Communications to the Editor

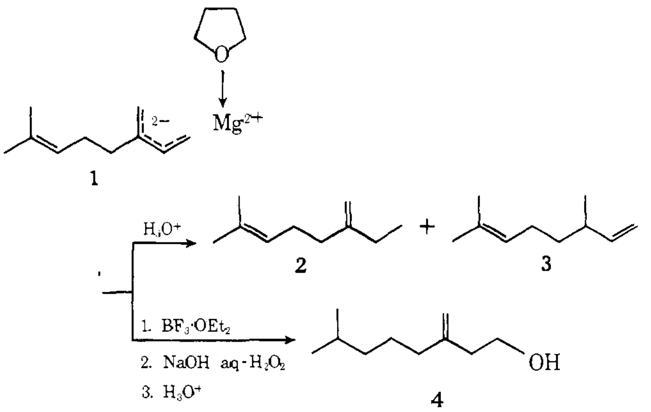
Metal-Assisted Terpenoid Synthesis. 3.[1] A Myrcene Magnesium Compound as a New Example of an Enediylmetal System[2] Formed from a Conjugated Diene and Its Synthetic Applications

Sir:

Butadiene or isoprene is known to react with activated magnesium metal to give a mixture of halide-free organomagnesium(II) compounds of which organic groups can be the diene monomer, dimers, and higher oligomers.[3e] The reaction may be catalyzed by transition metal compounds but results in increase of the product variety.[3] For synthetic purposes, it is desirable to obtain selectively a single magnesium compound. We wish to report here such an example using myrcene as the diene.

A mixture of myrcene (1.0 mol) and magnesium (1.5 mol), activated by a small amount of iodine and/or ethyl bromide, in THF (1l.) was heated at 45–50 °C for 3–4 h in the presence of a Lewis acid such as $BF_3{\cdot}OEt_2$, $Al(Oi\text{-}C_3H_7)_3$, or $ZnCl_2$ (0.02 mol) to give a light olive solution which leaves, upon vacuum removal of solvent, a dark colored, highly viscous, apparently polymeric substance (**1**); λ_{max}, 237 nm (THF). Acid hydrolysis of **1** yields 1 mol each of THF and $C_{10}H_{18}$ hydrocarbons per magnesium atom. The hydrocarbons were found to be a mixture of 2-methyl-6-methylene-2-octene (**2**) (87%) and 2,6-dimethyl-1,7-octadiene (**3**) (13%). Hence **1** can be formulated as $[Mg(C_{10}H_{16})(THF)]_n$. The hydrocarbon moiety may be regarded as the myrcene dianion[2] which receives two protons upon hydrolysis. A precedent for this result is the formation of butene-d_2 and octadiene-d_2 upon deuterolysis of the butadiene-magnesium compound.[3d] The absence of the myrcene dimer is significant and contrasts to the oligomer formation in the similar preparation of butadiene-magnesium compounds.

Scheme I



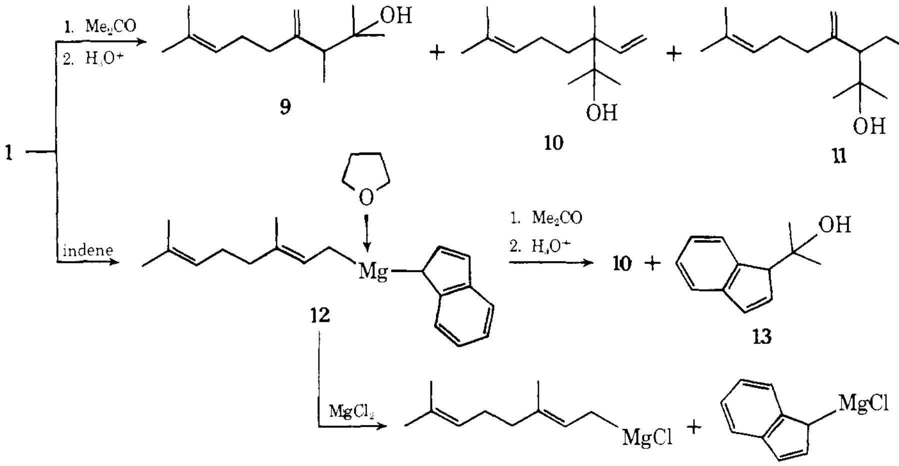
The function of a Lewis acid in the preparation is apparently to lower the lowest unoccupied MO(LUMO) level of the conjugated diene facilitating transfer of two electrons from magnesium to the diene LUMO.[4] The ESR spectrum (modulating width 12.5 G) of **1** in THF shows the absence of a radical anion.

The reaction pattern of **1** deserves scrutiny in view of the versatility of ordinary Grignard reagents which contain a monobasic carbanion. A THF solution of **1** (0.1 mol) was treated with $BF_3{\cdot}OEt_2$ (0.12 mol) at 10 °C for 1 h and subsequently oxidized at 0–5 °C by an alkaline hydrogen peroxide solution (10% aqueous NaOH 50 ml, 30% H_2O_2 15 ml). Usual workup, after acid hydrolysis, gave 7-methyl-3-methylene-6-octen-1-ol (isogeraniol, **4**) in 78% yield based on **1** (Scheme I). Isogeraniol was also obtained by a one batch process without isolating **1**. Thus, a mixture of magnesium (0.2 mol), myrcene (0.2 mol), and triethyl borate (0.22 mol) in THF (300 ml) was heated at 60 °C for 4 h[5] to give, after oxidation with alkaline H_2O_2 solution, **4** in 72% isolated yield. The regioselective terminal alcohol formation from a conjugated diene is noteworthy since usual alcohol synthesis through hydroboration of conjugated dienes gives glycols.[6]

The reaction of **1** (prepared from 0.5 mol of myrcene) with an excess (1.5 mol) of acetone in THF gave two monoalcohols, 2,3,8-trimethyl-4-methylene-7-nonen-2-ol (**9**) (89%) and 2,3,7-trimethyl-3-vinyl-6-octen-2-ol (**10**) (6%), and one diol, 3-(5-methyl-1-methylene-4-hexenyl)-2,5-dimethyl-2,5-hexanediol (**11**) (5%) (Scheme II). These products, inter alia **11**, are consistent with the formulation of **1** as an enediyl-metal species.

We have found a simple procedure to convert **1** into a dienyl(enyl)magnesium compound. For example, after treating a THF solution of **1** (0.1 mol) with indene (0.12 mol) at 10 °C

Scheme II



for 2 h, a new compound, $Mg(C_{10}H_{17})(C_9H_7)(THF)$ (**12**),[7] was isolated as a pale yellow, extremely air-sensitive solid upon high-vacuum concentration of the yellow reaction mixture. Supports for this formulation are: (1) acid hydrolysis affords 1 mol each of hydrocarbon $C_{10}H_{18}$ (mainly **3**), indene, and THF, (2) the reaction with acetone gives quantitative yield of two tertiary alcohols, **10** and **13**, in exactly 1:1 mole ratio, and (3) the NMR (60 MHz) spectrum in C_6D_6 shows signals[8] assignable in terms of the substituted allyl magnesium compound.[9]

Compound **12** reacts readily (at 25 °C for 2 h in THF) with an equivalent amount of anhydrous $MgCl_2$ to give 3,7-dimethyl-2,6-octadienylmagnesium chloride and indenylmagnesium chloride (Scheme II). As the latter is much less soluble in THF, these two compounds can be separated by filtration.

The present preparation of the endiyl compounds can be applied to isoprene and 2,3-dimethylbutadiene and their analogues. Terminally substituted conjugate dienes like piperylene or cyclic dienes such as 1,3-cyclooctadiene do not undergo the reaction. The halide-free endiylmagnesium compounds promise to have a great potential for organic and inorganic synthesis.

References and Notes

(1) For part 2 see S. Akutagawa, T. Taketomi, and S. Otsuka, *Chem. Lett.*, 485 (1976).

(2) A simplified description of two polar σ-bonds between a conjugated diene system and Mg.

(3) (a) H. E. Ramsden and J. Engelhart, 153rd Meeting of the American Chemical Society, Miami Beach, Fla., 1967, abstract PO-41; (b) M. Yang, K. Yamamoto, N. Otake, M. Ando, and K. Takase, *Tetrahedron Lett.*, 3843 (1970); (c) M. Yang, M. Ando, and K. Takase, *ibid.*, 3529 (1971); (d) Y. Nakano, K. Natsukawa, H. Yasuda, and H. Tani, *ibid.*, 2833 (1972); (e) K. Fujita, Y. Ohnuma, H. Yasuda, and H. Tani, *J. Organomet. Chem.*, **113**, 201 (1976).

(4) G. I. Gray and R. Robinson, *J. Am. Chem. Soc.*, **83**, 249 (1961).

(5) Neither the activation of magnesium nor the addition of Lewis acid was required in this case.

(6) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962, p 24.

(7) The stereochemistry of the double bond in **12** could not be determined by the NMR spectrum. The geometry is likely to be trans since **12** gave 2,6-dimethyl-2,6-*trans*-undecadiene and *n*-propylindene by the reaction with $n\text{-}C_3H_7I$ in HMPA.

(8) Chemical shifts (δ ppm), coupling constants (Hz), and intensities for important signals: 0.92 (d), $-CH_2Mg-$, 2 H; 1.90 (d), $-MgCH{=}$(Indenyl), 1 H; 3.45 (t), $\llcorner(CH_2CH_2)_2\text{-}O\lrcorner$, 4 H; 6.01 (t), $=CHCH_2Mg-$, 1 H; 6.18 (d), H^3 (indenyl), 1 H; 6.66 (d), H^2 (indenyl), 1 H; 7.15 (m), H^{4-7} (indenyl), 4 H.

(9) D. A. Hutchinson, K. R. Beck, R. A. Benkeser, and J. B. Grutzner, *J. Am. Chem. Soc.*, **95**, 7075 (1973).

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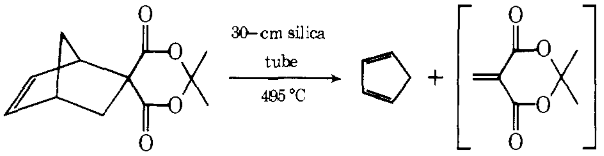
Evidence for the Pyrolytic Generation of Methylene Ketene (Propadienone)

Sir:

Flash vacuum pyrolysis of 5-arylidene- and 5-alkylidene-1,3 dioxan-4,6-diones is a general method for the generation of substituted methylene ketenes. The formation of these highly reactive species has been established[1] by low-temperature infrared spectrometry, by their conversion into substituted acrylic acid derivatives, and by isolation of their dimerization products, 2,4-bis(arylidene or alkylidene)cyclobutane-1,3-diones. Substituted methylene ketenes are also involved in gas-phase rearrangements leading to the synthesis of new aromatic rings,[2] in various thermal or base-catalyzed reactions[3] in solution, and in photochemically induced reactions.[4] Evidence is now presented to show that flash vacuum pyrolysis of the cyclopentadiene adduct (**1**) of 2,2-dimethyl-5-methylene-1,3-dioxan-4,6-dione leads to formation of this 5-methylene compound (**2**) in the gas phase and to its decomposition into acetone, carbon dioxide, and methylene ketene (**3**).



1 **2**

$$\longrightarrow CH_3COCH_3 + CH_2{=}C{=}C{=}O + CO_2$$

3

The cyclopentadiene adduct **1** could not be prepared directly[5] from the readily available bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic acid,[6] but was made indirectly by peracid oxidation of 5-phenylseleno-2,2,5-trimethyl-1,3-dioxan-4,6-dione and trapping of the unstable intermediate 2,2-dimethyl-5-methylene-1,3-dioxan-4,6-dione (**2**) with cyclopentadiene. Treatment of the sodium salt of 2,2,5-trimethyl-1,3-dioxan-4,6-dione suspended in methylene chloride with phenylselenenyl bromide (1.0 equiv) at room temperature afforded the 5-phenylseleno compound (67%) as pale yellow needles from ether/hexane, mp 66.6–68.5 °C. Oxidation of the 5-phenylseleno compound with *m*-chloroperbenzoic acid (2.1 equiv) in methylene chloride at −10 °C for 5 min followed by addition of excess cyclopentadiene at −10 °C gave the cyclopentadiene adduct **1** (53%) as colorless needles from ether/hexane, mp 86.5–88 °C.[7] Hydrolysis of adduct **1** with 2 M sodium hydroxide followed by acidification gave bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic acid (93%).

Direct examination of the pyrolysate of adduct **1**, formed in the temperature range 460–570 °C, by passing it into a quadrupole mass spectrometer showed that four of the principal ions which occurred at *m/e* 66, 58, 54, and 44 corresponded to the four products shown. Optimum formation of methylene ketene as indicated by the abundance of the ion at *m/e* 54 occurred between 490 and 520 °C. The abundance of the ion at *m/e* 26 increased markedly from 520 to 570 °C. This we attribute to the decomposition of methylene ketene into acetylene (*m/e* 26) and carbon monoxide, a general mode of fragmentation for methylene ketenes.[8]

The infrared spectrum of a pyrolysate formed at 495 °C (0.005 mm) and condensed directly onto a sodium chloride disk cooled conductively by liquid nitrogen showed a strong, sharp nonsymmetrical absorption band at 2100 cm^{-1}, in good agreement with the frequency range (2080–2113 cm^{-1}) found[1] for aryl- and alkyl-substituted methylene ketenes. The spectrum also showed bands attributed to cyclopentadiene and acetone, and separate examination of the volatile products confirmed the presence of carbon dioxide.

Efficient trapping of methylene ketene with aniline or methanol could only be achieved when the vaporized reagent was introduced ca. 8 cm before the outlet from the heated zone. Acrylanilide and methyl acrylate were obtained in yields of 24 and 25%, respectively.[9]

Pyrolysis of large samples (150–500 mg) of the cyclopentadiene adduct **1** at 495 °C (0.1 mm) and passage of the pyrolysate through a Pyrex tube at room temperature caused deposition of a glassy solid over a narrow zone in the tube; a liquid containing mainly cyclopentadiene and acetone collected in the cold trap. The glassy solid on occasion appeared partly crystalline, but was clearly a mixture. It was unstable to moisture and dissolved in water to give an acidic solution. The