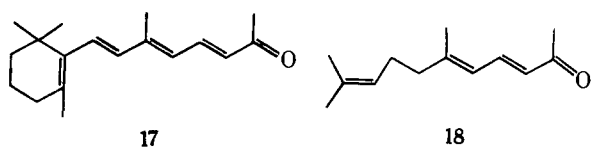
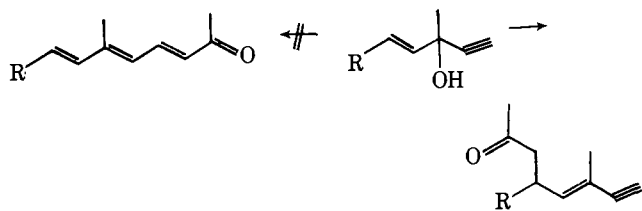


5.5 (d,  $J = 16$  Hz), and 6.2 (br d,  $J = 16$  Hz,  $\text{HC}=\text{CH}$ ).<sup>6</sup> The crude aldol was reduced in benzene with 1.2 equiv of sodium bis-2-methoxyethoxyaluminum hydride (2 h,  $\sim 15^\circ$ ). Acidification to pH 2 with 1:7 sulfuric acid-ice water was followed by workup and purification by passing through silica gel (elution with methylene chloride). The vinyllogous aldol **14** (40% from **11**) had  $R_f$  0.15 on silica gel,  $\lambda$  2.91, 5.98  $\mu$ ; NMR  $\delta$  1.4 (s,  $\text{HOCCCH}_3$ ), 2.3 (s,  $\text{O}=\text{CCH}_3$ ), 2.5 (br d,  $J = 7$  Hz,  $\text{HOCCCH}_2\text{C}=\text{C}$ ), and 6.0-7.2 (m,  $-\text{HC}=\text{CHC}(=\text{O})\text{CH}_3$ ). The vinyllogous aldols **15** and **16** from 6-methyl-5-heptene-2-one and hexanal, respectively, were prepared similarly in  $\sim 50\%$  overall yields. Dehydration of the vinyllogous aldols to conjugated dienones is easily achieved, as we illustrate for the preparation of the  $\text{C}_{18}$  ketone **17**: methanesulfonyl chloride<sup>7</sup> (2 equiv in tetrahydrofuran) was added slowly to the vinyllogous aldol **14** (0.5 M in tetrahydrofuran containing 7 equiv of triethylamine at  $0^\circ$ ). Workup after 1 h (extraction with petroleum ether, filtration through silica gel) then gave the known **17** in 74% yield.<sup>8,9</sup> The known dienone **18**<sup>10</sup> (pseudoinone) was prepared similarly from **15**.



Although the overall yields of vinyllogous aldols are only moderate (40-50%), the simplicity of the sequence and its compatibility with the existence of sensitive functionality (e.g., polyenes) should make it generally useful.<sup>11</sup> It is also worth emphasizing that the present method is of some importance in the construction of polyenones in general. There are at least two excellent methods<sup>12</sup> for the construction of conjugated dienones. They are, however, not suitable for the construction of more highly conjugated systems, such as **17**, because in such a situation the intermediates would un-



dergo chain extension by rearrangement toward the double rather than the triple bond.

**Acknowledgment.** We thank the National Institutes of Health and the National Science Foundation for their support of this work.

## References and Notes

- (1) Cf. H. O. House, "Modern Synthetic Reactions," 2d ed., W. A. Benjamin, Menlo Park, Calif., 1972.
- (2) G. Stork and R. Danheiser, *J. Org. Chem.*, **38**, 1775 (1973).
- (3) These are readily available by either of two methods: enol ether formation starting with symmetrical 1,3-diketones (cf. ref 5) or, in general, by alkoxide addition to conjugated ethynyl ketones.
- (4) G. Stork, G. A. Kraus, and G. Garcia, *J. Org. Chem.*, **39**, 3459 (1974).
- (5) Prepared from trimethyl orthoformate, acetyl acetone, and a small amount of *p*-toluenesulfonic acid in benzene-methanol at room temperature for 2 days, followed by distillation, according to unpublished results by R. Borch in this laboratory. For another, less convenient, method, cf. D. V. C. Aurang, *Can. J. Chem.*, **49**, 2672 (1971).
- (6) NMR spectra are in deuteriochloroform and IR spectra are taken neat.
- (7) In some related cases, superior results were obtained by the use of *p*-toluene sulfonylisocyanate as the dehydrating agent. (cf. L. C. Roach and W. H. Daly, *Chem. Commun.*, 606 (1970)).
- (8) We thank Professor K. Nakanishi for the authentic sample which had been prepared according to J. F. Arens and D. A. Van Dorp, *Recl. Trav. Chim. Pays-Bas*, **65**, 338 (1946).
- (9) The  $\text{C}_{18}$  ketone **17** thus obtained is an 85:15 *E:Z* mixture around the 9-10 double bond.
- (10) Identified by comparison with an authentic sample.
- (11) We have, for instance, used the vinyllogous aldol **16** as the starting material for an "ene synthesis" of prostaglandins: G. Stork and G. A. Kraus, in preparation.
- (12) W. Kimel, N. W. Sax, S. Kaiser, G. C. Eichmann, G. O. Chase, and A. Ofner, *J. Org. Chem.*, **23**, 153 (1958), and especially, G. Saucy and R. Marbet, *Helv. Chim. Acta*, **50**, 1158 (1967).

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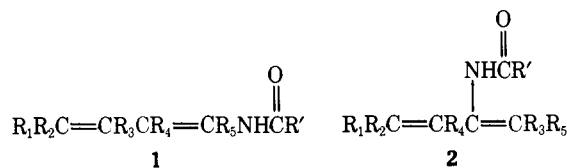
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## Synthesis of Trichloroacetamido-1,3-dienes. Useful Aminobutadiene Equivalents for the Diels-Alder Reaction

Sir:

Nitrogen substituted 1,3-dienes have received little study.<sup>1,2</sup> The most common examples are the sensitive *N,N*-disubstituted dieneamines, which are available by condensation of an unsaturated carbonyl compound with a secondary amine.<sup>2,3</sup> Acyclic dieneamides such as **1** and **2** are



virtually unexplored.<sup>2</sup> For example, in the parent butadiene system only a single report exists of the synthesis of the 2-acetamido- and 2-benzamido derivatives,<sup>4</sup> while the corresponding 1-isomers are apparently unknown.<sup>5</sup> In this communication we report that thermolysis of propargylic trichloroacetimidates affords a general, one-step route to a variety of trichloroacetamido-substituted 1,3-dienes (**1** and **2**,  $\text{R}'=\text{CCl}_3$ ,  $\text{R}_4=\text{H}$ ). The thermal rearrangement of propargylic imidates has not to our knowledge been previously reported.<sup>10</sup> Since the trichloroacetyl group can be removed by treatment with dilute base,<sup>11</sup> dienes such as **1** and **2** ( $\text{R}'=\text{CCl}_3$ ) hold particular synthetic interest as amino-1,3-diene equivalents for the Diels-Alder reaction. Few ni-

Table I. Synthesis of Trichloroacetamido 1,3-Dienes by Thermolysis of Propargylic Trichloroacetimidates<sup>a</sup>

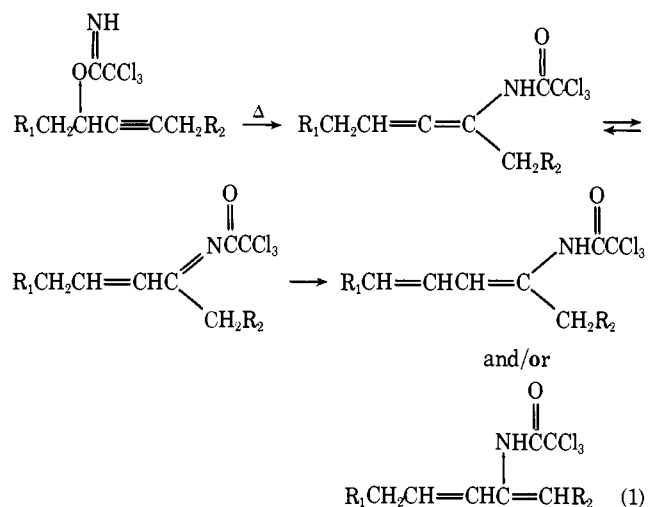
Alkynyl trichloroacetimidate	Trichloroacetamido-1,3-diene <sup>b</sup>	Mp, °C	Pyrolysis conditions <sup>c</sup> (°C, h)	Isolated yield, %
$\text{CH}_3\text{C}\equiv\text{CH}-\text{O}(\text{C}=\text{NH})\text{CCl}_3$		88–88.5	138°, 12	38
$\text{CH}_3\text{C}\equiv\text{CCH}_2\text{O}(\text{C}=\text{NH})\text{CCl}_3$		27–30	180°, 0.5	14 (28) <sup>d</sup>
$n\text{-C}_3\text{H}_7\text{C}\equiv\text{CH}-\text{O}(\text{C}=\text{NH})\text{CCl}_3$	$\text{C}_2\text{H}_5\text{CH}=\text{CHCH}=\text{CHNHCOCCl}_3$ <sup>e</sup>	34–47 (isomer mixture)	138°, 8	80
$n\text{-C}_5\text{H}_{11}\text{C}\equiv\text{CCH}_2\text{O}(\text{C}=\text{NH})\text{CCl}_3$		3 38–40 4 an oil	180°, 2	78
$(\text{CH}_3)_3\text{CCH}_2\text{CHC}\equiv\text{CC}(\text{CH}_3)_3$ 5		142.5–143	138°, 4	85
$\text{C}_6\text{H}_5\text{CH}_2\text{CHC}\equiv\text{CC}(\text{CH}_3)_3$		121–122	138°, 9	66
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_2\text{C}_2\text{H}_5$	$\text{C}_6\text{H}_5\text{C}=\text{CHCH}=\text{CHCH}_3$	129–130	110°, 12	45 (major isomer)

<sup>a</sup> No attempt has been made to optimize yields. <sup>b</sup> These compounds showed ir and NMR spectra consistent with the indicated structures and correct combustion analysis ( $\pm 0.4\%$ ) or exact mass measurements by high resolution mass spectrometry. <sup>c</sup> Solvents: toluene (110°), xylenes (135–140°), *o*-dichlorobenzene (180°). <sup>d</sup> Percent conversion, corrected for recovered starting material. <sup>e</sup> A combustion analysis was not obtained for this compound since it was moderately air sensitive. It is stable when stored under nitrogen at 0°. <sup>f</sup> Presumed stereochemistry in analogy with 6.

nitrogen substituted dienes, with the exception of *N,N*-disubstituted 1-amino-1,3-butadienes,<sup>12</sup> have found use in the Diels–Alder reaction,<sup>2–4,8,9,12–15</sup> and no useful synthetic equivalents for amino-1,3-dienes currently exist.<sup>14</sup> A preliminary account of the Diels–Alder reaction of three representative trichloroacetamido-1,3-dienes is reported.

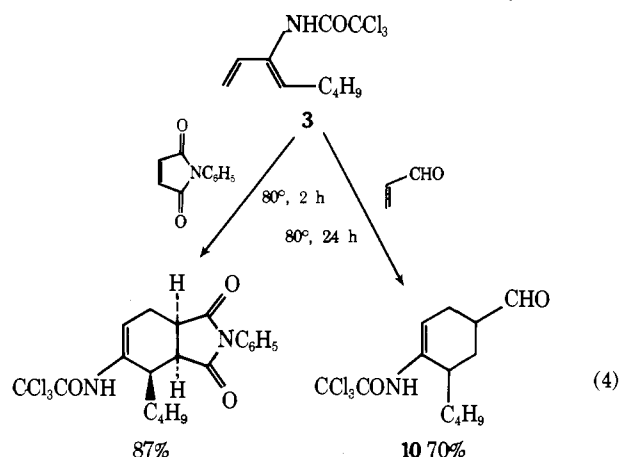
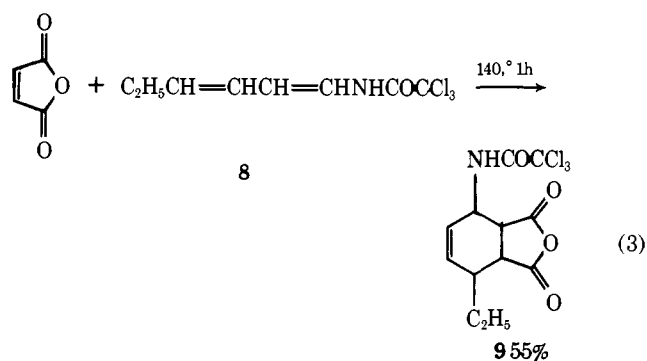
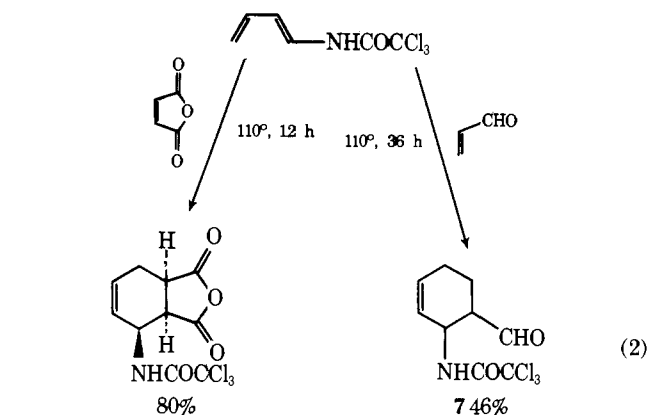
Propargylic alcohols are converted in high yields into the corresponding trichloroacetimidic esters by condensation with trichloroacetonitrile at 0°. Solution thermolysis of these esters results in 1,3-transposition of the oxygen and nitrogen atoms of the imidate moiety to afford, often in synthetically useful yields, 1,3-dieneamides (Table I). The parent 1,3-butadienes are formed in somewhat lower yields, and this is attributed to their further reaction under the thermolysis conditions.<sup>18</sup> Only a single isomer of 1-trichloroacetamido-1,3-butadiene was obtained. It is assigned the (*E*)-configuration on the basis of its 300-MHz <sup>1</sup>H NMR spectrum which showed no 1,4-trans-trans coupling for the trans C-4 vinylic hydrogen.<sup>19,20</sup> The stereochemical assignments for **3** and **4** also follow from the <sup>1</sup>H NMR spectra (300 MHz) which showed a larger downfield shift<sup>22</sup> ( $\delta$  6.09 vs. 5.60) for the C-4 vinylic hydrogen of **4**, and a long-range coupling of 1.7 Hz, attributed to 1,4-trans-trans coupling,<sup>19</sup> for the trans C-1 vinylic hydrogen of this isomer. Thermolysis of imidate **5** afforded in 92% yield a mixture of dienes of which the *E*, *Z*-isomer, **6**, was the major (~90%) component. The stereochemical assignment for **6** follows from <sup>1</sup>H NMR paramagnetic shift experiments (Eu(dpm)<sub>3</sub>) which gave the largest induced shift for the central vinylic hydrogen, and resolved the vinylic coupling constants ( $J = 14.3$  and 10.3 Hz).

A mechanistic rationale for the reactions described is illustrated in eq 1. The facile tautomerization of nitrogen substituted allene intermediates in thermal rearrangements is precedented.<sup>23</sup>



Diels–Alder reactions of three representative trichloroacetamido-1,3-dienes are illustrated in eq 2–4. As is apparent in eq 2 and 3 the 1-substituted isomers react quite sluggishly.<sup>2,13</sup> The reaction of *trans*-1-trichloroacetamido-1,3-butadiene with acrolein was, however, highly regioselective and afforded **7**<sup>24</sup> as a 3:1 mixture of *cis* and *trans* stereoisomers.<sup>25</sup> Dieneamide **8** must be at least 60% a single isomer (presumably *E,E*) since only one maleic anhydride adduct, **9**, mp 168.5–169.5 °C, was isolated. Diene **3**, with 2-trichloroacetamido substitution, is much more reactive and readily undergoes cycloaddition in refluxing benzene with maleic anhydride, *N*-phenylmaleimide (eq 4), and acrolein (eq 4). Addition of **3** to acrolein was also highly regioselective and afforded as the major product adduct **10**<sup>26</sup> as a 4:1 mixture of *cis* and *trans* stereoisomers.<sup>25</sup>

We are continuing to explore the thermal and catalyzed



Diels-Alder reactions of trichloroacetamido-1,3-dienes as well as attempting to prepare, by similar routes, more reactive Diels-Alder 1,3-dieneamides.

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## References and Notes

- (1) For example, the diene volume of "Houben-Weyl" devotes only 6 pages to such dienes.<sup>2</sup>
- (2) "Houben-Weyl", 4th ed, Vol. 5/1C, Thieme Verlag, Stuttgart, Germany, 1970, in particular pp 198-200, 513-514.
- (3) Cf. S. Hunig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957); recent examples include: H. Leotte, *Rev. Port. Quim.*, **7**, 214 (1965); *Chem. Abstr.*, **65**, 13647f (1966); G. Satzinger, *Justus Liebigs Ann. Chem.*, **728**, 64 (1969).
- (4) Reportedly prepared by acylation of 2-amino-1,3-butadiene which was formed from 2-amino-3-butyne by pyrolysis at 200-350 °C: J. B. Dickey, U.S. Patent 2 446 172 (1948); *Chem. Abstr.*, **42**, 8209i (1948).
- (5) The 1-phthalimido- and 2-phthalimido-1,3-butadienes are known. They are prepared by multistep sequences in low overall yield from 1,3-butadiene<sup>6</sup> and ethyl acetoacetate,<sup>7</sup> respectively. Recently the synthesis of a cyclic acetamido-1,3-diene from isophorone oxime was reported.<sup>8</sup> An apparently general synthesis of *trans*-N-acyl-N-alkyl-1-amino-1,3-dienes has also recently appeared.<sup>9</sup>
- (6) A. Terada, *Nippon Kagaku Zasshi*, **81**, 1773 (1960); A. Terada and K. Murata, *ibid.*, **83**, 490 (1962).

- (7) A. Terada and S. Takahashi, *Nippon Kagaku Zasshi*, **83**, 485 (1962).
- (8) R. B. Boar, J. F. McGhie, M. Robinson, D. H. R. Barton, D. C. Horwell, and R. V. Stick, *J. Chem. Soc., Perkin Trans. 1*, 1237 (1975).
- (9) W. Opolzer and W. Frostl, *Helv. Chim. Acta*, **58**, 587 (1975).
- (10) A previous report from our laboratory described the corresponding rearrangement of allylic trichloroacetimidates: L. E. Overman, *J. Am. Chem. Soc.*, **96**, 597 (1974).
- (11) (a) L. E. Overman, *Tetrahedron Lett.*, 1149 (1975); (b) L. E. Overman, *J. Am. Chem. Soc.*, in press.
- (12) For several recent examples see (a) W. G. Dauben and A. P. Kozikowski, *J. Am. Chem. Soc.*, **96**, 3664 (1974); (b) G. Satzinger, *Justus Liebigs Ann. Chem.*, **728**, 64 (1969).
- (13) A. S. Onishchenko, "Diene Synthesis", Israel Program of Scientific Translations, Daniel Davy and Co., New York, N.Y., 1964.
- (14) Successful Diels-Alder reactions of 1- and 2-phthalimido-1,3-butadienes have been reported.<sup>15</sup>
- (15) A. Terada and K. Murata, *Bull. Soc. Chem. Jpn.*, **40**, 1644 (1967).
- (16) These esters are prepared in yields of 80-100% by the base-catalyzed addition of alcohols to trichloroacetonitrile.<sup>17</sup> The procedure we have found most reproducible is to utilize the corresponding potassium alkoxide (0.1-0.2 equiv, from KH) as the catalyst and carry out the condensation with trichloroacetonitrile at 0° in an ethereal solvent.<sup>11b</sup> For tertiary and secondary alcohols it is essential that the ethereal alcohol-alkoxide solution be added to an ethereal solution of trichloroacetonitrile at 0°.
- (17) F. Cramer, K. Pawelzik, and H. J. Baldauf, *Chem. Ber.*, **91**, 1049 (1958); F. Cramer and H. J. Baldauf, *ibid.*, **92**, 370 (1959).
- (18) The yields were not significantly improved by adding up to 10% of *tert*-butylcatechol as a free radical inhibitor.
- (19) A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3445, 3451 (1965).
- (20) The observed magnitude ( $J = 9.5$  Hz) of the coupling constant for the vinylic hydrogens at C-1 and C-2 was inconclusive.<sup>21</sup>
- (21) Cf. the *cis*- and *trans*-1-alkoxy-1,3-butadienes: J. P. Dorie, M. L. Martin, S. Odiot, and F. Tonnard, *Org. Magn. Reson.*, **5**, 265 (1973).
- (22) In a possibly related system the *cis*-vinylic hydrogen of an enol acetate is more deshielded (larger  $\delta$ ) than a *trans*-vinylic hydrogen: H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).
- (23) R. W. Jemison, T. Laird, and W. D. Ollis, *J. Chem. Soc., Chem. Commun.*, 556 (1972).
- (24) A colorless liquid:  $\text{C}_9\text{H}_{10}\text{Cl}_3\text{NO}_2$  (MS);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 10.03 (d,  $J = 0.8$  Hz) and 9.97 (d,  $J = 1.6$  Hz) (CHO), 6.8 (m, NH), 5.4-6.2 (m,  $\text{CH}=\text{CH}$ ), and 4.7 (m,  $\text{CH-NHCOCCl}_3$ ).
- (25) Preferential endo-addition is assumed.<sup>2,13</sup>
- (26) A colorless liquid:  $\text{C}_{13}\text{H}_{18}\text{Cl}_3\text{NO}_2$  (MS);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 9.97 and 9.87 (br s, CHO), 7.6 (m, NH), and 6.17 (br t,  $J = 4$  Hz,  $=\text{CH}$ ).
- (27) (a) A. P. Sloan Foundation Fellow, 1975-1977; (b) Earl C. Anthony predoctoral fellow, 1974-1975.

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## Association of Isocyanide Complexes of Rhodium(I) and Rhodium(III) in Solution

Sir:

We have found that rhodium complexes of the type  $(\text{RNC})_4\text{Rh}^+$  and *trans*- $(\text{RNC})_4\text{RhX}_2^+$  (R = alkyl; X = halide) undergo appreciable association in solution. Previously, three other types of interaction between  $d^8$  and  $d^6$  complexes have been recognized. (1) A number of Pt(II) and Pt(IV) complexes associate in the solid state to form columns constructed of alternating quasi-planar Pt(II) and six-coordinate Pt(IV) centers.<sup>1</sup> In these columns halide ligands are located between platinum atoms in the column and no direct metal-metal bonding is present. (2) A different arrangement occurs in Krogmann's salt,  $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.32}(\text{H}_2\text{O})_{2.6}$ . In this case, reaction of  $\text{Pt}(\text{CN})_4^{2-}$  with  $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$  produces a solid which consists of stacks of  $\text{Pt}(\text{CN})_4$  units with direct platinum-platinum bonds.<sup>2</sup> (3) In solution the Pt(II)-catalyzed substitution reactions of Pt(IV) complexes are conventionally interpreted as involving a transient, ligand-bridged Pt(II)-Pt(IV) species.<sup>3</sup>

Electronic spectra, infrared spectra, and synthetic studies demonstrate the occurrence of the equilibrium shown in (1). Solutions containing both  $(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}^+$  and *trans*-