mixture of cis and trans isomers.[11] This mixture (3) was reacted with olivetol in the presence of boron trifluoride diethyl etherate[12] (0.4 equiv of BF_3, 1% (v/v) in CH_2Cl_2, 0 °C, then room temperature for 25 min) to afford 11-(methylthio)-Δ^9-tetrahydrocannabinol (23%) as a 1:1 mixture of the trans and cis isomers 7 and 8, separable by column chromatography [medium-pressure N_2, 230–400 mesh SiO_2, 1:3 Et_2O–petroleum ether (40–60 °C)] from the expected trans–cis mixture of regioisomers (9, 18%) formed by condensation at the 4-position of olivetol.[13] It is notable that the double bond retains its original position in all these products (7, 8, and 9) in agreement with our own[2] and other[5] observations on the stability of sulfur-containing Δ^9-tetrahydrocannabinoids toward Lewis acids.

The trans and cis isomers (7 and 8) of 11-(methylthio)-Δ^9-tetrahydrocannabinol were separated by column chromatography [medium-pressure N_2, 230–400 mesh SiO_2, 1:6 Et_2O–petroleum ether (40–60 °C)] as their acetates (10 and 11)[14] (3 equiv of Ac_2O–pyridine, room temperature, 1 h), obtained in 10 and 8% overall yield, respectively, from the terpenoid synthon 3. Conversion of the methylthio function in the trans isomer 10 into the acetoxy function of 12 was effected via the sulfonium tetrafluoroborate 13 formed with trimethyloxonium tetrafluoroborate (1.1 equiv, CH_3NO_2, room temperature, 25 min). Displacement at the allylic sulfonium center with acetate anion (3 equiv of n-$Bu_4N^+OAc^-$,[15] acetone, reflux, 30 min) completed the conversion in 95% overall yield. Ammonolysis (NH_3–MeOH, room temperature, 48 h) of the diacetate 12 gave *trans*-11-OH-Δ^9-THC (1, 92%), identified by comparison (NMR, IR, and mass spectra) with authentic material.

cis-11-OH-Δ^9-THC (4)[16] was similarly prepared from the *cis*-11-methylthio isomer 11 via the salt 14 and the diacetate 15. The mass spectra and R_F values on TLC of the *cis* and *trans* isomers (4 and 1) of 11-OH-Δ^9-THC and the retention times on GLC of their corresponding bis(trimethylsilyl) ethers are extremely similar and could be misleading in metabolic studies where both isomers of the parent Δ^9-THC compounds are involved. ^{1}H NMR spectra ($(CD_3)_2CO$), however, distinguish these two 11-hydroxy isomers. The *cis* isomer 4 shows the geminal methyl singlets at δ 1.17 and 1.26 and the multiplets of C10a H and C10 H at δ 3.48 and 6.47, whereas the corresponding resonances in the *trans* isomer 1 are at δ 1.00, 1.31, 3.18 (J_{trans} = 11 Hz), and 6.70, respectively. The *cis* and *trans* isomers (5 and 2) of Δ^9-THC itself show similar features.[17]

The terpenoid synthon 3 affords access to a variety of 11-substituted Δ^9-tetrahydrocannabinoids. Retention of the methylthio function until the cannabinoid skeleton is formed not only controls the double bond position but its subsequent displacement also permits the introduction of various nucleophiles at C11. For example, reaction of the sulfonium tetrafluoroborate 13 with thioacetate anion (2 equiv of n-$Bu_4N^+SAC^-$,[18] acetone, room temperature, 15 min) gives the diacetate 16. Subsequent reduction[19] of both esters (30 equiv of $NaBH_4$, EtOH, room temperature, 20 h) then yields *trans*-11-SH-Δ^9-THC (17),[20] the 11-mercapto analogue of 11-OH-Δ^9-THC (1). Alternatively, condensation of the terpenoid synthon 3 with suitably substituted resorcinols[2,21] would lead to metabolites of Δ^9-THC hydroxylated both at C11 and in the alkyl side chain.[2,22]

Acknowledgment. We thank Mr. P. J. Green and Mr. A. J. Herlt for technical assistance and Dr. R. E. Willette of the National Institute on Drug Abuse for an authentic sample of 11-OH-Δ^9-THC.

Registry No. 1, 28623-60-1; 2, 3556-79-4; 3, cis isomer, 72377-96-9; 3, trans isomer, 72377-97-0; 4, 72402-25-6; 5, 6087-73-6; 6, 72377-98-1; 7, 72377-99-2; 8, 72378-00-8; 9, cis isomer, 72378-01-9; 9, trans isomer, 72378-02-0; 10, 72390-08-0; 11, 72378-03-1; 12, 72402-26-7; 13, 72378-05-3; 14, 72378-07-5; 15, 72402-27-8; 16, 72378-08-6; 17, 72378-09-7; olivetol, 500-66-3; diethyl [2-(cyclohexylamino)vinyl]-phosphonate lithium salt, 72378-10-0.

(11) Data: bp 85 °C (0.03 mm) (Kugelrohr); cis/trans ratio 47:53; NMR ($CDCl_3$) δ 1.64, 1.70 (2 s, 6, Me_2C=), 2.01 and 2.03 (2 s, 3, SMe), 2.0–2.5 (m, 2, CH_2CH=), 2.75 (t, 2, J = 7 Hz, $CH_2C(CH_2SMe)$=), 3.24 and 3.61 (2 s, 2, CH_2SMe), 5.12 (br m, 1, $W_{1/2}$ = 16 Hz, CH=CMe_2), 5.90 and 6.30 (2 d, 1, J = 8 Hz, trans and cis =CHCHO), 9.96 (d, 1, J = 8 Hz, CHO); IR (film) 1670 (C=O), 1620 (C=C) cm^{-1}. The mixture had a satisfactory C, H, and S analysis.

(12) Mechoulam, R.; Braun, P.; Gaoni, Y. *J. Am. Chem. Soc.* **1972**, *94*, 6159.

(13) Petrzilka, T.; Haefliger, W.; Sikemeier, C. *Helv. Chim. Acta* **1969**, *52*, 1102.

(14) The trans isomer 10 was the first to elute: NMR (CCl_4) δ 0.92 (t, 3, J = 6 Hz, CH_2Me), 1.09 (s, 3, Me), 1.38 (s, 3, Me), 1.92 (s, 3, SMe), 2.20 (s, 3, ArOCOMe), 2.60 (t, 2, J = 7 Hz, $ArCH_2$), 2.98 (br s, 2, SCH_2C=) superimposed upon 3.08 (m, 1, C10a H), 6.11 (m, 1, C10 H), 6.30 and 6.45 (2 m, 2, ArH); IR (film) 1763 (C=O), 1623, 1563 cm^{-1}; mass spectrum, m/z (relative intensity) 402 (21) (high resolution, 402.2229; calcd for $C_{24}H_{34}O_3S$, 402.2228), 313 (100). Cis isomer 11: NMR (CCl_4) δ 0.90 (t, 3, J = 6 Hz, CH_2Me), 1.25 (s, 3, Me), 1.36 (s, 3, Me), 1.87 (s, 3, SMe), 2.25 (s, 3, ArOCOMe), 2.48 (t, 2, J = 7 Hz, $ArCH_2$), 2.96 (br s, 2, SCH_2C=), 3.48 (m, 1, C10a H), 5.98 (d, 1, J = 5 Hz, C10 H), 6.28 and 6.42 (2 m, 2, ArH); IR (film) 1765 (C=O), 1668, 1625, 1565 cm^{-1}; mass spectrum, m/z (relative intensity) 402 (18) (high resolution, 402.2223; calcd for $C_{24}H_{34}O_3S$, 402.2228), 313 (100).

(15) Baker, R.; Hudec, J.; Rabone, K. L. *J. Chem. Soc. C* **1969**, 1605.

(16) Cis isomer 4: NMR ($(CD_3)_2CO$) δ 0.80 (t, 3, J = 6 Hz, CH_2Me), 1.17 (s, 3, Me), 1.26 (s, 3, Me), 2.34 (t, 2, J = 7.5 Hz, $ArCH_2$), 3.32 (t, 1, J = 6 Hz, CH_2OH), 3.48 (m, 1, C10a H), 3.82 (dm, 2, CH_2OH), 5.99 and 6.15 (2 m, 2, ArH), 6.47 (m, 1, C10 H), 7.95 (br s, 1, ArOH); IR (CCl_4) 3610 (OH), 3350 (OH), 1625 cm^{-1}; mass spectrum, m/z (relative intensity) 330 (30) (high resolution, 330.2197; calcd for $C_{21}H_{30}O_3$, 330.2195), 312 (19), 299 (100). The bis(trimethylsilyl) ether of 4 showed the following: mass spectrum, m/z (relative intensity) 474 (5), 459 (4), 413 (2), 403 (3), 384 (4), 371 (100); GLC (2% OV-17 on Gaschrom Q, 250 °C) retention time 1.82 relative to the derivative of (-)-Δ^9-THC (2); cf. 1.88 for the derivative of the *trans* isomer 1.

(17) Uliss, D. B.; Razdan, R. K.; Dalzell, H. C.; Handrick, G. R. *Tetrahedron* **1977**, *33*, 2055.

(18) Prepared by neutralization of n-$Bu_4N^+OH^-$ with HSAc as described[15] for n-$Bu_4N^+OAc^-$ and recrystallized from EtOAc.

(19) Brown, M. S.; Rapoport, H. *J. Org. Chem.* **1963**, *28*, 3261.

(20) NMR (CCl_4) δ 3.19 (m, 2, CH_2SH), otherwise very similar to that of 1, δ 3.90 (m, 2, CH_2OH); mass spectrum, m/z (relative intensity) 346 (17) (high resolution, 346.1966; calcd for $C_{21}H_{30}O_2S$, 346.1966), 331 (17), 313 (100), 312 (15), 299 (43), 297 (11).

(21) Pitt, C. G.; Seltzman, H. H.; Sayed, Y.; Twine, C. E.; Williams, D. L. *J. Org. Chem.* **1979**, *44*, 677.

(22) Wall, M. E.; Brine, D. R., p 51 in ref 1d.

Rodney W. Rickards,* William P. Watson
Research School of Chemistry
Australian National University
Canberra, ACT 2600, Australia
Received September 17, 1979

Efficient Enantioselective Synthesis of the Antitumor Agent Sarkomycin

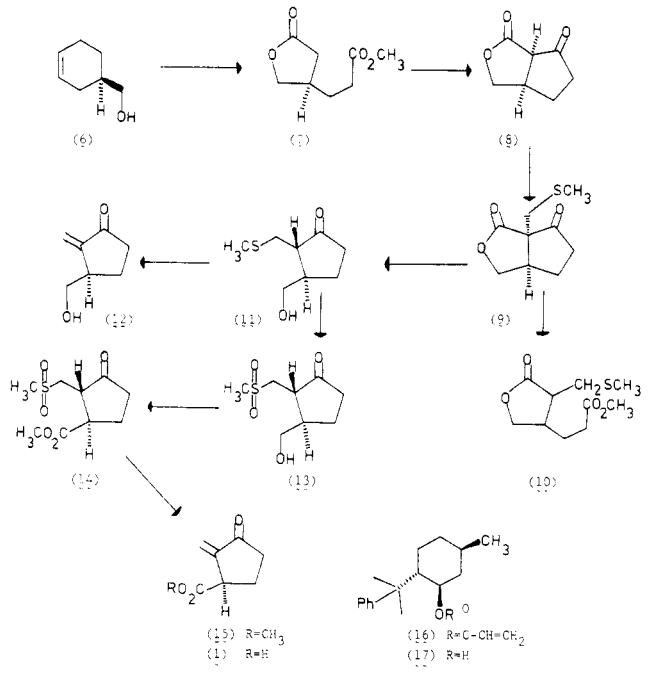
Summary: An efficient total synthesis of (±)-sarkomycin (1) is described via bicyclic lactone 8. Preparation of a key precursor (*R*)-(+)-6 via an asymmetric Diels–Alder reaction affords the correct enantiomer for the preparation of natural (*R*)-(-)-sarkomycin (1) in high optical yield.

Sir: The antibiotic (*R*)-(-)-sarkomycin (1), discovered by Umezawa et al in 1953,[1] was subsequently shown to have substantial inhibitory effect on Erlich ascites tumors in mice.[2] Further pharmacological studies[3] led to the mar-

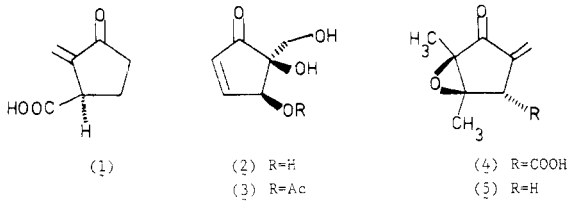
(1) Umezawa, H.; Takeuchi, T.; Nitta, K.; Yamamoto, T.; Yamaoka, S. *J. Antibiot., Ser. A* **1953**, *6*, 101.

0022-3263/80/1945-0752$01.00/0

Scheme I



keting in Japan of a preparation containing this substance as an antitumor drug.[4] Structural analysis[5] revealed the simple carboxylic acid **1**, whose absolute configuration was assigned as *S*[6] and later revised by Hill to *R*.[7] Several nonregiospecific syntheses of sarkomycin have appeared.[8,9] There has been considerable recent interest in the synthesis of the general class of cyclopentanone antitumor antibiotics exemplified by the pentenomycins **2** and **3** and methylenomycins **4** and **5**.[10] Herein we describe our efforts directed toward sarkomycin (**1**).



Since sarkomycin (**1**) contains but a single asymmetric center, it was a central consideration that the synthetic route be readily adaptable to the preparation of the chiral antibiotic. Futhermore, early efforts established the need to carefully control the regiochemistry during introduction of the methylene function.[7,8]

The synthetic route (Scheme I) was initiated by ozonolysis of 3-cyclohexene-1-methanol (**6**) in HOAc/HCOOH at 0 °C. Oxidative workup with H_2O_2 followed by Fischer esterification (CH_3OH/HCl) afforded the lactone ester **7** in 74% overall yield.[11] Dieckmann cyclization of **7** was effected by treatment with KO-*t*-Bu (2.14 equiv) in THF at −78 °C, followed by quenching at −78 °C with gaseous HCl, affording the crystalline (mp 54–55 °C) bicyclic keto lactone **8** in ~80% yield.[12,13] Introduction of the required one-carbon unit was then accomplished by alkylation (KO-*t*-Bu/THF/−25 °C) with CH_3SCH_2I generated in situ,[14] providing the bicyclic lactone **9** (mp 44–46 °C) in 76% yield.[12] It was then desired to effect lactone cleavage and decarboxylation. However, treatment of **9** under a variety of acidic and basic conditions resulted in rupture of the cyclopentanone ring, affording **10**. Subsequently, it was found that the desired mode of cleavage could be obtained by treatment of **9** with 10% aqueous HCl in ethanol [~3:10 (v/v)] under reflux for 24 h which gave keto alcohol **11** in 60–80% yield. Elimination of methanethiol from **11** could be cleanly accomplished by methylation (CH_3I) to the sulfonium salt followed by treatment with aqueous $NaHCO_3$ in CH_2Cl_2 (two phase), affording methylene ketone **12** in 94% yield.[12] However, attempted oxidation of **12** to (±)-sarkomycin (**1**) under a variety of conditions has been unsuccessful thus far.

Alternatively, oxidation of **11** to sulfone **13** with MCPBA (2 equiv, room temperature, 18 h) proceeded smoothly.[13] Further oxidation of **13** with CrO_3/acetone followed by methylation (CH_2N_2/ether) gave the keto ester **14** (mp 93–97 °C) in 67% overall yield. Elimination to (±)-sarkomycin methyl ester (**15**) was then effected by treatment of **14** with K_2CO_3 in THF at 25 °C for 0.8 h (78%).[15] (±)-Sarkomycin ester **15** has been previously converted to (±)-**1** by acidic hydrolysis.[8] The final transformation to **15** was performed under mild conditions, and deuterium incorporation studies verified that no racemization will occur during this conversion in the optically active series. We then set out to establish a route to chiral **6** of the proper absolute configuration (*R*) to afford (*R*)-(−)-sarkomycin. It was predicted from Walborsky's model[16] that the Lewis acid catalyzed Diels–Alder reaction between (−)-menthyl acrylate and butadiene, followed by LAH reduction, should produce (*R*)-(+)-**6**, and the validity of this was established experimentally. Consequently, acrylate **16** was utilized to obtain both the correct absolute configuration and high optical yields.[17] The highest optical yield (ee) was obtained by treatment of **16** with butadiene (10 equiv) in the presence of $TiCl_4$ (1.5 equiv) at −20 °C for 24 h. Direct LAH reduction permitted recovery

(2) Umezawa, H.; Yamamoto, T.; Takeuchi, T.; Osato, T.; Okami, Y.; Yamaoka, S.; Okuda, T.; Nitta, K.; Yagishita, K.; Utahara, R.; Umezawa, S. *Antibiot. Chemother. (Washington, D.C.)* **1954**, *4*, 514.

(3) (a) Oboshi, S.; Aoki, K. *Chemotherapy (Tokyo)* **1956**, *4*, 91. (b) Sung, S. C.; Quastel, J. H. *Cancer Res.* **1963**, *23*, 1549.

(4) Banyu Pharmaceutical Co., Ltd., Tokyo.

(5) Hooper, I. R.; Cheney, L. C.; Corn, M. J.; Fardig, O. B.; Johnson, D. A.; Johnson, D. L.; Palermiti, F. M.; Schmitz, H.; Wheatley, W. B. *Antibiot. Chemother. (Washington, D.C.)* **1955**, *5*, 585.

(6) Sato, Y.; Nishioka, S.; Yonemitsu, O.; Ban, Y. *Chem. Pharm. Bull.* **1963**, *11*, 829.

(7) Hill, R. K.; Foley, Jr., P. J.; Gardella, L. A. *J. Org. Chem.* **1967**, *32*, 2330.

(8) (a) Toki, K. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 450. (b) *Ibid.* **1958**, *31*, 333.

(9) (a) Shemyakin, M. M.; Ravdel, G. A.; Chaman, Y. S.; Shvetsov, Y. B.; Vinagradova, Y. I. *Chem. Ind. (London)* **1957**, 1320. (b) *Izv. Akad. Nauk Uzb. SSR, Ser. Khim. Nauk.* **1959**, 2188.

(10) Branca, S. J.; Smith, III, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 7767. Scarborough, Jr., R. M.; Smith, III, A. B. *Ibid.* **1977**, *99*, 7087.

(11) (a) Ceder, O.; Hansson, B. *Acta Chem. Scand.* **1970**, *24*, 2693. (b) Ceder, O.; Nilsson, H. G. *Acta Chem. Scand., Ser. B* **1977**, *31*, 189.

(12) Spectral data are as follows. **8**: IR 1775, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.65 (m, 1 H), 4.12 (m, 1 H), 3.45 (br s, 2 H). **9**: IR 1780, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.74–4.00 (m, 2 H), 3.00 (s, 3 H), 2.60–2.25 (m, 5 H), 2.10 (br s, 3 H). **11**: IR 3600–3200, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (br d, *J* = 3 Hz, 2 H), 3.35–2.30 (m, 8 H), 2.15 (s, 3 H). **12**: IR 3600–3200, 1725, 1640; ^1H NMR ($CDCl_3$) δ 6.10 (d, *J* = 3 Hz, 1 H), 5.50 (d, *J* = 3 Hz, 1 H), 3.78 (d, *J* = 4 Hz, 2 H), 2.65–1.70 (m, 5 H). **13**: IR 3600–3200, 1740, 1300, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (br d, *J* = 3 Hz, 2 H), 3.33 (d, *J* = 5 Hz, 2 H), 3.35–2.30 (m, 8 H), 2.15 (s, 3 H). **14**: IR 1740, 1300, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77 (s, 3 H), 3.60–3.16 (m, 3 H), 3.00 (s, 3 H), 2.60–2.13 (m, 5 H). **15**: IR 1740, 1725, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.20 (d, *J* = 2 Hz, 1 H), 5.60 (d, *J* = 2 Hz, 1 H), 3.74 (s, 3 H), 3.60–2.0 (m, 5 H).

(13) All new compounds gave satisfactory spectral data and exact mass spectral or combustion analysis.

(14) Ronald, R. C. *Tetrahedron Lett.* **1973**, 3831.

(15) Comparison of spectral data with literature values and exact mass analysis were utilized to establish identity with methyl sarkomycin derived from natural sources.

(16) Walborsky, H. M.; Barash, L.; Davis, T. C. *Tetrahedron* **1963**, *19*, 2333.

(17) A synthetic route to the enantiomeric substance has been described: Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908.

of (*R*)-(+)-**6** in 70% chemical yield and 86–91% ee.[18] This procedure also facilitated recovery of the chiral alcohol **17** for recycling. Assignment of the absolute configuration and assessment of the optical purity of (*R*)-(+)-**6** is based upon Ceder's correlation. This, then, represents an efficient chiral synthesis of (*R*)-(−)-sarkomycin which should be amenable to scale up if desired.

Acknowledgment. This investigation was supported by reasearch grants awarded by the National Cancer Institute (CA 17154) and the National Institute of General Medical Sciences (GM 25982) of the National Institutes of Health, DHEW.

Note Added in Proof. Another new regiospecific synthesis has recently been described: Marx, J. N.; Minaskanian, G. *Tetrahedron Lett.* **1979**, 4175.

Registry No. (±)-**1**, 72581-31-8; (*R*)-(−)-**1**, 489-21-4; (±)-**6**, 72581-32-9; (*R*)-(+)-**6**, 5709-99-9; (±)-**7**, 72581-33-0; (±)-**8**, 72525-94-1; (±)-**9**, 72525-95-2; (±)-**11**, 72525-96-3; (±)-**12**, 72525-97-4; (±)-**13**, 72525-98-5; (±)-**14**, 72542-01-9; (±)-**15**, 72525-99-6; (−)-**16**, 72526-00-2; butadiene, 106-99-0.

(18) Other Lewis acid catalysts such as $AlCl_3$ and $SnCl_4$ were inferior to $TiCl_4$ in terms of either chemical or optical yields.

(19) (a) Fellow of the Alfred P. Sloan Foundation (1976–1980); recipient of a Career Development Award (CA-00273) from the National Cancer Institute, NIH.

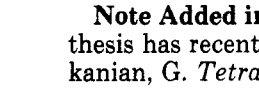
Robert K. Boeckman, Jr.,*[19] Paul C. Naegely
Samuel D. Arthur
Department of Chemistry, Wayne State University
Detroit, Michigan 48202
Received October 3, 1979

Hindered Amines. Novel Synthesis of 1,3,3,5,5-Pentasubstituted 2-Piperazinones

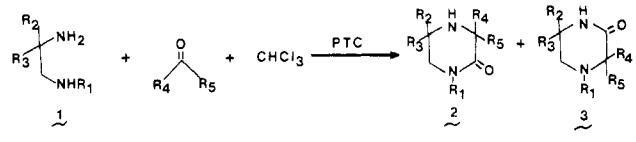
Summary: 1,3,3,5,5-Pentasubstituted 2-piperazinones (**2**) are prepared from easily available N^1,2,2-trisubstituted 1,2-ethanediamine (**1**), chloroform, and ketones in phase transfer catalyzed reactions and probably not through the dichlorocarbene intermediate.

Sir: Hindered amines, especially cyclic ones, are highly effective in the protection of polymers against ultraviolet light.[1] Their nitroxyl radicals are used extensively as spin labels in biological studies.[2] Their lithio salts, as strong and nonnucleophilic bases, are of considerable synthetic interest.[3] Although many types of hindered amines are known, only a few can be made practically, even in the laboratory.[2] In this communication, I wish to report a simple synthesis of novel 1,3,3,5,5-pentasubstituted 2-piperazinones[4] (**2**) from easily available N^1,2,2-trisubstituted 1,2-ethanediamines[5] (**1**), chloroform, and ketones in a phase transfer catalyzed (PTC) reaction.[6]

Table I. Synthesis of 2 and 3[a,b]

	R_1[c]	R_4	R_5	yield ratio[d,e] 2	3	mp[f] [bp],[g] °C
1a	*n*-C_3H_7	CH_3	CH_3	73	27	[118-121 (10 mm)]
b	*i*-C_3H_7	CH_3	CH_3	73 (52)	27	82-84
c	*i*-C_3H_7	$-(CH_2)_5-$		85 (67)	15	77-78
d	*i*-C_3H_7	CH_3	C_2H_5	70	30	[93-96 (1.2 mm)]
e	*t*-C_4H_9	CH_3	CH_3	74 (50)	26	103-105
f	*t*-C_8H_{17}	$-(CH_2)_5-$		76 (55)	24	102-103
g	Ph	CH_3	CH_3	87 (51)	12	93-95
h	$C(CH_3)_2CH_2OH$	CH_3	CH_3	80 (51)	20	83-85
i		CH_3	CH_3	68 (41)	32	53-55

[a] Yields are essentially quantitative by GC analysis. [b] All compounds gave satisfactory elemental analysis. [c] All R_2 and R_3 are CH_3 except for **1i**. [d] Determined by GC and/or ^1H NMR from different chemical shifts of ring methylene protons in **2** and **3**. [e] Numbers in parentheses are yields of pure **2**. [f] Of recrystallized **2**. [g] Of the mixture of **2** and **3**.



Under PTC conditions, chloroform is known to react with ketones, e.g., cyclohexanone, to form α-chloro- and α-hydroxycyclohexanecarboxylic acids,[7] secondary amines to form formamides,[8] and primary amines to form isocyanides.[9] However, the synthesis of **2** and **3** (see Table I) is remarkably selective. At ice-bath temperatures with 2–5% catalyst and a slight excess of chloroform, the reaction is complete overnight without detectable formation of these side products. Hydroxyl groups, which are reported to react with chloroform to form, e.g., chlorides,[10] under PTC conditions, do not interfere. This is important in spin-label studies when the nitroxyl radical is to be attached to a biological system. When **2** is solid, it can usually be isolated free from **3** after a single recrystallization. The following illustrates a general procedure: **1b** (50 mmol, Aldrich Chemical, 98% pure), chloroform (60 mmol), acetone (100 mmol), benzyltriethylammonium chloride (BTAC) (2 mmol), and 50 mL of CH_2Cl_2 are mixed and cooled while 50% NaOH (220 mmol) is added dropwise to keep the temperature below 5 °C. The reaction is stirred at 5 °C overnight and is worked up in the usual manner to obtain a clear oil which solidifies upon standing: IR (neat) 1610, 3310 (**2b**), 1665 (**3b**) cm^{-1}; ^1H NMR ($CDCl_3$) for **2b** δ 4.94 (hept, 1 H), 3.08 (s, 2 H), 1.50–1.30 (br, 1 H), 1.35 (s, 6 H), 1.18 (s, 6 H), 1.15 and 1.03 (d, 6 H); for **3b** δ 7.78 (br, 1 H), 2.78 (hept, 1 H), 2.59 (s, 2 H), 1.73 (s, 6 H), 1.35 (s, 6 H), 1.35 and 1.16 (d, 6 H).

(1) Patent literature has been flooded with this subject in recent years. See also: Ranby, B.; Rabek, J. F. "Photodegradation, Photo-oxidation and Photostabilization of Polymers"; Wiley: New York, 1975; pp 407–8.

(2) (a) "Spin Labeling, Theory and Applications"; Berliner, L. J., Ed.; Academic Press: New York, 1976. (b) Roaztsev, E. G. "Free Nitroxyl Radicals"; Plenum Press: New York, 1970.

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