of benzyl diazomethyl sulfone (**5**) [as a mixture with 0.17 g (0.00086 mol) of TsN$_3$ (**4**); see above], and stirring was continued for 2 h. Et$_2$O (150 mL) was added and the solution was washed thoroughly with water, dried (MgSO$_4$), and evaporated, leaving 0.97 g of yellow crystals shown by ^{1}H NMR to be composed of **6** (87 mol %) and **4** (13 mol %). Trituration with hexane removed **4**, 0.17 g (0.00086 mol, 100% recovery), leaving **6**: white crystals; mp 147–150 °C; 0.77 g (0.0023 mol, 88%); mp 151–152 °C (hexane/benzene; EtOH); IR (Nujol) 1380 and 1180 (strong, SO$_3$), 1345 and 1130 (strong, SO$_2$) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.84 (d, J = 8 Hz, 2, o-SO$_3$Ar H), 7.5–7.3 (m, 7, m-SO$_3$Ar H, Ph), 4.66 (s, 2, SCH$_2$O), 4.30 (s, 2, CH$_2$Ph), 2.47 (s, 3, CH$_3$). Anal. Calcd for $C_{15}H_{16}O_5S_2$: C, 52.93; H, 4.74; S, 18.84. Found: C, 52.91; H, 4.85; S, 18.78.

Registry No. 1, 4403-73-0; **2**, 70-23-5; **3**, 73178-38-8; **4**, 941-55-9; **5**, 1588-80-3; **6**, 73178-37-7; p-toluenesulfonic acid, 104-15-4.

---

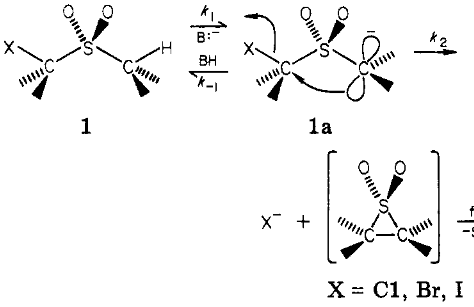
[24] This recrystallized material is the monohydrate: ^{1}H NMR (CD$_3$COCD$_3$) δ 8.57 (s, 3, OH), 7.78 (d, J = 8 Hz, 2, o-SO$_3$Ar H), 7.28 (d, J = 8 Hz, 2, m-SO$_3$Ar H), 2.40 (s, 3, CH$_3$). We did not find it necessary to use anhydrous TsOH (cf. ref 4).

Communications

Unexpected Behavior of an α-Tosyloxy Sulfone Compared with an α-Chloro Sulfone in Base-Induced Reactions

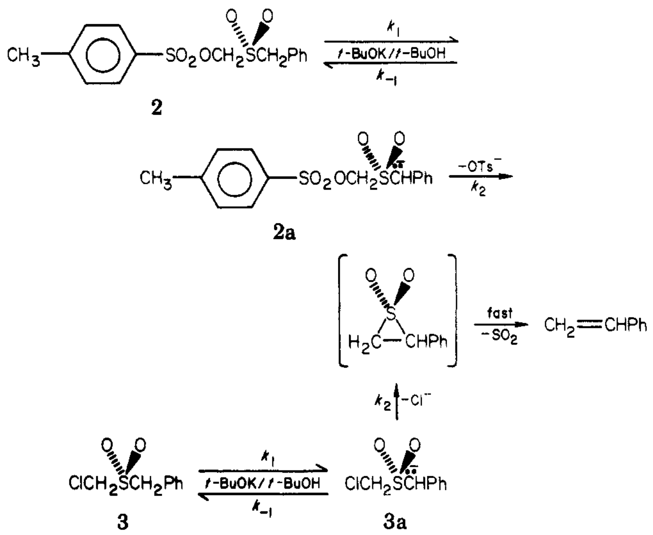
Summary: Unexpectedly, a rate ratio for $k_{\mathrm{OTs}}/k_{\mathrm{Cl}}$ of 0.0011 was observed in 1,3 eliminations of (tosyloxy)methyl benzyl sulfone and chloromethyl benzyl sulfone in t-BuOK/t-BuOH (25 °C), while in MeONa/MeOH (25 °C) neither 1,3 elimination occurred; instead, the α-tosyloxy sulfone underwent facile S–O cleavage to provide methyl p-toluenesulfonate and α-toluenesulfinic acid.

Sir: It is generally believed that base-induced 1,3-elimination reactions of α-halo sulfones (**1**) (Ramberg–Bäcklund reactions) proceed via intramolecular nucleophilic displacement from the semi-W conformation of the α′ carbanion (**1a**) and that the elimination step is rate limiting insofar as halide ion and alkene are formed from **1a** at the same rate, k_2.[1] Although the conventional order of leaving-group reactivity for ionic displacements and eliminations is exhibited in these reactions ($k_{\mathrm{I}} > k_{\mathrm{Br}} > k_{\mathrm{Cl}}$), the values of $k_{\mathrm{I}}/k_{\mathrm{Cl}}$ and $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ are as much as 10 times the expected values, even compared to those of other intramolecular nucleophilic displacements.[2]



Unfortunately, tosylate, one of the most commonly used leaving groups, was not included in these comparative rate studies; indeed, the Ramberg–Bäcklund reaction of α-tosyloxy sulfones has not been previously investigated, primarily because of the difficulty posed by their preparation. In nucleophilic displacement reactions, OTs is a much better leaving group than Cl; e.g., values of $k_{\mathrm{OTs}}/k_{\mathrm{Cl}}$ in the range of 70–3500 were recently reported by Harris and co-workers,[3] while Lowry and Richardson[4] tabulated a range of 60–1500. The successful preparation of (tosyloxy)methyl benzyl sulfone (**2**)[5a] finally afforded the opportunity to investigate the base-induced reactivity of this type of sulfone and to determine the value of $k_{\mathrm{OTs}}/k_{\mathrm{Cl}}$ in these 1,3 eliminations, the results of which might help to evaluate the significance of the surprisingly large values of $k_{\mathrm{I}}/k_{\mathrm{Cl}}$ and $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ previously reported.

In t-BuOK/t-BuOH. We were intrigued to find that in t-BuOK/t-BuOH (6.7 × 10^{-2} N, 25 °C) 1,3 elimination of OTs$^-$ from **2** was much *slower* than 1,3 elimination of Cl$^-$ from the counterpart chloromethyl benzyl sulfone (**3**),[5b] the value of $k_{\mathrm{obsd(OTs)}}/k_{\mathrm{obsd(Cl)}}$ being 0.0011. In each run of the series required for this kinetic study, styrene was



---

[1] These reactions have been reviewed: (a) Bordwell, F. G. In "Organosulfur Chemistry"; Janssen, M. J., Ed.; Interscience: New York, 1967; Chapter 16. (b) Paquette, L. A. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Interscience: New York, 1968; Vol. 1, pp 121–56. (c) *Acc. Chem. Res.* **1968**, *1*, 209–16. (d) *Org. React.* **1977**, *25*, 1–71. (e) Meyers, C. Y.; Matthews, W. S.; Ho, L. L.; Kolb, V. M.; Parady, T. E. In "Catalysis in Organic Syntheses"; Smith, G. V., Ed.; Academic Press: New York, 1977; pp 197–278. (f) Meyers, C. Y. In "Topics in Organic Sulfur Chemistry"; Tišler, M., Ed.; University Press: Ljubljana, Yugoslavia, 1978; pp 207–60.

[2] (a) Bordwell, F. G.; Wolfinger, M. D. *J. Org. Chem.* **1974**, *39*, 2521–5. (b) Bordwell, F. G.; Williams, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 435–9.

[3] Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295–3300. [Rate ratios are estimated and are corrected to reflect reactions at 25 °C: solvolysis in 70% (v/v) aqueous ethanol of p-Y-C$_6$H$_4$CH$_2$(OTs or Cl), Y = NO$_2$, Cl, H, CH$_3$.]

[4] Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; pp 192–3. [Reactions at 25 °C in ethanol: n-C$_3$H$_7$(OTs or Cl) + p-CH$_3$C$_6$H$_4$S$^-$ and C$_2$H$_5$(OTs or Cl) + C$_2$H$_5$O$^-$.]

[5] (a) Mp 151.5–152.5 °C. Synthetic details are described by: Hua, D. H.; Peacock, N. J.; Meyers, C. Y. *J. Org. Chem.*, see companion note in this issue. (b) Mp 102–103 °C [lit. mp 103 °C (Böhme, H.; Fischer, H.; Frank, R. *Justus Liebigs Ann. Chem.* **1949**, *563*, 54–72); lit. mp 103–104 °C (Bordwell, F. G.; Cooper, G. D. *J. Am. Chem. Soc.* **1951**, *73*, 5184–6)].

0022-3263/80/1945-1719$01.00/0 © 1980 American Chemical Society

formed and isolated as the only product, and the material balance (styrene + residual sulfone) was essentially quantitative.[6] The plotted data showed that for **2**, $t_{1/2}$ = 4500 s and $k_{\mathrm{obsd}} = 1.56 \times 10^{-4}$ M^{-1} s^{-1}; for **3**, $t_{1/2}$ = 5 s and $k_{\mathrm{obsd}} = 1.34 \times 10^{-1}$ M^{-1} s^{-1}.

Bordwell has described the kinetic relationship that applies to these reactions with α-halo sulfones, provided that $k_{-1} \gg k_2$:[2b]

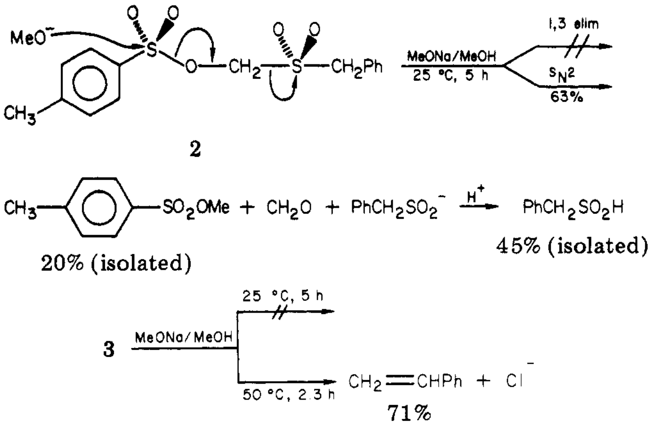
$$k_{\mathrm{obsd}} = k_1 k_2 / k_{-1} = K_{\mathrm{eq}} k_2$$

In *t*-BuOK/*t*-BuOD (9.0×10^{-4} N, 50 °C; 8.0×10^{-5} N, 25 °C), **2** as well as **3** underwent α′ D/H exchange before any 1,3 elimination was detected; the deuterated sulfones were quantitatively isolated.[7] In our reactions, then, $k_{-1} \gg k_2$ and the Bordwell relationship should apply. The fact that OTs and Cl have similar inductive effects[8] suggested that in our reactions K_{eq} for $\mathbf{2} \rightleftharpoons \mathbf{2a}$ and $\mathbf{3} \rightleftharpoons \mathbf{3a}$ should be similar, by analogy with the reasoning used by Bordwell et al., who assigned the same value for K_{eq} to the counterpart α-halo sulfones and calculated the values of k_2 from this and the respective values of k_{obsd}. Their k_2 ratios and k_{obsd} ratios, therefore, were identical.

On this basis, the value for $k_{2(\mathrm{OTs})}/k_{2(\mathrm{Cl})}$ for our reactions would be estimated as ca. 0.001. However, our D/H exchange studies revealed the striking fact that, despite the slightly larger σ_{I} value for OTs than for Cl,[8] **2** underwent exchange much *slower* than **3**. When the rates were adjusted for identical conditions, it was determined that $k_{1(\mathrm{Cl})}/k_{1(\mathrm{OTs})} \simeq 500$. Considering that reprotonation of carbanions **2a** and **3a** in *t*-BuOH is probably diffusion controlled, or at least that $k_{-1(\mathrm{Cl})} \simeq k_{-1(\mathrm{OTs})}$, then K_{eq} = constant × k_1 for these reactions[9] and $k_{2(\mathrm{OTs})}/k_{2(\mathrm{Cl})} = k_{\mathrm{obsd(OTs)}}/k_{\mathrm{obsd(Cl)}} \times k_{1(\mathrm{Cl})}/k_{1(\mathrm{OTs})} \simeq 0.55$.

If the forces responsible for reducing the value of $K_{\mathrm{eq(OTs)}}$ relative to $K_{\mathrm{eq(Cl)}}$ also operate to reduce the value of $k_{2(\mathrm{OTs})}$ relative to $k_{2(\mathrm{Cl})}$ by a similar factor,[10] then the ratio for $k_{\mathrm{obsd(OTs)}}/k_{\mathrm{obsd(Cl)}}$ would be lower than that "expected" by a factor of about 500 × 500, or roughly 10^5. When this factor is applied to the ratio for k_{obsd} in our reactions, a value in the neighborhood of 10^2 emerges, which is within the range of ratios for $k_{\mathrm{OTs}}/k_{\mathrm{Cl}}$ reported for nucleophilic displacement reactions. While the origin of these deviations has yet to be established, our results suggest that the rate comparisons previously reported for 1,3 eliminations of α-chloro, α-bromo, and α-iodo sulfones might require reexamination.

In MeONa/MeOH. The behavior of α-tosyloxy sulfone **2** was also unexpected when we attempted to study these elimination reactions in MeONa/MeOH (4×10^{-1} N).[11] Neither sulfone underwent 1,3 elimination at 25 °C during 5 h. However, while **3** was quantitatively recovered, **2** underwent S_N2 attack *at the sulfonate sulfur* (63%) which led to the formation of methyl *p*-toluenesulfonate and α-toluenesulfinic acid.[12] At 50 °C, **3** underwent 1,3 elimination (71%) in 2.3 h.



The fact that OTs⁻ was not displaced by MeO⁻ indicates that as an α substituent in sulfones, OTs apparently resembles halogen inasmuch as intermolecular S_N2 displacement of halide from α-halo sulfones is energetically very unfavorable.[13] However, nucleophilic attack at sulfonyl sulfur of alkyl tosylates (S–O cleavage) also is generally an unfavorable process compared to displacement of OTs⁻.[14] The facile S–O cleavage of **2** by nucleophilic attack of MeO⁻ under these mild conditions is, therefore, surprising. The ease of this reaction is also reflected by the fact that it proceeded at a rate similar to that of C–O cleavage of the methyl tosylate formed.[15] Undoubtedly, the large electron-withdrawing effect of the sulfone sulfonyl

---

[6] For each reaction, a sclution of 0.0010 mol of sulfone in 150 mL of anhydrous *t*-BuOH (freshly distilled from potassium metal), to which a solution of 0.014 mol of *t*-BuOK (freshly sublimed) in 50 mL of *t*-BuOH was added, was maintainea at 25 °C under N_2 and quenched with water at the end of the required time. The extent of reaction was based on the determination of Cl⁻, residual sulfone, or styrene formed, at least two of these methods always being used to confirm the results; for quantitative determinations with ¹H NMR, the internal standard was CH_2Br_2.

[7] In **2** as well as **3**, α′ D/H exchange was only slightly faster than α D/H exchange; $k_{1(\alpha')}/k_{1(\alpha)} \simeq 1.4$ in both cases.

[8] σ_{I} values (±0.01–0.03 for the halogens): OTs, 0.58 ± 0.10; F, 0.54; Cl and Br, 0.47; I, 0.40. Charton, M. *Prog. Phys. Org. Chem.*, in press. We are grateful to Dr. Charton for providing us with these values in advance of publication. Almost identical values have now been tabulated by: Exner, O. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 10.

[9] Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; Chapter I, especially p 14.

[10] Conformational influences may play an important role here. For example: (a) Conformational factors in the formation and reprotonation of α-sulfonyl carbanions have been described by: Corey, E. J.; Lowry, T. H. *Tetrahedron Lett.* **1965**, 793–801, 803–9. Corey, E. J.; König, H.; Lowry, T. H. *Ibid.* **1962**, 515–20. (b) Conformational preference in the formation of α′-sulfonyl carbanions in Ramberg–Bäcklund reactions has been reported by: Paquette, L. A.; Wittenbrook, L. S. *J. Am. Chem. Soc.* **1968**, *90*, 6783–9. (c) Overall conformational requirements for Ramberg–Bäcklund reactions have been reported by: Bordwell, F. G.; Doomes, E. *J. Org. Chem.* **1974**, *39*, 2526–31. Bordwell, F. G.; Doomes, E.; Corfield, P. W. R. *J. Am. Chem. Soc.* **1970**, *92*, 2581–3. Bordwell, F. G.; Jarvis, B. B.; Corfield, P. W. R. *Ibid.* **1968**, *90*, 5298–9.

[11] Freshly prepared NaOMe (0.020 mol) was added at once to a solution of 0.0020 mol of the sulfone in 50 mL of MeOH maintained under N_2.

[12] About 37% of **2** was recovered and separated from MeOTs in the ether extract of the water-quenched reaction mixture. $PhCH_2SO_2H$ was extracted from the acidified aqueous residue and isolated as waxy crystals whose spectra were superimposable with those exhibited by this acid prepared unequivocally by the method of: Rothstein, E. *J. Chem. Soc.* **1934**, 684–7 [IR (neat) 3700–2100 (two strong, broad bands, OH), 1070 (strong, SO_2H) cm^{-1}; ¹H NMR ($CDCl_3$) δ 8.80 (s, 1 H, OH), 7.60–7.10 (m, 5 H, Ar), 4.00 (s, 2 H, CH_2)].

[13] This unfavorability has been ascribed to the sulfonyl's steric and field effects in blocking incoming nucleophiles (Bordwell et al., ref 5b; Meyers, C. Y. *Tetrahedron Lett.* **1962**, 1125–32; Bordwell, F. G.; Brannen, W. T. *J. Am. Chem. Soc.* **1964**, *86*, 4645–50). However, the same results might be associated with the large electron-withdrawing effect of sulfonyl, which makes the α-halogen atom very "positive"; loss of halogen with a pair of electrons (i.e., as halide) in ionic displacement and elimination reactions in such systems should be energetically unfavorable (see ref 1e, 1f, and Kolb, V. M. Ph.D. Dissertation, Southern Illinois University, Carbondale, IL, 1976).

[14] (a) Kaiser, E. T. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; Chapter 12. (b) Suter, C. M. "Organic Chemistry of Sulfur"; Wiley: New York, 1944; Chapter V.

[15] The S–O cleavage reaction of **2** proceeded to the extent of 63%, while about 67% of the MeOTs so formed underwent C–O cleavage (into Me_2O and NaOTs; not isolated). However, under conditions required for S–O cleavage of neopentyl tosylate with NaOMe, the MeOTs formed was not detected per se because it underwent C–O cleavage too rapidly (Bordwell, F. G.; Pitt, B. M.; Knell, M. *J. Am. Chem. Soc.* **1951**, *73*, 5004).

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

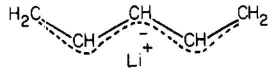
Department of Chemistry
Southern Illinois University
Carbondale, Illinois 62901

Received August 22, 1979

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

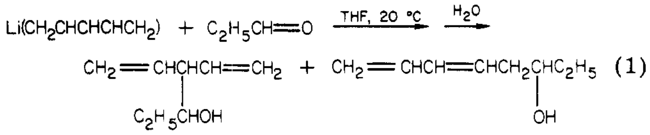
Summary: Pentadienyllithium reacts with trimethylchlorosilane to give (2,4-pentadienyl)trimethylsilane, $Me_3SiCH_2CH{=}CHCH{=}CH_2$, as the exclusive product. This silane reacts with aliphatic and aromatic aldehydes and ketones in the presence of $TiCl_4$ in dichloromethane at −40 °C to give, after 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



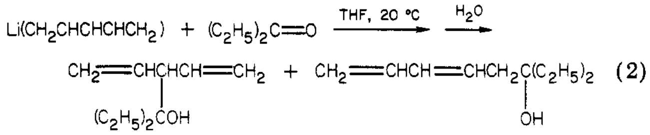
I

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,



$$Li(CH_2CHCHCHCH_2) + C_2H_5CH{=}O \xrightarrow{THF,\ 20\ ^\circ C} \xrightarrow{H_2O} \underset{C_2H_5CHOH}{CH_2{=}CH\overset{|}{C}HCH{=}CH_2} + CH_2{=}CHCH{=}CHCH_2\underset{OH}{CH}C_2H_5 \quad (1)$$

31 parts 69 parts



$$Li(CH_2CHCHCHCH_2) + (C_2H_5)_2C{=}O \xrightarrow{THF,\ 20\ ^\circ C} \xrightarrow{H_2O} \underset{(C_2H_5)_2COH}{CH_2{=}CH\overset{|}{C}HCH{=}CH_2} + CH_2{=}CHCH{=}CHCH_2\underset{OH}{C}(C_2H_5)_2 \quad (2)$$

44 parts 56 parts

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

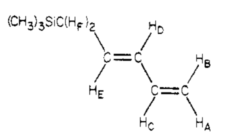
---

(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").

0022-3263/80/1945-1721$01.00/0 © 1980 American Chemical Society