Mild Procedures for Interconverting Allylic Oxygen Functionality. Cyclization-Induced [3,3] Sigmatropic Rearrangement of Allylic Carbamates

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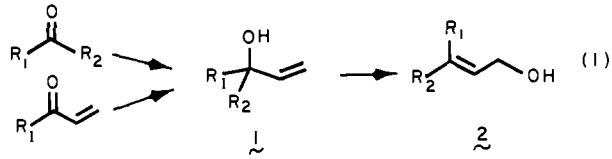
Abstract: Mercuric trifluoracetate (0.2–0.6 equiv) is shown to be an effective catalyst for equilibrating *N,N*-dimethylcarbamic esters of allylic alcohols at room temperature. Acyclic, cyclic, terpene, and steroid examples are reported. Yields are uniformly high (Tables I–III), and side reactions typically encountered in acid-catalyzed isomerizations are not observed. This method for allylically transposing oxygen functionality would appear to be the method of choice in cases where "classical" acid-catalyzed methods fail. When an excess of mercuric trifluoroacetate (1.1–3.0 equiv) is employed, a significant amount of the allylic carbamates is bound as covalent adducts. This observation forms the basis of a method for achieving contrathermodynamic allylic isomerizations (eq 3). The method is limited in scope and preparatively significant contrathermodynamic isomer enrichments were obtained only with the 2-alken-1-yl carbamates **3** and **18.** Future applications of this methodology are discussed in terms of the semiquantitative model of Scheme I. The mechanism of the mercury (II)-catalyzed allylic rearrangement is considered in detail. An ionization–recombination mechanism is ruled out by (a) the inability to detect allyl cation intermediates, (b) the formation of rearranged carbamates rather than amines, and (c) the inversion of the allyl fragment which is observed in the catalyzed rearrangement of thionocarbamate **27.** The experimental observations are most consistent with a mechanism (eq 8) in which the mercuric catalyst interacts with the carbon–carbon π bond to promote an intramolecular cyclization to yield a 1,3-dioxanium ion intermediate. We suggest the name cyclization-induced rearrangement for this catalysis mechanism (eq 6). More general implications of the cyclization-induced rearrangement mechanism are also considered.

Besides being one of the focal points for the evolution of mechanistic organic chemistry, the allylic rearrangement of allylic alcohols and their derivatives occupies a position of some importance in synthetic organic chemistry.[3] Often the more readily accessible allylic isomer is not the desired one. If in such cases, the desired isomer predominates at equilibrium, or is favored under kinetically controlled conditions, a synthetic strategy involving an allylic rearrangement may be utilized. The former version is the more common, and a typical example is illustrated in eq 1.[4] The early studies on the synthesis of vitamin A represent pioneering investigations of the use of allylic rearrangements in the natural products area.[5] The sulfuric acid catalyzed rearrangement of allylic alcohol **1** (R_1,R_2 = CH_3, C≡CH) to the conjugated isomer **2** (R_1,R_2 = CH_3, C≡CH)[6] was utilized in the original "C_{14}-aldehyde" route to vitamin A,[7] and multiple allylic rearrangements are characteristic features of more recent vitamin A total syntheses.[8] Allylic transpositions of oxygen functionality have found application in many natural products areas. The total syntheses of strychnine[9] and crinine[4] are notable examples in the alkaloid area,[10] and numerous illustrations are to be found in the terpene[11,12] and steroid fields.[13]



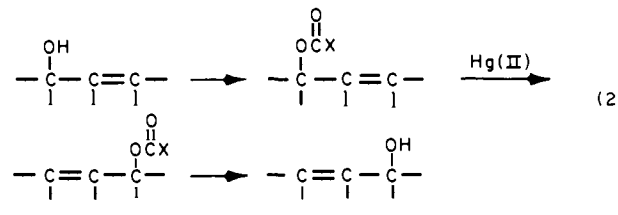
(1)

The classical method for effecting the allylic equilibration of an allylic alcohol or ester is the addition of a strong protic or Lewis acid catalyst,[3,5-8,11-13] In favorable cases this method succeeds splendidly, and near quantitative yields have been obtained,[8b] More typically, the yields are only moderate, as allyl cation (or ion-pair) intermediates[3] are diverted in part along other reaction pathways. Typically encountered side reactions are elimination to yield dienes,[3,13a,b,14] skeletal rearrangement,[3,15] cyclization,[3,16,17] and the formation of resinous materials.[3,14a] Although recent studies have recorded some success in suppressing these side reactions by the use of more selective protic acid catalyst mixtures[13b,17] and transition-metal catalysts,[18,19] the development of alternate solutions remains highly desirable.

Previous investigations from our laboratory have shown that allylic transpositions may be dramatically catalyzed by mercury(II) salts,[20,21] Since these transformations are not believed to involve allyl cation or related intermediates,[20] we anticipated that this methodology would be applicable to the allylic equilibration of oxygen functionality and would likely avoid many of the side reactions encountered in the "classical" acid-catalyzed methods. In this paper we report that these expectations have been realized. In particular, we show that mercuric trifluoroacetate is an effective catalyst at room temperature for the high-yield equilibration of *N,N*-dimethylcarbamic esters of allylic alcohols. We also report that in certain cases a modification of this process achieves a contrathermodynamic isomerization to specifically afford the terminal alkenic isomer. The mechanism of mercury(II) catalysis is considered in detail, and the experimental observations to date are shown to be most consistent with a cyclization-induced rearrangement process. The more general implications of this catalytic mechanism are also considered.

Results

Exploratory Studies. The general sequence is illustrated in eq 2. Previous investigations in our laboratory had shown that



(2)

alkyl and aryl esters underwent mercury(II)-catalyzed interconversion only very slowly at room temperature,[2] and as a result the more reactive[21] carbamic esters (X = NR_2) were utilized in this investigation. The allylic rearrangement of the *N,N*-dimethylcarbamic ester of (*E*)-2-hexen-1-ol (**3**) was chosen for our exploratory studies. Treatment of **3** at room temperature in THF with less than stoichiometric amounts of mercuric trifluoracetate resulted in the rapid formation of the

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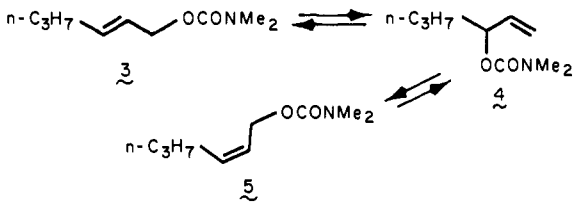
Table I. Mercury(II)-Catalyzed Isomerization of Hexenyl Carbamates **3**–**5**[a]

entry	carbamate (M)	equiv of HgX_2	reaction time, h	% carbamate recovery	product composition: % terminal alkene (**4**)	product composition: % internal alkene (**3** and **5**)	*E*/*Z* ratio (**3**:**5**)[b]
1	**3** (0.2)	0.4	0.3	90	28	72	
2	**3** (0.2)	0.4	3	89	35	65	
3	**3** (0.2)	0.4	5	91	38	62	
4	**3** (0.2)	0.6	5	86	37	63	
5	**3** (0.2)	0.06	5	100	12	88	
6	**3** (0.1)	0.35	4–6	100[c]	35[c]	65[c]	90:10[c]
7	**3** (0.1)	0.4	7	100	48	52	
8	**3** (0.1)	0.4	12–27	96	43	57	
9	**4** (0,1)	0.6	7	81	44	56	
10	**4** (0.15)	0.6	60–90	81[d,e]	41[d]	59[d]	
11	**4** (0.1)	0.9	7	70	44	56	
12	**4** (0.1)	0.35	24	90	48	52	90:10
13	**5** (0.1)	0.4	2	89	25	75	36:64
14	**5** (0.1)	0.4	91	67[f]	24	76	28:72
15	**5** (0.2)	0.6	4–9	70[g]	28	72	44:56
16	**3** (0.1)	$Hg(ClO_4)_2$ 0.4	1	46	28	72	90:10
17	**3** (0.1)	$Hg(ClO_4)_2$ 0.4	6	49	41	59	87:13
18	**3** (0.3)	$Hg(NO_3)_2$ 0.4	0.3	83	29	71	90:10
19	**3** (0.3)	$Hg(NO_3)_2$ 0.4	2–15	80[c]	39[c]	61	90:10

[a] In THF at room temperature. The catalyst was mercuric trifluoroacetate unless otherwise noted. Carbamate recoveries and isomer ratios were determined by GLC analysis (*p*-dichlorobenzene internal standard). [b] A dash indicates that this ratio was not determined. [c] Average of three determinations over the time period. Apparent equilibrium had been reached. [d] Average of seven determinations over the time period. Apparent equilibrium had been reached. [e] Hydrolysis products were detected: 1-hexen-3-ol (2–9%), (*E*)-2-hexen-1-ol (<1%). [f] Hydrolysis products were detected: 1-hexen-3-ol (19%). [g] Hydrolysis products were detected: 1-hexen-3-ol (7–14%).

isomeric carbamates **4** and **5**. Results are summarized in Table I.[22] The use of 0.4 equiv of mercuric trifluoroacetate yielded an isomer mixture whose composition became constant after approximately 4 h (entries 1–3 and 6). A similar mixture was obtained with 0.6 equiv of the mercuric catalyst; however, the use of 0.06 equiv of catalyst resulted in only partial conversion after 5 h. The overall recovery of the hexenyl isomers was excellent (>90%) when 0.4 equiv or less of catalyst was employed and decreased at higher catalyst concentrations and long reaction times. Treatment of **3** with 0.3 equiv of mercuric trifluoroacetate resulted in the formation of carbamate products only, since careful examination of the crude reaction mixture failed to detect the presence of 3-dimethylamino-1-hexene (0.3% detection limit). Similar, though not identical, isomer mixtures were obtained from mercuric trifluoroacetate treatment of the terminal hexenyl carbamate **4**. In this case,



longer reaction times were required before a constant isomer composition was obtained. The qualitatively similar isomer mixture (52 ± 4% **3**, 41 ± 3% **4**, 7 ± 1% **5**) obtained at long reaction times from both **3** and **4** (entries 3,4,6,8–11) approximates closely the expected[23,24] equilibrium isomer mixture. Similar conditions did not, however, totally equilibrate the cis isomer **5**. When long reaction times were employed (entries 14 and 15), carbamate hydrolysis by adventitious moisture became a significant side reaction. Unexpectedly, such hydrolysis afforded 1-hexen-3-ol almost exclusively.

Mercuric perchlorate and mercuric nitrate are also effective catalysts (entries 16–19). However, mercuric trifluoroacetate is the catalyst of choice, since isomer recoveries are higher with this reagent. A comparison of the initial rate of the mercuric trifluoroacetate catalyzed isomerization of **3** in THF with the thermal isomerization of several 2-butenyl derivatives[25] allows one to estimate[26] a rate enhancement of 10^{12}–10^{14} (1 M catalyst) for the catalyzed reaction.

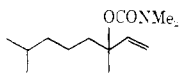
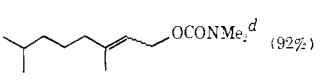
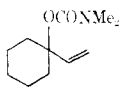
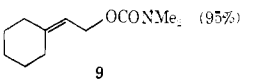
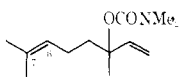
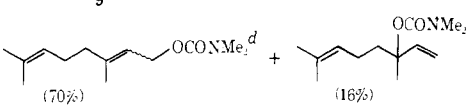
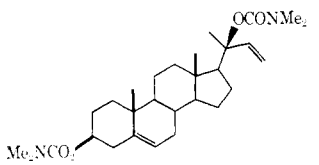
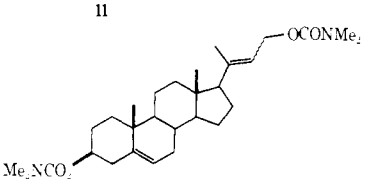
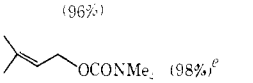
We next examined the extent to which the hexenyl carbamates were bound as mercury(II) adducts under these reaction conditions. In our previous experiments (Table I), products were analyzed by direct GLC analysis of reaction aliquots, and it was not clear, if such adducts were present, whether they would have been undetected or would have fragmented to alkenyl carbamates in the GLC injector. Mercuric trifluoroacetate is well established to reversibly form covalent adducts with alkenes in nonnucleophilic solvents,[27] and a number of mercuriophilic reagents [e.g., norbornene,[27a] pyridine,[27b] and triphenylphosphine (Ph_3P)][20,21] have been utilized to regenerate the alkene from such complexes. We thus felt that higher yields, and perhaps somewhat different isomer ratios, would be observed in mercuric trifluoroacetate catalyzed equilibrations if the catalyst was sequestered, and any bound alkene liberated, before product isolation or analysis. When low catalyst concentrations (0.3–0.4 equiv) were employed, quenching with Ph_3P, sodium borohydride, or methanol had only small effects on yield and product ratios (Table II). Although methanol and sodium borohydride are not expected to regenerate an alkene from a covalent mercury(II) adduct, they should detect the presence of such adducts by converting them to the corresponding methoxymercurated[28] or demercurated[29] compounds. We interpret these experiments to imply that when low catalyst concentrations are employed at most only small amounts of the hexenyl carbamates are bound.[30] The situation is very different at higher catalyst concentrations. Thus, while the carbamate recovery was only 78% after 1.6 h in an unquenched experiment (1.1 equiv of HgX_2) a quantitative carbamate recovery was observed under identical conditions

Table II. Mercuric Trifluoroacetate Catalyzed Isomerization of Hexenyl Carbamate **3.** Quenching with Mercuriophiles[a]

equiv of HgX_2	quenching agent (equiv)	reaction time, h	% carbamate recovery	quenched product composition: % terminal alkene (**4**)	quenched product composition: % internal alkene (**3** and **5**)	quenched product composition: E/Z ratio (**3**:**5**)
0.35	none	5.1	97	35	65	89:11
0.35	none	6.0	104	36	64	91:9
0.35	CH_3OH (20)[b]	6.8	102	36	64	91:9
0.30	$NaBH_4$ (6)[c]	4.7	90	29	71	97:3
0.30	Ph_3P (1.1)	9.0	95	35	65	94.6
1.1	none	1.6	78	42	58	83:17
1.1	none	5.2	74	45	55	84:16
1.1	none	17.0	63[d]	45[d]	55[d]	83:17[d]
1.1	pyridine (11)	2.3	79[e]	41	59	91:9
1.1	Ph_3P (4)[f]	2.3	101[e]	44	56	93:7
1.1	Ph_3P (4)[f]	5.2	88[g]	55	45	93:7

[a] In THF at room temperature. Initial carbamate concentration = 0.10 M. Carbamate recoveries and isomer ratios were determined by GLC analysis (*p*-dichlorobenzene internal standard). [b] The amount of **4** present decreases with time; 20 h after quenching it is present to the extent of only 17%. [c] Number of hydride equivalents. An aqueous solution of sodium borohydride (0.5 M $NaBH_4$, 3 M NaOH) was employed. [d] Average of two determinations made at 16.5 and 17.1 h. [e] Identical reaction aliquots were utilized in these two experiments. [f] Similar results were obtained when 2 equiv of Ph_3P was employed. [g] 1-Hexen-3-ol (ca. 10%) was also produced.

Table III. Preparative Scale Mercuric Trifluoroacetate Catalyzed Allylic Carbamate Isomerizations[a]

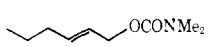
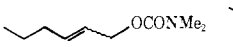
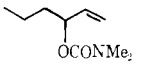
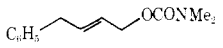
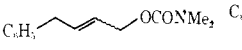
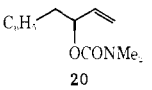
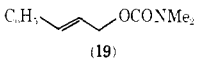
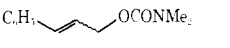
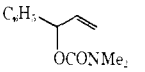
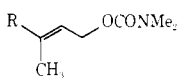
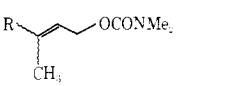
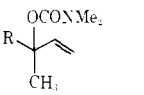
starting carbamate	conditions[b]: equiv of HgX_2	conditions[b]: time, h	products (isolated yield)[c]
 6	0.3	4	 (92%) 7
 8	0.3	2	 (95%) 9
 10	0.3 0.6	3 3	 (70%) + (16%) (73%) (4%) 11
 12	0.3	1	 13
 14	0.3	1	(96%)  (98%)[e] 15

[a] Yields have not been maximized. [b] In THF at room temperature. Carbamate concentration = 0.10 M. Reactions were quenched by adding 2.5 equiv of Ph_3P (per equiv of catalyst). [c] Yields refer to products purified by chromatography and bulb to bulb distillation or crystallization. [d] A 7:3 mixture of *E* and *Z* isomers. [e] GLC yield (*p*-dichlorobenzene internal standard), 1.5% of **14** was also present.

after 2.3 h when a Ph_3P quench was employed. Although the recoveries, as expected, were somewhat lower at longer reaction times, particularly noteworthy in the Ph_3P-quenched experiments was the increased formation of the terminal alkenyl isomer **4** (vide infra). *Clearly at higher catalyst concentrations significant amounts of the hexenyl isomers are bound as covalent adducts, and Ph_3P (but not pyridine) is an effective reagent for liberating bound alkene from such adducts.*

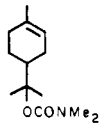
Synthetic Applications of Mercuric Trifluoroacetate Promoted Equilibrations. The exploratory hexenyl carbamate studies indicated that high-yield oxygen equilibrations should be possible under mild conditions if mercuric trifluoroacetate is employed at low concentrations and the mercuric catalyst is removed by complexation with Ph_3P before product isolation. The application of this method for the preparative scale isomerization of a representative group of tertiary allylic carbamates to their more stable, internal double-bond, isomers is summarized in Table III. The starting carbamic esters were prepared from the corresponding alcohol and dimethylcarbamyl chloride in good yield (>70%; see Experimental Section). In all cases, isomerization was achieved within a few hours at room temperature. The yields were nearly quantitative for all but the linalyl carbamic ester **10.** The lower yields, and the requirement for higher catalyst concentrations, observed with **10** are attributed to competing reactions (presumably oxidation)[31] at the 6,7 double bond. Of considerable significance is the total absence of cyclized products derived from the linalyl ester **10.** The *N,N*-dimethylcarbamic ester of α-terpi-

Table IV. Contrathermodynamic Isomerization of 2-Alken-1-yl *N,N*-Dimethylcarbamates. Excess Anhydrous Mercuric Trifluoroacetate Catalyst

	conditions[a]					product composition[c]		
starting isomer	concn M	equiv of HgX_2	solvent	time h	yield,[b] %	internal isomer, %	terminal isomer, %	internal isomer *E/Z* ratio[d]
 (3)							 4	
	0.1	1.1	THF	9	(80)	43	57	88:12
	0.1	1.1	THF	16	(98)	35	65	83:17
	0.1	1.1	THF	48	(81)	37	63	
	0.1	1.1	C_6H_6	8	89[e]	17	83	58:42
	0.1	3.0	THF	8	87	16	84	66:34
	0.1	3.0	THF	24	(80)	13	87	
	0.1	3.0	THF	72	(72)	13	87	
	1.0	3.0	THF	24	(98)	6	94	
	1.0	3.0	THF	24	75	5	95	
	1.0	3.0	THF	48	(80)	5	95	
 (18)							 20	
	0.1	1.1	THF	9	(88)	43	57	
	0.1	1.1	C_6H_6	8	86	29	71	
 (19)								
	0.1	1.1	THF	4–50	(>95)	100	0	
	0.1	1.1	C_6H_6	3–50	(50–70)	89	11	
 R = $(CH_2)_3CH(CH_3)_2$ (6)								
	0.1	3.0	THF	0.1	(61)	88	12	
	0.1	3.0	THF	0.25	(61)	85	15	
	0.1	3.0	THF	0.50	(48)	95	5	
	1.0	3.0	THF	0.03	(49)	67	33	
	1.0	3.0	THF	0.5	(28)	65	35	
	1.0	3.0	THF	2.0	(20)	82	18	
R = $(CH_2)_2CH{=}C(CH_3)_2$ (10)	0.1	1.1	THF	20	(68)	99	1	

[a] In THF at room temperature. Reactions were quenched with Ph_3P (2.5–3.6 equiv). [b] Isolated yield, after chromatography, of the isomer mixture. Yields in parentheses refer to precent recoveries based on GLC or ^1H NMR analysis. [c] The reported internal/terminal isomer ratios were determined by both ^1H NMR and GLC analysis. The two methods agreed within ±2%. [d] A dash indicates that this ratio was not determined. [e] 1-Hexen-3ol was formed in 3% yield. For all other table entries it was produced in only trace (<0.3%) amounts.

neol **16** was not observed by careful GLC analysis of the crude reaction mixture under conditions where 0.2% of this material was easily detected. The use of other carbamic esters was briefly explored. The methylcarbamate **17** (R = CH_3) behaved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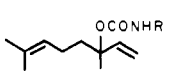
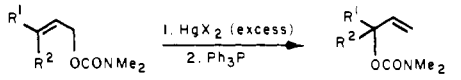

17

similarly to **10;** however, the corresponding phenyl carbamate **17** (R = C_6H_5) was clearly inferior. For example, treatment of **17** (R = C_6H_5) with 0.3 equiv of mercuric trifluoroacetate for 3 h resulted in only 35% conversion of the corresponding geranyl and neryl isomers, and only 50% conversion when 0.6 equiv of catalyst was employed. Hydrolysis of the product carbamates to the corresponding alcohols was demonstrated for carbamate **11** which was converted in 96% yield to a mixture of geraniol and nerol when treated with methanolic KOH.

Contrathermodynamic Allylic Isomerizations. The possibility of converting an internal allylic isomer to the less stable terminal alkenic isomer by use of excess mercuric trifluoroacetate and a Ph_3P quench was investigated (eq 3). The result of a


(3)

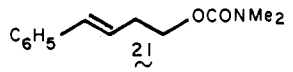
number of preparative scale experiments is summarized in Table IV. The conversion of the internal hexenyl carbamate **3** to the terminal isomer **4** was examined in greatest detail. Preliminary experiments indicated that isomer compositions became essentially constant after 8–24 h. As summarized in Table IV, the extent of conversion of a 0.10 M solution of **3** to the terminal isomer **4** increased with increasing mercuric trifluoroacetate concentration in THF, and for the same mercuric salt concentration was higher in benzene than THF. When 3.0 equiv of mercuric trifluoroacetate was employed, the terminal isomer yield was also greater when the starting carbamate concentration was 1.0 M. Under the best conditions (3.0 equiv of HgX_2, 1 M carbamate, THF), **3** was converted in 75% isolated yield to an isomer mixture which contained *95% of the less stable terminal isomer 4.*

Significant in the conversion of **18** to the terminal alkenic isomer **20** was the absence of the more stable styrene isomer

Table V. Treatment of Hexenyl Carbamate **3** with Acid Catalysts[a]

entry	carbamate concn, M	catalyst (equiv)	solvent	reaction time, h	% carbamate recovery	product composition: % terminal[b] carbamate (**4**)	product composition: noncarbamate[c] products
1	0.8	CF_3CO_2H (0.1)	THF	23	100	0	
2	0.2	CF_3CO_2H (33)	THF	4	89	2	$C_3H_7CH{=}CHCH_2OCOCF_3$ (2%)[d]
3	0.2	CF_3CO_2H (33)	THF	30[d]	61	5	$C_3H_7CH{=}CHCH_2OCOCF_3$ (15%)[d]
4	0.2	$BF_3{\cdot}Et_2O$ (0.5)	THF	12	100	1	
5	0.15	$BF_3{\cdot}Et_2O$ (0.5)	CH_2Cl_2	7	91	6	
6	0.15	$BF_3{\cdot}Et_2O$ (0.8)	CH_2Cl_2	18	63	14	
7	0.1	$BF_3{\cdot}Et_2O$ (1.2)	*m*-xylene	2.4	68	6	**26** ($C_{14}H_{20}$) (30%)
8	0.1	$BF_3{\cdot}Et_2O$ (1.2)	*m*-xylene	21	44	9	**26** ($C_{14}H_{20}$) (40%)
9	0.2	$Hg(OCOCF_3)_2$ (0.4)	*m*-xylene	3	98	39	*e*
10	0.2	$Hg(OCOCF_3)_2$ (0.4)	*m*-xylene	18	87	40	*e*

[a] At room temperature. Product compositions were determined by GLC analysis (*p*-dichlorobenzene internal standard). [b] Percentage of the recovered carbamate isomer mixture which is the rearranged terminal isomer. [c] A dash indicates none were detected. [d] An identical experiment starting with the terminal isomer **4** resulted in 5% isomerization to the internal isomer **3**. [e] No arylated hexene was detected, under GLC conditions where 1% was detectable.

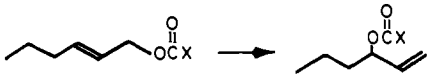


21

21 (2% would have been detected). Although the small conversions of the cinnamyl carbamate **19,** and the trisubstituted allylic carbamate **6,** to the corresponding terminal alkenic isomers represent significant enrichments in the less stable isomer, they are of no preparative significance. Isomer recoveries, moreover, decreased rapidly with time in the case of the trisubstituted isomers **6** and **10.**

The purity of the mercuric trifluoroacetate is critically important in these conversions which employ large amounts of this reagent. For example, treatment of carbamate **3** for 6 h in THF with 2.0 equiv of commercial mercuric trifluoroacetate (mp <160 °C, partially hydrated) resulted in significant carbamate hydrolysis: 1-hexen-3-ol and (*E*)-2-hexen-1-ol were formed in yields of 32 and 2%, respectively, after quenching with Ph_3P. The amount of hydrolysis obtained increased to 65% after 17 h in a similar reaction to which 5 equiv of water was added, This competing hydrolysis was totally suppressed if anhydrous mercuric trifluoroacetate (mp 166–168 °C; see Experimental Section) was employed, and standard precautions were taken to exclude atmospheric moisture.

Preliminary experiments revealed that terminal isomer enrichments could also be achieved with other allylic alcohol derivatives. For example, in a single experiment, treatment of the phenyl carbamate **22** with 1.2 equiv of mercuric trifluo-

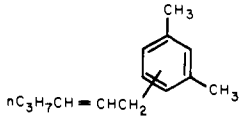


22, X = NHC_6H_5 **23**, X = NHC_6H_5

24, X = 4-$OCH_3C_6H_4$ **25**, X = 4-$OCH_3C_6H_4$

roacetate in THF for 19 h followed by a Ph_3P quench afforded, in 78% yield, a hexenyl isomer mixture containing 64% of the terminal isomer **23.** Similarly, treatment of anisate **24**[2] with 1.0 equiv of mercuric trifluoroacetate in benzene for 53 h afforded an isomer mixture (85% yield) containing 69% of the terminal isomer **25.**

Treatment of Carbamate 3 with Other Catalysts. Boron trifluoride etherate and trifluoroacetic acid were chosen as typical Bronsted and Lewis acid catalysts, and the results obtained when carbamate **3** was treated with these reagents are summarized in Table V. Carbamate **3** was uneffected by catalytic amounts of trifluoroacetic acid (a possible impurity in mercuric trifluoroacetate) in THF, and afforded only trace amounts of the rearranged carbamate **4** when the acid concentration was 6 M (entries 2 and 3). Carbamate **3** was similarly uneffected by catalytic amounts of boron trifluoride etherate in THF but was slowly converted to the terminal isomer in the less complexing solvent dichloromethane. In an effort to intercept intermediates formed by BF_3-promoted ionization, carbamate **3** was treated with 1.2 equiv of boron trifluoride etherate in *m*-xylene, Under these conditions, the arylated hexene **26** (a 3:1 mixture of isomers; see Experimental



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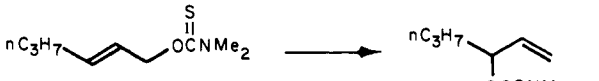
Section) was formed as the major product, and carbamate **3** was only partially equilibrated with the terminal isomer **4.** In contrast, similar treatment of **3** with mercuric trifluoroacetate in *m*-xylene resulted in the rapid and high-yield formation of the equilibrium mixture of hexenyl carbamate isomers (entries 9, 10). *Significantly, the arylated product* ***26*** *was not produced in the mercury(II)-catalyzed reaction.*

Catalyzed Rearrangement of Thionocarbamates. The related rearrangement of allyl thionocarbamates[32] is catalyzed by mercuric trifluoroacetate at room temperature. Treatment of thionocarbamate **27** with 0.3 equiv of mercuric trifluoroacetate for 12 h followed by quenching with Ph_3P afforded thiocarbamate **28** in 52% isolated yield. Careful GLC analysis of the



27 **28**

crude reaction mixture showed that the thiocarbamate with an unrearranged 2-hexen-1-yl carbon skeleton was formed in trace amounts (<5%) only, and that 3-dimethylamino-1-hexene was not produced.

Discussion

Synthetic Applications of Mercuric Trifluoroacetate Catalyzed Equilibrations of Oxygen Functionality. The yields obtained in the mercuric trifluoroacetate catalyzed allylic carbamate equilibration are uniformly good, and isolated yields (after chromatography and bulb to bulb distillation) are often greater than 90% (Table III). These represent some of the highest yields ever reported for the allylic isomerization of oxygen functional groups,[3-18] *In no case have products arising*

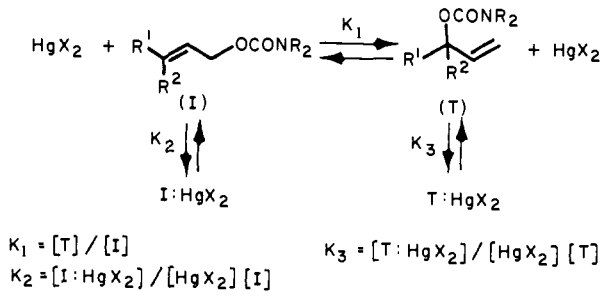
from cyclization, or hydrogen, alkyl, or aryl migration been detected. Carbamic esters of primary, secondary, and tertiary alcohols are successfully equilibrated by the mercury(II)-catalyzed procedure at room temperature. In contrast the acid-catalyzed isomerization of primary and secondary (but not tertiary) allylic alcohols and their ester derivatives generally requires elevated temperatures,[3]

As a method for allylic alcohol equilibration, the mercury(II)-catalyzed carbamate equilibration is noteworthy, since strongly acidic conditions are not required. However, this methodology has the serious disadvantage that the carbamic ester intermediate must be prepared and ultimately cleaved. As a result, for allylic alcohols for which "classical" acid-catalyzed isomerization succeeds, the more complex (and expensive) mercury(II)-promoted process offers no practical advantage. However, in cases where skeletal rearrangement, cyclization, or elimination are menacing complications, or where intramolecular delivery of the allylic oxygen offers stereochemical advantages, the mercuric trifluoroacetate catalyzed process would appear to be the method of choice. With this methodology, linalool was converted in 60% overall yield to a mixture of geraniol and nerol which was uncontaminated with cyclic terpene isomers. In contrast, rearrangement of linalool or linayl acetate is accomplished in only low to moderate yield by protic or Lewis acid catalysis, with cyclic terpene isomers being formed in significant amounts,[16] often as the major products.[17,33] The advantages of the mercury(II) methodology are also apparent in the allylic rearrangement of the carbamic ester **12** of 20-vinylpregn-5-ene-3β,20*S*-diol (**43**) to afford **13** in 96% isolated yield. Tertiary C-20 sterols are notorious for the ease with which they undergo dehydration and skeletal rearrangement.[34] In a recent study, sterol **43** was reported to be converted exclusively to diene products when treated with a dioxane solution of sulfuric acid and under the best conditions afforded only a 50% yield of the rearranged allylic alcohol.[13a]

Contrathermodynamic Allylic Isomerizations. Catalyzed Equilibration and Selective Binding. Equilibrium constants for the formation of covalent alkene-mercuric trifluoroacetate adducts have been measured in THF[27a] and benzene.[27b] These formation constants are considerably higher for mono- than disubstituted alkenes and in general decrease with increasing double-bond substitution. One would thus anticipate that treatment of an internal allylic isomer, such as the hexenyl carbamate **3,** with an excess of mercuric trifluoroacetate, followed by the addition of a mercuriophile should yield an isomer mixture rich in the less stable terminal isomer **4.** That is, the excess catalyst is expected to preferentially trap the terminal alkene isomer as a covalent adduct,[35] thus, selectively removing it from the equilibrating isomer pool. This expectation has been realized (Table IV), and **3** was converted virtually completely to the less stable terminal isomer **4** by this method. Although similar results were obtained with carbamate **18,** only modest success was realized with the cinnamyl carbamate **19** and the trisubstituted alkenic carbamate **6.** Preparatively significant contrathermodynamic allylic isomer enrichments were obtained only for the conversion of carbamic esters of 2-alken-1-ols, which contain a disubstituted double bond, to the corresponding 1-alken-3-ol derivatives.

A general description of the product mixture produced when an allylic carbamate is treated with a mercuric salt is depicted in Scheme I, where T:HgX_2 and I:HgX_2 represent the covalent adducts produced from mercuric trifluoroacetate and the terminal and internal alkenic isomers, respectively.[35] If R^1 and R^2 are not identical, such a scheme could be elaborated to include both the cis and trans internal allylic isomers and their corresponding HgX_2 adducts. In terms of Scheme I, our interpretation of the observed effects of catalyst concentration on isomer composition goes as follows. At low catalyst concentrations in THF, quenching with the mercuriophile Ph_3P has little effect on isomer composition, since little of the alkene isomers are bound as covalent adducts. Steady-state isomer compositions attained in this way, therefore, approximate equilibrium values. At high catalyst concentrations, on the other hand, significant amounts of the alkenic isomers are bound as HgX_2 adducts. When such a reaction mixture is quenched with Ph_3P, the amount of each isomer produced represents the sum of the amount which was free in solution and bound as an HgX_2 adduct. Since $K_3 \gg K_2$, the amount of terminal isomer produced increases as a larger fraction of the alkene isomers is bound. Quantitative calculations based on this scheme are instructive. These are easily accomplished (see Experimental Section) if K_2 and K_3 can be estimated, and in cases where $R^1 \neq R^2$ the internal isomers are grouped together.[36] Direct measurements of K_2 and K_3 are not generally possible, since the mercuric salt promotes interconversion of the allylic isomers. Table VI summarizes a few such calculations, in which K_2 and K_3 were estimated using literature values for internal and terminal alkenes as models for the allylic carbamates.[27a] Before discussing these results it is important to realize that this model is expected to overestimate the amount of the alkene isomers which are bound as covalent adducts since non-hydrogen (i.e., $OCONR_2$) substitution at the allylic position is expected to decrease the equilibrium constants for HgX_2 adduct formation.[27a]

Scheme I



Although the terminal isomer compositions predicted by Scheme I are, as expected, somewhat greater than actually observed, the calculated effect of the mercuric trifluoroacetate-carbamate molar ratio and the starting carbamate concentration parallel nicely the experimental results obtained with the hexenyl carbamates. The calculated terminal isomer compositions for the isomerization of **3** at 0.1 M correspond to having 50% and >99% of the hexenyl isomers bound as covalent adducts when 0.3 and 3.0 equiv, respectively, of catalyst are employed. Equilibrium constants for forming mercuric trifluoroacetate-alkene adducts appear to be higher in the less coordinating solvent benzene than THF; however, few examples have been studied.[27] Calculations similar to those of Table VI for this solvent would reproduce the experimentally observed trend of greater terminal isomer enrichment in benzene than THF, since a larger fraction of the hexenyl isomers would be bound, at similar catalyst concentrations, in the former solvent. Particularly interesting are the results calculated for the cinnamyl carbamate **19.** Clearly, if the thermodynamic equilibrium strongly favors the internal alkenic isomer, even unattainably large catalyst concentrations are predicted to afford only modest yields of the less stable terminal isomer, as was observed. This result obtains in spite of the fact that nearly all the alkene isomers would be bound as covalent adducts (e.g., 80 and 99.4% at 3.0 and 100 equiv of catalyst, respectively) under these conditions. A similar lack of success in achieving synthetically useful terminal isomer yields is predicted for the trisubstituted alkenic carbamate **6.** In this case, the larger equilibrium constant K_1 is offset by the lower HgX_2 binding affinity for the 3-methyl-substituted terminal isomer.

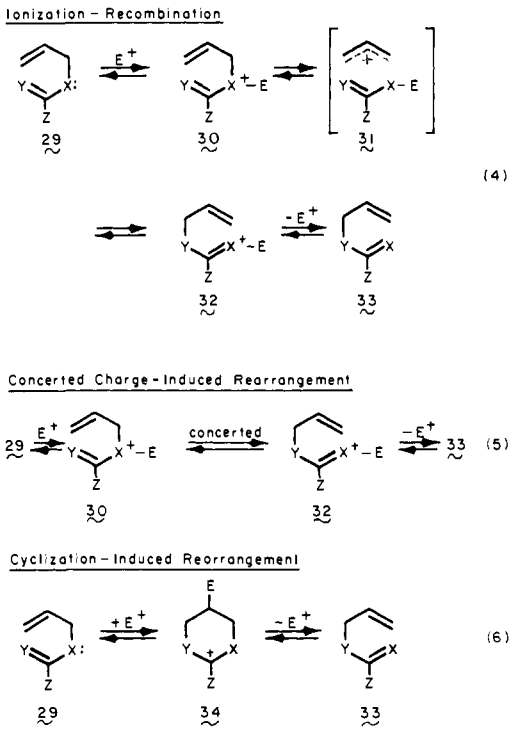
Table VI. Calculated Isomer Compositions in THF According to Scheme I

starting internal isomer	concn, M[a]	$[HgX_2]$ M[b]	K_1	K_2, M^{-1}	K_3, M^{-1}	calcd terminal isomer content, %	obsd terminal isomer content, %[c]
3	0.1	0.001	0.7[d]	9.2[e]	830[f]	42	
	0.1	0.01				47	
	0.1	0.03				58	41
	0.1	0.11				92	65
	0.1	0.30				97	87
	1.0	1.1				97	
	1.0	3.0				98	95
19	0.1	0.11	0.005[g]	14[h]	830[f]	12	0
	0.1	0.3				18	
	0.1	10.0				23	
6	0.1	0.3	0.015[i]	4.4[j]	93[k]	15	(5-15)[l]
	0.1	10.0				27	
	1.0	3.0				22	(18-35)[l]

[a] Initial internal allylic carbamate concentration. [b] Initial mercuric trifluoroacetate concentration. [c] After quenching with Ph_3P. [d] The cis and trans internal isomers are treated together. [e] For *trans*-2-hexene.[27a] For 1-hexene.[27a] [g] The thermodynamic equilibrium constant for the corresponding isomeric acetates.[24] [h] For styrene. [i] From the equilibrium ratio of **14** and **15** at low HgX_2 concentration (Table III). [j] For 1-methylcyclohexene.[27a] [k] For 3,3-dimethyl-1-butene.[27a] [l] Isomer recoveries were low and changed rapidly with time.

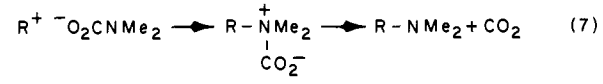
The results of these simple calculations would appear to be useful guides for any subsequent investigations of this method for contrathermodynamic allylic isomerization. In cases where the two isomers are energetically close, the terminal-internal binding selectivity exhibited by mercuric trifluoroacetate is sufficient to achieve essentially quantitative isomerization to the terminal isomer if the conditions are chosen such that all the alkene isomers are bound as HgX_2 adducts. However, if the thermodynamic equilibrium to overcome is highly unfavorable, a binding agent of greater selectivity will be required. We note that, in principle, the same agent need not be employed to effect both isomer equilibration and selective binding.[37]

Mechanism of the Mercury(II)-Catalyzed Rearrangement. That electrophiles may catalyze what are formally [3,3]-sigmatropic rearrangements[38,39] has been noted for years.[3,20,21,40-43] At least three general mechanisms have been suggested, These are illustrated in eq 4-6 for the specific case of a 1,5-unsaturated system with a heteroatom at position 3 (e.g., allylic carbamate, allyl vinyl ether, etc.), In the catalytic mechanisms of eq 4 and 5, the electrophilic catalyst is suggested to bind with the substrate at the heteroatom X.[44] In the *ionization-recombination* mechanism, such complexation promotes heterolysis of the carbon-X bond of complex **30** to yield **31,** which can recombine at atom Y to give the rearranged complex **32** and ultimately **33.** The acid-catalyzed rearrangement of allylic esters is a good example of a reaction which is believed to proceed in this fashion, and numerous studies over the past 20 years have dealt with the exact nature of the intermediate **31.**[3] Such a mechanism would be expected to afford mixtures of regioisomers in cases where $X \neq Y$, as well as other allyl cation-derived products. Another possibility, termed a *charge-induced* [3,3]-sigmatropic rearrangement by Schmid, Hansen, and co-workers,[43a] is for the complex **30** to rearrange concertedly to **32.** Catalysis would be observed if **30** underwent concerted thermal rearrangement more rapidly than the uncomplexed starting material.[41a,42,43a,45] The concerted charge-induced rearrangement mechanism has been suggested for trifluoroacetic acid[41c] and boron trichloride[41a] catalyzed aromatic Claisen rearrangements and for sulfuric acid[42b] and zinc chloride[42a] catalyzed aromatic amino Claisen rearrangements. A third totally different mechanism, for which we suggest the name *cyclization-induced rearrangement,* is outlined in eq 6. In this mechanism, the electrophilic catalyst rather than complexing with the heteroatom X, interacts with the carbon-carbon π bond to promote an intramolecular cyclization to yield **34** as a pivotal intermediate.[46] Fragmentation of the cyclic intermediate **34** in the alternate sense would yield the rearranged product **33.** To our knowledge a cyclization-induced rearrangement mechanism was first suggested by Henry[47] in a kinetic study of the palladium(II)-catalyzed isomerization of allylic propionate esters. We have subsequently proposed a cyclization-induced mechanism for the mercury(II)-catalyzed [3,3]-sigmatropic rearrangement of allylic imidates,[20] and a related mechanism was recently suggested by Lutz[43e] for a Cope rearrangement catalyzed by alumina.[48-50]



An ionization-recombination mechanism for the mercury(II)-catalyzed allylic carbamate rearrangement is easily ruled out by the following observations. (*a*) *Failure to trap allyl cation intermediates.* Arylated hexenes were not formed when the hexenyl carbamate **3** was treated for 8 h with mercuric trifluoroacetate in *m*-xylene. Such treatment yielded the

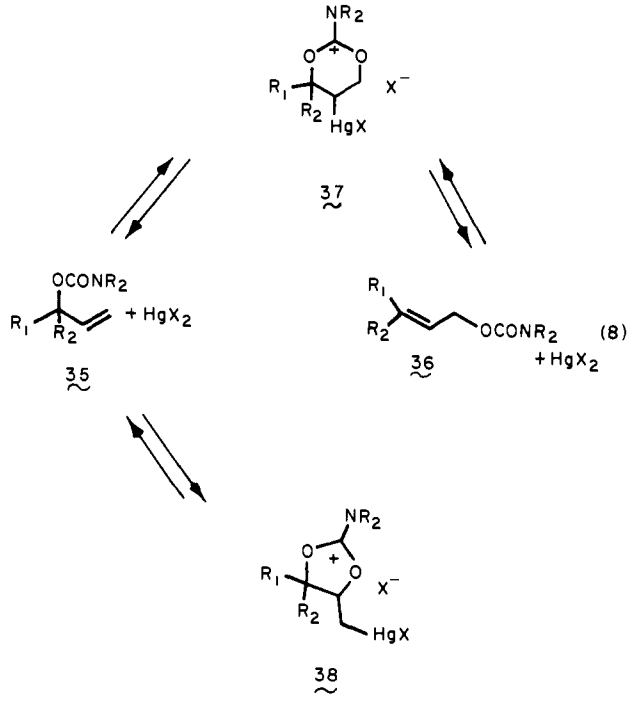
equilibrium mixture of hexenyl carbamates within 2 h and thus provides a sensitive test for the intervention of trappable intermediates,[51,52] since numerous isomer interconversions occurred under these conditions. In contrast, treatment of carbamate **3** in *m*-xylene with boron trifluoride etherate gave as major products the arylated hexenes **26.** Intramolecular traps have also failed to detect the presence of allyl cation intermediates in the mercury(II)-catalyzed process. For example, mercuric trifluoroacetate treatment of the *N,N*-dimethyl carbamic ester (**10**) of linalool yielded the allylically rearranged acyclic geraniol and nerol isomers **11** rather than the cyclic α-terpienol derivative **16.** Cyclization is the characteristic reaction of allyl cation intermediates formed from ionization of linalyl, geranyl, and neryl derivatives.[16,17,33] (*b*) *The formation of rearranged carbamates rather than amines.* The mercuric trifluoroacetate catalyzed rearrangement afforded allylic carbamate products in high yield (Tables I–III). In the case of the rearrangement of carbamate **3,** 3-dimethylamino-1-hexene was specifically looked for and shown not to be present (<0.3%). If rearrangement had occurred via an ionization–recombination process, the formation of amines would have been expected (eq 7).[53,54] (*c*) *Inversion of the allylic fragment.* Mercuric trifluoroacetate catalyzed rearrangement of thionocarbamate **27** was highly regiospecific. Similar regiospecificity was observed in the mercuric trifluoroacetate catalyzed rearrangement of trichloroacetimidic esters of 2-alken-1-ols.[20]



(7)

A cyclization-induced or concerted charge-induced rearrangement mechanism would be consistent with the observations summarized above. Both mechanisms involve intramolecular reorganization of a catalyst–substrate complex and thus avoid the formation of allyl-cation intermediates. Although these mechanisms differ in both the structure of the catalyst–substrate complex and the timing of bond-making and bond-breaking steps, unambigous distinction between the two processes, although certainly possible, is not simple. A particularly difficult complication is the likely possibility that, if intramolecular cyclization does occur, the favored mode of cyclization would be to form the "nonproductive" cyclic complex **38.**[55] This represents nothing more than a detour on the cyclization-induced rearrangement pathway (**35** → **37** → **36**), since **38** would have no reaction alternative available to it, except reversal to the starting components. The intervention of **38,** however, seriously complicates experiments addressed at trapping[56] or detecting the catalytically "productive" cyclic complex **37.**[57]

Although a concerted charge-induced rearrangement mechanism cannot be unambiguously ruled out, we favor a cyclization-induced rearrangement mechanism for the mercury(II)-catalyzed allylic carbamate rearrangement for several reasons: (a) Mercury(II) salts are well known to promote the addition of a variety of oxygen nucleophiles to carbon–carbon π bonds,[58] and numerous intramolecular examples have been reported.[59] Deoxymercuration is also known to be rapid in oxymercurated adducts derived from mercuric trifluoroacetate,[27,59] Thus, both steps of the cyclization-induced rearrangement mechanism are well precedented if the electrophile is mercuric trifluoroacetate and the solvent is nonnucleophilic. (b) The cyclic adduct **37,** a 1,3-dioxanium ion, should be a reasonably stable reaction intermediate. 1,3-Dioxanium ions have been isolated as crystalline perchlorate salts.[60] (c) Mercuric trifluoroacetate and mercuric nitrate are dramatically more effective, at comparable concentrations, than trifluoroacetic acid or boron trifluoride etherate in promoting the rearrangement of carbamate **3.** This trend is consistent with



(8)

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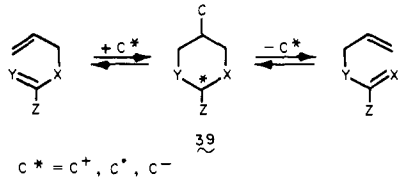
the great efficiency of mercury(II) salts in promoting the addition of nucleophiles to carbon–carbon π bonds,[58]

General Implications of Cyclization-Induced Catalysis. The cyclization-induced rearrangement mechanism may be a general pathway for electrophile-catalyzed [3,3]-sigmatropic rearrangements and clearly has been neglected in past considerations of these catalyzed transformations.[40–43] For example, a cyclization-induced rearrangement mechanism does not appear to be ruled out by the variety of evidence amassed and used to support the concerted charge-induced rearrangement pathway for the acid-catalyzed aromatic Claisen[41] and amino Claisen[42] rearrangements.[61] In general, one would expect "soft" electrophiles[62] with their higher affinities for carbon–carbon π-bond complexation to favor a cyclization-induced rearrangement pathway, while "hard" electrophiles, with their higher affinities for heteroatom complexation, should favor ionization–recombination or concerted charge-induced rearrangement pathways.

Anionic and free-radical agents, in principle, could also catalyze [3,3]-sigmatropic rearrangements by cyclization-induced pathways, eq 9. To our knowledge nucleophilic (or

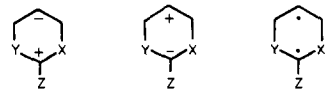


(9)

39

C* = C⁺, C·, C⁻

base) catalysis[63] of this type has not been suggested. We also note that formally the cyclic intermediates **39** may be considered as resulting from σ bond formation between a catalyst C* and the dipolar or diradical intermediates **40–42.** This view



40 **41** **42**

of cyclization-induced catalysis is of particular interest in light of recent evidence that both 1,4-cyclohexadiyls[64,65] and 1,4-cyclohexazwitterions[66] may be intermediates in a number of thermal [3,3]-sigmatropic rearrangements.

Conclusion. Mercuric trifluoroacetate is an effective catalyst

for promoting the equilibration of allylic carbamate esters at room temperature. Yields are uniformly high, and side-reactions typically encountered in acid-catalyzed isomerizations, such as skeletal rearrangement, cyclization, and elimination, are not observed. This method for the allylic transposition of oxygen functionality would appear to be the procedure of choice in cases where "classical" acid-catalyzed methods fail. A modification of this procedure, which utilizes mercuric trifluoroacetate in molar excess amounts, provides in some cases a method for achieving contrathermodynamic allylic isomerizations.

The mechanism of the mercury(II)-catalyzed allylic rearrangement was considered in detail. The experimental observations to date are most consistent with a mechanism (eq 8) in which the mercuric catalyst interacts with the carbon–carbon π bond to promote an intramolecular oxymercuration to form the 1,3-dioxanium ion **37** as the central intermediate. The name *cyclization-induced rearrangement* is proposed for catalysis mechanisms of this type. The concept of cyclization-induced catalysis is a potentially general one (eq 9), and we suggest that a variety of catalyzed reactions may follow this course.

Experimental Section

Allylic and propargylic alcohols (purity 97% or better) were purchased from Aldrich Chemical Co. or Chemical Samples Co. (*Z*)-2-Hexen-1-ol was prepared by catalytic hydrogenation ($Pd/BaSO_4$) of 2-hexyn-1-ol and was purified by preparative gas liquid chromatography (GLC). 1-Phenyl-2-propen-1-ol and 3,7-dimethyl-1-octen-3-ol were prepared by Grignard addition of vinylmagnesium bromide.[67] (*E*)-4-Phenyl-2-buten-1-ol was prepared by diisobutylaluminum hydride reduction[68] of ethyl 4-phenyl-2-butenoate[69] and was purified by preparative GLC. (20*S*)-20-Vinylpregn-5-ene-3β,20-diol (**43**) was prepared from pregnenolone acetate as described.[13a] Tetrahydrofuran (THF) was distilled from sodium and benzophenone immediately before use. Benzene was distilled from calcium hydride and stored over activated type 4A molecular sieve. Anhydrous mercuric trifluoroacetate (mp 166–167 °C) was prepared by the procedure of Brown[28] and could be stored in vials desiccated over KOH for up to 9 months with little depression (mp 165–168 °C) in the melting point. Some samples of commercial material contain considerable water and melt as low as 100 °C. Such samples can be purified by recrystallization from trifluoroacetic acid and vacuum drying over KOH. It is essential that anhydrous mercuric trifluoroacetate (mp >165 °C) be used. Mercuric nitrate and mercuric perchlorate were purchased from Aldrich Chemical Co. and Ventron Corp., respectively, and were used as received. *N,N*-Dimethylcarbamyl chloride was purified by distillation (bp 47 °C, 10 mm).

Microanalyses were performed by Chemalytics, Tempe, Ariz., or Galbraith Laboratories, Knoxville, Tenn. Analyses agreed with the theoretical values within ±0.3% unless otherwise noted. High-resolution mass spectra were obtained from the Research Triangle Institute, N.C. Melting points were determined in sealed capillaries with a Thomas-Hoover capillary melting point apparatus, which was calibrated with known standards.

Proton magnetic resonance (^{1}H NMR) spectra were recorded at 60 MHz on either a Varian A-56/60 or EM-360 spectrometer using tetramethylsilane as the internal reference. Chemical shifts are given as δ values in ppm relative to tetramethylsilane = 0. Apparent coupling constants (J) are reported in Hz; abbreviations used are: s, singlet; d, doublet; t, triplet; m, multiplet. Infrared spectra were recorded with either a Perkin-Elmer Model 137 or Beckman Acculab 2 spectrometer. Hewlett-Packard Models 5771A and 5700 dual flame-ionization detector (FID) gas chromatographs and a Varian Model 3700 gas chromatograph equipped with a differential thermal-conductivity (TC) detector were used for analytical gas chromatographic analyses (GLC). A Varian Aerograph Model 90-P gas chromatograph was used for preparative GLC. GLC chromatogram peak areas were determined either with a DISC integrator or by the Xerox-cut-weigh method. All quantitative GLC experiments were performed with *p*-dichlorobenzene as the internal standard and were corrected for detector response. When the FID detector was employed, the response factors were determined every few days.

Thin-layer (TLC) and preparative-layer TLC chromatography separations were done with E. Merck silica gel (GF- and PF-254). Dry column chromatography used Woelm silica gel for dry column chromatography, or W. R. Grace silica gel (grade 62) to which a fluorescent indicator was added.

All reactions were performed under a nitrogen atmosphere, and solvent transfers were with a syringe. Concentrations were done using a rotary evaporator at reduced pressure. Bulb to bulb distillations were carried out at <150 °C (<0.01 mm) in a Kugelrohr apparatus.

Preparation of *N,N*-Dimethylcarbamates. In our early experiments, *N,N*-dimethylcarbamates were prepared by adding a THF solution of the lithium (from butyllithium) or sodium (from NaH) alkoxide to a THF solution of *N,N*-dimethylcarbamyl chloride. The use of the potassium alkoxide (from KH) and a normal addition procedure, however, is preferred, since this procedure is simpler, the reaction is considerably faster with tertiary alcohols, and yields are higher. A representative procedure utilizing KH is detailed below.

3,7-Dimethyl-1,6-octadien-3-yl *N,N*-Dimethylcarbamate (10). (Linalyl Carbamate) Preferred KH Procedure. A suspension of potassium hydride [1.16 g of a 22.7% dispersion in oil (29 mmol), previously washed with hexane] and 10 mL of dry THF was added dropwise (double-needle transfer) at −10 to 0 °C to a stirred solution of 3.58 g (23.2 mmol) of linalool (3,7-dimethyl-1,6-octadien-3-ol) and 20 mL of THF. Addition was complete within 30 min, and the mixture was allowed to warm to room temperature, maintained there for 30 min, and recooled to −10 °C. *N,N*-Dimethylcarbamyl chloride (2.35 mL, 25.5 mmol) was added dropwise while maintaining the temperature between −10 and 0 °C. The cooling bath was removed and the progress of the reaction was followed by GLC.[70] After 1 h at room temperature, the reaction mixture was diluted with 100 mL of ether, washed with saturated sodium bicarbonate solution, dried ($MgSO_4$), and concentrated to afford 4.96 g of a yellow liquid which contained 4.25 g of **10** (81%) by GLC analysis (biphenyl internal standard), with the remainder being unreacted starting material. Bulb to bulb distillation of a 206-mg sample afforded 200 mg of **10** (86% pure). The analytical sample was prepared by spinning-band distillation (55 °C, 0.01 mm): ν_{max} (film) 1710 (C=O) and 1200 cm$^-$ (CO); ^{1}H NMR ($CDCl_3$) δ 6.00 (apparent dd, J = 17 and 10 Hz, $-CH{=}CH_2$), 4.8–5.3 (complex m, C-1 and C-6 hydrogens), 2.85 [s,$N(CH_3)_2$], 1.55 (s, CH_3), 1.60 (s, CH_3), and 1.67 (s, CH_3). Anal. ($C_{13}H_{23}NO_2$) C, H, N.

The following carbamates were prepared in a similar fashion.

1-Vinylcyclohexyl *N,N*-dimethylcarbamate (8) was prepared as above in 75% yield (>95% pure by ^{1}H NMR). The analytical sample was prepared by spinning-band distillation (83 °C, 0.2 mm): ν_{max} (film) 1700 (C=O), 1190 (CO), 917 and 984 cm^{-1}($-CH{=}CH_2$); ^{1}H NMR (CCl_4) δ 6.10 [apparent dd, J = 10 and 18 Hz, $-CH{=}CH_2$), 4.7–5.2 (m, $-CH{=}CH_2$), 2.80 (s, $N(CH_3)_2$]. Anal. ($C_{11}H_{19}NO_2$) C, H, N.

3,7-Dimethyl-1-octen-3-yl *N,N*-dimethylcarbamate (6) was prepared as above in 84% yield (98% pure by GLC[70]). The analytical sample was prepared by spinning-band distillation (90 °C, 0.01 mm); ν_{max} (film) 1702 (C=O), 1190 (CO), 913 and 990 cm^{-1} ($-CH{=}CH_2$); ^{1}H NMR ($CDCl_3$) δ 6.00 (apparent dd, J = 10 and 17 Hz, $-CH{=}CH_2$), 4.8–5.3 (m, $-CH{=}CH_2$), 2.85 [s, $N(CH_3)_2$], 1.52 (s, CCH_3), 0.86 [d, J = 5 Hz, $CH(CH_3)_2$]. Anal. ($C_{13}H_{25}NO_2$) C, H, N.

(20*S*)-20-Vinylpregn-5-ene-3β,20-diol *N,N*-dimethylcarbamate (12). A solution of diol **43**[13a] (2.50 g, 7.24 mmol) and 8 mL of dry hexamethylphosphoramide was treated dropwise at room temperature with 3.5 mL of a mineral oil suspension of potassium hydride (24% in oil, 490 mg, 18.2 mmol). After stirring for 1 h, 4.68 g (43.6 mmol) of *N,N*-dimethylcarbamyl chloride was added dropwise. After 24 h no **43** remained (TLC analysis, 1:1 hexane–ethyl acetate) and the reaction mixture was diluted with ether, washed with water, dried (Na_2SO_4), and concentrated to afford 3.52 g of a yellow semisolid material. TLC analysis (1:1 hexane–ethyl acetate) showed the presence of two products, R_f 0.7 (monocarbamate) and R_f 0.6 (dicarbamate), and this sample was therefore resubmitted to the identical carbamylation conditions. Recrystallization of the crude product (3.96 g) thus obtained afforded 2.84 g (81%) of a white solid, mp 178–184 °C. Quantitative ^{1}H NMR analysis showed that this sample of **12** was contaminated with 10% of the corresponding monocarbamate. An analytical sample of **12** was prepared by preparative layer chromatography (85:15 hexane–ethyl acetate, developed three times) and recrystallization from ethyl acetate: mp 190–191 °C; ν_{max} (KBr) 1704

(C=O), and 1190 cm^{-1}(CO); ^1H NMR ($CDCl_3$)δ 6.08 (q, J = 19 and 10.5 Hz, -CH=CH_2), 5.3-4.8 (complex m, -CH=CH_2 and C-6 hydrogen), 4.46 (m, C-3 hydrogen), 2.87 [s, $N(CH_3)_2$]. Anal. ($C_{29}H_{46}N_2O_4$)C, H, N.

(*E*)-2-Hexen-1-yl *N,N*-dimethylthioncarbamate (27) was prepared as above in 79% yield from (*E*)-2-hexen-1-ol and dimethylthiocarbamoyl chloride. Purification was achieved by chromatography on silica gel (9:1 hexane-ethyl acetate): ν_{max} (film) 1520 (C=S) and 1180 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 5.5-5.8 (m, CH=CH), 4.75 (d, J = 5 Hz, $-CH_2O-$), 3.26 (s, NCH_3), 3.07 (s, NCH_3). Anal. ($C_9H_{17}NOS$) C, H, N.

The following carbamates were prepared in 45-84% yield using *n*-butyllithium or sodium hydride to form the alkoxide. Details may be found in reference 2.

(*E*)-2-Hexen-1-yl *N,N*-Dimethylcarbamate (3). Purified by column chromatography on silica gel (benzene-acetone): 99.1% pure by GLC;[72] ν_{max} (film) 1704 (C=O), 1190 (CO), and 976 cm^{-1} (*trans*-CH=CH-); ^1H NMR ($CDCl_3$) δ 5.3-6.1 (m, -CH=CH-), 4.52 (d, J = 6 Hz, $-CH_2O-$), 2.90 [s, $N(CH_3)_2$]. Anal. ($C_9H_{17}NO_2$) C, H, N.

1-Hexen-3-yl *N,N*-Dimethylcarbamate (4). Purified by preparative GLC:[71] 98% pure by GLC;[72] ν_{max} (film) 1704 (C=O), 1183 (CO), 990 and 926 cm^{-1} (-CH=CH_2); ^1H NMR ($CDCl_3$) δ 5.0-6.2 (m, vinylic hydrogens and >CHO-), 2.90 [s, $N(CH_3)_2$]. Anal. ($C_9H_{17}NO_2$) C, H, N.

(*Z*)-2-Hexen-1-yl *N,N*-Dimethylcarbamate (5). Purified by preparative GLC:[71] 99.3% pure by GLC;[72] ν_{max} (film) 1704 (C=O), 1179 (CO), and 767 cm^{-} (*cis*-CH=CH-); ^1H NMR ($CDCl_3$) δ 5.2-5.8 (m, -CH=CH-), 4.60 (d, J = 6 Hz, $-CH_2O-$), 2.85 [s, $N(CH_3)_2$]. Anal. ($C_9H_{17}NO_2$) C, H, N.

(*E*)-3,7-Dimethyl-2,6-octadien-1-yl *N,N*-Dimethylcarbamate [(*E*)-11]. Purified by chromatography on silica gel (hexane-ethyl acetate) and bulb to bulb distillation: 99.5% pure by GLC;[72] ν_{max} (film) 1704 (C=O) and 1180 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 4.8-5.3 (m, two vinylic hydrogens), 4.57 (d, J = 7 Hz, $-CH_2O-$), 2.87 [s, $N(CH_3)_2$], 1.68 and 1.58 (singlets, three CH_3). Anal. ($C_{13}H_{23}NO_2$) C, H, N.

2-Methyl-3-buten-2-yl *N,N*-Dimethylcarbamate (14). Purified by spinning-band distillation (bp 70-71 °C, 12 mm): 99.7% pure by GLC;[72] ν_{max} (film) 1712 (C=O), 1199 (CO), 986 and 918 cm^{-1} (-CH=CH_2); ^1H NMR ($CDCl_3$) δ 4.8-6.5 (m, -CH=CH_2), 2.80 [s, $N(CH_3)_2$], 1.48 (s, CH_3). Anal. ($C_8H_{15}NO_2$) C, H, N.

3-Methyl-2-buten-1-yl *N,N*-Dimethylcarbamate (15). Purified by preparative GLC:[71] >98% pure by GLC;[72] ν_{max} (film) 1712 (C=O) and 1185 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (broadened t, J = 7 Hz, =CH), 4.50 (d, J = 7 Hz, $-CH_2O-$), 2.70 [s, $N(CH_3)_2$], 1.72 [broadened s, $=C(CH_3)_2$]. Anal. ($C_8H_{15}NO_2$) C, H, N.

(*E*)-4-Phenyl-2-buten-1-yl *N,N*-Dimethylcarbamate (18). Purified by preparative GLC:[71] >99% pure by GLC;[72] ν_{max} (film) 1705 (C=O), 1178 (CO), and 969 (*trans*-CH=CH); ^1H NMR ($CDCl_3$) δ 7.28 (apparent s, C_6H_5), 5.5-6.2 (m, -CH=CH-), 4.55 (d, J = 4 Hz, $-CH_2O-$), 3.38 (d, $C_6H_5CH_2-$), 2.88 [s, $N(CH_3)_2$]. Anal. ($C_{13}H_{17}NO_2$), C, H, N.

(*E*)-3-Phenyl-2-propen-1-yl *N,N*-Dimethylcarbamate (19). Purified by dry column chromatography (9:1 hexane-acetone) and bulb to bulb distillation: 95% pure by GLC;[72] ν_{max} (film) 1704 (C=O), 1188 (CO) and 971 cm^{-1} (*trans*-CH=CH); ^1H NMR ($CDCl_3$) δ 6.9-7.5 (m, C_6H_5), 5.9-6.8 (m, -CH=CH), 4.66 (d, J = 5 Hz, $-CH_2O$), 2.82 [s, $N(CH_3)_2$]; mass spectrum 205.110 ($C_{12}H_{15}NO_2$ requires 205.110).

1-Phenyl-2-propen-1-yl *N,N*-Dimethylcarbamate. Purified by column chromatography on silica gel (3:1 hexane-ethyl acetate) and bulb to bulb distillation: >99% pure by GLC;[70] ν_{max} (film) 1712 (C=O), 1649 (aromatic), 1185 (CO), 926 and 976 cm^{-1} (-CH=CH_2); ^1H NMR ($CDCl_3$) δ 7.4 (s, C_6H_5), 4.8-6.4 (m, -CH=CH_2 and -CHO-), 2.82 [s, $N(CH_3)_2$]. Anal. ($C_{11}H_{15}NO_2$) C, H, N.

Preparation of 3-(*N,N*-Dimethylamino)-1-hexene. 3-Amino-1-hexene was prepared by alkaline hydrolysis of 2,2-trichloro-*N*-(1-hexen-3-yl) acetamide[20] as described.[20] A solution of 3-amino-1-hexene (810 mg, 82 mmol), formalin (5.9 g, 200 mmol), and formic acid (6.4 g, 140 mmol) was refluxed for 4 h. Concentrated HCl (1 mL) was added and the acidic solution was evaporated to dryness on a rotary evaporator. The resulting solid was dissolved in a minimum amount (ca. 10 mL) of concentrated NH_4OH, and the basic solution was extracted with pentane. The pentane extracts were concentrated and purified by preparative GLC[73] to give a pure sample of 3-(*N,N*-dimethylamino)-1-hexene: ν_{max} (film) 2980 (CH), 1430 (N-CH_3), 990 and 930 cm^{-1} (-CH=CH_2); ^1H NMR ($CDCl_3$) δ 4.9-5.7 (m, -CH=CH_2 and CHN) and 2.20 [s, $N(CH_3)_2$]. Anal ($C_8H_{17}N$) C, H, N.

Analytical Scale Mercuric Trifluoroacetate Promoted Isomerizations. A. Unquenched. All experiments were performed at room temperature. In a typical unquenched experiment (Tables I, II, and V), 15-200 mg of the *N,N*-dimethylcarbamate and 10-200 mg of *p*-dichlorobenzene (internal standard) were weighed into an oven-dried round-bottom flask equipped with a magnetic stir bar. The flask was flushed with nitrogen, covered with a rubber septum, and maintained under an atmosphere of nitrogen. Isomerizations involving long reaction times (>8 h) were stoppered with well-greased glass stoppers and were not maintained under a nitrogen atmosphere. Sufficient solvent was added to achieve the desired concentration, and mercuric trifluoroacetate (or other catalytic agent) was added while stirring. In early experiments, mercuric trifluoroacetate was added as a THF or benzene solution. Due to the discoloration of THF stock solutions and slow benzene mercuration,[74] the addition of solid mercuric trifluoroacetate is preferred and this method was utilized in a majority of the experiments. No difference in product composition was observed in comparable experiments which employed solid catalyst or a freshly prepared stock catalyst solution. Reaction aliquots were directly analyzed by GLC,[72] and all products were confirmed by enhancement experiments.

B. Quenched. The procedure was the same as in part A, except that at the indicated time reaction aliquots were treated with the quenching reagent before GLC analysis. Methanol and pyridine were added via syringe, and triphenylphosphine (Ph_3P) was added as a THF solution. With these quenching reagents the product composition was the same immediately, or 24 h after quenching. In Ph_3P-quenched experiments, bis(triphenylphosphine) bis(trifluoroacetate) mercury(II), mp 136 °C, usually precipitated immediately, although cooling and scratching were occasionally required when benzene was the solvent. This precipitate was allowed to settle, and the decantate was directly analyzed by GLC. The sodium borohydride quenched experiments were performed as follows. A reaction mixture containing 0.11 mmol of mercuric trifluoroacetate was treated in rapid succession with 0.3 mL of a 3 M aqueous solution of sodium hydroxide and 0.3 mL of an 0.5 M solution of sodium borohydride in 3 M sodium hydroxide. Metallic mercury formed immediately, and the slurry was stirred for 5 min. Solid potassium chloride was added, and after the solids settled the decantate was analyzed by GLC. Product compositions are not regarded as too reliable, since they changed with time (see Table II).

Preparative Scale Equilibrations. Catalytic Mercuric Trifluoroacetate. Preparation of (*E*)- and (*Z*)-3,7-Dimethyl-2-octen-1-yl *N,N*-Dimethylcarbamate (7). (Representative Procedure). A dry 50 mL-round bottom flask was equipped with a magnetic stirring bar and charged with 595 mg (2.50 mmol) of carbamate **6**. The flask was flushed with nitrogen and covered with a rubber septum, and 25 mL of dry THF was added. The septum was briefly removed, 319 mg (0.75 mmol) of anhydrous mercuric trifluoroacetate was added in one portion, and the rubber septum was replaced. The reaction was stirred under a nitrogen atmosphere at room temperature for 4 h, at which time GLC analysis[70] indicated that no **6** remained. Solid triphenylphosphine (1.31 g, 5 mmol) was then added, followed by 50 mL of pentane, and the bulk of the bis(triphenylphosphine) bis(trifluoroacetate) mercury(II) was allowed to precipitate overnight at −10 °C (refrigerator). Filtration and concentration yielded 1.60 g of a colorless oil which was purified by chromatography on silica gel (9:1 hexane-ethyl acetate) and bulb to bulb distillation to afford 548 mg (92%) of pure **7**; a 7:3 mixture of (*E*) and (*Z*) isomers (GLC analysis);[70] ν_{max} (film) 1700 (C=O) and 1200 cm^{-} (CO); ^1H NMR ($CDCl_3$) δ 5.40 (broadened t, J = 7 Hz, =CH), 4.58 (d, J = 7 Hz, $-CH_2O-$), 2.89 [s,$N(CH_3)_2$], 0.88 [d, J = 6 Hz, $CH(CH_3)_2$].

(*E*)- and (*Z*)-3,7-Dimethyl-2,6-octadien-1-yl *N,N*-Dimethylcarbamate (11). In a similar fashion, 1.09 g (4.86 mmol) of **10** was treated for 3 h with 1.25 g (2.92 mmol, 0.60 equiv) of mercuric trifluoroacetate to afford, after chromatography (silica gel, 9:1 hexane-ethyl acetate) and bulb to bulb distillation, 829 mg (77%) of a colorless oil: TLC (R_f 0.2, 9:1 hexane-ethyl acetate); ν_{max} (film) 1700 (C=O) and 1185 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 5.39 (broadened t, J = 7 Hz, C-2 vinylic hydrogen), 5.1 (m, C-6 vinylic hydrogen), 4.57 (d, J = 7 Hz, $-CH_2O-$), 2.88 [s, $N(CH_3)$]. GLC analysis[70] showed that this material was a 7:3 mixture of (*E*)- and (*Z*)-**11**, contaminated with

5% of the starting isomer **10**. Assignments for **10** and (*E*)-**11** were confirmed by peak-enhancement experiments with authentic samples. No GLC peak could be observed for the α-terpineol isomer **16**. Identical GLC analysis of product mixtures spiked with **16** indicated that 0.2% (but not 0.1%) of **16** would have been detected.

Similar scale experiments employing 0.3 equiv of mercuric trifluoroacetate afforded the results summarized in Table III.

2-Cyclohexylideneethyl *N,N*-Dimethylcarbamate (9). In a similar fashion, 101 mg (0.52 mmol) of **8** was treated for 2.5 h with 63.9 mg (0.30 equiv) of mercuric trifluoroacetate to afford, after chromatography (silica gel, 9:1 hexane–ethyl acetate) and bulb to bulb distillation, 93.3 mg (92%) of pure **9**: ν_{max} (film) 1700 (C=O) and 1190 cm^{-} (CO); ^{1}H NMR ($CDCl_3$) δ 5.23 (t, J = 7 Hz, =CH), 4.53 (d, J = 7 Hz, $=CH_2O-$), 2.90 [s, $N(CH_3)_2$].

24-Norchola-5,20(22)-diene-3,23-diol Di-*N*-dimethyl Carbamate (13). In a similar fashion, 54 mg (0.11 mmol) of **12** (mp 190–191 °C) was treated for 1 h with 14.2 mg (0.30 equiv) of mercuric trifluoroacetate to afford, after chromatography (silica gel, 7:3 hexane–ethyl acetate), 52 mg of pure **13**, mp 128–130 °C, TLC (R_f 0.3, 7:3 hexane–ethyl acetate). Recrystallization from hexane afforded an analytical specimen: mp 129–130 °C; ν_{max} (KBr) 1710 (C=O) and 1190 cm^{-1} (CO); ^{1}H NMR (CCl_4) δ 5.2 (broad s, two vinylic hydrogens), 4.6–3.8 (broad m, C-3 hydrogen), 4.4 (d, J = 3 Hz, CH_2O-), 2.72 [s, $N(CH_3)_2$]. Anal. ($C_{29}H_{46}N_2O_4$) C, H, N.

Equilibration of (*E*)-2-Hexen-1-yl *N,N*-Dimethylcarbamate (3). In a similar fashion, 646 mg (3.77 mmol) of **3** was treated for 24 h with 483 mg (0.3 equiv) of mercuric trifluoroacetate to afford, after chromatography (silica gel, 9:1 hexane–ethyl acetate) and bulb to bulb distillation, 594 mg (92%) of a mixture of hexenyl carbamates **4** (35%), **5** (4%), and **3** (61%). A comparable reaction was carefully examined after 24 h by GLC[73] and 3-dimethylamino-1-hexene could not be detected. Under these conditions, 3-dimethylamino-1-hexene was detectable at the 0.3% level.

1-Hexen-3-yl *N,N*-Dimethylthiocarbamate (28). In a similar fashion, 522 mg (2.79 mmol) of **27** was treated for 18 h with 342 mg (0.29 equiv) of mercuric trifluoroacetate to afford, after chromatography (silica gel, 9:1 hexane–ethyl acetate), 272 mg (52%) of **28**, a colorless liquid, pure by GLC:[73,75] ν_{max} (film) 1660 (C=O), 1100 (CS), and 910 cm^{-1} (CH=CH_2); ^{1}H NMR ($CDCl_3$) δ 4.9–6.2 (m, -CH=CH_2 and CHS), 2.99 [s, $N(CH_3)_2$]. Anal. ($C_8H_{17}NOS$) C, H, N.

A comparable reaction was examined by GLC[73,75] for the presence of (*E*)-2-hexen-1-yl *N,N*-dimethylthiocarbamate (**44**) and 3-dimethylamino-1-hexene. After 2 h, the formation of **28** reached a maximum, and at this time **28** and **44** were present in a ratio of 12:1, respectively (uncorrected for detector response). Thiocarbamate **44** may not be a primary reaction product, since the amount of **44** present increased slowly with time. An authentic sample of **44** was prepared from thermolysis of 1-hexene-3-yl *N,N*-dimethylthionocarbamate and was identical (^{1}NMR) with a sample of **44** isolated from the catalyzed rearrangement of **28**. 3-Dimethylamino-1-hexene was not detectable (<1%).

Contrathermodynamic Isomerizations with Excess Mercuric Trifluoroacetate. Conversion of Carbamate 3 to the Terminal Isomer 4 (Representative Procedure). A dry 10-mL flask was equipped with a magnetic stirring bar, flushed with nitrogen, and charged with 646 mg (3.77 mmol) of **3** and 4 mL of dry THF. Anhydrous mercuric trifluoroacetate (4.83 g, 11.3 mmol, mp 165–168 °C) was added in one portion and the reaction was maintained at room temperature under a nitrogen atmosphere. After 24 h the isomerization was quenched by adding a solution of 7.4 g (28 mmol) of triphenylphosphine and 10 mL of THF. Mercuric bis(triphenylphosphine) trifluoroacetate (mp 136 °C) precipitated almost immediately. After 30 min the mixture was vacuum filtered, the insoluble mercuric complex was washed with two 10-mL portions or pentane, and the filtrate was concentrated to give 2.3 g of a colorless oil. Analytical GLC analysis[75] indicated a 94.3:5.7 ratio of allylic carbamates **4** and **3**, respectively. TLC analysis (9:1 hexane:acetone) showed carbamates **3** and **4** (R_f 0.3–0.4), Ph_3P (R_f 0.7), and $(Ph_3P)_2Hg(OCOCF_3)_2$ (R_f <0.1). Chromatography on 200 g of silica gel (9:1 hexane–ethyl acetate) and bulb to bulb distillation afforded 484 mg (75%) of the terminal carbamate **4**, which was contaminated with 5% of the internal carbamate **3** (GLC analysis[75]).

Table IV summarizes the results obtained in other preparative scale isomerizations of carbamate **3** which were conducted in a similar fashion. When benzene was utilized as the solvent, concentrations of mercuric trifluoroacetate greater than 0.11 M resulted in the formation of a collodial precipitate.

Isomerization (*E*)-4-Phenyl-2-buten-1-yl *N,N*-Dimethylcarbamate (18) with 1.1 Equiv of Mercuric Trifluoroacetate in THF. In a similar fashion, 91 mg (0.42 mmol) of carbamate **18** was treated for 8 h with 198 mg (0.47 mmol, 1.1 equiv) of mercuric trifluoroacetate. After purification by preparative TLC (7:3 hexane–ethyl acetate) and bulb to bulb distillation, 78 mg (86% recovery) of a colorless liquid was obtained. GLC and ^{1}H NMR analysis indicated that this liquid was a 67:32 mixture of carbamates **18** and **20**. An analytical sample of 4-phenyl-1-buten-3-yl *N,N*-dimethylcarbamate (**20**) was isolated by preparative GLC: ν_{max} (film) 1705 (C=O), 1178 (CO), 981 and 918 cm^{-1} (-CH=CH_2); ^{1}H NMR ($CDCl_3$) δ 7.33 (apparent s, C_6H_5), 4.85–6.27 (complex m, -CH=CH_2, and CHO), 2.82 (d, J = 7 Hz, $-CH_2CH=$), 2.90 [s, $N(CH_3)_3$]. Anal. ($C_{13}H_{17}NO_2$) C, H, N.

Treatment of Carbamate 3 with BF_3 Etherate in *m*-Xylene. Isolation of Arylated Hexenes 26. A solution of 216 mg (1.26 mmol) of **3** and 2.0 mL of *m*-xylene was treated at room temperature with 0.2 mL (2 mmol) of BF_3 etherate under a nitrogen atmosphere. Additional BF_3 etherate was added at 22 (0.2 mL) and 45 h (0.15 mL) when GLC analysis[73] indicated that carbamates **3** and **4** were still present. After 64 hr, the reaction mixture was partitioned between 0.5 mL of water and ether, and the ether layer was washed with water and dried ($MgSO_4$). Concentration, and preparative GLC[73] afforded **26**; a 3:1 mixture of isomers by GLC:[73] ν_{max} (film) 1880 and 1700 cm^{-1} (1, 3,5- or 1,2,4-trisubstituted aromatic) and 1610 cm^{-} (C=C); ^{1}H NMR ($CDCl_3$) δ 7.02 (s, ArH), 5.03–5.93 (m, -CH=CH-), 3.2–3.4 (overlapping d, $-CH_2CH=$ of two isomers), 2.27 (s, $ArCH_3$), 2.25 (s, $ArCH_3$). Anal. ($C_{14}H_{20}$) C, H.

Calculated Equilibrium Isomer Compositions. For the five-component equilibrium of Scheme I, the mass conservation equations $[HgX_2]_0 = [HgX_2] + [I:HgX_2] + [T:HgX_2]$ and $[I]_0 = [I] + [T] + [I:HgX_2] + [T:HgX_2]$ can be written, where $[HgX_2]_0$ is the concentration of mercuric trifluoroacetate employed, $[I]_0$ is the initial concentration of the starting internal alkene isomer, and all other concentrations are for the respective species at equilibrium. Combining these equations with the equations which define the equilibrium constants K_1, K_2, and K_3 yields eq 10–13.

$$(K_1K_3 + K_2)[HgX_2] + [(1 + K_1) + (K_1K_3 + K_2)([I]_0 - [HgX_2]_0)][HgX_2] - (1 + K_1)[HgX_2]_0 = 0 \quad (10)$$

$$[I] = \frac{[HgX_2]_0 - [HgX_2]}{[HgX_2](K_1K_3 + K_2)} \quad (11)$$

$$[T] = K_1[I] \quad (12)$$

$$[T:HgX_2] = K_1K_3[I][HgX_2] \quad (13)$$

Using the values for the equilibrium constants shown in Table VI, these equations were solved for various $[HgX_2]_0$ and $[I]_0$ to yield the results summarized in Table VI.

Acknowledgment. The support of the National Science Foundation (GP-38634X and CHE 76-06101) and the Sloan Foundation is gratefully acknowledged. We thank Mr. Bernard J. Kane of Glidden-Durkee Corp. for generous gifts of high-purity geraniol and nerol.

References and Notes

(1) A. P. Sloan Foundation Fellow, 1975–1977; Camille and Henry Dreyfus Teacher–Scholar Award Recipient, 1976–1981.
(2) Abstracted in part from the Ph.D. dissertation of C. B. Campbell, University of California, Irvine, Calif., 1976.
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(45) The greater delocalization which is possible in the transition state of the charge-promoted process was the subject of a recent Huckel MO study.[42b]

(46) The **29–33** pathway could involve other intermediates. However, the formation at some point on the reaction coordinate of the σ-bonded cyclic intermediate **34** is considered to be the central feature of this mechanism.

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(48) The mechanisms of eq 4–6 are best considered as general mechanistic categories. For the ionization–recombination and cyclization-induced rearrangement mechanisms, for example, the possibility exists for different steps to be rate limiting or for either of these mechanisms to be elaborated to include participation by a counterion or nucleophilic solvent.

(49) Although the mechanisms of eq 4–6 form a reasonable framework for mechanistic discussion, other possibilities certainly exist, since a variety of structures[50] could be considered for a catalytically productive catalyst–substrate complex.

(50) For example, the transition-state geometry could involve coordination of the catalyst in a tri-, tetra-, or hexahapto sense: cf. M. Hargittai and I. Hargittai, "Molecular Geometries of Coordination Compounds in the Vapor Phase", Elsevier, New York, N.Y., 1977, pp 222–223.

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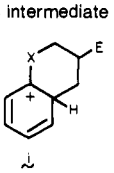
(61) The formation of the cyclic intermediate i (X = O, NH; E = electrophile)



i

would be the central feature of a cyclization-induced mechanism for these rearrangements. We are not suggesting, however, that this is a more reasonable formulation for these reactions.

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(69) W. S. Wadsworth, Jr., and W. D. Emmons, *Org. Synth.*, **45**, 44 (1965).

(70) A 6 ft × $\frac{1}{8}$ in. 3% SP-2401 on 100/120 Supelcoport column was used.

(71) A 8 ft × $\frac{1}{4}$ in. 5% STAP on 80/100 Chromosorb WAW column was used.

(72) A 18 ft × $\frac{1}{8}$ in. 10% Carbowax 20M on 80/100 Chromosorb WAW-DMCS column was used. A temperature program of 50–200 °C at 5 °C/min separated all the carbamate isomers and hydrolysis products.

(73) A 6 ft × $\frac{1}{8}$ in. 3% SP-2100 on 100/120 Supelcoport column was used.

(74) H. C. Brown and R. A. Wirkkala, *J. Am. Chem. Soc.*, **88**, 1447 (1966).

(75) A 6 ft × $\frac{1}{8}$ in. 10% SP-2330 on 100/120 Supelcoport column was used.

Free-Radical Participation in the Reactions of Selected Metalate Anions with Alkyl Halides[1]

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Received December 19, 1977

Abstract: The reactions of lithium, sodium, and potassium trimethyltin with *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide (**1** and **2**), chloride, and tosylate and cyclopropylcarbinyl chloride, bromide, iodide, and tosylate (**5**, X = Cl, Br, I, OTs) have been examined. Treatment of $(CH_3)_3SnLi$, -Na, -K with **1** and **2** at 0 °C in THF produces a mixture of *cis*- and *trans*-4-*tert*-butylcyclohexyltrimethyltin (**3** and **4**), (**4**:**3**, Li, 72:28; Na, 64:36; K, 64:36). In DME at 0 °C somewhat different values are observed: **4**:**3**, Li, 79:21; Na, 47:53; K, 53:47. Thus, alkylation of these bromides proceeds in all instances with stereochemical equilibration. Intermediate 4-*tert*-butylcyclohexyl radicals are implicated. Product isomer ratios for reactions carried out at lower temperatures (−70 °C) indicate that the alkylation of both $(CH_3)_3SnNa$ and $(CH_3)_3SnK$ with **1** and **2** produce slightly different ratios of **4**:**3** than the values observed at 0 °C, but nonetheless still proceed with complete loss of stereochemical integrity. Under similar conditions, reaction of $(CH_3)_3SnLi$ with **1**, but not **2**, yields an enhanced predominance of the trans product **4**, corresponding to a net increase in inversion of configuration. These results suggest that at least one stereospecific pathway is operating at low temperatures in addition to any nonstereospecific reaction(s). By comparison, reaction of *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylate with $(CH_3)_3SnLi$ produces only **4** and **3**, respectively, and thus proceeds with complete inversion of configuration. The reaction of $(CH_3)_3SnLi$ with *cis*- and *trans*-4-*tert*-butylcyclohexyl chloride presumably provides an intermediate in the transition between these two extremes, since it does not occur with complete stereochemical equilibration. The contention that the reaction of alkyl halides with $(CH_3)_3SnLi$, -Na, and -K proceeds by two (or more) competing reaction pathways, one of which involves intermediate free alkyl radicals, is supported by the observation that the reaction of lithium, sodium, and potassium trimethyltin with cyclopropylcarbinyl bromide and iodide, but not chloride or tosylate, yields two alkylation products: trimethyl(cyclopropylcarbinyl)tin (**6**) and trimethyl(allylcarbinyl)tin (**7**). The yield of **7** is a function of halide, temperature, solvent, gegenion, and concentration. These observations are compatible with a reaction mechanism involving free, noncaged, cyclopropylcarbinyl radicals as intermediates. A similar study of the reaction of $CpFe(CO)_2Na$ with **5** leads to the conclusion that only the reaction with cyclopropylcarbinyl iodide involves free cyclopropylcarbinyl radicals to any significant degree. In contrast, the reaction of PhSeNa with **5** produce only cyclopropylcarbinyl phenyl selenide and presumably does not proceed through the intermediacy of free alkyl radicals.

The displacement of halides and other groups from alkyl substrates by metalate anions represents one of the most important routes for the formation of metal-carbon σ bonds. Because of its importance, considerable attention has been paid to the mechanism of these reactions and their generally high stereoselectivity has been widely interpreted as evidence against the intermediacy of free alkyl radicals and in favor of an S_N2 pathway.[2,3]

Stereochemical studies provide the single most valuable type of information available in characterizing the mechanism of any transformation involving the rupture or formation of a bond at a tetrahedral carbon. However, the serious shortcomings associated with the application of traditional stereochemical studies to organometallic systems, particularly transition metal alkyls, are well known. Alternative procedures have been developed which circumvent some of these problems, although these alternatives are not without their own limitations.[2,4]

As an adjunct to information obtained from stereochemical studies of organometallic systems, we have employed the cyclopropylcarbinyl moiety. There are several practical advantages that accrue from the use of this system as a diagnostic probe with which to investigate the reaction of metalate anions. First, cyclopropylcarbinyl halides are generally stable compounds which are readily prepared in high purity. Second, the homoallyl rearrangement which characterizes the free cyclopropylcarbinyl radical is a particularly well understood radical rearrangement.[5-7] Rearrangement is too slow a process ($k = 1.3 \times 10^8\ s^{-1}$ at 25 °C)[6] to compete effectively with diffusion of the intermediate radical out of the solvent cage in which it is initially formed:[8] homoallyl rearrangement in this system is not concerted with the formation of the radical. Thus, and most usefully for the interpretation of the work reported here, the origins of organometallic products containing the allylcarbinyl moiety can be couched in terms of a relatively straightforward reaction sequence involving kinetically free

0002-7863/78/1500-4834$01.00/0