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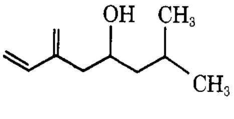
Received July 6, 1976

Terpene Synthesis via Pentadienyl Anions

Summary: The introduction of the terminal isoprenoid 1,3-diene unit using pentadienyllithiums is illustrated by the synthesis of monoterpenes from Ho-leaf oil and *Ledum palustre* oil.

Sir: The formation of terpenes by head-to-tail linking of isoprene units has long been an objective of organic synthesis.[1] Although 1,5-dienes are more common among acyclic terpenes,[2] terpenoids with terminal isoprene residues present as 1,3-dienes of three types occur in nature. For example, tagetol[3] (**1**) is a sex attractant of *Ips confusus*, compound **2**[4] is a volatile constituent of *Ledum palustre* essential oil, and hotrienol[5] (**3**) is a component of Japanese Ho-leaf oil.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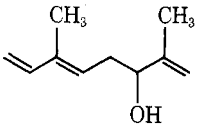
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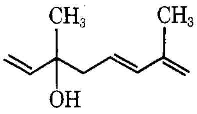
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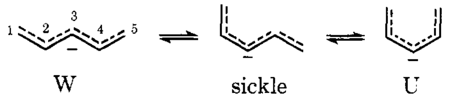
We have recently reported[6] a general method for the introduction of terminal isoprenoid 1,3-dienes of type **1**. We now report a convenient method for the stereoselective production of isoprenoid (*E*)-1,3-dienes of the two remaining types.

Pentadienyl anions have been studied for some time,[7] particularly with regard to the conformations in eq 1. The three planar conformations, W, sickle, an U have been used to rationalize the sites of protonation in various derivatives. In general the W conformer protonates at C-1 and the U conformer at C-3 (the sickle form is intermediate). A recent ^{13}C NMR determination[8] indicated that 3-methylpentadienyllithium **4** exists almost exclusively as the W form from −80 to +40 °C. Thus protonation of 3-methylpentadienyllithium (**4**) gives 96% **5** (R = H, 95% *E*) and 4% **6** (R = H).

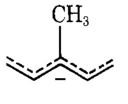


(1)

Table I. Reaction of 4 with Electrophiles at 0 °C

Entry	Electrophile	% **5**	% **6**
1	H_2O	96[a]	4
2	Adamantanone	75[b]	0
3	Methacrolein	65[b,c]	0
4	$CH_2{=}C(CH_3)(CH_2)_2CHO$	40[b]	60
5	$CH_3(CH_2)_5CHO$	38[b]	48
6	PhCHO	70[b]	30
7	$CH_3(CH_2)_4CH_2I$	38[d]	54
8	$CH_3(CH_2)_4CH_2I$	58[d,e]	34
9	Cyclohexene oxide	28[b]	72

[a] Reference 8. [b] Isolated yields. [c] +9% compound **8**. [d] GC yield. [e] With $CuBr{\cdot}SMe_2$ (−78 °C).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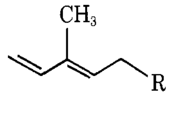
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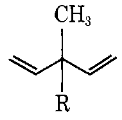
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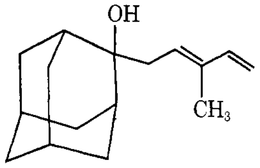
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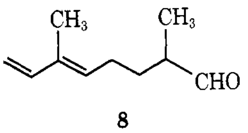
Reaction of anion **4** with adamantanone gave **7**[9] (mp 59–61 °C) as the exclusive product (75% yield, >96% *E*). The pentadienyl anion **4** consequently gives us a convenient method for the introduction of the terminal 1,3-diene of type **2**. Reaction of **4** with methacrolein gives the monoterpene **2** in 65% yield. Interestingly, the only other product, isolated in 9% yield, was the conjugate addition product **8** (99% *E*). Since the uncatalyzed 1,4 addition of an organolithium is rather unusual we felt that the copper catalyzed reaction might be very good. Surprisingly, with **4** and 1 equiv of CuI (THF, −78 °C), compound **8** was formed in only 30% yield and the 1,2 adduct **9** *at the 3 position* was isolated in 25% yield![10] The scope of the reaction of **4** with various electrophiles (Table I) indicates that some exploratory work must be done in order to find optimal conditions for 1,3-diene production.[11]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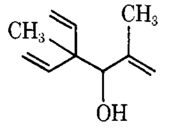
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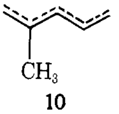
The synthesis of hotrienol **3**, the last type of terpenoid 1,3-diene, was achieved using 2-methylpentadienyllithium **10**. Compound **10** in contrast to **4** exists as a mixture of con-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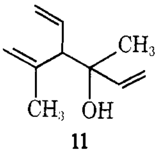
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formers[7] and consequently yields about a 1:1 mixture of hotrienol **3** and compound **11** on reaction with methyl vinyl ketone. Hotrienol can be isolated by chromatography in 35% yield.[9] This one-step synthesis of hotrienol (**3**) compares favorably with the published[12] synthesis.

Acknowledgment. We gratefully acknowledge the generous support of the Indiana University Department of Chemistry. S.R.W. thanks the Indiana University Research Fund for a Summer Faculty Fellowship.

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(9) All new substances possessed spectral data in accord with the assigned structures. Synthetic **2** and **3** had spectral properties identical with those reported.[4,5]

(10) Compound **9** was never observed in the uncatalyzed reaction, and compound **2** was not detected in the catalyzed reaction. In the presence of CuBr·S(CH$_3$)$_2$ only the normal 1,4 adduct **8** is obtained; thus, the origin of compound **9** may involve a RCu species.

(11) Temperature has been shown to affect the degree of ionization of pentadienyl anion and thus the ratio of kinetic C-1 or C-3 addition. We have also determined that adduct **6** can isomerize to **5** under the reaction conditions.

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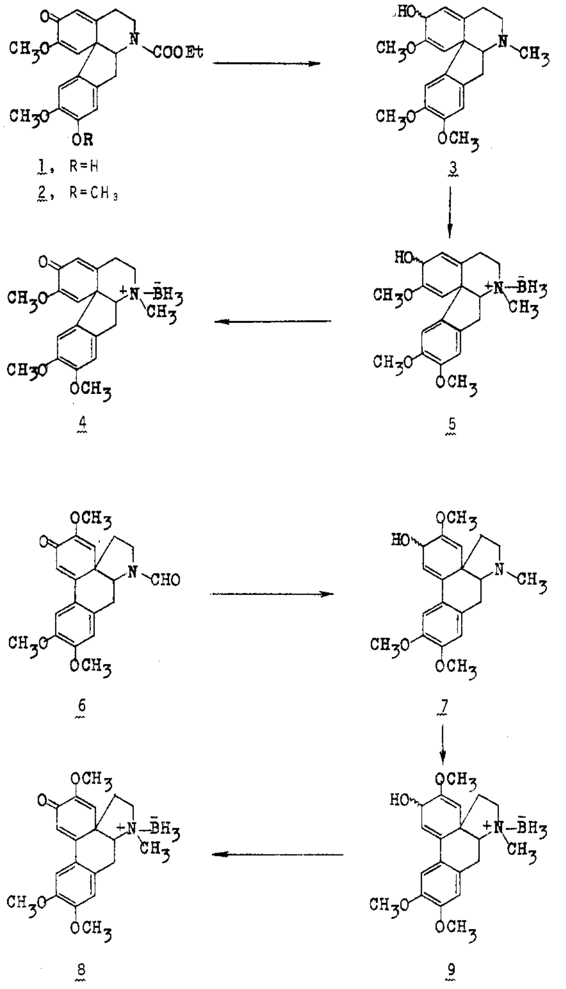
Received June 10, 1976

The Synthesis and Chemistry of Elusive Spirodienone Alkaloid Precursors[1]

Summary: *N*-Methylproerythrinadienone and *N*-methylneospirinedienone derivatives, elusive spirodienone intermediates, have been synthesized as borane complexes and shown to be genuine precursors of aporphine and dibenzazonine alkaloids.

Sir: In earlier studies we have shown that spirodienones derived from benzylisoquinolines play important roles in biomimetic syntheses of alkaloids.[2-6] Thus morphinandienones are effective in vitro precursors of aporphine and dibenzazonine alkaloids, and acid-catalyzed rearrangement of morphinandienones to aporphines and dibenzazonines may proceed via the intermediacy of proerythrinadienones and neospirinedienones, respectively.[4,5] The proerythrinadienones have also been proposed as biosynthetic precursors of aporphine[7] and *Erythrina* alkaloids.[8] Attempts to synthesize such spirodienones have failed when the nitrogen atoms were unprotected[8,9] and attempted transformation of *N*-acylproerythrinadienones to aporphines and dibenzazonines has also been unsuccessful.[10] We describe herein the synthesis of the borane complexes[11] of *N*-methylproerythrinadienone (**4**) and *N*-methylneospirinedienone (**8**) derivatives and the first reported laboratory transformation of a proerythrinadienone to an aporphine. In addition, the temperature dependence of rearrangements of these spirodienones is described.

Methylation of (±)-*N*-ethoxycarbonylproerythrinadienone (**1**)[12] with CH$_3$I–K$_2$CO$_3$ in acetone gave **2** (84%, mp 87–89 °C).[13] Reduction of **2** with LiAlH$_4$ in THF gave a mixture of the epimeric dienols (**3**, 73%) which, upon treatment with BH$_3$–THF followed by MnO$_2$ oxidation, yielded the (±)-*N*-methylproerythrinadienone–borane complex (**4**, 51% from **3**): mp 135–137 °C (CHCl$_3$–Et$_2$O); uv $\lambda_{\max}^{\mathrm{EtOH}}$(log ϵ) 286 (3.87), 244 (4.27) nm; ir (CHCl$_3$) 4.21 (B–H), 6.01, 6.11, 6.21 (cyclohexadienone C=O) μ; NMR (CDCl$_3$) δ 6.78, 6.41, 6.16, 5.82 (each s, 4 H, aromatic and olefinic H), 3.88, 3.73, 3.67 (each s, 9 H, 3-OCH$_3$), 2.71 (s, 3 H, -NCH$_3$); mass spectrum *m/e* (rel %) 355 (6, M$^+$), 341 (100), 311 (15). Similarly, (±)-*N*-methylneospirinedienone–borane complex (**8**) was prepared by reduction of (±)-*N*-formylneospirinedienone (**6**)[2] with LiAlH$_4$ to the epimeric dienols (**7**, 72%), treatment of **7** with BH$_3$–THF to give **9**, and oxidation of **9** with MnO$_2$ to **8** (47% from **7**): mp 156–158 °C (CHCl$_3$–Et$_2$O); uv $\lambda_{\max}^{\mathrm{EtOH}}$ (log ϵ) 356 (3.92), 290 (4.09), 262 (4.15), 234 (sh, 4.29) nm; ir (CHCl$_3$) 4.20 (B–H), 6.01, 6.10, 6.22 (cyclohexadienone C=O) μ; NMR (CDCl$_3$) δ 6.96, 6.74, 6.34, 6.30 (each s, 4 H, aromatic and olefinic H), 3.92 (s, 6 H, 2-OCH$_3$), 3.76 (s, 3 H, 1-OCH$_3$), 2.54 (s, 3 H, -NCH$_3$); mass spectrum *m/e* (rel %) 355 (7, M$^+$), 341 (100), 326 (70), 310 (28), 298 (59). Thus the spirodienones postulated earlier[4] as intermediates in the acid-catalyzed rearrangements of morphinandienones to aporphines and dibenzazonines were isolated as borane complexes.



Heating the (±)-*N*-methylproerythrinadienone–borane complex (**4**) in concentrated hydrochloric acid on a steam bath