

MERCURY IN ORGANIC CHEMISTRY

XVI *. SYNTHESIS OF 1,4-DIENES VIA ALLYLATION OF VINYL MERCURIALS **

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Summary

Vinylmercurials react readily with allylic halides, lithium chloride and palladium chloride in tetrahydrofuran to give 1,4-dienes. Some reactions proceed well using only catalytic amounts of palladium chloride while others require stoichiometric amounts. The yields decrease with increasing substitution about the carbon-carbon double bond of the allylic halide. The reactions appear to proceed through the addition of vinylpalladium species to the carbon-carbon double bond of the allylic halide, and subsequent palladium chloride elimination. The overall result is S_N2' substitution of the allylic halide.

Introduction

1,4-Dienes are common in naturally occurring fatty acids such as arachidonic acid, the biological precursor to the prostaglandins, and other polyunsaturated fatty acids. Several methods for the synthesis of 1,4-dienes utilizing organometallic reagents have appeared recently. Zweifel has treated vinylalanes with allylic halides in the presence of cuprous chloride to obtain 1,4-dienes [2]. Alkenyltrialkylaluminum complexes also react with allylic halides to give 1,4-dienes [3–5]. Yamamoto has obtained 1,4-dienes by treating divinylchloroboranes with allylic halides and methyl copper [6]. Normant [7] and Henrick and Siddall [8] have treated vinylcopper reagents with allyl bromide to obtain 1,4-dienes. Using a different approach Corey and Semmelhack treated vinyl bromide with π -methallylnickel bromide and obtained the corresponding 1,4-diene [9].

During our studies on the synthetic utility of vinylmercurials [10], we have

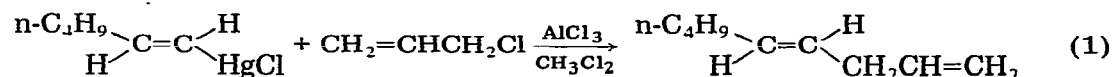
* For Part XV see ref. 1.

** Dedicated to Professor H.C. Brown for his many contributions to chemistry.

discovered a number of interesting new routes to dienes and polyenes [1,11,12]. Using reactions suggested by previous work of Heck [13], we now wish to report a new route to 1,4-dienes via vinylmercurials.

Results and discussion

Electrophilic approaches. After our earlier success with the synthesis of α,β -unsaturated ketones by electrophilic cleavage of vinylmercurials [14], we decided to examine the Lewis acid catalyzed reaction of allyl chloride and *trans*-1-hexenylmercuric chloride (eq. 1). Reaction of the mercurial and one equivalent each of



aluminum chloride and allyl chloride at room temperature in dichloromethane provided a precipitate presumed to be mercuric chloride, but no 1,4-diene was observed by gas chromatographic analysis. Reducing the amount of aluminum chloride to 0.1 equivalent again resulted in precipitation, but still no 1,4-diene was observed. Lowering the temperature to 0°C or -78°C with one equivalent of aluminum chloride did not improve the situation. One equivalent of titanium tetrachloride or ferric chloride at 0°C likewise produced no diene products. Thus, although it appears that aluminum chloride catalyzes the reaction of vinylmercurials and allyl chloride, either the desired 1,4-diene is never formed or it is destroyed under the reaction conditions as fast as it is formed.

Palladium chloride promoted coupling. The success of Heck's earlier palladium chloride-catalyzed coupling of arylmercuric chlorides and allylic chlorides to

TABLE 1

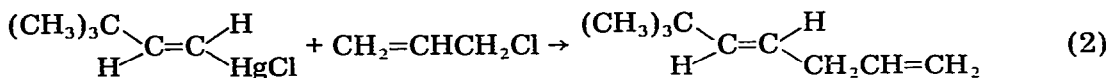
STOICHIOMETRY STUDIES ON THE REACTION OF *trans*-3,3-DIMETHYL-1-BUTENYLMERCURIC CHLORIDE AND ALLYL CHLORIDE (eq. 2)^a

Solvent	PdCl ₂	LiCl	CuCl ₂	CH ₂ =CHCH ₂ Cl	Yield of 1,4-diene (%) ^b	
THF	1	0	0	1	0	
		2			46	
		4			45	
		2		2	78	
	0.1			5	98	
					96	
	0.01				10	
				2	37 ^c	
	1			0	1	48 ^d
						47 ^e
Et ₂ O					30	
CH ₂ Cl ₂					34	
CH ₃ OH					6	
CH ₃ CN					23	
HMPA					<3 ^f	
C ₆ H ₆	0.1			5	43 ^f	

^a Ten ml solvent and 1 mmol mercurial starting at -78°C. ^b GLC yield corrected by the use of an internal standard. ^c A second product, presumed to be *trans*-1-chloro-3,3-dimethyl-1-butene, is observed. ^d Start reaction at -22°C. ^e Start reaction at 25°C. ^f Start reaction at 0°C.

give allylic aromatics [13] suggested that palladium chloride might also catalyze the reaction of vinylmercuric chlorides and allylic halides to form 1,4-dienes. That possibility has been examined in detail.

The first system chosen for study was the reaction of *trans*-3,3-dimethyl-1-butenylmercuric chloride and allyl chloride (eq. 2). The effects of solvent, lithi-

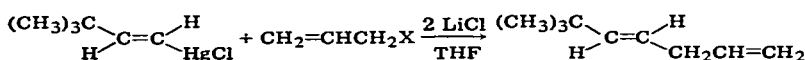


um chloride, cupric chloride, varying amounts of palladium chloride, and the quantity of allyl chloride on the yield of 1,4-diene were studied. The results of this study are summarized in Table 1. Tetrahydrofuran (THF) proved to be the best solvent for the reaction. As with the palladium chloride promoted synthesis of symmetrical 1,3-dienes [11], lithium chloride was essential for the reaction. Five equivalents of allyl chloride provided optimum yields of the 1,4-diene. Ten percent palladium chloride worked as well as one equivalent, but 1% catalyst resulted in only a 10% yield. Added cupric chloride improved the reaction only slightly and a second product, possibly *trans*-1-chloro-3,3-dimethyl-1-butene, was observed. This second product was also observed in the reaction of the vinyl mercurial with cupric chloride and lithium chloride, in the absence of palladium chloride and allyl chloride. Starting the reaction at -22°C or 25°C appeared to have no effect on the reaction. The reaction at room temperature was observed to occur immediately upon mixing of the reagents. A starting temperature of -78°C was chosen for further reactions in order to allow complete mixing of the reagents before reaction occurred. In attempting to scale up the reaction, it was found that ten equivalents of allyl chloride were necessary to maintain the near quantitative yield.

Other allyl derivatives were also examined. Allyl bromide was found to be as effective as allyl chloride, but allyl iodide appeared to be more erratic and seems to give poorer yields of 1,4-dienes. The reaction is also not limited to halides,

TABLE 2

REACTION OF *trans*-3,3-DIMETHYL-1-BUTENYLMERCURIC CHLORIDE WITH OTHER ALLYL DERIVATIVES^a



PdCl ₂ (mmol)	CH ₂ =CHCH ₂ X		Yield of 1,4-diene (%) ^b
	X	mmol	
1	Cl	1	46
	Br		40-69
	I		13-50
	OAc		33
		5	65
0.1			14

^a One mmol of mercurial, two mmol lithium chloride and 10 ml of solvent, reaction started at -78°C and allowed to slowly warm to room temperature overnight. ^b GLC yield corrected by the use of an internal standard.

TABLE 3

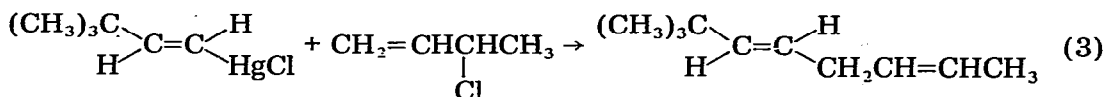
REACTION OF *trans*-3,3-DIMETHYL-1-BUTENYLMERCURIC CHLORIDE AND 3-CHLORO-1-BUTENE (eq. 3)^a

Solvent	PdCl ₂	CuCl ₂	CH ₂ =CHCH(Cl)CH ₃	Yield of diene(%) ^b	
				1,4	1,3 ^c
THF	0.1	0	5	44	20
		2		52	37
		0	10	39	10
	1.0	2		40	24
		0	5	38	6
			10	49	10
Et ₂ O	0.1	2		32	36
		0		9	30
		2		51	11

^a Ten ml of solvent, 1 mmol of vinylmercurial and 2 mmol LiCl starting at -78°C and allowing to slowly warm to room temperature overnight. ^b GLC yield corrected by the use of an internal standard. ^c 1,3-Diene \equiv *trans,trans*-2,2,7,7-tetramethyl-3,5-octadiene; yield calculated on the basis of mercurial used.

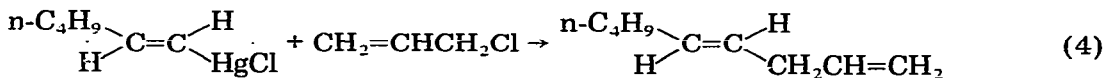
but gives a modest yield of 1,4-diene when using allyl acetate. The results of these studies are summarized in Table 2.

Two other systems then were studied in detail. The reaction of *trans*-3,3-dimethyl-1-butenylmercuric chloride and 3-chloro-1-butene is summarized in Table 3 (eq. 3). It should be noted that the product obtained is that of an S_N2'



allylic displacement rather than direct substitution. This is discussed in more detail in the mechanistic section. Under most conditions significant yields of the symmetrical 1,3-diene, *trans,trans*-2,2,7,7-tetramethyl-3,5-octadiene, were observed along with the desired 1,4-diene. No conditions were found which would completely eliminate its formation. One equivalent of palladium chloride and ten equivalents of allylic chloride proved to be the optimum conditions in this system. GLC analysis of the resulting 1,4-diene indicated approximately a 60/40 mixture of compounds stereoisomeric about the C(2)–C(3) double bond and presumed to be *trans/cis*.

The reaction of *trans*-1-hexenylmercuric chloride and allyl chloride also required additional study since the conditions used for *trans*-3,3-dimethyl-1-butenylmercuric chloride and allyl chloride were not successful in this system (eq. 4). Again, one equivalent of palladium chloride and ten equivalents of allyl



chloride proved to be the optimum reaction conditions. Other solvents were tried, but none were as effective as THF.

Mechanisms can be written which would result in the generation of HCl in the reaction (see the mechanistic discussion). Therefore, the effect of the added bases magnesium oxide, potassium carbonate, and triethylamine was studied. None of

TABLE 4
SYNTHESIS OF 1,4-DIENES

Vinylmercurial	Allylic chloride ^a	1,4-Diene	Yield (%) ^b
	CH ₂ =CHCH ₂ Cl		96 ^c
			46 ^d
			28 ^d
			49 ^d
	CH ₃ CH=CHCH ₂ Cl		32 ^d
	CH ₂ =CHCH ₂ Cl		71 (52)
			39
	CH ₂ =CHCH ₂ Cl		80 (76)
			73
			100 ^c
			99 98 ^e

^a Ten equivalents and 1 equivalent of palladium chloride unless otherwise indicated. ^b GLC yield (isolated yield). ^c Five equivalents of allyl chloride and 0.1 equivalents of palladium chloride. ^d A dimeric product is also seen, probably *trans,trans*-2,2,7,7-tetramethyl-3,5-octadiene. ^e 10% palladium chloride.

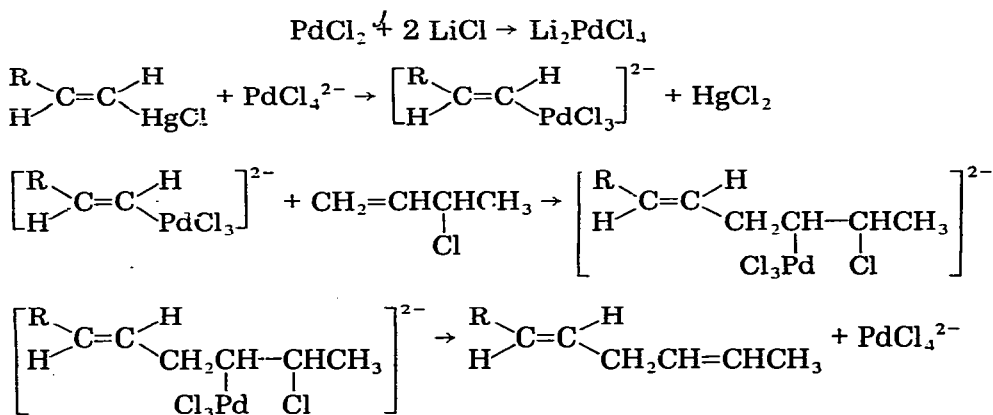
the bases studied resulted in an increase in the yield of 1,4-diene.

The synthesis of 1,4-dienes. The full scope of the reaction then was investigated on a series of allylic chlorides and vinylmercurials. The reactions studied fell into two categories, those that were catalytic and those that required a full equivalent of palladium chloride. The results are listed in Table 4. Three vinylmercurials gave excellent yields with 10% palladium chloride and 10 equivalents of allyl chloride: *trans*-3,3-dimethyl-1-butenylmercuric chloride, *trans*-1-cyclohexenyl-ethenylmercuric chloride, and *E*-2-chloromercuri-4,4-dimethyl-2-pentene. All other mercurials examined required a full equivalent of palladium chloride in order to obtain a good yield of 1,4-diene. No trends are apparent in comparing the structures of the mercurials and the yields of 1,4-dienes.

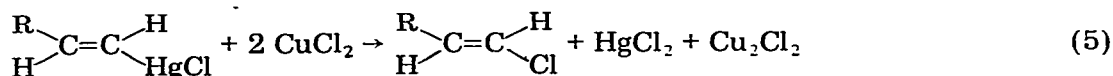
No other allylic chlorides provided 1,4-dienes in as good a yield as allyl chloride itself. Substitution on either the allylic carbon or the internal carbon lowers the yield of 1,4-diene to approximately the same extent. Allylic chlorides containing internal double bonds appear to give still lower yields. The reactions of methallyl chloride, 3-chloro-1-butene and 2,3-dichloro-1-propene all gave substantial yields of 1,3-diene derived from symmetrical dimerization of the vinylmercurial. These reactions, as well as the reaction of crotyl chloride, also produced two or three minor products (by GLC analysis). In the reaction of 2,3-dichloro-1-propene, the symmetrical 1,3-diene and the desired 1,4-diene overlapped substantially upon GLC analysis on a 10' DC-550 column. The product was identified by GLC-mass spectrometric analysis (1/8" column) and high resolution mass spectrometric analysis on the mixture of 1,4- and 1,3-dienes obtained by preparative GLC.

Mechanism. The mechanism of the palladium chloride promoted reaction is suggested by the reaction of *trans*-3,3-dimethyl-1-butenylmercuric chloride with 3-chloro-1-butene, and by analogy to the previously reported palladium chloride-catalyzed reaction of arylmercurials and allylic halides [13]. The first step is presumably a transmetalation reaction between the vinylmercurial and PdCl_4^{2-} to generate a vinylpalladium species. The latter then adds to the carbon-carbon double bond of the allylic halide to generate an alkylpalladium chloride which then eliminates PdCl_4^{2-} to form the 1,4-diene (Scheme 1). This mechanism suggests that the reaction ought to be catalytic, which indeed it is.

SCHEME 1



One pathway for removal of palladium chloride is suggested by the major side product observed in these reactions, the symmetrical 1,3-diene formed by dimerization of the vinylmercurial. We have observed previously that this reaction requires a stoichiometric amount of palladium chloride for optimum yields and that metallic palladium is produced in the reaction [11]. Likewise, in many of these reactions the rust red color of palladium chloride is replaced by the black color of finely divided palladium metal as the reaction proceeds. Anhydrous cupric chloride can be employed to reoxidize the palladium and the yields are generally improved. However, chlorination of the vinylmercurial often becomes an important side reaction, particularly when the reaction is run in polar solvents (eq. 5).



Other methods for the removal of palladium chloride also can be envisioned. If the intermediate palladium species undergoes β -hydride elimination rather than β -chloride elimination, the resulting palladium hydride would be expected to eliminate palladium metal and generate HCl. The HCl thus produced could cause cleavage of the carbon—palladium bond in either of the two key organopalladium intermediates, further reducing the yield of 1,3-diene. This protonolysis reaction does not appear to be important, however, since added bases, such as MgO, K_2CO_3 , and Et_3N , do not improve the yields in the reaction of *trans*-1-hexenylmercuric chloride and allyl chloride.

Conclusion. The palladium promoted reaction of vinylmercuric chlorides and allylic chlorides provides a new method for the synthesis of 1,4-dienes. The reaction, unfortunately, requires an excess of the allylic halide to produce high yields. Furthermore, although the reaction is catalytic in palladium chloride, best yields are generally obtained by using one equivalent of palladium chloride. The reaction proceeds by $\text{S}_{\text{N}}2'$ displacement on the allylic halide, presumably by addition of a vinylpalladium species to the carbon—carbon double bond of the allylic halide and subsequent β elimination of the tetrachloropalladate anion.

Experimental

Reagents. All reagents were used directly as obtained commercially unless otherwise indicated. Tetrahydrofuran and ether were distilled from lithium aluminum hydride. All allylic chlorides were distilled before use. Dichloromethane was shaken with concentrated sulfuric acid, washed with water and saturated sodium chloride, dried over calcium chloride, and distilled.

The vinylmercuric chlorides were prepared using the published literature procedure [15]. Palladium chloride was generously supplied by Matthey Bishop and Engelhard Industries.

All GLC yields are corrected by the use of appropriate hydrocarbon internal standards and calculated correction factors.

Electrophilic approaches. The reaction of *trans*-1-hexenylmercuric chloride with allyl chloride and aluminum chloride at 0°C is representative of the procedure used for these studies. A 25 ml round bottom flask was flushed with nitro-

gen, charged with dichloromethane (10 ml), *trans*-1-hexenylmercuric chloride (1.0 mmol), allyl chloride (1.0 mmol), and decane (0.26 mmol). The mixture was cooled to 0°C in an ice bath and aluminum chloride (1.0 mmol) was added. Samples were removed at 0.25, 0.5, 1, 2, 6 and 12 h and quenched in a 1/1 mixture of saturated sodium potassium tartrate and saturated sodium carbonate. GLC analysis of the samples showed no 1,4-diene in the reaction mixture.

Initial stoichiometry studies. All GLC reactions in this section were carried out using a similar procedure. A 50 ml round bottom flask was flushed with nitrogen, charged with 10 ml of solvent, usually THF, and cooled to -78°C in a dry ice/acetone bath. The mercurial (1 mmol), lithium chloride (2 mmol), allylic chloride (1, 2, 5, or 10 mmol) and an internal standard (0.25 or 0.50 mmol of nonane, decane, or dodecane depending on the system under study) were then added and the reaction stirred under nitrogen and allowed to warm to room temperature slowly. The reaction was quenched by the addition of saturated ammonium chloride and the THF layer analyzed by GLC (10' DC-550 or 10' SE-30 columns at 90°C to 150°C depending on the system and standard chosen for the reaction).

The synthesis of 1,4-dienes. All GLC yields were determined as discussed above. Authentic samples of *trans*-6,6-dimethyl-1,4-heptadiene, 3-(*trans*-1-hexenyl)cyclohexene, *trans*-1-cyclohexyl-1,4-pentadiene, and *trans*-1-cyclohexenyl-1,4-pentadiene were obtained from Professor G. Zweifel and were used for calculating correction factors and for verification of the stereochemistry of the products obtained. Correction factors for the remaining 1,4-dienes were obtained from the products isolated by preparative GLC from the various reactions.

The following procedure for the preparation of *trans*-1-phenyl-1,4-pentadiene is representative of the procedure used in obtaining isolated yields. A 250 ml round bottom flask equipped with a gas-inlet tube and a side arm capped with a rubber septum was flushed with nitrogen, charged with THF (100 ml) and cooled to -78°C in an acetone/dry ice bath. Styrylmercuric chloride (10 mmol), lithium chloride (20 mmol), allyl chloride (100 mmol), and palladium chloride (10 mmol) were added and the reaction stirred magnetically while allowing the cooling bath to slowly warm to room temperature overnight. The reaction was quenched by adding saturated ammonium chloride. After separating the layers the ammonium chloride solution was washed with two volumes of hexanes (mixture of isomers). The organic layers were then washed twice with saturated sodium chloride, and dried over anhydrous sodium sulfate. Removal of the solvent by careful distillation yields a yellow oil. Distillation (Kugelrohr) at reduced pressure (25 mmHg, 100°C) results in 1.09 g (76%) of a colorless liquid: ¹H NMR (CCl₄) δ 2.9 (2 H, t, *J* 6 Hz, =CHCH₂CH=), 5.0 (2 H, m, =CH₂), 5.5–6.2 (3 H, m, remaining vinyls), 7.2 ppm (5 H, br s, C₆H₅), IR (thin film) (max) 3090, 3070, 3040, 3010, 2980, 2900, 2840, 1950, 1880, 1805, 1640, 1605, 1580, 1500, 1450, 1430, 1415, 1310, 1265, 1075, 1030, 995, 970, 915, 740, and 690 cm⁻¹; *m/e* 144.0917 ± 15 (C₁₁H₁₂ calcd. 144.0939).

trans-1,4-Nonadiene was isolated in like manner (care must be taken in distilling off the solvent since the 1,4-diene is fairly volatile): ¹H NMR (CCl₄) δ 0.95 (3 H, t, *J* 6 Hz, CH₃), 1.4 (4 H, m, CH₂'s), 2.05 (2 H, m, =CHCH₂CH₂), 2.75 (2 H, m, =CHCH₂CH=), 5.0 (2 H, m, =CH₂), 5.4 (2 H, m, CH=CH), and 5.75 ppm (1 H, m, CH=CH₂); IR (thin film) (max) 3080, 3030, 3010, 2960, 2930, 2880, 2860,

1640, 1465, 1430, 1375, 990, 970, and 910 cm^{-1} ; m/e 124.1234 \pm 15 (C_9H_{16} calcd. 124.1252).

The following dienes were characterized after isolation by preparative GLC (10' DC-550). *trans*-2,6,6-Trimethyl-1,4-heptadiene (GLC of the product mixture shows several side products including *trans,trans*-2,2,7,7-tetramethyl-3,5-octadiene): ^1H NMR (CCl_4) δ 1.0 (9 H, s, *t*-butyl), 1.7 (3 H, s, $\text{CH}_3\text{C}=\text{}$), 2.7 (2 H, m, $=\text{CHCH}_2$), 4.7 (2 H, m, $=\text{CH}_2$), 5.4 ppm (2 H, m, $\text{CH}=\text{CH}$), IR (thin film) (max) 3070, 3010, 2960, 2900, 2860, 1650, 1470, 1460, 1360, 1260, 970, and 880 cm^{-1} ; m/e 138.1392 \pm 12 ($\text{C}_{10}\text{H}_{18}$ calcd. m/e 138.1409). *trans,trans*- and *cis,trans*-7,7-Dimethyl-2,5-octadiene (~60/40 ratio of isomers by GLC on a 50 m SE-30 glass capillary column, identity of the respective peaks was not established): ^1H NMR δ 1.0 (9 H, s, *t*-butyl), 1.65 (3 H, m, $=\text{CHCH}_3$), 2.70 (2 H, m, $=\text{CHCH}_2\text{CH}=\text{}$), and 5.25 ppm (4 H, m, vinyls); IR (thin film) (max) 3030, 2960, 2900, 2870, 2830, 1475, 1460, 1390, 1360, 1270, 1200, 1080, 1020, and 970 cm^{-1} ; m/e 138.1397 \pm 9 ($\text{C}_{10}\text{H}_{18}$ calcd. 138.1409). *trans*-4,6,6-Trimethyl-1,4-heptadiene: ^1H NMR (CCl_4) δ 1.1 (9 H, s, *t*-butyl), 1.7 (3 H, d, J 1 Hz, $\text{CH}_3\text{C}=\text{}$), 2.6 (2 H, d of d, J 1 Hz, 6 Hz, $\text{CH}_2\text{CH}=\text{}$), 4.9 (1 H, br m, $\text{CH}=\text{}$), 5.2 ppm (3 H, m, $\text{CH}=\text{CH}_2$); IR (thin film) (max) 3080, 3010, 2960, 2910, 2870, 1640, 1480, 1470, 1440, 1390, 1370, 1225, 1205, 1155, 1030, 995, 915, 850, and 815 cm^{-1} ; m/e 138.1389 \pm 14 ($\text{C}_{10}\text{H}_{18}$ calcd. 138.1409). *trans*-2-Chloro-6,6-dimethyl-1,4-heptadiene (two products were obtained which were inseparable by preparative GLC): ^1H NMR (CCl_4) (taken on the mixture obtained) δ 1.0 (9 H, overlapping *t*-butyls), 3.0 (2 H, m, CH_2), 4.7–5.9 ppm (4 H, m, vinyls); IR (thin film on the mixture) (max) 3100, 3040, 2960, 2900, 2870, 1740, 1635, 1620, 1480, 1465, 1430, 1390, 1365, 1260, 1200, 1130, 970, 890, 880, and 690 cm^{-1} ; two parent ions were seen by mass spec., m/e 158.0846 \pm 10 ($\text{C}_9\text{H}_{15}\text{Cl}$ calcd. 158.0862) and m/e 166.1697 \pm 15 ($\text{C}_{12}\text{H}_{22}$ calcd. 166.1722), which were verified as being derived from the isolated mixture (as opposed to being an artifact from preparative GLC) by GLC/mass spectrometry. *trans*-3,6,6-Trimethyl-1,4-heptadiene: the correction factor for *trans*-2,6,6-trimethyl-1,4-heptadiene was used in determining this yield: four products were seen by GLC, two were identified as having molecular weights indicating isomers of the desired 1,4-diene by GLC/mass spectrometry (m/e 138) and one as being derived from two organic groups from the mercurial, possibly the symmetrical 1,3-diene, *trans,trans*-2,2,7,7-tetramethyl-3,5-octadiene (m/e 166 for $\text{C}_{12}\text{H}_{22}$); the products were not isolated due to the low yield and complexity of the mixture.

Acknowledgments

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