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REACTIONS OF GRIGNARD REAGENTS FROM 1-HALOGENOALLENES. ALLENES—XXXIII[1]

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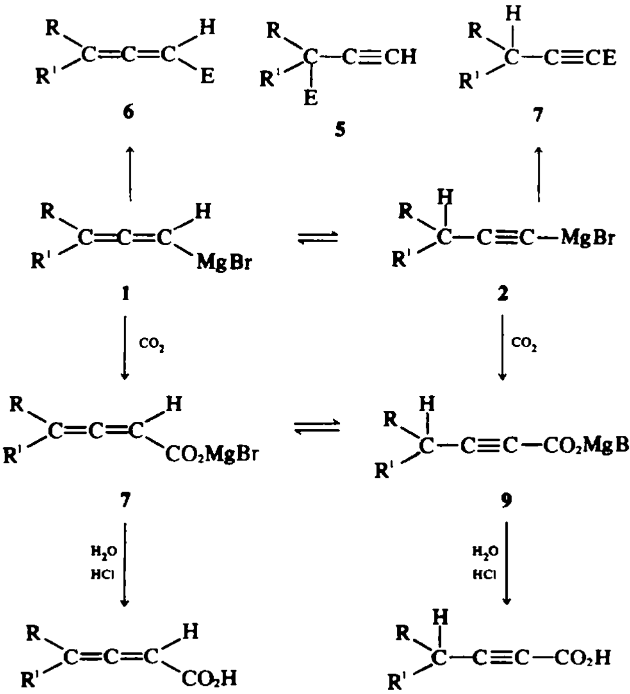
Abstract—Grignard reagents have been prepared from 1-bromo-3,3-dialkylallenes in ether or tetrahydrofuran. The allenic acids, 4,4-dialkylbuta-2,3-dienoic acids together with 4,4-dialkylbut-2-ynoic acids are formed with carbon dioxide to the exclusion of acids with a terminal acetylene group. Two coupled products, 3,4-diethyl-3,4-dimethylhexa-1,5-diyne and 3-ethyl-3,6-dimethylocta-4,5-dien-1-yne, which are formed as byproducts in reactions of 3-methylpenta-1,2-dienyl magnesium bromide with electrophiles (CO_2, H_2O, Me_2CO), are obtained in high yield by passing oxygen through the solution of the Grignard reagent.

Allenyl Grignard reagents have previously been prepared from a variety of substituted propargyl halides.[2-4] Evidence for their allenyl (rather than propargylic) structure rests on the absorption in the IR at 1880 cm^{-1}, which is characteristic of the coupled C=C=C stretching vibration displaced from the normal 1950 cm^{-1} by bonding to magnesium,[2,6d] PMR signals for =C=CH̲–[5] and the fact that Grignard reagents with identical IR spectra in THF were obtained from propargyl bromide and 1-bromopropadiene.[4] Despite previous reports[6a] concerning lack of reaction of 1-halogeno-allenes, we have found that 1-bromoallenes and (in one case a 1-chloroallene) are readily converted to Grignard derivatives in ether or THF with excess magnesium.‡ Generally, electrophiles react with allenyl magnesium bromide at C_3 to give only terminal acetylenic products (**5** R = R' = H):§ An exception appears to be carbon dioxide[6a] which yields mixtures in which the allenic product predominates. Treatment of six 3,3-disubstituted allenyl Grignard reagents with carbon dioxide gave allenic acids in 18–60% yield (Table 1) which were contaminated with 4,4-dialkylbut-2-ynoic acids (**4**) but not with acids with a terminal acetylene of the type **5** (E = CO_2H).

Partial, or in some cases (such as acids with bulky substituents) complete, separation of the allenic and acetylenic acids may be achieved by preferential extraction of the more acidic acetylenic acids into sodium bicarbonate solution (p*K* MeC≡C–COOH 2·7; p*K* MeCH=CH–COOH 4·7; the p*K* value for the corresponding allenic acid CH_2=C=CHCOOH is not known but would be expected to be closer to that of crotonic acid).[6b] Hydrolysis of the allenyl Grignard compound **1** (R = Me,



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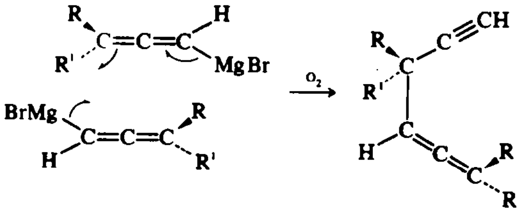
‡ Grignard reagents were prepared from optically active 1-chloro- and 1-bromo-3,4,4-trimethylpenta-1,2-diene in THF as solvent and mercuric chloride was used catalyst.[7]

§ The product from exceptionally sterically hindered electrophiles, e.g. di-t-butyl ketone contains up to 20% of allene.

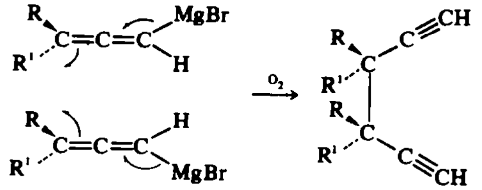
$R^1 = Et$) gave a 3:1 hydrocarbon mixture of allene **6** ($E = H$, $R = Me$, $R = Et$) to terminal acetylene **5** or **7** ($E = H$, $R = Me$, $R^1 = Et$). The reaction with acetone gave five products, the major compound being the crystalline alcohol [**7**, $R = Me$, $R^1 = Et$, $E = Me_2C(OH)$] (31%); the other products were not identified, but GLC indicated that two minor components were the same hydrocarbons obtained previously from the hydrolysis. With acetone, 2,2,6-trimethylcyclohexylidinevinyl magnesium chloride in THF gave a mixture of the alcohols of the type **6** and **7** [$E = Me_2C(OH)$] which was not separated. The corresponding alcohols **5** with a terminal acetylene were not detected amongst the products in either case suggesting that electrophilic addition does not take place at the 3-position of 3,3-disubstituted allenyl Grignard compounds. However, a more thorough investigation is needed to confirm this. In all these reactions with allenyl Grignard compounds small quantities of a high boiling mixture of hydrocarbons† were obtained as a byproduct. The same hydrocarbon mixture† could be prepared in almost quantitative yield by passing oxygen into the solution of allenyl Grignard reagent (**1**, $R = Me$, $R^1 = Et$); separation by preparative GLC gave 3 - ethyl - 3,6 - dimethylocta - 4,5 - dien - 1 - yne (63%) and 3,4 - diethyl - 3,4 - dimethylhexa - 1,4 - diyne (34%).‡ Variable small quantities of acetylenic alcohol, MeEtC(OH)C≡CH were also detected.

The results obtained are consistent with the initial formation of allenyl Grignard reagent (**1**) which undergoes a slow prototropic rearrangement to give a mixture of allenyl and acetylenic Grignard reagents during the time needed (2–4 hr) to complete the reaction with magnesium.§ The mixture of Grignard reagents then reacts with added electrophiles to give allenic and acetylenic products (**3** and **4**; **6** and **7**). It can readily be shown by spectroscopic means that the products do not isomerise during work up but the possibility of intermediate Grignard complexes (**8**), formed with the electrophile, isomerising cannot be excluded. Although Glaser coupling of copper(I) acetylides with oxygen is well known[6c] no report of a similar coupling reaction of Grignard derivatives has appeared. Allenyl Grignard reagents react exothermically with oxygen to give products which are best explained by postulating 1,3-coupling (**A**) and 3,3-coupling (**B**).

No product from the 1,1-coupling of either the allenyl Grignard reagent (**1**) or the acetylenic Grignard reagent (**2**) was detected and it may be assumed that such coupling reactions do not take place in the presence of oxygen.



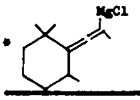
(A)



(B)

Table 1. Reaction of allenyl Grignard reagents with electrophiles

$$RR^1C{=}C{=}CHMgBr \xrightarrow[2\ H_2O]{1.\ E} RR^1C{=}C{=}CHEH + RR^1CH{-}C{\equiv}C{-}EH$$

R	R^1	$E = Me_2CO$		$E = CO_2$	$RR^1C{=}C{=}CHCOOH$			
		mixed alcohols yield %	acetylenic alcohol yield %	Mixed acids yield %	yield %	ν_{max} cm^{-1}	λ_{max} nm	ε
Me	Me			28	20^a	1950		
Me	Et	65	31^b	60	45^a	1960		
Et	Et			49	35^a	1960		
Me	Bu^t			45	34^{cd}	1960	212	(11550)
• Pr^i	Pr^i			40	30^{ce}	1975	213	(9850)
Me	Ph			-	18^f	1950	207	(32000)
							248	(15000)
• 		68	30^g	61	40^a	1950		

[a] Only partial separation obtained; ratio estimated from IR and GLC (on esters); [b] acetylenic alcohol crystallised from distillate; [c] three extractions with a deficiency of $NaHCO_3$ solution left solid allenic acid; the extract was acidified and the process repeated; [d] m.p. 48–49° (lit[7] m.p. 47–48°); [e] m.p. 54°, Found C, 70·8, H, 9·4, O, 19·0. $C_{10}H_{16}O_2$ requires C, 71·4, H, 9·6, O, 19·0%; [f] lit[8] m.p. for (+)-acid 101–102°; m.p. of (±) acid 129–130°; [g] not separated, ratio estimated form IR; in THF, ether gave lower yields.

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†The ratio of the two hydrocarbon compounds as determined by GLC varied from 3:1 to 2:1 according to variations in the conditions (time 1–4 hr, temperature, gentle or vigorous reflux).

‡Occasionally a third compound (m.p. 101°, 10%) was isolated; the transparent, white crystals rapidly turned pink and then red. Where $R = Me$ and $R' = Et$ it analysed as a diiodo compound (Found: C, 33·2, H, 4·6. $C_{12}H_{16}I_2$ requires: C, 34·8 H, 3·9%) and it was only obtained if methyl iodide and iodine were used to start the reaction. It is tentatively formulated as MeEtCI–C≡C–C≡C–CIMeEt and could arise from the following sequence of reactions: $MeEtC{=}C{=}CHMgBr + MgI_2 \rightarrow MeEtCI{-}C{\equiv}CH + MeEtC{=}C{=}CHMgBr \rightarrow MeEtCI{-}C{\equiv}MgBr + I_2 \rightarrow MeEtCIC{\equiv}C{-}C{\equiv}CIMeEt$.

§IR spectra show broad bands 1870–1890 and above 2000 cm^{-1}.

EXPERIMENTAL

GLC was carried out with a Griffin and George II and a Pye 104 instrument using thermal and flame ionisation detectors and glass columns. IR spectra were determined with Perkin Elmer Infracord and 237 spectrometers, UV spectra with a Bausch and Lombe Spectronic 505 and a Pye-Unicam 1800 instrument. NMR spectra with a Varian T60 on Perkin-Elmer R10 spectrometer in $CDCl_3$ using Me_4Si as internal standard.

General method for the preparation of allenic acids. A typical allenic acid, 4,5,5 - trimethylhexa - 2,3 - dienoic acid was prepared as follows: Clean Mg turnings (1·83 g, 0·075 mol) dry ether (60 ml) and a crystal of I_2 under oxygen-free N_2 was treated with a small quantity (< 1 ml) of 1-bromo-3,4,4-trimethylpentadiene. After the reaction had started the rest of the 1-bromoallene (15 g, 0·075 mol) in ether (30 ml) was added dropwise at such a rate as to barely maintain gentle reflux and then for a further 1 hr with minimal heating. The resulting suspension was cooled to 0° and dry CO_2 passed through at such a rate so as to maintain the internal temp between 0 and 5° and then at a fast rate for a further 1 hr. The mixture was acidified with dil HCl and when the inorganic salts had dissolved the ether layer was separated and the aqueous layer extracted further with ether. The ethereal layer was extracted with $NaHCO_3$ aq (5 × 30 ml) and the combined bicarbonate soln extracted with ether. Acidification with dil HCl, extraction with ether and evaporation gave the crude, oily mixed acids (5·7 g; 45%). The acid mixture was dissolved in ether and extracted with a minimum of $NaHCO_3$ aq (3 × 10 ml). The ether layer was dried and evaporated leaving the solid allenic acid. The soln of Na- salts was acidified, extracted with ether and the ethereal layer extracted with $NaHCO_3$ aq (3 × 8 ml) and the cycle repeated 4 times. The first 3 times the residue was solid allenic acid, the fourth time an oily mixture of allenic and acetylenic acids resulted. Recrystallisation of the combined solid acids from pentane gave 4,5,5-trimethylhexa-2,3-dienoic acid (4·3 g, 34%), m.p. 48–49° (Table 1).

Allenic acids with different alkyl substituents were prepared similarly (Table 1).

Reaction of 3-*methylpenta*-1,2-*dienylmagnesium bromide with water.* The Grignard reagent (prepared as described above from Mg, 1·8 g and 1-bromo-3-methylpenta-1,2-diene, 12 g) was cooled to 5° and water (20 ml) was added. Work up and distillation gave a mixture of 3-methyl-penta-1,2-diene and 3-methylpent-1-yne (2·5 g, 41%) GLC silicone oil; 17°; t_R 12 min (75%) and t_R 10 min (25%), identified by comparison with authentic samples.[9]

Reaction of 2,2,6-*trimethylcyclohexylidenevinyl magnesium chloride and water* (with L. A. Goodson). The Grignard reagent prepared as above in dry THF from 2,2,6-trimethylcyclohexylidenevinylchloride (18·5 g, 0·1 mol) and Mg (2·6 g, 0·11 mol, using a crystal of mercuric chloride) was poured onto crushed ice. Work up and distillation gave a mixture of hydrocarbons (9·4 g, 62·5%). The mixture (4·8 g) was warmed with $AgNO_3$ (5·7 g) in abs EtOH (70 ml) for 2 hr and then refrigerated overnight. Filtration, addition of ether and repeated washing of the ethereal soln with water, drying ($MgSO_4$) and evaporation of ether gave 1 - vinylidene - 2,2,6 - trimethylcyclohexane (3·0 g, 62·5%) (Found: C, 87·8; H, 12·1. $C_{11}H_{18}$ requires: C, 87·9; H, 12·1%) ν_{max} 1950 (C=C=C) and 845 cm^{-1} (=C=CH_2). The crystalline Ag salt was warmed with NaCN (4 g) in water (50 ml) for 2 hr, the soln extracted with ether, the ethereal soln dried and distilled yielding 1 - ethynyl - 2,2,6 - trimethylcyclohexane (1·0 g, 21%) (Found: C, 87·7; H, 11·8. $C_{11}H_{18}$ requires: C, 87·9; H, 12·1%) ν_{max} 3300 and 2120 cm^{-1}.

Reaction of 3-*methylpenta*-1,2-*dienylmagnesium bromide with acetone.* To the Grignard reagent prepared as described above from Mg, (2·4 g) and 1 - bromo - 3 - methylpenta - 1,2 - diene, (16·1 g) dry redistilled acetone (6·4 g, 0·11 mol) was slowly added. After heating under reflux for 1 hr, the reaction was worked up. Fractionation gave two fractions containing mixtures of hydrocarbons and allenic and acetylenic alcohols and then 2,5-dimethylhept-3-yn-2-ol (4·4 g, 31%) b.p. 94–100° at 1·5 mmHg, m.p. 41° from hexane) ν_{max} 3400 (OH) 2260 (–C≡C–) and 940 cm^{-1} (lit.[10]).

Reaction of 2,2,6-*trimethylcyclohexylidenevinyl magnesium chloride and acetone* (with L. A. Goodson). To the Grignard reagent prepared as above from 2,2,6-trimethylcyclohexylidenevinyl chloride (9·3 g) and Mg (1·3 g) in THF dry acetone was slowly added. Work up and distillation gave a mixture of 2 - methyl - 4 - (2,2,6 - trimethylcyclohexylidene)but - 3 - en - 2 - ol and 2 - methyl - 4 - (2,2,6 - trimethylcyclohexyl)but - 3 - yn - 2 - ol (7·1 g, 68%) b.p. 88–92° at 1·0 mm Hg (Found: C, 79·8; H, 11·3. $C_{14}H_{24}O$ requires: C, 80·7; H, 11·6%), ν_{max} 3400 (OH), 2240 (–C≡C–), 1960 (C=C=C) cm^{-1}.

Coupling reaction of 3-*methylpenta*-1,2-*dienyl magnesium bromide in the presence of oxygen.* Through a soln of the Grignard reagent prepared from Mg (2·7 g) and 1 - bromo - 3 - methylpenta - 1,2 - diene (16·1 g) as described above dry O_2 was passed slowly until the exothermic reaction subsided and then vigorously for 1 hr. Work up gave the product (8·0 g, 98·7%), GLC 10% carbonwax 20 M (2m): 70° t_R 10 min (70%) t_R 24 min (30%). Prep GLC on 30% Carbonwax 20 M (3m) gave 3 - ethyl - 3,6 - dimethylocta - 4,5 - dien - 1 - yne, GLC 10% carbonwax 20 M (2m) 70°, t_R 10 min (Found: C, 88·6; H, 11·1. $C_{12}H_{18}$ requires: C, 88·8; H, 11·2%); ν_{max} 3310 (–C≡CH), 2110 (C≡CH), 1960 cm^{-1} (C=C=C); no λ_{max} in the UV; τ 9·0 (6H, t, $C\underline{H}_3CH_2$), 8·8 (3H, s, $CH_3{-}\overset{|}{\underset{|}{C}}{-}$), 8·4 (2H, q, $CH_3C\underline{H}_2$) 8·24 (3H, d, $C\underline{H}_3$–C=C=CH, $J_{9,4}$ 3·5 Hz), 8·2 (2H, m, $CH_3C\underline{H}_2$), 8·0 (1H, d, C≡C$\underline{H}$), 4·9 (1H, m, =C=CH, $J_{4,9}$ 3·5 Hz) and 3,4 - diethyl - 3,4 - dimethylhexa - 1,5 - diyne, GLC 10% carbonwax 20 M; 70°, t_R 24 min (Found: C, 88·7; H, 11·1. $C_{12}H_{18}$ requires: C, 88·8; H, 11·2%) ν_{max} 3320 C≡CH, 2110 cm^{-1} (C≡CH); no λ_{max} in UV; τ 8·98 (6H, t, $C\underline{H}_3$–CH_2), 8·78 (6H, s, $C\underline{H}_3$), 8·37 and 8·40 (4 H, q, $CH_3C\underline{H}_2$ nonequivalent), 8·0 (2H, s, C≡C$\underline{H}$).

Experiments in which the bromoallene was added very quickly (< 1 hr) and vigorous reflux was maintained, gave variable quantities (10–30%) of 3-methylpent-1-yn-3-ol (identified by GLC, silicone oil; 80°, t_R 7 min and mixed with authentic specimen gave a single peak t_R 7 min).

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