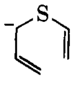
Treatment of allyl vinyl sulfide, bp 38° (37 mm),[4,5] in dry tetrahydrofuran at −78° with 1 equiv of *sec*-butyllithium in pentane gave a yellow solution containing the anion **1**, which is stable at that temperature but which decomposes slowly at 0°. The formation of the anion **1** was verified by reaction with 1 equiv of benzyl bromide (−78° for 30 min, then −30° for 30 min) to give the sulfide **2** ($R = CH_2C_6H_5$), shown by nmr analysis to be >85% pure. The crude sulfide was dissolved in dimethoxyethane (DME) and water (3:1) in the presence of calcium carbonate (~3 equiv), and the mixture was heated at reflux for 12 hr. After purification by thin layer chromatography (tlc), the desired aldehyde **3** ($R = CH_2C_6H_5$) was obtained in 62% over-all yield: mass *m/e* 174 (M^+); ir (neat) 2730, 1730 (s, C=O), 970 cm^{-1} (s, trans C=C); nmr (CCl_4, TMS) δ 5.4–5.7 (m, 2 H, olefinic proton), 9.76 (t, 1 H, J = 1 Hz, CHO). The gas chromatographic (glpc, t_r 4.50 min, using 1-m of 5% OV-1 column at 130°) and silver nitrate-silica gel tlc (R_f 0.67, CH_2Cl_2) analyses showed the absence of detectable amounts (<1%) of the geometrically isomeric olefin.



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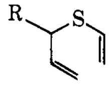

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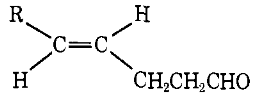
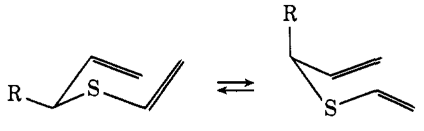


3

In a similar experiment[6] octyl bromide and geranyl bromide gave the corresponding aldehyde **3**, $R = n\text{-}C_8H_{17}$ (57%)[7] and R = geranyl (62%),[8] respectively.

The basis for the high stereoselectivity in this reaction can be explained by essentially the same arguments used to rationalize the stereochemical outcome of Claisen rearrangement;[9] conformer **4**, a precursor to trans olefin in the transition state, is favored over **5** which leads to cis product, because the alkyl substituent has preference for occupying an equatorial position.



4 **5**

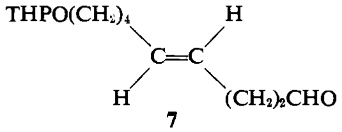
Comment is required on the choice of conditions for the above described reaction sequence.

1. In general, the combination of 1,4-diazabicyclo[2.2.2]octane (DABCO) and *n*-butyllithium is the most satisfactory base for the metalation of allyl sulfides,[10,11] while *n*-alkyllithium reagents alone are poor. However, the lithiation of allyl phenyl sulfide with the DABCO-*n*-butyllithium system followed by alkylation gave a mixture of α and γ alkylated product (α/γ = *ca.* 7:3).[11] In contrast, *sec*-butyllithium *without* DABCO in tetrahydrofuran proved to be an excellent reagent for the metalation–alkylation process of allyl phenyl sulfide to give the α-alkylated product almost exclusively (>95% selectivity and quantitative yield with methyl iodide).

2. Heating **2** ($R = CH_2C_6H_5$) at 180–200° with or without red mercuric oxide[2b] afforded only an intractable tar but no desired aldehyde **3** ($R = CH_2C_6H_5$). The DME–water method, on the contrary, gave most satisfactory results under sufficiently mild conditions and therefore should broaden the scope and utility of the thio-Claisen rearrangement.

The remarkably stereoselective and simple synthesis of **3** ($R = CH_2C_6H_5$) provided the essential information leading to a facile stereoselective synthesis of the sex attractant of the pink bollworm moth, *Pectinophora gossypiella Saunders*, so-called propylure.[12] Starting with readily available iodide **6**,[13] and using the same procedure as described for the conversion of benzyl bromide to the aldehyde **3** ($R = CH_2C_6H_5$), we obtained 9-(2′-tetrahydropyranyloxy)-*trans*-4-nonenal (**7**)[14] cleanly in 55% yield. In view of the earlier synthesis of propylure from **7** (simple Wittig reaction),[15] the synthesis of the latter by the route described above constitutes a formal total synthesis of this hormone. This route is apparently most advantageous in comparison to the previous ones[15,16] requiring a lengthy and conventional chain-extension reaction and giving very low yields of the final product.

$ICH_2CH_2CH_2CH_2OTHP$
6



7

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[4] Prepared from lithium ethenethiolate [L. Brandsma and P. J. W. Schuijl, *Recl. Trav. Chim. Pays-Bas*, **88**, 513 (1969)] and allyl bromide in liquid ammonia (62% after distillation).

[5] All new compounds reported in this communication have been characterized spectrometrically and analytically.

[6] Alkyl bromides and iodides were found to give most satisfactory results for this reaction. Alkyl chlorides were much less reactive to **1** except for benzylic and allylic cases.

[7] Mass *m/e* 196 (M^+); ir (neat) 2725, 1730 (s, C=O), 970 cm^{-1} (s, trans C=C); nmr (CCl_4, TMS) δ 5.3–5.5 (m, 2 H, olefinic proton), 9.65 (t, 1 H, J = 1 Hz, CHO); homogeneous by glpc and $AgNO_3$–SiO_2 tlc assay.

[8] Mass *m/e* 220 (M^+); ir (neat) 2720, 1728 (s, C=O), 970 cm^{-1} (s, trans C=C); nmr (CCl_4, TMS) δ 9.63 (t, 1 H, J = 1 Hz, CHO); homogeneous by glpc and $AgNO_3$–SiO_2 tlc assay.

[9] P. Vittorelli, T. Winkler, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **51**, 1457 (1967).

[10] The combination of DABCO-*n*-butyllithium: E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).

[11] J. F. Biellmann and J. B. Ducep, *Tetrahedron Lett.*, 5629 (1968); see also, V. Rautenstrauch, *Helv. Chim. Acta*, **54**, 739 (1971); E. E. van Tamelen, R. A. Holton, R. E. Hopla, and W. E. Konz, *J. Amer. Chem. Soc.*, **94**, 8228 (1972).

[12] Isolated and identified as 1-acetoxy-10-*n*-propyltrideca-*trans*-5,9-diene: W. A. Jones, M. Jacobson, and D. F. Martin, *Science*, **152**, 1516 (1966); W. A. Jones and M. Jacobson, *ibid.*, **159**, 99 (1968).

[13] This iodide was prepared by the sequence: 1,4-butanediol monotetrahydropyranyl ether [E. J. Corey, H. Yamamoto, D. K. Herron, and K. Achiwa, *J. Amer. Chem. Soc.*, **92**, 6635 (1970)] → ROTs (*p*-toluenesulfonyl chloride–pyridine at 0°) → RI (sodium iodide–acetone at 25°) (65% over-all yield).

[14] Identical in all respects with the reported one (ref 15).

[15] G. Pattenden, *J. Chem. Soc. C*, 2385 (1968).

[16] A. I. Meyers and E. W. Collington, *Tetrahedron*, **27**, 5979 (1971), and references cited therein.

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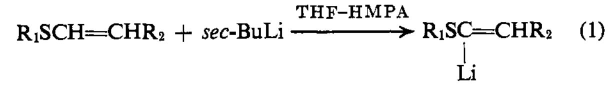
A New Synthesis of Ketones Using 1-(Alkylthio)vinyllithium

Sir:

Addition of *sec*-butyllithium to a solution of vinyl sulfides in tetrahydrofuran–hexamethylphosphoric triamide (THF:HMPA = 9:1) at −78° results in essentially quantitative formation of 1-(alkylthio)vinyllithium **1** (eq 1), which is stable at this temperature for



$$R_1SCH{=}CHR_2 + sec\text{-}BuLi \xrightarrow{\text{THF-HMPA}} \underset{\displaystyle Li}{R_1SC}{=}CHR_2 \qquad (1)$$

1

at least 6 hr. At −78°, the anion **1** reacts smoothly with halides, aldehydes, and epoxides to provide, after hydrolysis with mercuric ion in aqueous acetonitrile,[1,2] good yields of the corresponding ketones, acyloins, and α,β-unsaturated ketones, respectively, as depicted below (Table I). The procedure is simpler[3] and potentially more versatile than the recently developed ketone syntheses.[4]

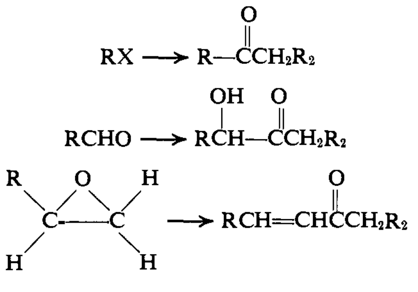


Table I. Reactions of 1-(Alkylthio)vinyllithium with Electrophile

$R_1SCH{=}CHR_2$				Yield,[b,c]
R_1	R_2	Electrophile	Product[a]	%
C_2H_5	H	*n*-Octyl bromide	*n*-$C_8H_{17}COCH_3$	90
CH_3	*n*-C_8H_{17}	*n*-Octyl bromide	*n*-$C_8H_{17}CO$-*n*-C_9H_{19}	82
CH_3	C_6H_5	*n*-Octyl bromide	*n*-$C_8H_{17}COCH_2C_6H_5$	65
C_2H_5	H	1,4-Dibromobutane	$CH_3CO(CH_2)_4COCH_3$	60
C_2H_5	H	1,3-Dibromopropane	3-Methyl-2-cyclohexenone[d]	52
C_2H_5	H	Benzaldehyde	$C_6H_5CHOHCOCH_3$	64
C_2H_5	H	Nonanal	*n*-$C_8H_{17}CHOHCOCH_3$	58
CH_3	C_6H_5	Benzaldehyde	$C_6H_5CHOHCOCH_2C_6H_5$	54
CH_3	*n*-C_8H_{17}	Benzaldehyde	$C_6H_5CHOHCO$-*n*-C_9H_{19}	51
C_2H_5	H	Styrene oxide	$C_6H_5CH{=}CHCOCH_3$	68
CH_3	C_6H_5	Propylene oxide	$CH_3CH{=}CHCOCH_2C_6H_5$	57

[a] All products exhibited spectral and physical properties in accordance with the assigned structures or with reported literature values. [b] Yield of product after isolation by preparative tlc. [c] The yields are not necessarily optimum since each run was performed only once. [d] 2,6-Heptadione could not be obtained after hydrolysis.

Although the potentiality of 1-(alkylthio)vinyllithium as a synthetic equivalent of acyl anion was proposed earlier by Corey,[5] the actual execution utilizing this type of reagent for ketone synthesis has never been developed to a useful level due to the lack of a satisfactory base–solvent system for converting a vinyl sulfide into a reactive anion **1**.[6] In an attempt to find the suitable system, we studied the reaction of ethyl vinyl sulfide with a variety of bases and solvents using octyl bromide as an electrophile (base, solvent, yield of 2-decanone after hydrolysis): *n*-BuLi, THF, 2–3%; *n*-BuLi–TMEDA, THF, 10–20%; *n*-BuLi, THF–HMPA, 68%; *sec*-BuLi, THF, 72%; *sec*-BuLi, THF–HMPA, 90%.

The details of the new ketone synthesis[9] are illustrated by the procedure for the synthesis of 2,7-octadione. To a solution of ethyl vinyl sulfide (0.422 g, 4.80 mmol) in THF–HMPA (9:1, 20 ml) was added *sec*-butyllithium (4.40 mmol in pentane) at −78°, and the solution was held there for 30 min. The resulting orange solution was treated with 1,4-dibromobutane (0.432 g, 2.00 mmol) and the mixture was stirred at −78° for 30 min and 25° for 30 min.[10] Addition of water, extraction with ether, and concentration gave a crude sulfide (0.510 g) which was dissolved in acetonitrile–water (3:1, 20 ml). The solution was treated with mercuric chloride (2.17 g) and the mixture was heated at reflux for 12 hr.[1] Extractive work-up followed by tlc purification (R_f 0.2–0.3, CH_2Cl_2) afforded pure 2,7-octadione as a colorless semisolid (0.170 g, 60%) which was spectroscopically identical with an authentic sample.

We are investigating further extension of this reaction as well as synthetic applications.

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(1) E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970).

(2) In many cases, the alkylated sulfides were isolated and characterized in pure states, but it was found that this delay of the sequence was unnecessary and the crude products were hydrolyzed directly with mercuric chloride to give the desired products efficiently.

(3) Vinyl sulfides are readily available by recently published methods: ref 1; I. Shahak and J. Almog, *Synthesis*, **1**, 170 (1969).

(4) 1,3-Dithiane method: E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075, 1077 (1965); dihydro-1,3-oxazine method: A. I. Meyers, E. M. Smith, and A. F. Jurjevich, *J. Amer. Chem. Soc.*, **93**, 2314 (1971); cyanohydrin anion method: G. Stork and L. Maldonado, *ibid.*, **93**, 5286 (1971); epoxysilane method: G. Stork and E. Colvin, *ibid.*, **93**, 2080 (1971); organocopper method: G. H. Posner, C. E. Whitten, and P. E. McFarland, *ibid.*, **94**, 5106 (1972); hydroboration method: H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 714 (1970).

(5) E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).

(6) Indeed, allenic ether, for example, can be readily metalated by sodium amide in liquid ammonia[7] and this is based on the enhanced acidity of sp^2 hydrogen relative to sp^3 hydrogens. It must be borne in mind, however, that to successfully form the anion **1** by metalation, Michael-type addition reaction and some other side reactions[8] must be suppressed.

(7) S. Hoff, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **87**, 916, 1179 (1968).

(8) W. E. Parham and R. F. Motter, *J. Amer. Chem. Soc.*, **81**, 2146 (1959); W. E. Parham, M. E. Kalnins, and D. R. Theissen, *J. Org. Chem.*, **27**, 2698 (1962).

(9) The reactivity of this new reagent was found to be very similar to that of 1,3-dithiane anion. Thus, it reacted with alkyl iodides and bromides smoothly at −78°, but proved much less reactive toward chlorides. For example, cyclohexyl chloride was almost inert and the yield of the corresponding ketone was less than 10%.

(10) Most of the color was discharged after 10 min at −78°.

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Hydrogen Cyanide Chemistry. V. Diazodicyanoimidazole and Dicyanoimidazole Halonium Ylides

Sir:

We report the synthesis of a new diazo compound, diazodicyanoimidazole (**3**), which eliminates nitrogen at approximately 80° in solution to form a highly reactive intermediate that inserts a 4,5-dicyanoimidazole