(guanosine) complexes of Bau[7] and Cramer,[8] suggesting again that the influence of the crystal packing forces prevails *even* at stoichiometry.

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Supplementary Material Available: Listing of hydrogen atom parameters and structural factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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Structural Factors in the Facile Carbomagnesiation of Isolated Carbon–Carbon Double Bonds[1]

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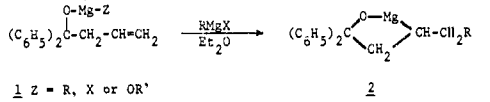
Abstract: The structural features in the carbinol and the Grignard reagent, the role of alternative coordination sites on the olefin, the effect of varying the donor solvent, and the role of transition metal catalysts were investigated for the carbomagnesiation of a series of 1,1-diphenyl-*n*-alken-1-ols, where n = 0, 1, 2, and 4. Allyl-, benzyl- and *tert*-butylmagnesium bromides in ethyl ether and diallylmagnesium in benzene were shown to add to such carbinols to yield either the corresponding carbinol or olefin in which the R group of the magnesium reagent was attached principally to the ω carbon or the original carbinol. In some reactions, and especially with 1-methoxy-1,1-diphenyl-3-butene, positional isomers of the resulting olefin indicated the occurrence of concurrent carbonium-ion rearrangements. The carbometalation is markedly promoted by transition metal catalysis, especially that by nickel. Strong donor solvents, such as tetrahydrofuran and amine coordination sites on the olefin substrate, caused a pronounced retardation of the carbomagnesiation. In light of these observations and other studies of the stereochemical course of reaction, a mechanism for the uncatalyzed carbomagnesiation is proposed involving the intramolecular rearrangement of an alkenoxy(alkyl)magnesium (**27**). In such a complex the incompletely coordinated magnesium is envisaged as initiating an electrophilic attack on the proximate olefinic π bond. Infrared and NMR spectroscopic studies of alkenols are drawn upon to support these views. The fostering action of nickel salts on such carbometalations is ascribed to the reactivity of π-allylnickel intermediates.

The tendency to add to, or to effect substitution at, a wide variety of functional groups has permitted Grignard reagents to exert a pervasive influence on organic synthesis. However, although diverse polar, unsaturated bonds, such as carbonyl, azomethine, cyano, and thiocarbonyl groups, do add such reagents readily, olefinic and acetylenic linkages have generally been found to be unreactive.[3] The one established exception has been an olefinic group, either conjugated with a carbonyl or similar group, or forming the exocyclic ethylenic unit of a fulvene,[4] where, by using copper catalysis[5] or by resorting to more reactive Grignard reagents (allylic or *tert*-alkyl), smooth addition can be achieved. However, in 1965 we observed another structural feature that facilitated the addition of Grignard reagents to carbon-carbon unsaturation, namely the presence of a neighboring hydroxyl group.[6] Thus, alkenols in the form of their magnesium salts were found to undergo ready addition of the carbon-magnesium bond to their olefinic linkage (carbomagnesiation) in refluxing ether, when allylic or *tert*-alkyl Grignard reagents were employed[7] (eq 1).



(1)

1 Z = R, X or OR' 2

This anchimeric assistance for carbomagnesiation has aroused considerable interest as to its scope and its mechanistic path. Subsequent studies in our laboratory and elsewhere have shown that this reaction can be realized with alkenols,[6-8] alkynols,[7,8] alkenyldialkylamines,[9] alkenylalkyl ethers,[7] and vinylic pyridines.[10] Similar, anchimerically assisted additions of organolithium[9,11] and -zinc[12] reagents have also been uncovered. These developments seem also to have prompted a renewed study of the carbomagnesiation of simple olefins under forcing conditions. By use of pressures of 30–70 atm and

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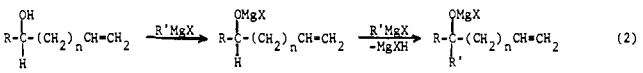
temperatures of 50–175 °C, first Shepherd in 1963[13] and later Lehmkuhl[14] were able to obtain 1:1 adducts of ethylene and other 1-alkenes with ethereal solutions of *sec*-alkyl, *tert*-alkyl, and allylic Grignard reagents. Yet the credit for the first carbomagnesiation of simple olefins under forcing conditions seems to be owed to Podall and Foster,[15] who in 1958 reported that diethylmagnesium in ether reacted with ethylene at 50 atm and 100 °C to yield dibutylmagnesium. These composite studies of the forced carbomagnesiation of olefins do serve to show how significant the anchimeric assistance of hydroxylate sites is in the carbomagnesiation of alkenols.

A class of organomagnesium reactions that is formally related to the hydroxlate-assisted additions described in this article is the intramolecular reaction of alkenyl- and alkynylmagnesium compounds, leading to cyclic or open-chain organomagnesium isomers. Such reactions constitute a valuable intramolecular model for evaluating the structural and mechanistic factors involved in the carbomagnesiation of olefins and acetylenes. Detailed mechanistic studies of such organomagnesium rearrangements by Roberts, Richey, Hill, and others have provided some superb insights into the chemistry of Grignard reagents,[15b] and heteroatom-assisted carbomagnesiation (ref 6–10 and this article) shows that these processes have many mechanistic similarities.

The present report analyzes the structural factors, both in the alkenols and in the Grignard reagent, that underlie this facile carbomagnesiation of unconjugated olefinic bonds. In attempting to plumb the nature of such anchimeric acceleration, the efficacy of alternative neighboring groups, such as ether and amine sites, the influence of various solvents, and the purity of the magnesium metal are also examined.

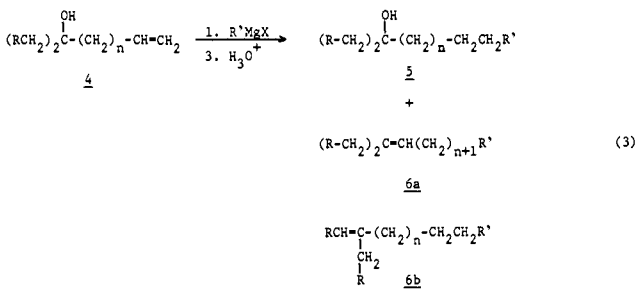
Results

The advantages of using a series of 1,1-diphenyl-*n*-alken-1-ols (**3**) for this study soon become apparent. First of all, 1,1-disubstituted alken-1-ols did not have the serious drawback of 1-substituted alkenols, namely the possibility of an interfering magnesium hydride transfer[16] (eq 2). Secondly, unlike



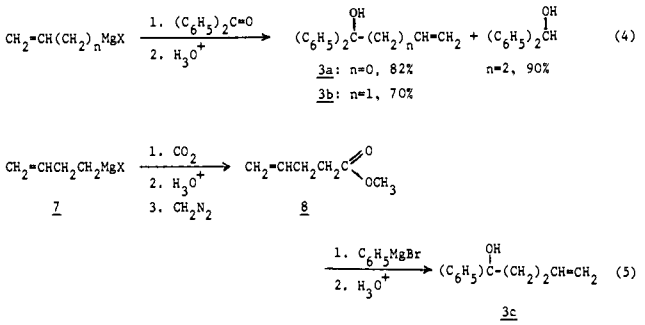
(2)

1,1-diphenyl-*n*-alken-1-ols (**3**), which yielded only one dehydration product, any concurrent dehydration of the starting 1,1-dialkyl-*n*-alkenol or its product carbinol (**4**) could yield two positionally isomeric alkenes (eq 3).



(3)

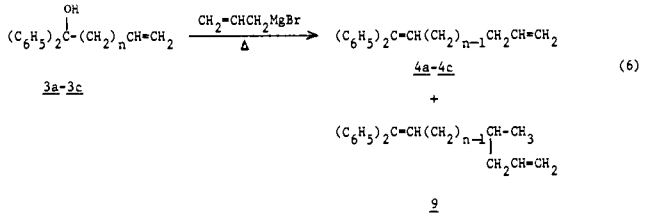
Accordingly, the series of 1,1-diphenyl-*n*-alken-1-ols (**3**) was chosen as substrates for the carbomagnesiation reaction. The homologues of **3**, where $n = 0$ and 1 (**3a** and **3b**), were prepared from benzophenone and the appropriate Grignard reagent. The homologue of **3**, where $n = 2$ (**3c**), could not be made analogously (eq 4) because the requisite 3-butenylmagnesium bromide (**7**) underwent magnesium hydride transfer almost exclusively, to yield benzhydrol (cf. eq 2). Consequently, **7** was converted into methyl 4-pentenoate (**8**) and this ester treated with phenylmagnesium bromide to yield **3c** (eq 5). Finally, the homologue of **3**, where $n = 4$ (**3d**), was readily available from our prototype reaction, the allylation of allyldiphenylcarbinol (cf. eq 1).



(4)

(5)

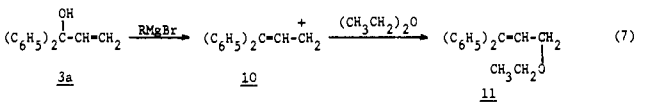
Reactivity of the Homologous Alkenols. Treatment of the alkenols **3a–d** with a 2.5-fold amount of allylmagnesium bromide in ether and stirring of the mixture at 20–30 °C for 60 h gave a satisfactory yield of the allylated alcohol **5b** only in the case of **3b** (56%). With **3a** and **3c** prolonged reaction times (240 h) or elevated temperatures (refluxing benzene) were required to form even modest amounts of the allylated, but dehydrated, products (**4a–c,** 10–30%) (eq 6). The identifiable



(6)

products were the corresponding 1,*n*-alkadienes; with **3c** spectral data indicated that the allylation might also have led to the branched olefin **9** (NMR doublet at 0.7–0.85 ppm). In contrast, 1,1-diphenyl-6-hepten-1-ol (**3d**) showed no sign of undergoing carbomagnesiation, even after prolonged reaction in refluxing benzene. Dehydration to yield 1,1-diphenyl-1,6-heptadiene was the only result.

The dehydration of either the starting alkenols (**3a–d**) or the carbinol products (**5a–d**) occurred during contact with allylmagnesium bromide itself and was favored by a large excess of the Grignard reagent (e.g., **3b** yielded a 78% yield of solely alkene **4b** when a 10-fold excess of the Grignard reagent was used) or by elevated temperatures (e.g., refluxing benzene). That carbonium reactions, presumably promoted by magnesium halides, may be involved in these dehydrations seems likely from the isolation of small amounts of 1-ethoxy-3,3-diphenyl-2-propene (**11**) from the reaction of **3a** in ethyl ether. The readily formed allylic carbonium ion **10** could coordinate with ethyl ether to form the allylic ether **11** (eq 7). With the



(7)

other diphenylcarbinols carbonium-ion formation would be followed by proton loss to RMgX and the formation of **4**.

Catalysis of the Allyl Grignard Additions. With carefully purified 1,1-diphenyl-3-buten-1-ol (**3b**), the effect of using allylmagnesium bromide prepared from magnesiums of different purity was explored. From mixtures of **3b** and the Grignard reagent in a 1:2.5 ratio, the following yields of 1,1-diphenyl-6-hepten-1-ol (**3d**) were obtained after 84 h at 25 °C: (1) >99.96 Mg, 62%; (2) 99.949 Mg, 70%; (3) ordinary 99.8% Mg, 85%; and (4) ordinary 99.8% Mg + 3.0% nickel(II) acetylacetonate, 93% (after 36 h, 91%).

A similar addition of $Ni(acac)_2$ to the reaction of 1,1-diphenyl-2-propen-1-ol (**3c**) enhanced the Grignard reaction in refluxing benzene and gave a 54% yield of 1,1-diphenyl-1,5-

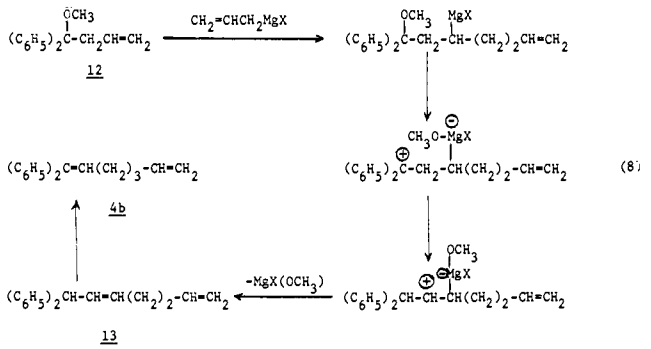
hexadiene (**4a**), but the addition of the nickel catalyst was of no avail in the attempted allylation of **3d**.

Solvent Effects. The interaction of allylmagnesium bromide with **3b** was strongly retarded when the majority of the ethyl ether was replaced either by tetrahydrofuran or by benzene. Yields under comparable conditions were as follows: C_6H_6, 4%; Et_2O, 60%; and THF, 1%. The retardation in benzene may have been due to the heterogeneity of the reaction mixture; the others were homogeneous.

By contrast, with diallylmagnesium **3b** reacted well in a homogeneous benzene solution (65%) but poorly in ether or THF solution (1%).

Behavior of Other Grignard Reagents toward 3b. As mentioned above, diallylmagnesium proved to be a very effective alkylating agent toward **3b,** but with solvent effects the opposite of allylmagnesium bromide. In accord with previous experience, active Grignard reagents such as benzyl and *tert*-butyl, were also capable of alkylating **3b,** but ordinary alkyl and aryl reagents were not.

Alternative Coordination Sites on Alkene Substrates. That magnesium salt formation at a hydroxyl group was not essential for assisted allylation was shown by the allylation of 1-methoxy-1,1-diphenyl-3-butene (**12**). By heating with allylmagnesium bromide in toluene, **12** underwent allylation and demethanolation. The formation of isomeric 1,1-diphenylheptadienes (**4b** and **13**) points again to carbonium-ion reactions that, in this instance, initiated a hydride shift (cf. eq 8).

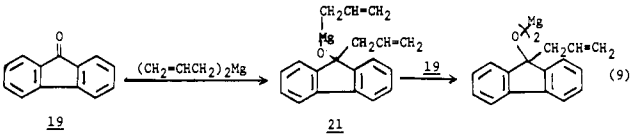


The preponderance of **13** at shorter reaction times demonstrates that **13** undergoes isomerization to **4b,** again possibly via Lewis acid generated carbonium ions.

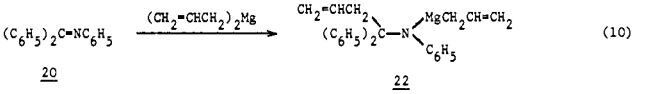
An alternative mode of formation of **13,** namely the demethanolation of **12** to yield 1,1-diphenyl-1,3-butadiene (**14**) and the addition of allylmagnesium bromide to **14,** was ruled out by heating pure **14** with the Grignard reagent in refluxing toluene for 48 h and finding no **13** in the recovered starting material.[17] Therefore, there is no doubt that the methoxyl group provides anchimeric assistance in the carbomagnesiation of **12**.

On the other hand, magnesium salt formation or simple coordination at a nitrogen site did not lead to anchimerically assisted allylation. Neither α-allylbenzhydrylaniline (**15**) nor 2-allyl-1-methyl-1,2-dihydroquinoline (**16**) underwent any

significant allylation with C_3H_5MgBr, although each should be able to bind RMgBr at nitrogen, proximate to the substrate's allyl group. The lack of allylation in **17** and **18** seems to be due to the stronger coordination of nitrogen with the magnesium, compared with the coordination of oxygen with the magnesium in **1** or in **12**. Evidence that a carbon-magnesium bond coordinated with nitrogen is less reactive than one coordinated with oxygen was gained in the following manner. Although both 9-fluorenone (**19**) and benzophenone anil (**20**) react individually with 1 molar equiv of allylmagnesium bromide essentially in a quantitative manner, diallylmagnesium exhibits a different behavior; 0.5 molar equiv of $(C_3H_5)_2Mg$ will react quantitatively with 1 molar equiv of 9-fluorenone. This finding means that intermediate **21** is still able to allylate



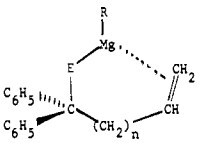
another equivalent of **19** (eq 9). **20,** however, reacts with 0.5 molar equiv of $(C_3H_5)_2Mg$ to give only a 50% conversion to **15**. Consequently, intermediate **22** must be unable to allylate the remaining half of **20** (eq 10). Thus, it is clear that nitrogen



coordination can strongly suppress the reactivity of the allylmagnesium bond. For this reason, no anchimerically assisted allylation was observed with **15** or **16**.

Discussion

Structure of the Reagents. The failure of the olefin, 1,1-diphenyl-1,3-butadiene (**14**), to react with the allyl Grignard reagent, even at 110 °C, plainly supports the anchimeric acceleration of the alcoholate function in the 1,1-diphenyl-*n*-alken-1-ols (**3a–d**). The ease of carbomagnesiation decreased in the series, 1,1-diphenyl-3-buten-1-ol (**3b**) > 1,1-diphenyl-2-propen-1-ol (**3a**) >> 1,1-diphenyl-4-penten-ol (**3c**) >>> 1,1-diphenyl-6-hepten-1-ol (**3d**). The heptenol actually could not be made to react either at elevated temperatures or by nickel catalysis. Since 1-methoxy-1,1-diphenyl-3-butene (**12**) could also be allylated by the allyl Grignard reagent, it can be concluded that an oxygen coordination site α, β, or γ to the olefinic linkage assists in these carbomagnesiations (**23**). As



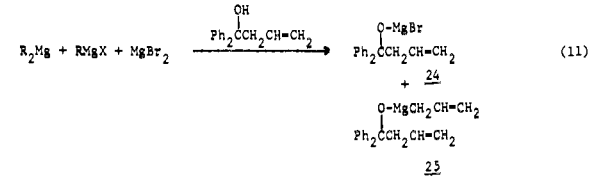
a precedent for such intramolecular interactions between an acidic site and an olefinic linkage, one could cite the hydrogen-bonding studies on unsaturated alcohols.[18] Some of these alcohols displayed shifts in the infrared hydroxyl absorption due to intramolecular hydrogen bonding (Δ (cm^{-1}), Δ (cal/mol)): $CH_2{=}CHCH_2OH$ (13, 36); $CH_2{=}CHCH_2CH_2OH$ (40, 114); and $CH_2{=}CHCH_2CH_2CH_2OH$ (0, 0). In a qualitative sense, the reactivity of the carbinols **3a–c** does parallel the tendency for such hydrogen bonding in the unsubstituted alkenols. Examination of the infrared C=C stretch and $CH_2{=}CH$ out-of-plane deformation frequencies for **3a–d** did show small reproducible variations: C=C, 1653 (**3a**), 1633 (**3b**), 1637 (**3c**), and 1637 cm^{-1} (**3d**); $CH_2{=}CH$, 910 (**3a**), 913 (**3b**), 910 (**3c**), and 910 (**3d**). All such data point to a maximum in the interaction between the hydroxy and olefinic groups for the butenol system. This conclusion supports the suggestion that an O-coordinated magnesium (**23**) would interact most effectively with the double bond when $n = 1$.

The ability of such reagents as allylmagnesium bromide, diallylmagnesium, benzylmagnesium bromide, and *tert*-butylmagnesium bromide to effect carbomagnesiation of the most reactive alkenol (**3b**) and the contrasting failure of aryl and primary alkyl Grignard reagents are in accord with reactivity trends established in other reactions.[19] Whether the

observed reactivity trend for carbomagnesiation is in better accord with a heterolysis or a homolysis of the carbon-magnesium bond will be considered later in this section.

Another important structural aspect of this reaction is the nature of the magnesium intermediate initially formed from the alcohol. Because of the Schlenk equilibrium allylmagnesium bromide, for example, consists of monomeric and dimeric forms of equal amounts of R_2Mg, $RMgBr$, and $MgBr_2$ at the concentration (0.25 M) employed in these studies.[20,21] Composite NMR and infrared spectral studies lead to the alternative conclusions either that the allyl group is bonded to magnesium in a σ manner, with ~50% ionic character, or that the allyl group is π bonded to magnesium, but undergoes rapid carbon-carbon bond rotations.[22,23]

When this Grignard reagent reacts with an alkenol, therefore, two different alkoxides can be expected (eq 11). From



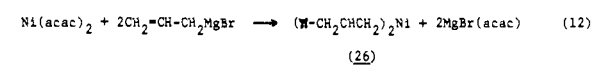
(11)

studies of alkylmagnesium alkoxides, it can be supposed that **24** and **25** would have a strong tendency to be dimeric.[24] The results obtained with **3b** and the allyl Grignard reagent prepared from triply sublimed magnesium (in a 2.5:1.0 ratio) suggest that equal amounts of **24** and **25** were initially formed. Since the carbomagnesiation virtually halted after a 50% conversion (36 h; slowly up to 62% in 84 h), it can be concluded that, barring catalytic influences, only **25** is important in the uncatalyzed allylation. Allylmagnesium bromide or diallylmagnesium present in the ether medium seems to react with **24** only very slowly to yield allylated product.

Solvent Effects and Coordination Sites on Olefinic Substrates. Although donor coordination sites on the substrate olefin foster the carbomagnesiation reaction, too great a Lewis basicity of the coordination sites on the substrate olefin or of the solvent strongly retards the allylation. Witness the inertness of α-allylbenzhydrylaniline (**15**) and 2-allyl-1-methyl-1,2-dihydroquinoline (**16**) and the inhibiting effect of tetrahydrofuran on the reactivity of allylmagnesium bromide or diallylmagnesium. Since **25** seems to be the reactive component, the allylation can be viewed as occurring through an electrophilic attack of magnesium on the C=C bond (cf. **23**). If the magnesium is coordinated either at a very basic amine site (E = NR) or with THF molecules (THF), its Lewis acidity toward the olefinic π cloud should be significantly lowered and hence its reactivity depressed.

Nickel Catalysis and Electron Spin Resonance Monitoring. With reagents prepared from triply sublimed magnesium, individual reaction mixtures of 1,1-diphenyl-3-buten-1-ol (**3b**) with allylmagnesium bromide (1:2.5) in diethyl ether and of the butenol with diallylmagnesium (1:1.25) in benzene were monitored by ESR spectroscopy immediately after admixing at 25°C and again at hourly intervals. No absorptions due to radicals could be observed, even though concentrations of radicals as low as 10^{-6} M could easily have been detected.

The remarkable effect of nickel salts on this allylation reaction had three interconnected advantages: more rapid reaction, higher conversion to product (with **3b**, almost a quantitative yield), and less dehydration of the product alcohol. The origin of the nickel catalysis seems to lie in the formation of bis(π-allyl)nickel (**26**) (eq 12). This nickel reagent[25-27] and

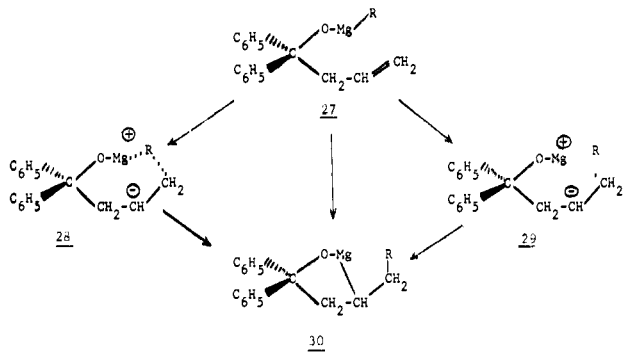


(12)

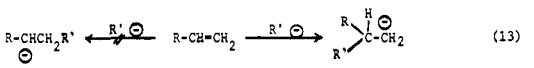
(26)

even allylnickel bromide[28] are known to allylate various olefinic, acetylenic, and carbonyl linkages. Accordingly, such nickel allyls seem able to allylate the alkenols (with anchimeric assistance through the alkoxides) more rapidly than their magnesium analogues. Furthermore, because the conversion of the butenol **3b** approaches 100%, these nickel allyls must be able to convert alkenoxymagnesium bromides (such as **24**) into alkenoxy(allyl)nickel or -magnesium (**25**) reagents, which are then capable of undergoing assisted allylation. Whether the nickel-promoted reaction proceeds by a mechanism similar to that displayed by the uncatalyzed reaction is uncertain.

Stereochemistry and Mechanism of the Uncatalyzed Carbomagnesiation. An integrated view of the influences of substrate, Grignard reagent, and medium effects leads to a mechanism involving the intramolecular rearrangement of an alkenoxy(alkyl)magnesium (**27**). Its passage to product **30** could occur by (a) an electrophilic attack of magnesium on the olefinic linkage, similar to the well-established mechanism for



the carbalumination of olefins[29] and acetylenes;[30] (b) a nucleophilic attack of a developing R^- on the C=C bond (**28**); or (c) an electron transfer leading to a radical-anionic transition state (**29**). First of all, a transition state involving carbanionic attack (**28**) does not accord either with solvent effects or with the regiochemistry of addition. In processes involving the formation of carbanions, the use of stronger donors (THF, TMEDA, HMPT) invariably increases the rates of reaction,[31,32] but the effect of stronger donors in these carbomagnesiations is to retard the reaction. In addition, carbanionic addition to a terminal alkene should be favored, for thereby the more stable terminal carbanion is formed. In carbomagnesiation a secondary carbanion would have been a postulated intermediate (eq 13).

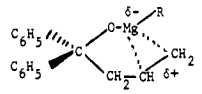


(13)

Secondly, an electron-transfer process is consistent with the nature of the effective R groups in carbomagnesiation. If R must assume some radical character in the transition state (**29**), then the reactivity of allyl, benzyl, and *tert*-butyl can be rationalized. Arguments against such electron transfer, however, seem superior. If electron transfer develops cationic character on magnesium, increasing the donor strength of the solvent should enhance the reaction.[33] As with a carbanionic view, this expectation conflicts with fact. Also, **29** implies the acceptance of an electron by the π^* orbital of an isolated C=C bond. The electron affinity of simple olefins make them unlikely to accept electrons even from more powerful electron sources, such as sodium.[33]

Finally, all efforts to detect paramagnetic intermediates were unsuccessful and no chemical byproducts of free-radical processes, such as dimers of **3b** or of its allylated derivative, could be detected.

Therefore, the evidence gathered in this study is in best accord with an electrophilic attack by magnesium in the rearrangement of **27**. The transition state **31** would lead to an increase of electron density at magnesium, labilizing R in an anionic sense (pseudo-*ate* complex).[34] The greater the electron



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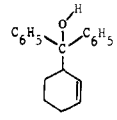
density available in the R–Mg bond, the more readily R would migrate to the olefinic bond. From this view it would follow that *tert*-butyl Grignard reagents owe their reactivity in carbomagnesiation to the inductive electron release by the substituent methyl groups. Allylic and benzylic Grignard reagents would be more reactive because electron delocalization would reduce the energy necessary to heterolyze the carbon-magnesium bond in **25** and **31**. Insofar as this mechanism parallels carbalumination, a known electrophilic process, such carbomagnesiation should be expected to proceed stereospecifically in a syn fashion. Indeed, carbomagnesiations of certain norbornenyl alcohols[35] and of **32**,[36] closely related to **3b**, have been



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shown to occur in a manner syn with respect to the hydroxyl-bearing substituent.

Experimental Section

General Procedures. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer spectrometer, Model 137 or Model 337, equipped with sodium chloride optics. Proton magnetic resonance spectra (^{1}H NMR) were obtained with a Varian spectrometer, Model A-60, on neat samples or on 10% solutions in pure solvents. The values are reported on the δ scale in parts per million with reference to internal or external tetramethylsilane, followed by the relative proton intensities and the coupling constants (J) in hertz. Vapor phase chromatographic analysis (VPC) and isolations were carried out on an F&M chromatograph, Model 720, equipped with a 6 ft × 0.25 in. column of 10% SE-30 silicone gum rubber on Chromosorb P. Mass spectra of solids and liquids were obtained on a Varian MAT spectrometer, Model CH5, and those of gases on a Consolidated Electrodynamics instrument, Model CEC-21-620A. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

All preparations and reactions involving air- and moisture-sensitive organometallic intermediates were conducted under an atmosphere of dry, oxygen-free nitrogen, with adherence to published procedures. Solvents of reagent grade were used in all reactions. The anhydrous ethyl ether (Fisher) was used directly; the benzene was dried just before use by distilling from the sodium ketyl of benzophenone under a dry nitrogen atmosphere; the tetrahydrofuran (Baker) was stored overnight over sodium hydroxide pellets, then heated at reflux for 24 h over freshly cut pieces of sodium metal, distilled under a nitrogen atmosphere from the sodium, and finally redistilled from lithium aluminum hydride just prior to use.

Hydrolyses were generally conducted by the slow addition of a saturated, aqueous ammonium chloride solution, and the organic product was extracted into ethyl ether. The solvent was removed by drying over anhydrous calcium sulfate and, where distillation was required, the product was fractionated through a stainless steel spinning band column (Nester-Faust).

Standard titrimetric procedures were used for the estimation of organomagnesium concentrations.

Starting Materials. 1,1-Diphenyl-2-propen-1-ol (3a). Vinylmagnesium chloride was prepared (88%) by the addition of vinyl chloride (62.0 g, 1.0 mol) dissolved in 300 mL of anhydrous tetrahydrofuran to a vigorously stirred suspension of 20.0 g (0.87 g-atom) of magnesium turnings in 100 mL of dry THF.[37] The resulting Grignard reagent was added dropwise over a period of 2 h to a solution of benzophenone (67.0 g, 0.37 mol) in 300 mL of dry THF. After 36 h at 25 °C, the reaction mixture was hydrolyzed and worked up with an iced, saturated ammonium chloride–sodium carbonate solution, so as to avoid acid-catalyzed rearrangement. The product distilled at 118–120 °C (0.4 mm): 63.0 g (82%); n^{25}D 1.5902; IR (neat) 3700, 3580 (OH), 3110 (arom CH), 2930 (aliph CH), 1650 (C=C), 985 and 915 cm^{-1} (CH=CH_2); NMR (neat) 7.10 (m, 10 H), 6.29 (q, CH=CH_2, J_{cis} = 10 Hz), J_{trans} = 16 Hz), 5.08 (q, 2 H, CH=CH_2), 2.76 (s, OH). Anal. Calcd for $C_{15}H_{14}O$: C, 85.78; H, 6.66. Found: C, 86.11; H, 6.71.

1,1-Diphenyl-3-buten-1-ol (3b). Allylmagnesium bromide was prepared in 95% yield in accord with a published procedure.[38] Using a 10% excess of the Grignard reagent with 0.60 mol of benzophenone provided, after 10 h at room temperature, a 70% isolated yield of the alcohol: bp 124–125 °C (0.2 mm); n^{25}D 1.5830 (lit.[19] bp 150–155 °C (3 mm); n^{25}D 1.5825); NMR (CCl_4) 7.0–7.5 (m, 10 H), 5.67 (q of t, CH=CH_2, J_{trans} = 17, J_{cis} = 9, J_{gem} = 6 Hz), 2.92 (d, 2 H, CH=CH_2), 2.58 (s, OH); IR (neat) 3580 (OH), 1650 (C=C), 990, 910 cm^{-1} (CH=CH_2).

1,1-Diphenyl-4-penten-1-ol (3c). Step A. 4-Pentenoic Acid. 3-Butenylmagnesium bromide was prepared in 87% yield by the addition of 42.0 g (0.32 mol) of 4-bromo-1-butene dissolved in 200 mL of anhydrous ethyl ether to a vigorously stirred suspension of magnesium turnings (8.0 g, 0.33 g-atom) in 100 mL of ether. The attempted synthesis of the alcohol by the addition of this Grignard reagent to 0.22 mol of benzophenone, however, led to a 90% yield of benzhydrol, mp 68–69 °C, from ethanol.

Therefore, an identical batch of the Grignard reagent was poured into a slurry of powdered solid carbon dioxide in ether. The thawed mixture was hydrolyzed with 2 N H_2SO_4, and the separated ether layer was extracted with 10% aqueous sodium carbonate. The aqueous extracts were acidified with 5 N HCl and then reextracted with ether. The ether extracts were dried ($MgSO_4$), the solvent evaporated, and the residue distilled to give 18.5 g (67%) of the 4-pentenoic acid, bp 83–85 °C (16 mm), n^{25}D 1.4310 (lit.[39] bp 95–97 °C (15 mm)).

Step B. Methyl 4-Pentenoate. The 4-pentenoic acid was esterified in ethyl ether with diazomethane prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide,[40] 47% yield, bp 126–127 °C (750 mm) (lit.[41] bp 127–128 °C).

Step C. 3c. An ethereal solution of phenylmagnesium bromide, prepared from 67.0 g (0.426 mol) of bromobenzene and 8.0 g (0.33 g-atom) of magnesium, was added to 10 g of **8** and the mixture allowed to stand for 40 h. Hydrolytic workup yielded 16.0 g of the alcohol: 67%; bp 145–148 °C (0.5 mm); n^{25}D 1.5710; NMR (CCl_4) 7.0–7.5 (m, 10), 5.75 (q, 1, CH=CH_2, J_{trans} = 17.5, J_{cis} = 9.5 Hz), 4.77 (q, 2, CH=CH_2), 2.34 (s, 1, OH), 2.15 (t, 4, CH_2CH_2); IR (neat) 3590 and 3700 (OH), 1650 (C=C), 995 and 910 cm^{-1} (CH=CH_2). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.58; H, 7.79.

1-Methoxy-1,1-diphenyl-3-butene. A solution of 0.12 mol of allylmagnesium bromide in 200 mL of ether was added to 25 g (0.11 mol) of benzophenone dimethyl ketal in 500 mL of dry toluene and the resulting solution was distilled to remove the ether (fresh, dry toluene being added until the temperature of the distillate attained 108–110 °C). Thereupon the resulting suspension was stirred under reflux for 120 h. Usual hydrolytic workup yielded 14 g (54%) of the desired product: bp 110–112 °C (0.3 mm); mp 59–61 °C; NMR ($CDCl_3$) 7.0–7.4 (m, 10), 5.57 (q, 1, CH=CH_2, J_{trans} = 18, J_{cis} = 9.0 Hz), 4.90 (q, 2, CH=CH_2), 3.02 (d, 2, CH_2, J = 6 Hz), 2.99 (s, 3, OCH_3); IR ($CHCl_3$) 3180 (arom CH), 1640 (C=C), 995 and 910 cm^{-1} (CH=CH_2). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.39; H, 7.84.

Diallylmagnesium. To 300 mL of an ethereal solution of allylmagnesium bromide (0.1 mol) was added 35 mL (0.41 mol) of freshly purified and distilled (over CaH_2) 1,4-dioxane. After stirring for 12 h the mixture was allowed to stand and the clear supernatant layer was siphoned off under nitrogen. The precipitate was washed with 100 mL of a 9:1 (v/v) mixture of dry ether and dioxane. The combined clear extracts gave a negative test for halogen when a sample was hydrolyzed and treated with silver nitrate. Analysis for magnesium by titration of a hydrolyzed sample showed a yield of 0.035 mol (lit.[21] 0.033 mol).

Magnesium. Unless otherwise specified, the magnesium turnings used for the preparation of organomagnesium reagents in this study were of 99.8% purity, obtained in reagent grade from the J.T. Baker Chemical Co. The reagent termed Dow magnesium was >99.96% pure and contained the following (percent): Al (<0.0011), Ca (<0.01), Cu (<0.001), Fe (<0.0005), Mn (<0.0005), Ni (<0.0005), Pb (<0.01), Si (<0.01), Sn (<0.01), and Zn (<0.003) (from the Dow Chemical Corp., courtesy of Dr. F. Johnson). The reagent termed United Mineral magnesium was 99.949% pure and contained the

following (percent): Al (0.0013), Ca (0.015), Cu (0.001), Fe (0.0005), Mn (0.0005), Ni (0.005), Pb (0.013), Si (0.001), Sn (0.015), and Zn (0.001) (from the United Mineral and Mining Corp.).

Organomagnesium Reactions. A. Effect of Chain Length. 1. Allylmagnesium Bromide and 3a. Admixture of 0.25 mol of the Grignard reagent in 360 mL of ether with 21 g (0.1 mol) of the alcohol dissolved in 140 mL of ether led to a vigorous reaction and the deposition of the magnesium alcoholate. After the mixture stirred for 240 h at 20–30 °C, the usual workup yielded 10.5 g (50%) of the starting material and 3.1 g (13.3%) of 1,1-diphenyl-1,5-hexadiene (**4a**): bp 129–129.5 °C (0.55 mm); n^{25}_D 1.5834; NMR ($CDCl_3$) 7.12 (m, 10 H), 6.02 (t, C=CH, J = 7 Hz), 5.88 (m, CH=CH_2, J_{trans} = 18, J_{cis} = 9 Hz), 4.95 (br q, CH=CH_2), 2.99 (4 H, CH_2CH_2); IR (neat) 3120, 2950, 1650 (C=C), 990 and 910 (CH=CH_2), 758, 695 cm^{-1}. Anal. Calcd for $C_{18}H_{18}$: C, 92.25; H, 7.75. Found: C, 92.08; H, 7.89.

In one run the magnesium alcoholate suspension was allowed to reflux. Workup yielded both **4a** and ~5% of 1-ethoxy-3,3-diphenyl-2-propene: NMR ($CDCl_3$) 7.17 (10 H), 6.0 (t, C=CH, J = 7.0 Hz), 3.98 (d, 2 H, J = 7.0 Hz), 3.35 (q, 2 H, J = 7.0 Hz), 0.97 (t, 3 H).

2. Allylmagnesium Bromide and 3b. Admixture of 0.13 mol of the Grignard reagent in 250 mL of ether with 11.2 g (0.05 mol) of the alcohol led to a vigorous reaction and the formation of a suspension. Stirring at 20–30 °C for 60 h and usual workup yielded 7.4 g (56%) of **3d**: bp 164–166 °C (0.8 mm); n^{25}_D 1.5630; NMR ($CDCl_3$) 7.30 (m, 10 H), 5.82 (m, CH=CH_2, J_{trans} = 18, J_{cis} = 10, J_{CH_2H} = 6 Hz), 4.99 (q, CH=CH_2), 2.60 (s, OH), 2.05 (m, 4 H), 1.30 (m, 4 H); IR (neat) 3620 (OH), 3120, 2980, 1645 (C=C), 1600, 990 and 910 (CH=CH_2), 745, 695 cm^{-1}.

In a reaction involving 0.1 mol of the alcohol **3b** and 1.05 mol of the Grignard reagent in a total volume of 1000 mL of ether, which was allowed to react for 60 h at 20–30 °C, the product was 1,1-diphenyl-1,6-heptadiene (**4b**), isolated in 78% yield: bp 132–133 °C (0.85 mm); n^{23}_D 1.5788; NMR (CCl_4) 7.15 (m, 10 H), 6.01 (t, C=CH, J = 7.5 Hz), 5.69 (q, CH=CH_2, J_{trans} = 16, J_{cis} = 7 Hz), 4.89 (q, CH=CH_2), 2.05 (br t, 4 H), 1.52 (q, 2 H). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.89; H, 7.96.

3. Allylmagnesium Bromide and 3c. Admixture of 0.13 mol of the Grignard reagent in 250 mL of ether with 11.9 g (0.05 mol) of the alcohol in 100 mL of dry benzene yielded a suspension from which the ether was replaced by benzene through distillation. The reaction mixture (500 mL) was then heated at reflux for 96 h, worked up by hydrolysis, and fractionally distilled to yield (1) 1.7 g (16%) of 1,1-diphenyl-1,4-pentadiene (bp 120–125 °C (0.4 mm); NMR ($CDCl_3$) 7.25 (s, 10 H), 6.05 (t, C=CH), 5.65 (m, CH=CH_2), 5.1 (m, CH=CH_2), 2.85 (t, CH_2)) and (2) 7.8 g (60%), bp 145–150 °C (0.4 mm), of a mixture that GLPC showed contained three components of similar retention times and in ca. equal proportions. Although these components were not completely separable, one component could be isolated in an enriched fraction and spectrally identified as 1,1-diphenyl-1,7-octadiene (**4c**): NMR (CCl_4) 7.25 (m, 10 H), 6.00 (t, C=CH), 5.45 (q, CH=CH_2, J_{trans} = 19, J_{cis} = 10 Hz), 4.90 (q, CH=CH_2), 2.05 (m, 4 H), and 1.52 (m, 4 H); IR (neat) 3080, 2950, 1650 (C=C), 1600, 990 and 910 (CH=CH_2), 755, 695 cm^{-1}. The other components had NMR and IR spectral features very similar to **4c** but displayed a broad doublet at 0.7–0.85 ppm, consistent with the presence of a $>CHCH_3$ group. Therefore, one of the olefinic components may be 4-methyl-1,1-diphenyl-1,6-heptadiene, the product resulting from allylating **3c** with a regiochemistry the reverse of that leading to **4c**.

4. Allylmagnesium Bromide and 3d. Neither the reaction of 2.5 equiv of the Grignard reagent with **3d** in ethereal solution at 25–30 °C nor a similar attempt in refluxing benzene led to any sign of addition to the double bond of **3d**, even after reaction times of several days. Elevated temperatures, however, did lead to some dehydration of the starting alcohol.

B. Various Grignard Reagents with 3b. 1. Benzylmagnesium Bromide. The Grignard reagent[42] (0.1 mol in ethyl ether) was allowed to react with **3b** (9.0 g, 0.04 mol) for 96 h at 25–30 °C. Workup and GLPC analysis indicated that a 20% yield of 1,1,5-triphenylpentene was obtained. Preparative GLPC (10% SE-30 silicone gum rubber on firebrick) gave a sample that was spectrally pure: bp 150–155 °C (0.35 mm); n^{25}_D 1.5932; NMR ($CDCl_3$) 7.0 (15 H), 6.10 (t, C=CH), 2.65 (m, $CH_2CH_2CH_2$), 1.00 ($CH_2CH_2CH_2$); IR (neat) 1600 cm^{-1} (C=C).

Attempts to increase the yield by conducting the reaction in refluxing ether or benzene caused extension dehydration of the starting carbinol (**3b**) and polymerization of the resulting butadiene. In these cases, the yields were <10%.

2. *tert*-Butylmagnesium Bromide. The Grignard reagent[43] (0.13 mol in ether) was allowed to react with **3b** (11.2 g, 0.05 mol). (During the addition of the first 0.05 mol of the Grignard reagent a transient bright red color was observed.) The ether solvent was then replaced by toluene (distillation) and the resulting mixture heated at reflux for 96 h. Workup and fractional distillation yielded (1) 800 mg (8%) of 1,1-diphenyl-1-butene (bp 100–102 °C (0.5 mm); NMR ($CDCl_3$) 7.30 (m, 10 H), 6.12 (t, C=CH), J = 7.5 Hz), 2.12 (m, $-CH_2-$), 1.02 (t, CH_3)) and (2) 5.0 g (38%) of 1,1-diphenyl-5,5-dimethyl-1-hexene (NMR ($CDCl_3$) 7.1–7.5 (m, 10 H), 6.23 (t, C=CH, J = 7.5 Hz), 2.00 (m, CH_2CH_2), 1.05 (s, CMe_3)).

The GLPC analysis and nmr spectrum of the main product revealed the presence of an impurity having similar properties; the presence of a *tert*-butyl group in this isomer suggests that it may be a double-bond isomer of this product.

No reaction occurred in ether at room temperature and <5% occurred in refluxing benzene after 96 h.

3. Phenylmagnesium Reagents. Interaction of 0.05 mol of the alcohol with 2.5 equiv of either phenylmagnesium bromide or diphenylmagnesium for 96 h in ether (36 °C), benzene (80 °C), or toluene (110 °C) gave no desired reaction. High recovery (~95%) of the alcohol **3b** or its dehydration product was the only result.

4. Diallylmagnesium. a. Ether. The interaction of 11.2 g (0.05 mol) of the alcohol **3b** with 0.063 mol of the magnesium reagent in 500 mL of ether for 96 h at room temperature gave <3% of the desired product **3d** and the starting material **3b** was recovered in 95% yield.

b. Benzene. By distillation the ether solvent in a 350-mL portion of 0.18 M diallylmagnesium was replaced by benzene. The benzene solution was then admixed with 0.05 mol of **3b** (total volume, 500 mL) and the reaction allowed to proceed at room temperature for 96 h. Workup yielded 65% **3d**, bp 164–166 °C (0.8 mm).

C. Solvent Effects. In addition to the aforementioned solvent effects with diallylmagnesium, the reactivity of allylmagnesium bromide toward **3b** was examined as a function of solvent. Thus, interaction of 0.13 mol of the Grignard reagent with 0.05 mol of **3b** in 500 mL of tetrahydrofuran gave <1% of addition after 96 h at 25–30 °C and 98% of **3b** was recovered.

Likewise, distillative replacement of the ether in 0.13 mol of the Grignard reagent by benzene and interaction of the resulting 500-mL solution with 0.05 mol for 96 h at 25–30 °C gave only 4% reaction and a 95% recovery of **3b**.

D. Additions of Allylmagnesium Bromide to Substrates Having Coordination Sites. 1. 1-Methoxy-1,1-diphenyl-3-butene (12). Admixture of 0.13 mol of the Grignard reagent with 11.9 g (0.05 mol) of **12**, distillative replacement of the ether by toluene, and heating the resulting mixture at reflux for 96 h at 110 °C yielded 50% starting material and 50% 1:1 mixture of two olefins, which were subjected to column chromatographic separation on silica gel: (1) 1,1-diphenyl-1,6-heptadiene (**4b**) and (2) 1,1-diphenyl-2,6-heptadiene (**13**) (bp 116–118 °C (0.5 mm); n^{25}_D 1.5653; NMR ($CDCl_3$) 7.10 (m, 10 H), 5.91 (m, CH=CH, CH=CH_2), 4.92 (q, CH=CH_2), 4.50 (d, $(C_6H_5)_2CH$), 2.10 (m, CH_2CH_2); IR (neat) 1650 (C=C), 910 and 990 (CH=CH_2), 975 cm^{-1} (trans CH=CH)). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.83; H, 8.00.

When the reaction was conducted as described above, but allowed to proceed for only 48 h, the 2,6-diene **13** was the exclusive product (40% yield).

2. 9-Fluorenone (19). a. Allylmagnesium Bromide. The interaction of 10.8 g (0.06 mol) of 9-fluorenone with 0.06 mol of 1.3 M allylmagnesium bromide in ether for 30 h at 25–30 °C gave, upon hydrolytic workup, column chromatographic separation on neutral alumina, and recrystallization from cyclohexane, 11.9 g (90%) of 9-allyl-9-fluorenol, mp 118–120 °C (lit.[44] mp 117–118 °C).

b. Diallylmagnesium. The corresponding reaction between 0.06 mol of the ketone and 0.03 mol of the magnesium reagent in ether (some dioxane from the preparation of the halogen-free reagent) for 30 h at 25–30 °C gave 12 g (92%) of 9-allyl-9-fluorenol.

3. Benzophenone Anil (20). a. Allylmagnesium Bromide. The interaction of 20.6 g (0.08 mol) of the anil **20** with 0.08 mol of the Grignard reagent in ether for 24 h at 25–30 °C gave, upon workup and recrystallization from petroleum ether (boiling point range 60–110 °C), 27 g (91%) of α-allylbenzhydrylaniline (**15**), mp 75–77 °C (lit.[45] mp 78.5–80 °C).

b. Diallylmagnesium. The interaction of 15.4 g (0.06 mol) of the

anil and 0.03 mol of the magnesium reagent in ether–dioxane for 30 h at 25–30 °C yielded, upon workup and column chromatography on neutral alumina, 9.1 g (51%) of the allyl adduct **15**, mp 75–77 °C, and ~50% starting anil.

In an attempt to liberate the magnesium reagent from any complex with **20** or the magnesium salt of **15**, a reaction was run, identical with the foregoing one but containing 2 mL of *N*-methylpyrrolidine. As before, however, again 50% **15** was obtained and the balance of anil **20** was recovered.

4. α-Allylbenzhydrylaniline (15).[46,47] To a solution of 3.0 g (10 mmol) of **20** in 60 mL of ether was added 100 mmol of allylmagnesium bromide in 15 mL of ether. After the reaction mixture was stirred at reflux for 20 h, the precipitate was collected and washed under a nitrogen atmosphere, suspended in 30 mL of dry benzene, and then heated under reflux for 6 days. Hydrolytic workup and analysis by TLC on silica gel plates, by use of a 10:1 mixture of petroleum ether–ether and a few drops of 1-butanol as a developer, showed the presence of much **15**, a modest amount of benzophenone anil, and a trace of an unknown at a small R_f value. No 1,1-diphenyl-1,6-heptadiene was discernible.

In a trial involving an excess of the Grignard reagent, 3.0 g (10 mmol) of **15** in 60 mL of ether and 36 mmol of the magnesium reagent in 45 mL of ether were heated at reflux for 10 h. Distillative replacement of the ether by dry benzene, heating the reaction mixture for 6 days at reflux, and hydrolytic workup gave a mixture of products. By TLC the predominant component was benzhydrylaniline; small amounts of aniline were detected, as were two minor components having R_f values similar to that of **15**. No more than a trace of 1,1-diphenyl-1,6-heptadiene was present. The NMR spectrum of this mixture was dominated by the absorption of **15**; minor absorptions in the regions of: 1.1, 1.2–1.5, and 2.5 ppm might indicate some allylation of **15**.

5. Other Substrates. Allylmagnesium bromide failed to add to the C=C linkages of the following substrates: (a) norbornadiene, when heated in refluxing ether for 3.5 days with 2 equiv of the Grignard reagent; (b) indole, when heated in either refluxing ether or benzene for 2 days, with 10 equiv of reagent; and (c) 2-allyl-1-methyl-1,2-dihydroquinoline, when heated in ether or refluxing benzene for 12 days with 2 equiv of reagent.

E. Catalysis of the Allyl Grignard Additions. For this work all reagents had to be protected from contact with any foreign metallic surfaces. Early work was invalidated because the starting alcohols, prior to use, had been distilled through a spinning-band column equipped with a stainless steel band. Apparently sufficient metallic impurities were introduced in this way to make the rates of reactions employing triply sublimed magnesium comparable with the rates of those reactions in which nickel had been intentionally used. Hence, in this study all starting alcohols were distilled in an all-glass apparatus just prior to use. Moreover, the comminution of triply sublimed magnesium pieces was not done on a lathe, but by sheathing the magnesium pieces in heavy plastic and hitting the brittle lumps through such a protective layer.

1. 3b. All reactions were conducted by preparing allylmagnesium bromide from the requisite grade of magnesium and then allowing 0.125 mol of this reagent to react with 0.05 mol of alcohol **3b** in ether in a total volume of 500 mL for 84 h at 25 °C. Usual workup and GLC analysis gave **3d** or 1,1-diphenyl-1,6-heptadiene (**4b**) in the following total yields: (a) ordinary Grignard Mg (99.8%), 85%; (b) ordinary Grignard Mg, to which Grignard reagent 3 mol % of nickel(II) acetylacetonate had been added, 93%; (c) Dow magnesium (>99.96%), 62%; and (d) United Mineral magnesium (99.949%), 70%.

2. 3a. To 21 g (0.1 mol of **3a** and 800 mg (3 mmol) of nickel(II) acetylacetonate in ether was added 0.26 mol of allylmagnesium bromide (99.8% Mg) in a total volume of 500 mL. Since no reaction occurred after 100 h in refluxing ether, the solvent was distillatively replaced by benzene. After 120 h at reflux, workup gave 12.5 g (54%) of 1,1-diphenyl-1,5-hexadiene.

3. Other Attempts. In a procedure analogous to the foregoing, 1,1-diphenyl-6-hepten-1-ol failed to react with the Grignard reagent and catalyst after 100 h in refluxing ether and a further 120 h in refluxing benzene (95% recovery). Likewise, 1,1-diphenyl-3-buten-1-ol failed to react with phenylmagnesium bromide and the nickel catalyst, even in refluxing toluene. Finally, 1,1-diphenyl-1,3-butadiene did not add allylmagnesium bromide (2.5 equiv) after 48 h in refluxing toluene.[17]

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References and Notes

(1) Part 15 of the series "Rearrangements of Organometallic Compounds"; cf. J. J. Eisch and J. E. Galle, *J. Organomet. Chem.*, **127**, C9 (1977), for part 14.
(2) Address correspondence to this author at The State University of New York at Binghamton.
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Evidence from X-ray Crystallography for the Diequatorial Disposition of a Five-Membered Ring in a Sulfurane[1]

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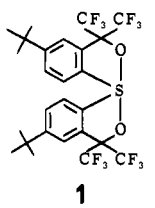
Abstract: The crystal and molecular structure of 1,1-bis[1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanolato]-5-methyl-3,3-bis(trifluoromethyl)[3*H*-2,1-benzoxathiole], trialkoxysulfurane **8**, was solved by X-ray crystallographic techniques. The compound crystallizes in space group $P2_12_12_1$ of the orthorhombic system with four molecules in a cell of dimensions a = 19.74 (3), b = 14.20 (2), c = 10.74 (1) Å. The X-ray structure analysis (R = 0.099) reveals trigonal bipyramidal geometry around sulfur similar to structures previously determined for other sulfuranes. The five-membered ring including the sulfur atom is, however, clearly in the diequatorial orientation, **8**. The axial S–O bond lengths are 1.840 (10) and 1.829 (10) Å while the equatorial S–O and S–C bond lengths are 1.630 (9) and 1.777 (14) Å, respectively. The equatorial C–S–O angle is 95.0 (6)° while the O(apical)–S–O(apical) angle is 172.0 (4)° (bent away from the lone pair of electrons on sulfur). Observations are made concerning the relationship of structure with reactivity of **8**.

Introduction

The X-ray structures of a number of sulfuranes having two five-membered rings, compounds **1–5**, have been reported.[2-5] In all of these cases, approximate trigonal bipyramidal geometry is observed around the sulfur atom and the five-membered rings have always been observed to be in the axial-equatorial orientation. Arguments have been advanced from a nuclear magnetic resonance spectral study[6] of **6** and from an infrared study[7] of **7** which support the axial-equatorial orientation of the five-membered ring for these compounds. The proton ortho to sulfur in the fused-ring system linked by apical and equatorial bonds to sulfur in compounds such as **6** and **7** is held very near the apical S–X bond linking the monodentate apical ligand X to sulfur. Much evidence has accumulated to support the generalization that such protons are shifted to very low fields.[8]



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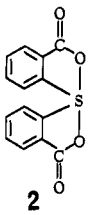

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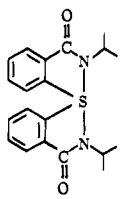

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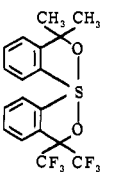

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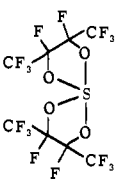

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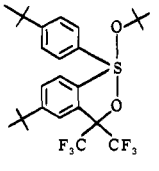

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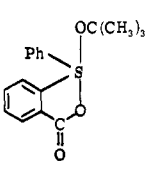

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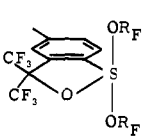
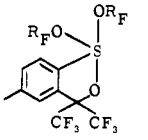
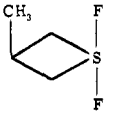
Astrologes and Martin have reported[8] the synthesis and reactions of trialkoxysulfurane **8**. A second covalent structure, **8a**, resembles structure **8** in that both satisfy both the electronegativity rules,[9,10] with apical fluoroalkoxy ligands, and the stricture against diapical linkage of five-membered rings. A nuclear magnetic resonance spectrum of the compound reveals an upfield shift of the proton ortho to the sulfur atom in the fused-ring system related to the ortho-proton resonances of other sulfuranes studied.[8,11] This has been interpreted[8] in terms of a preference for the geometry (**8**) with a diequatorial five-membered ring.





8, $R_F = OC(CF_3)_2C_6H_5$ **8a**

Denny has shown[12] from NMR evidence that difluorosulfurane **9** exists in a conformation with a diequatorial four-membered ring. In this case the preference for the geometry **9** with two apical fluorines over that (**10**) with one apical car-



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