

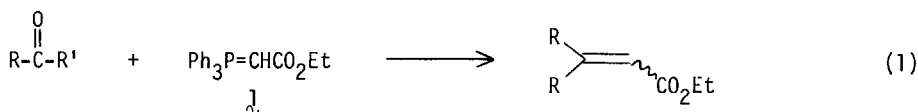
THERMODYNAMIC AND KINETIC CONTROL IN THE REACTION OF CARBOETHOXYMETHYLENE-
TRIPHENYLPHOSPHORANE AND ETHYL LITHIOTRIMETHYLSILYLACETATE WITH 2-
(t-BUTYLDIMETHYLSILYLOXY)CYCLOALKANONES.

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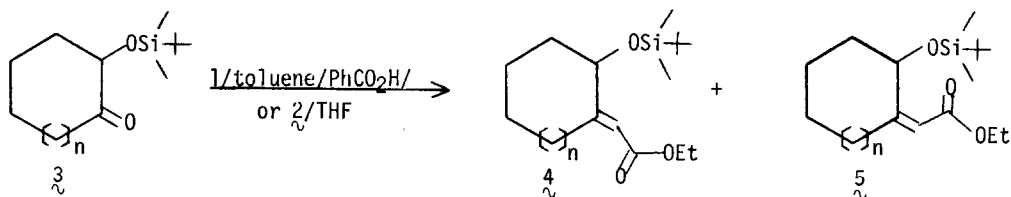
The reaction of 2-t-butyltrimethylsilyloxy cycloalkanones (5,6 and 7 membered rings) with carboethoxymethylenetriphenylphosphorane gives almost exclusively the E isomeric Wittig products, whereas reaction with ethyl lithiotrimethylsilylacetate gives predominantly the Z isomers. The Z products show the methine proton at ca. 5.5 ppm, an unusually large chemical shift for this type of proton.

It is well known that α,β -unsaturated esters can be prepared from ketones or aldehydes via reaction with carboethoxymethylenetriphenylphosphorane, **1**,² or ethyl lithiotrimethylsilylacetate, **2**.³ The recent report on the synthesis of acyclic Z-trisubstituted allylic alcohols from the Wittig reaction on protected α -hydroxy ketones⁴ prompts us to report our findings at similar reactions on α -t-butylsilyloxycycloalkanones. Thus, we wish to report herein on: 1) the reaction of **1** and **2** with α -t-butyl-



dimethylsilyloxycycloalkanones, **3**; 2) the change in stereochemistry in the reactions of **1** and **2** with the silylated acylons, **3** and 3) an extremely low field resonance for the C-2 methine proton in Z-2-(t-butyltrimethylsilyloxy)carboethoxymethylenecycloalkanes.

Reaction of $\mathfrak{3}$ with $\mathfrak{1}$ in refluxing toluene containing a small amount of benzoic acid⁵ gave a 96:4 mixture of E and Z silyloxy esters, $\mathfrak{4}$ and $\mathfrak{5}$, respectively. Conversely, the reaction of $\mathfrak{3}$ with reagent $\mathfrak{2}$ gives predominantly the Z isomer, $\mathfrak{5}$ (see Table 1). The best explanation for these results is that the Wittig reagent, $\mathfrak{1}$, occurs with thermodynamic control, whereas the silyl reagent, $\mathfrak{2}$, is



under kinetic control. It is known that the addition of $\mathfrak{1}$ to aldehydes or ketones is reversible with the reverse reaction being faster than decomposition of the betaine in many cases.⁶ This favors the formation of the thermodynamically more stable E isomer, $\mathfrak{4}$. On the other hand, the addition of $\mathfrak{2}$, although possibly reversible, proceeds to give product at a faster rate than the betaine,⁷ thus leading to kinetic control in this reaction.

The structural assignments of products $\mathfrak{4}$ and $\mathfrak{5}$ purified by flash chromatography rests on their ¹H-NMR spectra, in particular the C-2 proton. The E isomers show a multiplet at ca. 3.95 ppm for the C-2 proton, an expected value for a proton on an allylic carbon bearing oxygen.⁸ The corresponding Z isomers, however, show two single proton multiplets at 5-6 ppm downfield with no resonance at 3.9 ppm. For example, compound $\mathfrak{5a}$ (n=0) showed multiplets at 5.78 and 5.46 ppm. Off-resonance experiments⁹ showed that the low field proton was coupled to the vinyl carbon at 165.4 ppm and the higher field proton to the oxygen bearing carbon at 59.5 ppm. Similar experiments on $\mathfrak{5b}$ (n=1) showed the vinyl proton to be at 5.57 ppm (m) and the methine proton at 5.68 ppm (bm). Compound $\mathfrak{5c}$ (n=2) showed the vinyl proton at 5.57 ppm (m) and the methine proton at 5.83 ppm (bm). Thus, the methine proton of C-2 in $\mathfrak{5b}$ and $\mathfrak{5c}$ are at lower field than the vinyl protons, the reverse of those in $\mathfrak{5a}$. Similar deshielding has been observed for cis allylic protons in methyl and ethyl cyclobutylideneacetates.¹⁰

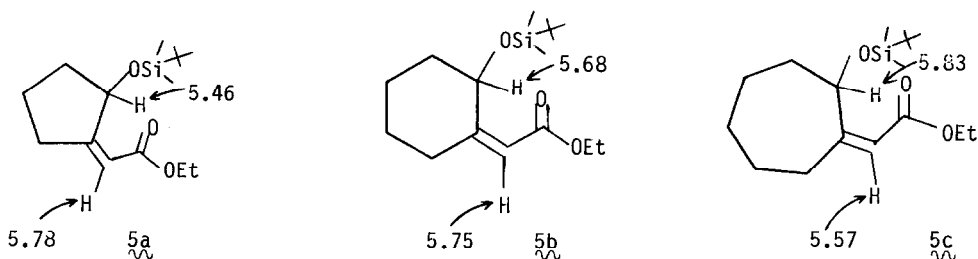


Table I. Products of the Carboethoxymethylenation of 2-(t-Butyldimethylsilyloxy)cycloalkanes.

Acyloin	Method	4 ^a	5 ^a	%Yield ^b
3a (n=0)	A ^c	97	3	52
	B ^d	33	67	64
3b (n=1)	A	96	4	80
	B	14	86	68
3c (n=2)	A	94	6	27
	B	8	92	50

a) Percent composition of the mixture determined by GC on a K20M column. b) Percent yield of isolated material; c) A mixture of the acyloin, 1 (10% excess) and a small amount of benzoic acid refluxed for several hours in toluene; d) A THF solution of LDA treated with Me₃SiCH₂CO₂Et at -78° (0.5h) followed by addition of the acyloin and warming to rt.

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- In two cases where either loss of a phosphorous or a silicon were possible the loss of silicon

to form the vinyl phosphorous species was observed.

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