2.20 and 2.23 two doublets (3H, 2-CH₃, $J^{5} = 1.22 \text{ Hz}$), 2.25 and 2.26 two singlets (3H, CH₃-C=0), 3.14 m (1H, 4-CH), 3.96-4.17 m (2H, 7-CH₂).

CONCLUSIONS

A synthesis is reported for 2,4-dimethyl-3-acetyl-1,6-dioxaspiro[4,4]non-2-ene, which is the first example of a trisubstituted spiroketal.

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CROSS COUPLING OF DIALKYLMAGNESIUM DERIVATIVES WITH ALLYLIC COMPOUNDS

CATALYZED BY COPPER SALTS

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The reaction of allylic compounds with Grignard reagents catalyzed by salts of copper [1, 2], nickel [3], iron and cobalt [4], titanium [5], and palladium [6] is a simple and efficient method for the preparation of unsaturated hydrocarbons. However, information concerning the use of dialkylmagnesium derivatives, which are more reactive than Grignard reagents, in these reactions is extremely limited [7].

In a continuation of a study of the cross coupling of allylic compounds with dialkylmagnesium derivatives in an effort to expand the scope of this reaction and elucidate the effect of the R_2Mg reagent structure on its reactivity, we investigated the reaction of dialkylmagnesium and diarylmagnesium reagents with allylic ethers and esters, thioethers, and amines by the action of transition metal salts.

In order to select optimal conditions, we studied the effect of the nature of the metal, structure of the electron donor ligand and of the solvents on the yield and composition of the reaction products in the case of the coupling of diphenylmagnesium with allyl acetate. Copper salts activated by Ph_9P have high catalytic activity (Table 1). In the absence of catalyst, Ph_2Mg reacts with allyl acetate primarily at the ester group to give diphenylmethylcarbinol. The yield of product (I) in these experiments does not exceed 10%. In the presence of copper salts, the yield of (I) may be increased to 40%. Activation of the catalyst by Ph_9P facilitates the exclusive formation of (I) in 98% yield.

$$Ph_2MeCOH \leftarrow Ph_2Mg + OAc \xrightarrow{[Cu] - Ln} Ph_-$$
 (I)

In light of these results, the subsequent experiments were carried out using the $Cu(acac)_2$ -Ph₃P catalyst system in THF at 40°C over 4 h. Under these conditions, Ph₂Mg and dihexylmagnesium react with allyl esters of acrylic, methacrylic, succinic, and benzoic acids to form (I) and 1-nonene (II) in high yields. The structure of the acid residue in the allyl esters has virtually no effect on the yield of the cross coupling products which was from 79% to 90%. In addition, dihexylmagnesium was found to be more reactive in these reactions with allylic compounds than Ph₂Mg. All our attempts to obtain branched olefins by

$$RCO_2 - + R_2^{1}Mg \rightarrow R^{1} - (I), (II)$$

 $R^1 = Ph$ (I); $n-C_6H_{13}$ (II); $R = CH_2CH = CH_2$; $CH_2CH = CHPh$, Ph, $CH(Me)C = CH_2$.

the coupling of dibutylmagnesium with 3-acetoxy-1-pentene were unsuccessful. In all the experiments, a \sim 1:2 ratio of cis-3-nonene (III) and trans-3-nonene (IV) was obtained, independently of the reaction conditions. In addition, 2,7-octadienyl acetate and diphenyl-, dibutyl- and dihexylmagnesium gave 1,6-E-dienes (V)-(VII). Then, we established that the

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TABLE 1. Effect of the Nature of the Catalyst on the Yield and Composition of the Products of the Reaction of Ph2Mg and Allyl Acetate at 40°C in THF (4 h, M:Ph₃P:allyl acetate: $Ph_2Mg = 1:2:50:25)$

Catalyst	Yield of (I), %	Catalyst	Yield of (I), %	
-	7	CuBr	79	
Cu (acac) 2	98		77 -	
CuLi₂Cl₄ CuI	96 96	CuCl ₂ CuCl	65 42	

TABLE 2. Influence of the Nature of the Solvent and the Activator Structure on the Yield of $(Cu(acac)_2:Ln: \bigcirc OAc:$ PhoMg = 1:2:50:25 40° 4 h THE $Ph_2Mg = 1:2:50:25, 40^\circ, 4 h, THF_0$

Solvent	Yield of (I), %	Activator	Yield of (I), %	Solvent	Yield of (I), %	Activator	Yield of (I), %
THF 1,4- Dioxane Ether Di (n-propy1) ether	98 90 75 65	$\begin{array}{c} - \\ Ph_{3}P \\ (PhO)_{3}P=O \\ \alpha', \alpha' - Dipy - \\ ridy1 \end{array}$	40 98 90 70	Diglyme Sulfolane Benzene Heptane	50 41 37 15	(<i>i</i> -C ₄ H ₉ O) ₃ P Ph ₃ P=O (C ₆ H ₁₁ O) ₃ P (PhO) ₃ P	66 63 62 30



R = Ph (V); *n*-Bu (VI); *n*-C₆H₁₃ (VII)

cross coupling of diphenyl-, dibutyl-, and dihexylmagnesium with allyl esters and thioethers, l-methoxy-, l-ethoxy-, and l-phenoxy-2,7-octadienes catalyzed by copper complexes also leads to monoolefins (I), (II), and (VIII) and 1,6-diolefins (V)-(VII) in high yields. In con-

 $\begin{array}{c} \text{RX-} & + \text{R}_{2}^{1}\text{Mg} \xrightarrow[84-96\%]{} \text{R}^{1} \xrightarrow[84-96\%]{} \text{R$ R = Me, Et, Ph; $R^1 = Ph$ (V); n-Bu (VI); n-C₆H₁₃ (VII)

trast to ethers and esters, dialkylallylamines react with these Grignard reagent analogs to give the cross coupling products in yields not greater than 10%. However, allylamines containing a more polarized C-N bond (as in ammonium salts) react rather readily with diarylmagnesium and dialkylmagnesium derivatives to form monoolefins in satisfactory yields.

$$\begin{array}{c} & \stackrel{+}{\longrightarrow} R^{1}R^{2}Me \ \bar{I} + R_{2}^{3}Mg \xrightarrow{32-50\%} R^{3} - \\ R^{1} = R^{2} = Et; \ R^{1} = Ph; \ R^{2} = Me; \ |R^{1} = Ph; \ R^{2} = CH_{2}CH = CH_{2}; \ R^{3} = Ph \ (I); \ n-C_{6}H_{13}; \\ (II); \ n-Bu \ (VIII). \end{array}$$

Thus, the cross coupling of dialkylmagnesium derivatives with allyl ethers, esters, sulfides, and quaternery allylamines is an efficient method for the synthesis of unsaturated hydrocarbons in high yields.

EXPERIMENTAL

The dialkylmagnesium derivatives were obtained according to Seifert [8] and Kamienski [9]. The gas-liquid chromatography was carried out on a Chrom-5 chromatograph with a flame ionization detector using a 1200 × 3 mm column packed with 15% PEG-6000 on Chromatone N-AW. The column temperature was 140°C and helium served as the gas carrier. The 'H NMR spectra

were taken on a Tesla BS-467 spectrometer for CCl_4 solutions with HMDS as the internal standard. The IR spectra were taken neat on a UR-20 spectrometer and the mass spectra were recorded on an MKh-13-06 mass spectrometer with 70 eV ionizing voltage and 200°C ionization chamber temperature.

<u>General Method for the Reaction of Dialkylmagnesium Derivaties with Allylic Compounds</u>. A sample of 25 mmoles organomagnesium reagent was added with vigorous stirring to a solution of 0.262 g (1 mmole) $Cu(acac)_2$, 0.524 g (2 mmoles) Ph_3P and 50 mmoles of the corresponding allylic compound in 10 ml THF cooled to $-5^{\circ}C$ in an argon stream. The mixture was maintained for about 10 min at $-5^{\circ}C$ and then transferred to a constant-temperature glass reactor and heated for 4 h at 40°C. At the end of the reaction, the catalysate was decomposed with saturated aq. NH_4C1 and extracted with ether. After removal of the solvent, the residue was distilled in vacuum.

cis-3-Nonene (III) + trans-3-nonene (IV), bp $63-64^{\circ}C$ (34 mm) [10], np^{2°} 1.4177, IR spectrum (v, cm⁻¹): 720, 975, 3020 (cis, trans-CH=CH). ¹H NMR spectrum (δ , ppm): 0.76-1.05 m (6H, CH₃), 1.11-1.58 m (6H, CH₂), 1.73-2.25 m (4H, CH₂-C=), 5.12-5.50 m (2H, CH=CH). ¹⁹C NMR spectrum (δ , ppm): for (III): 14.11 q (C¹), 25.72 t (C²), 131.87 d (C³), 129.40 d (C⁴), 32.68 t (C⁵), 29.50 t (C⁶), 31.55 t (C⁷), 22.69 t (C⁸), 14.07 q (C⁹); for (IV): 14.41 q (C¹), 20.59 t (C²), 131.51 d (C³), 129.34 d (C⁴), 27.16 (C⁵), 29.58 t (C⁶), 31.84 t (C⁷), 22.82 t (C⁸), 14.07 (C⁹) M⁺ 126.

Olefins (I), (II), and (VIII) and 1,6-dienes (V)-(VII) were identified with authentic samples [7, 10].

CONCLUSIONS

The feasibility was demonstrated for the preparation of unsaturated hydrocarbons of given structure by the cross coupling of dialkylmagnesium derivatives with functional allylic compounds by the action of catalytic amounts of copper complexes.

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