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MERCURY IN ORGANIC CHEMISTRY VIII.
A CONVENIENT SYNTHESIS OF α,β-UNSATURATED KETONES

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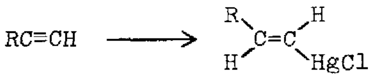
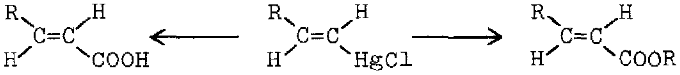
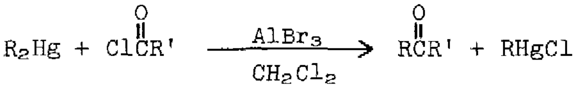
Recently, vinylmercurials have become available by a variety of acetylene addition reactions.[3-6] These reactions appear to accommodate considerable organic functionality. The vinylmercurials themselves possess a number of characteristics making them attractive as synthetic intermediates. Recently we reported that they can be readily converted into α,β-unsaturated carboxylic acids and esters in excellent yield.[7] We now wish to report that vinylmercurials can be readily acylated to give the corresponding α,β-unsaturated ketones in near quantitative yield.

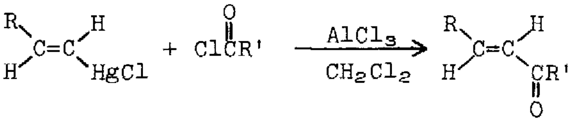




Most organomercurials are completely unreactive towards acid halides. Only a few exceptions have been noted.[8-15] However, aluminum halides promote the rapid acylation of both di-n-alkyl- and diarylmercurials.[16,17] Unfortunately, only one of the two organic groups of the organomercurial reacts. We have recently found that vinylmercuric chlorides, unlike the alkyl- and arylmercuric chlorides, react with acid chlorides in minutes at room temperature in the presence of aluminum trichloride to give excel-



$$R_2Hg + Cl\overset{O}{\overset{\|}{C}}R' \xrightarrow[CH_2Cl_2]{AlBr_3} R\overset{O}{\overset{\|}{C}}R' + RHgCl$$



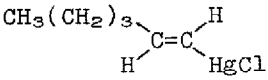
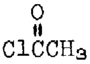
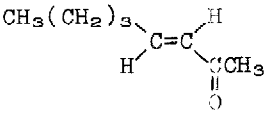
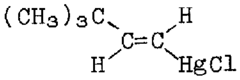
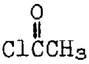
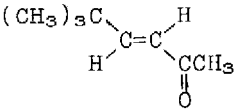
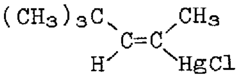
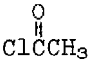
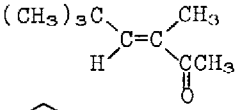
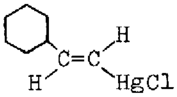
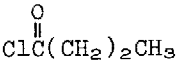
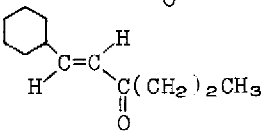
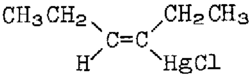
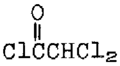
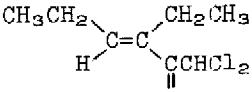
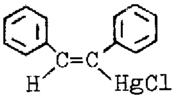
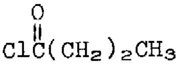
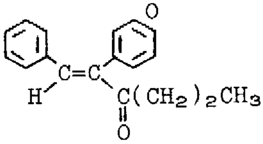
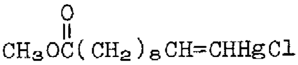
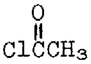
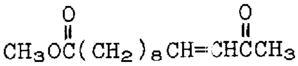
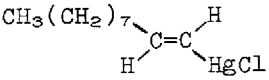
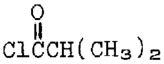
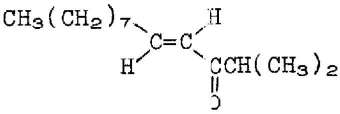
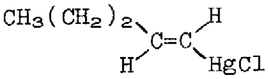
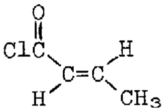
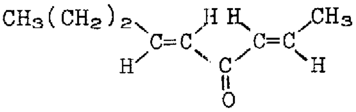
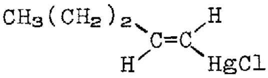
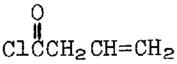
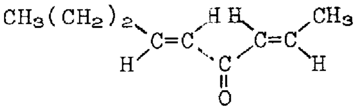
lent yields of α,β-unsaturated ketones with retention of configuration.

The following synthesis of trans-3-octen-2-one is representative. To a thoroughly dried round bottom flask equipped with a septum inlet and flushed with nitrogen is added 100 ml of methylene chloride, 1.33 g of aluminum trichloride (10 mmol) and 0.80 ml of acetyl chloride (10 mmol). After stirring briefly, 3.19 g of trans-1-hexenylmercuric chloride (10 mmol) is added while backflushing with nitrogen, and the reaction is stirred for five minutes. A white solid (presumably mercuric chloride) precipitates almost immediately. The reaction mixture is then poured into water and the layers separated. The aqueous layer is extracted with methylene chloride. The organic layer is then washed with 5% sodium bicarbonate, 3M sodium thiosulfate and water. The combined aqueous washes are re-extracted with methylene chloride, and the organic layers combined and dried over anhydrous sodium sulfate. Removal of the solvent yields 1.22 g (97%) of essentially pure trans-3-octen-2-one as a colorless oil. Gas chromatography showed 5% or less of the undesired cis isomer. PMR (CCl_4): δ0.92 (3H, triplet not fully resolved), 1.40 (4H, m), 2.18 (3H, s), 2.2 (2H, m), 5.95 (1H, d, J=17Hz), and 6.80 (1H, d of t, J=17 and 7Hz). IR (thin film): 1675 (s) and 980 (s) cm^{-1}. M.S. parent ion 126.1042 ± .0006, calc. for $C_8H_{14}O$ 126.1045.

As indicated in the table, the reaction appears to be quite general. Alkyl, aryl and functionally substituted vinylmercurials all work well. Both aliphatic and α,β-unsaturated acid chlorides give excellent yields. β,γ-Unsaturated acid chlorides also react but the major product is the corresponding α,β-unsaturated dienone. Aromatic acid chlorides give very poor yields.

At least three possible mechanisms can be invoked to account for this reaction; (1) generation and acylation of a vinylalane, (2) direct electrophilic substitution at the carbon-mercury bond, and (3) addition of the acid chloride complex to the double bond of the vinylmercurial followed by mercuric chloride elimination. Since vinylmercuric chlorides do not appear to react with aluminum trichloride, the first possibility is unlikely. While direct substitution appears likely, we have in one instance observed a carbon skeleton rearrangement suggesting attack upon the double bond. Furthermore, substitution of titanium tetrachloride for aluminum chloride produces substantial amounts of the thermodynamically less stable, stereochemically inverted enones, suggesting the presence of an addition-elimination mechanism. Full synthetic and mechanistic details will be published in the full paper.

TABLE. Synthesis of ∝,β-Unsaturated Ketones

VINYLMERCURIAL	ACID CHLORIDE	KETONE	% YIELD[18]
	 $Cl\overset{\overset{O}{\Vert}}{C}CH_3$		97
	 $Cl\overset{\overset{O}{\Vert}}{C}CH_3$		95
	 $Cl\overset{\overset{O}{\Vert}}{C}CH_3$		99
	 $Cl\overset{\overset{O}{\Vert}}{C}(CH_2)_2CH_3$		96
	 $Cl\overset{\overset{O}{\Vert}}{C}CHCl_2$		89[a]
	 $Cl\overset{\overset{O}{\Vert}}{C}(CH_2)_2CH_3$		72[b]
 $CH_3O\overset{\overset{O}{\Vert}}{C}(CH_2)_8CH{=}CHHgCl$	 $Cl\overset{\overset{O}{\Vert}}{C}CH_3$	 $CH_3O\overset{\overset{O}{\Vert}}{C}(CH_2)_8CH{=}CH\overset{\overset{O}{\Vert}}{C}CH_3$	100[c]
	 $Cl\overset{\overset{O}{\Vert}}{C}CH(CH_3)_2$		97
			97
	 $Cl\overset{\overset{O}{\Vert}}{C}CH_2CH{=}CH_2$		91

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[a] Ketone decomposes readily.

[b] Ketone separated from a mixture of cis- and trans-stilbene by column chromatography.

[c] Both the vinylmercurial and ketone are cis,trans mixtures.

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