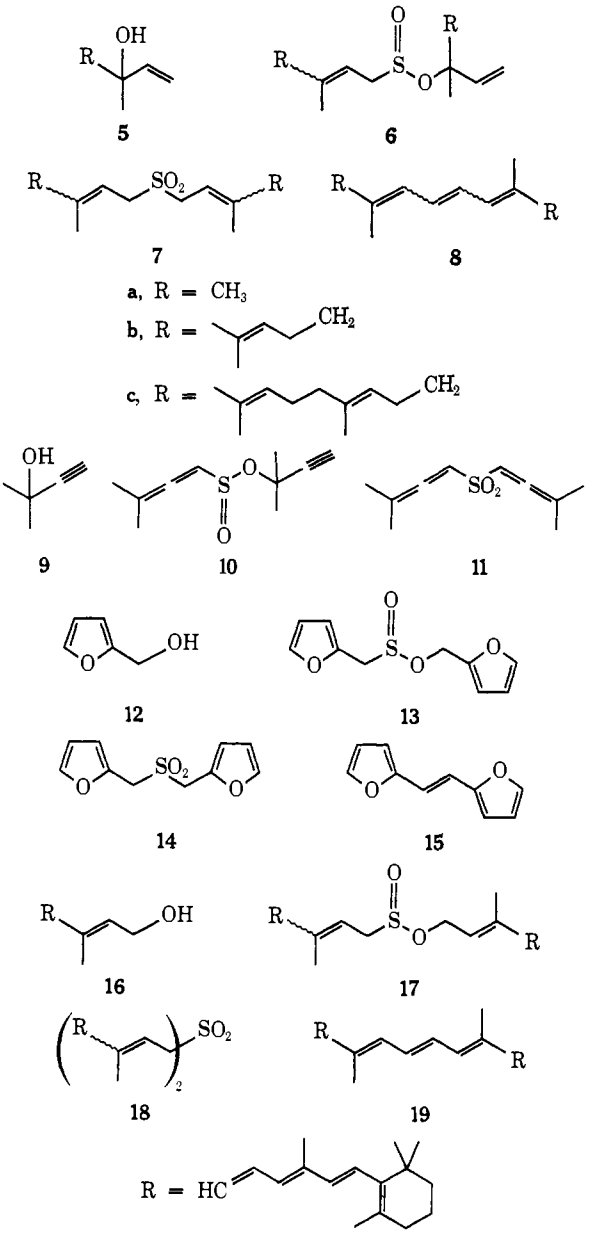
ments[7] or subsequent isomerization of the sulfones. Vitamin A (**16**) afforded β-retinyl sulfone (**18**) in analogy



to the rearrangement of cinnamyl trichloromethanesulfenate to cinnamyl trichloromethyl sulfoxide[8] and β-ionyl *p*-toluenesulfinate to β-ionyl *p*-tolyl sulfone.[9] In these cases an allylic shift would have resulted in loss of conjugation and/or increased steric interactions.

Carbon tetrachloride in the presence of potassium hydroxide[10] at room temperature converted sulfones **7a**, **b**, **c**, and **14** rapidly to the olefins **8a**, **b**, **c**, and **15** (method D) (Table I). No dichlorocarbene adducts were detected. The Ramberg–Bäcklund reaction of

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Table I

Alcohol	Sulfone	Method of preparation	% yield	Olefin	Method of preparation	% yield
5a	**7a** mp 37–38°	A	83	**8a**	D	78[a]
5a	**7a**	B	48			
5b	**7b** oil	B	66[b]	**8b**	D	69[b]
5c	**7c** oil	B	74[b]	**8c**	D	89[b]
9	**11** mp 62°	B	28			
12	**14** mp 76–78°	B	32	**15**	D	18[c]
16	**18** amorphous	A	46[b]	**19**		
16	**18**	C	74[b]	**19**	E	24[c]

[a] 3:1 mixture of geometric isomers by glc. [b] Undetermined mixture of isomers. [c] All-trans isomer.

sulfone **14** required 60° and failed for β-retinyl sulfone (**18**). A mixture of stereoisomeric β-carotenes was prepared by treatment of the α,α′-dianion[11] (produced with *n*-butyllithium or lithium diisopropylamide in tetrahydrofuran at 0°) with iodine or bromine (method E). Thermal or iodine catalyzed isomerization[12] gave crystalline all-*trans*-β-carotene. The new transformation of a sulfone dianion to an olefin with halogens may be viewed as proceeding through an α-halo sulfone analogous to the Ramberg–Bäcklund transformation or as a two-electron oxidation to the episulfone followed by loss of sulfur dioxide.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM 09868) for financial support.

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(13) National Institues of Health, Predoctoral Fellow 1972–present.

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Total Synthesis of *dl*-Shionone, a Tetracyclic Triterpene[1]

Sir:

As an integral part of our program directed toward the total synthesis of polycyclic triterpenes,[2] we have investigated the total synthesis of the tetracyclic triterpene shionone (**15**)[3]—an interesting objective in itself and a useful model for some of the transformations necessary in a total synthesis of friedelin[4] and its derivatives. The successful approach we report here for this total synthesis incorporates the tetracyclic ketone **10**[5]

(1) This work was made possible through the support of the National Science Foundation and a grant from the Hoffman-LaRoche Foundation.

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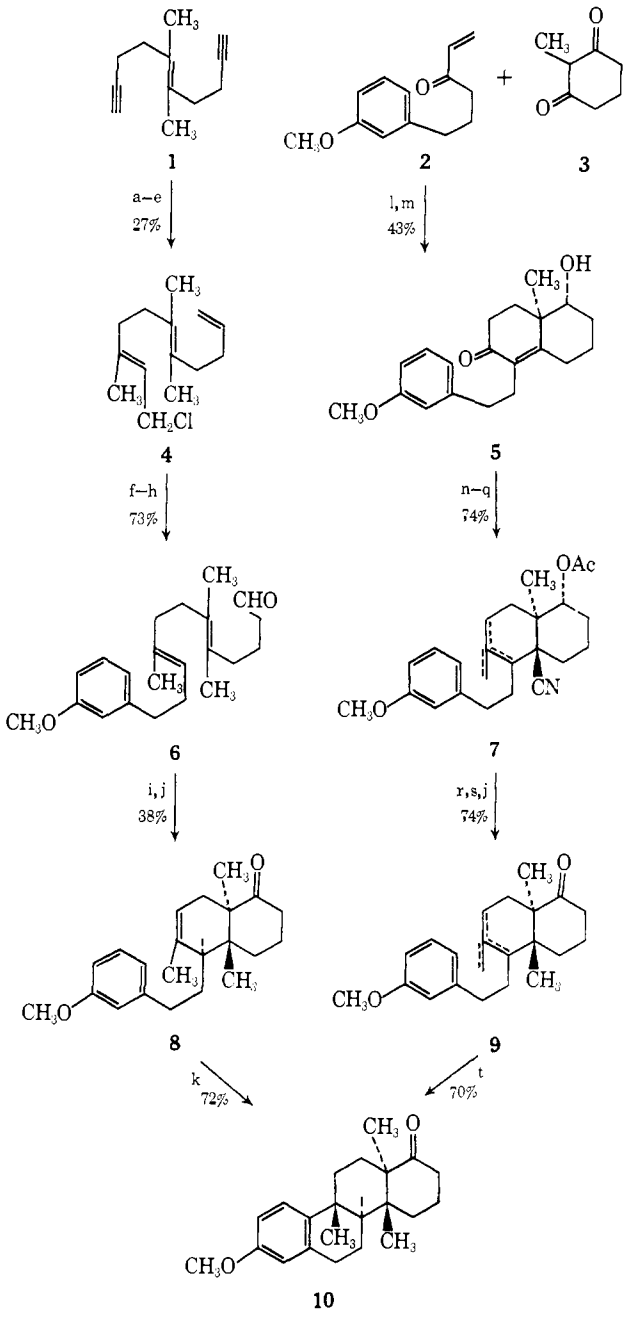
(5) The structural formulas containing one or more asymmetric carbon atoms depict one enantiomer but refer to racemic compounds throughout. All intermediates were characterized by ir and nmr spectroscopy which are fully consistent with the structures shown. All new substances gave satisfactory combustion analyses.

as the key intermediate, and we have developed two independent syntheses of this material (Chart I).

Chart I. Syntheses of the Tetracyclic Ketone **10**[5,a]



[a] (a) Sia_2BH, THF, HOAc; (b) EtMgCl, CH_2O; (c) $LiAlH_4$, NaOMe, THF, I_2; (d) $LiCuMe_2$, THF; (e) Ph_3P, CCl_4; (f) *m*-$MeOC_6H_4CH_2MgCl$, Et_2O–HMPA; (g) Sia_2BH, H_2O_2, OH^-; (h) $CrO_3 \cdot 2Py$, CH_2Cl_2; (i) 0.5 equiv of $SnCl_4$, C_6H_6, 25°, 65 sec; (j) 8 *N* H_2CrO_4, acetone; (k) TsOH, $C_6H_5CH_3$, reflux; (l), Et_3N, CH_3OH, 25°, $C_6H_5CO_2H$, Et_3N, xylene, reflux; (m) $NaBH_4$, EtOH; (n) Et_3Al, HCN, THF; (o) CH_3MgI; (p) AC_2O, pyr; (q) $SOCl_2$, pyr; (r) $(i\text{-Bu})_2AlH$, C_6H_6; (s) $N_2H_4 \cdot 2HCl$, $N_2H_4 \cdot H_2O$, KOH, TEG; (t) CF_3CO_2H, reflux.

As was the case in the recent alnusenone synthesis,[2a] the correct stereochemical disposition of the angular methyl groups about the tetracyclic nucleus of ketone **10** was the initial objective. One scheme that was designed to accomplish this goal was a nonenzymic polyene cyclization approach.[6] In the present case a nonbiogenetic polyene precursor that contained an acyclic tetrasubstituted double bond was chosen so as to generate the desired angular methyl pattern of ketone **10**. Previous work[7] had provided means for the synthesis of systems containing the required trans-tetrasubstituted olefinic linkage and demonstrated its utility in acid catalyzed cyclizations for the synthesis of trans diangularly methylated decalones. For the construction of the tetracyclic ketone **10**, the olefinic aldehyde **6** was prepared from the enediyne **1**[8] (Chart I). Cyclization of the aldehyde **6** was investigated under a variety of conditions, and the optimum procedure developed entailed the intermediate isolation of the octalinone **8** and then subsequent protonic acid catalyzed closure of the B ring. Direct conversion of aldehyde **6** to the tetracyclic ketone **10** in benzene–stannic chloride led to a lower overall yield due to the more vigorous conditions necessary to effect cyclization into the aromatic ring and to the formation of both ortho and para aromatic substitution products.[6c]

This polyene cyclization sequence is effective for the synthesis of ketone **10**, but the 5.5% overall yield is poor compared to that of the second approach. This alternate approach is patterned closely after the scheme used for the construction of alnusenone intermediates[2a] and has as its central feature the triethylaluminum catalyzed conjugate addition of cyanide[9] to the bicyclic enone **5**[10] (Chart I). By this approach the tetracyclic intermediate **10** was available in 16.5% overall yield.

The conversion of the ketone **10** to *dl*-shionone (**15**) entailed first the addition of the rudiments of the side chain, modification of the aromatic A ring and finally completion of the side chain construction (Chart II). Several points in this process are worthy of note.

The conversion of ketone **10** to aldehyde **11** was conveniently accomplished through first formation of the chloroaldehyde in the Vilsmeier reaction[11] and then methylation of the aldehyde enolate that results from lithium–ammonia reduction. This process effectively converts an α-decalone system to the desired β,β-disubstituted decalin system and in this case is quite stereoselective.

Second, the crucial A ring modification was conveniently accomplished through a sequence that entails the opening of enone **12** by the Eschenmoser cleavage[12] of the derived epoxide. After methyllithium addition, the resulting acetylenic tertiary alcohol cyclizes[13] stereoselectively and in high yield when treated with trifluoroacetic acid and generates the enol trifluoroacetate directly. This enol trifluoroacetate serves as an efficient precursor of the desired C3(4) enolate when treated with lithium diisopropylamide (*not* methyl-

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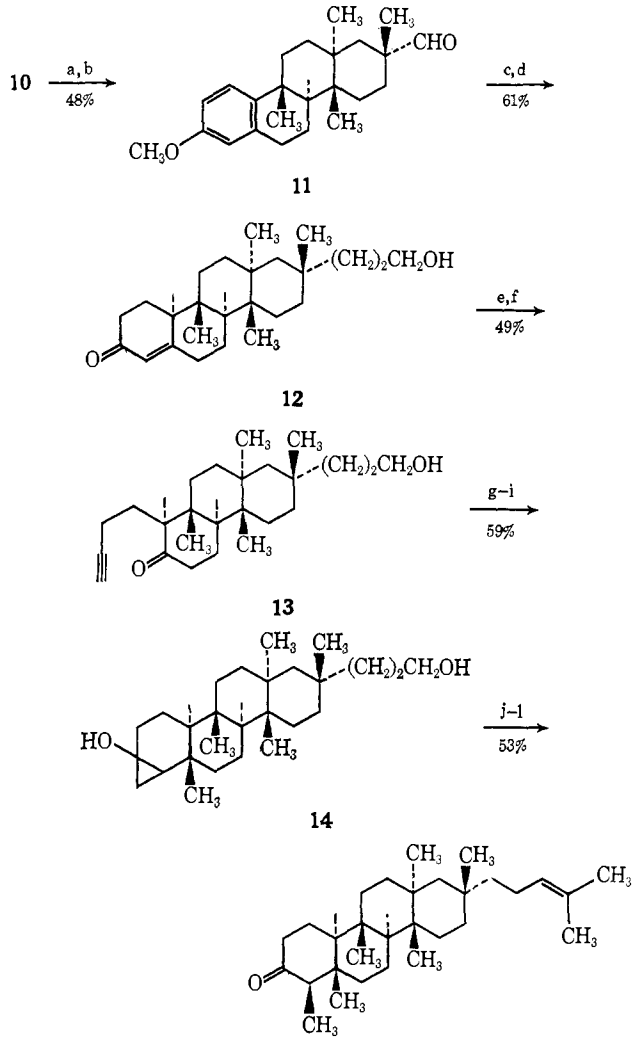
Chart II. Conversion of Tetracyclic Ketone **10** to *dl*-Shionone (**15**)[b,a]



[a] (a) $POCl_3$, DMF, 60°; (b) Li, NH_3, THF, CH_3I; (c) $[(EtO)_2POCHCH{=}NC_6H_{11}]^-Na^+$, THF, 60°; 1% aqueous $(CO_2H)_2$, C_8H_6; (d) Li, NH_3, EtOH, H_3O^+, EtOH, reflux; (e) H_2O_2, aqueous NaOH, CH_3OH–CH_2Cl_2; (f) $TsNHNH_2$, HOAc–CH_2Cl_2; (g) MeLi, THF; (h) CF_3CO_2H, $(CF_3CO)O$, −25°; (i) $(i\text{-}Pr)_2NLi$, THF, $ICH_2ZnI(Ag)$, Et_2O; (j) H_3O^+, EtOH, reflux; (k) $CrO_3 \cdot 2Py$, CH_2Cl_2; (l) $(CH_3)_2C{=}PPh_3$, THF.

lithium). The final C4 methyl group can conveniently be added through treatment of this enolate with the Simmons–Smith reagent[14] and then acid catalyzed cleavage of the resulting cyclopropanol **14**. This sequence, particularly important for future friedelin synthetic work, can be accomplished in 25% overall yield and in our hands is significantly better than a conjugate addition–methylation approach that might seem more apparent.

Completion of the synthesis required only the addition of the terminal isopropylidene grouping with the Wittig reagent, and *dl*-shionone (mp 161.5–163° (vac); C, 84.38%; H, 11.90%) was in hand. This synthetic material had identical solution infrared and nmr spectra and R_f value on tlc (silica gel, ether) with those of natural shionone, which was kindly provided by Professor G. Ourisson (University of Strasbourg). Further work on the friedelin synthesis is underway.

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(16) National Institute of Health Trainee, 1969–1973.
(17) National Science Foundation Fellow, 1968–1972.
(18) National Defense Education Act Trainee, 1971–1974.

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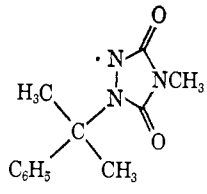
Non-Aryl Hydrazyls. I. Synthesis, Isolation, and Characterization of 1-α-Cumyl-4-methylurazolyl

Sir:

We wish to report the synthesis and characterization of 1-α-cumyl-4-methylurazolyl (**1**), a stable, cyclic non-



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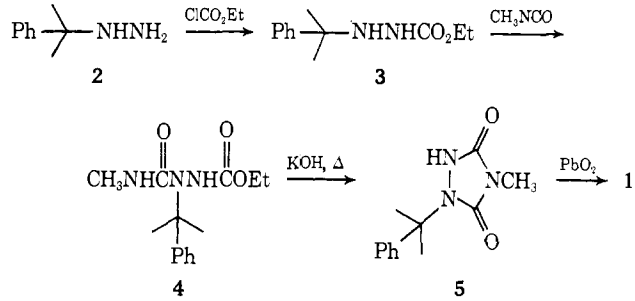
aryl hydrazyl, isolatable as its dimer, a tetrazane. Although triarylhydrazyls such as diphenylpicrylhydrazyl (DPPH) are among the most stable and extensively studied free radicals known,[1] only recently have hydrazyls, lacking a directly bonded aromatic group, been examined.[2–9] Heretofore, non-aryl hydrazyls have been

Scheme I



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