

production of 0.1-0.2 mmole of corresponding alcohol depending on the reactants, ketones. (It should be noted that the reductive elimination, $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2 \rightarrow \text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2 + \text{H}_2$, is significant at 70°C for 5 hours.)

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Reaction of 1-Ethoxy-1-(Trimethylsiloxy)-2-(Trimethylsilyl) Propene with Aldehydes-Synthesis of α, β -Unsaturated Carboxylic Esters

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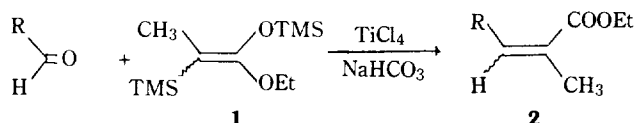
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Peterson olefination is referred to as an elimination reaction of β -hydroxyalkylsilanes¹. Recently, it was reported that 4,5-dihydro-5-methyl-2-(trimethylsiloxy)-3-(trimethylsilyl) furan reacts with aldehydes to produce α -ethylidene- γ -butyrolactones². We have also reported³ that the reaction of bis(trimethylsiloxy)ketene acetal of trimethylsilylacetic acid with carbonyl compounds directly afforded α, β -unsaturated carboxylic acids in moderate to good yields.

Because of our interest in the use of the ketene acetals of α -(trimethylsilyl)carboxylates for the olefination^{4,5} of carbonyl compounds, we have examined the reaction of the ketene acetal of ethyl 2-(trimethylsilyl)propanoate, 1-ethoxy-1-(trimethylsiloxy)-2-(trimethylsilyl)propene (**1**), with aldehydes in the presence of titanium tetrachloride.



The ketene acetal **1** (bp: 70-72°C/12 mmHg)⁶ was prepared in 65% yields by silylating⁷ ethyl 2-(trimethylsilyl)propanoate, which was obtained by the reaction⁸ of ethyl propanoate with trimethylsilyl triflate in the presence of triethylamine. Reaction of this ketene acetal **1** with aldehydes produced the mixture of *cis*- and *trans*- α, β -unsaturated carboxylic esters **2** in moderate yields (see Table). The ratio of *cis*- and *trans*-isomers was esti-

Table 1. Synthesis of α -methyl- α, β -unsaturated Carboxylic Acid Ethyl Esters

R	Yield (%) ^a	E/Z ratio ^b
Phenyl	67	1.4
m-NO ₂ -Ph	70	1
p-NO ₂ -Ph	62	1
p-MeO-Ph	72	1.6
PhCH=CH-	65	1
CH ₃ CH=CH-	68	1
PhCH ₂ CH ₂ -	62	1.2
CH ₃ CH ₂ CH ₂ -	43	1

^aIsolated by silica gel column chromatography. ^bBased on the ¹H-nmr integration data of the olefinic methyl protons of the products.

mated from the proton nmr spectral data and found to be nearly unity (see Table).

A typical procedure for the olefination of aldehydes with the above ketene acetal **1** is exemplified as follows. To a stirred solution (-78°C) of 0.3 ml (3.0 mmol) of benzaldehyde in 15 ml of dry dichloromethane, was added dropwise 10 ml of 1.0 M solution of titanium tetrachloride in dichloromethane followed by a solution of 3.5 mmol of the ketene acetal **1** in 5 ml of dichloromethane. After stirred for 5 hr at -78°C, the mixture was treated with 0.1 ml of 5% aqueous sodium bicarbonate solution and allowed to warm to room temperature.

The mixture was dried over anhydrous magnesium sulfate, filtered and the filtrate concentrated under reduced pressure. Purification of the residue by column chromatography afforded ethyl α -methylcinnamate in 67% yield.

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6. The ^1H -nmr spectral data of this ketene acetal **1** in CDCl_3 is as follows. $\delta = 0.10$ (s, 9H, -TMS), 0.21 (s, 9H, -OTMS), 1.22 (t, $J = 6.0$ Hz, 3H, $-\text{CH}_3$ of ethyl), 1.55 (s, 3H, $-\text{CH}_3$), 3.78 ppm (q, $J = 6.0$ Hz, 2H, $-\text{CH}_2$ of ethyl).
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Adsorption of Benzenethiol on $\gamma\text{-Al}_2\text{O}_3$ supported Ni and Mo; Infrared Spectroscopic Study

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For more than two decades infrared absorption spectroscopy has been successfully applied to the analysis of high surface area materials and related adsorption complexes¹⁻³. However, there is still little understanding of the interactions between sulfur compounds and various dispersed metal particles⁴. In this respect, we have previously applied infrared spectroscopy to the benzenethiol molecule adsorbed on the silver surface⁵. We present in this communication further infrared spectroscopic information on the interaction of benzenethiol with the gamma-alumina supported nickel and molybdenum.

The γ -alumina was supplied by Morton Thiokol Corporation. Benzenethiol purchased from Aldrich Chemical Company was dried under vacuum at the dry-ice temperature and stored in a vacuum bulb which was connected to the conventional vacuum apparatus maintaining a dynamic vacuum of $\sim 10^{-4}$ Nm⁻². The glass part of the vacuum system was heated with a heating tape. The design of the infrared cell was similar to that of Ramamoorthy *et al.*^{6,7} Infrared spectra were recorded with a Perkin-Elmer model 283 spectrophotometer.

Initially, well-ground γ -alumina was impregnated with aqueous solutions of reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The samples, dried in air at 378 K for 72 hrs, were ground to a fine powder and pressed into self-supporting discs, 2 cm in diameter and less than 0.05 cm thick. The pellet was reduced in a furnace under the stream of deoxygenated H_2 at 773 K for 15 hrs, and then transferred into the stainless steel holder, which was suspended by a stainless wire in the infrared cell. The pellet was treated further in the cell with the static pressure of 200 Torr H_2 at 773 K for 3 hrs, after which the hydrogen gas was pumped off and the cell was cooled down to ambient temperature. The details of the infrared measurement were already described

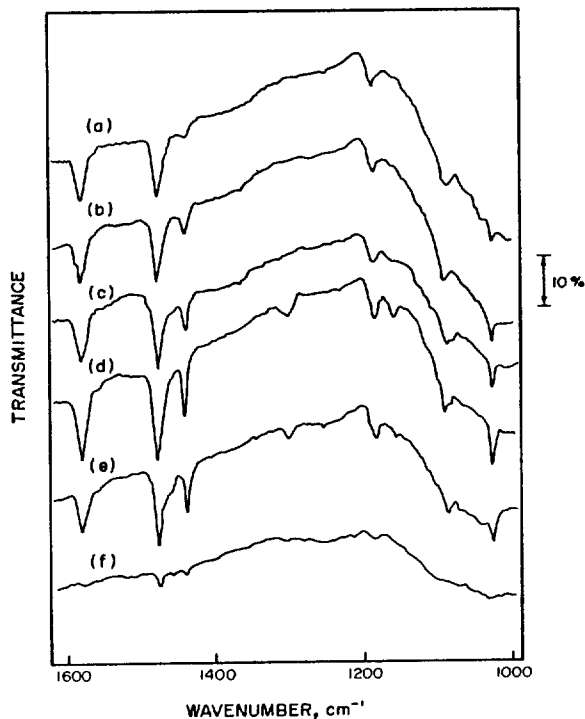


Figure 1. Infrared spectra, in the limited region 1600-1000 cm^{-1} , of benzenethiol adsorbed on 15.0 wt% Ni/ $\gamma\text{-Al}_2\text{O}_3$ at 50(a), 150(b), 500 m Torr(c), and 1 Torr(d), and taken after evacuation for 2 hrs at 298 K(e) and 1 hr at 573 K(f).

in the previous report^{5,7}, and will not be repeated here.

Infrared spectra of benzenethiol adsorbed on 15.0 wt% Ni/ $\gamma\text{-Al}_2\text{O}_3$ (the average particle size of nickel metal