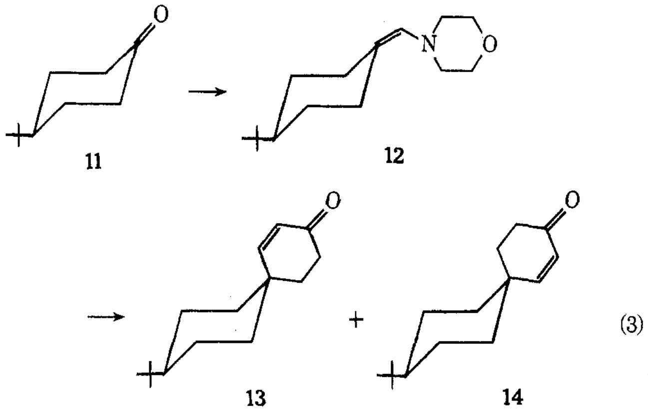
that this synthetic sequence proceeds with a considerable degree of stereoselectivity. For example, 4-*tert*-butylcyclohexanone (**11**) was smoothly converted to a diastereomeric mixture of the spiro[5.5]undecenones **13** and **14** in a ratio of 9:1 (eq 3).[12] This result is in accord with the expectation that



11 **12** **13** **14** (3)

the initial reaction of methyl vinyl ketone with the enamine **12** will occur from the less hindered, equatorial face of **12**.

The application of this new spiroannelation procedure to the synthesis of spiro sesquiterpene natural products as well as alkaloid natural products containing spirocyclic rings and quaternary carbon atoms is presently under investigation.

Acknowledgment. We wish to thank the Research Corporation and the University Research Institute of the University of Texas at Austin for their generous financial support of this program.

Supplementary Material Available. Characterization of all new compounds, together with representative experimental details (5 pages). Ordering information is given on any current masthead page.

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(11) All compounds were adequately characterized by spectral methods (ir, NMR, MS), and all new compounds gave satisfactory high resolution mass spectral and/or combustion analytical data.

(12) Although the two isomers **13** (major) and **14** (minor) were inseparable by preparative chromatographic techniques, their presence is easily detected by analytical GLC and ^{1}H and ^{13}C NMR spectra: **13**, ^{1}H NMR ($CDCl_3$, TMS) δ 7.17 (d, J = 10 Hz, $-CH{=}CHCO-$) and ^{13}C NMR ($CDCl_3$, TMS) δ 155.4 ($-\mathbf{C}H{=}CHCO-$); **14**, ^{1}H NMR ($CDCl_3$, TMS) δ 6.52 (d, J = 10 Hz, $-CH{=}CHCO-$) and ^{13}C NMR ($CDCl_3$, TMS) δ 160.7 ($-\mathbf{C}H{=}CHCO-$). The stereochemical assignment with respect to the newly created chiral center may be made on the basis of the ^{1}H and ^{13}C NMR spectra. The β-vinyl proton of the major isomer **13** is *deshielded* relative to the β-vinyl proton of **14**, owing to steric crowding. As expected the β-vinyl carbon of **13** is *shielded* relative to the β-vinyl carbon of **14** owing to steric compression.

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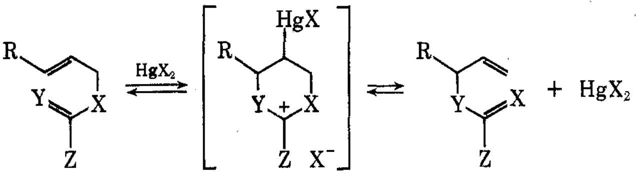
Mercury(II)-Catalyzed 3,3-Sigmatropic Rearrangements of Allylic *N,N*-Dimethylcarbamates. A Mild Method for Allylic Equilibrations and Contrathermodynamic Allylic Isomer Enrichments

Summary: Allylic *N,N*-dimethylcarbamates undergo allylic equilibration in high yield when treated at 25 °C in THF with catalytic amounts of mercuric trifluoroacetate. In certain cases the use of excess mercuric trifluoroacetate allows the less stable allylic isomer to be trapped.

Sir: The 1,3-isomerization of allylic alcohols and allylic alcohol derivatives has been investigated mechanistically for years,[1-3] and plays a key role in several synthetic[4] and commercial processes.[5] Popular methods for affecting this transformation include Lewis acid, protic acid, and transition metal catalyzed isomerization of allylic alcohols, or the corresponding acetates. Overall yields vary from 25 to 85%, and isomer conversions often only approach the equilibrium values.[1-5] Although methodology is well established[6] for the contrathermodynamic isomerization of alkenes, to our knowledge, no method exists for achieving contrathermodynamic *allylic* isomerizations.

The first examples of mercuric ion catalyzed [3,3]-sigmatropic rearrangements were recently reported from our laboratory.[7] This study revealed that trichloroacetimidic esters of 2-alken-1-ols **1** ($X = O$, $Y = NH$, $Z = CCl_3$) underwent rapid isomerization to the corresponding allylic trichloroacetamides **3** ($X = O$, $Y = NH$, $Z = CCl_3$) when treated in an aprotic solvent, at room temperature, with a catalytic amount of mercuric trifluoroacetate. The intramolecular iminomercuration–deoxymercuration mechanism of eq 1 ($X = O$, $Y = NH$, $Z = CCl_3$) was suggested for this catalyzed transformation.[7-9] We anticipated that mercury(II) salts would catalyze the allylic isomerization (**1** → **3**) of other functional groups, and subsequent work in this laboratory has confirmed this expectation. In this communication we wish to report that mercuric trifluoroacetate is an effective catalyst at room temperature for the allylic equilibrium of *N,N*-dimethylcarbamic esters of allylic alcohols. Moreover, we wish to report that in certain cases a modification of this process results in the first approach to achieving contrathermodynamic allylic isomerizations.



1 **2** **3** (1)

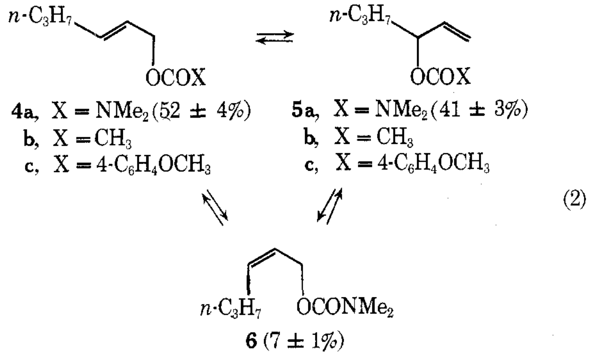
Treatment of the allylic carbamate isomers **4a** and **5a** at room temperature for 4–11 h with 0.4 equiv of *anhydrous* mercuric trifluoroacetate in dry tetrahydorfuran (THF) re-

Table I. Anhydrous Mercuric Trifluoroacetate Catalyzed Allylic Isomerization of 2-Alken-1-yl *N,N*-Dimethylcarbamates ($R_1R_2C{=}CHCH_2OCONMe_2$)[a]

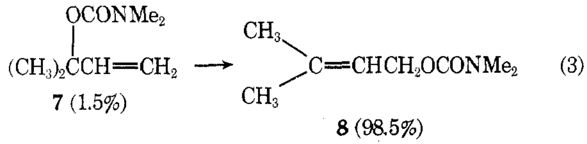
Starting internal alkene isomer							Quenched product composition[e]	
R_1	R_2	No.	Equiv[b] of HgX_2	Solvent[c]	Reaction time, hr	% yield[d]	% terminal alkene	% internal alkene
n-C_3H_7	H	**4a**	0.3	THF	9	(97)	34	66[f]
n-C_3H_7	H	**4a**	1.1	THF	9	(80)	58	42[f]
n-C_3H_7	H	**4a**	1.1	THF	16	(98)	65	35[f]
n-C_3H_7	H	**4a**	3.0	THF	8	87	81	19[f]
n-C_3H_7	H	**4a**	1.1	C_6H_6	8	89	83	17[f]
$C_6H_5CH_2$	H	**10**	1.1	THF	9	(88)	57	43[f]
$C_6H_5CH_2$	H	**10**	1.1	C_6H_6	8	86	71	29[f]
CH_3	CH_3	**8**	1.2	THF	8–17	(66)	2	98

[a] Carbamate, 0.1 M. Reactions were quenched by adding 3.6 equiv of Ph_3P, dissolved in a small volume of the solvent, per equivalent of catalyst. Bis(triphenylphosphine)bis(trifluoroacetato)mercury(II) precipitates within minutes when induced by scratching and cooling. Chromatography is necessary to remove the last traces of this complex. [b] Prepared by the procedure of Brown,[20] mp 166–167 °C, and stored in a desiccator over KOH. [c] THF was distilled from sodium and benzophenone immediately before use. Benzene was distilled from CaH_2 and stored over molecular sieves. If water is not rigorously excluded considerable carbamate hydrolysis occurs. [d] Isolated yields, after chromatography, of the isomer mixture. Yields in parentheses refer to percent recoveries based on GLC or ^1H NMR analysis. [e] Internal/terminal isomer ratios were determined by both ^1H NMR and GLC analysis. In all cases the two methods agreed within 3%. [f] An *E*/*Z* isomer mixture.

sulted in the formation, in >90% yield, of the apparent equilibrium mixture[10] of isomers shown in eq 2. Similar treatment of acetate **4b** or anisate **4c** with up to 1.2 equiv of $Hg(OCOCF_3)_2$ afforded <10% of the corresponding terminal isomers **5b** or **5c**. A comparison of the initial rate of the catalyzed isomerization of **4a** in THF with the thermal, gas phase isomerization of several 2-butenyl derivatives,[12] allows one to make a rough estimate[13] for the rate enhancement of the catalyzed process (1 M catalyst) of 10^{13}. Under similar conditions (0.3 equiv of $Hg(OCOCF_3)_2$, 30 min, 25 °C) the tertiary allylic carbamate **7** is converted in 95% yield into a mixture of carbamate isomers containing 98.5% of the more stable[2b,4c] trisubstituted alkene isomer **8**.



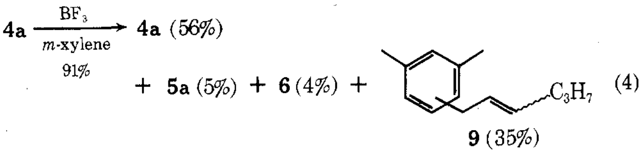
4a, X = NMe_2 (52 ± 4%) **5a**, X = NMe_2 (41 ± 3%)
b, X = CH_3 **b**, X = CH_3
c, X = 4-$C_6H_4OCH_3$ **c**, X = 4-$C_6H_4OCH_3$
6 (7 ± 1%)



$$(CH_3)_2\overset{\displaystyle OCONMe_2}{\overset{|}{C}}CH{=}CH_2 \longrightarrow (CH_3)_2C{=}CHCH_2OCONMe_2 \quad (3)$$

7 (1.5%) **8** (98.5%)

Permissive evidence that the mercuric catalyzed equilibrations are occuring by the two-step mechanism of eq 1 (X = Y = O, Z = NMe_2), comes from our inability to trap allylic carbonium ions in the mercuric catalyzed reaction. For example, treatment (8 h, 25 °C) of carbamate **4a** in *m*-xylene as solvent with 0.4 equiv of $Hg(OCOCF_3)_2$ resulted in production (93% recovery) of the equilibrium mixture of carbamate isomers shown in eq 2. No trace of the allyl cation–Friedel-Crafts product, **9**, could be found. In contrast, treatment of carbamate **4a** in *m*-xylene with 2.5 equiv of boron trifluoride etherate (25 °C, 8 h) yielded the product mixture shown in eq 4.[14]



9 (35%)

Equilibrium constants for formation of covalent alkene–mercuric trifluoroacetate adducts have been measured in THF[15] and benzene,[16] and are considerably higher for mono- than for disubstituted alkenes. The addition of mercuriophilic reagents [for example norbornene,[15] pyridine,[15] or triphenylphosphine (Ph_3P)[7]] to these covalent adducts has also been shown to result in quantitative liberation of the alkene. Thus, treatment of an internal allylic carbamate such as **4a** with an excess of $Hg(OCOCF_3)_2$, followed by the addition of a mercuriophile, should yield an isomer mixture rich in the contrathermodynamic terminal isomer **5a**. That is, the excess catalyst is expected to preferentially trap the terminal alkene isomer as a covalent adduct,[17] thus selectively removing it from the equilibrating isomer pool. That this expectation has indeed been realized is apparent from the data in Table I. Thus, treatment of carbamate **4a** with 1.1 equiv of $Hg(OCOCF_3)_2$ in benzene for 8 h at room temperature, followed by quenching with Ph_3P and chromatographic workup, afforded, in 89% yield, an isomer mixture containing 83% terminal isomer, **5a**. Two trends are apparent. The contrathermodynamic isomer preference in THF increases with increasing catalyst concentration, and, for the same catalyst concentration, this preference is higher in benzene than THF. Both trends would be expected if this isomerization occurred as we have suggested since a larger fraction of the alkene isomers should, at comparable catalyst concentrations, be bound as covalent adducts in benzene[15,16] and also at higher catalyst concentrations. The mildness of this method is well demonstrated by the allylic isomerization of carbamate **10** to the corresponding terminal alkene isomer without the formation of even a trace of the more stable styrene isomer. This method fails, however, if the starting 2-alken-1-yl carbamate is disubstituted at C-3. Thus carbamate **8** yields only a trace of the tertiary allylic isomer **7** (i.e., the reverse of eq 3) when treated with 1.2 equiv of $Hg(OCOCF_3)_2$ in THF.[18]

The mercuric trifluoroacetate promoted[19] allylic carbamate equilibrium is notable for the mildness of the reaction conditions and the high isolated yields. Unwanted skeletal isomerizations would appear precluded since allylic carbonium ions are not intermediates. The method reported here for contrathermodynamic allylic isomer enrichment is limited to the conversion of carbamic esters of 2-alken-1-ols, which contain a disubstituted double bond, to the correspondinng 1-alken-3-ol derivatives. Although this method represents a general approach for achieving contrathermodynamic allylic isomerizations, the reaction conditions we have thus far investigated do not specifically afford only the contrathermodynamic isomer. One can imagine, however, that similar catalysts, which have even higher selectivities for binding specifically the terminal alkene isomer, may overcome this limitation.

Acknowledgment. We thank the National Science Foundation for support of this work under Grant No. GP-38634X.

Supplementary Material Available. Experimental procedure (2 pages). Ordering information is given on any current masthead page.

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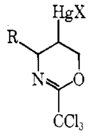
(8) Since in this case Y contains a protic hydrogen, the ion pair **2** would be in equilibrium with HX and the neutral adduct i.



i

(9) A mechanism similar to that shown in eq 1 has been suggested for the palladium(II)-catalyzed isomerization of allylic esters: P. M. Henry, *J. Am. Chem. Soc.*, **94**, 5200 (1972).

(10) Equilibration of the butenyl acetates in acetic acid by treatment with *p*-toluenesulfonic acid (0.3 M, 60 °C, 9–16 days)[2b] or perchloric acid (8.3 mM, 75 °C, 3–5 h)[11b] has been reported.[11] Recoveries varied from 30 to 84% and the equilibrium composition[11b] was 38.2% α-methylallyl acetate, 51.4% *trans*-crotyl acetate, and 10.4% *cis*-crotyl acetate.

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(13) At 25 °C in THF the rate constant for the catalyzed conversion of **4a** to **5a** was measured by the initial rate method: $k_{cat} = 4 \pm 3 \times 10^{-3}$ mol l.$^{-1}$ s^{-1} (five determinations). The extent of reaction ranged from 3 to 30% and the equivalent of catalyst varied from 0.05 to 1.0.[14] The corresponding rate constant for the thermal, gas phase, isomerization was estimated by extrapolating rate constants[12] for the conversion of $CH_3CH{=}CHCH_2O(C{=}O)Z$ to $CH_3CHO(C{=}O)ZCH{=}CH_2$ (Z = CF_3, CH_3, and OCH_3) from 325 to 25 °C, plotting the logarithm of these extrapolated rate constants vs. σ_m (correlation coefficient, 1.00), and estimating $K_{thermal}$ for the conversion of **4a** to **5a** from this plot using the σ_m constant for the $N(CH_3)_2$ group; $k_{thermal} = 3 \times 10^{-17}$ s^{-1}.

(14) Details will be reported in the subsequent full paper and the Ph.D. thesis of C. B. Campbell.

(15) H. C. Brown and M.-H. Rei, *J. Chem. Soc., Chem. Commun.*, 1296 (1969).

(16) H. C. Brown, M.-H. Rei, and K.-T. Liu, *J. Am. Chem. Soc.*, **92**, 1760 (1970).

(17) A variety of structures would appear possible for these postulated covalent adducts. This aspect is under investigation.

(18) This result is not unexpected. The equilibrium constant for the formation of the mercuric trifluoroacetate complex of 3,3-dimethyl-1-butene is nine times less than that of 1-hexene.[15] A competing oxidation reaction also becomes important here at long reaction times.

(19) Winstein and coworkers[11a] have reported that the crotyl and α-methyl allyl acetates may be equilibrated by treatment at 75 °C for 23 h with 1.1–1.3 equiv of mercuric acetate in acetic acid. Less than 48% of the allylic esters were recovered from this treatment. An intermolecular acetoxymercuration–deactoxymercuration mechanism was suggested for this process.

(20) H. C. Brown and M.-H. Rei. *J. Am. Chem. Soc.*, **91**, 5646 (1969).

(21) A. P. Sloan Foundation Fellow, 1975–1977.

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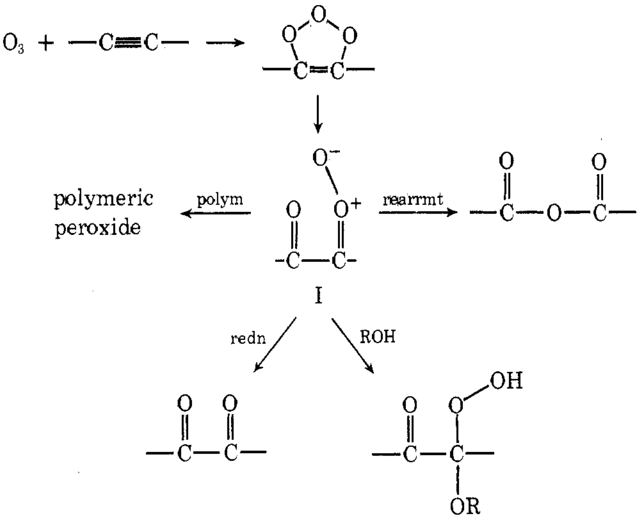
Reductive Trapping in the Ozonolysis of Diphenylacetylene

Summary: Evidence is presented that establishes the existence of a relatively stable (half-life ~35 min, −42 °C) reducible intermediate in the ozonolysis of diphenylacetylene.

Sir: The reaction of ozone with alkenes has been the subject of extensive study.[1] By comparison the number of mechanistic studies of the ozonolysis of alkynes has been relatively small, although recently there has been renewed interest.[2–10] The mechanism suggested by Criegee and Lederer is analogous to that for alkenes and a slightly modified version is depicted in Scheme I.[5]

Scheme I



The intermediacy of I, an α-carbonyl carbonyl oxide, is supported by solvent trapping,[5,6] reductive trapping,[8,9] and spectroscopic work.[7] The stability of I, whether it is a long-lived intermediate, and its mode of rearrangement to the anhydride products are open questions. In this work the reaction of diphenylacetylene and ozone has been studied in an effort to answer some of those questions.

Previous work has shown the products of the reaction of diphenylacetylene and ozone to be benzil, benzoic anhydride,