with methylene chloride; the methylene chloride solution is washed repeatedly with dilute aqueous NaCl and then dried ($MgSO_4$). The solvent is removed under reduced pressure, and the residual oil on Kugelrohr distillation at 70 °C (0.005 mm) gives 0.466 g (95% yield) of pure **2**.[25]

A 60% oil dispersion of NaH[20] (0.100 g, 2.5 mmol) is washed with pentane, and the oil-free hydride is transferred to a nitrogen-filled flask with the aid of 10 mL of *tert*-butyl alcohol. The mixture is stirred for 10 min under N_2, and then a solution of nitro ester **2** (0.245 g, 1 mmol) in 10 mL of *tert*-butyl alcohol is added. One minute later, 200 mL of ice-cold pentane[26,27] is added, and this is followed at once by 25 g of ice and an ice-cold solution of $KMnO_4$ (0.115 g, 0.73 mmol, 110% of the required amount) in 40 mL of water. The resulting mixture is stirred vigorously for 10 min, and then 1 mL (1 mmol) of 1 M sodium metabisulfite is added; this is followed by 2 mL (2 mmol) of 1 M H_2SO_4 whereupon the brown mixture is rapidly decolorized. The pentane phase is isolated, and the aqueous layer is extracted with more pentane. The combined pentane solutions are washed thoroughly with ice-cold water and dried ($MgSO_4$) under N_2. Removal of the pentane under N_2[28] gives 0.195 g (91% yield) of pure,[25] colorless aldehyde **3**.[29]

There are well-defined methods for converting CH_2NO_2 into a variety of other functions, e.g., COOH, CN, and CH_2NH_2, and, consequently, quaternary carbon compounds with a wide range of functions now become readily available. And if, as seems quite possible, the replacement of tertiary nitro groups by the anions of higher primary nitroparaffins proves feasible, this will provide a further demonstration of the synthetic utility of electron-transfer substitution reactions.

Acknowledgment. We are indebted to the National Science Foundation for support of this investigation.

Registry No. 1, 68896-18-4; **2**, 76173-36-9; **3**, 76173-37-0; 2-methyl-2-nitropropane, 594-70-7; 1,1,3,3-tetramethyl-1-nitrobutane, 5342-78-9; 2-methyl-2-nitrotridecane, 76173-38-1; ethyl 2-methyl-2-nitropropanoate, 5342-77-8; 2-cyano-2,3-dimethyl-3-nitrobutane, 29770-62-5; *tert*-butyl 2-methyl-2-(1-nitrocyclohexyl)propanoate, 76173-39-2; 1-(2-nitro-2-propyl)-1-cyanocyclohexane, 76173-40-5; 1-(2-cyano-2-propyl)-1-nitrocyclohexane, 29770-63-6; 1-(1-(tetrahydropyranyloxy)ethyl]-1-nitrocyclohexane, 76173-41-6; 2-nitro-2-phenylpropane, 3457-58-7; 2-nitro-2-(3,5-bis(trifluoromethyl)-phenyl)propane, 58324-86-0; 2-nitro-2-(*p*-cyanophenyl)propane, 58324-82-6; 2-nitro-2-(*p*-(phenylsulfonyl)phenyl)propane, 58324-84-8; 2,3-dimethyl-2-nitro-3-phenylbutane, 65638-49-5; 2,3-dimethyl-2-nitro-3-(3,5-bis(trifluoromethyl)phenyl)butane, 65338-72-9; 2,3-dimethyl-2-nitro-3-(*p*-cyanophenyl)butane, 65253-37-4; 2,2-dimethyl-1-nitropropane, 34715-98-5; 2,2,4,4-tetramethyl-1-nitrobutane, 76173-42-7; 2,2-dimethyl-1-nitrotridecane, 76173-43-8; ethyl 2,2-dimethyl-3-nitropropanoate, 76173-44-9; 2-cyano-2,3,3-trimethyl-4-nitrobutane, 76173-45-0; *tert*-butyl 2-methyl-2-(1-(nitromethyl)-cyclohexyl)propanoate, 76173-46-1; 2-(1-cyanocyclohexyl)-2-methyl-1-nitropropane, 76173-47-2; 2-cyano-2-(1-(nitromethyl)-cyclohexyl)propane, 76173-48-3; 1-(1-(nitromethyl)cyclohexyl)-ethanol, 76173-49-4; 2-methyl-1-nitro-2-phenylpropane, 76173-50-7; 2-methyl-1-nitro-2-(3,5-bis(trifluoromethyl)phenyl)propane, 76173-51-8; 2-(*p*-cyanophenyl)-2-methyl-1-nitropropane, 76173-52-9; 2-methyl-1-nitro-2-(*p*-(phenylsulfonyl)phenyl)propane, 76173-53-0; 2,2,3-trimethyl-1-nitro-3-phenylbutane, 76173-54-1; 2,2,3-trimethyl-1-nitro-3-(3,5-bis(trifluoromethyl)phenyl)butane, 76173-55-2; 3-(*p*-cyanophenyl)-2,2,3-trimethyl-1-nitrobutane, 76173-56-3; 2,2-dimethyltridecanal, 76173-57-4; 2-(1-cyanocyclohexyl)-2-methylpropanal, 76173-58-5; 2-methyl-2-(3,5-bis(trifluoromethyl)phenyl)-propanal, 76173-59-6; 2-(*p*-cyanophenyl)-2-methylpropanal, 76173-60-9; 2-(*p*-(phenylsulfonyl)phenyl)-2-methylpropanal, 76173-61-0; 2,2,3-trimethyl-3-phenylbutanal, 76173-62-1.

(25) Satisfactory elemental analyses and NMR spectra were obtained for all new compounds.

(26) Pentane usually contains small amounts of impurities which $KMnO_4$ oxidizes to compounds that are not easily separated from low-boiling aldehydes. The pentane is purified by being stirred with concentrated H_2SO_4 containing $Na_2Cr_2O_7$ at 25 °C; cooling may be necessary. This is followed by distillation from CaH_2.

(27) When, as in several of our cases, the aldehyde is not soluble in pentane, ethyl acetate is substituted for pentane.

(28) There are indications that the aldehydes of Table II are rather sensitive to oxygen. They are stable for at least 1 week under N_2 at −78 °C.

(29) For some of the aldehydes passage through a short column of silica gel was required to give a pure product.

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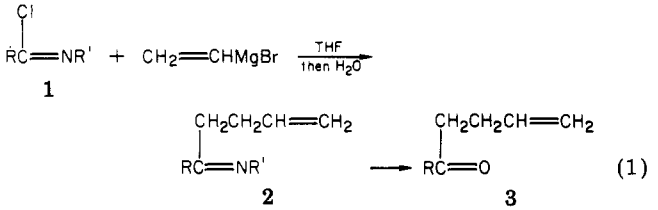
Coupling Reactions of Vinylmagnesium Bromide with Imidoyl Chlorides and with Amides. Synthesis of Enol Imines, γ,δ-Unsaturated Ketones, and Ketimines

Summary: Vinylmagnesium bromide undergoes successive addition to imidoyl chlorides and to amides to give unsaturated ketones, imines, enol imines, or enamines, depending on the reaction conditions.

Sir: One of us has recently described several coupling reactions of imidoyl chlorides with transition-metal organometallics resulting in the formation of mesoionic compounds[2] and 1,4-diaza-1,3-butadienes.[3] Related to the latter are 1-aza-1,3-butadienes, substituted derivatives of which can be generated by treatment of alkenylmagnesium halides with imidoyl chlorides.[4] We expected the very reactive alkenyl Grignard vinylmagnesium bromide to undergo successive additions to an imidoyl chloride to produce a metallo enamine, which could be intercepted by reaction with appropriate acylating and alkylating reagents. Some elegant synthetic applications of metallo enamines have recently been described.[5] We now report that imidoyl chloride (and amide)–vinylmagnesium bromide reactions provide an entry into a variety of useful organic compounds. The observation of an unusual N-alkylation of a metallo enamine is also described.

Treatment of **1** (R = Ph, R′ = *p*-ClC_6H_4) with 2 equiv of vinylmagnesium bromide in tetrahydrofuran (THF) for 30 min at room temperature affords the γ,δ-unsaturated imine **2** in 75% yield (eq 1). Reaction workup by chromatography on silica gel or acidic alumina gave the unsaturated ketone 1-phenyl-4-penten-1-one (**3**, R = Ph) in 70–75% yield. Compounds **2** and **3** (R = *p*-BrC_6H_4, *p*-ClC_6H_4; R′ = Ph, *p*-ClC_6H_4) were similarly obtained in very good yields (80–86%, Table I). Repetition of these experiments in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium resulted in little change in product yields.



(1) E. W. R. Steacie Fellow, 1980–1982.

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(4) Normant, H.; Martin, G. *Bull. Soc. Chim. Fr.* **1957**, 429.

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0022-3263/81/1946-1039$01.25/0

Table I. Pertinent Spectral Data for 2, 3, 8, and 10

reactant	2, 3, 8, or 10,[a] R, R', R''	mp or bp (mm Hg), °C	yield, %	^{1}H NMR ($CDCl_3$), δ	mass spectrum, m/e
1	2, Ph, *p*-ClC_6H_4	oil	75	2.26 (m, 2 H, CH_2CN), 2.76 (m, 2 H,	271
4			89	$CH_2CH=CH_2$), 4.66-6.00 (m, 3 H, olefinic protons), 6.73 (d, 2 H, *J* = 8 Hz, protons ortho to N-bearing carbon), 7.30 (d, 2 H, protons ortho to Cl-bearing carbon), 7.45 (m, 5 H, Ph)	269
1	2, *p*-BrC_6H_4, Ph	oil	80	2.32 (m, 2 H, CH_2CN), 2.70 (m, 2 H, $CH_2CH=CH_2$), 4.70-6.00 (m, 3 H, olefinic), 6.8-7.8 (m, 8 H, aromatic	315, 313
1	3, Ph	115-117 (7)[b]	70-75	2.51 (m, 2 H, $CH_2CH=CH_2$), 3.00 (t,	160
4			88	2 H, *J* = 7 Hz, CH_2CO), 4.80-6.00 (m, 3 H, olefinic protons), 7.50 (m, 3 H, meta and para protons), 7.98 (m, 2 H, ortho protons)	
1	3, *p*-BrC_6H_4	185-187 (1.5)	86	2.50 (m, 2 H, $CH_2CH=CH_2$), 3.03 (t, 2 H, *J* = 6 Hz, CH_2CO), 4.70-6.00 (m, 3 H, olefinic), 7.60 (d, 2 H, *J* = 8 Hz, protons ortho to bromine substituted carbon), 7.83 (d, 2 H, protons ortho to carbonyl)	240, 238
1	3, *p*-ClC_6H_4	160-162 (10)[c]	84	2.28 (m, 2 H, $CH_2CH=CH_2$), 2.79 (t, 2 H, *J* = 7 Hz, CH_2CO), 4.70-6.00 (m, 3 H, olefinic protons), 7.46 (d, 2 H, *J* = 8 Hz, protons ortho to Cl), 7.97 (d, 2 H, protons ortho to CO)	196, 194
4	8, Ph, *p*-ClC_6H_4, Ph	121-123	46	2.92 (m, 2 H, CH_2), 4.66-5.90 (m, 3 H, olefinic protons), 6.60 (d, 2 H, *J* = 8 Hz, protons ortho to N substituent), 7.05 (d, 2 H, protons meta to N substituent), 7.43 (m, 10 H, Ph groups), 13.54 (br s, 1 H, OH)	375, 373
4	8, Ph, *p*-ClC_6H_4, $CH_3CH=CH$	32-34	62	1.95 (d, 3 H, *J* = 6 Hz, $CH_3CH=$), 2.90 (m, 2 H, CH_2), 4.66-6.30 (m, 5 H, olefinic protons), 6.53 (d, 2 H, *J* = 8 Hz, protons ortho to N substituent), 7.00 (d, 2 H, protons meta to N substituent), 7.30 (m, 5 H, Ph), 14.13 (br s, 1 H, OH)	339, 337
1	8, Ph, *p*-ClC_6H_4, CH_3	71-72	72	2.26 (s, 3 H, CH_3), 2.86 (m, 2 H, CH_2), 4.73-6.00 (m, 3 H, olefinic), 6.50 (d, 2 H, *J* = 8 Hz, protons ortho to N substituent), 6.98 (d, 2 H, protons meta to N substituent), 7.33 (m, 5 H, Ph), 13.56 (br s, 1 H, OH)	313, 311
1	10, Ph, *p*-ClC_6H_4	oil	48	2.76 (m, 2 H, CH_2), 3.03 (s, 3 H, NCH_3), 4.8-5.9 (m, 3 H, vinyl protons), 6.00 (t, 1 H, remaining olefinic proton), 6.63 (d, 2 H, *J* = 8 Hz, protons ortho to N substituent), 7.13 (d, 2 H, protons meta to N substituent), 7.26 (s, 5 H, Ph)	285, 283

[a] Satisfactory (±0.4%) C, H, and N analyses were obtained for all new compounds. [b] Lit.[6] bp 108.2-108.8 °C (5 mm). [c] Lit.[6] bp 80-82 °C (0.07 mm). [d] Isolated (not GC) yields.

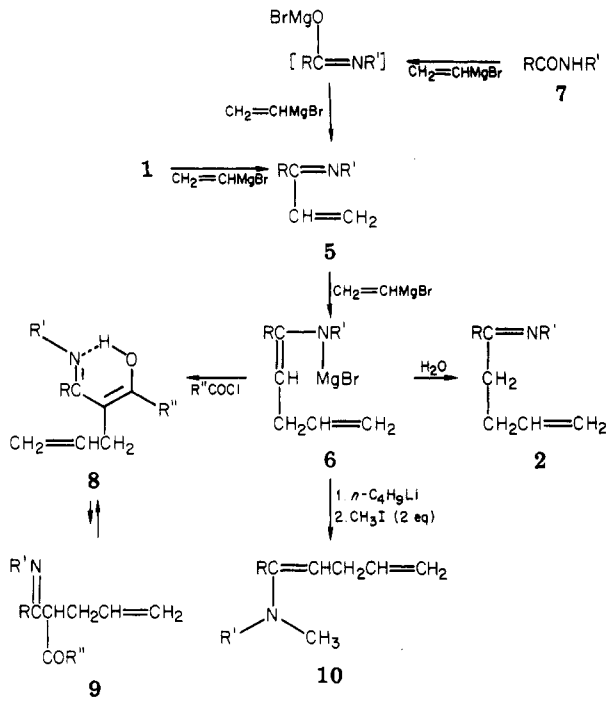
One can use secondary amides in place of imidoyl chlorides for reaction with vinylmagnesium bromide to generate **5** and the metallo enamine **6** (Scheme I). Reaction of **4** (R = Ph, R' = *p*-ClC_6H_4) with the vinylmagnesium reagent (3:1 ratio of C_2H_3MgBr to **4**) in THF at room temperature for 3 h afforded **2** (R = Ph, R' = *p*-ClC_6H_4) in only 22% yield. However, use of a 4.3/1.0 molar ratio of Grignard/**4** and refluxing in THF for 18 h gave **2** (R = Ph, R' = *p*-ClC_6H_4) in 89% yield. The latter was quantitatively converted to the γ,δ-unsaturated ketone as described above. The imidoyl chloride reaction is effected under milder conditions than the amide route; however, the yields of **2** and **3** are slightly better with the latter method. γ,δ-Unsaturated ketones and imines are useful compounds in their own right (e.g., as sources of 1,5-dienes and for intramolecular cyclization reactions).[6]

Addition of acid chloride **7** (R'' = CH_3, Ph, $CH_3CH=$CH) to metallo enamine **6**, generated in situ from **1** or **4**, gave the enol imine **8**. The enolic proton of **8** occurred at low field (δ 13.54-14.13) in the proton magnetic resonance spectrum. It is noteworthy that there was no detectable amount of any keto–imine tautomer (**9**) in these reactions.

When **6** (R = Ph, R' = *p*-ClC_6H_4) was first treated with butyllithium at −78 °C and then with methyl iodide, the enamine **10** was formed. Hydrolytic cleavage of **10** gave

(6) E.g.: Marvell, E. N.; Li, T. H.-C. *J. Am. Chem. Soc.* **1978**, *100*, 883.

Scheme I



3 (R = Ph) and *p*-chloro-*N*-methylaniline. The formation of **10** is an exceptional case of N-alkylation of metallo enamines, since the latter generally experience C-alkylation.[5]

The following general procedure was used. To a vigorously stirred solution of **1** (1.70 mmol) in dry THF (15 mL) was added, in one portion, 3.50 mmol of vinylmagnesium bromide in 4 mL of THF. The reaction was exothermic, and the color of the solution became red-brown. After 30 min, the reaction mixture was poured into water and extracted with ether, and the ether extract was dried ($MgSO_4$) and concentrated. Analytically pure **2** was obtained by distillation or recrystallization. For the preparation of the enol imines **8**, an acid chloride was added to the red-brown solution, and the reaction mixture was stirred for 8–10 min and then poured into water. The methylated compound **10** was obtained by first adding 1.5 equiv of *n*-butyllithium to the red-brown solution (cooled to −78 °C), and then, after gradual warming to room temperature, methyl iodide (2 equiv) in THF (2 mL) was added dropwise. After being stirred for 30–60 min, the solution was worked up in the usual manner.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. 1 (R = Ph; R′ = *p*-ClC_6H_4), 34918-76-8; 1 (R = *p*-BrC_6H_4; R′ = Ph), 68695-50-1; 1 (R = R′ = *p*-ClC_6H_4), 29955-57-5; 2 (R = Ph; R′ = *p*-ClC_6H_4), 76173-06-3; 2 (R = *p*-BrC_6H_4; R′ = Ph), 76173-07-4; 3 (R = Ph), 3240-29-7; 3 (R = *p*-BrC_6H_4), 76173-08-5; 3 (R = *p*-ClC_6H_4), 35204-91-2; 4 (R = Ph; R′ = *p*-ClC_6H_4), 2866-82-2; 6 (R = Ph; R′ = *p*-ClC_6H_4), 76173-09-6; 7 (R″ = CH_3), 75-36-5; 7 (R″ = Ph), 98-88-4; 7 (R″ = $CH_3CH{=}CH$), 10487-71-5; 8 (R = Ph; R′ = *p*-ClC_6H_4; R″ = Ph), 76173-10-9; 8 (R = Ph; R′ = *p*-ClC_6H_4; R″ = $CH_3CH{=}CH$), 76173-11-0; 8 (R = Ph; R′ = *p*-ClC_6H_4; R″ = CH_3), 76173-12-1; 10 (R = Ph; R′ = *p*-ClC_6H_4), 76173-13-2; vinyl bromide, 593-60-2.

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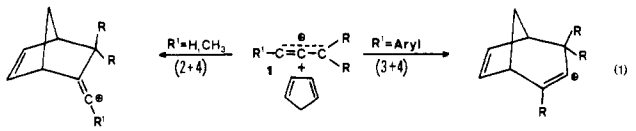
Stepwise [2 + 2] and [3 + 2] "Cycloaddition" Reactions of Allenyl Cations with Olefins

Summary: Propargyl halides $R^1C{\equiv}CCHalR^2R^3$ and olefins react under zinc halide catalysis to give α-halobenzylidenecyclobutanes (R^1 = phenyl) or 1-halocyclopentenes (R^1 = methyl).

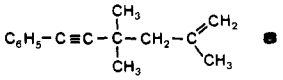
Sir: Allenyl cations (**1**) have been established as reactive intermediates in solvolysis reactions of allenyl and propargyl derivatives;[1] they can be observed as stable species in superacidic solutions.[2] Recently we demonstrated their ability to undergo [2 + 4] and [3 + 4] cycloadditions with cyclopentadiene (eq 1).[3] In this paper we report the Lewis



(1)

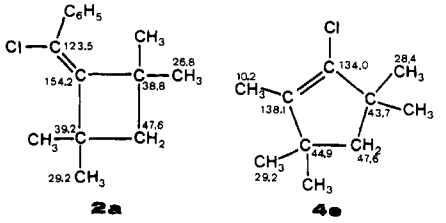
acid catalyzed formation of vinylcyclobutanes **2** and cyclopentenes **4** from propargyl halides **3** and olefins via stepwise [2 + 2] and [3 + 2] cycloadditions of intermediate allenyl cations **1** (Scheme I).

Vinyl halides **2** and **4** are accessible in moderate to good yields when equimolar mixtures of propargyl halides **3** and olefins are treated with the homogenous catalyst system 1:1.5 $ZnHal_2$–Et_2O in methylene chloride.[4] Best yields were usually obtained when **3** and 1–2 equiv of olefin in methylene chloride solution were added to the catalyst at −78 °C and subsequently warmed up to 0 °C (Table I). In addition to **2a** and **2b**, reactions a and b (Table I) yielded mixtures of enynes (~20%) from which **8** was isolated as the major component.[5]



8

Methylenecyclobutanes **2** and cyclopentenes **4** can be differentiated on the basis of their ^{13}C NMR spectra. As expected from increment calculations,[6] the vinylic resonances are very similar in the cyclopentenes (**4e**, Δ = 4.1 ppm) but differ considerably in the benzylidenecyclobutanes (**2a**, Δ = 30.7 ppm).



2a **4e**

In the mass spectra, the cyclobutanes **2** are characterized by strong peaks corresponding to ions **1**, whereas this type of fragmentation is not observed for cyclopentenes **4**. Treatment of **2b** with silver trifluoroacetate in ether and subsequent alkaline hydrolysis gave cyclobutyl phenyl ketone **9**;[7] the cyclopentene framework in compounds **4** was

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(3) (a) Mayr, H.; Grubmüller, B. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 130. (b) Mayr, H.; Halberstadt, I. K. *Ibid.* **1980**, *19*, 814.
(4) For a description of the catalyst see ref 3b.
(5) For **8**: ^1H NMR (CCl_4) δ 1.30 (s, $C(CH_3)_2$), 1.98 (s, CH_3), 2.24 (s, CH_2), 4.82 and 4.91 (br s, $=CH_2$), 7.27 (mc, C_6H_5).
(6) Hesse, M.; Meier, H.; Zeeh, B. "Spektroskopische Methoden in der organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1979; p 234.

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