and the fact that CH_2O and $PhCH_2SO_2^-$ are good leaving groups (compared to RO^-) contribute to the facility of S–O cleavage in this system.

Acknowledgment. Discussions with Dr. F. G. Bordwell in the course of this work were especially helpful.

Registry No. 2, 73178-37-7; **3**, 5335-44-4; α-toluenesulfinic acid, 4403-73-0; styrene, 100-42-5; MeOTs, 80-48-8.

Cal Y. Meyers,* Duy H. Hua, Nancy J. Peacock

Department of Chemistry
Southern Illinois University
Carbondale, Illinois 62901

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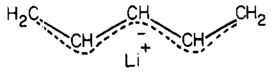
(2,4-Pentadienyl)trimethylsilane: A Useful Pentadienylation Reagent

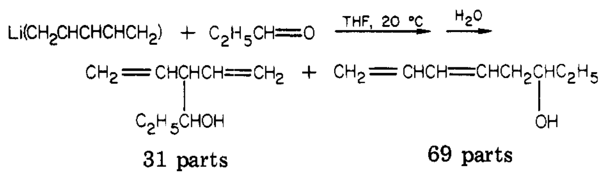
Summary: Pentadienyllithium reacts with trimethylchlorosilane to give (2,4-pentadienyl)trimethylsilane, $Me_3SiCH_2CH{=}CHCH{=}CH_2$, as the exclusive product. This silane reacts with aliphatic and aromatic aldehydes and ketones in the presence of $TiCl_4$ in dichloromethane at −40 °C to give, after hydrolytic workup, exclusively products of the type $RR'C(OH)CH_2CH{=}CHCH{=}CH_2$ in good yield. With α,β-unsaturated carbonyl compounds a $TiCl_4$-induced Diels-Alder reaction of the dienylsilane interferes.

Sir: The pentadienyllithium reagent, I, which is obtained

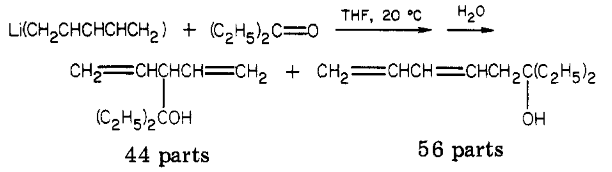


I

by treatment of 1,4-pentadiene with *n*-butyllithium in tetrahydrofuran at −60 °C[1] reacts with aldehydes[2] and ketones[3] to give a mixture of isomeric alcohols, e.g., eq 1 and 2. The addition of this reagent to dialkyl ketones,



$$Li(CH_2CHCHCHCH_2) + C_2H_5CH{=}O \xrightarrow{THF,\ 20\ °C} \xrightarrow{H_2O} \underset{31\ \text{parts}}{\underset{C_2H_5CHOH}{CH_2{=}CH\underset{|}{C}HCH{=}CH_2}} + \underset{69\ \text{parts}}{CH_2{=}CHCH{=}CHCH_2\underset{\underset{OH}{|}}{C}HC_2H_5} \quad (1)$$



$$Li(CH_2CHCHCHCH_2) + (C_2H_5)_2C{=}O \xrightarrow{THF,\ 20\ °C} \xrightarrow{H_2O} \underset{44\ \text{parts}}{\underset{(C_2H_5)_2COH}{CH_2{=}CH\underset{|}{C}HCH{=}CH_2}} + \underset{56\ \text{parts}}{CH_2{=}CHCH{=}CHCH_2\underset{\underset{OH}{|}}{C}(C_2H_5)_2} \quad (2)$$

but not to aliphatic aldehydes, is reversible, and heating the THF solution of the lithium alkoxide mixture formed in the room-temperature reaction for 5 h at 60 °C in some (but not all) cases converts the mixture to a single isomer, the homodienyl alcoholate, $CH_2{=}CHCH{=}CHCH_2CR_2OLi$. Thus, in the case of pentan-3-one, such treatment, followed by hydrolysis, gave $CH_2{=}CHCH{=}CHCH_2C(OH)(C_2H_5)_2$ in 62% yield and none of the other isomer.[3] The corresponding zinc reagent, $CH_2{=}CHCH{=}CHCH_2ZnBr$, reacts with aldehydes in THF at room temperature to give only one of the two isomeric alcohols, $(CH_2{=}CH)_2CHCH(OH)R$,[2] and with ketones under the same conditions to produce, depending on the ketone, one of the two possible isomeric alcohols as the sole product or a mixture of both.[3] Here also, heating the reaction mixture (at 100 °C in diglyme or hexamethylphosphoric triamide in the case of the aldehyde reactions and in THF at 60 °C in the case of the ketone reactions) converted the product mixture to exclusively the $CH_2{=}CHCH{=}CHCH_2$-substituted zinc alkoxide.

We report here the preparation and utilization of an alternate pentadienylation reagent, one which may be prepared in high yield, which is stable on storage as the pure compound, and which reacts with both aldehydes and ketones under mild conditions to give $CH_2{=}CHCH{=}CHCH_2$-substituted alcohols in good yield. We have found that pentadienyllithium, I, reacts with trimethylchlorosilane in THF at room temperature to give exclusively (2,4-pentadienyl)trimethylsilane, $Me_3SiCH_2CH{=}CHCH{=}CH_2$, a stable liquid, in excellent (~85%) yield.[4] This compound, in a sense, is an allylic silane, and thus it seemed possible that it would undergo Lewis acid induced addition to the C=O bond of aldehydes and ketones, which is now well-known as a general (and very useful) reaction of allylic silanes.[5] We have found that this is indeed the case.

In a typical reaction, 6 mmol of an aldehyde (aliphatic or aromatic) is added (under argon, with stirring) to 6 mL of dry dichloromethane; the solution is cooled to −40 °C, 2 mmol of titanium tetrachloride then is added, and the resulting mixture is stirred for 5 min. Subsequently, 4 mmol of $Me_3SiCH_2CH{=}CHCH{=}CH_2$ is added, and the reaction mixture is stirred under argon while it is allowed to warm to 5 °C during the course of 5 min. It then is poured into 25 mL of saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether (3 × 20 mL). The organic layer is dried (K_2CO_3) and distilled at reduced pressure. Isolation of products and yield determinations were accomplished by using gas–liquid chromatography (10% Carbowax 20M). The products were identified by analysis (if new) and ^1H NMR spectroscopy. Results are presented in Table I.

In the reactions with ketones, the ketone and $TiCl_4$ were mixed in dichloromethane at −40 °C as above. This solution then was allowed to warm to room temperature before the $Me_3SiCH_2CH{=}CHCH{=}CH_2$ was added. A 2-h period of stirring at room temperature was followed by workup as above. Results are given in Table I.

It is clear that a new and very useful procedure for the

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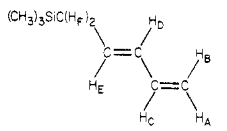
(1) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199, 205 (1967).

(2) F. Gérard and P. Miginiac, *Bull. Soc. Chim. Fr.*, 1924 (1974).

(3) F. Gérard and P. Miginiac, *Bull. Soc. Chim. Fr.*, 2527 (1974).

(4) This compound has a boiling point of 41 °C (36 mm Hg) and an $n^{26}{}_D$ of 1.4570 and is the *E* isomer, according to its 270-MHz ^1H NMR spectrum (in CCl_4): 0.00 (s, 9 H, Me_3Si), 1.59 (d, J_{FE} = 8 Hz, 2 H CH_2), 4.83 (d, J_{AC} = 10.3 Hz, 1 H, H_A), 4.98 (d, J_{BC} = 16.8 Hz, 1 H, H_B), 5.69 (dt, J_{ED} = 15.2 Hz, J_{EF} = 8 Hz, 1 H, H_E), 5.92 (dd, J_{DC} = 10.3 Hz, J_{DE} = 15.2 Hz, 1 H, H_D), 6.28 ppm (ddd, J_{CA} = 10.3 Hz, J_{CB} = 16.8 Hz, J_{CD} = 10.3 Hz, 1 H, H_C).



(5) (a) J. A. Mangravite, *J. Organomet. Chem. Libr.*, 7, 45 (1979) (review); (b) G. M. Rubottom, *ibid.*, 8, 322 (1979) (and earlier annual surveys of "Silicon-Application to Organic Synthesis").

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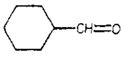
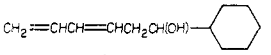
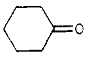
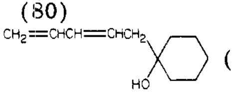
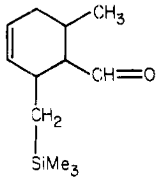
Table I. $TiCl_4$-Induced Pentadienylation of Aldehydes and Ketones by (2,4-Pentadienyl)trimethylsilane

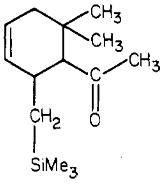
carbonyl compd	product alcohol (% yield)[a]
$CH_3CH_2CH{=}O$	$CH_2{=}CHCH{=}CHCH_2CH(OH)CH_2CH_3$ (79)
$(CH_3)_2CHCH{=}O$	$CH_2{=}CHCH{=}CHCH_2CH(OH)CH(CH_3)_2$ (80)
$(CH_3)_3CCH{=}O$	$CH_2{=}CHCH{=}CHCH_2CH(OH)C(CH_3)_3$ (60)
	 (58)
$C_6H_5CH{=}O$	$CH_2{=}CHCH{=}CHCH_2CH(OH)C_6H_5$ (51)
$(C_2H_5)_2C{=}O$	$CH_2{=}CHCH{=}CHCH_2C(OH)(C_2H_5)_2$ (55)
$(n\text{-}C_3H_7)_2C{=}O$	$CH_2{=}CHCH{=}CHCH_2C(OH)(C_3H_7\text{-}n)_2$ (80)
	 (64)

[a] In a few cases the 250-MHz ^1H NMR spectrum of the product was measured. It was found that the *E* isomer was the sole isomer present. All products were characterized by combustion analysis and by their IR and 60-MHz proton NMR spectra.

preparation of alcohols of the type $CH_2{=}CHCH{=}CHCH_2C(OH)RR'$ is in hand. The yields are fair to good and very likely can be improved when the reactions are carried out on a larger scale. The reaction conditions are quite mild, and the products which are obtained are isomerically pure. This reaction, however, is not readily applicable to the pentadienylation of α,β-unsaturated carbonyl compounds because of a competitive $TiCl_4$-induced Diels–Alder reaction.[6] Thus the reaction of crotonaldehyde with $Me_3SiCH_2CH{=}CHCH{=}CH_2$ in the presence of $TiCl_4$ under these conditions gave a 40% yield of II, while a similar reaction with mesityl oxide produced a mixture of the Diels–Alder adduct (III, 24% yield) and the 1,4-addition product $[CH_2{=}CHCH{=}CHCH_2C(CH_3)_2CH_2C(O)CH_3]$ in 35% yield.



II



III

The mechanism of these pentadienylsilane addition reactions is not known as yet. Allylsilanes react with aldehydes and ketones in the presence of Lewis acids with allylic transposition, e.g., eq 3.[7] Experiments with appropriately substituted (2,4-pentadienyl)silanes will have to be carried out to determine whether or not the reactions proceed with pentadienyl transposition; i.e., is eq 4 applicable? Such studies are intended, as are further investigations of the chemical reactivity of $Me_3SiCH_2CH{=}CHCH{=}CH_2$ and related compounds.

$$Me_3SiCH_2CH{=}CHCH_3 + R_2C{=}O \xrightarrow{TiCl_4} \xrightarrow{H_2O} CH_2{=}CHC(CH_3)HC(OH)R_2 \quad (3)$$

$$Me_3SiCH_2CH{=}CHCH{=}CHCH_3 + R_2C{=}O \xrightarrow{TiCl_4} \xrightarrow{H_2O} R_2C(OH)C(CH_3)HCH{=}CHCH{=}CH_2 \quad (4)$$

Acknowledgment. The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC (Grant No. AF-AFOSR-79-0007) for support of this research. J.P. acknowledges with thanks a leave of absence from the University of Poitiers and the award of a NATO Postdoctoral Fellowship.

Registry No. II, 72952-63-7; III, 72952-64-8; propanal, 123-38-6; 2-methylpropanal, 78-84-2; 2,2-dimethylpropanal, 630-19-3; cyclohexanecarboxaldehyde, 2043-61-0; benzaldehyde, 100-52-7; 3-pentanone, 96-22-0; 4-heptanone, 123-19-3; cyclohexanone, 108-94-1; (*E*)-5,7-octadien-3-ol, 72952-65-9; (*E*)-2-methyl-5,7-octadien-3-ol, 72952-66-0; (*E*)-2,2-dimethyl-5,7-octadien-3-ol, 72952-67-1; (*E*)-1-cyclohexyl-3,5-hexadien-1-ol, 72952-68-2; (*E*)-1-phenyl-3,5-hexadien-1-ol, 72952-69-3; (*E*)-3-ethyl-5,7-octadien-3-ol, 72952-70-6; (*E*)-4-propyl-6,8-nonadien-4-ol, 72952-71-7; (*E*)-1-(2,4-pentadienyl)cyclohexanol, 72952-72-8; (*E*)-(2,4-pentadienyl)trimethylsilane, 72952-73-9; crotonaldehyde, 4170-30-3; mesityl oxide, 141-79-7; (*E*)-4,4-dimethyl-6,8-nonadien-2-one, 72952-74-0.

Dietmar Seyferth,* Jacques Pornet

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Reductive Alkylation of 2,5-Dimethoxybenzoic Acid: A Direct Synthesis of Dihydrofluoren-2-ones

Summary: A two-operation procedure is described for the synthesis of 3,4-dihydrofluoren-2(1*H*)-ones from "reductive alkylation" of 2,5-dimethoxybenzoic acid with benzyl halides, followed by cyclodehydration of the adducts, with concomitant decarboxylation.

Sir: 3,4-Dihydrofluoren-2(1*H*)-ones have been employed as intermediates in syntheses of C-nor-D-homosteroids[1] and have good potential for gibberellin synthesis,[2] but published procedures for their preparation are generally long, are inefficient, and lack flexibility.[1-3] Alkylation of dianion **1** by phenethyl iodides, followed by acid-promoted cyclodehydration of the adducts has provided a very direct and flexible route to tetrahydrophenanthren-2-ones.[4] We now report an adaptation of this alkylation–cyclodehydration strategy to the synthesis of dihydrofluoren-2-ones.

Dianion **1**, prepared by lithium–ammonia reduction of 2,5-dimethoxybenzoic acid, was rapidly alkylated in situ by a range of benzyl bromides, and acids **2a**–**e**[5] were obtained in good yield after removal of the ammonia and careful acidification to pH 5.5. Cyclization of acid **2a** in polyphosphoric acid (2 h, 25 °C) and of acid **2b** in 85%

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(5) All compounds were obtained as crystalline solids, characterized by C and H elemental analysis (±0.3%), accurate mass measurement, and IR, ^1H NMR, and mass spectra. Percentage yields of pure, isolated products are indicated in parentheses.

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