179 (2.9), 137 (100), 136 (15), 135 (22), 130 (7.1), 109 (5.8), 102 (12), 77 (5.7); mass measurement by high-resolution mass spectroscopy *m/e* 266.0807 (calcd for $C_{13}H_{14}O_6$, 266.0790).

Anal. Calcd for $C_{13}H_{14}O_6$: C, 58.65; H, 5.30. Found: C, 58.80; H, 5.43.

Hydrogenolysis of 7.—Lactone **7** (889 mg, 3.3 mmol) and 300 mg of 10% Pd/C in CH_3OH (50 ml) was treated with H_2 (3.7 atm) for 9 days. The solution was filtered and evaporated *in vacuo*. Chromatography of the residue on silica gel (Et_2O–hexane elution) gave 586 mg of an oil which, although homogeneous by tlc, was shown by nmr and uv spectra to be a mixture of **3** and another component, provisionally assigned as **8**. Preparative tlc, preparative glc, distillation, and further column chromatography failed to separate the components, but an adequate separation on an analytical scale could be obtained by glc. Direct introduction of the glc column effluent into the mass spectrometer gave spectra of the two components.[8] The spectrum of **3** was identical with the spectrum of trimethylated **1**. The spectrum of the second component was consistent with the assignment as dimethyl 2-(4-methoxycyclohexylmethyl)malate (**8**): mass spectrum *m/e* 288 (0.9%, $m \cdot^+$), 270 (1.3), 256 (13), 229 (15), 197 (77), 179 (15), 165 (16), 161 (16), 123 (72), 117 (36), 101 (34), 95 (55), 81 (100), 71 (78).

Assay of Germination Inhibition.—The test consisted of placing 100 *Arenaria patula* seeds on Whatman No. 1 filter paper in each of three Petri plates. Each plate was moistened with 5 ml of an aqueous solution of **1**. Controls employed 5 ml of distilled, deionized H_2O. After 2 weeks at 20° under a 12/12 photoperiod, germination counts were made. In a test using a 0.4 m*M* solution of **1**, germination in both the control and the test samples was 75%; however, with a 5 m*M* solution of **1**, 22% germination was observed as compared with 73% in the control samples. The latter represents an inhibition of 70%.

Acknowledgment.—This work was supported by a grant (GB-12439) from the National Science Foundation.

Registry No.—**1**, 42151-32-6; **2**, 42151-33-7; **3**, 42151-34-8; **4**, 42151-35-9; **5**, 42151-36-0; **7**, 42151-37-1; **8**, 42151-38-2; CH_2N_2, 334-88-3; CH_3I, 74-88-4; OsO_4, 20816-12-0.

(8) A trace of a third component (*m/e* 296) was observed; it is probably an ethyl analog of **7**.

A Short Nonannelation Approach to Synthesis of Oxygenated Eudesmane Sesquiterpenes

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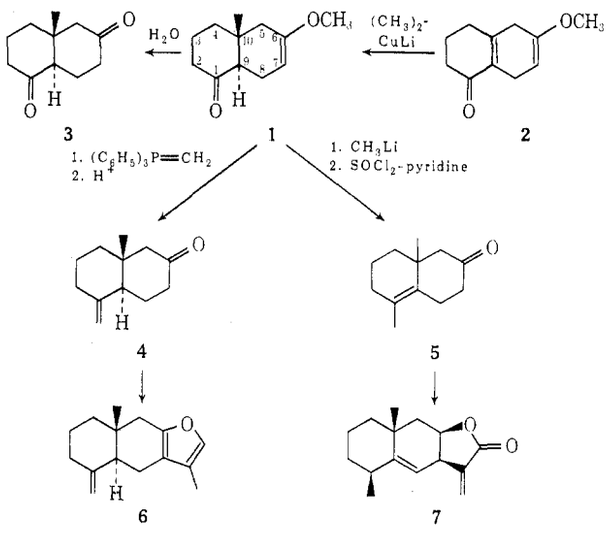
Many syntheses of eudesmane sesquiterpenes have been accomplished within the past 10 years.[1] Most approaches have involved constructing the bicyclic carbon framework of the decalin system *via* Robinson annelation reactions.[2] Although such annelation reactions have been thoroughly studied and reviewed, they are often low-yield procedures which require substantial experimentation before optimum conditions can be achieved, and they may be subject to stereochemical complications when substituents are present in either the Michael donor or the Michael acceptor. Recently β-eudesmol, a simple member of the eudesmane class of sesquiterpenes, has been prepared *via* a stereoselective nonannelation approach starting with a naphthalene derivative.[3] We have extended and generalized this type of approach so that various oxygenated (*e.g.*, furan and lactone) eudesmane sesquiterpenes can be prepared stereoselectively from naphthalene precursors.

SCHEME I



Our primary synthetic effort involved developing a direct nonannelation synthesis of keto enol ether **1**. This compound was attractive for several reasons: (1) the C-1 carbonyl group would allow epimerization (and possibly alkylation) at C-9; (2) the C-1 carbonyl group could be easily transformed into a variety of other functional groups (*e.g.*, methylene or tertiary alcohol); (3) the masked C-6 carbonyl group would allow regioselective alkylation of the *trans*-decalin system at C-7; and (4) the C-6 oxygen atom could be removed or incorporated into furan or lactone rings as, for example, in atractylon (**6**)[4] or alantolactone (**7**).[5] We selected dienone **2** as immediate precursor to keto enol ether **1** because dienone **2** is easily prepared from 6-methoxy-1-tetralone,[6] and it was expected to undergo a conjugate addition reaction with lithium dimethylcuprate(I) to produce enol ether **1** (Scheme I).[7]

Dienone **2**, prepared in 40% yield from 6-methoxy-

(1) (a) J. A. Marshall, M. T. Pike, and R. D. Carroll, *J. Org. Chem.*, **31**, 2933 (1966); (b) D. C. Humber, A. O. Pinder, and R. A. Williams, *ibid.*, **32**, 2335 (1967); (c) R. K. Mathur and A. S. Rao, *Tetrahedron*, **23**, 1259 (1967); (d) C. H. Heathcock and T. R. Kelly, *ibid.*, **24**, 1801 (1968); (e) D. L. Robinson and D. W. Theobald, *ibid.*, **24**, 5227 (1968); (f) J. A. Marshall and M. T. Pike, *J. Org. Chem.*, **33**, 435 (1968); (g) H. Minato and T. Nagasaki, *J. Chem. Soc. C*, 622 (1968); (h) J. Naemura and M. Nagasaki, *Tetrahedron Lett.*, 33 (1969); (i) for stereochemical relationships in the eudesmane group of sesquiterpenes, see W. Cocker and B. H. McMurry, *Tetrahedron*, **8**, 181 (1960); (j) for a review of synthetic approaches to decalin sesquiterpenes, see J. M. Mellor and S. Munavelli, *Quart. Rev., Chem. Soc.*, **18**, 270 (1964).

(2) (a) E. C. DuFeu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937); (b) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, **10**, 179; (c) J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964); (d) B. P. Mundy, *J. Chem. Educ.*, **50**, 110 (1973).

(3) (a) J. W. Huffman and M. L. Mole, *J. Org. Chem.*, **37**, 13 (1972). (b) See also R. G. Carlson and E. G. Zey, *ibid.*, **37**, 2468 (1972), for a similar approach. (c) After submission of this manuscript, we learned that Professor R. B. Miller was also pursuing this approach: R. B. Miller and R. D. Nash, *J. Org. Chem.* **38**, 4424 (1973).

(4) (a) H. Minato and I. Horibe, *J. Chem. Soc. C*, 1575 (1967); (b) H. Minato and T. Nagasaki, *ibid.*, 1866 (1966); (c) H. Minato and T. Nagasaki, *Chem. Commun.*, 377 (1965).

(5) J. A. Marshall, N. Cohen, and A. R. Hochstetler, *J. Amer. Chem. Soc.*, **88**, 3408 (1966).

(6) (a) A. J. Birch, J. A. K. Quartey, and H. Smith, *J. Chem. Soc.*, 1768 (1952); (b) H. O. House and R. W. Bashe, II, *J. Org. Chem.*, **30**, 2942 (1965).

(7) G. H. Posner, *Org. React.*, **19**, 1 (1972).

1-tetralone,[6] was found to be contaminated by about 6% of a conjugated dienone.[8,9]

Conjugate addition reactions of organocopper reagents have been used effectively to attach a wide variety of hydrocarbon groups to the β-carbon atom of many types of α,β-ethylenic ketones.[7,10] Dienone **2**, however, poses an unusual problem; the C-5 hydrogen atoms, which are allylic and vinylogously α to the C-1 carbonyl group, may be sufficiently acidic to be abstracted by the organocopper reagent. It was gratifying, therefore, that reaction of dienone **2** with a large excess of lithium dimethylcuprate produced conjugate adduct **1**, which was isolated in approximately 50% yield by preparative tlc using pH 7 buffered plates. The nature of the remaining material formed in this reaction was elusive; deuterium oxide quenching of the reaction in the hope of recovering deuterated dienone **2** led to adduct **1** and an unstable oil and treating the crude reaction products with lithium dimethylcuprate led to no dramatic increase in the amount of conjugate adduct **1**. It should be noted that enolate ions formed *via* organocopper conjugate addition to enones have been trapped as enol acetates and enol silyl ethers[10f,11] which can be converted to lithium enolates;[11b,12] thus indirect alkylation at C-9 may be possible.[13,14]

To confirm the gross structure of conjugate adduct **1**, this liquid enol ether was hydrolyzed in good yield to crystalline diketone **3**. 1,6-Decaldione **3** has not been reported previously.

Treating conjugate adduct **1** with methylenetriphenylphosphorane[15] led upon acidic work-up directly to enone **4**, which had spectral properties identical with those of enone **4** prepared previously by Minato and Horibe.[4,16] Reaction of adduct **1** with methyllithium and then thionyl chloride in pyridine[17] led directly to enone **5**, which had spectral data identical with those of enone **5** prepared previously by Marshall, Cohen, and Hochstetler.[5,18]

(8) A. J. Birch and K. P. Dastur, *Tetrahedron Lett.*, 4195 (1972).

(9) M. V. R. Koteswara Rao, G. S. Khrishna Rao, and S. Dev, *Tetrahedron*, **22**, 1977 (1966).

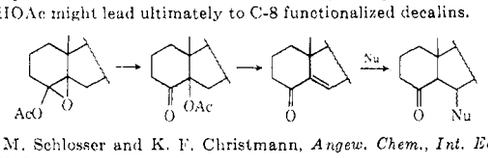
(10) Several organocopper conjugate additions to octalones have been reported: (a) A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1943); (b) A. J. Birch and M. Smith, *Proc. Chem. Soc., London*, 356 (1962); (c) J. A. Marshall and H. Roebke, *J. Org. Chem.*, **33**, 840 (1968); (d) J. A. Marshall, W. I. Fanta, and H. Roebke, *ibid.*, **37**, 1016 (1966); (e) R. E. Ireland, M. I. Dawson, J. Bordner, and R. E. Dickerson, *J. Amer. Chem. Soc.*, **92**, 2568 (1970); (f) E. Piers, W. de Waal, and R. Britton, *ibid.*, **93**, 5113 (1971); (g) R. S. Matthews and R. E. Meteyer, *Chem. Commun.*, 1576 (1971).

(11) (a) K. Heusler, J. Kebrle, C. Meystre, H. Ueberwasser, P. Wieland, G. Anner, and A. Wettstein, *Helv. Chim. Acta*, **42**, 2043 (1959); (b) G. Stork and F. Hudrlick, *J. Amer. Chem. Soc.*, **90**, 4462 (1968).

(12) (a) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, Chapter 9; (b) H. O. House, M. Gall, and H. O. Ohmstead, *J. Org. Chem.*, **36**, 2361 (1971), and references therein.

(13) Depending on the stereochemistry of C-9 alkylation, an entry might be available into the *cis*-9,10-dimethyldecalin system, which is characteristic of valerane sesquiterpenes.

(14) Epoxidation of the initial enol acetate, rearrangement, and elimination of HOAc might lead ultimately to C-8 functionalized decalins.



(15) M. Schlosser and K. F. Christmann, *Angew. Chem., Int. Ed. Engl.*, **3**, 636 (1964).

(16) We thank Professor Minato for providing us with a copy of his ir spectrum of enone **4**.

(17) Thionyl chloride in pyridine is known to favor formation of endocyclic rather than exocyclic olefins: R. M. Coates and R. L. Sowerby, *J. Amer. Chem. Soc.*, **94**, 5386 (1972).

(18) We thank Professor Marshall for providing us with copies of his ir and nmr spectra of enone **5**.

The stereochemistry of conjugate adduct **1**, of the corresponding diketone **3**, and of methylene derivative **4** was determined by nuclear magnetic resonance (nmr) spectral data according to the method of Williamson, Howell, and Spencer.[19] The data are summarized in Table I. Since the $\Delta W_{1/2}$ values are substantially

TABLE I
NMR DATA FOR ANGULAR METHYL GROUPS IN KETONES **1**, **3**, AND **4**

Ketone	Chemical shift, ppm	$\Delta W_{1/2}$,[a] Hz
1	0.80	1.01
3	0.78	1.58
4	0.72	1.05

[a] The $\Delta W_{1/2}$ values were determined by using the formula $\Delta W_{1/2} = W_{1/2}(CH_3) - W_{1/2}(TMS)$, where $W_{1/2}(CH_3)$ is the half band width of the angular methyl group and $W_{1/2}(TMS)$ is the half band width of the TMS signal.

larger than 0.25 associated with *cis*-9-methyldecalins and are in the range of those reported for *trans*-9-methyldecalins, the methyldecalins **1**, **3**, and **4** are assigned trans ring fusions. It is noteworthy that *trans*-10-methyldecalin (**1**) is formed stereoselectively under the conditions of the conjugate addition reaction.

Because enone **4** has previously been converted to isoalantolactone and atractylon (**6**)[4] and enone **5** has previously been transformed to telekin and alantolactone (**7**),[5] our synthesis of **4** and **5** constitutes a formal total synthesis of these four furanoeudesmane and eudesmanolide sesquiterpenes. In addition, keto enol ether **1** might be a useful intermediate in synthesis of other sesquiterpenes containing the 10-methyl-1,6-decaldione functionality or derivatives thereof.

Experimental Section

General.—Melting points are uncorrected. The ir spectra were determined with a Perkin-Elmer Model 457 ir spectrophotometer. Nmr spectra were determined with either a Varian A-60 or a Jeol MH-100 spectrometer. The mass spectra were determined on a Hitachi Model RMU6 high-resolution mass spectrometer. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz. Analytical gas–liquid chromatography utilized a Varian Model 1200 gas chromatograph with flame ionization detector. Preparative gas–liquid chromatography utilized a Varian Model 90-P gas chromatograph with a thermal conductivity detector. Thin layer chromatography plates were prepared from silica gel PF-254 which was obtained from EM Laboratories, Inc.

Methyllithium was obtained as a ~2.0 *M* solution in ether from Alpha Inorganics and was titrated[20] before each use. Cuprous iodide was obtained from Fisher Scientific Co. and was extracted with tetrahydrofuran and then dried *in vacuo* before use. Triphenylmethylphosphonium bromide was obtained from Aldrich Chemical Co. and was used without further purification. Potassium *tert*-butoxide was obtained from Alpha Inorganics and was sublimed before use.

Preparation of Keto Enol Ether 1.—To a 50-ml three-neck flask fitted with two serum stoppers and a T-joint with a nitrogen filled balloon attached was added 5.05 g (26.8 mmol) of cuprous iodide. The flask was alternately evacuated while being flamed and purged with nitrogen from the balloon. To the flask was added 19.0 ml of anhydrous ether *via* hypodermic syringe and the flask was cooled to 0°. To this stirred suspension of cuprous iodide in ether was added 27.0 ml of a 1.98 *M* (53.6 mmol) methyllithium, followed by 600 mg (3.37 mmol) of enone **2** in 2.0 ml of anhydrous ether. The reaction mixture was allowed to

(19) K. L. Williamson, T. Howell, and T. Spencer, *J. Amer. Chem. Soc.*, **88**, 325 (1966).

(20) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

stir for 2.0 hr at 0° after which time it was quenched by cautiously pouring it into 100 ml of saturated aqueous sodium bicarbonate. The entire mixture was vacuum filtered to remove all solids, the ether layer was separated, and the aqueous portion was extracted with two additional 20-ml portions of ether. The combined ethereal solutions were washed with 50 ml of brine, dried (anhydrous potassium carbonate), and concentrated *in vacuo* to afford 654 mg of a yellow oil. Preparative tlc on pH 7 buffered silica plates[21] eluted with 9:1 carbon tetrachloride:ethyl acetate gave three distinct bands. The fastest migrating band ($R_f \approx 0.5$) was collected to afford 307 mg (48%) of ketone **1** as a pale yellow oil. This material was not further purified for use in subsequent reactions: nmr ($CDCl_3$) δ 0.80 (s, 3 H), 1.20–2.80 (m, 11 H), 3.45 (s, 3 H), 4.52 (unresolved m, 1 H); ir ($CHCl_3$) 1715 cm^{-1} (C=O).

10-Methyldecal-1,6-dione (3).—Preparative tlc of ketone **1** on a nonbuffered silica plate yielded white crystalline material of mp 74–77°. Three recrystallizations from hexane containing a trace of ether afforded an analytical sample of dione **3** as white needles: mp 84–85°; ir ($CHCl_3$) 1710 (C=O), 1378 (CH_3 bend) cm^{-1}; nmr ($CDCl_3$) δ 0.78 (s, 3 H), 1.50–2.82 (m, 13 H); mass spectrum (70 eV) *m/e* 180 (M^+), 165 ($M^+ - CH_3$), 137 (165 − CO), 124, 111, 96, 95, 55.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.32; H, 8.98.

Preparation of Ketone 4.—In a 10-ml three-neck flask 555 mg (1.55 mmol) of triphenylmethylphosphonium bromide and 150 mg (1.34 mmol) of freshly sublimed potassium *tert*-butoxide were intimately mixed under a nitrogen atmosphere. Anhydrous ether (6.0 ml) was introduced and the mixture turned bright yellow. To this solution of methylene triphenylphosphorane was added 60 mg (0.31 mmol) of ketone **1** in 3.0 ml of anhydrous ether and the reaction was allowed to stir at room temperature for 10 hr. The reaction was quenched by the addition of 5 ml of 1 *N* hydrochloric acid followed by 5 ml of water. The ether layer was separated and the aqueous portion was washed with two additional portions of ether. The combined ethereal extracts were washed with saturated aqueous bicarbonate and brine, dried (magnesium sulfate), and concentrated *in vacuo* to afford 293 mg of an oil with traces of solid.[22] The yield of ketone **4** as determined by glpc[23] using hexadecane as an added calibrated internal standard was 48%. A pure sample (24 mg, 43% yield) was obtained by preparative silica gel tlc which was eluted with 9:1 hexane:ether ($R_f \approx 0.30$): ir (thin film) 3090, 1713, 1645, 895, 887 cm^{-1}; nmr (CCl_4) δ 4.48 (s, 1 H), 4.78 (s, 1 H), 0.72 (s, 3 H), 2.5–0.90 (m, all other protons); mass spectrum (70 eV) *m/e* 178 (M^+, base), 163 ($M^+ - CH_3$), 150 (M^+ − CO), 135, 79.

Preparation of Ketone 5.—Into a 10-ml three-neck flask in which a nitrogen atmosphere was maintained was introduced 60 mg (0.31 mmol) of ketone **1** in 2.0 ml of anhydrous ether. The solution was cooled to 0° and 0.5 ml of 2.0 *M* (1.0 mmol) methyllithium was added. After stirring for 20 min at 0°, the reaction was allowed to warm to room temperature, and 5.0 ml of saturated aqueous sodium bicarbonate was cautiously added. An additional 10 ml of ether was added and the organic layer was separated. The aqueous phase was extracted with two additional 10-ml portions of ether. The combined extracts were washed with 10 ml of brine, dried (anhydrous potassium carbonate), and concentrated *in vacuo* to afford 64 mg of an oil. This crude methyllithium adduct was dissolved in 2.0 ml of freshly dried pyridine and to this solution was added 2.0 ml of a solution made from 0.4 ml of thionyl chloride in 20 ml of pyridine. The reaction mixture was allowed to stir at room temperature for 15 min after which time it was poured into 15 g of ice and acidified with 1 *N* hydrochloric acid to pH 2. The mixture was extracted with two 15-ml portions of ether. The combined ether extracts were washed with water, saturated aqueous sodium bicarbonate, and brine, dried (magnesium sulfate), and concentrated *in vacuo* to afford 35 mg (70%) of ketone **5** as an oil. A pure sample of **5** was obtained *via* preparative gas–liquid chromatography:[24] nmr (CCl_4) δ 1.70 (s, CH_3), 1.00 (s, CH_3); ir (thin film) 1712, 1455, 1265; mass spectrum (70 eV) *m/e* 178 (M^+), 163 ($M^+ - CH_3$), 150 (M^+ − CO), 135, 121, 107, 105, 93, 79.

(21) Plates were prepared in the standard manner except that an aqueous solution containing 1% of a standard pH 7 buffer solution was used in place of pure water. These plates were dried at room temperature for at least 24 hr prior to use.

(22) Most of this crude material consists of phosphine oxides.

(23) In a 7 ft × 1/8 in. SE-30 column at 160° with a helium flow rate of 45 ml/min.

(24) In a 20 × 3/8 in. QF-1 column at 175° with a helium flow rate of 100 ml/min. A smaller peak (<10%) was also detected but was not isolated.

Acknowledgment.—This work was supported by Public Health Service Research Grant No. 1 RO1 CA-12658 from the National Cancer Institute.

Registry No.—**1**, 42246-15-1; **2**, 2844-80-6; **3**, 42246-17-3; **4**, 3241-65-4; **5**, 2658-95-9.

Chemistry of Heterocyclic Compounds. 12. Preparation and Reactions of 2-Pyridylacetylenes[1]

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The preparation of 2-pyridylacetylenes has been besieged by sporadic results; for example, dehydrobromination of stilbazole dibromide (**2a**) has been shown to give stilbazole, bromostilbazole, and/or 2-phenylethynylpyridine, depending upon reaction conditions. Scheuing and Winterhalder[2] were the first to isolate 2-phenylethynylpyridine (**3a**) by treatment of the dibromide **2a** with refluxing ethanolic potassium hydroxide. Attempted repetition of this reaction afforded, in one case,[3] only stilbazole (**1a**) and an unstipulated bromostilbazole, whereas others[4] obtained **3a**, bromostilbazole, and α-(2-pyridyl)acetophenone.[5] Recently, Acheson and Bridson,[7] utilizing these reaction conditions,[2] obtained 2-phenylethynylpyridine (**3a**) containing at best approximately 30% of bromostilbazole, which was identified as 2-(1-bromo-*cis*-2-phenylvinyl)pyridine. The pure acetylene **3a** was prepared[7] (83%) by using potassium *tert*-butoxide, as the dehydrobromination reagent, in refluxing *tert*-butyl alcohol.

During the course of our studies, we needed the previously prepared di(2-pyridyl)acetylene (**7a**)[8] and di(6-methyl-2-pyridyl)acetylene (**7b**). We herein describe the preparation of pure **7**, as well as the structural determination of the major side products, which arise when more rigorous conditions[2] are utilized.

(1) This research has been supported by Public Health Service Grant No. 5-RO1-MS-09930 from the National Institute of Neurological Diseases and Stroke, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp.

(2) G. Scheuing and L. Winterhalder, *Justus Liebigs Ann. Chem.*, **473**, 126 (1929).

(3) J. W. Blood and B. D. Shaw, *J. Chem. Soc.*, 504 (1930).

(4) T. Katsumoto and A. Honda, *J. Chem. Soc. Jap.*, **84**, 527 (1963).

(5) Preparations of other phenylethynyl heterocycles[6] have utiliized the original, or slightly modified, procedure of Scheuing and Winterhalder.[2] Analyses of the acetylenic products are generally outside the acceptable analytical limits, which are indicative of halogenated contaminants.

(6) (a) J. M. Smith, Jr., H. W. Stewart, B. Roth, and E. H. Northey, J. *Amer. Chem. Soc.*, **70**, 3997 (1948); (b) K. Schofield and T. Swain, *J. Chem. Soc.*, 2393 (1949); (c) H. C. Beyerman, W. Eveleens, and Y. M. F. Muller, *Recl. Trav. Chim. Pays-Bas*, **75**, 63 (1956); (d) T. Nakashima, *Yakugaku Zasshi*, **77**, 1298 (1957); (e) A. I. Kiprianov and G. G. Dyadyusha, *Zh. Obshch. Khim.*, **30**, 3647 (1960); (f) I. Ernest, *Collect. Czech. Chem. Commun.*, **25**, 748 (1960).

(7) R. M. Acheson and J. N. Bridson, *J. Chem. Soc. C*, 1143 (1969).

(8) D. Jerchel and W. Melloh, *Justus Liebigs Ann. Chem.*, **622**, 53 (1959).