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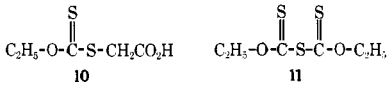
(3) Compare with the following. (a) Phthaloyl group: F. E. King and D. A. Kidd, *J. Chem. Soc.*, 3315 (1949); J. C. Sheehan and V. S. Frank, *J. Am. Chem. Soc.*, **71**, 1856 (1949). (b) 4,5-Diphenyl-4-oxazolin-2-one (Ox) group: J. C. Sheehan and F. Guziec, Jr., *J. Am. Chem. Soc.*, **94**, 6561 (1972); *J. Org. Chem.*, **38**, 3034 (1973). For recent reviews on amino protection, see (c) L. A. Carpino, *Acc. Chem. Res.*, **6**, 191 (1973); (d) J. W. Barton in J. F. W. McOmie, Ed., "Protective Groups in Organic Chemistry", Plenum Press, New York, N.Y., 1973, pp 43–93.
(4) An *orthogonal* system is defined as a set of completely independent classes of protecting groups. In a system of this kind, each class of groups can be removed in any order and in the presence of all other classes.
(5) Prepared by partial hydrolysis of trichloromethanesulfenyl chloride according to W. Weiss, German Patent 1 224 720 (Nov 11, 1964); *Chem. Abstr.*, **65**, 12112h (1966).
(6) Derivatives **3** were generally prepared in essentially quantitative yields by reaction of the parent amines with *O*-ethyl-*S*-carboxymethyl dithiocarbonate (**10**)[7] or bis(ethyloxythiocarbonyl) sulfide (**11**)[8]: G. Barany, B. W. Fulpius, and T. P. King, unpublished work.



10 **11**

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(10) Yields are intrinsically dependent on the nature of the substituent R. For amino acid ester derivatives **1d**, yields are typically 70–90%.
(11) We prepared **7**, bp 85–87 °C (27 mm), in excellent yield by thermolysis of the addition product between methyloxythiocarbonyl chloride[12] and chlorocarbonylsulfenyl chloride.[5] (b) Reported as part of partial hydrolysate mixture of bis(trichloromethyl)disulfane: N. Kobayashi, A. Osawa, and T. Fujisawa, *Chem. Lett.*, 1315 (1973).
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(15) Satisfactory elemental analyses have been obtained for all new compounds. The reported melting points are uncorrected.
(16) Generally detected on basis of UV absorbance. An especially useful method designed to specifically distinguish Dts compounds involved spraying thin layer plates first with 5% β-mercaptoethanol in 1-butanol, followed by 0.2% ninhydrin in 1-butanol, to develop spots of the characteristic color.
(17) Dts compounds can be determined directly on standard amino acid analyzers. For example, Dts-glycine ethyl ester and Dts-glycine eluted, respectively, near lysine and aspartic acid, with integration constants ranging from 25 to 33% of a norleucine internal standard. Apparently, the active reducing agent is hydrindantin, and the released amine reacts in situ with ninhydrin to give a purple color.
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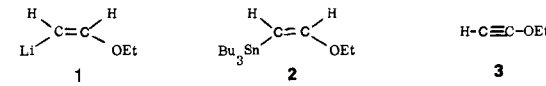
A Nucleophilic Acetaldehyde Equivalent. Preparation and Synthetic Applications of *cis*-2-Ethoxyvinyllithium

Sir:

Reactions which convert aldehydes or ketones to α,β-unsaturated aldehydes with simultaneous chain extension by two carbon atoms are highly useful synthetic operations. Unfortunately, a simple solution to this problem involving an aldol condensation between acetaldehyde and a carbonyl partner is not applicable owing to the facile self-condensation of acetaldehyde.[1,2] To overcome this restriction, a number of new reagents and processes have recently appeared. For example, the excellent process of Wittig involves masking of the nucleophilic aldehyde component as the metalated ethylidenecyclohexylamide.[2] Condensation with carbonyl compounds and subsequent hydrolysis has represented one of the most useful and simple procedures hitherto reported. The aldehyde component has also been masked as the corresponding dihydro-1,3-oxazine,[3] 2-oxazoline,[4] thiazole,[5] and thiazoline[6] and as the *N,N*-dimethylhydrazone.[7] Reactions based on Wittig-type condensations, for example, with the resonance-stabilized ylide formylmethylenetriphenylphosphorane,[8] diethyl carboxaldehydomethylphosphonate,[9] diethyl 2-(cyclohexylamino)vinylphosphonate,[10] and 1,3-dioxan-2-ylmethylenetriphenylphosphorane[11] have also been used for aldehyde synthesis. Recently, methods involving Lewis acid catalyzed condensations of an enol ether and a carbonyl group[12] or a ketal[13] were reported. In addition, aldehydes have been obtained by multistep procedures which involve addition of acetylide[14] and vinylmetallic reagents[15] to carbonyl groups.

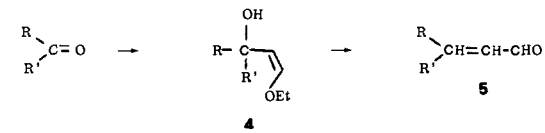
Despite the availability of this array of approaches, the known reagents are frequently unsatisfactory either as a result of their low reactivity or the necessity for subsequent acidic or multistep procedures to free the initially masked aldehyde, often resulting in poor overall yields.

We wish to report our finding that *cis*-2-ethoxyvinyllithium (**1**)[16] is a conveniently prepared and relatively stable nucleophilic acetaldehyde equivalent of considerable synthetic value. Formation of anion **1** proceeds smoothly and essentially quantitatively by reaction of *cis*-1-ethoxy-2-tri-*n*-butylstannylethylene (**2**), prepared by hydrostannation of the commercially available compound ethoxyacetylene (**3**, 94%),[17] with 1.1 equiv of *n*-butyllithium in THF at −78 °C for 1 h.[18] At −78 °C, the anion **1** reacts with aldehydes and ketones to produce the allylic alcohols **4** in excellent yields (Scheme I).



1 **2** **3**

Scheme I

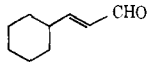
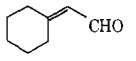
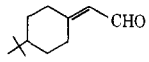
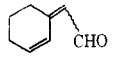
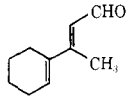
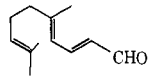
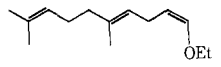


4 **5**

The most notable advantage of our procedure for carbonyl homologation compared with the Wittig directed aldol approach is the ease by which the intermediate enol ethers of type **4** are converted into α,β-unsaturated aldehydes under essentially nonacidic conditions. Thus, chromatography of these substances on silica gel or Florisil is sufficient to cause complete allylic rearrangement to the aldehydes **5** (Table I).[19] By contrast, the intermediate aldimine adducts prepared by the Wittig approach[2] require fairly vigorous acid hydrolysis for conversion to aldehydes. These acidic conditions not only result in lower overall yields but may also be incompatible with complex synthetic intermediates, particularly with functional groups protected as acid labile derivatives.

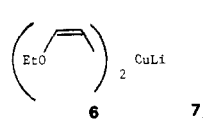
The reaction of **1** with halides was also investigated. In THF at −78 °C, alkylation of **1** with 1-bromo- or 1-iododecane requires HMPA as cosolvent (1 equiv). In the absence of HMPA the starting halides were completely recovered under similar conditions or even after slow warming to room temperature over 5 h.[20] The allylic halide, geranyl bromide, is more reactive and can be smoothly alkylated without HMPA as cosolvent. These intermediate enol ethers are converted by mild acid treatment (3:2:1 acetic acid–THF–water, 40 °C) to their corresponding carbonyl compounds, dodecanal and *trans*-5,9-dimethyl-4,8-decadienal,[21] in >95% isolated yields. We were, however, unsuccessful in alkylating **1** with benzyl bromide which gave only 1,2-diphenylethane, presumably by initial metal–halogen exchange to generate benzyllithium as an intermediate.

Table I. Reaction of *cis*-2-Ethoxyvinyllithium with Electrophiles

Electrophile	Adduct	Yield, %[a]
Cyclohexanecarboxaldehyde		89[b]
Cyclohexanone		97[b]
4-*tert*-Butylcyclohexanone		85
Benzaldehyde	$C_6H_5CH{=}CHCHO$	76[b,c]
2-Cyclohexen-1-one		66
1-Acetyl-1-cyclohexene		84
Geranial		95[b]
Geranyl bromide		70
1-Iododecane	$CH_3(CH_2)_{10}CHO$	82[b,d,e]

[a] The yields were based on products isolated by preparative TLC or column chromatography. All products exhibited satisfactory NMR, IR, and microanalytical data. Unless otherwise indicated the reaction was run in THF. [b] Melting points of 2,4-DNP derivatives were compared to literature values and found satisfactory. [c] This compound was compared by GLC analysis with an authentic sample. [d] Reaction in THF/HMPA. [e] The intermediate enol ether was hydrolyzed directly without purification.

Finally, we have investigated the preparation and synthetic utility of a vinylcuprate reagent derived from **1.** Addition of a THF solution of cuprous iodide and dimethyl sulfide[22] to a −78 °C solution of anion **1** produces the red-brown, soluble reagent **6.** The effectiveness of **6** as a nucleophile was demonstrated for both conjugate addition and direct displacement reactions. For example, using only 1.05–1.1 equiv of this reagent the conjugate adducts **7–9** were obtained from the corresponding unsaturated compounds as indicated (conditions, yield). With the halides 3-bromocyclohexene[23] and benzyl bromide the vinylated products **10** and **11** were formed at −78 °C in 79 and 80% yields, respectively. Typical experimental procedures follow.



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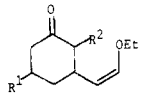
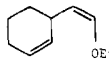


7, R^1, R^2 = H (-78 to -40° for 1.5 h, 82%)

8, R^1 =  ; R^2 = Me (-78 to -30° for 6 h, 70%)

9 (-78° to -10° for 5 h, 65%)



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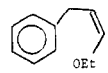

11

The generation and reaction of **1** with electrophiles is illustrated in the preparation of cyclohexylideneacetaldehyde. To a solution of 940 mg (2.60 mmol) of *cis*-1-ethoxy-2-tri-*n*-butylstannylethylene[17] in 10 mL of dry THF at −78 °C was added dropwise 1.70 mL (2.72 mmol) of 1.60 M *n*-butyllithium. After stirring for 1 h at −78 °C, 232 mg (2.36 mmol) of cyclohexanone was added over 1 min. The mixture was stirred at this temperature for 1 h and warmed to room temperature for 5 min. Aqueous sodium bicarbonate (2 mL) was added, the mixture was extracted with ether, and the isolated crude product was purified by column chromatography on silica gel to give 283 mg (97%) of the desired aldehyde.

The generation and reaction of cuprate **6** with electrophiles is demonstrated with 2-cyclohexen-1-one. A solution of **1** prepared as above from 2.18 g (6.04 mmol) of *cis*-1-ethoxy-2-tri-*n*-butylstannylethylene[17] in 15 mL of THF was cooled to −78 °C. A solution of 0.577 g (3.03 mmol) of purified cuprous iodide and 0.890 mL (12.1 mmol) of dimethyl sulfide[22] in 5 mL of THF was added over 5 min. After stirring for 1 h at this temperature, 0.264 g (2.75 mmol) of 2-cyclohexen-1-one in 5 mL of THF was added over 10 min. After stirring for 1 h, the mixture was warmed to −40 °C during 30 min, quenched with 20% NH_4Cl, and extracted with ether. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as eluent affording 379 mg (82%) of 3-(*cis*-2-ethoxyethenyl)cyclohexan-1-one (**7**): IR (film) 1715, 1668, 1125 cm^{-1}; NMR ($CDCl_3$) δ 5.93 (d, J = 6 Hz, 1 H), 4.28 (dd, J = 6 and 9 Hz, 1 H), 3.78 (q, J = 7 Hz, 2 H), 1.42–3.30 (br m, 9 H), 1.22 (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.78; H, 9.79.

In summary, *cis*-2-ethoxyvinyllithium (**1**) is a conveniently prepared reagent which provides a highly efficient route to α,β-unsaturated aldehydes from carbonyl compounds and a simple method for the two-carbon chain extension of halides to aldehydes. Further, a vinylcuprate reagent derived from **1** is easily prepared and undergoes smooth conjugate additions with α,β-unsaturated carbonyl compounds and complements the reactivity of **1** with regard to alkylation of halides.

Acknowledgments. We gratefully acknowledge support of this work by a National Starch and Chemical Corporation grant of Research Corporation and by a Biomedical Support grant of the National Institutes of Health to Stanford University.

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(16) A previous attempt to prepare anion **1** by transmetalation of *cis*-1-bromo-2-ethoxyethylene with *n*-butyllithium at −100 °C met with only limited success. See J. Ficini and J.-C. Depezay, *Tetrahedron Lett.*, 937 (1968).
(17) Examination of the NMR spectrum of **2** before and after distillation (bp 110 °C at 0.3 mm) revealed that within detectable limits the reaction affords only the cis isomer, consistent with previous studies (see A. J. Leusink, H. A. Budding, and J. W. Marsman, *J. Organomet. Chem.*, **9**, 285 (1967); A. J. Leusink, H. A. Budding, and W. Drenth, *ibid.*, **11**, 541 (1968)).
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J. Am. Chem. Soc., **99**, 4836 (1977); E. J. Corey, P. Ulrich, and J. M. Fitzpatrick, *ibid.*, 98, 222 (1976).
(19) The corresponding diethyl acetals are also readily prepared from **4** (*p*-TsOH, EtOH, 5 min, 0 °C).
(20) We are presently investigating the thermal stability of anion **1**.
(21) This compound was previously prepared in 10% overall yield from geranyl bromide by application of the reagent 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine (see ref 3). The low yield was attributed to the vigorous acid hydrolysis step required by this procedure. See T. Kato, H. Maeda, M. Tsunakawa, and Y. Kitahara, *Bull. Chem. Soc. Jpn.*, **44**, 3437 (1971).
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(23) With lithio reagent **1**, the halide was recovered unchanged (in THF containing 1 equiv of HMPA) at temperatures between −78 to 0 °C.

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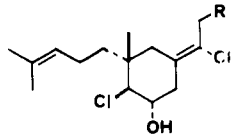
Carbonimidic Dichlorides from the Marine Sponge *Pseudaxinyssa pitys*

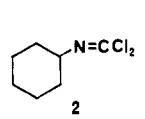
Sir:

Terpenoid isonitriles have been isolated from several sponges, mainly those of the order Halichondrida.[1] The isonitriles often coexist with the corresponding isothiocyanates, formamides, and primary amines.[2] We wish to report the isolation and structural elucidation of two carbonimidic dichlorides,[3] the first natural products found to contain this rare functionality.

The air-dried sponge *Pseudaxinyssa pitys* de Laubenfels (Axinellidae, Halichondrida)[4] was extracted with methanol. The chloroform-soluble material from the methanol extracts was chromatographed on Florisil to obtain the carbonimidic dichloride **1**, $C_{16}H_{23}NOCl_4$, $[\alpha]^{20}_D$ +36° (*c* 1.1, $CHCl_3$), as a clear oil (0.9% dry weight). The mass spectrum of **1** contained an $[M - Cl]^+$· cluster as the highest molecular weight peaks, as did the mass spectrum of cyclohexyl carbonimidic dichloride **2**, prepared by the method of Kühle et al.[3a] The ^{13}C NMR spectrum[5] of **1** contained 16 signals, including a low intensity signal at δ 127.1 ppm, assigned to the carbon atom in the carbonimidic dichloride functionality (cf. δ 122.0 for **2**). The infrared spectrum contained a strong $N{=}CCl_2$ band at 1647 cm^{-1} (lit.[3a] 1645–1660 cm^{-1}). Reduction of the carbonimidic dichloride **1** with lithium aluminum hydride in anhydrous tetrahydrofuran at −78 °C gave an isonitrile **3** (IR 2145 cm^{-1}) having the molecular formula $C_{16}H_{23}NOCl_2$.[6] The isonitrile **3** was converted into a formamide **4**[7] (IR 1680 cm^{-1}) by the action of 98% acetic acid.[1e] Treatment of the carbonimidic dichloride **1** with 0.1 N phosphoric acid in 95% methanol at 50 °C for ½ h resulted in the formation of a 2:1 mixture of the primary amine **5** (IR 3200 cm^{-1}) and the methylurethane **6**[8] (IR 3300, 1715 cm^{-1}). Each of these reactions was performed on cyclohexane carbonimidic dichloride **2** with similar results, confirming the presence of the carbonimidic dichloride functionality in **1**.



1 R = -N=CCl₂
3 R = -N⁺≡C⁻
4 R = -NHCHO
5 R = -NH₂
6 R = -NHCOOMe



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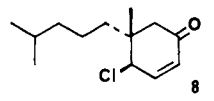

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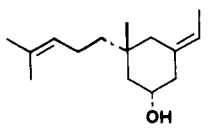
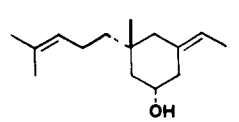


9a



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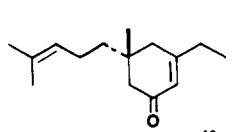
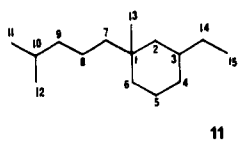


10



11

The ^1H NMR spectrum[9] of the carbonimidic dichloride **1** was almost identical with those of the isonitrile **3**,[6] formamide **4**,[7] and methyl urethane **6**,[8] except for variation of the chemical shift and multiplicity of a two-proton signal which appeared at δ 4.36 (s, 2 H) in **1**. Comparison of the chemical shift data for the two-proton signal in **1**, **3**, **4**, and **6** with suitable model compounds suggested that the carbonimidic dichloride was bonded to a methylene on an olefinic bond. The ^{13}C NMR spectrum[5] indicated the presence of trisubstituted and tetrasubstituted olefinic bonds, a carbon bearing hydroxyl (IR 3400 cm^{-1}) at δ 74.8 (d), a carbon bearing chlorine at 70.8 (d), a carbon bearing nitrogen at 57.4 (t), and one other tetrasubstituted carbon at 40.7 ppm. The carbon skeleton of **1** must therefore be monocyclic with the remaining chlorine atom on an olefinic bond.

The terminal trisubstituted olefinic bond gave rise to ^1H NMR signals at δ 1.62 (s, 3 H), 1.70 (s, 3 H), and 5.10 (br t, 1 H, J = 6 Hz). Hydrogenation of **1** over 10% palladium/charcoal gave a 9,10-dihydro derivative **7** having an isopropyl signal at δ 0.89 (d, 6 H, J = 6 Hz) in the ^1H NMR spectrum. Ozonolysis of **7** in methanol at −78 °C, followed by treatment with dimethyl sulfide, gave a γ-chloro-α,β-unsaturated ketone **8**. In the ^1H NMR spectrum[10] of **8**, all protons on the cyclohexenone ring were observed and their relationships determined by spin-decoupling experiments. Assuming that the hydroxy group had been eliminated from an intermediate β-hydroxy ketone formed by ozonolysis of the tetrasubstituted olefinic bond, we could place all the substituents on the six-membered ring of **1**. The ^1H NMR spectrum of **1** contained an α-chloro proton at δ 3.83 coupled to an α-hydroxy proton at δ 3.77 which was, in turn, coupled to two mutually coupled protons at 3.49 and 1.98 ppm. The lower field equatorial proton at C-4 exhibited a long-range coupling to an equatorial ring methylene proton at δ 2.52 which was, in turn, coupled to an axial methylene proton at 2.10 ppm. The tetrasubstituted carbon atom bearing a methyl group and the isoprenoid side chain must be located between the carbon bearing chlorine and the ring methylene. The coupling constants indicated that the chlorine and hydroxyl groups were both equatorial. The coupling constants were observed more clearly in the ^1H NMR spectrum[11] of the acetate of methylurethane **6**.

The relationship between the hydroxy group and the two-carbon side chain was confirmed by the following sequence. Reduction of **1** with lithium in liquid ammonia gave a 4:1 mixture of alcohols **9a** and **9b**. In the ^1H NMR spectrum of the mixture of alcohols, two quartets were observed at δ 5.35 (q, 0.8 H, J = 7 Hz) and 5.23 (q, 0.2 H, J = 7 Hz) and two doublets at 1.64 (d, 0.6 H, J = 7 Hz) and 1.57 (d, 2.4 H, J = 7 Hz), indicating that the alcohols were stereoisomeric at the newly formed trisubstituted olefinic bond. Oxidation of the alcohol mixture with Jones reagent, followed by isomerization of the olefinic bond into conjugation, using *p*-toluenesulfonic acid in benzene, gave the α,β-unsaturated ketone **10**,[12] which had an ethyl group at the β carbon.