−0.1 to 0.1 (m, 1, secondary cyclopropyl), and −0.5 to −0.7 (m, 1, secondary cyclopropyl); *m/e* (calcd) 211.0997, (obsd) 211.1000.

Acknowledgment. We wish to express our appreciation to the National Science Foundation for financial support and to Ronald K. Russell for assistance in recording the 100-MHz NMR spectra.

Registry No.—**1**, 7092-05-9; **2**, 56960-48-6; **3**, 57029-75-1; **4**, 41411-75-0; **6**, 57029-76-2; **7**, 56960-49-7; **8**, 56960-50-0; **9**, 57029-77-3; **10**, 56960-51-1; **11**, 7322-47-6; **12**, 56960-52-2; **13**, 57029-78-4; **14**, 56960-53-3; **15**, 57029-79-5; **16**, 56960-54-4; maleic acid-2,3-d_2, 24461-33-4; dimethyl acetylenedicarboxylate, 762-42-5; succinic acid, 110-15-6; cycloheptatriene, 544-25-2; diacid, mp 159–167°, 57029-80-8; chlorosulfonyl isocyanate, 1189-71-5; diiodomethane, 75-11-6.

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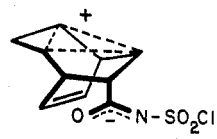

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Direct Determinations of *R/S* Enantiomer Ratios of Citronellic Acid and Related Substances by Nuclear Magnetic Resonance Spectroscopy and High Pressure Liquid Chromatography

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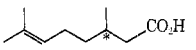
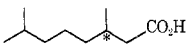
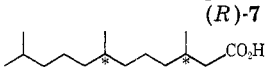
Two methods are described for direct determination of the enantiomer ratios of optically active 3,7-dimethyl-6-octenoic acid (citronellic acid), 3,7-dimethyloctanoic acid, and the homologous 3,7,11-trimethyldodecanoic acid. The first method is based on analysis of the C_3 methyl signal in the NMR spectra of methyl esters obtained in CS_2 in the presence of a chiral europium shift reagent. The second method is based on analytical separations by high pressure liquid chromatography of diastereomeric amides obtained by reaction of (*R*)-(+)-α-methyl-*p*-nitrobenzylamine with, e.g., citronellic acid. Both methods give directly *R/S* enantiomer ratios on samples of citronellic acid and epimer ratios on 3,7,11-trimethyldodecanoic acid. Using these methods citronellic acid samples from natural citronellal and (+)-pulegone have been shown to be respectively 80 and 96–98% excesses of the (3*R*)-(+) enantiomer.

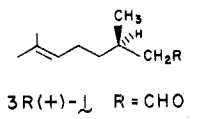
Citronellal is a relatively inexpensive chiral substance which is found in over 50 essential oils,[1] typically as a mixture of *R* and *S* enantiomers with one predominating. Citronellal obtained from its most important source, Java citronella oil,[2] has been assigned the (3*R*)-(+)-1 configuration[3] but is known to be only about 75% optically pure.[4,5] This paper describes two convenient methods for direct determination of the enantiomeric composition of citronellic acid (**2**) which is readily derived from citronellal. One method involves analysis of NMR spectra of **3** obtained in the presence of the chiral shift reagent Eu(dcm)$_3$, **4**.[6] The other involves analytical separation by high pressure liquid chromatography of diastereomeric amides **6** obtained from reaction of **5** with excess (*R*)-(+)-α-methyl-*p*-nitrobenzylamine.[7]

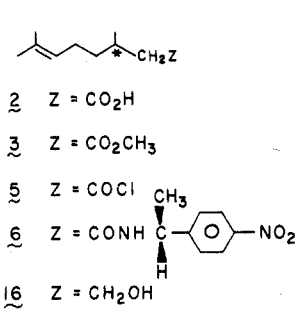
Both methods have been used to determine the enantiomeric compositions of samples of **2** and **7** obtained from racemic citronellol, from natural citronellal having $[\alpha]^{25}D$

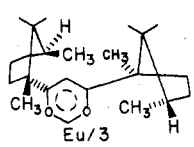
Table I
Enantiomeric Compositions of C_{10} and C_{15} Substrates by NMR and HPLC Methods

Substrate		$[\alpha]^{25}D$	R/S determinations of esters by NMR	Percentage of R and S enantiomer amides by HPLC	Percent enantiomeric excess[d]
	rac-2	0° (c 5.0, $CHCl_3$)	R/S = 1	54.4% R, 45.6% S	~0
	nat-2[a]	+7.73° (c 5.3, $CHCl_3$)	R/S = 9	90.2% R, 9.8% S	80.4
	pin-2	+8.70° (c 5.0, $CHCl_3$)	R/S = 12	92.5% R, 7.5% S[b]	85
	(R)-2	+10.3° (c 5.0, $CHCl_3$)	R only	99% R, 1% S	98
	rac-7	0°	R/S = 1	50.0% R, 50.01 S[b]	~0
	nat-7	+5.50° (c 5.0, $CHCl_3$)	R/S = 9	90.8% R, 9.2% S	82
	pin-7	+8.70° (c 5.0, $CHCl_3$)	R/S = 12	91.5% R, 8.5% S[b]	83
	(R)-7	+7.0° (c 5.0, $CHCl_3$)	R only	96.6% R, 3.4% S	93
					
(3R,7R(phytol))-14		+5.43° (c 5.0, $CHCl_3$)	3R,7R only	100% 3R	100 (C_3), 100 (C_7)
(3R(nat),7RS)-14		c	3R/3S ≃ 9, 7R/7S ≃ 1	90.5% 3R, 9.5% 3S	81 (C_3), 0 (C_7)
(3R(R),7RS)-14		+6.05° (c 5.0, $CHCl_3$)	3R only, 7R/7S = 1	98.3% 3R, 1.7% 3S	96 (C_3), 0 (C_7)
(3RS,7RS)-14		0°	3R/3S = 7R/7S = 1	49.4% 3R, 50.6% 3S[b]	0 (C_3), 0 (C_7)
(3RS,7R(nat))-14		c	Not determined	51.2% 3R, 48.8% 3S	0 (C_3), 80 (C_7)

[a] Natural citronellal, $[\alpha]^{25}D$ +12.00° (neat), was used to prepare nat-2. [b] Multiple determination. Typical precision limits ±0.5%. Other values are based upon single determinations. [c] Not obtained on free acid. [d] In the case of 14, numerical values given refer to the excess of R epimer over S epimer at C_3 or C_7 (i.e. % R epimer − % S epimer).







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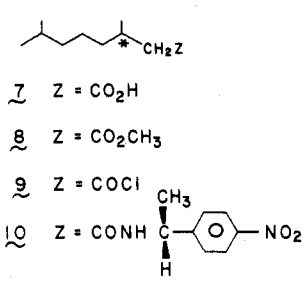
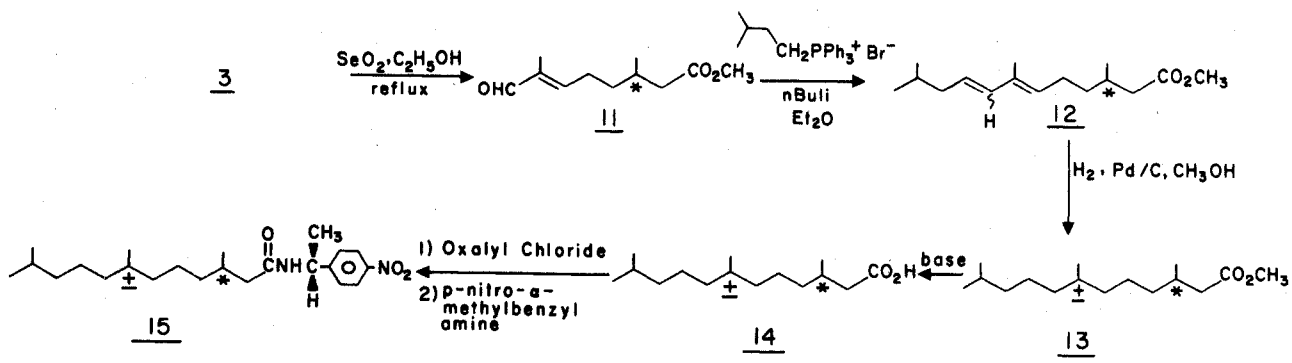


+12.00° (neat), from pulegone[8] and from (+)-citronellol derived from (−)-β-pinene obtained from U.S. sulfate turpentine.[9] These samples are herein designated as rac-2, nat-2, (R)-2, and pin-2, respectively, and are shown below to be respectively 0, 80–82, 96–98, and 84–86% enantiomeric excess of (3R)-(+)-2 or (3R)-(+)-7. The R/S epimer ratios at both C_3 and C_7 in the homologous C_{15} acid 14 were determined by NMR on 13 and HPLC on 15. A sample of (3RS,7RS)-14 was obtained from addition of triethyl phosphonoacetate to 6RS,10-dimethylundecan-2-one[12] followed by hydrogenation and hydrolysis; samples of (3R,7RS)-14 were obtained both from nat-3 and (R)-3 as shown in Scheme I and a sample of (3RS,7R)-14 was obtained from natural citronellal by reaction with methyl diethyl phosphonosenecioate. Properties of all these substances are given in Table I.

Determination of the enantiomeric composition of 3 or 8 by NMR was accomplished by integration of the pair of C_3 methyl group signals observed at 4.2 ppm on solutions of the ester and 1.2 equiv of 4 in CS_2 and Me_4Si. The procedure given in the Experimental Section was optimized with respect to which ester of 2 was used, the molar ratio 4/3, the solvent, and the probe temperature, to obtain best analytical results on a Varian T-60 spectrometer with T-6057 lock/decoupler. The recommended conditions produce an enantiomeric shift difference ($\Delta\Delta\delta$) of the C_3 methyl group signals for 3 of ca. 0.015 ppm, sufficient to allow semiquantitative determination of R/S ratios in the range $1/9 < R/S < 9/1$ and to permit detection of ca. 3–5% of a minor enantiomer when suitable reference samples are available. Typical spectra are shown in Figures 1a–c which show respectively that rac-8 is a 1:1 mixture of enantiomers, that nat-3 is a 9:1 R:S mixture, and that no S enantiomer was detected in (R)-3.

Application of the NMR method to (3RS,7RS)-13 gave the interesting C_3 methyl group signals shown as Figures 2a and 2b which were obtained at 60 and 100 MHz, respectively. These complex C_3 methyl group signals arise because

Scheme I



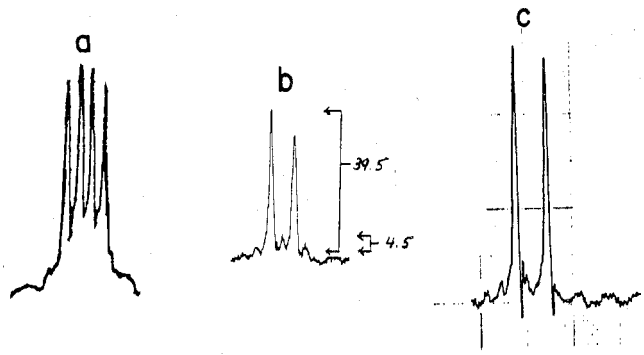


Figure 1. C_3 methyl group signals from **3** and **8** in the presence of $Eu(dcm)_3$: a, rac-**8**; b, nat-**3**; c, (*R*)-**3**.

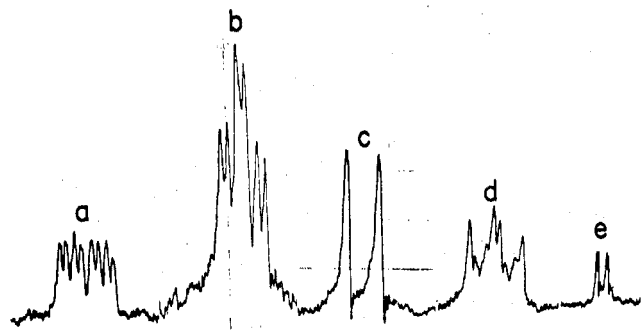
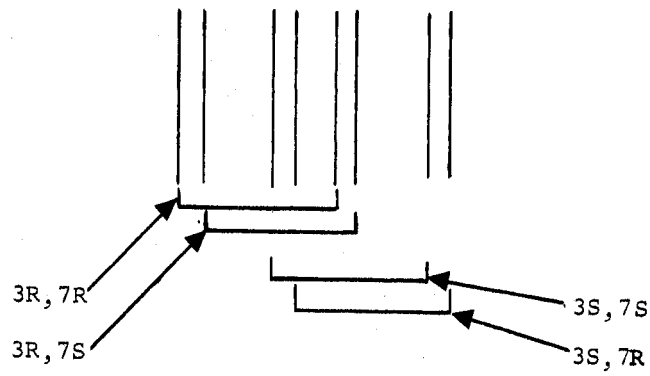


Figure 2. C_3 methyl group signals from **13** in the presence of $Eu(dcm)_3$: a, 3*RS*,7*RS* at 60 MHz; total width 11 Hz; b, same at 100 MHz; total width 15 Hz; c, 3*R*,7*R* (60 MHz); d, 3*RS*,7*R*(nat) + 3*RS*,7*RS* at 60 MHz; e, 3*R*(nat),7*RS* at 60 MHz. Sweep width is 250 Hz for a, c, d and 500 Hz for b, e.

$\Delta\Delta\delta$ is different for each of the four components of (3*RS*,7*RS*)-**13**: (3*R*,7*R*)-**13**, (3*R*,7*S*)-**13**; (3*S*,7*S*)-**13**, and (3*S*,7*R*)-**13**, listed in order of decreasing δ observed in the presence of $Eu(dmc)_3$. Full assignment of the spectrum as indicated in Figure 3 was made based on the appearance of spectra obtained for samples: (a) of (3*R*,7*R*)-**13** (Figure 2c); (b) of (3*RS*,7*R*)(nat)-**13** and (3*RS*,7*RS*)-**13** (Figure 2d); (c) of (3*R*(nat),7*RS*)-**13** (Figure 2e). These spectra can be used analytically to determine the *R*/*S* ratio at C_3 with roughly the same limits of accuracy as for C_{10} systems and to estimate the *R*/*S* ratio at C_7. The limit of detectability of a minor epimer at C_7 using 60-MHz spectra with reference compounds lies between 5 and 10%.

A somewhat more complicated but inherently more accurate and sensitive determination of *R*/*S* ratios in **2** and **7** and at C_3 (but not C_7) in **14** can be made by analytical HPLC of amides **6**, **10**, and **15**, prepared by reaction of the appropriate acid chlorides with excess (*R*)-(+)-α-methyl-*p*-nitrobenzylamine.[7] The crude amide was analyzed to avoid possible epimeric fractionations. Data obtained on a variety of C_{10} and C_{15} systems are given in Table I. In the cases, e.g., of racemic **10** and of **15** which was known from its method of synthesis to be a 1:1 epimer mixture at both C_3 and C_7, repeated analyses on the same sample revealed two well-separated component peaks with areas in the ratio 3*R* = 50.0 ± 0.6 and 3*S* = 50.0 ± 0.6.

Analysis of (3*R*(nat),7*RS*)-**15** gave two peaks in about 9:1 ratio while analysis of (3*RS*,7*R*(nat))-**15** gave two peaks in ca. 1:1 ratio. Hence, one peak of **15** is due to those diastereomers containing 3*R* epimers (i.e., 3*R*,*R* and 3*R*,7*S*) and the other peak is due to those diastereomers containing 3*S* epimers (i.e., 3*S*,7*R* and 3*S*,7*S*). Analysis of (3*R*,7*R*)-**15** from natural phytol[8] revealed no 3*S* compounds. Since the limit of detectability of the HPLC method is probably below 0.5% of minor components, the last result demonstrates that the (*R*)-(+)-α-methyl-*p*-nitrobenzylamine used was essentially pure (*R*)-(+) enantiomer and that the 3*R* chiral center derived from phytol was also epimerically pure. Analogous results were obtained on the C_{10} derivatives **6** and **10**. Analyses of **6**, **10**, and (3*R*,7*RS*)-**15** from natural citronellal all indicated about 90–91% of *R* and 9–10% of *S* enantiomer in the natural material. Analyses of **6** and **10** from (−)-β-pinene indicated about 92.5 parts *R* and 7.5 parts *S* enantiomer. Analyses of **6**, **10**, and **15** from pulegone indicated that (3*R*)-(+)-**2** from pulegone contained 1–2% of the *S* enantiomer. Thus, samples of **2** from natural citronellal, from (−)-β-pinene, and from pulegone are respectively 80–82, 84–86, and 96–98% enantiomeric excesses of (3*R*)-(+)-**2**.



		Hz
$\Delta\Delta\delta$ =	3R, 7R vs 3R, 7S	1.3
	3R, 7R vs 3S, 7S	3.0
	3R, 7R vs 3S, 7R	4.5
	3R, 7S vs 3S, 7S	1.7
	3R, 7S vs 3S, 7R	3.2
	3S, 7S vs 3S, 7R	1.5

J_{HC-CH_3} = 6.5 Hz

Figure 3. Schematic representation of the C_3 methyl group signal of (3*RS*,7*RS*)-**13** at 60 MHz in the presence of $Eu(dcm)_3$.

It is unfortunate that natural citronellal and citronellol from (−)-β-pinene are not pure enantiomers because these otherwise useful chiral intermediates are not easy to transform into pure (3*R*)-(+)-**1** derivatives. The NMR and LC methods described here should be useful in connection with attempts to obtain enantiomerically pure citronellyl derivatives. For instance, the highest rotation previously reported for (+)-citronellol, **16**, is $[\alpha]_D$ +5.2° (neat) on a sample obtained by pyrolysis of *cis*-pinane.[13,14] The sample of **16** obtained in this work from pulegone had $[\alpha]_D$ +5.37° (neat) and it contains measurable amounts of (3*S*)-(−) enantiomer. Applications of NMR and HPLC methods similar to those described here are possible to determination of enantiomeric excess in a wide variety of aliphatic carboxylic acids derivable from C_5, C_{10}, and C_{15} chiral substances. A study of a number of α-methyl carboxylic acids and shift reagents recently appeared;[15] and many similar applications should be possible.

Experimental Section

Citronellal [$[\alpha]^{25}D$ +12.00° (neat)] from Java citronella oil was oxidized to citronellic acid, nat-**2**, using silver oxide. A sample of

(+)-citronellol obtained from (−)-β-pinene in a technical scale synthesis was obtained from Mr. B. J. Kane of Glidden-Durkee. A commercial sample of racemic citronellol was oxidized to racemic citronellal using CrO_3–pyridine. Conversion of **2** to **3** was accomplished with CH_2N_2 or acidic methanol.

Preparation and Analysis of (*R*)-(+)-*p*-Nitro-α-methylbenzylamides by HPLC. The acid (0.50 mmol) and oxalyl chloride (1.50 mmol) were refluxed for 30 min in 5 ml of benzene. Solvent and excess oxalyl chloride were removed at 45° and 20 mm. The crude acid chloride was dissolved in 5 ml of ether and cooled in an ice bath. A solution of (*R*)-(+)-α-methyl-*p*-nitrobenzylamine,[7] $[\alpha]^{25}D$ +17.7° (neat) (2.0 mmol), in 3 ml of ether was added in small portions. The mixture was stirred for 1 hr at 0–5° and then diluted with 100 ml of ether, washed successively with 1 *N* HCl, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. Crude amide, obtained by evaporation of the ether, was analyzed by HPLC without further purification.

Six microliters of a 1% solution of the crude amide in ethyl acetate (5 mg in 0.5 ml) was injected into a 4 mm i.d. × 100 cm chromatographic column obtained by connecting, in series with minimum volume fittings, two 50-cm stainless steel columns which had been slurry packed with 10 μm silica gel (Partisil 10 from H. Reeve Angel & Co., Inc.). The mobile phase was 20% v/v tetrahydrofuran (distilled in glass from Burdick and Jackson) in spectral grade *n*-heptane pumped at a flow rate of 1.5 ml min^{-1}. The column effluent was monitored at 254 nm (Model 1222 uv monitor from Laboratory Data Control) and quantitative results were obtained from peak area measurements. The HETP values for all components ranged from 0.17 mm to 0.23 mm. Corrected elution volumes ($V_R{}^1 = V - V_m$) and capacity ratios (k^1) for the diastereoisomers were as follows.

Compd	Confign,	$V_R{}^1$, ml	k^1	Confign,	$V_R{}^1$, ml	k^1
6	*RR*	108.5	7.2	*SR*	121.0	8.1
10	*RR*	94.0	6.3	*SR*	114.0	7.6
15	*RRR*	77.0	5.1	*RSR*	95.0	6.3
	SRR			*SSR*		

Analysis of 3, 8, or 13 for Enantiomeric Excess by NMR. In a dry tube under argon were combined 170 mg of $Eu(dcm)_3$, 0.35 ml of CS_2, and then 0.023 g of **3** or 8 or 0.028 g of **13**. The solution was filtered through a cotton plug into a Wilmad Glass Co. 507PP NMR tube and ca. 0.05 ml of Me_4Si was added. The NMR spectra of solutions prepared as above were taken within 30 min on a Varian T-60 spectrometer equipped with a T6057 lock-decoupler. It was preferred to lock the spectrometer on Me_4Si, whose signal was the strongest in the spectrum. The C_3 methyl doublets analyzed were found at ca. 4.2 ppm (for **3** and 8) and ca. 3.95 ppm (for **13**) downfield from the Me_4Si beat signal. Careful adjustment of the resolution was necessary to obtain good spectra. Aged solutions gave poor spectra.

Preparation of Methyl (3*R*)-7-Formylcitronellate [(*R*)-11]. A solution of 5.2 g of (*R*)-**3** and 6.3 g of SeO_2 in 565 ml of ethanol was refluxed for 12 hr, cooled, filtered, and concentrated under reduced pressure at 30°. The residue was dissolved in 50 ml of ether, filtered, and cautiously treated with 3 × 50 ml of saturated $NaHCO_3$ solution. The ether layer was washed with 2 × 50 ml of H_2O, dried over $MgSO_4$, and evaporated under reduced pressure to give a red oil which was quickly distilled under vacuum, then fractionated to give 3.0 g (54%) of the 7-formyl ester as a colorless oil: bp 80–84° (0.03 mm); ν_{CO} 1688, 1738 cm^{-1} ($CHCl_3$). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.46; H, 9.20. $[\alpha]^{25}D$ +10.67° (*c* 5.0, $CHCl_3$).

Treatment of nat-**3** in the same way gave nat-**11** in 58% yield, $[\alpha]^{25}D$ +8.55° (*c* 5.0, $CHCl_3$). Anal. Found: C, 66.47; H, 9.31.

Methyl (3*R*,7*RS*)-3,7,11-Trimethyldodecanoate (13). Following the general procedure of Inhoffen et al.,[16] 0.0051 mol of 3-methylbutyltriphenylphosphorane[16] was condensed with 0.0025 mol of (*R*)-**11**, giving after work-up 1.6 g of a mixture of methyl (3*R*)-3,7,11-trimethyldodeca-6*E*,8*EZ*-dienoate and triphenylphosphine oxide. This was taken up in ether cooled in dry ice–acetone, most of the phosphine oxide was removed by filtration, and the filtrate was chromatographed on 20 g of silica gel from which the ester was eluted with 3:1 benzene–hexane and vacuum distilled on the Kugelrohr, bp 107° (0.12 mm). The yield was 0.5 g (79%). Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.34; H, 11.26. The (3*R*)(nat),7*RS* analogue was prepared similarly: $[\alpha]^{25}D$ +8.13° (*c* 5.0, $CHCl_3$); ν_{CO} 1730 cm^{-1} ($CHCl_3$). Anal. Found: C, 76.28; H, 11.33. Hydrogenation of the dienoate over Pd/C in methanol gave methyl (3*R*,7*RS*)-3,7,11-trimethyldodecanoate [(3*R*,7*RS*)-**13**]: $[\alpha]^{25}D$ +5.13° (*c* 5.0, $CHCl_3$); ν_{CO} 1745 cm^{-1} ($CHCl_3$). Anal. Calcd for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58. Found: C, 74.83; H, 12.71. Similarly, we obtained ((3*R*)(nat),7*RS*)-**13**: $[\alpha]^{25}D$ +4.25° (*c* 5.03, $CHCl_3$); ν_{CO} 1745 cm^{-1} $(CHCl)_3$. Anal. Found: C, 74.66; H, 12.77.

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Registry No.—rac-**2**, 57030-77-0; (*R*)-**2**, 18951-85-4; (*S*)-**2**, 2111-53-7; rac-**3**, 57030-78-1; (*R*)-**3**, 20425-48-3; (*S*)-**3**, 56994-89-9; (*RR*)-**6**, 56994-90-2; (*SR*)-**6**, 56994-91-3; rac-**7**, 57030-79-2; (*R*)-**7**, 32531-52-5; rac-**8**, 57030-80-5; (*RR*)-**10**, 56994-92-4; (*SR*)-**10**, 56994-93-5; (*R*)-**11**, 56994-94-6; (3*R*,7*R*)-**13**, 13955-72-1; (3*R*,7*S*)-**13**, 56994-95-7; (3*S*,7*S*)-**13**, 56994-96-8; (3*S*,7*R*)-**13**, 13852-95-4; (*RR*)-**14**, 13955-73-2; (*RS*)-**14**, 57030-81-6; (*SR*)-**14**, 13852-96-5; (*SS*)-**14**, 42763-75-7; (*RRR*)-**5**, 56994-97-9; (*SRR*)-**15**, 57030-82-7; (*RSR*)-**15**, 57030-83-8; (*SSR*)-**15**, 57030-84-9; oxalyl chloride, 79-37-8; (*R*)-(+)-α-methyl-*p*-nitrobenzylamine, 22038-87-5.

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(9) We are grateful to Mr. B. J. Kane of Glidden-Durkee for supplying us with a sample of (+)-citronellol from (−)β-pinene. This sample of citronellol was obtained from (−)-3,7-dimethyl-1,6-octadiene by reaction with diisobutylaluminum hydride, oxidation, hydrolysis and distillation. The (−)-3,7-dimethyl-1,6-octadiene had been prepared on a commercial scale from U.S. sulfate turpentine (ref 10).
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