(12) D. Taub, R. D. Hoffsommer, and N. L. Wendler, *J. Org. Chem.*, **29**, 3486 (1964).

(13) R. A. Bartsch and D. M. Cook, *J. Org. Chem.*, **35**, 1714 (1970).

(14) C. J. M. Stirling, *J. Chem. Soc.*, 255 (1960).

(15) P. F. Hudrlik and M. M. Mohtady, *J. Org. Chem.*, **40**, 2692 (1975).

(16) (a) K. B. Wiberg and G. W. Klein, *Tetrahedron Lett.*, 1043 (1963); (b) S. Julia and C. Gueremy, *Bull., Soc., Chim. Fr.*, 2994 (1965); (c) F. Nerdel, D. Frank, and H. Marshall, *Chem. Ber.*, **100**, 720 (1967); for more recent studies of related systems, see H. Marschall and W. B. Mühlenkamp, *Chem. Ber.*, **109**, 2785 (1976); (d) E. Wenkert, P. Bakuzis, R. J. Baumgarten, C. L. Leicht, and H. P. Schenk, *J. Am. Chem. Soc.*, **93**, 3208 (1971); (e) S. Wolff and W. C. Agosta, *J. Chem. Soc., Chem., Commun.*, 771 (1973); (f) for study of a comparable cyclopentanone derivative, see K. Ebisu, L. B. Batty, J. M. Higaki, and H. O. Larson, *J. Am. Chem. Soc.*, **88**, 1995 (1966).

(17) D. H. Aue, M. J. Meshishnek, and D. F. Shellhamer, *Tetrahedron Lett.*, 4799 (1973).

(18) H. O. House and J. M. Wilkins, submitted for publication.

(19) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated $MgSO_4$ was employed as a drying agent. The IR spectra were determined with a Perkin-Elmer Model 257 infrared recording spectrophotometer fitted with a grating. The UV spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The proton NMR spectra were determined at 60 MHz with a Varian Model A-60 or Model T-60-A NMR spectrometer and the ^{13}C NMR spectra were determined at 25 MHz with a JEOL Fourier transform spectrometer, Model PTF-100. The chemical shift values are expressed in δ values (ppm) relative to a Me_4Si internal standard. The mass spectra were obtained with a Hitachi (Perkin-Elmer) Model RMU-7 mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

(20) The solution was titrated with a standard solution of *sec*-BuOH in xylene employing 2,2′-bipyridyl as an indicator. For the detailed procedure, see M. Gall and H. O. House, *Org. Synth.*, **52**, 39 (1972).

(21) (a) W. L. Howard and N. B. Lorette, *"Organic Synthesis,"* Collect. Vol. 5, Wiley, New York, N.Y., 1973, p 292; (b) *ibid.*, p 25.

(22) K. B. Becker, *Helv. Chim. Acta*, **60**, 68 (1977).

(23) S. O. Lawesson, E. H. Larson, G. Sundström, and H. J. Jakobsen, *Acta Chem. Scand.*, **17**, 2216 (1963).

(24) (a) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960); (b) C. J. Timmons, *Chem. Commun.*, 576 (1965).

(25) (a) W. D. Closson, S. F. Brady, and P. J. Orenski, *J. Org. Chem.*, **30**, 4026 (1965); (b) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(26) These measurements were performed in our laboratory by Mr. Ronald Sieloff.

(27) (a) R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969, pp 143–158; (b) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Am. Chem. Soc.*, **92**, 2783 (1970); (c) H. O. House and E. F. Kinloch, *J. Org. Chem.*, **39**, 1173 (1974); (d) H. O. House, D. Koepsell, and W. Jaeger, *ibid.*, **38**, 1167 (1973).

(28) H. O. House, C. Y, Chu, J. M. Wilkins, and M. J. Umen, *J. Org. Chem.*, **40**, 1460 (1975).

(29) Higher reaction temperatures or longer reaction times resulted in the formation of more high molecular weight by-products and a lower yield of ketone **63**.

(30) (a) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963); (b) J. D. Chanley, *J. Am. Chem. Soc.*, **70**, 244 (1948).

(31) This experiment was first performed in our laboratories by Dr. A. V. Prabhu.

(32) (a) H. O. House and J. M. Wilkins, *J. Org. Chem.*, **41**, 4031 (1976); (b) H. O. House and E. F. Kinloch, *ibid.*, **39**, 1173 (1974).

(33) (a) A. Jonczyk, B. Serafin, and M. Makosza, *Rocz. Chem.*, **45**, 1027 (1971); (b) *ibid.*, **45**, 2097 (1971).

(34) D. M. Bailey, J. E. Bowers, and C. D. Gutsche, *J. Org. Chem.*, **28**, 610 (1963).

(35) W. C. Agosta and D. K. Herron, *J. Org. Chem.*, **34**, 2782 (1969).

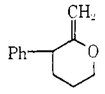
(36) (a) J. M. Conia and J. Salaun, *Bull. Soc. Chim. Fr.*, 1957 (1964); (b) N. J. Turro and W. B. Hammond, *Tetrahedron*, **24**, 6017 (1968). We are grateful to Professor N. J. Turro for providing us with copies of the IR and NMR spectra of ketones **52** and **53**.

(37) H. O. House and E. J. Grubbs, *J. Am. Chem. Soc.*, **81**, 4733 (1959).

(38) A. H. Homeyer, F. C. Whitmore, and V. H. Wallingford, *J. Am. Chem. Soc.*, **55**, 4209 (1933).

(39) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1965).

(40) G. Descotes, J. C. Martin, and G. Labrit, *Bull. Soc. Chim. Fr.*, 4151 (1969). These authors report that the isomeric liquid enol ether i has n^{25}_{D} 1.5475.



i

(41) J. V. Braun, J. Gruber, and G. Kirschbaum, *Ber.*, **55**, 3664 (1922).

(42) E. L. Alpen, W. D. Kumler, and L. A. Strait, *J. Am. Chem. Soc.*, **72**, 4558 (1950).

(43) D. E. Butler and J. C. Pollatz, *J. Org. Chem.*, **36**, 1308 (1971).

(44) M. Makosza and B. Serafin, *Rocz. Chem.*, **40**, 1647 (1966); *Chem. Abstr.*, **66**, 94792 (1967).

(45) F. H. Case, *J. Am. Chem. Soc.*, **55**, 2927 (1933); **56**, 715 (1934).

(46) S. MacKenzie, S. F. Marsocci, and H. C. Lampe, *J. Org. Chem.*, **30**, 3328 (1965).

(47) K. Okazaki, *J. Pharm. Soc. Jpn.*, **63**, 629 (1943); *Chem. Abstr.*, **45**, 2884 (1951).

(48) L. Skattebøl, E. R. H. Jones, and M. C. Whiting, "Organic Syntheses", Collect. Vol. 4, Wiley, New York, N.Y., 1963, p 792.

(49) P. S. Pinkney and C. S. Marvel, *J. Am. Chem. Soc.*, **59**, 2669 (1937).

(50) I. Heilbron, E. R. H. Jones, J. B. Toogood, and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).

(51) R. B. Turner, *J. Am. Chem. Soc.*, **72**, 878 (1950).

(52) M. J. Jorgenson, A. J. Brattesani, and A. F. Thacher, *J. Org. Chem.*, **34**, 1103 (1969).

Mercury in Organic Chemistry. 13.[1] Stereospecific Synthesis of α,β-Unsaturated Ketones via Acylation of Vinylmercurials[2]

Richard C. Larock*[3,4] and John C. Bernhardt[5]

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received May 13, 1977

Treatment of vinylmercuric chlorides with acid chlorides and aluminum trichloride for 5 min at room temperature in methylene chloride solvent provides a very mild, convenient method for the synthesis of α,β-unsaturated ketones in excellent yields and high stereochemical purity. The reaction is applicable to the synthesis of functionally substituted enones as well as dienones. Rhodium(I) and palladium(0) reagents also promote the reaction, but in lower yield. The use of titanium tetrachloride instead of aluminum trichloride leads to enones of inverted stereochemistry in some cases, but the reaction is not synthetically useful due to its irreproducibility. Both the aluminum trichloride and titanium tetrachloride reactions appear to proceed through addition of the complexed acid chloride to the carbon–carbon double bond of the vinylmercurial, followed by mercuric chloride elimination. However, direct substitution at the carbon–mercury bond cannot be ruled out in the aluminum trichloride reactions.

A variety of methods presently exist for the synthesis of α,β-unsaturated ketones. The aldol condensation is one important approach to the synthesis of α,β-unsaturated ketones.[6] Another important method employs the Friedel–Crafts reaction of acid chlorides, acids, or anhydrides with olefins.[7] Recently a new procedure involving the hydrozirconation of acetylenes and subsequent aluminum chloride promoted acylation of the resulting vinylzirconium compounds has been added to the list of important methods of preparing α,β-unsaturated ketones.[8] The acylation of vinylmercurials appeared to be an equally promising route to enones since vinylmercurials are readily available directly from acetylenes.[9,10] We wish now to report in detail our studies on the successful development of just such a procedure.

Although a number of reactions of organomercurials which lead to ketones have been reported previously, there are only isolated examples of the direct reaction of acid chlorides with organomercuric chlorides to give ketones.[11] Most of the ex-

0022-3263/78/1943-0710$01.00/0

amples involve the reaction of acid halides and activated arylmercuric chlorides, and some of these reactions even require forcing conditions. None of these reactions appear to be very general. However, the use of Lewis acids has been found to promote some of these reactions. Skoldinov and Koschkov used aluminum chloride to promote the reaction of benzoyl chloride and phenylmercuric chloride or diphenylmercury (eq 1 and 2).[12] Reutov and co-workers have used aluminum bromide in dichloromethane to prepare ketones (eq 3).[13] Either dialkyl- or diarylmercury compounds could be used with either aliphatic or aromatic acid halides. The reaction occurs very quickly, often in minutes, and transfers only one aryl or alkyl group from mercury to the acid chloride.

$$(C_6H_5)_2Hg + C_6H_5COCl \xrightarrow[CS_2]{AlCl_3} (C_6H_5)_2C{=}O \qquad (1)$$

$$C_6H_5HgCl + C_6H_5COCl \xrightarrow[neat]{AlCl_3} (C_6H_5)_2C{=}O \qquad (2)$$

$$R_2Hg + R'COCl \xrightarrow[CH_2Cl_2]{AlBr_3} RR'C{=}O + RHgCl \qquad (3)$$

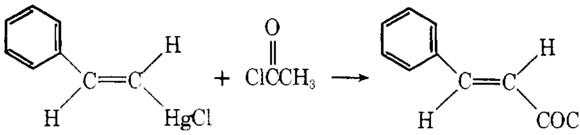
One example of a transition metal catalyzed reaction of dialkyl- or diarylmercurials with acid bromides has also appeared recently. Tetrakis(triphenylphosphine)palladium(0) catalyzes the reaction of acid halides with organomercurials (eq 4).[14] Unfortunately, the reaction requires the use of hexamethylphosphoramide (HMPA) and fails for alkyl- and arylmercuric chlorides.

$$R_2Hg + R'COBr \xrightarrow[HMPA]{Pd(PPh_3)_4} R'RC{=}O + RHgBr \qquad (4)$$

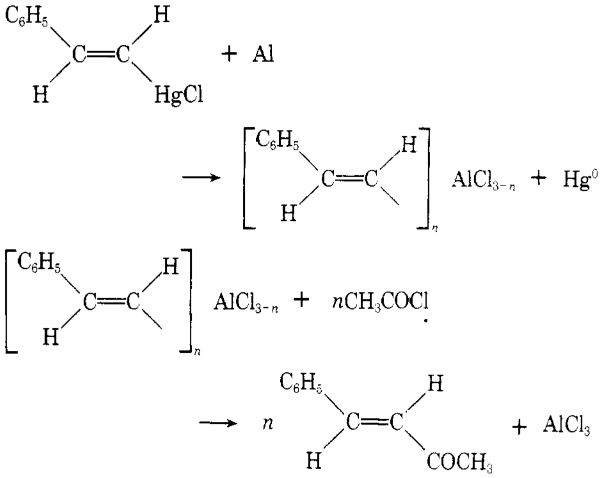
We have developed the first synthesis of α,β-unsaturated ketones from vinylmercuric chlorides and acid chlorides. The reaction proceeds to give high yields of α,β-unsaturated ketones greater than 95% stereochemically pure. The reaction works very well with aliphatic acid chlorides and moderately well with aromatic acid chlorides. Unfortunately, not all functional groups are tolerated, and the reaction conditions, although relatively mild, tend to cause rearrangements in some systems. With these limitations in mind, however, the reaction appears to be fairly general.

Results and Discussion

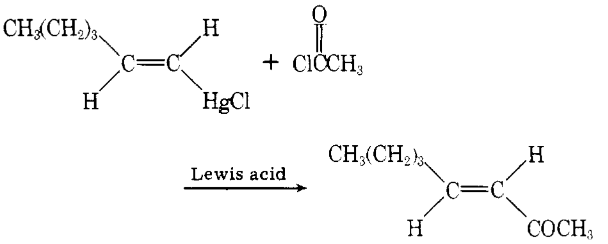
Reaction of Styrylmercuric Chloride with Acetyl Chloride. Reutov's report[13] on the synthesis of ketones from diaryl- or dialkylmercurials prompted us to study the reaction of vinylmercuric chlorides with acid chlorides. Styrylmercuric chloride and acetyl chloride were initially chosen as a model system for study (eq 5). Reutov's reaction conditions, aluminum bromide in dichloromethane at room temperature, gave no enone whatsoever. Therefore, a large number of other reaction conditions were examined. The best results were obtained using 4 equiv of aluminum powder in dichloromethane (48% yield). This reaction presumably proceeds via transmetallation to a more reactive vinylalane (eq 6 and 7).


(5)

Treatment of distyrylmercury with acetyl chloride and aluminum chloride in methylene chloride gave a much better reaction and a 53% yield of enone. Distyrylmercury is significantly more soluble in dichloromethane than is styrylmercuric chloride. As a result, the success of this reaction may be due to a combination of increased reactivity and increased solubility of the distyrylmercury. Both the aluminum powder and distyrylmercury reactions result in utilization of roughly half of the styryl groups available and therefore appear to be equally useful synthetically.


(6)
(7)

Reaction of trans-1-Hexenylmercuric Chloride with Acetyl Chloride. A new model system was then investigated to determine if the difficulties encountered in the styryl system were unique to that system or a general characteristic of all vinylmercuric chlorides (eq 8). *trans*-1-Hexenylmercuric chloride was treated with acetyl chloride and aluminum bromide in dichloromethane for 1 h at 0 °C. Analysis of the reaction mixture by GLC showed an excellent yield of enone, although a mixture of approximately equal quantities of *cis*- and *trans*-3-octen-2-one was obtained.



(8)

In an effort to improve the stereospecificity of the reaction, studies on the effect of the Lewis acid (Table I) and solvent (Table II) were carried out. Titanium tetrachloride, aluminum bromide, and aluminum chloride were found to be the only synthetically useful Lewis acids. Antimony pentachloride, stannic chloride, and boron trichloride showed evidence of undergoing transmetallation reactions with the vinylmercuric chloride, although no ketone products were seen by GLC. A precipitate, presumably mercuric chloride, is observed in the successful reactions, and a similar precipitate was observed in these three nonketone-forming reactions as well. Although it is not known exactly what is happening in these reactions, it is assumed that a transmetallation reaction occurs leading to new vinylmetallics, which do not provide any enone product.

As can be seen in Table II, dichloromethane was a significantly better solvent for the reaction than any other solvent tested. Polar solvents are necessary to dissolve the vinylmercuric chloride, but solvents which are capable of coordinating with the Lewis acid are undesirable since they weaken the ability of the Lewis acid to promote acylation. One difficulty with styrylmercuric chloride was its insolubility in dichloromethane, which probably explains its lack of reaction under conditions where other vinylmercuric chlorides react readily.

The effect of reaction temperature on the stereospecificity of the three Lewis acid systems which were found to be effective in this reaction was studied (Table III). The stereospecificity obtained with aluminum bromide was found to improve on lowering the temperature to −78 °C. However, the

Table I. Effect of Lewis Acids on the Reaction of *trans*-1-Hexenylmercuric Chloride and Acetyl Chloride[a]

Lewis acid	Time, h	% yield of 3-octen-2-one[b] Cis	Trans	Total
$SbCl_5$	0.1	0	0	0[c]
$SbCl_3$	24	0	0	0
$SnCl_4$	1	0	0	0[c]
SbF_3	24	0	0	0
$BF_3 \cdot Et_2O$		6	7	13
$ZnCl_2$	6	7	5	12
BCl_3		0	3	3[c]
$FeCl_3$	0.1	2	23	25
Al powder	24	7	41	48
$TiCl_4$	0.25	23	76	99
$AlBr_3$	0.50	44	49	93
$AlCl_3$	0.25	5	95	100

[a] A 1-mmol amount each of Lewis acid, acetyl chloride, and *trans*-1-hexenylmercuric chloride in 10 mL of CH_2Cl_2 at ~25 °C. [b] GLC yield corrected by the use of an internal standard. [c] Transmetalation reaction possible.

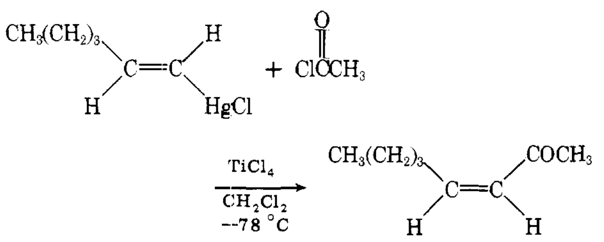
Table II. Effect of Solvents on the Reaction of *trans*-1-Hexenylmercuric Chloride and Acetyl Chloride[a]

Lewis acid	Time, h	Solvent	% yield of 3-octen-2-one[b] Cis	Trans	Total
$AlBr_3$	24	DMF[c]	1	2	3
		HMPA[d]	0	4	4
	0.25	$CHCl_3$	9	6	15
		$C_6H_5NO_2$	13	13	26
		CH_3NO_2	Trace	21	21
		CH_2Cl_2	44	49	93
$AlCl_3$	24	DMF[c]	0	0	0
		Et_2O	0	0	0
		HMPA[d]	0	2	2
	0.25	$CHCl_3$	0	4	4
	18	THF[e]	3	19	22
	0.25	$C_6H_5NO_2$	19	19	38
		CH_3NO_2	14	26	40
		CH_2Cl_2	5	95	100

[a] A 1-mmol amount each of Lewis acid, acetyl chloride, and *trans*-1-hexenylmercuric chloride in 10 mL of solvent at ~25 °C. [b] GLC yield corrected by the use of an internal standard. [c] DMF, *N*,*N*-dimethylformamide. [d] HMPA, hexamethylphosphoramide. [e] THF, tetrahydrofuran.

improvement never equalled the stereospecificity of the room-temperature reaction of aluminum chloride. The stereospecificity observed with aluminum chloride was relatively insensitive to changes in reaction temperature.

The stereospecificity of the titanium tetrachloride reaction was especially interesting. At −78 °C the major product observed was the cis-enone resulting from inversion of stereochemistry about the carbon-carbon double bond (eq 9). This reaction will be discussed in greater detail later.


(9)

Studies to determine the optimum reaction time showed that the aluminum chloride reaction was complete in less than 5 min, while aluminum bromide required 30 min to reach completion (Table IV).

Table III. Effect of Temperature on Stereospecificity in the Reaction of *trans*-1-Hexenylmercuric Chloride and Acetyl Chloride[a]

Lewis acid	Temp, °C	Time, h	% yield of 3-octen-2-one[b] Cis	Trans	Total
$AlBr_3$	25	0.5	44	49	93
	0		35	64	99
	−22		37	61	98
	−78		16	84	100
$AlCl_3$	25	0.25	5	95	100
	0		8	86	94
	−22		8	92	100
	−78		5	88	93
$TiCl_4$	25	0.25	23	76	99
	−78		29	6	35
		3	91	3	94

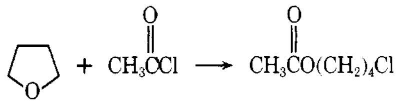
[a] A 1-mmol amount each of *trans*-1-hexenylmercuric chloride, acetyl chloride, and Lewis acid in 10 mL of CH_2Cl_2. [b] GLC yield corrected by the use of an internal standard.

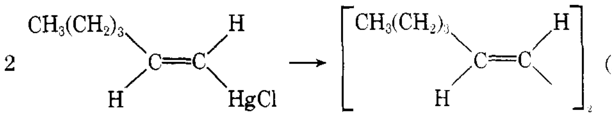
Table IV. Effect of Time on the Reaction of *trans*-1-Hexenylmercuric Chloride and Acetyl Chloride at 25 °C[a]

Lewis acid	Time, min	% yield of 3-octen-2-one[b] Cis	Trans	Total
$AlBr_3$	1	18	41	59
	5	19	41	60
	20	23	42	65
	30	44	49	93
	1440	0	51	51
$AlCl_3$	1	5	86	91
	5	5	95	100
	15	5	95	100
	30	7	93	100
	60	6	94	100
	1440	10	90	100

[a] A 1-mmol amount each of *trans*-1-hexenylmercuric chloride, acetyl chloride, and Lewis acid in 10 mL of CH_2Cl_2. [b] GLC yield corrected by the use of an internal standard.

The recent report that $Pd(PPh_3)_4$ catalyzes the reaction of dialkyl- or diarylmercurials with acid bromides[14] led us also to try various transition-metal catalysts on this system. The results of this study are summarized in Table V. Only two systems proved to be of any utility, $Pd(PPh_3)_4$ in HMPA and $[ClRh(CO)_2]_2$ in dichloromethane. Neither of these systems worked as well as the aluminum chloride promoted reaction. Some interesting observations were made, however. Two reactions were observed when the rhodium catalysts were tried in THF, neither of which was expected. The acetyl chloride reacted with the solvent to give 1-acetoxy-4-chlorobutane (eq 10), while the vinylmercuric chloride reacted with itself to form a symmetrical 1,3-diene (eq 11). In HMPA only the symmetrical 1,3-diene was observed. This latter reaction provided the basis for our recently reported catalytic procedure for the synthesis of symmetrical 1,3-dienes.[15]


(10)


(11)

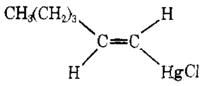
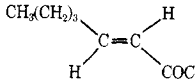
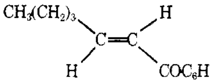
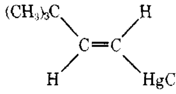
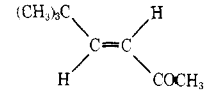
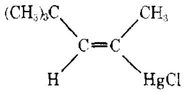
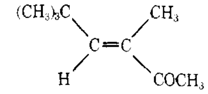
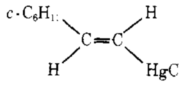
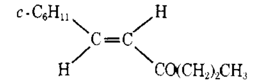
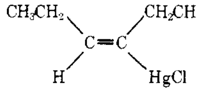
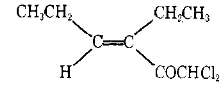
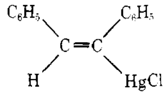
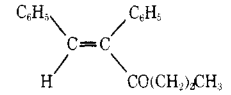
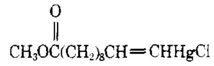
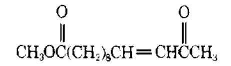
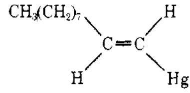
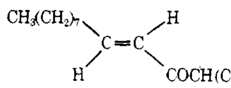
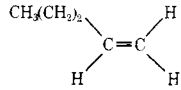
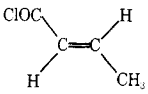
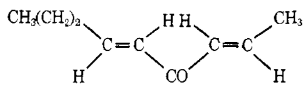
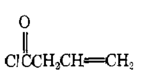
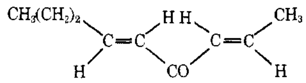
Synthesis of α,β-Unsaturated Ketones. Using our best reaction conditions, aluminum chloride in dichloromethane, we have examined the scope of this new α,β-unsaturated ketone synthesis. All reactions were carried out at room tem-

Table V. Transition Metal Catalyzed Reaction of *trans*-1-Hexenylmercuric Chloride and Acetyl Chloride[a]

Catalyst[b]	Solvent[c]	Time, h	Temp, °C	% yield of 3-octen-2-one[d] Cis	Trans	Total
$[(C_6H_5)_3P]_2Rh(CO)Cl$	CH_2Cl_2	0.5	0	7	7	14
		6	25	4	12	16
	THF	24		0	7	7[e]
$[(C_6H_5)_3P]_3RhCl$	THF	24	25	0	0	0
$Pd[P(C_6H_5)_3]_4$	THF	24	25	0	0	0
	HMPA	6		0	45	45[f]
			60	0	46	46[f]
				0	58	58
			100	0	45	45[f]
$[ClRh(CO)_2]_2$[g]	CH_2Cl_2	1	25	0	24	24[h]
	THF	6		0	0	0[e]
	HMPA	1.5		0	0	0[i]

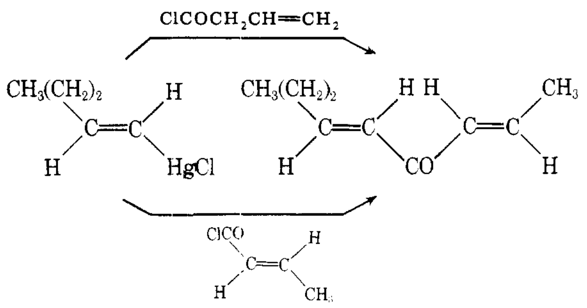
[a] A 1-mmol amount each of *trans*-1-hexenylmercuric chloride and acetyl chloride. [b] A 10% catalyst based on vinylmercuric chloride. [c] A 10-mL volume. [d] GLC yield corrected by the use of an internal standard. [e] The two major products were 1-acetoxy-4-chlorobutane and *trans,trans*-5,7-dodecadiene. [f] A 1% palladium reagent. [g] A 5% dimeric rhodium catalyst. [h] *trans,trans*-5,7-Dodecadiene is also seen. [i] Only *trans,trans*-5,7-dodecadiene is seen.

Table VI. Synthesis of α,β-Unsaturated Ketones[a]

Vinylmercurial	Registry no.	Acid chloride	Registry no.	Ketone	Registry no.	Isolated yield %
	50874-36-7	$ClCOCH_3$	75-36-5		18402-82-9	97
		$ClCOC_6H_5$	98-88-4		64235-53-6	64[b]
	36525-02-7	$ClCOCH_3$			20859-11-4	95
	38010-69-4				23732-17-4	99
	36525-01-6	$ClCO(CH_2)_2CH_3$	141-75-3		61759-47-5	96
	36525-04-9	$ClCOCHCl_2$	79-36-7		61759-48-6	89[c]
	16188-35-5	$ClCO(CH_2)_2CH_3$			61798-66-1	72[d]
 $CH_3O\overset{\overset{O}{\|}}{C}(CH_2)_8CH{=}CHHgCl$		$ClCOCH_3$		 $CH_3O\overset{\overset{O}{\|}}{C}(CH_2)_8CH{=}CH\overset{\overset{O}{\|}}{C}CH_3$		100[e]
	56453-77-1	$ClCOCH(CH_3)_2$	79-30-1		61759-50-0	97
	36525-00-5		625-35-4		61759-51-1	97
		 $Cl\overset{\overset{O}{\|}}{C}CH_2CH{=}CH_2$	1470-91-3			91

[a] A 10-mmol amount each of vinylmercurial, acid chloride, and aluminum chloride in 100 mL of CH_2Cl_2 stirred for 5 min at room temperature. [b] GLC yield containing 14% cis ketone. [c] Ketone decomposes readily. [d] Ketone separated from a mixture of *cis-* and *trans*-stilbene by column chromatography. [e] Both the vinylmercuric chloride and ketone are cis, trans mixtures.

perature for 5 min. A series of vinylmercurials and acid chlorides were examined. The results are summarized in Table VI. The isolated yields are generally greater than 95%, with stereochemical purity also greater than 95% in most cases. Alkyl-, aryl-, and functionally substituted vinylmercurials were all found to work well. Aliphatic, unsaturated, and aryl acid chlorides were also found to work satisfactorily. α,β-Unsaturated acid chlorides reacted cleanly to produce fully conjugated dienones in high yield. β,γ-Unsaturated acid chlorides, on the other hand, react to produce the same dienones as the α,β isomers (eq 12). Esters are tolerated in the mercurial



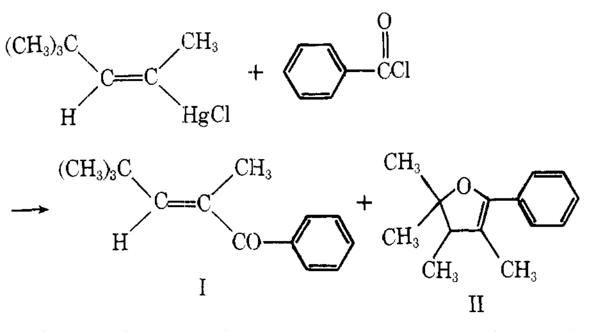
(12)

component, and halides should be tolerated in either component of the reaction.

Six systems were tried unsuccessfully. Pivaloyl chloride decarbonylated under the influence of aluminum chloride before the vinylmercurial could be added to the reaction flask. Neither levulinyl chloride nor methylsuccinyl chloride (prepared from succinic anhydride[16]) reacted as desired. Vinylmercuric chloride reacted with 3,3-dimethylbutyryl chloride to produce 5,5-dimethyl-1-hexen-3-one and 1-chloro-5,5-dimethyl-3-hexanone in approximately equal amounts (eq 13). We were unable readily to eliminate HCl from the β-chloro ketone on treatment with base. (E)-3-Acetoxy-2-chloromercuri-2-butene was reacted with isobutyryl chloride, but the product mixture obtained showed an NMR spectrum much too complex to be the desired product.

$$\begin{aligned}&(CH_3)_3CCH_2COCl + CH_2{=}CHHgCl\\&\quad\rightarrow (CH_3)_3CCH_2COCH{=}CH_2\\&\qquad + (CH_3)_3CCH_2COCH_2CH_2Cl \quad (13)\end{aligned}$$

Two products, I and II, were obtained when benzoyl chloride was reacted with (E)-2-chloromercuri-4,4-dimethyl-2-pentene (eq 14). This reaction takes longer than with aliphatic



(14)

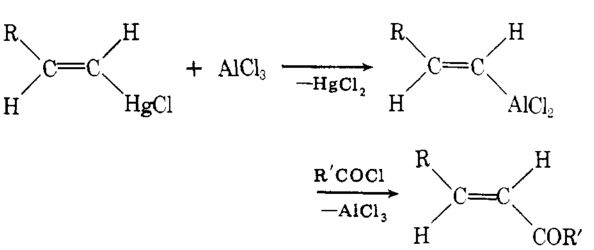
acid chlorides. Initially the two products are obtained in approximately equal amounts, but by the time the reaction is complete the dihydrofuran predominates. Further discussion of this reaction will be put off until the mechanistic discussion.

Reactions with Titanium Tetrachloride. As indicated earlier, unusual stereochemical results were found when examining the reaction of *trans*-1-hexenylmercuric chloride, acetyl chloride, and titanium tetrachloride at −78 °C. When this reaction was scaled up to 10 mmol an isolated yield of 78% *cis*-3-octen-2-one was obtained. A 3-h reaction period was necessary, and less than 3% of the trans isomer was seen by NMR.

A number of other acid chlorides and vinylmercurials were examined in this reaction. Three acid chlorides were tried with *trans*-1-decenylmercuric chloride, but it appears that this mercurial is very unreactive toward acid chlorides and titanium tetrachloride. Both *trans*-cyclohexylethenylmercuric chloride and *trans*-3,3-dimethyl-1-butenylmercuric chloride also failed to react with acetyl chloride at −78 °C after 3 h. Raising the reaction temperature to −45 °C gave only the trans enone.

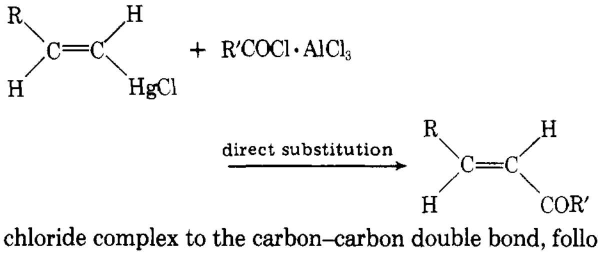
Three other acid chlorides, butyryl chloride, 3-methylbutyryl chloride, and 3,3-dimethylbutyryl chloride, were then tried with *trans*-1-hexenylmercuric chloride, but mixtures of cis and trans enones were always obtained. Finally, the reaction of *trans*-1-hexenylmercuric chloride and butyryl chloride was chosen as a model system for further studies. In studying this reaction the following variables were investigated: reaction time (6 h was usually optimum), reaction temperature (warmer than −78 °C decreased the amount of cis isomer seen), stoichiometry, and the order and mode of addition of the reagents. Only a random array of yields were obtained, and after much frustration it was decided that this reaction was not sufficiently reproducible to make it of value synthetically.

Mechanism. There are at least three possible mechanisms that can be written for the aluminum chloride promoted reactions: (1) the formation of a vinylalane by transmetallation with aluminum chloride, followed by acylation (eq 15); (2)



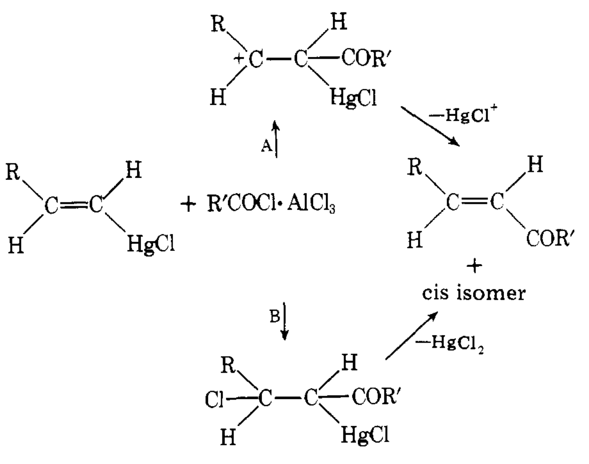
(15)

direct electrophilic substitution at the carbon–mercury bond (eq 16); and (3) addition of the acid chloride–aluminum



(16)

chloride complex to the carbon–carbon double bond, followed by elimination of mercuric chloride to form the α,β-unsaturated ketone (eq 17).



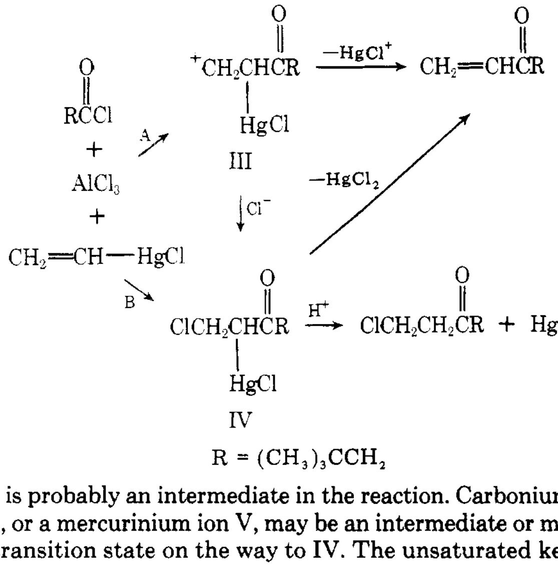
(17)

In order to investigate the first possible mechanism, two exchange reactions were investigated. Aluminum chloride was reacted with either *trans*-1-decenylmercuric chloride or stilbenylmercuric chloride in methylene chloride, and the reaction was quenched with 10% sodium hydroxide. If exchange occurred, the vinylalane formed would be expected to react with water to form a hydrocarbon. If no exchange occurred, no hydrocarbon would be observed. A basic quench was used to prevent the generation of acid from hydrolysis of the unreacted aluminum chloride, which could then cleave the carbon–mercury bond. Quenching the stilbenylmercuric chloride–aluminum chloride mixture after 5 min at room temperature led to a 14% yield of *cis*- and *trans*-stilbenes. The reaction of *trans*-1-decenylmercuric chloride and aluminum chloride resulted in a 7% yield of 1-decene when quenched after 5 min. Quenching after 3 h did not increase the yield of hydrocarbon in either reaction. *trans*-1-Decenylmercuric chloride was chosen for the ease of analyzing the resultant hydrocarbon, while stilbenylmercuric chloride was chosen because stilbene was seen in its reaction with butyryl chloride (see Table VI). From these results it appears that stilbene may have arisen from acid cleavage of the starting mercurial. In conclusion, it appears that the first mechanism (vinylmercurial exchange with aluminum chloride) is unlikely since exchange does not occur quickly enough to account for a near-quantitative yield of ketone in less than 5 min. However, one cannot rule out the very rapid acylation of a vinylalane generated in only minor amounts through an unfavorable transmetallation equilibrium.

The second and third mechanisms must both be considered seriously. Direct electrophilic cleavage at the carbon–mercury bond would be expected to result in complete retention of stereochemistry. A large portion of the reaction could be occurring by this route since the reaction is highly stereospecific. However, the presence of small quantities of *cis*-α,β-unsaturated ketone suggests that at least some of the product might arise from an addition–elimination mechanism. Another possibility is that the cis isomer arises from Lewis acid isomerization of the trans enone. Isomerization of the enones in this fashion does not appear to occur, as will be discussed later in this section.

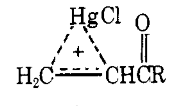
Three reactions tend to support the addition–elimination mechanism: (1) the reaction of 3,3-dimethylbutyryl chloride with vinylmercuric chloride, which gives 5,5-dimethyl-1-hexen-3-one and 1-chloro-5,5-dimethyl-3-hexanone (eq 13); (2) the reaction of benzoyl chloride with (*E*)-4,4-dimethyl-2-chloromercuri-2-pentene, which gives (*E*)-1-phenyl-2,4,4-trimethyl-2-penten-1-one (I) and 4,5-dihydro-2-phenyl-3,4,5,5-tetramethylfuran (II) (eq 14); and (3) the titanium tetrachloride promoted reactions, which result in a high percentage of stereochemically inverted enones. Each of these will be discussed in turn.

In the reaction of vinylmercuric chloride with 3,3-dimethylbutyryl chloride, the formation of the β-chloro ketone could arise from either route shown in eq 18. The β-chloromercurial



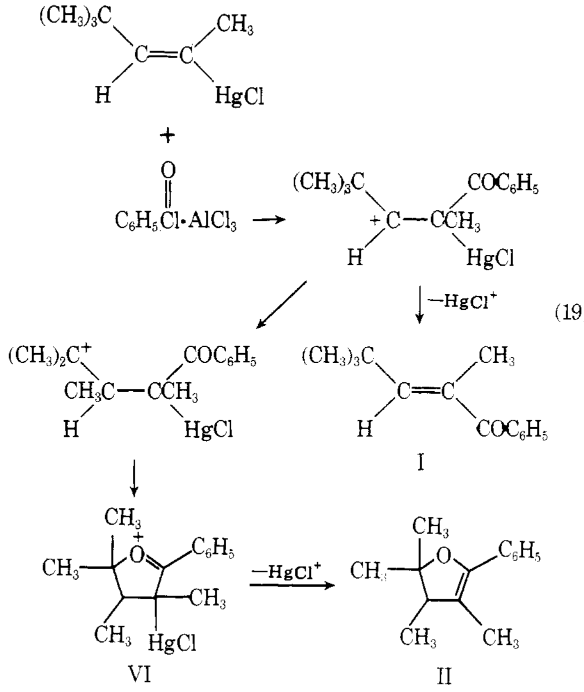
(18)

IV is probably an intermediate in the reaction. Carbonium ion III, or a mercurinium ion V, may be an intermediate or merely a transition state on the way to IV. The unsaturated ketone can arise from either III by elimination of a chloromercury ion or IV by elimination of mercuric chloride. The β-chloro ketone probably comes from IV by acid cleavage of the carbon–mercury bond. α-Chloromercuri ketones, such as IV, have previously been reported to be especially vulnerable to acid cleavage.[17] The acid could arise either from an impurity in aluminum chloride or on aqueous workup.



V

Studies on the reaction of benzoyl chloride and (*E*)-4,4-dimethyl-2-chloromercuri-2-pentene (eq 14) suggest that the dihydrofuran II arises directly from starting materials by rearrangement of an intermediate carbonium ion (eq 19).

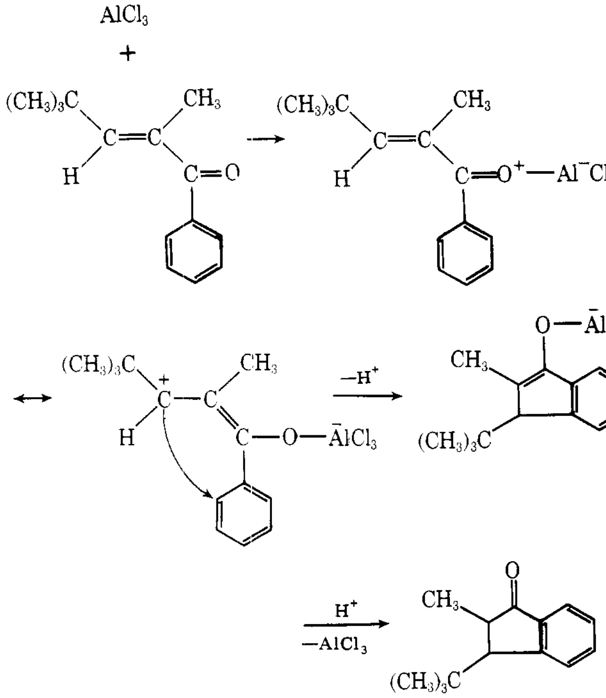


(19)

Sampling the reaction after short reaction times showed that both enone I and dihydrofuran II were present in the reaction shortly after mixing, but enone I reached a maximum yield of 31% in 1 h and then decreased to 20%, while the yield of dihydrofuran II continued to rise until reaching 45% after 6 h. Dihydrofuran II is stable under the reaction conditions. Stirring II with aluminum chloride does not result in rearrangement. Stirring enone I with equimolar amounts of aluminum chloride and mercuric chloride did not result in any rearrangement. However, excess aluminum chloride caused complete rearrangement to 2-methyl-3-*tert*-butyl-1-indanone (VII) (eq 20). Small amounts of indanone VII were also observed in the reaction of benzoyl chloride and (*E*)-4,4-dimethyl-2-chloromercuri-2-pentene. The structures of the rearrangement products II and VII were assigned on the basis of spectral data. Since both enone I and dihydrofuran II arise directly as the reaction progresses, it appears that this reaction at least occurs by an addition–elimination mechanism.

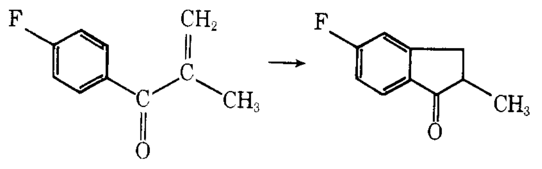
Literature precedent exists for much of the chemistry observed in this system. Pines observed that 4′-fluoro-2-methylacrylophenone cyclized to 2-methyl-5-fluoro-1-indanone under the influence of aluminum chloride or sulfuric acid (eq 21).[18] A cyclic oxonium ion was also observed by ^{13}C NMR in their studies (eq 22). This shows the plausibility of intermediate VI (eq 19), which would be expected to lose HgCl$^+$ and form the dihydrofuran II.

The titanium tetrachloride reaction probably proceeds by an addition–elimination reaction as well. Either a trans-

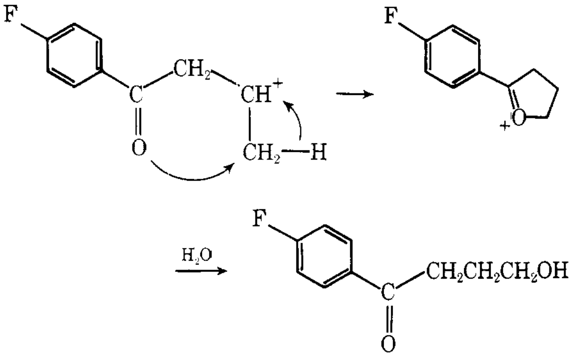


VII

(20)

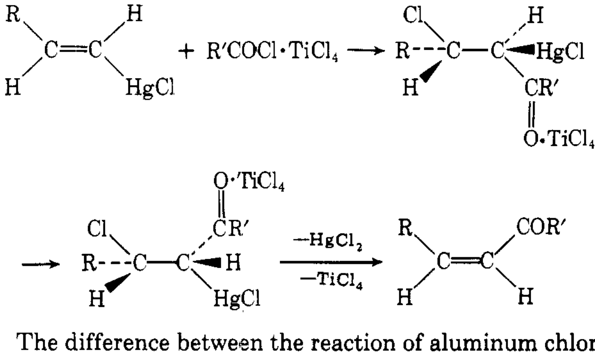


(21)



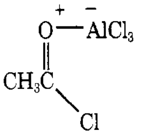
(22)

addition, trans-elimination or cis-addition, cis-elimination sequence would be expected to result in stereochemical inversion of the carbon–carbon double bond. Such a trans-addition, trans-elimination sequence has been proposed previously to explain the formation of a *trans*-vinyl bromide from the bromination of a *cis*-alkenylmercuric bromide.[19] A similar scheme may be invoked to explain the inversion of stereochemistry here (eq 23).



(23)

The difference between the reaction of aluminum chloride and titanium tetrachloride may be in the nature of the complex formed with the acid chloride or in the formation of different intermediates in the two reactions. In an effort to determine if a difference in the Lewis acid complex was responsible for the difference in the course of these reactions, infrared studies on the $TiCl_4$- and $AlCl_3$–acetyl chloride complexes were carried out. Cook reported that, if acetyl chloride is complexed through the oxygen (VIII), the C=O stretch is lowered from 1808 to 1637 cm^{-1}, while formation of an acylium ion (IX) raises the absorption to 2307 and 2203 cm^{-1}.[20] Cook found all three absorptions in a neat mixture of acetyl chloride and aluminum chloride, while in chloroform only the 1637-cm^{-1} absorption was seen. We have found that equal amounts of aluminum chloride and acetyl chloride in dichloromethane at 25 °C gives rise to absorptions at 1805 and 1640 cm^{-1} with little decrease in the strength of the 1805-cm^{-1} band. Likewise, equimolar amounts of $TiCl_4$ and acetyl chloride at 25 °C give rise to both the 1805- and 1630-cm^{-1} bands. The slight difference in frequencies for the complexes may indicate slightly tighter complexing for $TiCl_4$ than for $AlCl_3$. The intensity of the 1805-cm^{-1} band in the titanium tetrachloride reaction decreased by ~10% on standing for 2 h, indicating a relatively small degree of complexation. Similar results were seen for aluminum chloride. These results do not appear to account for the differences in the stereochemistry of the two reactions.



VIII

$$CH_3C\equiv\overset{+}{O}\quad \overset{-}{AlCl_4}$$

IX

The final point of discussion concerns the stability of the products under the reaction conditions. Stirring *trans*-3-octen-2-one with 1 equiv of aluminum chloride at room temperature in dichloromethane, or with equimolar amounts of aluminum chloride and mercuric chloride, showed that 96 and 91%, respectively, of the trans enone was still present in the reaction mixture after 8 h. After 27 h, the yields of ketone were 86 and 87%, respectively. No cis enone was seen in either reaction. Quite clearly the cis product is not arising by isomerization of the trans enone.

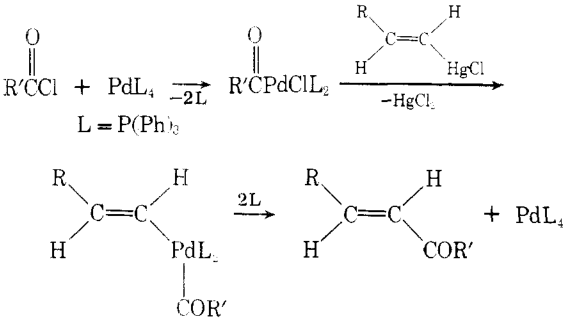
The isomerization of cis enones was studied on *cis*-5-decen-4-one. Stirring the cis enone with aluminum chloride at room temperature resulted in a 91:5% cis/trans mixture after 5 min and a 43:22% mixture of enones after 24 h. An equimolar mixture of aluminum chloride and mercuric chloride resulted in a 95:5% cis/trans mixture after 5 min and a 5:35% mixture after 24 h. The titanium tetrachloride isomerization was studied in the same manner. With the cis enone, after 5 min no trans enone was seen and 88% of the cis enone remained. After 24 h, only traces of either enone were observed. After 5 min with equimolar amounts of titanium tetrachloride and mercuric chloride, 3% trans enone was observed while 84% of the cis enone remained. After 24 h, 2% of each enone was observed.

Based on the evidence obtained, it appears that the Lewis acid promoted acylation of vinylmercuric chlorides proceeds by way of an addition–elimination reaction. While the evidence is not conclusive, all of the side reactions discussed, as well as the formation of small amounts of cis enone observed in most reactions, may be explained by this mechanism. However, none of the data available precludes a direct substitution reaction as being the major route with small amounts of addition–elimination, accounting for the small amounts of the less stable cis enones.

The titanium tetrachloride reaction most likely proceeds via trans addition, trans elimination or cis addition, cis elimination, both of which would result in inversion of stereochemistry around the carbon–carbon double bond. However, experimental evidence which could either prove or disprove this proposal is lacking.

Enone isomerization probably does not account for the small amounts of cis enone observed with aluminum chloride or the substantial yields of cis enone with titanium tetrachloride.

The transition metal catalyzed reaction is envisioned as involving an initial oxidative addition between $Pd(PPh_3)_4$ and the acid chloride. Transfer of the vinyl group from the mercurial to the resulting acylpalladium species and subsequent reductive elimination would then provide the α,β-unsaturated ketone and regenerate the catalyst (eq 24). An identical mechanism has been suggested previously for the palladium(0)-catalyzed acylation of dialkyl- and diarylmercurials[14] and is entirely consistent with the known chemistry of palladium.



Conclusion

α,β-Unsaturated ketones can be readily prepared from vinylmercurials and acid chlorides. Best yields and stereochemical purity are obtained when one employs 1 equiv of aluminum trichloride in methylene chloride and the reaction is run 5 min at room temperature. Substitution of titanium tetrachloride for aluminum chloride at −78 °C gives enones of inverted stereochemistry, but the results are not reproducible. Catalytic amounts of $Pd(PPh_3)_4$ in HMPA will also promote acylation of the vinylmercurials, but the yields are lower than the aluminum trichloride reactions. Rhodium(I) catalysts give still lower yields. Mechanistically, the formation of the major side products and stereochemically inverted enones seems best explained by a mechanism involving the addition of a Lewis acid–acid chloride complex to the carbon–carbon double bond of the vinylmercurial and subsequent mercuric chloride elimination. It is not possible at present to decide whether the major products are produced by the same mechanism or by direct electrophilic acylation of the carbon–mercury bond.

Experimental Section

Reagents. All chemicals were used directly as obtained commercially unless otherwise noted. HMPA was distilled from lithium aluminum hydride under vacuum. Dichloromethane was shaken with concentrated sulfuric acid, washed with water and saturated sodium chloride, dried over calcium chloride, and distilled. Ether and THF were distilled from $LiAlH_4$.

The vinylmercuric chlorides used were prepared according to literature procedures and have all been described previously.[9,10,15]

$(Ph_3P)_2Rh(CO)Cl$ (Alfa Inorganics–Ventron), $[ClRh(CO)_2]_2$ (PCR), aluminum chloride (Fisher Scientific), and aluminum bromide (Fisher Scientific) were all used directly as obtained commercially. Wilkinson's catalyst, $(Ph_3P)_3RhCl$, was prepared according to published procedures.[21]

All GLC yields are corrected by the use of appropriate hydrocarbon internal standards and calculated correction factors.

Reaction of Styrylmercuric Chloride with Acetyl Chloride. The following procedure for the reaction of styrylmercuric chloride and acetyl chloride is representative. Styrylmercuric chloride (1.0mmol), acetyl chloride (1.0 mmol), and an internal hydrocarbon standard were dissolved in *N,N*-dimethylformamide (DMF) (10 mL) under nitrogen. Aluminum bromide (1.0 mmol) was then added, and the reaction was stirred for 24 h at 25 °C. A solid formed in the reaction, and the liquid was decanted into 3 M sodium thiosulfate and ether was added. The ether was then analyzed by GLC (10′ DC-550 at 200 °C).

Distyrylmercury (0.5 mmol) was used in some reactions in the place of styrylmercuric chloride (1.0 mmol). When water-immiscible solvents were used for the reaction, samples were taken and quenched with water before GLC analysis.

The GLC correction factor was calculated using a commercial sample of *trans*-4-phenyl-3-buten-2-one. The product was verified by comparison with the commercial authentic sample.

Reaction of *trans*-1-Hexenylmercuric Chloride and Acetyl Chloride. An authentic sample of *trans*-3-octen-2-one was prepared according to the literature procedure.[22] 1-Hexene (12.5 mL, 100 mmol) was dissolved in a mixture of acetic acid (5.6 mL) and trifluoroacetic anhydride (14.0 mL) and stirred at room temperature for 20 min, then 40 °C for 1.5 h, and finally at room temperature overnight. The product was distilled under aspirator vacuum and then GLC prepped: ^1H NMR (CCl_4) δ 0.92 (3 H, not resolved, CH_3), 1.40 (4 H, m, $-CH_2CH_2-$), 2.18 (3 H, s, $COCH_3$), 2.2 (2 H, m, $CH_2CH=$), 5.95 (1 H, d, J = 17 Hz, $COCH=$), 6.80 (1 H, d t, J = 17, 7 Hz, $COCH=CH$); IR (max) (thin film) 2970, 2950, 2860, 1675, 1630, 1460, 1430, 1360, 1255, 1180, 980, 930, 735 cm^{-1}; MS *m/e* 126.1042 ± 0.0006 (calcd for $C_8H_{14}O$, 126.1045). Further samples of *trans*-3-octen-2-one were prepared by the procedure developed in this work.

The following procedure is representative of that used in the model studies in this section. Tetradecane, *trans*-1-hexenylmercuric chloride (1.0 mmol), and acetyl chloride (1.0 mmol) were dissolved in dichloromethane (10 mL). Aluminum bromide (1.0 mmol) was added and the reaction stirred at room temperature under nitrogen. Samples (0.5 mL) were taken, added to water, and then analyzed by GLC.

When temperatures other than room temperature were desired, the vinylmercurial and acid chloride were added and cooled down to the desired temperature in the appropriate temperature bath before the Lewis acid was added. Samples were taken as above. Addition of the vinylmercurial to a solution of Lewis acid and acid chloride also results in a satisfactory reaction.

In studying the effect of various Lewis acids (Table I), all variables were kept constant except reaction time and the Lewis acid. The solvents were investigated at room temperature for the time periods listed in Table II. Likewise, the effects of temperature, Table III, and reaction time, Table IV, were studied holding all other variables constant.

The transition metal catalyzed reactions were studied as with the Lewis-acid reactions. The transition-metal complex (0.1 mmol) was added to a solution of the vinylmercuric chloride and acid chloride in the appropriate solvent and analyzed by GLC after the appropriate workup. The ether and dichloromethane reactions were quenched with water. The THF reactions were quenched with saturated ammonium chloride, and the HMPA reactions were quenched by adding water and ether and then analyzing the ether layer, or by analyzing without quenching.

The side products in the transition-metal reactions were identified as follows. In THF, the product from the reaction of acetyl chloride and THF, 1-acetoxy-4-chlorobutane, had a GLC retention time (10% DC-550, 10 ft, 150 °C) very similar to that for *trans*-3-octen-2-one and was determined to be different by coinjecting ketone and the reaction mixture and observing two peaks. The side product was confirmed to have come from THF by stirring the rhodium catalyst, THF, and acetyl chloride in the absence of vinylmercurial and observing a product of identical retention time by coinjection with the above reaction mixture. 1-Acetoxy-4-chlorobutane (prepped by GLC): ^1H NMR (CCl_4) δ 1.8 (4 H, m, $-CH_2CH_2-$), 2.02 (3 H, s, $COCH_3$), 3.6 (2 H, m, CH_2Cl), 4.1 (2 H, m, CH_2OCOCH_3); IR (max) (thin film) 2960, 1740, 1450, 1240, 1045, 950, 880, 750, 720 cm^{-1}.

The structure of the symmetrical 1,3-diene from the reaction of *trans*-1-hexenylmercuric chloride and the rhodium catalyst in the presence of acetyl chloride (eq 11) was confirmed by spectral data and GLC comparison with an authentic sample of diene prepared by our own published procedure.[15]

Synthesis of α,β-Unsaturated Ketones. 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 was added dichloromethane (100 mL), aluminum chloride (1.33 g, 10 mmol), and acetyl chloride (0.80 mL, 10 mmol). After stirring briefly *trans*-1-hexenylmercuric chloride (3.1 g, 10 mmol) was added while backflushing with nitrogen, and the reaction was stirred for 5 min. A white solid (presumably mercuric chloride) precipitated almost immediately. The reaction mixture was then poured into water, and the layers were separated. The aqueous layer was extracted with dichloromethane. The organic layer was then washed with 5% sodium bicarbonate, 3 M sodium thiosulfate, and water. The combined aqueous washes were reextracted with dichloromethane, and the combined organic layers were dried over anhydrous sodium sulfate. Removal of solvent yielded 1.22 g (97%) of essentially pure *trans*-3-octen-2-one as a colorless oil. GLC analysis showed 5% or less of the undesired cis isomer. Spectral properties were identical with those of an authentic sample prepared earlier by an alternate method.

The following compounds were prepared in like manner.

***trans*-5,5-Dimethyl-3-hexen-2-one:** ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.10 (9 H, s, $\mathrm{C(CH_3)_3}$), 2.15 (3 H, s, $\mathrm{COCH_3}$), 5.90 (1 H, d, J = 16 Hz, $\mathrm{COC\mathbf{H}{=}}$), 6.70 (1 H, d, J = 16 Hz, $\mathrm{COCH{=}C\mathbf{H}}$); IR (max) (thin film) 3030, 2950, 2860, 1680, 1620, 1365, 1290, 1250, 980 cm^{-1}; MS *m/e* 126.1044 ± 0.0006 (calcd for $\mathrm{C_8H_{14}O}$, 126.1045).

(*E*)-3,5,5-Trimethyl-3-hexen-2-one: ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.20 (9 H, s, $\mathrm{C(CH_3)_3}$), 1.83 (3 H, d, J = 1.5 Hz, $\mathrm{{=}CCH_3}$), 2.20 (3 H, s, $\mathrm{COCH_3}$), 6.50 (1 H, q, J = 1.5 Hz, $\mathrm{CH{=}}$); IR (max) (thin film) 2960, 2860, 1680, 1640, 1470, 1370, 1250, 1200, 1030 cm^{-1}; MS *m/e* 140.1201 ± 0.0007 (calcd for $\mathrm{C_9H_{16}O}$, 140.1201).

***trans*-1-Cyclohexyl-1-hexen-3-one:** ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.9 (3 H, t, J = 6 Hz, $\mathrm{CH_2C\mathbf{H}_3}$), 1–2 (13 H, m, c-$\mathrm{C_6H_{11}}$ and $\mathrm{C\mathbf{H}_2CH_3}$), 2.3 (2 H, t, J = 7 Hz, $\mathrm{COCH_2}$), 5.90 (1 H, d, J = 16 Hz, $\mathrm{COC\mathbf{H}{=}CH}$), 6.65 (1 H, d d, J = 16, 6 Hz, $\mathrm{COCH{=}C\mathbf{H}}$); IR (max) (thin film) 2920, 2840, 1670, 1620, 1448, 1365, 1190, 978 cm^{-1}; MS *m/e* 180.1512 ± 0.0009 (calcd for $\mathrm{C_{12}H_{20}O}$, 180.1514).

(*E*)-1,1-Dichloro-3-ethyl-3-hexen-2-one: ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.1 (6 H, overlapping triplets, J = 7 Hz, $\mathrm{CH_3}$'s), 2–2.6 (4 H, m, J = 7 Hz, $\mathrm{CH_2}$'s), 5.5 (1 H, t, J = 7 Hz, $\mathrm{CH{=}C}$), 6.0 (1 H, s, $\mathrm{COCHCl_2}$); IR (max) (thin film) 2950, 2920, 2860, 1660–1640, 1460, 1375, 1310, 1250, 1210, 1140, 1080, 990, 790, 760, 735 cm^{-1}; sample decomposed before mass spectra could be obtained.

(*E*)-1,2-Diphenyl-1-hexen-3-one: ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.90 (3 H, t, J = 7 Hz, $\mathrm{CH_3}$), 1.65 (2 H, sextet, J = 7 Hz, $\mathrm{C\mathbf{H}_2CH_2CO}$), 2.50 (2 H, t, J = 7 Hz, $\mathrm{CH_2CO}$), 7–7.7 (11 H, m, $\mathrm{C_6H_5CH{=}CC_6H_5}$); IR (max) (thin film) 3060, 3030, 1685, 1615, 1595, 1495, 1450, 1200, 1135, 1070, 765, 700 cm^{-1}; MS *m/e* 250.1359 ± 0.0013 (calcd for $\mathrm{C_{18}H_{18}O}$, 250.1358).

12-Carbomethoxy-3-dodecen-2-one: ^{1}H NMR δ 1.3 (12 H, br s, $\mathrm{CH_2}$'s), 2.1 (3 H, s, $\mathrm{COCH_3}$), 2.2 (4 H, m, $\mathrm{{=}CHC\mathbf{H}_2}$ and $\mathrm{C\mathbf{H}_2COOCH_3}$), 3.55 (3 H, s, $\mathrm{COOCH_3}$), 5.95 (1 H, d, J = 16 Hz, $\mathrm{COCH{=}}$), 6.7 (1 H, d t, J = 16, 7 Hz, $\mathrm{COCH{=}C\mathbf{H}}$) (there is evidence in the NMR of the cis isomer being present as well, but the peaks are poorly resolved); IR (max) (KBr) 2980, 2920, 2850, 1745, 1680, 1600, 1470, 1440, 1385, 1340, 1320, 1280, 1245, 1205, 1175, 1000, 980, 880, 720, 690 cm^{-1}; MS *m/e* 240.1721 ± 0.0008 (calcd for $\mathrm{C_{14}H_{24}O_3}$, 240.1726).

***trans*-2-Methyl-4-tridecen-3-one:** ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.00 (3 H, t, J = 7 Hz, $\mathrm{CH_2C\mathbf{H}_3}$), 1.05 (6 H, d, J = 7 Hz, $\mathrm{CH(C\mathbf{H}_3)_2}$), 1.3 (12 H, br s, $\mathrm{CH_2}$), 2.2 (2 H, m, $\mathrm{C\mathbf{H}_2CH{=}}$), 2.7 (1 H, septet, J = 7 Hz, $\mathrm{C\mathbf{H}(CH_3)_2}$), 6.0 (1 H, d, J = 16 Hz, $\mathrm{COCH{=}}$), 6.75 (1 H, dt, J = 16, 7 Hz, $\mathrm{COCH{=}C\mathbf{H}}$); MS *m/e* 210.1989 ± 2.7 (calcd for $\mathrm{C_{14}H_{26}O}$, 210.1984).

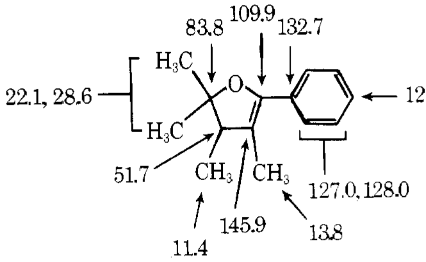
***trans, trans*-2,5-Nonadien-4-one:** ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.00 (3 H, t, J = 7 Hz, $\mathrm{CH_2C\mathbf{H}_3}$), 1.5 (2 H, sextet, J = 7 Hz, $\mathrm{C\mathbf{H}_2CH_3}$), 1.94 (3 H, d, J = 7 Hz, $\mathrm{{=}CHC\mathbf{H}_3}$), 2.20 (2 H, t, J = 7 Hz, $\mathrm{{=}CHCH_2}$), 6.15 (2 H, d, J = 16 Hz, $\mathrm{COC\mathbf{H}{=}}$'s), 6.80 (2 H, d t, J = 16, 7 Hz, $\mathrm{COCH{=}C\mathbf{H}}$'s); IR (max) (thin film) 3040, 3020, 2950, 2940, 2860, 1665, 1640–1620, 1440, 1380, 1335, 1300, 1200, 1150, 1080, 1040, 980 cm^{-1}; MS *m/e* 138.1040 ± 3.6 (calcd for $\mathrm{C_9H_{14}O}$, 138.1045).

***trans*-1-Phenyl-2-hepten-1-one:** ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.00 (3 H, t, J = 7 Hz, $\mathrm{CH_3}$), 1.5 (4 H. m, $\mathrm{CH_2CH_2}$), 2.3 (2 H, m, $\mathrm{{=}CHC\mathbf{H}_2}$), 6.85 (2 H, m, vinyl), 7.4 (3 H, m, $\mathrm{H_{3-5}}$ of COPh), 7.85, (2 H, m, $\mathrm{H_{2,6}}$ of COPh); IR (max) (thin film) 3060, 2960, 2930, 2870, 1670, 1620, 1600, 1580, 1450, 1390, 1280, 1220, 1180, 1000, 980, 920, 880, 860, 790 cm^{-1}; sample identical with a sample prepared from condensing the lithium enolate of acetophenone (lithium diisopropylamide, THF, −78 °C) with valeraldehyde followed by dehydration.[23]

In most reactions the stereochemically inverted enone was evident to the extent of 2–5% by close examination of the vinyl region of the NMR spectrum (chemical shift and coupling constants). These compounds were not, however, characterized further, and it is not clear whether this is a valid representation of the stereochemistry of the reaction or simply an indication of the stereochemical purity of the vinylmercurial starting material.

Reactions with Titanium Tetrachloride. These reactions were investigated in the same manner as were the Lewis-acid reactions previously discussed. Two cis enones were isolated and characterized, *cis*-3-octen-2-one and *cis*-5-decen-4-one. The correction factor used for *cis*-3-dodecene-2-one was measured from a sample of the trans isomer. *cis*- and *trans*-3-octen-2-one agree within ±2% for their correction factors, so that errors introduced by the use of the trans isomer are minimal.

Chart I



Spectral data on the compounds not previously given follow.

***cis*-3-Octen-2-one:** ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.9 (3 H, t, J = 7 Hz, $\mathrm{CH_2C\mathbf{H}_3}$), 1.4 (2 H, sextet, J = 8 Hz, $\mathrm{C\mathbf{H}_2CH_3}$), 2.1 (5 H, m with s superimposed, $\mathrm{COCH_3}$ and $\mathrm{{=}CHCH_2C\mathbf{H}_2}$), 3.0 (2 H, t, J = 4 Hz, $\mathrm{{=}CHC\mathbf{H}_2}$), 5.5 (2 H, m, $\mathrm{CH{=}CH}$); IR (max) (thin film) 2940, 2910, 2860, 1715, 1680, 1365, 1160, 965 cm^{-1}; MS *m/e* 126.1047 ± 0.0006 (calcd for $\mathrm{C_8H_{14}O}$, 126.1045).

***cis*-5-Decen-4-one:** ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.90 (6 H, t, J = 7 Hz, $\mathrm{CH_3}$'s), 1.2–2.1 (6 H, m, 3 $\mathrm{CH_2}$), 2.35 (2 H, t, J = 7 Hz, $\mathrm{COCH_2}$), 3.0 (2 H, m, $\mathrm{C\mathbf{H}_2CH{=}}$), 5.5 (2 H, m, $\mathrm{CH{=}CH}$); MS *m/e* 154.1354 ± 2.7 (calcd for $\mathrm{C_{10}H_{18}O}$, 154.1358).

***trans*-5-Decen-4-one:** ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.90 (6 H, t, J = 7 Hz, $\mathrm{CH_3}$'s), 1.4 (6 H, m, 3 $\mathrm{CH_2}$), 2.3 (2 H, m, $\mathrm{{=}CHC\mathbf{H}_2}$), 2.4 (2 H, t, J = 7 Hz, $\mathrm{COC\mathbf{H}_2}$), 6.1 (1 H, d, J = 16 Hz, $\mathrm{COCH{=}}$), 6.8 (1 H, d t, J = 16, 7 Hz, $\mathrm{COCH{=}C\mathbf{H}}$); MS *m/e* 154.1357 ± 0.6 (calcd for $\mathrm{C_{10}H_{18}O}$, 154.1358).

Mechanism. The exchange reactions of stilbenylmercuric chloride and *trans*-1-decenylmercuric chloride with aluminum chloride were studied as follows. The mercurial (1.0 mmol) and an appropriate internal hydrocarbon standard were dissolved in dichloromethane (10 mL). Aluminum chloride (1.0 mmol) was added, and the reaction mixture was stirred at room temperature. A sample was taken after 5 min and quenched by pouring into 10% sodium hydroxide. Samples were analyzed by GLC. Correction factors were calculated from authentic samples of 1-decene and stilbene.

The isomerization of *trans*-3-octen-2-one by aluminum chloride was studied as follows. *trans*-3-Octen-2-one (0.216 mmol) and an internal standard were dissolved in dichloromethane (2.3 mL). Aluminum chloride (0.271 mmol) was added, and the mixture was stirred at room temperature. Samples were taken at 0.5, 1, 4, 8, and 27 h and quenched with water before GLC analysis. Other isomerizations were studied in like manner. When mercuric chloride was used, it was added in approximately equimolar amounts.

Studies on the reaction of (*E*)-4,4-dimethyl-2-chloromercuri-2-pentene and benzoyl chloride were carried out in the same manner as the reactions of *trans*-1-hexenylmercuric chloride with acetyl chloride.

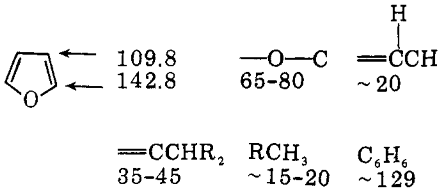
(*E*)-1-Phenyl-2,4,4-trimethyl-2-penten-1-one: ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.3 (9 H, s, $\mathrm{C(CH_3)_3}$), 2.1 (3 H, d, J = 1 Hz, $\mathrm{{=}CCH_3}$), 6.15 (1 H, q, J = 1 Hz, $\mathrm{COC{=}CH}$), 7.5 (5 H, m, $\mathrm{C_6H_5}$); ^{13}C NMR ($\mathrm{CDCl_3}$) 13.4 ppm ($\mathrm{{=}CCH_3}$), 30.1 ($\mathrm{C(\mathbf{C}H_3)_3}$), 33.7 ($\mathrm{\mathbf{C}(CH_3)_3}$), 127.9 and 129.4 ($\mathrm{C_{2,3}}$ of Ph), 131.3 ($\mathrm{C_4}$ of Ph), 134.8 ($\mathrm{COC{=}C}$), 138.6 $\mathrm{C_1}$ of Ph), 154.6 ($\mathrm{COC{=}\mathbf{C}}$), 200.1 (CO); IR (max) (thin film) 3060, 3030, 2960, 2870, 1650, 1600, 1580, 1470, 1450, 1370, 1315, 1300, 1290, 1210, 1040, 965, 875, 710 cm^{-1}.

4,5-Dihydro-2-phenyl-3,4,5,5-tetramethylfuran: ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.05 (3 H, d, J = 6 Hz, $\mathrm{CHC\mathbf{H}_3}$), 1.28 and 1.38 (3 H, s, $\mathrm{(CH_3)_2C}$), 1.85 (3 H, s, $\mathrm{{=}CC\mathbf{H}_3}$), 2.57 (1 H, q, J = 6 Hz, $\mathrm{C\mathbf{H}CH_3}$), 7.2–7.5 (5 H, m, $\mathrm{C_6H_5}$); ^{13}C NMR ($\mathrm{CDCl_3}$) 11.4 ppm ($\mathrm{CH\mathbf{C}H_3}$), 13.8 ($\mathrm{{=}C\mathbf{C}H_3}$), 22.1 and 28.6 ($\mathrm{(\mathbf{C}H_3)_2C}$), 51.7 ($\mathrm{\mathbf{C}HCH_3}$), 83.8 ($\mathrm{(CH_3)_2\mathbf{C}}$), 109.9 ($\mathrm{{=}\mathbf{C}Ph}$), 127.0 and 128.0 ($\mathrm{C_{2,3}}$ of Ph), 127.3 ($\mathrm{C_4}$ of Ph), 132.7 ($\mathrm{C_1}$ of Ph), 145.9 ($\mathrm{C{=}\mathbf{C}CH_3}$); IR (max) (thin film) 3080, 3060, 3020, 2985, 2920, 2860, 1670, 1600, 1500, 1450, 1380, 1365, 1260, 1100, 1070, 990, 860, 770, 690 cm^{-1}; MS *m/e* 202 (parent, 51), 200 (19), 187 (66), 185 (16), 129 (22), 121 (17), 105 (base peak, 100), 97 (19), 77 (36).

2-Methyl-3-*tert*-butyl-1-indanone: ^{1}H NMR ($\mathrm{CCl_4}$) δ 1.00 (9 H, s, $\mathrm{C(CH_3)_3}$), 1.23 (3 H, d, J = 7 Hz, $\mathrm{CHC\mathbf{H}_3}$), 2.50 (1 H, d q, J = 2, 7 Hz, $\mathrm{CHCH_3}$), 2.72 (1 H, d, J = 2 Hz, CHC), 7.2–7.8 (4 H, m, $\mathrm{C_6H_4}$); IR (thin film) (max) 3070, 2960, 2870, 1725, 1610, 1460, 1395, 1365, 1325, 1290, 1270, 1230, 1210, 1150, 1085, 960, 930, 920, 790, 745 cm^{-1}; MS *m/e* 202 (parent, 2), 187 (3), 174 (2), 158 (3), 145 (100, parent − *t*-Bu), 131 (27), 116 (15) 104 (6), 57 (17, *t*-Bu).

The ^{13}C NMR assignments (in ppm) for dihydrofuran II are shown in Chart I. The bases for these assignments (in ppm) were taken from

Chart II



"The Chemist's Companion" and are listed in Chart II.[24] Isomerization studies in this system were carried out in the same manner as the isomerization of enones already discussed.

In the reaction of 3,3-dimethylbutyryl chloride with vinylmercuric chloride, **5,5-dimethyl-1-hexen-3-one** was identified by its ^{1}H NMR spectrum: δ 1.0 (9 H, s, $C(CH_3)_3$), 2.4 (2 H, s, CH_2CO), 5.65 (1 H, d d, $J = 4, 8$ Hz, COCH=), 6.15 (2 H, m, $COCH{=}CH_2$). Further characterization was not carried out.

1-Chloro-5,5-dimethyl-3-hexanone was characterized fully: ^{1}H NMR (CCl_4) δ 1.0 (9 H, s, $C(CH_3)_3$), 2.25 (2 H, s, CCH_2CO), 2.75 (2 H, t, $J = 7$ Hz, $COCH_2CH_2Cl$), 3.6 (2 H, t, $J = 7$ Hz, CH_2Cl); IR (max) (thin film) 2940, 1710, 1360, 1180, 830 cm^{-1}; MS m/e 162.0812 ± 0.0008 (calcd for $C_8H_{15}OCl$, 162.0812).

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for financial support (R.C.L.) and the National Science Foundation for an NSF Traineeship (J.C.B.).

Registry No.—1-Acetoxy-4-chlorobutane, 6962-92-1; *trans*-11-chloromercuriundec-10-enoic acid, 56453-79-3; *cis*-11-chloromercuriundec-10-enoic acid, 56453-80-6; *trans*-12-carbomethoxy-3-dodecen-2-one, 61759-52-2; *cis*-12-carbomethoxy-3-dodecen-2-one, 61759-49-7; *cis*-3-octen-2-one, 51193-77-2; *cis*-5-decen-4-one, 64235-54-7; *trans*-5-decen-4-one, 64235-55-8; (*E*)-1-phenyl-2,4,4-trimethyl-2-penten-1-one, 64235-56-9; 4,5-dihydro-2-phenyl-3,4,5,5-tetramethylfuran, 64235-57-0; 2-methyl-3-*tert*-butyl-1-indanone, 64235-58-1; 3,3-dimethylbutyryl chloride, 7065-46-5; 5,5-dimethyl-1-hepten-3-one, 2177-33-5; 1-chloro-5,5-dimethyl-3-hexanone, 64235-59-2.

References and Notes

(1) Part 12: R. C. Larock and J. C. Bernhardt, *J. Org. Chem.*, **43**, 000 (1978).
(2) Preliminary communication: R. C. Larock and J. C. Bernhardt, *Tetrahedron Lett.*, 3097 (1976).
(3) DuPont Young Faculty Scholar, 1975–1976.
(4) Alfred P. Sloan Foundation Fellow, 1977–1979.
(5) National Science Foundation Trainee, 1973–1977.
(6) (a) A. T. Nielsen and W. J. Houlihan, *Org. React.*, **16** (1968); (b) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N.Y., 1972, Chapter 10; (c) H. Stetter, *Methoden Org. Chem. (Houben-Weyl), 4th Ed. 1952–*, **7**, Part 2, 1449–1526 (1976).
(7) (a) C. D. Nenitzescu and A. T. Balaban, *Friedel-Crafts Relat. React.*, **3**, Part 2, 1035–1071 (1964); (b) C. W. Schellhammer, *Methoden Org. Chem. (Houben-Weyl), 4th Ed. 1952–*, **7**, Part 1, 427–461 (1973).
(8) D. B. Carr and J. Schwartz, *J. Am. Chem. Soc.*, **99**, 639 (1977).
(9) R. C. Larock and H. C. Brown, *J. Organomet. Chem.*, **36**, 1 (1972).
(10) R. C. Larock, S. K. Gupta, and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 4371 (1972).
(11) (a) J. Volhard, *Justus Liebigs Ann. Chem.*, **267**, 172 (1892); (b) W. Steinkopf and A. Killingstad, *ibid.*, **532**, 288 (1937); (c) S. Umezawa, *Bull. Chem. Soc. Jpn.*, **14**, 155 (1939); (d) H. Gilman and G. F. Wright, *J. Am. Chem. Soc.*, **55**, 3302 (1933); (e) I. Kuwajima, K. Narasaka, and T. Mukaiyama, *Tetrahedron Lett.*, 4281 (1967).
(12) A. P. Skoldinov and K. A. Koschkov, *Zh. Obshch. Khim.*, **12**, 398 (1942); *Chem. Abstr.*, **37**, 3064 (1943).
(13) A. L. Kurts, I. P. Beletskaya, I. A. Savchenko, and O. A. Reutov, *J. Organomet. Chem.*, **17**, 21 (1969).
(14) K. Takagi, T. Okamoto, Y. Sukakibara, A. Ohno, S. Oka, and N. Hayami, *Chem. Lett.*, 951 (1975).
(15) R. C. Larock and J. C. Bernhardt, *J. Org. Chem.*, **42**, 1680 (1977).
(16) J. Cason, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 169.
(17) (a) W. Schrauth and H. Bauerschmidt, *Chem. Ber.*, **47**, 2736 (1914); (b) F. C. Whitmore, "Organic Compounds of Mercury", Reinhold, New York, N.Y., 1921, p 45; (c) H. R. Rodgers, J. X. McDermott, and G. M. Whitesides, *J. Org. Chem.*, **40**, 3577 (1975).
(18) S. H. Pines and A. W. Douglas, *J. Am. Chem. Soc.*, **98**, 8119 (1976).
(19) C. P. Casey, G. M. Whitesides, and J. Kurth, *J. Org. Chem.*, **38**, 3406 (1973).
(20) D. Cook, *Can. J. Chem.*, **37**, 48 (1959).
(21) J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, **10**, 67 (1967).
(22) A. L. Henne and J. M. Tedder, *J. Chem. Soc.*, 3628 (1953).
(23) M. W. Myddleton, A. W. Barrett, and J. H. Seager, *J. Am. Chem. Soc.*, **52**, 4405 (1930).
(24) A. J. Gordon and R. A. Ford, "The Chemist's Companion. A Handbook of Practical Data, Techniques, and References", Wiley, New York, N.Y., 1972, pp 280–288.

Intramolecular Phenoxymercuration of 2-Allylphenols. Regioselectivity and Stereochemistry

Takahiro Hosokawa,* Shyogo Miyagi, Shun-Ichi Murahashi, and Akio Sonoda

Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560, Japan

Yoshiki Matsuura, Shigeki Tanimoto, and Masao Kakudo

Institute for Protein Research, Osaka University, Yamada-kami, Suita, Osaka 5311, Japan

Received June 27, 1977

Intramolecular phenoxymercuration of 2-(2-cyclohexenyl)-4-methoxyphenol (1) using $Hg(OAc)_2$ gave 1,2,3,4,4a,9b-hexahydro-4-acetoxymercuri-8-methoxydibenzofuran (**2a**, 59%) as the sole product. The use of $HgCl_2$ in this reaction afforded only 2,4-propano-3-chloromercuri-6-methoxychroman (**3b**, 53%), indicating a change in the regioselectivity of the reaction. The stereochemistry of these mercurials was established by x-ray analyses which showed a trans arrangement of the Hg and the oxygen atom in both cases. That is, the reaction proceeds by an antarafacial addition to the C=C double bond of **1**. The use of mercuric chloroacetates in this reaction, e.g., $Hg(OCOCH_2Cl)_2$, gave both types of products, **2** and **3**, and the formation of the chroman compound **3** increased with increasing the electron-withdrawing property of the acetoxy ligands in $Hg(OCOCX_3)_2$: $OCOCH_3 < OCOCH_2Cl < OCOCHCl_2 < OCOCCl_3$. This suggests that the difference in regioselectivity observed with $Hg(OAc)_2$ and $HgCl_2$ depends on the electronic effect of the ligands on HgX_2. The use of HgX_2 having ligands more electronegative than acetate, such as X = NO_3 and ClO_4, led to the chroman compound **3**.

The reaction of 2-allylphenols with palladium(II) salts, which we have recently studied,[1,2] generally gives 2-substituted benzo- and/or dihydrobenzofurans. These products are considered to arise from an intramolecular phenoxypalladation process, but the palladation adduct is not isolated in this reaction. A way to produce this adduct may be by a metal-exchange reaction between the corresponding organomercury and palladium salts. Since palladium exchange with orga-

0022-3263/78/1943-0719$01.00/0