Freshly sublimed **3**,[3] reacted with the sodium salt of diisopropyl (carboethoxy)methylphosphonate [$(i\text{-}C_3H_7O)_2POCH_2CO_2CH_2CH_3$], gave (87% yield) the unsaturated ester **5**, mp 135–137 °C, $[\alpha]_D$ −10.8° (*c* 1.96, $CHCl_3$).[4] On treatment with magnesium monoethyl malonate,[5] **5** was smoothly converted (77% yield) into the diester **6**, mp 48–49 °C, $[\alpha]_D$ −9.5° (*c* 0.71, $CHCl_3$). The required imide ring was then readily introduced by reaction of diester **6** with ammonium hydroxide (50 °C, 24 h) followed by removal of the solvent and pyrolysis (155 °C, 35 min; 210 °C, 15 min)[6] to give (68% yield) the imide **7**, mp 261–262 °C, $[\alpha]_D$ −34.4° (*c* 0.64, H_2O).

We then turned our attention to selective hydrolysis of that acetal ring derived from a combination of primary and secondary alcohols. This was carried out by reacting **7** with a mixture of trifluoroacetic anhydride (TFAA, 3.0 equiv) and acetic acid (3.0 equiv) at 22 °C for 6 h.[7] After addition of saturated sodium bicarbonate and stirring and adjusting the pH of the reaction mixture to 6.5, the primary acetate **8** (87% yield) could be isolated, mp 188–189 °C, $[\alpha]_D$ −13.0° (*c* 1.44, H_2O). The secondary hydroxyl group of **8** was then protected with *tert*-butyldiphenylsilyl triflate, (TBDPSOTf, 4.0 equiv)[8] in CH_2Cl_2 solution containing 2,6-lutidine (5.0 equiv) to afford (100% yield) compound **9**, mp 181–182 °C, $[\alpha]_D$ +7.3° (*c* 1.01, $CHCl_3$). Reduction of the primary acetate residue of **9** with diisobutylaluminum hydride (1.0 equiv of DiBAl-H, −78 °C, THF, 5 min; then 3.0 equiv of additional DiBAl-H, −78 to 0 °C, 2 h) gave (97% yield) the corresponding alcohol **10**, mp 144–145 °C, $[\alpha]_D$ +7.8° (*c* 1.02, $CHCl_3$), without competing reduction of the imide residue. Finally, Swern oxidation[9] of **10** gave (97% crude yield) the aldehyde **4**.[10]

At this juncture, it was our intention to add the readily fabricated crotylstannane derivative **11**[11] to the aldehyde **4** in the presence of a Lewis acid.[12] To this end, we treated a CH_2Cl_2 solution of **4** containing magnesium bromide etherate (2.0 equiv) with the stannane **11** (2.0 equiv) at −78 °C followed by warming to −40 °C and stirring for 48 h. Much to our disappointment, this reaction gave a 4:1 mixture (83% yield) of compounds **12** and **13**, respectively. These substances were identified as epimers about the C-11 carbon atom; the major constituent, **12**, being the unwanted α-methyl isomer.[13]

After an exhaustive examination of the effect of various Lewis acids on the stereochemistry of this reaction, it was found that an acceptable yield of the desired β-methyl epimer at C-11 was obtained with borontrifluoride etherate ($BF_3{\cdot}Et_2O$). Thus, to a mixture of **4** (1.0 equiv) and **11** (2.0 equiv) in CH_2Cl_2 (0.1 M) at −78 °C was added $BF_3{\cdot}Et_2O$ (1.5 equiv, −78 °C, 5.5 h). Hydrolysis of this reaction at −78 °C with saturated aqueous $NaHCO_3$ gave (51% yield) the C-11 β-methyl compound **13** (mixture of alcohol epimers at C-10) together with (32% yield) its α-methyl isomer, compound **12** (single alcohol epimer at C-10). These substances, **13** and **12**, were readily separated by chromatography and independently carried forward.[14]

Swern oxidation of **13** (C-10 alcohol epimers) gave (63% yield, 89% yield based on recovered **13**) a single ketone **14**, mp 73–76 °C, $[\alpha]_D$ +73.4° (*c* 1.40, $CHCl_3$), which on treatment with a 3:1:1 mixture of HOAc–THF–H_2O (22 °C, 4.3 h)[15] afforded (100% yield) compound **1**, as a white solid from CH_2Cl_2/Et_2O, mp 154.5–155.5 °C, $[\alpha]_D$ −56.9° (*c* 0.21, $CHCl_3$) and $[\alpha]_D$ +6.0° (*c* 0.27, CH_3OH). Naturally occuring sesbanimide A (compound **2**), as obtained from Dr. R. G. Powell (USDA), mp 154.5–156 °C, exhibited the following optical rotations: $[\alpha]_D$ +52.6° (*c* 0.26, $CHCl_3$) and $[\alpha]_D$ −6.3° (*c* 0.32, CH_3OH).[16] The same two-step sequence carried out on **12** gave (89% overall yield) **15**, as white amorphous solid, mp 78–86 °C, $[\alpha]_D$ +15.7° (*c* 2.68, $CHCl_3$).[17] The synthetic sequence to (−)-sesbanimide A (**1**) requires 10 steps from the known aldehyde **3**[18] and occurs in an overall yield of 12% (17% based on recovered starting material, Swern oxidation **13** to **14**).

Acknowledgment. Financial support from the NIH and the Merck Corp. are gratefully acknowledged.

(4) Satisfactory spectral (^1H, ^{13}C, IR, MS, and HRMS) and physical data were collected, except in cases of instability, for all new compounds.
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(10) The crude aldehyde formed in this reaction was quite pure, as determined by ^1H NMR. However, this substance decomposed on chromatography, and, hence, its optical rotation was not measured.
(11) The preparation of **11** requires three steps starting from methyl-2-methylene-3-acetoxybutyrate, a substance described, as its ethyl ester analogue, by: Drewes, S. E.; Emslie, N. D. *J. Chem. Soc., Perkin Trans 1* **1982**, 2079. These steps are: (a) treatment of the ester with $Bu_3SnCu{\cdot}DMS{\cdot}LiBr$ (1.2 equiv); (b) reduction of the ester residue with DiBAl-H (2.5 equiv, −78 °C); (c) protection of the alcohol residue with TBSCl.
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(13) The ultimate proof for the structures assigned to compounds **12** and **13** came not from their NMR spectra but rather from their two-step conversion into sesbanimide B and sesbanimide A, respectively.
(14) The major and minor C-10 alcohol epimers of **13** could be separated upon additional chromatography, although this was not usually done. Physical characteristics for these compounds are: major isomer, mp 182–188 °C; $[\alpha]_D$ +29.4° (*c* 2.57, $CHCl_3$); minor isomer, mp 53–58 °C; $[\alpha]_D$ −5.8° (*c* 0.80, $CHCl_3$).
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(16) We thank Dr. R. G. Powell (USDA) for a generous sample of (+)-sesbanimide A.
(17) Compound **15**, according to its ^1H and ^{13}C spectra, is sesbanimide B as described in ref 1c.
(18) The optical antipode of **3** is an unknown compound. We are currently working on a short synthesis of this substance starting from D-(+)-xylose.

R. H. Schlessinger,* J. L. Wood
Department of Chemistry
University of Rochester
Rochester, New York 14627
Received February 20, 1986

Mercury in Organic Chemistry. 33. A Convenient Synthesis of Allenic and Propargylic Ketones via Acylation of Propargylic and Allenic Organomercurials, Respectively[1]

Summary: The low-temperature reaction of carboxylic acid chlorides, aluminum halides, and propargylic and allenic organomercurials affords the corresponding rearranged allenic and propargylic ketones, respectively, in high yields. The propargylic ketones rearrange smoothly to the corresponding allenic ketones when passed through a column of aluminum oxide.

(1) For "Mercury in Organic Chemistry. 32. Bromination and Iodination of Allenic and Propargylic Organomercurials: A Convenient Synthesis of 3-Halo-1,2-alkadienes", see: Larock, R. C.; Chow, M. S. *Organometallics* **1986**, *5*, 603.

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Table I. Acylation of Propargylic and Allenic Organomercurials[a]

entry	organomercurial	acid chloride	product[b]	isolated yield, %
1	$CH_3C{\equiv}CCH_2HgI$	$CH_3(CH_2)_2C(=O)Cl$	$CH_3(CH_2)_2C(=O)(CH_3)C{=}C{=}CH_2$	85
2		$Cl(CH_2)_3C(=O)Cl$	$Cl(CH_2)_3C(=O)(CH_3)C{=}C{=}CH_2$	90
3		$CH_3CH_2OC(=O)C(=O)Cl$	$CH_3CH_2OC(=O)C(=O)(CH_3)C{=}C{=}CH_2$	91[c]
4	$C_6H_5C{\equiv}CCH_2HgI$	$CH_3(CH_2)_2C(=O)Cl$	$CH_3(CH_2)_2C(=O)(C_6H_5)C{=}C{=}CH_2$	92
5	$CH_3CH{=}C{=}CHHgCl$	$CH_3(CH_2)_2C(=O)Cl$	$CH_3(CH_2)_2C(=O)CH(CH_3)C{\equiv}CH$	82
6		(*E*)-$CH_3CH{=}CHC(=O)Cl$	(*E*)-$CH_3CH{=}CHC(=O)CH(CH_3)C{\equiv}CH$	87
7		(*E*)-$C_6H_5CH{=}CHC(=O)Cl$	(*E*)-$C_6H_5CH{=}CHC(=O)CH(CH_3)C{\equiv}CH$	92

[a] All reactions were run by stirring 0.5 mmol each of $AlCl_3$, acid chloride, and organomercurial in 5 mL of CH_2Cl_2 for 3–6 min at −30 to −40 °C and quenching with 5 mL of 5% aqueous $NaHCO_3$ unless otherwise stated. [b] All products gave correct ^1H NMR, IR, and exact mass spectral data. [c] $AlBr_3$ was used instead of $AlCl_3$.

Sir: Allenic[2] and propargylic ketones are valuable substrates in organic chemistry, but relatively few methods exist for their preparation. Those methods that do exist frequently result in mixtures of products and can accommodate little functionality. We recently developed a convenient method for the preparation of propargylic and allenic mercurials (eq 1 and 2)[3] and reported that their

$$RC{\equiv}CCH_2I + Hg \rightarrow RC{\equiv}CCH_2HgI \quad (1)$$

$$RCH(I)C{\equiv}CH + Hg \rightarrow RCH{=}C{=}CHHgI \quad (2)$$

halogenation affords a convenient route to the corresponding rearranged allenic and propargylic bromides and iodides.[1] We now wish to report that these organomercurials undergo facile acylation with rearrangement to afford the corresponding allenic and propargylic ketones in high yields (eq 3 and 4). Our results are summarized in Table I.

$$RC{\equiv}CCH_2HgI + R'COCl \xrightarrow{AlCl_3} R'CORC{=}C{=}CH_2 \quad (3)$$

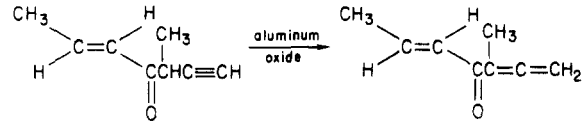
$$RCH{=}C{=}CHHgI + R'COCl \xrightarrow{AlCl_3} R'COCHRC{\equiv}CH \quad (4)$$

The acylation of alkyl-, aryl-, and vinylmercurials is well-known.[4] Using the reaction conditions developed earlier by us for the acylation of vinylmercurials ($AlCl_3$, CH_2Cl_2, 5 min at room temperature),[5] we observed that the acylation of propargylic and allenic organomercurials afforded the anticipated rearranged ketones, but they were contaminated by apparent HCl addition products. By simply lowering the reaction temperature to between −30 and −40 °C and quenching with 5% aqueous $NaHCO_3$, we were able to obtain excellent yields of the desired ketones free of any HCl adducts or any of the ketones expected from acylation with retention of the original organomercurial structure. With allenic mercurials we have been able to employ both aliphatic and α,β-unsaturated acid chlorides, but we obtained low yields when aromatic acid chlorides were employed. On the other hand, propargylic mercurials only react well with aliphatic acid chlorides.

The ketone products appear to be relatively unstable and are best stored under nitrogen in the cold. In attempting to purify the propargylic ketones, we observed that simple column chromatography over silica gel or basic aluminum oxide (J. T. Baker Chemical Co., Brockmann activity grade 1) cleanly rearranges these compounds in high yield to the corresponding allenic ketones,[2] thus further extending our approach to this valuable class of compounds (eq 5 and 6). Note that even the highly unsaturated allenic ketone derived from rearrangement of a propargylic enone survives the mild conditions employed here (eq 6). This isomerizaton process thus allows us to prepare allenic enones that we were unable to prepare by the direct reaction of propargylic mercurials and α,β-unsaturated acid chlorides.

$$CH_3(CH_2)_2C(=O)CH(CH_3)C{\equiv}CH \xrightarrow[\text{oxide}]{\text{aluminum}} CH_3(CH_2)_2C(=O)C(CH_3){=}C{=}CH_2 \quad (5)$$

68%



62% (6)

In view of the ready availability of functionality substituted propargylic and allenic organomercurials and the ease with which they undergo acylation to the corresponding allenic and propargylic ketones, respectively, we believe that this method for the preparation of these compounds should be particularly valuable. As a route to allenic ketones, it offers clear advantages over the reactions of allenylmagnesium compounds with amides and esters;[6] allenyllithium reagents and amides;[7] or propargylic silanes, acid chlorides, and aluminum trichloride;[8,9] since the first two organometallics can accommodate little functionality and afford mixtures of products, while the silanes are not as readily available and generally acylate in only poor to modest yields.

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Richard C. Larock,* Min-Shine Chow
Sarah J. Smith
Department of Chemistry
Iowa State University
Ames, Iowa 50011
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