$$K^+{}^-CHBrCH{=}CHCO_2C_2H_5 + \text{OH} \quad (5)$$

$$Et_3B + [{}^-CHBrCH{=}CHCO_2C_2H_5]K^+ \longrightarrow [Et_3B{-}CH(Br){-}CH{=}CHCO_2C_2H_5]^-K^+ \quad (6)$$

$$[Et_2B{-}CH(Et){-}CH{=}CHCO_2C_2H_5]^-K^+ \longrightarrow Et_2B{-}CH(Et){-}CH{=}CHCO_2C_2H_5 + KBr \quad (7)$$



(8)

ROH = 2,6-di-*t*-butylphenol

In the corresponding reaction involving the α-bromoacetates,[6] it was noted that the protonolysis of the boron intermediate by the 2,6-di-*t*-butylphenol was relatively slow. Consequently, *t*-butyl alcohol was added to facilitate liberation of the ester product. However, in the present case the reaction intermediate appears to undergo protonolysis much more readily, so that examination of the reaction mixture by glpc revealed the presence of the product in high yield without addition of an external protonolysis agent. This observation suggests that the rapid hydrolysis in this case may be a consequence of the high reactivity of allylic boron derivatives,[8] possibly facilitated by a cyclic transition state, as indicated (eq 8).

The reaction was applied to a number of organoboranes produced by hydroboration from olefins of representative structures. In all cases the reactions proceeded smoothly and satisfactory yields were realized. In each case migration of the double bond

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occurred, placing it out of conjugation into the $\Delta^{3,4}$ position. The results are summarized in Table I.

The following procedure for the reaction of tri-*n*-butylborane with ethyl 4-bromocrotonate is representative. To a 200-ml three-necked flask equipped with a dropping funnel, a septum inlet, condenser, and magnetic stirring bar was placed 11.4 g (55 mmol) of 2,6-di-*t*-butylphenol in 30 ml of purified tetrahydrofuran (THF). The flask was flushed with nitrogen and 50 ml of 1.0 *M* potassium *t*-butoxide in THF was injected into the flask. The flask was immersed in an ice bath and 12.1 ml (50 mmol) of tri-*n*-butylborane was added, followed by the dropwise addition over 30 min of 9.65 g (50 mmol) of ethyl 4-bromocrotonate in 20 ml of THF. The resulting mixture was allowed to stir for 1 hr at 0°. Glpc analysis, following addition of *n*-octane as an internal standard, indicated a 72% yield of ethyl 3-octenoate. The flask was cooled with a water bath. To destroy residual organoboron intermediates the reaction mixture was treated with 16.5 ml of 3 *M* sodium acetate followed by 12 ml of 30% hydrogen peroxide at a rate sufficient to maintain the temperature below 35°. After stirring for a further 30 min, the reaction mixture was saturated with sodium chloride. The organic phase was separated, dried over sodium sulfate, filtered, and distilled. There was obtained 5.1 g (60% yield) of ethyl 3-octenoate, bp 93–95° (10 mm), n^{20}D 1.4362.[9]

It is evident that the present reaction provides a highly convenient procedure for achieving a C-4 homologation. At the same time it provides a simple route for the synthesis of $\Delta^{3,4}$-olefinic esters. Of considerable interest is the unusual migration of the double bond from the conjugated $\Delta^{2,3}$ position to the unconjugated $\Delta^{3,4}$ position achieved in this reaction. Not only does this make these nonconjugated unsaturated esters and acids readily available, but the apparent stereospecificity of the migration would appear to have important theoretical implications.

(9) In all cases glpc examination indicated the presence of only one isomer and the ir spectrum corresponded to the presence of the *trans* isomer. However, glpc examination of the alcohols, obtained by reducing the esters with lithium aluminum hydride, revealed the presence of minor amounts of the *cis* isomer.

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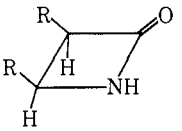
Stereochemistry of the Thermal Fragmentation of β-Lactams. Comparison with the Pyrolysis of 1-Azetines[1]

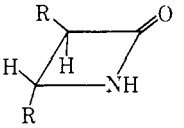
Sir:

Although thermal [2 + 2] cycloaddition reactions of olefins can be symmetry allowed and therefore concerted if the $[{}_{\pi}2_s + {}_{\pi}2_a]$ combination mode is followed,[2] only one authenticated example of this phenomenon has been reported to date.[3] Presumably this is because steric hindrance and angle strain factors generally develop to rather prohibitive levels as the two π bonds attempt to attain the requisite orthogonality. In contrast, cycloadditions of olefins to allenes,[4] ketenes,[5] and reactive isocyanates[6] are known to proceed with very high degrees of stereospecificity, thereby suggesting that cumulative π-bond systems can function more readily as ${}_{\pi}2_a$ donors than isolated double bonds.

If reversal of cyclobutane formation in any of the above examples is to be concerted, the process necessarily must take place *via* the $[{}_{\sigma}2_s + {}_{\sigma}2_a]$ pathway. Relevant studies on the pyrolysis of simple cyclobutane derivatives have been regarded as uniquely consistent with a stepwise decomposition involving tetramethylene diradicals.[7] It would appear that the total stereochemical inversion demanded of one of the four-membered ring carbons obtains with significant difficulty. To our knowledge, no information has been available concerning the stereochemical course of retrograde olefin–cumulene cycloadditions. This communication deals with the thermal cleavage of β-lactams **1** and **2**[8] and contrasts the remarkable stereospecificity noted in these examples with the pyrolytic behavior of the related 1-azetines **5** and **6**.



1a, R = CH_3
b, R = CH_2CH_3



2a, R = CH_3
b, R = CH_2CH_3

The four β-lactams were prepared by means of the known[6] stereospecific addition of chlorosulfonyl isocyanate to the appropriate *cis*- and *trans*-olefins and hydrolysis of the resulting N-(chlorosulfonyl)azetidin-2-ones with aqueous sodium hydroxide in acetone solution. Under conditions where the individual β-lactams were slowly introduced in the gas phase (12 mm, N_2 stream) through a quartz tube packed with glass beads (contact time, ~2 sec), these compounds were seen to be stable to 500°. At 600°, however, there resulted virtually complete fragmentation of the four-membered rings, accompanied by the formation of an alkene (>90% yield) and cyanuric acid (80–90%). The olefin composition was analyzed by vpc using either a 100 ft × 0.02 in. squalane-coated capillary column at 30°[9a] for the isomeric 2-butenes or a 22 ft × 0.25 in. column packed with 15% β,β′-oxydi-

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(8) The susceptibility of β-lactams to thermal fragmentation has been noted earlier, but not in stereochemical terms: (a) H. Staudinger, *Ber.*, **44**, 521 (1911); (b) A. M. Van Leusen and J. F. Arens, *Rec. Trav. Chim Pays-Bas*, **78**, 551 (1959).

(9) (a) Employed in conjunction with a flame ionization detector and a calibrated Infotronics CRS-11 HSB Digital Readout system; (b) employed in conjunction with a calibrated thermal conductivity detector (manual integration).