

yield, mp 205–206°,<sup>6</sup> desulfurized with Raney Nickel to *N*-phenyl-*N*-methyloxamide. Warming solutions of these dimers (9, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> or CH<sub>2</sub>CH=CH<sub>2</sub>) in chloroform or other nonpolar solvents, in the absence of oxygen, resulted in their smooth conversion to the stable dimers (7), thus proving their intermediacy in the transformation of the benzothiazolium salts (3). When the allyl substituents in 3 were marked by alkyl groups, as crotyl and dimethylallyl, less than 100% inversion of the migrating allylic group was observed in the product dimer 7, indicative of the presence of a competing [1,3]-sigmatropic migration of the allylic function. The contribution of this pathway was favored by higher temperatures, as is shown in Table I. The products of these reactions were stable to the reaction conditions.<sup>7</sup>

The above results show that ethylenes (9, R = CH<sub>2</sub>-CH=CR<sub>2</sub>) rearrange by two competing pathways, a thermally allowed [3,3]-sigmatropic process and a formally forbidden [1,3]-sigmatropic pathway,<sup>8</sup> as shown

(6) The substance 10 (R = CH<sub>3</sub>) was originally formulated as the isomeric cyclic thiocarbamate. This oxidative rearrangement has precedent in the autoxidation of tetrathioethylenes: cf. W. Adam and J. C. Liu, *J. Amer. Chem. Soc.*, **94**, 1206 (1972); W. Ando, J. Suzuki, T. Arai, and T. Migita, *Tetrahedron*, **29**, 1507 (1973).

(7) Since the dissociation of electron-rich ethylenes, such as 9, to nucleophilic carbenes has been shown not to be occur, this pathway, via 4, cannot be involved in the rearrangement of 9: cf. R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **7**, 754 (1968). Furthermore the remote possibility of acid-catalyzed formation of 4 from 8, with subsequent rearrangement at the level of 4 and recombination to 7, was excluded by noting that 2-alkylbenzothiazoles are unable to intercept any intermediate in the conversion of 3 (R = CH<sub>2</sub>CH=CH<sub>2</sub>, X = Br) to 7 (R = CH<sub>2</sub>CH=CH<sub>2</sub>).

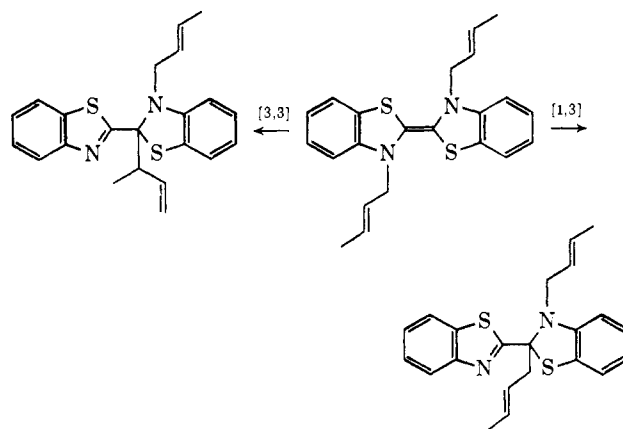
Table I

Salt 3 (X = Br) R	% [3,3]-sigmatropic pathway to compound 7 at °C <sup>a</sup>			<i>t</i> <sub>1/2</sub> , 34° CHCl <sub>3</sub> (min)
	25°	75°	100°	
CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> <sup>b</sup>				100
CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ( <i>p</i> -NO <sub>2</sub> ) <sup>b</sup>				<10
CH <sub>2</sub> CH=CD <sub>2</sub>	100			15
CH <sub>2</sub> CH=CHCH <sub>3</sub> (t)	90	85	75	10
CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	60		30	10

<sup>a</sup> Determined *via* acidic degradation by pathway shown in 8.

<sup>b</sup> These benzyl derivatives provide only [1,3] products.

Scheme I



in Scheme I. Although we cannot exclude the possibility that the latter process is an example of a forbidden yet concerted reaction<sup>9,10</sup> the effect of *p*-nitro substitution, Table I, is typical of that found in the Stevens [1,2]-rearrangement, a process clearly radical in character,<sup>11b</sup> and suggests to us that the same duality of concerted *vs.* radical pathways found in the [2,3]-sigmatropic reaction also operates in certain circumstances in the [3,3]-sigmatropic reaction.

**Acknowledgments.** We wish to thank the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Eli Lilly and Co. for support.

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(9) J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).

(10) Attempts to observe CIDNP effects in these rearrangements have been unsuccessful.

(11) (a) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970); (b) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

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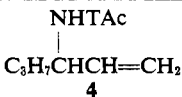
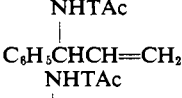


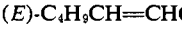
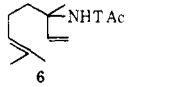
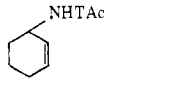

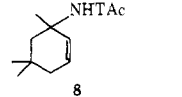
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### Thermal and Mercuric Ion Catalyzed [3,3]-Sigmatropic Rearrangement of Allylic Trichloroacetimidates. The 1,3 Transposition of Alcohol and Amine Functions

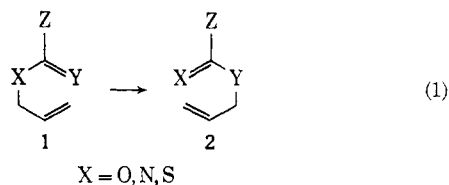
Sir:

The [3,3]-sigmatropic rearrangement of 3-heteroatomic-1,5-diene species (eq 1) is an important method for the stereospecific construction of unsaturated sys-

Table I. Thermal and Mercuric Trifluoroacetate Catalyzed Rearrangement of Allylic Trichloroacetimidates

Alkyl trichloroacetimidate (ROC(=NH)CCl <sub>3</sub> )	Trichloroacetamide <sup>a</sup>	Thermal <sup>b</sup>		Catalyzed <sup>c</sup>	
		Time, hr	% yield <sup>d</sup>	Equiv of Hg(OCOCF <sub>3</sub> ) <sub>2</sub>	% yield <sup>d</sup>
(E)-2-Hexen-1-yl 3	 $C_6H_{13}CHCH=CH_2$ 4	9	81 (95)	0.1	79 (92)
Cinnamyl	 $C_6H_5CHCH=CH_2$ NHTAc	6	77	0.2	45 (65) <sup>e</sup>
2-Buten-1-yl	 $CH_3CHCH=CH_2$ NHTAc	12	83	0.2	78
Allyl	 $CH_2=CHCH_2NHTAc$	12	82	0.2-0.4	0 <sup>f</sup>
1-Hepten-3-yl	 $(E)-C_4H_9CH=CHCH_2NHTAc$	1	69 (92)	0.2-0.4	0 <sup>f</sup>
Geranyl 5	 6	6	92 (96)	0.2	79 (88)
2-Cyclohexen-1-yl	 NHTAc	1	79 (94)	0.2-1.0	0 <sup>f</sup>
  8	0.75	80	0.2	20	

<sup>a</sup> TAc = trichloroacetyl. All new compounds showed ir and nmr spectra consistent with the indicated structures and correct combustion analyses ( $\pm 0.3\%$ ). <sup>b</sup> In refluxing *m*-xylene (138–139°). <sup>c</sup> In tetrahydrofuran at 0°. <sup>d</sup> Isolated yield of purified product. Yields in parentheses were determined by nmr or glc analysis using internal standards. <sup>e</sup> 30% cinnamyl trichloroacetimidate was recovered. <sup>f</sup> No rearranged product observable by nmr analysis. <sup>g</sup> At least 98%; only one isomer could be detected by nmr or glc.



tems.<sup>1,2</sup> We wish to report the facile [3,3]-sigmatropic rearrangement of allylic trichloroacetimidates (1; X = O, Z = CCl<sub>3</sub>, Y = NH) to afford the corresponding trichloroacetamides (2; X = O, Z = CCl<sub>3</sub>, Y = NH), a synthetic operation which results in the 1,3 transposition of alcohol and amine functions. Moreover we wish to report that this transformation is markedly catalyzed by the addition of mercuric salts.

Although the thermal [3,3]-sigmatropic rearrangement of a few allylic imidates has previously been reported,<sup>3</sup> the relatively low yield preparation of the

(1) Recently reviewed by J. Jefferson and F. Scheinmann, *Quart. Rev., Chem. Soc.*, **22**, 391 (1968).

(2) Recent synthetic applications include: (a) G. Saucy and R. Marbet, *Helv. Chim. Acta*, **50**, 2091, 2095 (1967); (b) K. Sadi, J. Ide, O. Oda, and N. Nakamura, *Tetrahedron Lett.*, 1287 (1972); (c) A. E. Wick, D. Felix, K. Steen, and A. Eschenmoser, *Helv. Chim. Acta*, **47**, 2425 (1964); (d) J. Ficini and C. Barbara, *Tetrahedron Lett.*, 6425 (1966); (e) W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T. Li, D. J. Faulkner, and M. R. Peterson, *J. Amer. Chem. Soc.*, **92**, 741 (1970); (f) R. E. Ireland and R. H. Mueller, *ibid.*, **94**, 5892 (1972); (g) J. E. Baldwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 117 (1973); (h) R. E. Hackler and T. W. Balko, *J. Org. Chem.*, **38**, 2106 (1973); (i) K. Oshima, H. Takahashi, Y. Yamamoto, and H. Kozaki, *J. Amer. Chem. Soc.*, **95**, 2694 (1973).

(3) O. Mumm and F. Moller, *Chem. Ber.*, **70**, 2214 (1937); W. M. Lauer and R. G. Lockwood, *J. Amer. Chem. Soc.*, **76**, 3974 (1954); W. M. Lauer and C. S. Benton, *J. Org. Chem.*, **24**, 804 (1959); R. M. Roberts and F. A. Hussein, *J. Amer. Chem. Soc.*, **82**, 1950 (1960); D. St. C. Black, F. W. Eastwood, R. Okraglik, A. J. Poynton, A. M. Wade, and C. H. Welker, *Aust. J. Chem.*, **25**, 1483 (1972).

requisite imidates and the harsh conditions required for the rearrangements have prevented these transformations from being of general synthetic use. In contrast we have found that a wide variety of allylic trichloroacetamides, which are easily prepared in nearly quantitative yield from the corresponding alcohol and trichloroacetoneitrile,<sup>4</sup> readily undergo thermal rearrangement within a few hours in refluxing *m*-xylene to afford the corresponding trichloroacetamides in isolated yields in excess of 80% (Table I).<sup>5-7</sup> In no case has the trichloroacetamide with an unrearranged carbon skeleton been detected. This transformation is formulated as a simple electrocyclic reaction on the basis of its stereo- and regiospecificity which is similar to that observed in related [3,3]-sigmatropic processes.<sup>2,8</sup> For example, the trichloroacetimidate of 1-hepten-3-ol affords 2-heptenyltrichloroacetamide with a *trans* to *cis* ratio of at least 98:2.

Dramatic catalysis by mercuric salts is observed. For example if 0.10 equiv of mercuric trifluoroacetate (or mercuric nitrate) is added to a tetrahydrofuran (THF) solution of imidate 3 in a pmr tube and the spectrum immediately recorded, only the rearranged amide 4 is observed. The catalyzed rearrangement is also

(4) F. Cramer, K. Pawelzik, and H. Baldauf, *Chem. Ber.*, **91**, 1049 (1958).

(5) Our results differ from a previous report that alkyl trichloroacetimidates were thermally stable at their boiling point and that at higher temperatures did not afford defined rearrangement products.<sup>6</sup>

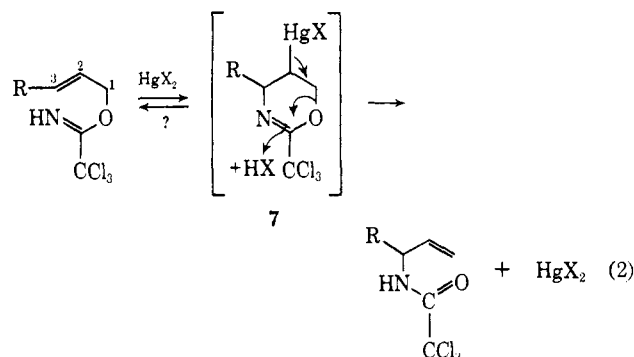
(6) F. Cramer and N. Hennrich, *Chem. Ber.*, **94**, 976 (1961).

(7) The rearrangements are easily monitored by tlc, ir, or nmr: *O*-allyl isomer ir 1660 cm<sup>-1</sup> (C=N), nmr  $\tau$  1.8 (N-H); *N*-allyl isomer ir 1690–1700 cm<sup>-1</sup> (C=O), nmr  $\tau$  3.4 (N-H).

(8) C. L. Perrin and D. J. Faulkner, *Tetrahedron Lett.*, 2783 (1969); D. J. Faulkner and M. R. Peterson, *ibid.*, 3243 (1969).

observed at  $-78^\circ$ ,<sup>9</sup> and a second double bond does not interfere as compound **6** can be obtained in 79% isolated yield. Catalysis is not observed with all the trichloroacetimidates studied and is most successful for derivatives of 3-substituted primary allylic alcohols (Table I).

Mercuric ion catalysis of a formal [3,3]-sigmatropic rearrangement is to our knowledge unprecedented. A two-step mechanism involving iminomercuriation-deoxymercuration is proposed. In the first step the mercuric electrophile adds to the carbon-carbon double bond to form a mercurinium ion (or its equivalent)<sup>11</sup> which is then captured intramolecularly at C-3 by the nucleophilic imino nitrogen to afford **7**.<sup>12,13</sup> Intermediate **7** can then suffer cleavage of the carbon-oxygen bond (deoxymercuration)<sup>14</sup> to afford the rearranged amide product. The success of this catalyzed reaction derives from the fact that in aprotic solvents adduct formation between an olefin and mercuric trifluoroacetate is both rapid and reversible,<sup>15</sup> a feature which we have utilized previously.<sup>16</sup> Evidence for the mechanism of eq 2 derives mainly from the observed de-



pendence of the catalyzed reaction on trichloroacetimidate structure. Thus the catalyzed reaction is successful for imidates with R groups which promote nucleophilic addition to C-3 and fails in cases such as allyl, 1-hepten-3-yl, and 2-cyclohexen-1-yl<sup>16</sup> where nucleophilic addition at C-2 is favored.<sup>17</sup> Consistent also with this mechanism is the failure of mercuric trifluoroacetate (or mercuric acetate) to catalyze the rearrangement of **5** in protic solvents such as methanol, and the failure of stronger Lewis acids such as aluminum chloride etherate,<sup>18</sup> silver fluoroborate,<sup>18</sup> or boron trifluoride etherate<sup>6,2d</sup> to promote this rearrangement.

(9) The catalyst was destroyed by reduction<sup>10</sup> at  $-78^\circ$  before workup.

(10) H. C. Brown, P. J. Geoghegan, Jr., G. L. Lynch, and J. T. Kurek, *J. Org. Chem.*, **37**, 1941 (1972).

(11) Cf. G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **95**, 6067 (1973), and references cited therein.

(12) Although aminomercuriation reactions are well known,<sup>13</sup> there are, to our knowledge, no previous reports of iminomercuriation. Iminomercuriation has, however, been observed in other unpublished work in our laboratory.<sup>17</sup>

(13) Cf. H. K. Hall, Jr., J. P. Schaefer, and R. J. Spangord, *J. Org. Chem.*, **37**, 3069 (1972), and references cited therein.

(14) M. M. Kreevoy and M. A. Turner, *J. Org. Chem.*, **30**, 373 (1965), and other papers in this series.

(15) (a) H. C. Brown and M.-H. Rei, *J. Chem. Soc. D*, 1296 (1969); (b) H. C. Brown, M.-H. Rei, and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 1760 (1970).

(16) L. Overman, *J. Chem. Soc., Chem. Commun.*, 1196 (1972).

(17) In these cases the use of 1 equiv of mercuric trifluoroacetate results in ring closure by the addition of the imino nitrogen atom at C-2. Subsequent transformation of these intermediates affords the corresponding 2-amino alcohols; details to be reported in a future publication.

(18) Such treatment in THF results in the disappearance of **3** without formation of any detectable **4**. Details of this conversion will be reported in a future publication.

The 1,3 transposition of the  $-OH$  and  $-NH_2$  groups reported here will likely be most useful in the synthesis of highly hindered amines (or amides), e.g., **6** and **8**, for which there are few alternate methods.<sup>19</sup> The ease of hydrolytic removal of the trichloroacetyl group<sup>20</sup> and the low temperature of the catalyzed conversion are two important features of the overall transformation.

The following procedure for the catalyzed reaction is representative. Geranyl trichloroacetimidate **5** (25 mmol, prepared in 92% yield from geraniol) was dissolved in 125 ml of THF and cooled to  $-78^\circ$  under nitrogen. A solution of mercuric trifluoroacetate<sup>21</sup> (25 ml of a 0.2 M THF solution) was added dropwise over 15 min. The resulting solution was allowed to warm to room temperature during 1 hr, and pyridine (8 ml) was added to complex free mercuric ion.<sup>15a</sup> THF and excess pyridine were removed *in vacuo*, ether was added, and the ether solution was washed with  $H_2O$  until the aqueous extracts gave a negative test for ionic mercury ( $NaBH_4-NaOH$ ).<sup>10</sup> Drying ( $MgSO_4$ ) and short-path distillation afforded 5.93 g (79%) of **6**: bp  $111-114^\circ$  (0.5 Torr);  $\nu_{max}$  1700 (C=O) and 3420  $cm^{-1}$  (N-H);  $\tau$  ( $CCl_4$ ) 3.41 (broad singlet, 1 H, O=CNH); 3.8-5.2 (multiplet, 4 H, =C-H), 8.33, 8.41, and 8.52 (singlets, 3 H each,  $CH_3$ ).

**Acknowledgment.** We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-38634X) and the Merck Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

(19) C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley-Interscience, New York, N. Y., 1970, Chapter 8.

(20) R. S. Goody and R. T. Walker, *Tetrahedron Lett.*, 289 (1967).

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

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## Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XX. $C_3H_7^+$ Cations with a Polarized Basis Set

Sir:

The structure of protonated cyclopropane and of the  $C_3H_7^+$  potential energy surface remains a problem intensively investigated by both experimental<sup>1-3</sup> and theoretical<sup>4,5</sup> means. Our previous study of the  $C_3H_7^+$

(1) M. Saunders, P. Vogel, E. L. Hagan, and J. Rosenfeld, *Accounts Chem. Res.*, **6**, 53 (1973) and references cited therein. Also see D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.*, **9**, 179 (1972).

(2) S.-L. Chong and J. L. Franklin, *J. Amer. Chem. Soc.*, **94**, 6347 (1972).

(3) D. J. McAdoo, F. W. McLafferty and P. F. Bente, *J. Amer. Chem. Soc.*, **94**, 2027 (1972).

(4) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971); *ibid.*, **94**, 311 (1972).

(5) (a) MINDO/2 has been applied to the  $C_3H_7^+$  surface, but the results are in poor agreement with experiment (N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **93**, 6686 (1971); N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972); M. J. S. Dewar, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., Vol. 1, July 1971, Butterworths, London, p 1). (b) A MINDO/3 study gives more reasonable results (M. J. S. Dewar, Abstracts, 23rd National Organic Chemistry Symposium of the American Chemical Society, Tallahassee, Fla., June 1973, p 26.)