A proton-noise-decoupled (PND) ^{13}C NMR spectrum revealed the presence of the same number of carbons (29) as for 1 and, together with a single-frequency off-resonance decoupled (SFORD) spectrum, demonstrated the presence of only six olefinic carbons (vs. eight for 1) and, notably, the absence of signals previously assigned to C-2′ and C-3′ in 1. Signals attributable to these two carbons appeared at 61.0 and 65.4 ppm and are both in the range expected for methine and quaternary carbons bonded to oxygen.[4] This observation suggested that the 2′,3′-acrylic ester double bond of 1 had been replaced with an epoxide function. The following evidence supported this conclusion and argued against epoxide formation at either the 7,8 site as in epoxyisororidin E and epoxyroridin H[5] or the 9,10 double bond as in baccharin and isobaccharin.[6] First, existence of the cis–trans diene system was mandated by the observation of proton and carbon-13 NMR signals in 2 (vide supra) which were essentially identical with respect to both chemical shift and multiplicity with those of the 7′,8′,9′,10′-diene system in 1 and the other roridins.[7] Second, the chemical shifts of H-10, 16-CH_3, C-9, and C-10 are virtually identical in 1 and 2, thus supporting the belief that this moiety exists unaltered in 2. This similarity in ^{13}C NMR data also extends to those signals assigned to C-4′, C-5′, C-6′, and C-12′ of the pyran ring in structures 1 and 2.

Satratoxin G, like 1, formed a diacetate derivative (mol wt 628), indicating the presence of two hydroxyl groups. The ^1H NMR spectrum of 2 also exhibited loss of two protons upon addition of D_2O, confirming the previous observation. The data presented thus far support the belief that 2 is an epoxidized variation of 1. Analogous epoxidations at the acrylic ester double bond have been reported for verrucarin B, roridin D[1], and a series of baccharin trichothecenes.[6]

MS, IR, and ^1H and ^{13}C NMR spectral data of 3 were found, in turn, to be very much like those of 1 and 2 (Tables I and II). Most of the arguments which were made concerning similarities between the NMR spectra and, therefore, the structures of 1 and 2, viz., common trichothecene and diene moieties, can be made for 3. Inspection of the ^{13}C NMR data of 3 reveals, moreover, the presence of two signals at 58.9 and 63.9 ppm, indicating that 3 possesses an epoxide group at C-2′ and C-3′, like 2, and not an acrylic ester double bond, like 1. However, two notable differences in the ^1H NMR spectrum of 3 are the appearance of a methyl, single-resonance line at δ 2.30, the concomitant absence of a methyl doublet at δ 1.20, and a methine quartet at ca. δ 3.7, which are characteristic of the methyl carbinol group found in most of the roridins.[1,5,6]

In addition, the molecular weight of 3 of 542 is just 2 mass units less than that of 2. This NMR and mass spectral data suggested that the methylcarbinol group at C-6′ of 2 had been oxidized to a ketone function in 3, an inference which was supported by the following evidence. First, 3 formed a monoacetate derivative of mol wt 584, indicating the presence of only one hydroxyl group. Second, a quartet at 29.7 ppm and a single line at 217 ppm appeared in an SFORD ^{13}C NMR spectrum. The former is in the range expected for an acyl methyl carbon, while the latter can be assigned to a ketonic carbonyl carbon.[4]

These data support the belief that 3 is an oxidized variation of 2. Satratoxin F is the first known member of the roridin family to possess an acyl group at C-6′ in place of the more common methylcarbinol function.

Comparison of the SFORD ^{13}C NMR spectra of these compounds reveals that the signal assigned to C-4′, which is observed as a triplet in 2 and 3, appears as a doublet of doublets in 1. Conversion of the acrylic ester double bond to an epoxide apparently changes the conformation of the macrocyclic ring in 2 and 3 sufficiently that both of the C-4′ methylene protons are relatively equidistant from the acrylic ester lactonic oxygen and, therefore, have similar chemical shifts. This is not the case in 1 where H-4′A (3.74 ppm) is considerably closer to the lactonic oxygen than H-4′B (2.6 ppm). It is this unusual difference in geminal proton chemical shift values which is responsible for the atypical appearance of the C-4′ signal in the SFORD spectrum of 1.[8]

Experimental Section

Satratoxins F and G were isolated according to the method of Eppley and Bailey.[2] Additional purification was achieved on silica gel with a Waters Prep LC/Systems 500 high-pressure liquid chromatograph. Elution with 3% methanol–chloroform gave complete separation into two fractions.

Satratoxin F (3). The residue from the first fraction was crystallized from chloroform–hexane to give 3: 40 mg; mp 140–143 °C; IR (KBr) 3460, 1748, 1715, 1183 cm^{-1}; mass spectrum (electron impact), m/e 542 ($M^{+\cdot}$) calcd for $C_{29}H_{34}O_{10}$.

Satratoxin G (2). Crystallization of the second fraction from chloroform-hexane gave 2: 87 mg; mp 132–136 °C; IR (KBr) 3450, 1747, 1710, 1185 cm^{-1}; mass spectrum (electron impact), m/e 544 ($M^{+\cdot}$) calcd for $C_{29}H_{36}O_{10}$.

General Methods. Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 180 recording spectrophotometer. Mass spectra of 2 and 3 were determined on a Varian MAT CH-5DF spectrometer and that of satratoxin G diacetate on a Finnigan 3300 by simultaneous pulsed positive/negative ion chemical ionization. Proton magnetic resonance spectra were recorded at 300 MHz for 1[3] and at 90 MHz on a Varian EM-390 spectrometer for 2 and 3. Carbon-13 magnetic resonance spectra were determined on a Varian CFT-20 spectrometer operating at 20 MHz. Signals were assigned by using SFORD and selective proton-decoupling experiments and chemical shift correlations[4] and by comparison with each other.

Registry No. 1, 53126-64-0; 2, 73513-00-5; 3, 73513-01-6.

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Marine Natural Products: Two New Acyclic Sesquiterpene Hydrocarbons from the Gorgonian *Plexaurella grisea*

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Although a variety of novel cyclic sesquiterpenes have been isolated from marine coelenterates, no simple farnesene derivatives or other acyclic sesquiterpenes appear to have been reported[1] from these organisms. Inci-

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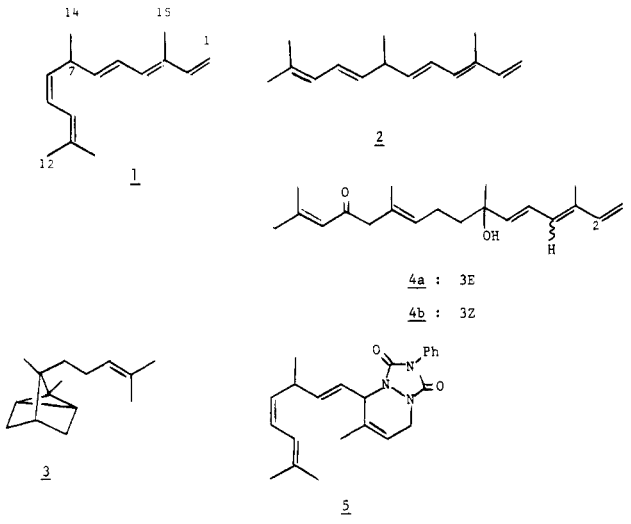
Table I. ^{1}H NMR Chemical Shift and Multiplicity Data (270 MHz, $CDCl_3$)

	1			2			5[b]		
H at C no.	δ	mult	J, Hz	δ	mult	J, Hz	δ	mult	J, Hz
1	5.16 (E)	d	17	5.17 (E)	d	17	3.96	br d	16
1	4.99 (Z)	d	11	5.00 (Z)	d	11	4.32	br d	16
2	6.38	dd	17, 11	6.39	dd	17, 11	5.62	br s	
4 (or 10)	6.08	d	11	5.80	d	11	4.66	d	8
5	6.36	ddd	15.5, 11, 1.6	6.35	ddd	15, 11, 1	5.36	pr of ddd	15.5, 8, 2
6	5.71	dd	15.5, 6.5	5.71	dd	15, 7	5.86	pr of dd	15.5, 6
7	3.44	sextet	~7	3.05	sextet	~7	3.36	sextet	~7.4
8	5.17	t	10	5.50	dd	15, 7	5.09	pr of t	10
9	6.16	dd	11, 10	6.22	dd	15, 11	6.14	dd	10, 11
10 (or 4)	6.03	d	11	6.05	d	11	6.00	d	11
12	1.82[a]	s		1.75[a]	s		1.73[a]	s	
13	1.76[a]	s		1.77[a]	s		1.76[a]	s	
14	1.13	d	7	1.15	d	7	1.08	d	7
15	1.85[a]	s		1.86[a]	s		1.80[a]	s	

[a] Signals may be interchanged. [b] Also δ 7.30-7.55 (5 H, m, aromatic).

dental to our continuing search for biologically active compounds from marine organisms, we have isolated two new acyclic sesquiterpene hydrocarbons, 1 and 2, from the



gorgonian *Plexaurella grisea* Kunze,[2] and we wish to report their structures herein. In addition, we isolated (+)-α-santalene (3), which is well-known from terrestrial sources but has not been reported previously from any marine organisms.

Isopropyl alcohol extracts of air-dried specimens collected off South Caicos Island were first subjected to solvent partitioning to concentrate the nonpolar components, and these were chromatographed over silica gel with hexane as eluent. The first few chromatographic fractions, which contained essentially one hydrocarbon, were pooled and rechromatographed over 10% silver nitrate–silica gel to give pure (+)-α-santalene (3).[3] The later fractions were quite complex as judged by gas chromatographic analysis, but two of the major components, 1 and 2 (representing approximately 50% of the total mixture), were well resolved and were isolated by preparative gas chromatography on OV-225.

Hydrocarbons 1 and 2 each showed molecular ions at *m/e* 202, corresponding to the molecular formula $C_{15}H_{22}$. Hydrogenation of pure 1 and a mixture of 1 and 2 in hexane over palladium on charcoal gave the same saturated hydrocarbon [GC analysis; *m/e* 212 (M^+), $C_{15}H_{32}$] identified as farnesane by comparison of ^{1}H NMR[4] and mass spectral[5] data. Hence, 1 and 2 were shown to be pentaunsaturated farnesanes.

Hydrocarbon 1 showed a large optical rotation, $[\alpha]^{25}_D$ +502°, and UV absorption indicative of both conjugated triene and diene moieties[6] [279, 271, and 264 nm (ε 46 240, 51 380, 39 640) and 237 nm (ε 24 960), respectively]. In the ^{1}H NMR spectrum (270 MHz) of 1 (Table I) the signals for all protons could be assigned with the aid of decoupling. Three olefinic methyl groups and one secondary aliphatic methyl group were evident from three-proton singlets at δ 1.76, 1.82, and 1.85 and one doublet at δ 1.13 (J = 7 Hz). The only other aliphatic proton signal in the spectrum of 1 was a one-hydrogen multiplet (sextet?) at δ 3.44, corresponding to a diallylic proton. Imposition of these groups on a farnesane skeleton, keeping in mind the requirement for conjugated diene and triene groups, leads unequivocally to structure 1 with unspecified stereochemistry.

The signals due to the terminal vinyl group, δ 4.99, 5.16, and 6.38, were identified by decoupling (irradiation at δ 4.99 and 5.16). Close correlation of the chemical shifts for the C-2 proton in 1 (δ 6.38) and in the known diterpene **4a**[6a] (δ 6.42) provided the basis for assigning the 3*E* configuration to 1. In the 3*Z* isomer **4b** and related compounds[6a] the C-2 proton absorbs at δ ~7.00.

Of the remaining olefinic proton signals for 1, one pair, δ 5.71 and 6.36, showed a large coupling (15.5 Hz) indicative of protons on a trans double bond. The location of this double bond was determined by analysis of the ^{1}H NMR data of the Diels–Alder adduct **5** prepared by reaction of 1 with 4-phenyl-1,2,4-triazoline-3,5-dione.[7] Comparison of the spectrum of **5** with that of 1 (see Table I) showed that the terminal vinyl group of 1 had clearly been involved in the formation of the adduct, and decoupling established that the protons of the trans double bond

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(7) J. Sauer and B. Schröder, *Chem. Ber.*, **100**, 678 (1967).

in **5**, δ 5.36 and 5.86 (J = 15.5 Hz), were both coupled to nonolefinic protons (δ 4.66 and 3.36, respectively). Hence the 5*E* configuration was confirmed. The remaining disubstituted double bond at C-8,9 was assigned the *Z* configuration on the basis of the 10-Hz coupling observed between the protons at these positions (see Table I). Thus, **1** was confirmed to be (3*E*,5*E*,8*Z*)-3,7,11-trimethyl-1,3,5,8,10-dodecapentaene.

The Diels–Alder product **5** would be expected to be a mixture of diastereomers, leading to possible added complexity in the ^{1}H NMR spectrum. In actuality, slight differences in chemical shift are observed between the diastereomers only for the protons at C-5, -6, and -7, resulting in a doubling of the multiplets for these protons (see Table I).

Hydrocarbon **2** was also optically active, $[\alpha]^{25}_D$ +55.1°, and had a UV spectrum (λ_{max} 279, 270, 264, and 236 nm; ϵ 36 360, 38 780, 32 320, and 20 600) similar to that of **1**. The ^{1}H NMR spectrum of **2** resembled closely that of **1** in terms of chemical shifts and multiplicities. The principal difference was that a 15-Hz coupling indicative of trans geometry was observed for the protons of both disubstituted double bonds in **2**, δ 5.71, 6.35 and 5.50, 6.22 assigned to H-5,6 and H-8,9, respectively. Since the chemical shifts of the C-2 protons in **1** and **2** are virtually identical, δ 6.38 and 6.39, **2** was also assigned the 3*E* configuration, yielding an overall stereochemical assignment for **2** of 3*E*,5*E*,8*E*.

It is of interest to note that the (+)-α-santalene isolated from *P. grisea* is the same enantiomer isolated from plants. This contrasts with the more general pattern observed to date, which is that sesquiterpenes isolated from coelenterates are antipodal to the same forms that have most commonly been isolated from terrestrial plants.[1]

P. grisea Kunze is reported in two review articles[1,8] to have yielded five sesquiterpene hydrocarbons, (+)-α-murolene, (−)-α-curcumene, (+)-β-curcumene, (+)-α-bisabolene, and (−)-β-bisabolene. However, a recent discussion with the authors of the earlier of these reviews[8] indicates that their statement "Three species of *Plexaurella* [*P. dicotoma* (Esper), *P. grisea* Kunze, and *P. fusifera* Kunze] contain..." is misleading. It was intended[9] to reflect the reviewers' opinion that the original source of the five sesquiterpenes was a mixed collection of these three *Plexaurella* species, rather than a homogeneous collection of *P. dichotoma* as reported by Youngblood.[10] Hence, the precise source of these sesquiterpenes is in doubt.

Experimental Section[11]

Isolation of Hydrocarbons 1, 2, and (+)-α-Santalene (3) from *Plexaurella grisea*. Specimens of *Plexaurella grisea* collected near South Caicos Island at ~−3 m were air-dried (800 g), broken into small pieces, and soaked in isopropyl alcohol for 2 months. The alcohol extract was concentrated in vacuo and the residue diluted with water and extracted with chloroform. The chloroform solubles (22 g) were partitioned between hexane and methanol–water (90:10). A portion (6.0 g) of this hexane fraction (13.9 g) was chromatographed over silica gel (250 g) with hexane as the eluting solvent. The first few fractions were pooled to give 400 mg of a clear oil (~90% one component by GC analysis) that was purified further by chromatography over 10% $AgNO_3$–silica gel. The major, pure hydrocarbon obtained was identified as (+)-α-santalene (**3**) (see spectral data below; 0.12% yield based on dry weight of specimen).

The later fractions eluted with hexane from the original silica gel column were found to be quite complex mixtures by GLC analysis, but two major components (70:30 ratio) comprised ~50% of the total mixture. These two components, hydrocarbons **1** and **2**, respectively, were isolated by preparative GLC on a 6 ft × $^1/_4$ in., 10% OV-225 column at 150 °C with respective relative retention times of 1.0 and 1.12 min (spectral data, see below). The yields of **1** and **2**, based on dry-specimen weight, were 0.25 and 0.11%, respectively.

Spectral Data. (a) (+)-α-Santalene (3): $[\alpha]^{25}_D$ +19.5° (*c* 5.20, $CHCl_3$) [lit. +12.5° (neat, 20 °C),[3c] +18.4° (neat, 26 °C),[3b] +16.5° (*c* 5.35, $CHCl_3$)[3a]]; IR (film) 3055, 1670 (v w), 855, 838 cm^{-1} (lit.[3b] 1670, 858, 840 cm^{-1}); ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.80 (2 H, s), 0.81 (3 H, s), 0.98 (3 H, s), 1.57 (3 H, s), 1.63 (3 H, s), 5.04 (1 H, t, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 10.7 (q), 17.5 (q), 19.6 (d), 23.3 (t), 25.7 (d), 27.4 (s), 31.0 (t), 31.5 (t), 34.6 (t), 38.2 (d), 45.9 (s), 125.5 (d), 130.6 (s); mass spectrum, *m/e* (relative intensity) 204 (M^+, 32), 189 (16), 161 (12), 137 (10), 107 (34), 94 (100), 93 (87), 79 (27), 69 (35), 41 (66).

(b) (3*E*,5*E*,8*Z*)-3,7,11-Trimethyl-1,3,5,8,10-dodecapentaene (1): oil; $[\alpha]^{25}_D$ +502° (*c* 0.327, $CHCl_3$), +474° (*c* 0.0974, EtOH); IR (film) 3090, 1640, 985, 960, 885, 755 cm^{-1}; UV (absolute EtOH), see text; ^{1}H NMR, see Table I; mass spectrum, *m/e* (relative intensity) 202 (M^+, 21), 187 (14), 173 (4), 160 (8), 159 (46), 157 (10), 146 (34), 145 (81), 133 (36), 131 (80), 119 (61), 115 (30), 107 (77), 105 (100), 91 (99), 77 (58), 67 (20), 65 (20), 55 (12), 53 (14).

(c) (3*E*,5*E*,8*E*)-3,7,11-Trimethyl-1,3,5,8,10-dodecapentaene (2): oil; $[\alpha]^{25}_D$ +55.1° (*c* 0.45, $CHCl_3$); IR (film) 3095, 1640, 986, 965, 890 cm^{-1}; UV (absolute EtOH), see text; ^{1}H NMR, see Table I; mass spectrum, *m/e* (relative intensity) 202 (M^+, 24), 187 (10), 173 (3), 160 (5), 159 (31), 157 (8), 146 (23), 145 (60), 133 (40), 131 (70), 119 (58), 115 (23), 107 (89), 105 (100), 91 (92), 77 (51), 67 (20), 65 (18), 55 (16), 53 (13).

Hydrogenation of 1 and Mixture of 1 and 2. Hydrocarbon **1** (7 mg) and a mixture of **1** and **2** (32 mg) were hydrogenated separately at atmospheric pressure and room temperature in hexane over 10% palladium on charcoal. The two clear oils obtained in essentially quantitative yields after removal of the catalyst by filtration and evaporation of the solvent exhibited identical GC retention times, mass spectra (*m/e* 212, M^+), and ^{1}H NMR spectra (100 MHz, $CDCl_3$). The ^{1}H NMR and mass spectra matched those reported for farnesane.[4,5]

Reaction of 1 with 4-Phenyl-1,2,4-triazoline-3,5-dione. Freshly prepared 4-phenyl-1,2,4-triazoline-3,5-dione[7] (10 mg) was added to a solution of 10 mg of **1** in 2 mL of dichloromethane at room temperature, and the reaction was stirred for 5 min. The residue obtained after evaporation of the solvent was chromatographed over silica gel with dichloromethane as eluent to give 9 mg of **5** as a colorless, viscous oil: IR ($CHCl_3$) 1770, 1710, 1600, 1500, 1420 cm^{-1}; UV (absolute ethanol) λ_{max} 234 nm (ϵ 24 000); ^{1}H NMR (270 MHz, $CDCl_3$), see Table I; mass spectrum, *m/e* (relative intensity) 377 (M^+, 100), 295 (7.5), 269 (10), 268 (56), 256 (61), 242 (82), 185 (20), 159 (19), 145 (50), 135 (59), 119 (48), 105 (37), 91 (74).

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(9) Private communication from L. S. Ciereszko and T. K. B. Karns, University of Oklahoma. Dr. Karns assisted in collection of the specimens in question.

(10) W. W. Youngblood, Ph.D. Thesis, University of Oklahoma, Norman, OK, 1969.

(11) ^{1}H NMR spectra were measured on Varian XL-100 or Bruker 270 MHz instruments; the ^{13}C NMR spectrum was taken on a JEOL FX 90Q spectrometer; IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer and UV spectra on a Cary 15 ultraviolet spectrophotometer. Optical rotations were measured on a Perkin-Elmer Model 141 instrument. Mass spectra were obtained on Du Pont 21-491 and Hewlett-Packard Model 5985A spectrometers. Silica gel 60, 230–400 mesh (E. Merck), was used for column chromatography. Analytical and preparative gas chromatographs used were Varian Models 1400 and 1200, respectively.

spectrometers and accessories.

Registry No. 1, 73368-16-8; 2, 73368-17-9; 3, 22527-23-7; 5, 73368-18-0; farnesane, 3891-98-3; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4.

Conversion of Methyl Ketones into Terminal Acetylenes and (*E*)-Trisubstituted Olefins of Terpenoid Origin

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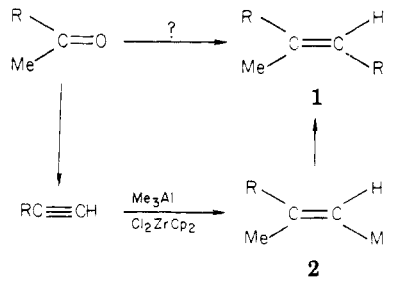
Carbonyl olefination reactions, such as the Wittig reaction, represent one of the most commonly used methods for the synthesis of olefins. Although the stereoselectivity of the conversion of aldehydes into olefins can be ≥95%, that of the ketone-to-olefin conversion has usually been disappointingly low[2] and hence represents an important synthetic problem to be solved. Although it appears difficult to provide a direct and generally applicable solution to this problem, there can be an indirect solution at least in a very important case of converting methyl ketones into methyl-substituted trisubstituted olefins (**1**) including various terpenes. Since we have recently developed a highly stereo- and regioselective Zr-catalyzed carbometallation procedure for converting terminal acetylenes into (*E*)-2-methyl-1-alkenylmetals (**2**)[3] as well as various reactions for converting **2** into trisubstituted olefins **1**,[4] we hoped to develop a convenient and widely applicable carbonyl olefination sequence such as that represented by Scheme I. As the isolation of **2** is not usually required, such a sequence would amount to a two-step but highly stereoselective alternative to conventional carbonyl olefination reactions.

In order to demonstrate the practicality of such a procedure, we decided to synthesize monocyclofarnesol (**3**)[5] from β-ionone (**4**) (see Scheme II). Unfortunately, however, our attempts to convert dihydro-β-ionone (**5**), obtained in quantitative yield by reducing **4** with $LiAlH_4$ and CuI,[6] into the required intermediate **6** by various known procedures[7] were disappointing. Even the best of those examined, which was developed by Craig and Moyle,[7f] yielded **6** only in <50% yield, which was contaminated with at least two isomeric products.

Clean conversion of **5** into **6** via enol derivatives would result if the "kinetic" enol phosphate **7** forms cleanly and β eliminates regioselectively. We have therefore tested several highly basic and sterically hindered amide bases

Scheme I



M = $AlMe_2$ and/or $ZrCp_2Cl$

Scheme II

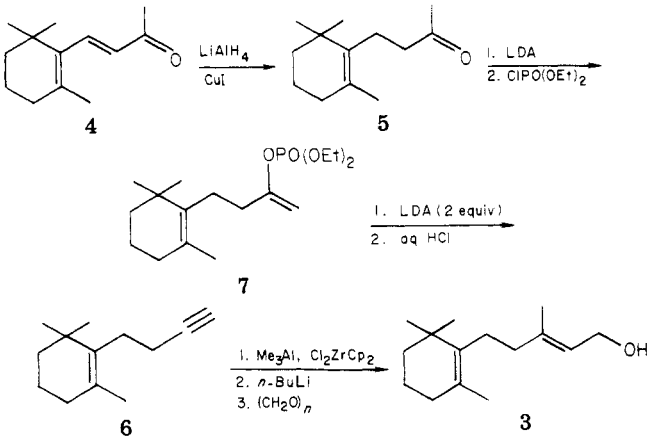


Table I. Conversion of Methyl Ketones into Terminal Acetylenes via Enol Phosphates

ketone	base	yield of acetylene, % GLC	yield of acetylene, % isolated
β-ionone (4)	LDA	95	85
dihydro-β-ionone (5)	LDA	90	85
acetophenone	LDA	85	80
pinacolone	LDA	90	78
cyclohexyl methyl ketone	LDA	85	80
2-octanone	LDA	23	
2-octanone	LTMP	75	
6-methyl-5-hepten-2-one	LDA	25	
6-methyl-5-hepten-2-one	LTMP	75	61

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(2) For reviews of various methods for the synthesis of olefins including carbonyl olefination reactions, see (a) D. J. Faulkner, *Synthesis*, 175 (1971); (b) J. Reucroft and P. G. Sammes, *Q. Rev., Chem. Soc.*, **25**, 135 (1971).

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(7) We note that essentially all of the highly successful examples of the methyl ketone-to-acetylene conversion reported previously involve those methyl ketones which do not contain α-methylene or α-methine hydrogens. In cases where methyl ketones contain α-methylene or α-methine hydrogens, the yields of the desired acetylenes are either low or unspecified, frequent major products being isomeric allenes. Various reagent combinations for the conversion of methyl ketones into terminal acetylenes that we have tested include the following: (a) PCl_5 in benzene, then $NaNH_2$ in NH_3 [R. S. Sweet and C. S. Marvel, *J. Am. Chem. Soc.*, **54**, 1184 (1932)]; (b) PCl_5 and 2,6-lutidine, then $NaNH_2$ in NH_3 [E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 4245 (1967)]; (c) $POCl_3$ in DMF, then NaOH [M. Rosenblum, N. Brawn, J. Papenmeier, and M. Applebaum, *J. Organomet. Chem.*, **6**, 173 (1966)]; (d) $(CF_3SO_2)_2O$, CCl_4, pyridine, then heat [R. J. Hargrove and P. J. Stang, *J. Org. Chem.*, **39**, 581 (1974)]; (e) NH_2NH_2 in Et_3N, and I_2 and Et_3N in THF, and finally methanolic KOH [A. M. Krubiner, N. Gottfried, and E. P. Oliveto, *J. Org. Chem.*, **34**, 3502 (1969)]; (f) NaOEt, then $ClPO(OEt)_2$, and finally $NaNH_2$ in NH_3 [J. C. Craig and M. Moyle, *J. Chem. Soc.*, 3713 (1963)].

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