justing the stereochemistry at C-5. This might involve, for example, epimerizing the amino group through a process related to that employed by Stork and Guthikonda in their yohimbine synthesis.[13] Alternatively, one could consider oxidizing the alcohol of the antipode corresponding to 11 to ketone, epimerizing the C-10 center, and then reducing ketone to the stereoinverted alcohol.

Since neither of these possibilities appeared especially attractive, we opted instead to simply vary the hydride agent used to reduce the isoxazolinium salt to isoxazolidine.[14] We hoped that by employing a reducing agent such as lithium aluminum hydride that would complex with the heterocyclic system, the C-9 substituent might better be able to exert its steric effect as a consequence of the tighter transition state. Reduction might then occur on the concave face of the molecule.[15] This did, in fact, prove to be the case. Although the cis-fused product **9** was still the major isomer of the lithium aluminum hydride reduction, a sufficient amount of the correct isomer was generated to complete the synthesis (ratio 2-3:1). Aluminum amalgam treatment of the mixture of **9** and **10**, chromatographic separation, and N,O-diacetylation of pure **10** gave an oil which was identical by TLC, IR, NMR, MS, and optical rotation [$[\alpha]^{25}_D$ -48.4° (*c* 0.0064, pyridine)] with the N,O-diacetylation product of natural (+)-paliclavine [$[\alpha]^{25}_D$ -49.6° (*c* 0.005, pyridine)].[16]

The work thus completes the first total synthesis of paliclavine, and does furthermore constitute the first total synthesis of a naturally occurring ergot alkaloid in optically active form. Since the reaction of (+)-paliclavine with acetaldehyde has been reported to yield (+)-paspaclavine (**13**),[2a] the synthesis of paliclavine does also constitute a total synthesis of the latter ergot alkaloid as well. The use of intermediate **5a** in the preparation of other ergot alkaloids as well as improvements in stereocontrol at C-5 are being examined.[17]

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(13) Stork, G.; Guthikonda, R. N. *J. Am. Chem. Soc.* **1972**, *94*, 5109.
(14) Yet another possibility would be to use a reducing agent that would cleave the N–O bond of the isoxazoline first and then effect reduction of the C–N bond. Sodium in ethanol is known to operate in this fashion. At present, however, we have not been able to obtain desirable products from this reduction procedure. See, for example, Jäger, V.; Buss, V. *Justus Liebigs Ann. Chem.* **1980**, 101.
(15) Reduction of isoxazolines by lithium aluminum hydride is believed to involve Li···O complexation during hydride transfer, see: Jäger, V.; Buss, V.; Schwab, W. *Justus Liebigs Ann. Chem.* **1980**, 122.
(16) We thank Dr. W. Acklin of the Eidgenössischen Technischen Hochschule and Dr. P. A. Stadler and Dr. T. Fehr of Sandoz Ltd. for generous samples of authentic paliclavine.
(17) All new compounds reported gave satisfactory spectral and analytical data or correct high-resolution mass spectral values for the molecular ion. The optical rotations were measured on a Perkin-Elmer 241 polarimeter.

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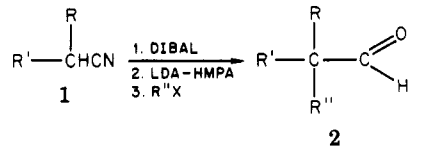
## Direct Conversion of Nitriles to α-Alkylated Aldehydes

*Summary:* An efficient one-pot process for direct conversion of primary and secondary nitriles to α-alkylated aldehydes has been developed.

*Sir:* We report a simple general method for direct conversion of primary and secondary nitriles (**1**) to α-alkylated aldehydes (**2**). This three-step one-pot synthesis is outlined by eq 1. Results of some applications of this method are presented in Table I. These reactions were carried out on 10–20-mmol scales and yields are for isolated pure products.



(1)

In most cases this synthesis offers important advantages over alternate routes to α-alkylated aldehydes with regard to availability of starting material, scope, convenience, and yield. Other methods include direct[1] and indirect[2-4] alkylation of aldehydes. Direct alkylation has been successful in certain cases; however, this method is very limited because of side reactions (viz.) self-condensation and O-alkylation).[1] Moreover, overalkylation can not be avoided if the aldehyde has two α-hydrogen atoms.[1b] Indirect methods that avoid these complications involve alkylation of imine[2,3] or hydrazone[4] derivatives of aldehydes. Alkylation of aldehydes via imines is a general method and has been used to prepare a number of alkylated aldehydes.[2] However, overall yields for the two steps are usually modest and the parent aldehyde is required. Modifications of this two-step process,[3] including a one-pot version,[3b] appear to offer little advantage over the original procedure.[2]

Aldehydes with two α-alkyl (or aryl) groups can be prepared from glycidic esters.[5] However, overall yields for preparation of glycidic esters and subsequent conversion to aldehydes are poor, and the method is limited to aldehydes with no more than two α-substituents.[5] Other routes to α-alkylated aldehydes include syntheses based on the dihydro-1,3-oxazine[6] and 2-thiazoline systems.[6] In general, these elegant aldehyde syntheses are not convenient for preparation of α-alkylated aldehydes.

The present method starts with generally readily available nitriles and gives good results with both primary and secondary nitriles (including cyclic nitriles, experiments 9 and 10) without complications from side reactions such as overalkylation or N-alkylation.[7] The first step involves treatment of the nitrile with diisobutylaluminum hydride (DIBAL) to form an aluminum imide (**3**). This reaction is very rapid in hexane at 0 °C. In experiment

(1) (a) Dietl, H. K.; Brannock, K. C. *Tetrahedron Lett.* **1973**, 1273. (b) Groenewegen, P.; Kallenberg, H.; Van der Gen, A. *Ibid.* **1978**, 491.
(2) (a) Stork, G.; Dowd, S. R. "Organic Syntheses"; Wiley: New York, 1974; Vol. 54, p 46. (b) Stork, G. U.S. Patent 3 230 216, 1966.
(3) (a) Cuvigny, Th.; Normant, H. *Bull. Soc. Chim. Fr.* **1970**, 3976. Curphey, T. J.; Hung, J. C.-Y. *Chem. Commun.* **1967**, 510. (b) Ho, T.-L.; Wong, C. M. *Synth. Commun.* **1974**, *4*, 147.
(4) Enders, D.; Eichenauer, H. *Tetrahedron Lett.* **1977**, 191.
(5) (a) Newman, M. S. "Organic Reactions"; Wiley: New York, 1949; Vol. 5, p 413. (b) Allen, C. F. H.; Van Allen, J. "Organic Syntheses", Collect. Vol. 3; Wiley: New York, 1955; p 733.
(6) Meyers, A. I. "Heterocycles in Organic Synthesis"; Wiley: New York, 1974; pp 201-212.
(7) Nitriles can also be converted to aldehydes directly by alkylation of the nitrile followed by reduction with DIBAL. However, with this sequence, overalkylation of primary nitriles is a serious side reaction.

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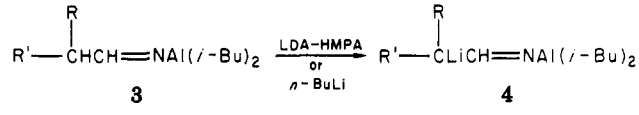
Table I. Conversion of Nitriles (1) to α-Alkylated Aldehydes (2)

| exp | nitrile (1) R′ | nitrile (1) R | R″X | % 2 isolated |
|---|---|---|---|---|
| 1 | Ph | H | *n*-BuBr | 70[a] |
| 2 | Ph | H | $Me_2SO_4$ | 64[b] |
| 3 | *n*-Bu | H | *n*-$C_5H_{11}Br$ | 85[c] |
| 4 | *n*-Bu | H | $CH_2$=$CHCH_2Br$ | 72[d] |
| 5 | *n*-Bu | H | $Me_2SO_4$ | 71[e] |
| 6 | *n*-Bu | H | *i*-PrBr | 55[f] |
| 7 | Me | Me | *n*-BuBr | 74[g] |
| 8 | Me | Me | $C_6H_5CH_2Br$ | 65[h] |
| 9 | $(CH_2)_4$ | | $C_6H_5CH_2Br$ | 63[i] |
| 10 | $(CH_2)_4$ | | *n*-$C_5H_{11}Br$ | 72[j] |

[a] **α-Butylbenzeneacetaldehyde**: bp 83–86 °C (1.7 mm); IR (neat) 3071 (w), 3051 (w), 3016 (w), 2946 (s), 2921 (s), 2861 (m), 2846 (m), 2801 (m), 2701 (w), 1725 (s), 1600 (w), 1492 (m), 1466 (m), 1458 (m), 1452 (m), 760 (m), 702 (s) $cm^{-1}$; 100-MHz. NMR ($CCl_4$) δ 9.44 (d, 1 H, $J$ = 3 Hz), 8.01–6.41 (m, 5 H), 3.34 (m, 1 H), 1.99 (m, 1 H), 1.68 (m, 1 H), 1.51–1.05 (m, 4 H), 1.05–0.61 (m, 3 H). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.27. 2,4-DNP, mp 113–114 °C. [b] 2,4-DNP, mp 135–136 °C (lit.[5b] mp 135 °C). Spectral features same as those of an authentic sample.[5b] [c] See text for properties of product. [d] **2-(2-Propenyl)hexanal**: bp 75–77 °C (17 mm); IR (neat) 3069 (m), 2949 (s), 2919 (s), 2864 (s), 2849 (s), 2797 (m, sh), 2699 (m), 1729 (s, sh), 1724 (s), 1639 (m), 1466 (m), 1456 (m), 1442 (m), 1418 (w), 994 (m), 919 (s), 729 $cm^{-1}$ (m); NMR ($CCl_4$) δ 9.44 (s, 1 H), 6.00–5.40 (m, 1 H), 5.20–4.80 (m, 2 H), 2.60–2.00 (m, 3 H), 1.80–1.05 (m, 6 H), 1.05–0.60 (br t, 3 H, $J$ = 4 Hz). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.99; H, 11.49. 2,4-DNP, mp 119 °C. [e] 2,4-DNP, mp 112–113.5 °C; semicarbazone, mp 94.5–95.5 °C (lit.[10] mp 92–93 °C). Spectral properties same as those for an authentic sample.[2b] [f] Product, bp 86–90 °C (38 mm) [lit.[11] bp 85–86 °C (40 mm)]; 2,4-DNP, mp 140–141 °C (lit.[11] mp 140.5–141 °C). [g] Product, bp 76–78 °C (60 mm) [lit.[2b] bp 65–67 °C (40 mm)]; 2,4-DNP, mp 135–136 °C (lit.[2b] mp 135–135.5 °C). [h] Product, bp 75–77 °C (2.6 mm) [lit.[2b] bp 70–73 °C (1.5 mm)]; 2,4-DNP, mp 151–152 °C (lit.[2b] mp 150–152 °C). [i] **1-Phenylmethylcyclopentanecarboxaldehyde**: bp 103 °C (1.6 mm); IR (neat) 3070 (w), 3050 (w), 3015 (m), 2945 (s), 2900 (m), 2857 (m), 2795 (w), 2710 (w), 2680 (w), 1719 (s), 1495 (m), 1452 (m), 760 (m), 730 (m), 703 $cm^{-1}$ (s); NMR ($CCl_4$) δ 9.44 (s, 1 H), 7.37–6.81 (m, 5 H), 2.86 (s, 2 H), 2.21–1.81 (m, 2 H), 1.81–1.27 (m, 6 H). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.05; H, 8.63. 2,4-DNP, mp 134 °C. [j] **1-Pentylcyclopentanecarboxaldehyde**: bp 66–69 °C (1.9 mm); IR (neat) 2945 (w), 2915 (s), 2855 (s), 2780 (m), 2700 (m), 2675 (m), 1722 (s), 1465 (m), 1457 (m), 1448 (m), 1440 (m), 1379 (m), 727 $cm^{-1}$ (m); NMR ($CCl_4$) δ 9.24 (s, 1 H), 2.13–1.81 (m, 2 H), 1.81–1.40 (m, 6 H), 1.40–1.02 (m, 8 H), 0.87 (br t, 3 H, $J$ = 6 Hz). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.38; H, 11.91. 2,4-DNP, mp 132.5–133.5 °C.

1, immediately after addition of DIBAL (in hexane) to a two-phase mixture of phenylacetonitrile and hexane, the infrared spectrum of the now homogeneous solution showed strong imine absorption (1665 $cm^{-1}$) and the cyano absorption (2250 $cm^{-1}$) was absent.

In the second step, **3** is converted to the lithium–aluminum complex of the dianion (**4**) by treatment with a suitable base.[7] Two methods were used for this step. In method A, **3** was treated with 1 equiv of lithium diisopropylamide (LDA) and a slight excess of hexamethylphosphoramide (HMPA) at −10 °C. *n*-Butyllithium gives complete conversion of **3** to **4** at −25 °C (method B), providing (a) the α-hydrogens are benzylic, and (b) sufficient ether is added so that the solvent is about a 1:1 ether/hexane mixture. Yields of final product are reduced sharply if ether is not present. Method B was used in experiments 1 and 2 and method A was used in the other experiments.[8]




**3** **4**

The final step in eq 1 is alkylation of **4**. The alkylation product is converted to aldehyde by acid hydrolysis. As can be seen from Table I, good results were obtained with a variety of alkylating reagents, including isopropyl bromide.

The following procedure for the preparation of 2-*n*-butylheptanal (experiment 3) is typical. A 100-mL flask was flushed with dry nitrogen and charged with 1.94 g of hexanenitrile (20 mmol) in 5 mL of anhydrous ether.[9a] The solution was chilled to −10 °C and 20 mL of DIBAL in hexane (20 mmol) was added. The resulting solution was stirred for 30 min after which 20 mmol of LDA (prepared by addition of 20 mmol of *n*-BuLi in 12 mL hexane to 2.02 g of diisopropylamine[9b] (20 mmol) in 27 mL of ether at −78 °C) was added. Addition of 4.5 g of HMPA[9c] (25 mmol) gave a clear yellow solution which was stirred for 1 h at room temperature (with secondary nitriles, yields are improved substantially if the reaction mixture is refluxed for 0.5–1.0 h at this point). The mixture was cooled to −10 °C and 3.32 g of 1-bromopentane (22 mmol) was added. The resulting solution was stirred at −10 °C for 5 h and at room temperature for 15 h and then refluxed for 1 h. The cooled reaction mixture was treated with 40 mL of 20% $H_2SO_4$ and steam distilled. The distillate (~300 mL) was extracted with ether. After the solvent was dried ($MgSO_4$) and removed, 2.88 g (85%) of colorless 2-*n*-butylheptanal, bp 85–86 °C (5.7 mm), was obtained by vacuum distillation. The 2,4-DNP derivative had a melting point of 108.5–109 °C (lit.[2b] mp 107.5–108 °C).

The above procedure is general and applicable to all nitriles and alkylation reactions included in Table I.

**Acknowledgment.** This work was supported by the National Science Foundation (Grant CHE-8108535).

(8) For systems in which the α-hydrogen atoms are not benzylic, method A was superior to several other base systems, including (1) *n*-BuLi, (2) *n*-BuLi–HMPA, (3) *n*-BuLi–TMEDA, (4) *t*-BuLi, and (5) LDA without HMPA.

(9) (a) Distilled from LAH before use. (b) Distilled from KOH. (c) Dried over calcium hydride, vacuum distilled, and stored over molecular sieve 13× in sealed container.

(10) Green, M. B.; Hickinbottom, W. J. *J. Chem. Soc.* **1957**, 3262.
(11) Rinehart, K. L., Jr.; Dolby, L. J. *J. Org. Chem.* **1957**, *22*, 13.

**Registry No.** 1 (R = H; R′ = Ph), 140-29-4; 1 (R = H; R′ = *n*-Bu), 628-73-9; 1 (R = R′ = Me), 78-82-0; 1 (R = R′ = $(CH_2)_4$), 4254-02-8; 2 (R = H; R′ = Ph; R″ = *n*-Bu), 73083-29-1; 2 (R = H; R′ = Ph; R″ = *n*-Bu) 2,4-DNP, 79792-46-4; 2 (R = H; R′ = Ph; R″ = Me), 93-53-8; 2 (R = H; R′ = Ph; R″ = Me) 2,4-DNP, 5530-36-9; 2 (R = H; R′ = *n*-Bu; R″ = *n*-$C_5H_{11}$), 998-62-9; 2 (R = H; R′ = *n*-Bu; R″ = *n*-$C_5H_{11}$) 2,4-DNP, 1243-29-4; 2 (R = H; R′ = *n*-Bu; R″ = $CH_2CH{=}CH_2$), 4456-87-5; 2 (R = H; R′ = *n*-Bu; R″ = $CH_2CH{=}CH_2$) 2,4-DNP, 30479-98-2; 2 (R = H; R′ = *n*-Bu; R″ = Me), 925-54-2; 2 (R = H; R′ = *n*-Bu; R″ = Me) 2,4-DNP, 23546-53-4; 2 (R = H; R′ = *n*-Bu; R″ = Me) semicarbazone, 1070-43-5; 2 (R = H; R′ = *n*-Bu; R″ = *i*-Pr), 79769-78-1; 2 (R = H; R′ = *n*-Bu; R″ = *i*-Pr) 2,4-DNP, 79769-79-2.

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## A Total Synthesis of Racemic Senepoxide: Formal Syntheses of Crotepoxide and Pipoxide

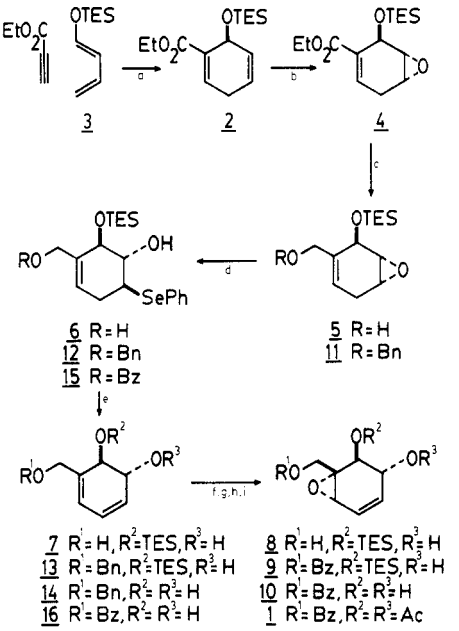
*Summary:* Diels–Alder reaction of 1-(triethylsiloxy)-buta-1,3-diene with ethyl propiolate affords an excellent yield of the dihydrobenzene adduct **2** which has been transformed into senepoxide. Formal syntheses of crotepoxide and pipoxide also have been carried out from **2**.

*Sir:* Senepoxide (**1**),[1] crotepoxide,[2] and pipoxide[3] belong to a small group of naturally occurring oxygenated cyclohexane derivatives. Our interest in these title substances arose from the realization that syntheses of them could be forthcoming from the dihydrobenzene derivative **2**. The ready tendency of substances like **2** to undergo thermal aromatization notwithstanding,[4] we report here the preparation of **2** using the Diels–Alder format. We also report the conversion of this adduct into the natural product **1**, as well as into synthetic intermediates which constitute formal syntheses of crotepoxide and pipoxide.[5]

Following the procedure used by Mukaiyama for the synthesis of 1-(trimethylsiloxy)buta-1,3-diene, we prepared the triethylsilyl analogue **3** (bp 120–125 °C).[6] Reaction of **3** with ethyl propiolate (1.1 equiv to 1.0 equiv, respectively; as a neat mixture to which had been added a crystal of methylene blue and then subjected to three freeze–thaw cycles at $10^{-6}$ torr and sealed under vacuum) at 80 °C for 120 h gave, after removal of the volatiles, crude **2** as a yellow oil in 87% yield (Scheme I). The structure of **2** followed from its $^1H$ spectrum recorded at 400 MHz.[7] This spectrum also indicated **2** to be 90% pure and as such its was used for all further reactions.[8]

In order to prepare senepoxide from **2**, we first monoepoxidized the diene using 95% *m*-chloroperbenzoic acid (*m*-CPBA) buffered with sodium bicarbonate in benzene solution to obtain the epoxide **4** contaminated with a small amount of its β isomer. This substance was then reduced with diisopropylaluminium hydride to give the corresponding allylic alcohol **5** which could be readily separated

**Scheme I**[a]




[a] (a) Compound **3** 1.1 equiv, ethyl propiolate 1.0 equiv, neat mixture, 10 mg of methylene blue, three freeze–thaw cycles at $10^{-6}$ torr, sealed under vacuum, 80 °C for 120 h, volatiles removed under vacuum. (b) Compound **2** 1.0 equiv, $NaHCO_3$ 3.1 equiv, *m*-CPBA 2.0 equiv, benzene (0.35 M), 22 °C, 48 h, standard workup. (c) Compound **4** 1.0 equiv, 0.1 M hexane, diisobutylaluminum hydride 2.1 equiv in hexane, −78 °C, 30 min, 0 °C quench with 2-propanol, standard workup. (d) Compound **5** 1.0 equiv, PhSeNa 2.0 equiv, EtOH 0.4 M, 80 °C, 3 h, standard workup, melting point of **6** 61–62 °C. (e) Compound **6** 1.0 equiv, $CH_2Cl_2$ 0.1 M, $NaHCO_3$ 2.0 equiv, −78 °C, dropwise addition of *m*-CPBA 1.0 equiv in $CH_2Cl_2$ 0.3 M, slowly warmed to 22 °C, stirred 8 h, standard workup. (f) Compound **7** 1.0 equiv, 0.1 M in $CH_2Cl_2$, −40 °C, *m*-CPBA 1.1 equiv in $CH_2Cl_2$ 0.3 M added dropwise, −40 °C for 30 min, 0 °C for 30 min, standard workup. (g) Compound **8** 1.0 equiv, 0.04 M $CH_2Cl_2$, $Et_3N$ 6 equiv, BzCl 3.0 equiv, −40 °C for 2 h, standard workup. (h) Compound **9** 1.0 equiv, MeOH 0.2 M at 0 °C add one drop of 5% HCl, 15 min at 0 °C standard workup. (i) Compound **10** 1.0 equiv, 0.5 M in $C_5H_5N$, 0 °C, $Ac_2O$ 6.5 equiv, 10 mg of DMAP, warm to 22 °C, 15 min, filtration chromatography, white solid mp 97–98 °C.

(1) For the isolation of senepoxide, see Hollands, R.; Becker, D.; Gaudemar, A.; Polonsky, J. *Tetrahedron* **1968**, *24*, 1633. The X-ray structure of senepoxide has been determined by Ducruix, A.; Pascard, C.; Polonsky, J. *Acta Crystallogr., Sect. B* **1976**, *32*, 1589.

(2) For the isolation of crotepoxide, see (a) Kupchan, S. M.; Hemingway, R. J.; Coggon, P.; McPhail, A. T.; Sim, G. A. *J. Am. Chem. Soc.* **1968**, *90*, 2982. (b) Kupchan, S. M.; Hemingway, R. J.; Smith, R. M. *J. Org. Chem.* **1969**, *34*, 3898. (c) Takahashi, S. *Phytochemistry* **1969**, *8*, 321. For a description of the X-ray structure of crotepoxide, see Coggon, P.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. B* **1969**, 534.

(3) For the isolation and publication of the incorrect structure of pipoxide, see Singh, J.; Dhar, K. L.; Atal, C. K. *Tetrahedron* **1970**, *26*, 4403. For the correct structure of pipoxide as well as its synthesis, see Holbert, G. W.; Ganem, B.; Van Egen, D.; Clardy, J.; Borsub, K.; Chantrapromma, K.; Sadavongvivad, C.; Thebtaranonth, Y. *Tetrahedron Lett.* **1979**, 715. (b) Joshi, B. S.; Gawd, D. H.; Fuhrer, H. *Ibid.* **1979**, 2427.

(4) For a recent experimental description of this type of phenomenon, see Wolinsky, J.; Login, R. B. *J. Org. Chem.* **1970**, *35*, 3205.

(5) For syntheses of senepoxide, see (a) Ichihara, A.; Oda, K.; Kobayashi, M.; Sakamura, S. *Tetrahedron Lett.* **1974**, 4235. (b) Holbert, G. W.; Ganem, B. *J. Am. Chem. Soc.* **1978**, *100*, 352. (c) Ganem, B.; Holbert, G. W.; Weiss, L. B.; Ishizumi, K.; *Ibid.* **1978**, *100*, 6438. (d) Ganem, B. *Tetrahedron* **1978**, *34*, 3353. (e) Ichihara, A.; Oda, K.; Kobayashi, M.; Sakamura, S. *Tetrahedron* **1980**, *36*, 183. For syntheses crotepoxide, see (a) Oda, K.; Ichihara, A.; Sakamura, S. *Tetrahedron Lett.* **1975**, 3187. (b) Demuth, M. R.; Garrett, P. E.; White, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 634. (c) Matsumoto, M.; Dobashi, S.; Kuroda, K. *Tetrahedron Lett.* **1977**, 3361. For the synthesis of pipoxide, see reference 3a.

(6) Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1161.

(7) We thank the National Science Foundation for funds that helped purchase the Bruker WH-400 spectrometer.

(8) Compound **2** could be purified only with great difficulty; however, this substance could be stored at −20 °C in the 90% pure state for long periods without decomposition.

0022-3263/81/1946-5252$01.25/0 