



5.5 (d, J = 16 Hz), and 6.2 (br d, J = 16 Hz, HC = CH).⁶ The crude aldol was reduced in benzene with 1.2 equiv of sodium bis-2-methoxyethoxyaluminum hydride (2 h, ~15°). 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 vinylogous aldol 14 (40% from 11) had $R_f 0.15$ on silica gel, λ 2.91, 5.98 μ ; NMR δ 1.4 (s, HOCCH₃), 2.3 (s, $O = CCH_3$), 2.5 (br d, J = 7 Hz, $HOCCH_2C = C$), and 6.0-7.2 (m, -HC=CHC(=O)CH₃). The vinylogous 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 vinylogous aldols to conjugated dienones is easily achieved, as we illustrate for the preparation of the C_{18} ketone 17: methanesulfonyl chloride⁷ (2 equiv in tetrahydrofuran) was added slowly to the vinylogous aldol 14 (0.5 M in tetrahydrofuran containing 7 equiv of triethylamine at 0°). Workup after 1 h (extraction with petroleum ether, filtration through silica gel) then gave the known 17 in 74% yield.8,9 The known dienone 1810 (pseudoionone) was prepared similarly from 15.



Although the overall yields of vinylogous 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.¹¹ 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 methods¹² for the construction of conjugated *di*enones. 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-



Journal of the American Chemical Society / 98:8 / April 14, 1976

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.
- G. Stork and R. Danheiser, J. Org. Chem, 38, 1775 (1973).
 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 ptoluene 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 C₁₈ ketone **17** thus obtained is an 85:15 *E:Z* mixture around the
- (9) The C₁₈ 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 vinylogous 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).

Gilbert Stork,* George A. Kraus

Department of Chemistry, Columbia University New York, New York 10027 Received December 24, 1975

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

Sir:

Nitrogen substituted 1,3-dienes have received little study.^{1,2} 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.^{2,3} Acyclic dieneamides such as 1 and 2 are



virtually unexplored.² For example, in the parent butadiene system only a single report exists of the synthesis of the 2acetamido- and 2-benzamido derivatives,⁴ while the corresponding 1-isomers are apparently unknown.⁵ 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, $R'=CCl_3$, $R_4=H$). The thermal rearrangement of propargylic imidates has not to our knowledge been previously reported.¹⁰ Since the trichloroacetyl group can be removed by treatment with dilute base,¹¹ dienes such as 1 and 2 ($R'=CCl_3$) 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 ^a
----------	--------------	--------------------	---------------	----------------	---------------	------------------------------------

Alkynyl trichloroacetimidate	Trichloroacetamido-1,3-diene ^b	Mp, ℃	Pyrolysis conditions ^c (°C, h)	Isolated yield, %
O(C=NH)CCl ₃				
CH ₃ CHC=CH	NHCOCCIs	88-88.5	138°, 12	38
CH ₃ C=CCH ₂ O(C=NH)CCl ₃ O(C=NH)CCl ₃		27-30	180°, 0.5	14 (28) ^d
<i>n</i> -C₃H ₇ CHC == CH	C ₂ H ₅ CH = CHCH=CHNHCOCCl ₃ ^e	34–47 (isomer mixture)	138°, 8	80
n-C ₅ H ₁₁ C=CCH ₂ O(C=NH)CCl ₃	$\begin{array}{c} \begin{array}{c} \text{NHCOCCl}_3 \\ \text{C}_4\text{H}_9 \end{array} + \begin{array}{c} \begin{array}{c} \text{NHCOCCl}_3 \\ \text{C}_4\text{H}_9 \end{array} \\ \begin{array}{c} \text{C}_4\text{H}_9 \end{array} \end{array}$	3 38–40 4 an oil	180°, 2	78
$\begin{array}{c} O(C \longrightarrow NH)CCl_{3} \\ (CH_{3})_{3}CCH_{2}CHC \longrightarrow CC(CH_{3})_{3} \\ 5 \end{array}$	(CH ₁) ₁ C 6	142.5-143	138°, 4	85
$O(C \longrightarrow NH)CCl_3$ $C_6H_5CH_2CHC \implies CC(CH_3)_3$ $O(C \implies NH)CCl_3$		121-122	138°, 9	66

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

129 - 130

CHCH=CHCH.

trogen substituted dienes, with the exception of N,N-disubstituted 1-amino-1,3-butadienes, 12 have found use in the Diels-Alder reaction, $^{2-4,8,9,12-15}$ and no useful synthetic equivalents for amino-1.3-dienes currently exist.¹⁴ A preliminary account of the Diels-Alder reaction of three representative trichloroacetamido-1,3-dienes is reported.

n

n

C.H.C==CCHC.H.

Propargylic alcohols are converted in high yields into the corresponding trichloroacetimidic esters by condensation with trichloroacetonitrile at 0°.16 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.¹⁸ 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 ¹H NMR spectrum which showed no 1,4-trans-trans coupling for the trans C-4 vinylic hydrogen.^{19,20} The stereochemical assignments for 3 and 4 also follow from the ¹H NMR spectra (300 MHz) which showed a larger downfield shift²² (δ 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,¹⁹ 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 (\sim 90%) component. The stereochemical assignment for 6 follows from ${}^{1}H$ NMR paramagnetic shift experiments (Eu(dpm)₃) 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.23



 $110^{\circ}, 12$

45

(major isomer)

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.^{2,13} The reaction of trans-1-trichloroacetamido-1,3-butadiene with acrolein was, however, highly regiospecific and afforded 7²⁴ as a 3:1 mixture of cis and trans stereoisomers.²⁵ 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 regiospecific and afforded as the major product adduct 10^{26} as a 4:1 mixture of cis and trans stereoisomers.²⁵

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.

Acknowledgment. We thank the National Science Foundation for support of this work under Grant No. GP-38634X and Mr. Everett R. Santee, Jr., of the University of Akron Institute of Polymer Science for assistance in obtaining the 300-MHz¹H NMR spectra.

References and Notes

- (1) For example, the diene volume of "Houben-Weyl" devotes only 6 pages to such dienes.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 exam-
- Bes 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, 8209*i* (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-butadiene⁶ and ethyl acetoacetate,⁷ respectively. Recently the synthesis of a cyclic acetamido-1,3-diene from isophorone oxime was reported.8 An apparently general synthesis of *trans-N*-acyl-*N*-alkyl-1-amino-1,3-dienes has also recently appeared.⁹
- (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. Oppolzer 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.
- Arn. Chem. Soc., in press.
 For several recent examples see (a) W. G. Dauben and A. P. Kozikow-ski, J. Am. Chem. Soc., 96, 3664 (1974); (b) G. Satzinger, Justus Lie-bigs Ann. Chem., 728, 64 (1969).
 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-buta-dienes have been reported.¹⁵
- (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.¹⁷ 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.^{11b} For tertiary and secondary alcohols it is essential that the ethereal alcoholalkoxide 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 tertbutylcatechol 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.2
- (21) Cf. the cis- and trans-1-alkoxy-1,3-butadienes: J. P. Dorie, M. L. Martin, S. Odot, 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 δ) than a trans-vinyite 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 coloriess liquid: $C_{9}H_{10}Cl_{3}NO_{2}$ (MS); ¹H NMR (CDCl₃, δ) 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, CH-CH), and 4.7 (m, CHNHCOCCI₃).
- (25) Preferential endo-addition is assumed.^{2, 13}
- (26) A colorless liquid: $C_{13}H_{18}Cl_3NO_2$ (MS); ¹H NMR (CDCl₃, δ) 9.97 and 9.87 (br s, CHO), 7.6 (m, NH), and 6.17 (br t, J = 4 Hz,==CH).
- (27) (a) A. P. Sloan Foundation Fellow, 1975-1977; (b) Earl C. Anthony predoctoral fellow, 1974-1975.

Larry E. Overman, *27a Lane A. Clizbe^{27b}

Department of Chemistry, University of California Irvine, California 92664 Received October 3, 1975

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

Sir:

We have found that rhodium complexes of the type $(RNC)_4Rh^+$ and trans- $(RNC)_4RhX_2^+$ (R = alkyl; X = halide) undergo appreciable association in solution. Previously, three other types of interaction between d⁸ and d⁶ 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.¹ 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. $K_2Pt(CN)_4Cl_{0.32}(H_2O)_{2.6}$. In this case, reaction of $Pt(CN)_4^{2-}$ with $Pt(CN)_4Cl_2^{2-}$ produces a solid which consists of stacks of Pt(CN)₄ units with direct platinum-platinum bonds.² (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.³

Electronic spectra, infrared spectra, and synthetic studies demonstrate the occurrence of the equilibrium shown in (1). Solutions containing both $(C_6H_{11}NC)_4Rh^+$ and trans-