# The Synthesis of Alkenes from Carbonyl Compounds and Carbanions α to Silicon. III. A Full Report and a Synthesis of the Sex Pheromone of Gypsy Moth[1,2]

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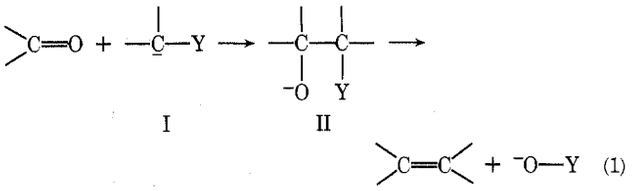
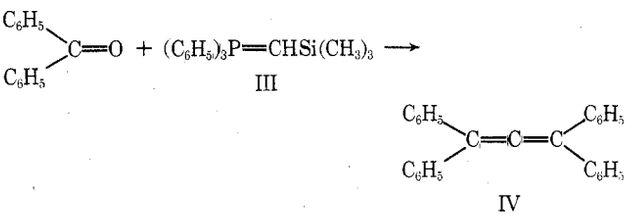
The synthesis of alkenes from carbonyl compounds and carbanions α to silicon is described. Methylenation of carbonyl compounds was accomplished by their reactions with trimethylsilylmethyl carbanion followed by treatment with thionyl chloride or acetyl chloride. Additions of organolithiums to triphenylvinylsilane were used as a method to generate α-silylalkyllithiums which reacted with carbonyl compounds to give the corresponding alkenes. A simple synthesis of the sex pheromone of gypsy moth by this method is reported.

A general method for the synthesis of alkenes can be represented by eq 1. The Wittig reaction[3] (Y = $PR_3^+$) and its many modifications are based on the key role of phosphorus in the carbanion formation as well as the elimination steps. An interesting alternative is Corey's olefin synthesis from sulfinamide derivatives (Y = $SONR_2$).[4] The use of other sulfur derivatives has subsequently been reported.[5,6] This paper describes our studies in the synthesis of alkenes from reaction of carbonyl compounds with carbanions α to silicon (Y = $SiR_3$).



I II (1)

In 1962, Gilman and Tomasi[7] studied the reaction of trimethylsilylmethylenetriphenylphosphorane (III) with benzophenone. They obtained tetraphenylallene (IV), a prod-



III IV

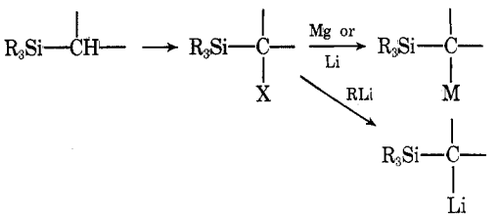
uct which they considered as rather unexpected. It was in 1968 that Peterson,[8] in extending his work on the generation of α-silyl carbanions,[9] demonstrated the alkene synthesis based on eq 1 (Y = $SiR_3$). Thus, the formation of IV from the reaction of III with benzophenone can be viewed as a special case of alkene synthesis *via* α-silyl carbanion.

At about the same time, we initiated our studies on the use of silicon compounds for a variety of organic syntheses.[10-12] This general interest led to a study of the olefination reaction using α-silyl carbanions. We have subsequently reported our preliminary results[1] on this reaction.

## Results and Discussion

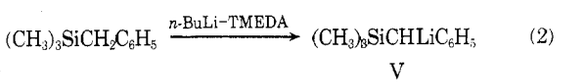
In order for the reaction (eq 1, Y = $SiR_3$) to be a viable method of forming the carbon–carbon double bond, two conditions must be met: first, a facile method of generating carbanions α to silicon must exist; and second, the elimination of the siloxy group from the β-silyl oxyanion adduct (II, Y = $SiR_3$) must occur readily. We shall now examine these two conditions.

**Methods of Generating Carbanions α to Silicon.** One of the simplest ways of preparing α-silyl carbanion is the reaction of α-halosilanes with magnesium[13,14] or lithium. The synthetic utility of this reaction is considerably enhanced by the fact that α-halosilanes can in turn be prepared by free-radical halogenation of alkylsilanes.[15] Alternatively, metal–halogen exchange reactions between α-halosilanes and alkyllithiums can lead also to the formation of α-silylalkyllithium compounds.[15]



M = MgBr or Li

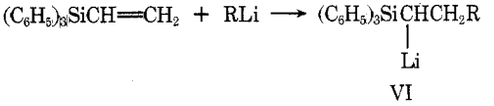
It has recently been shown by Peterson[9,16] that the highly reactive *n*-butyllithium–tetramethylethylenediamine complex (*n*-BuLi–TMEDA) can metalate a number of weakly acidic heteroatom-substituted methanes. This provides a useful method for preparing α-silylakyllithium compounds, especially when the alkyl group is further activated, for example, eq 2. We found that benzyltrimethylsil-



V (2)

ane can also be metalated by alkyllithium in hexamethylphosphoramide (HMPA). However, neither of these methods can be used to generate carbanions on long-chain alkyl carbon moieties. Peterson metalated *n*-butyltrimethylsilane with *n*-BuLi–TMEDA and found that metalation occurred mainly on the methyl carbons.[17] We have also attempted the metalation of *n*-hexyltriphenylsilane and found the metalation not to occur on the alkyl chain.

A solution to this problem is to take advantage of the discovery by Cason and Brooks that alkyllithium can add across the double bond of triphenylvinylsilane to give a metalated silane.[18] Thus, carbanions of general structure VI can be generated by the reaction of equimolar quantities of organolithium compound and triphenylvinylsilane in ether.



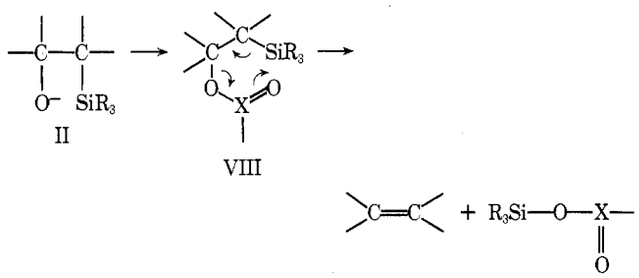
VI

The usefulness of this method may be further extended by the recent report of Buell, *et al.*,[19] which indicated that Grignard reagents can also add to activated vinylsilanes, for example, eq 3. It is therefore apparent that with a judi-

$$(CH_3)_2SiCH{=}CH_2 + RMgX \longrightarrow (CH_3)_2SiCH(CH_2R)MgX \quad (3)$$
$$OC_2H_5 \qquad\qquad OC_2H_5$$
VII

cious choice of one of the above methods, $\alpha$-silyl carbanions of diverse structures can be synthesized.

**Elimination of the $\beta$-Silyl Oxyanion Adduct II.** The formation of alkene and siloxy anion from the adduct II was found to occur spontaneously when the alkene was nonterminal. Although there is no direct evidence, decomposition is assumed to proceed through a four-membered cyclic transition state.[20,21] When the alkene was terminal, the lithium or magnesium salt of the adduct II did not decompose under the reaction conditions. On working up, the $\beta$-silylcarbinol can be obtained in good yield. While $\beta$-elimination of silylcarbinol under acidic conditions may be effected,[22] the resultant alkene may isomerize and thus it cannot be considered as a good synthetic method. Peterson[8] overcame this problem by converting the $\beta$-silylcarbinol to the corresponding sodium salt, which would then decompose in refluxing tetrahydrofuran to the alkene. He attributed the difference to the more ionic character of the sodium salt. We found that a satisfactory solution to this problem is to treat the adduct II *in situ* with either thionyl chloride or acetyl chloride. The alkene can in general be formed in good yield without contamination of other double-bond isomers. The reaction is assumed to proceed *via* the derivative VIII.[24]




**Methylenation.** Trimethylsilylmethylmagnesium chloride or trimethylsilylmethyllithium was prepared in ether by reported procedures.[13-15] The appropriate carbonyl compound in ether was added and the reaction mixture was refluxed for 1–2 hr. To the reaction mixture, a slight excess of thionyl chloride or acetyl chloride was added and stirred for 1 hr. After working up, the product could be isolated in moderately good yield (Table I). The terminal alkene thus obtained was generally free from contamination with other double-bond isomers. Also, an isolated double bond in other parts of the molecule was not affected. Because of the ready availability of chloromethyltrimethylsilane and thus the corresponding organometallics, this method offers an attractively simple way of converting carbonyl compounds to the corresponding methylene derivatives. In certain cases, it is superior to the Wittig reaction.[23]

This method of methylenation is applicable to $\alpha,\beta$-unsaturated ketones. $\beta$-Ionone was converted in reasonable yield to the corresponding methylene derivative. On the other hand, methylenation of cyclohex-2-enone gave only a 20% yield of 3-methylenecyclohexene. It seemed that 1,4-addition as well as polymerization predominated in this case.

**Benzylidene Formation.** The trimethylsilylbenzyl carbanion V was prepared from trimethylbenzylsilane and *n*-

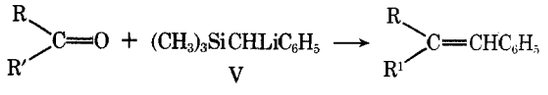


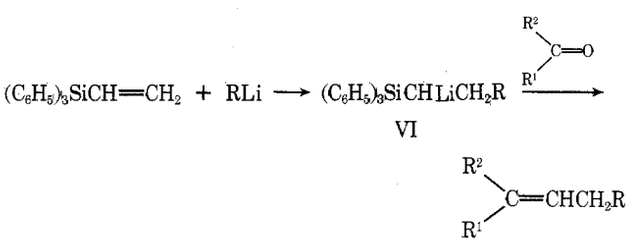

**Table I**
**Methylenation of Carbonyl Compounds**

| Carbonyl compd | Organometallic reagent used | Decompn agent used | Yield of olefin,[a] % |
|---|---|---|---|
| 2-Methylhept-2-en-6-one | $(CH_3)_3SiCH_2MgCl$ | $SOCl_2$ | 57 |
| 2-Methylhept-2-en-6-one | $(CH_3)_3SiCH_2Li$ | $SOCl_2$ | 53 |
| Cyclohexanone | $(CH_3)_3SiCH_2MgCl$ | $CH_3COCl$ | Quant[b] |
| $\beta$-Ionone | $(CH_3)_3SiCH_2MgCl$ | $CH_3COCl$ | 52 |
| Cyclohex-2-enone | $(CH_3)_3SiCH_2Li$ | $CH_3COCl$ | 20[c] |

[a] Isolated yield except where noted. [b] Determined by nmr. [c] By comparison with authentic sample prepared according to W. J. Barley and J. C. Goossens, *J. Amer. Chem. Soc.*, 78, 2804 (1956).

butyllithium or methyllithium in HMPA. The existence of the carbanion was demonstrated by quenching the mixture with $D_2O$ and was recovered and found to be >85% deuterated at the benzyl group by nmr. The red carbanion solution was treated with the appropriate carbonyl compound. The mixture, after stirring at room temperature, gave the alkene directly in reasonable yield. We have obtained stilbene from benzaldehyde and 1,2-diphenylpropene from acetophenone. In both these cases as well as subsequent ones, where *E–Z* isomerism is possible, both isomers were obtained. We have not examined the effect of solvents or additives on the ratio of isomers.[24]

**Substituted Ethylidenes.** Carbanions of structure VI were generated by the reaction of equimolar quantities of



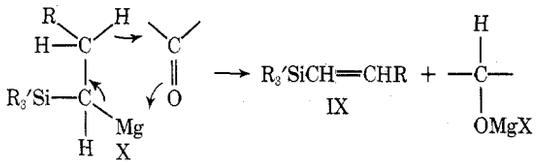

organolithium and triphenylvinylsilane in ether.[18] Quenching experiments with $D_2O$ indicated that the carbanion deteriorated on standing, since the percentage of deuterium incorporation in the isolated substituted ethyltriphenylsilane decreased rapidly. To the carbanion solution, the appropriate carbonyl compound was added. The mixture, on working up, gave the corresponding alkene in good yield. We have prepared 1-phenyl-1-heptene, 2-methyl-6-heptadecene, 2,6-dimethyl-2,6-dodecadiene, and 1,3-diphenylpropene by this method (Table II).

We have also examined the efficacy of the $\alpha$-silylalkylmagnesium halide (VII), prepared by the addition of Grignard reagent ot an activated vinylsilane, in this olefination. In agreement with the report by Buell, *et al.*,[19] we found that isopropylmagnesium chloride indeed added to dimethylvinylethoxysilane to generate the corresponding adduct VII (R = *i*-Pr). When benzaldehyde was added to a solution of adduct VII, a reaction occurred. The reaction mixture was quenched with acetyl chloride. On working up, the products were found to be benzyl acetate and tetramethylbis[1-(3-methyl-1-(*E*)-butenyl)]disiloxane (IX). There was no trace of product which could be identified as due to the addition of the carbonyl compound to the Grignard reagent VII. While the formation of benzyl alcohol (as the acetate) is not entirely unexpected and can be accounted for satisfactorily by the usual hydride transfer mechanism, we are nevertheless surprised by the dominance of reduction over the addition process. This seems to be the common feature of VII on reaction with carbonyl

**Table II**
**Olefination of Carbonyl Compounds by α-Silyl Carbanions Formed from Addition of Organolithium to Vinyltriphenylsilane**

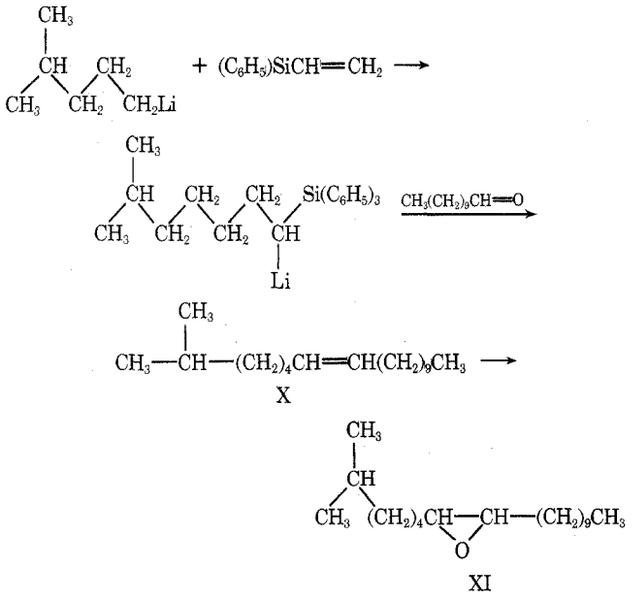
| Carbonyl compd | Organolithium | α-Silyl carbanion | Product | Yield, % (E:Z) |
|---|---|---|---|---|
| $C_6H_5CHO$ | *n*-BuLi | $CH_3(CH_2)_2CHSi(C_6H_5)_3$ | 1-Phenyl-1-heptene[a] | 50(1:1) |
| $CH_3(CH_2)_9CHO$ | 3-Methylbutyllithium | $(CH_3)_2CH(CH_2)_3CHSi(C_6H_5)_3$ | 2-Methyl-6-heptadecene[b] | 69(1:1) |
| 2-Methylhept-2-en-6-one | *n*-BuLi | $CH_3(CH_2)_4CHSi(C_6H_5)_3$ | 2,6-Dimethyl-2,6-dodecadiene[c] | 34(1:1) |
| $C_6H_5CHO$ | $C_6H_5Li$ | $C_6H_5CH_2CH-Si(C_6H_5)_3$ | 1,3-Diphenylpropene[d] | 40(1:1) |
| $CH_3(CH_2)_9CHO$ | 4-Methylpentyllithium | $(CH_3)_2CH(CH_2)_4CHSi(C_6H_5)_3$ | 2-Methyl-7-octadecene[e] | 50(1:1) |

[a] Reference 34. [b] Bp 111–112° (0.35 nm); nmr ($CDCl_3$) 0.95 (m, 9 H), 1.4 (broad s, 20 H), 2.05 (m, 5 H), 5.45 ppm (m, 2 H); mass spectrum $M^+$ 252. [c] Bp 58–60° (0.1 mm); nmr (neat) 0.95 (t, 3 H), 1.25 (broad, 5 H), 1.58 and 1.62 (s, 9 H), 2.0 (broad, 6 H), 5.05 (t, 2 H); mass spectrum $M^+$ 194. [d] Spectroscopic data in agreement with literature values: E.K. Ramino and W.A. Bonner, *J. Org. Chem.*, **31**, 396 (1966). [e] See Experimental Section.



compounds which we have examined. Thus, acetophenone and 2-methylhept-2-en-6-one also gave the corresponding alcohols, which were characterized as the acetates. The other products in these reactions were the disiloxanes IX. The ease of hydride transfer may be a reflection of the "β effect" of silicon.[25,26] It is known, for example, that carbene insertion into alkylsilanes occurred exclusively at the β position.[27]

**Sex Pheromone of Gypsy Moth.** The structure of the sex pheromone of gypsy moth (Disparlure) has recently been identified as *cis*-7,8-epoxy-2-methyloctadecane[28] (XI).



A simple synthesis of this compound was achieved by the silicon method.[29] 4-Methylpentyllithium, prepared from the corresponding chloro compound, was allowed to react *in situ* with triphenylvinylsilane. Undecanal was added to the reaction mixture. On working up, a 50% yield of 2-methyl-7-octadecenes (X) was obtained. This was converted to the corresponding epoxides by *m*-chloroperbenzoic acid in quantitative yield. The epoxides, on nmr analysis, were found to be a 1:1 mixture of cis and trans isomers. They were identical in all respects with an authentic mixture.[30] Under field test, they showed the appropriate biological activities.[30]

## Experimental Section

All reactions were conducted in glassware that was dried, either overnight in an oven at 130° or by flame drying under nitrogen. The reactions were all conducted under a nitrogen atmosphere up to the hydrolysis step. Stirring was done with magnetic stirring bars unless otherwise noted. HMPA and TMEDA were distilled and stored over molecular sieves. Absolute diethyl ether was stored over sodium ribbon and used without further purification. Boiling and melting points were uncorrected. Spectra were recorded on the following instruments: nmr, Varian T-60 and A-60; ir, Perkin-Elmer 257; uv, Unicam SP-800; mass spectra, AEI MS-902 at 70 eV. Vpc was done on a Hewlett-Packard 7570 gas chromatograph and the columns were 12 ft of UCW-98 or SE-30 unless otherwise noted. Column chromatography was carried out with silica gel, mesh size 100–200, by Grace.

**I. Methylenation. A. Reaction of 2-Methylhept-2-en-6-one–Trimethylsilylmethylmagnesium Chloride Adduct with Thionyl Chloride.** To a stirred solution of trimethylsilylmethylmagnesium chloride, made from 2.5 g (0.02 mol) of chloromethyltrimethylsilane and 0.5 g (0.02 mol) of magnesium turnings in 25 ml of diethyl ether, was added a solution of 2.5 g (0.02 mol) of 2-methylhept-2-en-6-one in 5 ml of diethyl ether.

The addition was done dropwise at such a rate that a gentle reflux of the mixture was maintained. The reaction mixture was refluxed with continued stirring. After 3 hr, the reaction mixture was cooled in an ice bath and 1.8 ml (0.025 mol) of thionyl chloride was added. The ice bath was removed and stirring was continued at room temperature. After 1 hr, the reaction mixture was hydrolyzed by the dropwise addition of a saturated ammonium chloride solution. The coagulated solid was filtered off and washed with diethyl ether. Distillation of the combined filtrate–washings gave 1.4 g (57%) of 2,6-dimethyl-1,5-heptadiene as a clear, colorless liquid: bp 135–136°; $n^{23}D$ 1.4385 [lit.[31] bp 69–70° (80 mm), $n^{18}D$ 1.4461]; nmr (neat) 1.52 (s, 3 H), 1.62 (s, 6 H), 2.06 (m, 4 H), 4.64 (s, 2 H), 5.06 ppm (m, 1H); ir (neat) 3080 (w), 2970, 2925 (s), 2865 (m), 1660 (m), 1460, 1452, 1390 (m), 895 $cm^{-1}$ (s).

**B. Reaction of β-Ionone–Trimethylsilylmethylmagnesium Chloride Adduct with Acetyl Chloride.** To a stirred solution of trimethylsilylmethylmagnesium chloride, made from 1.25 g (0.01 mol) of chloromethyltrimethylsilane and 0.25 g (0.01 mol) of magnesium turnings in 15 ml of diethyl ether, was added dropwise 1.9 g (0.01 mol) of β-ionone in 5 ml of diethyl ether. After the mixture was refluxed with stirring for 3 hr, the reaction mixture was allowed to cool to room temperature and 0.8 g (0.01 mol) of acetyl chloride was added to the stirred solution. Stirring was continued at room temperature for 1 hr, whence the reaction mixture was hydrolyzed by a saturated ammonium chloride solution. The coagulated solid was filtered off and washed with diethyl ether. The combined filtrate–washings were evaporated to remove the solvent to give 2.0 g of pale brown oil. High-vacuum distillation of this oil afforded 1.1 g (52%) of olefin as a clear colorless liquid:[33] bp 46–47° (0.05 mm) [lit.[32] bp 113–115° (15 mm)]; $n^{21}D$ 1.5147; uv (etha-

**Table III**

| Reaction time,[a] hr | Wt crude, g | % starting material left[b] | Wt product recrystd, g | % yield | Mp,[c] °C | Abs[d] at 2160 cm$^{-1}$ |
|---|---|---|---|---|---|---|
| 1.25 | 0.35 | 30.3 | 0.20 | 60 | 74–76 | 0.29 |
| 1.75 | 0.40 | 29.2 | 0.20 | 60 | 74–77 | 0.275 |
| 2.25 | 0.35 | 27.8 | 0.20 | 60 | 74–77 | 0.26 |
| 3.25 | 0.40 | 25.2 | 0.15 | 45 | 73–76 | 0.20 |
| 4.25 | 0.25 | 25.5 | 0.10 | 42 | 73–77 | 0.083 |

[a] Includes time for addition. [b] Calculated from the relative integration per olefinic *vs.* aromatic proton, respectively. [c] Reported mp 77–78° for *n*-hexyltriphenylsilane. [d] For a concentration of 250 mg/cc. Value given is corrected for absorption (0.030) observed for nondeuterated *n*-hexyltriphenylsilane.

nol) 228 nm (ε 10,600), 262 (10,200) [lit.[32] 228 nm (ε 633), 262 (611)]; nmr ($CCl_4$) 0.96 (s, 6 H), 1.6 (s, 3 H), 1.82 (s, 3 H), 2.28 (m, 6 H), 4.8 (s, 2 H), 5.95 ppm (s, 2 H); ir (neat) 3100 (w), 2930, 2940, 2880 (s), 2840 (m), 1612, 1460, 1393, 1381, 1370 (m), 985, 900 cm$^{-1}$ (s).

**II. Benzylidene Formation. Reaction of Trimethylsilylbenzyl Anion with Benzaldehyde.** To a stirred, ice-cooled solution of 1.64 g (0.1 mol) of benzyltrimethylsilane in 10 ml of HMPA was added 0.01 mol of methyllithium in pentane. Stirring was continued for 2 hr, when a solution of 1.1 g (0.01 mol) of benzaldehyde in 5 ml of diethyl ether was added. The ice bath was removed and the reaction mixture was stirred at room temperature. After 1 hr, the mixture was poured into 25 ml of ice-cooled 1% hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with two 10-ml portions of ether. The combined ether extracts was washed with water, dried over sodium sulfate–sodium carbonate, and then film evaporated to give 2.4 g of brown liquid. Recrystallization of the crude material from ethanol gave 0.6 g of *trans*-stilbene, mp 124–125°. The filtrate was evaporated and distillation of the resulting liquid gave 0.3 g of *cis*-stilbene, bp 105–106° (5 mm) (total yield of stilbene, 50%).

**III. Substituted Ethylidenes. A. Quenching Experiments. Reaction of *n*-Butyllithium with Triphenylvinylsilane.** To a stirred solution of 2.5 ml (0.005 mol) of *n*-butyllithium–hexane was added a solution of 1.43 g (0.005 mol) of triphenylvinylsilane in 50 ml of diethyl ether dropwise over 1.25 hr. At the completion of addition, 10 ml of the reaction mixture was withdrawn and added to 2 ml of frozen $D_2O$. The ether layer was separated, dried over sodium sulfate, and evaporated to give *n*-hexyltriphenylsilane. Similar samples were taken at intervals of additional stirring of 0.5, 1, 2, and 3 hr. The nmr ($CCl_4$) of the crude product was recorded in each instance. The samples were then purified by recrystallization (absolute ethanol) and dried, and the ir ($CCl_4$) was recorded from 1900 to 2800 cm$^{-1}$ for C–D absorption (~2160 cm$^{-1}$). The results are given in Table III. The 1.25-hr sample showed 77% D incorporation by mass spectrometry.

**B. Olefination. Reaction of 1-Triphenylsilyl-1-hexyllithium with Benzaldehyde.** To a stirred solution of 2.2 ml (0.005 mol) of *n*-butyllithium–ether was added a solution of 1.43 g (0.005 mol) of triphenylvinylsilane in 50 ml of diethyl ether dropwise over 1.75 hr. After 5 min, to the stirred mixture was added 0.53 g (0.005 mol) of benzaldehyde over 15 min. The reaction mixture was stirred under reflux for 30 hr. The cooled mixture was poured into 50 ml of 10% aqueous ammonium chloride solution and the ether layer was separated. The aqueous layer was extracted with two 25-ml portions of ether. The ether fractions were combined, dried over sodium sulfate, and evaporated to give 2.2 g of a mixture of pale yellow oil and white solid. Treatment with *n*-pentane and filtration afforded 0.6 g of triphenylsilanol, mp 156–157.5°. The filtrate was evaporated to an oil, which was distilled to give 0.4 g (46%) of 1-phenylheptene (1:1 *E*:*Z* by vpc): bp 46° (0.01 mm) [lit.[34] bp 90–94° (3–4 mm)] ir (neat) 2910 (w), 2830 (s), 2770 (m), 1610 (w), 1502 (m), 1478, 1458 (m), 973 (s), 772 (m), 747 (s), 704, 697 cm$^{-1}$ (s); nmr ($CCl_4$) 0.9 (t, 3 H), 1.48 (m, 6 H), 2.2 (m, 2 H), 6.13 (m, 2 H), 7.23 ppm (s, broad, 5 H); mass spectrum M$^+$ *m/e* 174.

**C. Sex Pheromone of Gypsy Moth. 1. Reaction of 1-Triphenylsilyl-6-methylheptyllithium with Undecanal.** To a stirred, ice-cooled solution of 13 ml (0.01 mol) of 4-methylpentyllithium and 1.2 g (0.01 mol) of tetramethylethylenediamine was added a solution of 2.8 g (0.01 mol) of triphenylvinylsilane in 50 ml of diethyl ether dropwise over 3 hr. The reaction mixture was stirred for 30 min more and a solution of 1.6 g (0.01 mol) of undecanal in 10 ml of diethyl ether was added over 15 min. The ice bath was removed and the mixture was refluxed for 45 hr. The cooled reaction mixture was poured into 50 ml of 10% aqueous ammonium chloride solution, the ether layer was separated, and the aqueous layer was extracted with two 25-ml portions of ether. The combined ether extracts were washed successively with 1 *N* hydrochloric acid and water, and dried over sodium sulfate–sodium carbonate. The dried ether solution was evaporated to give 4.75 g of a mixture of white solid and liquid. The mixture was treated with 50 ml of *n*-hexane, cooled, and filtered to give 1.02 g of triphenylsilanol, mp 149–153°. The filtrate was film evaporated to give 3.57 g of light brown liquid, which was column chromatographed (hexane and hexane–chloroform) to give 1.82 g of crude product and 0.46 g (0.0016 mol) of unreacted triphenylvinylsilane. Distillation of the crude material gave 1.2 g (50%, based on silane) of 2-methyl-7-octadecene (*E*–*Z* mixture): bp 101–103° (0.09 mm); $n^{25}$D 1.4444; nmr ($CDCl_3$) 0.93 (m, 9 H), 1.33 (s, broad, 22 H), 2.01 (m, 5 H), 5.46 ppm (m, 2 H); ir (neat) 3002 (w) 2920, 2862, 2843 (s), 1468 (m), 1386, 1380, 1369 (w), 970 (m), 728 cm$^{-1}$ (w); mass spectrum M$^+$ *m/e* 266.[28]

**2. Biological Activities.** Two compounds, 6,7-epoxy-2-methylheptadecane (cis:trans 1:1) and 7,8-epoxy-2-methyloctadecane (cis:trans 1:1), synthesized by the silicon method, were tested for activity toward gypsy moth[30] with the following results (Table IV). Insects trapped were the total in three replecates. Chemicals were formulated with 2 mg keeper/trap.

**Table IV**

| Compd | μg/trap | Insects trapped |
|---|---|---|
| 6,7-Epoxy-2-methylheptadecane | 20 | 23 |
| | 2 | 16 |
| | 0.2 | 6 |
| 7,8-Epoxy-2-methyloctadecane | 20 | 40 |
| | 2 | 30 |
| | 0.2 | 25 |
| Disparlure (85% cis) | 20 | 71 |
| | 2 | 36 |
| | 0.2 | 28 |

**D. Reaction of Benzaldehyde–1-(Dimethylethoxysilyl)-3-methylbutylmagnesium Chloride Adduct with Acetyl Chloride.** A solution of isopropylmagnesium chloride [made from 1.57 g (0.2 mol) of isopropyl chloride and 0.5 g (0.2 mol) of magnesium turnings in 5 ml of diethyl ether] and 2.6 g (0.2 mol) of vinyldimethylethoxysilane was refluxed with stirring for 20 hr. To the stirred, cooled (to room temperature) reaction mixture was added a solution of 2.1 g (0.02 mol) of benzaldehyde in 5 ml of diethyl ether dropwise over 15 min. After stirring for 1 hr more, 1.45 ml (0.02 mol) of acetyl chloride was added and the mixture was stirred at reflux. After 5 hr, heating was discontinued and the mixture was left standing at room temperature. After 43 hr, the reaction mixture was hydrolyzed by dropwise addition of saturated ammonium chloride solution. The combined filtrate–washings were evaporated to give 4.5 g of brown liquid. Attempted distillation gave mixtures as evidenced by vpc. Further purification by column chromatography (hexane and hexane–$CHCl_3$ mixtures) gave 1.3 g (50%, based on silane used) of tetramethylbis[1-(3-methyl-1-(*E*)-butenyl)]disiloxane [bp 67.5° (6 mm); nmr ($CCl_4$) 0.13 (s, 6 H), 0.96 (d, $J$ = 7 Hz, 6 H), 2.11 (m, 1 H), 5.17 (d, $J$ = 17.5 Hz, 1 H), 5.73 ppm (d of d, $J$ = 17.5 and 5 Hz, 1 H); ir (neat) 2960 (vs), 2876 (s), 1630 (s), 15 (m), 1415, 1388, 1370, 1325 (w), 1260 (vs), 1225, 1175 (w), 1080 (s), 1050 (vs), 995 (s), 840, 805, 790 cm$^{-1}$ (vs); mass spectrum M$^+$ *m/e* 270] and 1.5 g (50%) of benzyl acetate, bp 82–83° (5 mm).

**Registry No.**—2-Methylhept-2-en-6-one, 110-93-0; chloromethyltrimethylsilane, 2344-80-1; thionyl chloride, 7719-09-7; 2,6-dimethyl-1,5-heptadiene, 6709-39-3; β-ionone, 14901-07-6; acetyl chloride, 75-36-5; β-ionone methylene derivative, 52260-01-2; benzyltrimethylsilane, 770-09-2; benzaldehyde, 100-52-7; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; triphenylvinylsilane, 18666-68-7; *n*-hexyltriphenylsilane, 18751-09-2; (*E*)-1-phenylheptene, 10201-58-8; (*Z*)-1-phenylheptene, 10201-59-9; undecanal, 112-44-7; 1-triphenylsilyl-6-methylheptyllithium, 52260-02-3; (*Z*)-2-methyl-7-octadecene, 35354-39-3; (*E*)-2-methyl-7-octadecene, 40302-56-5; *cis*-6,7-epoxy-2-methylheptadecane, 52260-03-4;

*trans*-6,7-epoxy-2-methylheptadecane, 52260-04-5; *cis*-7,8-epoxy-2-methyloctadecane, 29804-22-6; *trans*-7,8-epoxy-2-methyloctadecane, 42991-03-7; vinyldimethylethoxysilane, 5356-83-2; isopropyl chloride, 75-29-6; tetramethylbis[1-(3-methyl-1-(*E*)-butenyl)]disiloxane, 52260-05-6.

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# Notes

## Products and Rates of Reaction of Trifluoroacetic Anhydride with Aldehydes. A Nuclear Magnetic Resonance Study


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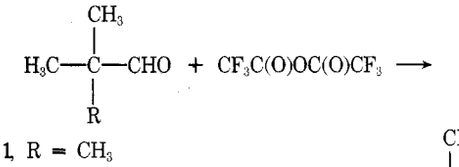
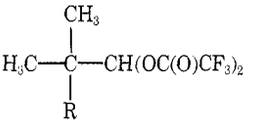
The reaction of carboxylic acid anhydrides with carbonyl compounds has been known since the beginning of this century.[1] These reactions appear to involve initial formation of a *gem*-bisester, $RC[OC(O)R']_2$, but may proceed to form other compounds, including enol esters.[2] While studies[3] have appeared on the synthetic aspects of this reaction, comparatively little has been done to elucidate the mechanism(s) of these reactions. The most extensive study to date appears to be that of Mazur and coworkers[4] on the reaction of ketones with trichloroacetic anhydride.

The broad application of trifluoroacetic anhydride (TFAA) to synthetic organic chemistry,[5] the greater reactivity of TFAA compared to trichloroacetic anhydride, TCAA, and the suitability of TFAA as an nmr solvent have prompted our investigation into the reaction(s) of TFAA with carbonyl compounds.[6] This report deals with the reaction of nonenolizable aliphatic and aromatic carboxaldehydes with TFAA.

**Aliphatic Carboxaldehydes.** Nonenolizable aliphatic carboxaldehydes were selected for study because they could not readily lose trifluoroacetic acid and would, therefore, lead to stable adducts.[7] The aldehydes selected for examination were 2,2-dimethylpropanol (pivalaldehyde, **1**), 2-methyl-2-phenylpropanal (**2**), and 2-methyl-2-*p*-methoxyphenylpropanal (**3**). These aldehydes reacted with excess TFAA to yield the anticipated 1,1-bis(trifluoroacetoxy)-2,2-dimethylpropane (**4**), 1,1-bis(trifluoroacetoxy)-2-methyl-2-phenylpropane (**5**), and 1,1-bis(trifluoroacetoxy)-2,2-dimethylpropane (**4**), 1,1-bis(trifluoroacetoxy)-tively. No other products could be detected by nmr; these products appear to be stable indefinitely in TFAA at 25°.



**1**, R = $CH_3$
**2**, R = $C_6H_5$
**3**, R = *p*-$CH_3OC_6H_4$



**4**, R = $CH_3$
**5**, R = $C_6H_5$
**6**, R = *p*-$CH_3OC_6H_4$

The rate of adduct formation was followed by integration of both the decreasing carboxaldehyde resonance and the new methine resonance in the product. The reaction exhibited pseudo-first-order behavior. The half-lives, $t_{1/2}$, for the reactions are similar but suggest some steric hindrance to adduct formation in going *from* **1** *to* **2** and **3** ($t^1_{1/2}$ = 20 min, $t^2_{1/2}$ = 125 min, $t^3_{1/2}$ = 130 min).[8]

The pmr spectra of these adducts are included in Table I. It is noteworthy that adduction "shifts" the aldehydic resonance upfield by *ca.* 2 ppm, since this, when necessary, can serve as a useful diagnostic tool for the presence of the carboxaldehyde group.

**Aromatic Carboxaldehydes.** Benzaldehydes, like the nonenolizable aliphatic carboxaldehydes, react with TFAA to produce *gem*-bis(trifluoroacetates). Again, these esters