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SYNTHESIS AND DIELS–ALDER REACTIONS OF E-1-TRIMETHYLSILYLBUTA-1,3-DIENE

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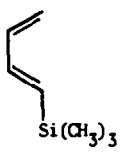
Abstract—A novel synthesis of E-1-trimethylsilylbuta-1,3-diene (1) has been achieved, and its Diels–Alder reactions with maleic anhydride, diethyl maleate, dimethyl fumarate, methyl propiolate, acrolein and acrylonitrile have been investigated. The structures of the products were studied to determine the stereoselectivity and regioselectivity of the reactions of this diene. In all cases with monosubstituted dienophiles the silyldiene 1 afforded the 1,3-disubstituted isomer (*meta* isomer) as the predominate regioisomer.

In the course of synthetic studies leading to the synthesis of crotepoxide,[1] several Diels–Alder reactions of E-1-trimethylsilylbuta-1,3-diene (1) have been examined as a model system for E,E-1-acetoxy-4-trimethylsilylbuta-1,3-diene (2). A novel route to diene 1 has been developed



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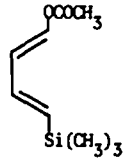

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and its reactions with various dienophiles have been examined. The structures of the adducts were determined by chemical and spectroscopic means, and some conclusions were drawn regarding the synthetic utility of this diene.

Prior to this work compounds such as 1 had been synthesized by addition of silicon hydrides to C–C multiple bonds.[2] The Diels–Alder reactions of these dienes with maleic anhydride and acrolein were reported, but the products were not structurally characterized.[2]

RESULTS AND DISCUSSION

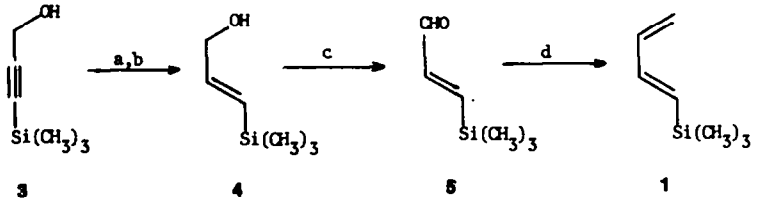
Preparation of the diene. The synthesis of diene 1 has been outlined in Scheme 1. The silylpropenol 4 was prepared as described in the literature[3] with one exception. When the silylpropynol 3 was added to the hydride in tetrahydrofuran at reflux as much as 40% of the product was the fully saturated 3-trimethylsilylpropanol; however when 3 was added slowly to the hydride with ice bath cooling followed by stirring at room temperature nearly pure unsaturated alcohol was formed. Oxidation of alcohol 4 was first carried out with a tenfold excess of manganese dioxide in pentane[4] in yields of 32–46%. Oxidation with pyridinium chlorochromate[5] afforded aldehyde 5 in yields of 56–67% without cumbersome handling of large quantities of manganese dioxide.

Initial attempts to carry out the Wittig alkylation using sodium methylsulfinylmethide in dimethyl sulfoxide were completely unsuccessful, leading to dark colored uncharacterizable material. Success was achieved using n-butyllithium in ether, however the yields were consistently in the range of 46–52% despite variations of temperature, reaction time and reactant ratios.

Note should be taken of the UV maxima of compounds 1 and 5 since little is known about the effect of silicon substituents on the spectra of conjugated chromophores. Diene 1 exhibits a maximum at 231 nm compared to 219 nm predicted for an alkyl-substituted butadiene, while aldehyde 5 exhibits a maximum at 220 nm compared to 222 nm predicted for a β-alkyl-substituted acrolein.

Diels–Alder reactions. Diels–Alder reactions of 1 with various common dienophiles (**6a–f**) were run to determine the reactivity and selectivity of this diene; these have been listed in Table 1. Maleic anhydride (**6a**) was reacted with 1 in refluxing benzene,[2a] and diethyl maleate (**6b**), dimethyl fumarate (**6c**), methyl propiolate (**6d**), acrolein (**6e**) and acrylonitrile (**6f**) were reacted with 1 by heating equimolar mixtures neat in sealed tubes at 150–180° for several hours. The Diels–Alder adducts 7 and/or 8 were obtained in moderate to good yields.

The maleic anhydride adduct **7a** was obtained pure in 43% yield after recrystallization. Analysis by PMR revealed that the mother liquor was indistinguishable from the crystalline product, thus indicating that a single isomer was present. This produce was assumed to possess the *endo* stereochemistry 9 as predicted by the

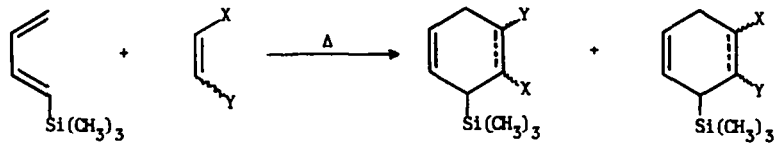


3 4 5 1

(a) $LiAl(OCH_3)_2H_2$, THF; (b) H_3O^+; (c) $C_5H_5N{\cdot}CrO_3{\cdot}HCl$, CH_2Cl_2; (d) $Ph_3P{=}CH_2$, Et, O

Scheme 1.

Table 1. Diels–Alder reactions of silylbutadiene 1

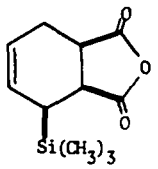


1 6 7 8

Compound	Dienophile	X	Y	Geometry	Reaction Conditions[a] Temperature (°C); Time (h)	Yield (%)	Ratio (7:8)
a	Maleic anhydride			Z	80;	22	43[b]
b	Diethyl maleate	$CO_2C_2H_5$	$CO_2C_2H_5$	Z	200;	9	64
c	Dimethyl fumarate	CO_2CH_3	CO_2CH_3	E	150;	2	84
d	Methyl propiolate	CO_2CH_3	H	-	180;	4	47
e	Acrolein	CHO	H	-	180;	5	31
f	Acrylonitrile	CN	H	-	180	4	58

[a]Reaction with **6a** run in refluxing benzene; all others run neat in sealed tubes.
[b]Recrystallized product; total yield of crude material was 78% (see Experimental).
[c]Complete ratios not determined, however in each case **8** was the predominate product formed.

Alder rules[6] and by analogy to numerous examples.[7] The diethyl maleate adduct **7b** was obtained as one nearly pure isomer (>90% by PMR) in 60–70% yield, however 30–40% diethyl maleate always remained even after 9 hr at 200°. This product was also assumed to possess the *endo* stereochemistry **10**, again by analogy.[6,7] Dimethyl fumarate (**6c**) afforded an 84% yield of an adduct (**7c**) whose PMR spectrum displayed two sets of signals in a ratio of 1:1. The stereochemistry was clearly a mixture as shown in structure **11**.



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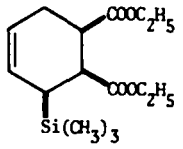

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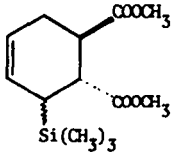

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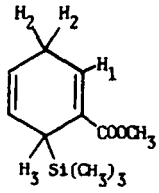
The outcome of the reactions with monosubstituted dienophiles was much more complex. Mixtures of isomers resulted, and their structures could not be unambigously assigned by spectroscopic means. Furthermore, although the crude products appeared to contain only the mixture of isomeric Diels–Alder adducts by PMR, with recoveries of 70–90%, purification by silica gel or alumina column chromatography afforded the products in yields of only 30–60%. It was not known if this was due to impurities which were not apparent by PMR or decomposition of the products during chromatography.

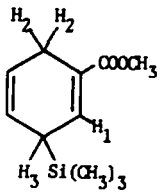
The methyl propiolate adducts **7d** and **8d** were obtained in yields of 21 and 26% respectively after column chromatography. The acrolein adducts were obtained as a mixture of at least three products, shown by PMR analysis to be present in a ratio of 1:2:3. Only the major product could be obtained pure after column chromatography, and a 31% recovery of all products was attained. The acrylonitrile adducts were partially separated by column chromatography, and a 58% yield of two adducts was obtained in a ratio of 1:2.

While this work was in progress a report of a similar study appeared.[8] This report presented several other routes to **1** and accounts of the reactions of **1** with several dienophiles including maleic anhydride (**6a**) and methyl propiolate (**6d**). Although the yield with **6d** was higher than that reported here, the structural assignments for the methyl propiolate adducts **7d** and **8d** were at slight variance with those reported below. No details were given as to purification of the products or the basis for the structural assignments.

Structural investigations. The structures of the methyl propiolate, acrolein, and acrylonitrile adducts were investigated by chemical and spectroscopic methods. Analysis of the propiolate adducts **7d** and **8d** by double-irradiation PMR and 251 MHz indicated that the minor, less polar isomer possessed structure **7d** and the major, more polar isomer possessed structure **8d**. The signal for the β-proton of the α,β-unsaturated ester (H_1) of **7d** was too complex to allow extraction of exact coupling constants. Irradiation at the ring methylene signal (H_2) led to a reduction width of the H_1 signal from $w_{1/2}$ = 9.6 Hz to $w_{1/2}$ = 3.2 Hz, while irradiation at the ring methine signal (H_3) led to $w_{1/2}$ = 8.8 Hz. In compound **8d** irradiation of the H_3 signal led to a reduction in width of the H_1 signal from $w_{1/2}$ = 12 Hz to $w_{1/2}$ = 5.6 Hz. The H_2



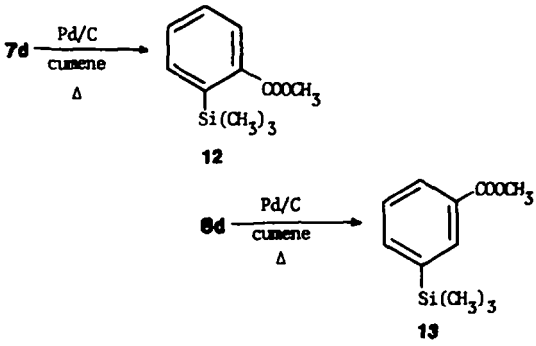
7d



8d

signal was too broad to permit efficient decoupling, however irradiation at the H_1 signal led to removal of only minor splittings in the H_2 signal.

The complexity of the PMR spectra of the propiolate adducts **7d** and **8d** left some doubt as to the structural assignments, so a chemical proof of structure was undertaken. Each propiolate adduct was separately dehydrogenated over palladium-carbon in refluxing cumene. Analysis of each aromatic product by PMR

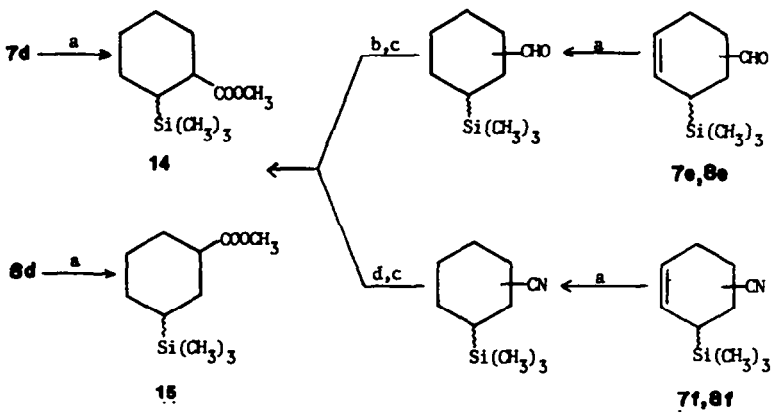


revealed that **7d** gave the *ortho*-substituted benzoate **12** and **8d** gave the *meta*-substituted benzoate **13** thereby firmly establishing the structures of **7d** and **8d**. The assignments of Fleming and Percival were the opposite of those given here.[8b] Their major product (40% yield) was assigned structure **7d** and their minor product (37% yield) was assigned structure **8d**. However, there is not a great difference between our *ortho*:*meta* ratio of 21:26 and Fleming's ratio of 40:37. In both cases, the ratio is essentially 1:1.

The PMR spectra of the acrolein and acrylonitrile adducts were too complex for meaningful analysis, and all attempts to dehydrogenate the cyclohexenes to aromatic products failed. An attempt was thus made to convert these compounds into compounds which could be related to the propiolate adducts as shown in Scheme 2. The propiolate adducts **7d** and **8d** were hydrogenated over palladium–carbon. A complex mixture of products resulted in each case, however analysis by GC-mass spectrometry identified one peak from **7d** to be an isomer of saturated ester **14** and two peaks from **8d** to be isomers of saturated ester **15**. Most of the products from hydrogenation of **7d** and **8d** were shown by GC-MS to be various unsaturated and aromatic derivatives, however further hydrogenation had no effect on them. The saturated esters **14** and **15** were clearly resolved by GC and could thus be related to the products derived from the other adducts to determine the regiochemistry of the acrolein and acrylonitrile Diels–Alder reactions.

The acrolein adducts **7e**, **8e** were obtained as a mixture whose PMR spectrum displayed three signals in the aldehyde region in a ratio of 3:2:1. The major isomer was obtained pure after column chromatography, and the two minor isomers were obtained as a mixture. The major isomer was hydrogenated, oxidized with silver oxide, and methylated with diazomethane to give a low yield (16%) of a product with corresponded to one of the isomers of **15** by GC analysis. The mixture of the two minor isomers was also submitted to this procedure and gave products which corresponded to both of the isomers of **15**. No peaks corresponding to **14** were observed in the GC of either sample. The major product and one of the minor products thus appear to be isomers of the "meta" structure **8e** while the other minor product appears to be either an isomer of the "ortho" structure **7e** which was lost during conversion to saturated ester **14** or an entirely different structure. The latter case is supported by the PMR spectra, which display an aldehyde doublet for the major product (49%) and one of the minor products (34%) but an aldehyde broad singlet for the other minor product (17%).

The acrylonitrile adducts **7f**, **8f** were separated, hydrogenated, hydrolyzed to the carboxylic acids, and methylated with diazomethane. The less polar, minor isomer gave a product which corresponded to one of the isomers of **15** with a small amount of a product which corresponded to an isomer of **14** by GC analysis. The more polar, major isomer gave only products which



(a) H_2, 10% Pd/C, EtOAc; (b) Ag_2O, NaOH, H_2O; (c) CH_2N_2, Et_2O; d) 37% aq. HCl, Δ

Scheme 2.

corresponded to the two isomers of 15 by GC analysis. The acrylonitrile adducts thus appear to be isomers of the "meta" structure 8f, possibly mixed with a small amount of 7f. The saturated esters were obtained in very low yields, and the assignments were not totally unambiguous.

Thus with acrolein and acrylonitrile the silyldiene 1 affords the *meta* isomers as the predominant products in contrast to Fleming's report of *ortho* selectivity in the reaction of 1 and methyl acrylate.[8b] However it should be stressed that our assignments are not totally unambiguous and thus this *meta* selectivity must be viewed with caution until more conclusive results are obtained.

CONCLUSIONS

The synthesis of diene 1 proceeded in a straightforward manner by a novel route, and yields were obtained which compared favorably with those reported elsewhere.[2,8a] The material obtained was pure by PMR analysis and was stereochemically homogeneous.

The Diels–Alder reactions of 1 proceeded under reasonably mild conditions in good to fair yields. The adducts obtained seemed to be reasonably unstable, possibly due to deterioration of the reactive allylic silane moiety. Future synthetic work with dienes of this type might well emphasize carrying the crude adducts through a subsequent transformation of the allylic silane prior to attempts at purification. Disubstituted, diactivated dienophiles appeared to react exclusively by the *endo* mode of addition, whereas monosubstituted dienophiles appeared to give mixtures of *endo* and *exo* products.

EXPERIMENTAL

General. Commercial reagents were used without further purification. PMR spectra were obtained on a Varian T-60 spectrometer in chloroform-d with TMS internal standard; IR spectra were obtained on a Perkin-Elmer Model 137 spectrometer, solids being run in KBr pellets and liquids between NaCl plates; UV spectra were obtained on a Cary 14 spectrometer; mass spectra were obtained on an AEI model MS-9 mass spectrometer; GC's were equipped with flame ionization detectors and utilized nitrogen carrier gas. Thin layer and column chromatography were carried out using Merck silica gel.

E-3-*Trimethylsilylprop*-2-*enol* (5). A soln of 4[3] (13 g; 0.1 mol) in CH_2Cl_2 (20 ml) was added to a stirred suspension of pyridinium chlorochromate[5] (32.3 g; 0.15 mol) in CH_2Cl_2 (20 ml). After 1 hr tlc analysis (silica gel; $CHCl_3$) showed the reaction to be complete and 200 ml ether was added to the black mixture. The supernatant was decanted and the residue was washed with three 50 ml portions of ether. The combined liquids were filtered through a short column of Florisil which was then washed with 50 ml ether. The greenish filtrate was concentrated by distillation of the solvents through a 30 cm Vigreux column, and the residue was distilled through a 10 cm Vigreux column at reduced pressure to yield 8.63 g aldehyde 5, b.p. 53–54°, 30 Torr (67%). This material darkened rapidly at room temp. but could be stored several weeks in the freezer. PMR δ 0.18 (s, 9H), 6.15 (dd, 1H, J = 7, 19 Hz), 7.52 (d, 1H, J = 19 Hz), 9.48 (d, 1H, J = 7 Hz); IR 2780 (w), 2680 (w), 1685, 1236 cm^{-1}; UV λ_{max} (EtOH) 220 nm ($\epsilon = 1.09 \times 10^4$).

E-1-*Trimethylsilylbuta*-1,3-*diene* (1). To a mixture of 300 ml dry ether and 35.25 ml *n*-BuLi (2.0 *M* in hexane, 70.5 mmol) under N_2 was added 25.2 g (70.5 mmol) methyltriphenylphosphonium bromide, and the resulting orange suspension was stirred at 3 hr at room temp. When 5 (9.02 g; 70.5 mmol) was added to the stirred ylide the color was discharged and a tan ppt formed. The mixture was refluxed 10 hr then cooled, filtered, and the filtrate was washed with 250 ml water and 100 ml NaCl aq. The organic phase was dried over $MgSO_4$, filtered, and concentrated by distillation of the solvents through a 30 cm Vigreux column. The residue was distilled through a 10 cm Vigreux column at reduced pressure to yield 4.58 g diene 1, b.p. 70–74°, 210 Torr (52%). PMR δ 0.8 (s, 9H), 5.0–7.4 (m, 5H); UV λ_{max} (EtOH) 231 nm ($\epsilon = 2.2 \times 10^4$).

cis,cis - 3 - *Trimethylsilylcyclohex* - 4 - *ene* - 1,2 - *dicarboxylic anhydride* (7a). A soln of 1 (126 mg; 1.0 mmol) in 4 ml dry benzene was added to 6a (98 mg; 1 mmol), and the mixture was refluxed 22 hr, whereupon GC analysis (6 ft × 1/8 in. SE-30, 10% on 60–80 mesh Chromosorb W) showed the diene to be nearly gone. The soln was evaporated and the residue recrystallized from acetone-petroleum ether to yield 97 mg anhydride 7a, m.p. 115–116° (43%). The mother liquor was evaporated to give 78 mg brown semisolid, indistinguishable from the pure product by PMR. PMR δ 0.17 (s, 9H), 1.67 (m, 1H), 2.43 (bm, 2H), 3.43 (m, 2H), 6.00 (m, 2H); IR 1840, 1780, 1240, 968, 940 cm^{-1}; mass spectrum *m/e* 209 (M^+–CH_3), 196, 181, 179, 152, 137, 135, 117, 103, 91, 73.

cis,cis - 3 - *Trimethylsilylcyclohex* - 4 - *ene* - 1,2 - *dicarboxylic acid diethyl ester* (7b). A mixture of 1 (504 mg; 4 mmol) 6b (688 mg; 4 mmol), and a trace of hydroquinone were heated in a sealed tube at 200° for 9 hr. The clear, yellow product was evaporated *in vacuo* to remove volatile components. The residue, 1.068 g, was shown by PMR to contain 29% 6b and 71% 7b (64%). PMR δ 0.04 (s, 9H), 1.16 (t, 3H, J = 7), 1.22 (t, 3H, J = 7), 1.6–3.6 (bm, 5H), 4.02 (q, 2H, J = 7), 4.05 (q, 2H, J = 7), 5.57 (m, 2H); IR 1725 cm^{-1}; mass spectrum *m/e* 298 (M^+), 283, 269, 253, 225, 209.

1,2 - trans - 3 - *Trimethylsilylcyclohex* - 4 - *ene* - 1,2 - *dicarboxylic acid dimethyl ester* (7c). Diene 1 was reacted with 6c as above on a 5 mmol scale at 150° for 2 hr. The crude material, 1.130 g, was shown by PMR analysis to be >90% pure 7c as a 1:1 mixture of isomers (84%). PMR δ 0.013 and 0.028 (s, 9H), 1.7–3.3 (m, 5H), 3.62 (s, 6H), 5.67 (bs, 2H); IR 1740, 1434, 1250 cm^{-1}; mass spectrum *m/e* 270 (M^+), 255, 239, 211, 195.

6 - *Trimethylsilylcyclohexa* - 1,4 - *diene* - 1 - *carboxylic acid methyl ester* (7d) and 3 - *Trimethylsilylcyclohexa* - 1,4 - *diene* - 1 - *carboxylic acid methyl ester* (8d). Diene 1 was reacted with 6d[9] as above on a 2.6 mmol scale at 180° for 4 hr. The crude product, 491 mg, was purified on 75 g silica gel eluted with 98:2 pentane:ether. Compound 7d was obtained first, 115 mg (21%), followed by compound 8d, 146 mg (26%). PMR (Compound 7d) δ 0.01 (s, 9H), 2.30 (m, 1H), 2.83 (m, 2H), 3.55 (s, 3H), 5.68 (m, 2H), 6.78 (m, 1H); double resonance:[10] irradiation at 2.83 caused the signal at 6.78 to narrow from $w_{1/2}$ = 9.6 Hz to $w_{1/2}$ = 3.2 Hz while irradiation at 2.30 caused the signal to narrow to $w_{1/2}$ = 8.8 Hz; (Compound 8d) δ 0.05 (s, 9H), 2.52 (m, 1H), 2.93 (m, 2H), 3.70 (s, 3H), 5.62 (m, 2H), 7.03 (m, 1H); double resonance:[10] irradiation at 2.52 caused the signal at 7.03 to narrow from $w_{1/2}$ = 12 Hz to $w_{1/2}$ = 5.6 Hz while irradiation at 7.03 caused the signal at 2.93 to simplify only slightly; IR (compound 7d) 1720, 1422, 1240, 1106, 1076, 1048, 838 cm^{-1}; (Compound 8d) 1710, 1424, 1294, 1248, 1088, 1066, 840 cm^{-1}; mass spectrum *m/e* 210 (M^+), 209, 195, 179, 163, 136, 121, 105, 77, 73 (fragmentation essentially the same for 7d and 8d).

Dehydrogenation of propiolate adducts (7d) and (8d): *Methyl* 3-*trimethylsilylbenzoate* (13). A mixture of 8d (50 mg), 10% Pd–C (25 mg), and cumene (1 ml) was refluxed for 2 hr while N_2 was slowly passed through the soln. The cooled mixture was centrifuged in pentane, the supernatant was evaporated, and the residue purified by preparative tlc (silica gel, benzene eluent). The major band (R_f = 0.62) yielded 13 (28 mg). PMR δ 0.33 (s, 9H), 3.97 (s, 3H), 7.47 (dd, 1H, J = 7, 8), 7.80 (ddd, 1H, J = 7, 2, 1.6), 8.08 (ddd, 1H, J = 8, 2, 1.6), 8.27 (bm, 1H).

Methyl 2-*trimethylsilylbenzoate* (12). In a similar reaction adduct 7d yielded 12 (R_f = 0.71). PMR δ 0.30 (s, 9H), 3.90 (s, 3H), 7.62 (d, 1H, J = 8), 7.83 (d, 1H, J = 8), 8.05 (dd, 1H, J = 7, 8), 8.14 (dd, 1H, J = 7, 8).

Reaction of diene 1 *with acrolein* (6e). Diene 1 was reacted with 6e as above on a 6 mmol scale at 180° for 5 hr. The crude product, 729 mg, was purified on 200 g activity III neutral alumina eluted with 40:1:1 pentane:ether:benzene. Analysis of the fractions by GC (6 ft × 1/8 in. Carbowax 20M, 10% on 60–80 mesh Chromosorb W) revealed that the first product appeared nearly

pure, 287 mg, followed by a mixture of two other products, 54 mg. Analysis of the crude mixture by PMR revealed three peaks in the aldehyde region: δ 9.55 (d, 49%), 9.65 (bs, 17%), 9.72 (d, 34%). The first product displayed a doublet at 9.55, and the mixture of the other two products displayed a broad singlet at 9.65 and a doublet at 9.72. Mass spectrum (mixture), *m/e* 182 (M^+), 167.

Reaction of diene 1 *with acrylonitrile* (6f). Diene 1 was reacted with 6f as above on a 4 mmol scale at 180° for 4 hr. The crude product, 622 mg, was purified on 100 g silica gel eluted with 98:2 pentane:ether. Analysis of the fractions by GC (6 ft × 1/8 in. Carbowax 20M, 10% on 60–80 mesh Chromosorb W) revealed that the first product appeared pure, 110 mg, followed by a mixture of the first product with a second produce, 93 mg, followed by the pure second component, 214 mg. PMR δ (First product) 0.16 (s, 9H), 0.8–2.4 (m, 5H), 3.05 (m, 1H), 5.67 (bs, 2H); (Second product) 0.10 (s, 9H), 0.8–2.4 (m, 5H), 2.78 (m, 1H), 5.63 (bs, 2H); IR (Mixture) 2232 (w), 1252 cm^{-1}; mass spectrum (mixture) *m/e* 179 (M^+), 164, 152, 137, 113, 111, 73.

Methyl 2-*trimethylsilylcyclohexanecarboxylate* (14). A soln of 7d (50 mg) in 15 ml EtOAc was stirred with 10% Pd–C (25 mg) under one atmosphere H_2 for 20 hr. The mixture was filtered and evaporated to give 21 mg product which was analyzed by GC (9 ft × 1/8 in. Carbowax 20M, 20% on 60–80 mesh Chromosorb W, 140°) and each peak was characterized by GC-mass spectrometry: 2.8 m [*m/e* 214 (M^+), 4.3 m [*m/e* 197 (M^+–CH_3)]. 5.2 m [*m/e* 212 (M^+), 197]. The peak at 2.8 m was assigned to one or both isomers of saturated ester 14.

Methyl 3-*trimethylsilylcyclohexanecarboxylate* (15). Similarly, 8d (50 mg) gave 29 mg product which was analyzed and characterized in the same manner: 3.2 m [*m/e* 214 (M^+), 199], 4.0 m [*m/e* 214 (M^+), 199], 6.6 m [*m/e* 212 (M^+)]. The peaks at 3.2 and 4.0 m were assigned to saturated esters 15.

Conversion of acrolein adducts 7e, 8e *to saturated esters.* The least polar, most abundant isomer of acrolein adducts 7e, 8e was hydrogenated in EtOAc over 10% Pd–C. The product was oxidized with a two-fold excess of silver oxide in NaOH aq, and the resulting acid was methylated with diazomethane in ether to give the corresponding saturated ester. Mass spectrum *m/e* 214 (M^+), 199. Analysis by GC revealed only one peak, which corresponded to the peak at 3.2 m from saturated esters 15. The mixture of the two minor acrolein adducts was also carried through this process. Analysis by GC revealed two peaks, which corresponded to the peaks at 3.2 m and 4.0 m from saturated ester 15.

Conversion of acrylonitrile adducts 7f, 8f *to saturated esters.* Each acrylonitrile adduct was separately hydrogenated in EtOAc over 10% Pd–C. The products were hydrolyzed in refluxing conc. HCl, and the resulting acids were methylated with diazomethane to give the corresponding saturated esters. The minor, less polar acrylonitrile adduct gave an ester which, upon GC analysis, revealed a large peak (≃87%) corresponding to the peak at 3.2 m from saturated ester 15 and a small peak (≃13%) peak corresponding to the peak at 2.8 m from saturated ester 14. The major, more polar acrylonitrile adduct gave an ester which, upon GC analysis, revealed a large and a small peak corresponding to the two peaks at 3.2 and 4.0 m from saturated ester 15.

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[10]Double resonance experiments were carried out on a 251 MHz superconducting NMR spectrometer.

[11]GC-mass spectrometry experiments were performed on a Hewlett-Packard Model 5980A spectrometer equipped with a glass column (6 ft × 1/8 in. Carbowax 20 M, 10% on 60–80 mesh Chromosorb W).