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Synthesis and Acylation of Allylic Mercuric Iodides: A Convenient Synthesis of Allylic Ketones[1]

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Allylic mercuric iodides are readily prepared by the reaction of mercury(0) and allylic iodides. They undergo efficient acylation with allylic rearrangement upon reaction with acyl chlorides and aluminum chloride to provide a convenient synthesis of allylic ketones. Artemisia ketone is prepared in two steps by this approach.

Introduction

The acylation of organometallics provides one of the most important synthetic routes to ketones.[2] Allylic ketones have been prepared by the reaction of allylic organometallics of silicon,[3] tin,[4] copper,[5] rhodium,[6] manganese[7] and titanium[8] with acyl halides (eq 1). Since these

$$H_2C{=}CHCH_2M + ClC(O)R \rightarrow H_2C{=}CHCH_2C(O)R \quad (1)$$

$$M = Si, Sn, Cu, Rh, Mn, Ti$$

organometallics are most commonly synthesized from the corresponding allylic alkali metal or magnesium compounds, little functionality can be accommodated by this process.

On the other hand, organomercurials are readily available by a wide variety of synthetic procedures.[9] Though they are toxic and should be handled with gloves in a hood, organomercurials are thermally and chemically quite stable and tolerate virtually all important organic functional groups. Since earlier reports in the literature suggested that allylic mercurials were readily available from the reaction of allylic halides and mercury,[10] and previous work on the acylation[11] of organomercurials suggested that this might provide a useful new route to the corresponding ketones, we decided to examine this overall approach to allylic ketones. We report first the development of a general synthesis of allylic mercuric iodides and then a convenient procedure for their acylation which does indeed provide a useful new approach to allylic ketones.

Synthesis of Allylic Mercuric Iodides

While there are miscellaneous reports of the reaction of allylic halides and metallic mercury providing allylic mercuric halides, relatively few such compounds have been isolated and well characterized, a variety of synthetic procedures have been employed, and the yields have usually been pretty low.[10] If our approach to allylic ketones were to be useful, we needed a convenient, general, high-yielding route to the allylic mercuric halides. We report here just such procedures.

Earlier, we reported a convenient synthesis of propargylic and allenic mercuric iodides by the reaction of 1 equiv of a propargylic iodide and 2 equiv of mercury in sunlight for 2 h in a sealed test tube flushed with nitrogen.[12] Using this procedure on allyl iodide for 20 min, a crude yield of allylmercuric iodide (**1**) of 60% was obtained (eq 2). Since

$$H_2C{=}CHCH_2I + Hg \rightarrow \underset{\mathbf{1}}{H_2C{=}CHCH_2HgI} \quad (2)$$

it appeared that allyl iodide was significantly more reactive than typical propargylic iodides, the reaction was rerun in indirect sunlight, and workup after 30 min afforded a 70% yield of compound **1**. It appeared that the reaction might be more conveniently effected in the presence of a solvent. Indeed, the same reaction carried out in tetrahydrofuran (THF) with vigorous stirring for almost 4 h at room temperature in room light, afforded a 98% isolated yield of allylmercuric iodide (**1**).

Since allylic bromides and chlorides are often easier to prepare and handle than allylic iodides, we examined the mercuration of these substrates. Allyl bromide gave none

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Table I. Preparation of Allylmercuric Iodide by the One-Pot Reaction of Allyl Bromide, Sodium Iodide, and Metallic Mercury[a]

entry	solvent	T_1 (h)	T_2 (h)	% isolated yield
1	$CH_3COC_2H_5$	24	18	42
2	CH_3COCH_3	2	4	61
3	THF	2	4	71
4	THF	2	8	92
5	THF	2	12	92

[a] All reactions were run at room temperature using 0.01 mol of allyl bromide, 0.02 mol of NaI, 0.02 g atoms of Hg, and 10 mL of solvent.

Table II. Preparation of Allylmercuric Iodide by the One-Pot Reaction of Allyl Chloride, Sodium Iodide, and Metallic Mercury[a]

entry	T_1 (h)	T_2 (h)	% isolated yield
1	2	8	58
2	2	30	58
3	4	24	78
4	2[b]	24	70
5	48	3	69

[a] All reactions were run at room temperature (unless so indicated) using 0.01 mol of allyl chloride, 0.02 mol of NaI, 0.02 g atoms of Hg and 10 mL of THF. [b] Refluxing in THF.

of the desired mercurial under the optimal conditions determined for allyl iodide. Even placing the reaction flask in an ultrasonic bath for 4 h while irradiating by sunlight or a high-pressure mercury lamp (Hanovia 679 A36) failed to initiate the mercuration of allyl bromide. Allyl chloride, likewise, proved to be inert.

Since allylic bromides or chlorides are readily available, but fail to react with metallic mercury directly, a two-step route to allylic mercuric iodides from allylic bromides or chlorides has been investigated. First, the allylic bromide or chloride is subjected to nucleophilic displacement by iodide anion, and the allylic iodide generated in situ is then treated with metallic mercury (eq 3). Various solvents have been examined for this process. The highest yield of compound 1 was obtained when allyl bromide was allowed to react with sodium iodide in THF for 2 h (T_1) and then continuously stirred for another 8–12 h (T_2) after the metallic mercury was added to the reaction mixture (procedure A; Table I, entries 4 and 5). With THF as the solvent, it is not necessary to remove the sodium salts produced in the first step, and the product formed is much cleaner than that formed in acetone.

$$\underset{X\,=\,Br,\,Cl}{H_2C{=}CHCH_2X} + NaI \xrightarrow[T_1]{solvent} H_2C{=}CHCH_2I \xrightarrow[T_2]{Hg} \underset{1}{H_2C{=}CHCH_2HgI} \qquad (3)$$

Allyl chloride was also allowed to react with sodium iodide and metallic mercury in THF under the same experimental conditions as allyl bromide (eq 3). The highest yield of compound 1 was obtained when the reaction time of the first step (T_1) was 4 h and the second reaction step (T_2) was run for 24 h (Table II, entry 3).

In order to demonstrate the synthetic utility of the two-step iodide displacement–mercuration procedure for the synthesis of allylic mercuric iodides, a variety of allylic bromides and chlorides was allowed to react with sodium iodide and metallic mercury in THF as described above (procedure A). As seen in Table III, most mercuration reactions of allylic chlorides and bromides were successfully run according to the sequence illustrated in eq 3. However, procedure A did not work well for the allylic halides shown in entries 7–9, where a simplified procedure (procedure B) which involves mixing all reagents plus the solvent together from the start and stirring the appropriate period of time at 0 °C. This procedure generally provides reasonable yields.

Methallyl chloride gave a 79% yield of methallylmercuric iodide (2) using procedure A (entry 4, Table III). The ^1H NMR spectral data for compound 2 indicate only two singlets [δ 3.94 (4 H), 1.80 (2 H)] proving the existence of an equilibrating process consistent with the data reported by Winstein and co-workers.[13]

The mercuration of crotyl bromide proceeds with no evidence of rearrangement (entry 5, Table III). The direct mercuration of crotyl bromide under sunlight in the absence of solvent failed to give any of the desired product.

According to the literature,[10d] cinnamylmercuric bromide can be prepared in significantly higher yield by shaking the allylic bromide with mercury for 15 min in 95% ethanol than by using our procedure (entry 6).

While the allylic bromides shown in entries 7–9 of Table III gave poor results using procedure A, satisfactory results were obtained using procedure B. While we have not examined the effect of functional groups other than an ester group, we would anticipate that other functionally-substituted allylic halides should provide the corresponding allylic mercurials.

All attempts to prepare secondary allylic mercurials from several different secondary allylic iodides, bromides, and chlorides proved unsuccessful.

The formation of organomercury compounds from organic halides and mercury appears to proceed by a radical chain mechanism.[14] To establish the free-radical nature of the reaction, oxygen was chosen as a radical chain inhibitor and galvinoxyl as a radical scavenger to see if these additives would suppress the radical chain reaction. While the reaction of allyl iodide and mercury in THF in the absence of oxygen after 4 h at 25 °C afforded a 95% isolated yield of allylmercuric iodide, the same reaction in the presence of oxygen gave only an 8% yield. The same reaction run in the absence of oxygen, but in the presence of galvinoxyl, gave only a 5% yield of allylic mercurial. These data clearly suggest the presence of a free-radical chain process. While a secondary carbon radical exhibits greater stability than its primary counterpart, the experimental fact is that only primary allylic iodides react with mercury to form the corresponding allylic mercurials. The high sensitivity of the reaction to steric effects suggests that a bulk mercury atom may be involved in the initiation process.

Synthesis of Allylic Ketones

With a number of allylic mercurials now readily available, we were ready to study their acylation as a potentially valuable new route to allylic ketones. Although alkyl,[15] aryl,[14,15b,c,16] vinylic,[17] allenic,[18] propargylic,[18] and alkynyl[19]

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Table III. Preparation of Allylic Mercuric Iodides

entry	allylic halide	proced[a]	reactn time(s) T_1 (h), T_2 (h)	allylic mercuric iodide	% isolated yield
	$H_2C{=}CHCH_2X$			$H_2C{=}CHCH_2HgI$ (**1**)	
1	X = I	*b*	–, 4		98
2	X = Br	A	2, 8		92
3	X = Cl	A	4, 24		78
4	$H_2C{=}C(CH_3)CH_2Cl$	A	8, 24	$H_2C{=}C(CH_3)CH_2HgI$ (**2**)	79
5	(*E*)-$CH_3CH{=}CHCH_2Br$	A	4, 24	(*E*)-$CH_3CH{=}CHCH_2HgI$ (**3**)	78
6	(*E*)-$PhCH{=}CHCH_2Br$	A	4, 24	(*E*)-$PhCH{=}CHCH_2HgI$ (**4**)	38
7	$(CH_3)_2C{=}CHCH_2Br$	B	6	$(CH_3)_2C{=}CHCH_2HgI$ (**5**)	44
8	(*E*)-$EtO_2CCH{=}CHCH_2Br$	B	3	(*E*)-$EtO_2CCH{=}CHCH_2HgI$ (**6**)	43
9	$H_2C{=}C(CO_2CH_3)CH_2Br$	B	1	$H_2C{=}C(CO_2CH_3)CH_2HgI$ (**7**)	47

[a] See the Experimental Section. [b] Commercially available allyl iodide was used directly, omitting the sodium iodide step.

Table IV. Preparation of Allylic Ketones[a]

entry	allylic mercurial	acid chloride	temp (°C), time (min)	allylic ketone	% isolated yield
1	1	*n*-$C_3H_7C(O)Cl$	0, 10	*n*-$C_3H_7C(O)CH_2CH{=}CH_2$ (**8**)	82
2		$PhC(O)Cl$	25, 6	$PhC(O)CH_2CH{=}CH_2$ (**9**)	87
3		(*E*)-$CH_3CH{=}CHC(O)Cl$	40, 4	(*E*)-$CH_3CH{=}CHC(O)CH_2CH{=}CH_2$ (**10**)	97
4		$(CH_3)_2CHC(O)Cl$	–78, 7	$(CH_3)_2CHC(O)CH_2CH{=}CH_2$ (**11**)	84
5		*p*-$CH_3OC_6H_4C(O)Cl$	0, 10	*p*-$CH_3OC_6H_4C(O)CH_2CH{=}CH_2$ (**12**)	90
6	**3**	*n*-$C_3H_7C(O)Cl$	0, 7	*n*-$C_3H_7C(O)C(CH_3)HCH{=}CH_2$ (**13**)	70
7	**5**	*n*-$C_3H_7C(O)Cl$	0, 10	*n*-$C_3H_7C(O)C(CH_3)_2CH{=}CH_2$ (**14**)	86
8		$(CH_3)_2CHC(O)Cl$	–60, 15	$(CH_3)_2CHC(O)C(CH_3)_2CH{=}CH_2$ (**15**)	93
9		$(CH_3)_2C{=}CHC(O)Cl$	–60, 15	$(CH_3)_2C{=}CHC(O)(CH_3)_2CH{=}CH_2$ (**16**)	96
10	**4**	$CH_3C(O)Cl$	–78, 10	$CH_3C(O)C(Ph)HCH{=}CH_2$ (**17**)	82
11		*n*-$C_3H_7C(O)Cl$	25, 10	*n*-$C_3H_7C(O)C(Ph)HCH{=}CH_2$ (**18**)	69
12	**6**	*n*-$C_3H_7C(O)Cl$	25, 10	*n*-$C_3H_7C(O)C(CO_2Et)HCH{=}CH_2$ (**19**)	89

[a] All reactions were run by adding 2 mmol of allylic mercurial to 20 mL of CH_2Cl_2 containing 2.2 mmol of $AlCl_3$ and 2 mmol of acyl chloride. After the appropriate reaction time, the reaction was quenched with 5% $NaHCO_3$, washed with 3 M $Na_2S_2O_3$ and saturated aqueous NaCl, and dried and the solvent removed.

mercurials undergo facile acylation by acyl halides either directly or preferably in the presence of aluminum chloride or $Pd(PPh_3)_4$ to form the corresponding ketones,[11] previous examples of the direct reaction of allylmercuric iodide with acyl halides afforded none of the anticipated allylic ketone, although it may initially have been formed (eqs 4 and 5).[20]

$$1 + ClC(O)CHPh_2 \xrightarrow[2.\ \text{alumina}]{1.\ \Delta} \underset{73\%}{CH_3CH{=}CHC(O)CHPh_2} \quad (4)$$

$$1 + 2ClC(O)CH_2R \xrightarrow{\Delta} \underset{40\text{–}52\%}{RCH{=}C(O_2CCH_2R)CH_2CH{=}CH_2} \quad (5)$$

With a variety of allylic mercurials in hand, we have examined their reaction with acyl halides and aluminum chloride in much the same manner as our previous successful work on the acylation of vinylic,[17] allenic,[18] and propargylic[18] mercuric iodides. Our results are summarized in Table IV.

The reaction of allylmercuric iodide and butyryl chloride was chosen as a model reaction for study (eq 6). Allylmercuric iodide was treated with butyryl chloride and $AlCl_3$ (1.1 equiv) in dichloromethane for 10 min at 0 °C to afford 1-hepten-4-one in 82% isolated yield without even optimizing conditions (Table IV, entry 1). No conjugated enone or 4-(acyloxy) 1,4-diene of the types reported previously for the analogous thermal reactions (see eqs 4 and 5) was observed. The amount of aluminum chloride does not seem to have a pronounced effect on the yield of the reaction, provided at least 1 equiv is present.

$$1 + n\text{-}C_3H_7C(O)Cl \xrightarrow[CH_2Cl_2]{AlCl_3} \underset{\mathbf{8}\ (82\%)}{n\text{-}C_3H_7C(O)CH_2CH{=}CH_2} \quad (6)$$

Under the same reaction conditions, the reaction of benzoyl chloride and allylmercuric iodide indicated the existence of a significant amount of impurities which appeared to contain two benzoyl fragments. It was subsequently found that this reaction proceeded at room temperature in only 6 min to afford the desired allylic ketone **9** in 87% isolated yield (Table IV, entry 2).

Crotonyl chloride was also allowed to react with allylmercuric iodide (**1**) in the presence of 1.1 equiv of $AlCl_3$. Best results were obtained by raising the reaction temperature and shortening the reaction time (0 °C, 8 min: 58% isolated yield of dienone **10**; 25 °C, 6 min: 64%; 40 °C, 4 min: 97%). When the reaction was run in refluxing dichloromethane for 4 min, a nearly quantitative yield of 1,5-heptadien-4-one (**10**) was obtained (entry 3).

With these encouraging results in hand, optimization of the acylation process using various allylic mercurials and acyl chlorides focused on the use of different combinations of reaction time and temperature. Our results are summarized in Table IV. The isolated yields obtained were generally greater than 80%. All reactions proceeded in a matter of minutes at room temperature or temperatures as low as –78 °C. Alkyl, aryl, and functionally-substituted allylic mercurials were all found to work well. While we have only examined the use of an ester-containing allylic mercurial (**6**) (entry 12 in Table IV), we anticipate that considerable functionality should be accommodated by this reaction. While allenic[18] and vinylic[17] mercurials react under similar conditions with aliphatic and α,β-

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unsaturated acyl chlorides, but not aromatic acyl chlorides, and propargylic[18] mercurials only react well with aliphatic acyl chlorides, allylic mercuric iodides give excellent yields with all three types of acyl chlorides.

All acylation reactions proceeded with allylic rearrangement, even when that involves attack at the more hindered end of the allylic system (entries 6–9) or that the double bond was removed from conjugation (entries 10–12). It appears that neither electronic effects nor steric hindrance are important factors in the acylation of allylic mercurials promoted by aluminum chloride. These results can be rationalized by the mechanism anticipated by Mukaiyama[20] in which electrophilic attack of the aluminum chloride-complexed butyryl chloride occurs at the γ-carbon atom of the allylic moiety of the allylic mercurial.

Calas and co-workers[3a] have found that allylic silanes prepared from Grignard reagents, in the presence of Lewis acids such as $AlCl_3$, react with acid chlorides to afford the corresponding allylically rearranged ketones. Using this methodology, the naturally-occurring monoterpene Artemisia ketone was synthesized.[3b] The high reactivity of 3-methyl-2-butenylmercuric iodide (**5**) toward acylation with acyl chlorides prompted us to examine the synthesis of Artemisia ketone (**16**). The intermediate allylic mercurial **5** can be readily prepared from the corresponding allylic bromide in only one step. Acylation afforded a 96% yield of Artemisia ketone, a yield higher than that obtained by the silane procedure (Table IV, entry 9).

By employing the crude allylic mercurial obtained from the mercuration step and simply changing the solvent, one can simplify the overall process still further. In this manner, allylmercuric iodide can be converted to 1-hepten-4-one in one pot in an overall yield of 78% (eq 7).

$$H_2C{=}CHCH_2I \xrightarrow[\text{THF, 25 °C, 4h}]{\text{Hg}} \xrightarrow[\text{CH}_2\text{Cl}_2\text{, 0 °C, 10 min}]{\text{AlCl}_3,\ n\text{-C}_3\text{H}_7\text{COCl}} \underset{\mathbf{8}\ (78\%)}{n\text{-}C_3H_7C(O)CH_2CH{=}CH_2} \quad (7)$$

Several acylation reactions were attempted without success. When the acylation was run using a benzoyl chloride bearing electron-withdrawing substituents on the benzene ring, the yield of the desired allylic ketone was reduced dramatically. For example, allylmercuric iodide was allowed to react with 3,5-dinitrobenzoyl chloride in the presence of $AlCl_3$ and dichloromethane, under various conditions and yields of only 6–15% were obtained. In contrast, when a benzoyl chloride with an electron-donating substituent on the aromatic ring was used as the acyl chloride, an excellent yield of the corresponding allylic ketone was obtained (see entry 5 in Table IV).

Other unsuccessful acyl chlorides are *o*-chlorobenzoyl chloride and chloro-substituted aliphatic acid chlorides, such as chloroacetyl chloride, γ-chlorobutyryl chloride, and dichloroacetyl chloride. Ethoxycarbonyl-substituted aliphatic acid chlorides, such as ethyl malonyl chloride and ethyl succinyl chloride, also failed to give any of the desired ketone products. However, when the ethoxycarbonyl group was attached to the allylic mercurial, a high yield of the desired allylic ketone was observed (see entry 12 in Table IV).

When methallylmercuric iodide was treated with butyryl chloride in the presence of $AlCl_3$ at 0 °C for 10 min, only an unexpected product 2-chloro-2-methyl-4-heptanone was isolated in 22% yield (eq 8). Unfortunately, we were unable to readily circumvent these difficulties.

$$H_2C{=}C(CH_3)CH_2HgI + n\text{-}C_3H_7C(O)Cl \xrightarrow[\text{0 °C, 10 min}]{\text{AlCl}_3/\text{CH}_2\text{Cl}_2} \underset{22\%}{n\text{-}C_3H_7C(O)CH_2C(Cl)(CH_3)_2} \quad (8)$$

Conclusion

Allylic mercuric iodides are readily prepared from the corresponding allylic halides and metallic mercury in good yields. It appears that a considerable amount of functionality can be tolerated in this procedure. Unfortunately, secondary allylic mercurials cannot be synthesized by this procedure.

The acylation of allylic mercuric iodides by an acyl chloride promoted by aluminum chloride provides a convenient synthesis of allylic ketones. This carbon–carbon bond-forming reaction proceeds with allylic rearrangement. A variety of allylic mercurials and acyl chlorides, including aliphatic, aromatic, and α,β-unsaturated acyl chlorides, can be employed successfully in this process. However, acyl chlorides containing an electron-withdrawing substituent often fail.

Experimental Section

General. All ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively. Thin-layer chromatography (TLC) was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short-wavelength UV light (254 nm) or basic $KMnO_4$ solution [3 g of $KMnO_4$ + 20 g of K_2CO_3 + 5 mL of NaOH (5%) + 300 mL of H_2O]. All melting points are uncorrected. All but one allylic halide and all acyl chlorides were purchased and distilled prior to use. Methyl α-(bromomethyl)acrylate was synthesized according to the procedure reported by Cassady and co-workers.[21] $AlCl_3$ and Hg were used directly as obtained commercially.

Preparation of Allylmercuric Iodide (1). A solution of allyl iodide (1.56 g, 0.01 mol) in 10 mL of dry THF was injected into a flask containing 4.0 g of Hg (0.02 g atoms) under N_2, and the reaction mixture was allowed to stir for 4 h at rt. The mixture was filtered through Celite to remove the unreacted Hg which was washed with 2 × 15 mL of THF. Removal of the solvent afforded crude allylmercuric iodide: 3.27 g, 98% yield; mp 130–131 °C (lit.[13] mp 129–131 °C, lit.[22] mp 133–135 °C); ^1H NMR (DMSO-d_6) δ 2.50 (br s, 2 H, $CH_2CH{=}CH_2$), 4.82 (br s, 2 H, $CH{=}CH_2$), 6.06 (dt, J = 8.7, 17.7 Hz, 1 H, $CH{=}CH_2$); ^1H NMR (DMSO-d_6, HgI_2) δ 3.70 (d, J = 11.0 Hz, 4 H, $CH_2CH{=}CH_2$), 6.04 (p, J = 11.0 Hz, 1 H, $CH_2CH{=}CH_2$) (consistent with literature[13]); IR (KBr) 1619 (C=C) cm^{-1}. Anal. Calcd for C_3H_5HgI: C, 9.87; H, 1.37. Found: C, 9.57; H, 1.45.

General Procedure for the Preparation of Allylic Mercuric Iodides from Allylic Halides. Procedure A. After 3.0 g of NaI (0.02 mol) and 10 mL of dry THF were stirred for 30 min, 0.01 mol of allylic bromide or chloride was added, and the reaction mixture was allowed to stir under N_2 for another 2–4 h at rt. Then 4.0 g of Hg was added to the flask, which was flushed with N_2, and stirring was continued. The reaction mixture was filtered through Celite which was washed with 2 × 15 mL of THF. Ether was then added to the combined organic solution, which was washed with 2 × 15 mL of H_2O and dried over $MgSO_4$. After removal of the solvent, the crude product was obtained. Recrystallization can be performed using EtOH as the solvent if necessary.

Procedure B. Procedure A was followed precisely, except that all reagents including mercury were stirred together from the start.

Spectral Data for Allylic Mercuric Iodides Prepared by the Above General Procedures. Methallylmercuric iodide

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[21] Cassady, J. M.; Howie, G. A.; Robinson, H. J.; Stamos, I. K. *Org. Synth.* **1983**, *61*, 77.

[22] Oppenheim, A. *Chem. Ber.* 1871, *4*, 1670.

(2): mp 200 °C dec; ^{1}H NMR (DMSO-d_6) δ 1.73 (s, 3 H, CH$_3$), 3.58 (br s, 4 H, C*H*$_2$C(CH$_3$)=C*H*$_2$); ^{1}H NMR (DMSO-d_6, HgI$_2$) δ 1.73 (s, 3 H, CH$_3$), 3.57 (sharp s, 4 H, C*H*$_2$C(CH$_3$)=C*H*$_2$); IR (KBr) 1626 (C=C), 878 (C=CH$_2$) cm^{-1}. Anal. Calcd for C_4H_7HgI: C, 12.56; H, 1.84. Found: C, 12.29; H, 1.98.

(*E*)-Crotylmercuric iodide (3): mp 103–105 °C (lit.[23] mp 102–105 °C); ^{1}H NMR (CDCl$_3$) δ 1.73 (d, *J* = 6.3 Hz, 3 H, CH$_3$), 2.77 (d, *J* = 7.2 Hz, 2 H, CH$_2$), 5.35–5.77 (m, 2 H, CH=CH); IR (KBr) 1614 (C=C), 959 ((*E*)-CH=CH) cm^{-1}.

(*E*)-Cinnamylmercuric iodide (4): mp 76–78 °C; ^{1}H NMR (CDCl$_3$) δ 2.39 (d, *J* = 10.2 Hz, 2 H, CH$_2$), 6.25 (dt, *J* = 15.9, 10.2 Hz, 1 H, CH=C*H*CH$_2$), 6.43 (d, *J* = 15.9 Hz, 1 H, PhCH=C), 7.20–7.34 (m, 5 H, aryl); IR (KBr) 1600 (C=C), 964 ((*E*)-CH=CH) cm^{-1}. Anal. Calcd for C_9H_9HgI: C, 24.20; H, 2.03. Found: C, 23.12; H, 2.01.

3-Methyl-2-butenylmercuric iodide (5): mp 66–67 °C; ^{1}H NMR (CDCl$_3$) δ 1.74 (d, *J* = ~1 Hz, 3 H, CH$_3$), 1.76 (d, *J* = ~1 Hz, 3 H, CH$_3$), 2.75 (d, *J* = 6.9 Hz, 2 H, CH$_2$), 5.74 (br t, *J* = 6.9 Hz, 1 H, C=CH); IR (KBr) 1626 (C=C) cm^{-1}. Anal. Calcd for C_5H_9HgI: C, 15.14; H, 2.29. Found: C, 15.06; H, 2.24.

(*E*)-Ethyl 4-(iodomercurio)crotonate (6): mp 117–18 °C; ^{1}H NMR (CDCl$_3$) δ 1.27 (t, *J* = 7.2 Hz, 3 H, CH$_3$), 2.88 (d, *J* = 9.0 Hz, 2 H, C=CCH$_2$), 4.19 (q, *J* = 7.2 Hz, 2 H, CH$_2$), 5.79 (d, *J* = 16.8 Hz, 1 H, COCH=C), 7.17 (dt, *J* = 16.8, 9.0 Hz, 1 H, CH=C*H*CH$_2$); IR (KBr) 1699 (C=O), 1624 (C=C), 980 ((*E*)-CH=CH) cm^{-1}. Anal. Calcd for $C_6H_9HgIO_2$: C, 16.35; H, 2.06. Found: C, 16.54; H, 1.99.

Methyl 2-[(iodomercurio)methyl]acrylate (7): mp 56–57 °C; ^{1}H NMR (DMSO-d_6) δ 2.60 (s, 2 H, CH$_2$Hg), 3.69 (s, 3 H, CH$_3$), 5.59 (s, 1 H, C=CH), 5.82 (s, 1 H, C=CH); IR (KBr) 1711 (C=O), 1610 (C=C), 890 (C=CH$_2$) cm^{-1}. Anal. Calcd for $C_6H_9HgIO_2$: C, 16.35; H, 2.06. Found: C, 16.11; H, 1.96.

General Procedure for the Acylation of Allylic Mercuric Iodides. After 25 mL of distilled CH$_2$Cl$_2$, 0.3 g of AlCl$_3$ (2.2 mmol), and the acyl chloride (2.0 mmol) were stirred under N$_2$ at the appropriate temperature for 10 min, the allylic mercuric iodide (2.0 mmol) was added directly (no solvent was used) to the flask under N$_2$, and the reaction mixture was stirred for the period of time required. Normally, a red or orange color appears. The mixture was poured into 30 mL of 5% NH$_4$Cl solution, stirred for 5 min, and separated, and the organic layer was washed several times with 5% NaHCO$_3$, 3 M Na$_2$S$_2$O$_3$, and H$_2$O and dried over MgSO$_4$. After removal of the solvent in vacuo, the crude product was obtained. Further distillation may be performed if necessary.

Spectral Data for the Allylic Ketones Prepared. 1-Hepten-4-one (8):[24] ^{1}H NMR (CDCl$_3$) δ 0.92 (t, *J* = 7.5 Hz, 3 H, CH$_3$), 1.67 (sextet, *J* = 7.5 Hz, 2 H, C*H*$_2$CH$_3$), 2.42 (t, *J* = 7.5 Hz, 2 H, COC*H*$_2$CH$_2$), 3.17 (d, *J* = 6.9 Hz, 2 H, COCH$_2$C=), 5.13 (dd, *J* = 16.8, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.18 (dd, *J* = 9.6, ~1 Hz, 1 H, (*Z*)-H$_2$C=C), 5.88–6.10 (m, 1 H, C*H*=CH$_2$); IR (neat) 1700 (C=O), 1635 (C=C) cm^{-1}; mass spectrum *m*/*z* 112.17250 (calcd for $C_7H_{12}O$, 112.17241).

1-Phenyl-3-buten-1-one (9):[25] ^{1}H NMR (CDCl$_3$) δ 3.76 (dt, *J* = 6.6, 1.2 Hz, 2 H, COCH$_2$), 5.21 (ddt, *J* = ~18.3, 1.5, ~1.5 Hz, 1 H, (*E*)-H$_2$C=C), 5.23 (ddt, *J* = 9.3, 1.5, ~1.5 Hz, 1 H, (*Z*)-H$_2$C=C), 6.09 (ddt, *J* = ~17.1, 10.2, 6.6 Hz, 1 H, C*H*=CH$_2$), 7.45 (t, *J* = 7.2 Hz, 2 H, *m*-H in Ph), 7.56 (t, *J* = 7.2 Hz, 1 H, *p*-H in Ph), 7.96 (d, *J* = 7.2 Hz, 2 H, *o*-H in Ph); IR (neat) 1690 (C=O), 1665 (C=C) cm^{-1}; mass spectrum *m*/*z* 146.18913, calcd for $C_{10}H_{10}O$ 146.18892.

(*E*)-1,5-Heptadien-4-one (10):[26] ^{1}H NMR (CDCl$_3$) δ 1.91 (dd, *J* = 6.6, 1.4 Hz, 3 H, CH$_3$), 3.31 (d, *J* = 6.9 Hz, 2 H, COCH$_2$), 5.14 (dd, *J* = 15.6, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.18 (dd, *J* = 10.0, ~1 Hz, 1 H, (*Z*)-C=CH$_2$), 5.90–5.99 (m, 1 H, C*H*=CH$_2$), 6.15 (dq, *J* = 15.6, 1.4 Hz, 1 H, COCH=C), 6.89 (dq, *J* = 6.6, 15.6 Hz, 1 H, COC=CH); IR (neat) 1695 (C=O), 1675 (C=C), 1633 (C=C), 973 ((*E*)-CH=CH) cm^{-1}; mass spectrum *m*/*z* 110.15620, calcd for $C_7H_{10}O$ 110.15639.

2-Methyl-5-hexen-3-one (11):[27] ^{1}H NMR (CDCl$_3$) δ 1.10 (d, *J* = 7.8 Hz, 6 H, CH$_3$), 2.67 (septet, *J* = 7.8 Hz, 1 H, CHC=O), 3.23 (d, *J* = 6.9 Hz, 2 H, CH$_2$C=), 5.13 (dd, *J* = 15.6, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.17 (dd, *J* = 9.0, ~1 Hz, 1 H, (*Z*)-H$_2$C=C), 5.60–5.89 (m, 1 H, C*H*=CH$_2$); IR (neat) 1723 (C=O), 1634 (C=C) cm^{-1}; mass spectrum *m*/*z* 112.17211, calcd for $C_7H_{12}O$ 112.17241.

1-(4-Methoxyphenyl)-3-buten-1-one (12):[28] ^{1}H NMR (CDCl$_3$) δ 3.72 (d, *J* = 6.6 Hz, 2 H, COCH$_2$), 3.89 (s, 3 H, CH$_3$), 5.20 (dd, *J* = 15.3, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.22 (dd, *J* = 9.0, ~1 Hz, 1 H, (*Z*)-H$_2$C=C), 6.09–6.15 (m, 1 H, C*H*=CH$_2$), 6.93 (d, *J* = 8.7 Hz, 2 H, aryl), 7.95 (d, *J* = 8.7 Hz, 2 H, aryl); IR (neat) 1668 (C=O), 1595 (C=C) cm^{-1}; mass spectrum *m*/*z* 176.08360, calcd for $C_{11}H_{12}O_2$ 176.08373.

3-Methyl-1-hepten-4-one (13):[29] ^{1}H NMR (CDCl$_3$) δ 0.90 (t, *J* = 7.5 Hz, 3 H, CH$_2$C*H*$_3$), 1.17 (d, *J* = 6.9 Hz, 3 H, CHC*H*$_3$), 1.58 (sextet, *J* = 7.5 Hz, 2 H, C*H*$_2$CH$_3$), 2.43 (t, *J* = 7.5 Hz, 2 H, COCH$_2$), 3.20 (p, *J* = 6.9 Hz, 1 H, C*H*CH$_3$), 5.13 (dd, *J* = 8.1, ~1 Hz, 1 H, (*Z*)-H$_2$C=C), 5.16 (dd, *J* = 17.4, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.71–5.86 (m, 1 H, C*H*=CH$_2$); IR (neat) 1720 (C=O), 1640 (C=C) cm^{-1}; mass spectrum *m*/*z* 126.19945, calcd for $C_8H_{14}O$ 126.19928.

3,3-Dimethyl-1-hepten-4-one (14):[30] ^{1}H NMR (CDCl$_3$) δ 0.88 (t, *J* = 7.5 Hz, 3 H, CH$_2$C*H*$_3$), 1.22 (s, 6 H, C(CH$_3$)$_2$), 1.57 (tq, *J* = 7.2, 7.5 Hz, 2 H, C*H*$_2$CH$_3$), 2.43 (t, *J* = 7.2 Hz, 2 H, COCH$_2$), 5.13 (dd, *J* = 10.3, ~1 Hz, 1 H, (*Z*)-H$_2$C=C), 5.13 (dd, *J* = 17.4, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.91 (dd, *J* = 10.2, 17.4 Hz, 1 H, C*H*=CH$_2$); IR (neat) 1709 (C=O), 1635 (C=C) cm^{-1}; mass spectrum *m*/*z* 252.39824, calcd for $C_9H_{16}O$ 252.39800.

2,4,4-Trimethyl-5-hexen-3-one (15): ^{1}H NMR (CDCl$_3$) δ 1.03 (d, *J* = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.23 (s, 6 H, C(CH$_3$)$_2$), 3.07 (septet, *J* = 6.6 Hz, 1 H, CHCO), 5.16 (dd, *J* = 17.2, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.18 (dd, *J* = 10.2, ~1 Hz, 1 H, (*Z*)-H$_2$C=C), 5.88 (dd, *J* = 10.2, 17.2 Hz, 1 H, C*H*=CH$_2$); IR (neat) (C=O), 1636 (C=C) cm^{-1}; mass spectrum *m*/*z* 140.12004, calcd for $C_9H_{16}O$ 140.12012.

2,5,5-Trimethyl-2,6-heptadien-4-one (16):[31] ^{1}H NMR (CDCl$_3$) δ 1.22 (s, 6 H, C(CH$_3$)$_2$), 1.88 (s, 3 H, =C(CH$_3$)$_2$), 2.12 (s, 3 H, =C(CH$_3$)$_2$), 5.13 (dd, *J* = 17.4, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.15 (dd, *J* = 10.8, ~1 Hz, 1 H, (*Z*)-H$_2$C=C), 5.93 (dd, *J* = 10.8, 17.4 Hz, 1 H, C*H*=CH$_2$), 6.24 (br s, 1 H, CH=C); IR (neat) 1684 (C=O), 1622 (C=C) cm^{-1}. Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.69; H, 10.52.

3-Phenyl-4-penten-2-one (17):[32] ^{1}H NMR (CDCl$_3$) δ 2.12 (s, 3 H, CH$_3$), 4.36 (d, *J* = 8.1 Hz, 1 H, PhCH), 5.07 (dd, *J* = 17.1, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.22 (dd, *J* = 10.2, ~1 Hz, 1 H, (*Z*)-C=CH$_2$), 6.24 (ddd, *J* = 8.1, 10.2, 17.1 Hz, 1 H, C*H*=CH$_2$), 7.21–7.37 (m, 5 H, aryl); IR (neat) 1713 (C=O), 1637 (C=C) cm^{-1}; mass spectrum *m*/*z* 160.00888, calcd for $C_{11}H_{12}O$ 160.00882.

3-Phenyl-1-hepten-4-one (18): ^{1}H NMR (CDCl$_3$) δ 0.82 (t, *J* = 7.5 Hz, 3 H, CH$_3$), 1.56 (sextet, *J* = 7.5 Hz, 2 H, CH$_2$), 2.41 (t, *J* = 7.5 Hz, 2 H, COCH$_2$), 4.36 (d, *J* = 8.1 Hz, 1 H, COCH), 5.07 (dd, *J* = 17.1, ~1 Hz, 1 H, (*E*)-H$_2$C=C), 5.20 (dd, *J* = 11.0, ~1 Hz, 1 H, (*Z*)-H$_2$C=C), 6.24 (ddd, *J* = 8.1, 11.0, 17.1 Hz, 1 H, C*H*=CH$_2$), 7.21–7.36 (m, 5 H, aryl); IR (neat) 1713 (C=O), 1605 (C=C) cm^{-1}; mass spectrum *m*/*z* 188.27034, calcd for $C_{13}H_{16}O$ 188.27001.

Ethyl 2-allyl-3-oxohexanoate (19): ^{1}H NMR (CDCl$_3$) δ 0.98 (t, *J* = 7.5 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 1.27 (t, *J* = 7.2 Hz, 3 H, OCH$_2$C*H*$_3$), 1.67 (sextet, *J* = 7.5 Hz, 2 H, CH$_2$C*H*$_2$CH$_3$), 2.34 (t, *J* = 7.5 Hz, 2 H, COCH$_2$), 3.09 (d, *J* = 6.9 Hz, 1 H, COCH), 4.15 (q, *J* = 7.2 Hz, 2 H, OCH$_2$), 5.14–5.18 (m, 2 H, C=CH$_2$), 5.86–6.00 (m, 1 H, C*H*=CH$_2$); IR (neat) 1711 (C=O), 1645 (C=O) cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.15; H, 8.75. Found: C, 65.03; H, 8.69.

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Supplementary Material Available: ^{1}H NMR spectra for all new ketones (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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