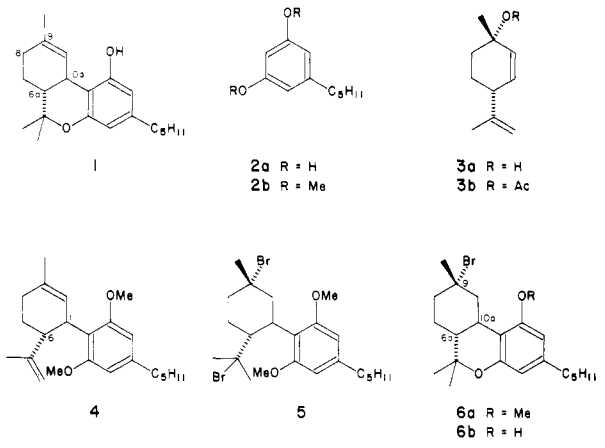
Chart I



For preparation purposes, however, it is inefficient and unnecessary to separate and purify the relatively unstable brominated intermediates **5**, **6a**, and **6b**. Instead the (−)-cannabidiol dimethyl ether (**4**) was subjected to successive hydrobromination (HBr, CH_2Cl_2, −20 °C), monodemethylation and cyclization (warmed to ambient, 5 h), and further demethylation [cooled to −76 °C, BBr_3 (9 equiv, 3.5 M in CH_2Cl_2) added, warmed to ambient, 7 h]. The resulting bromide **6b** obtained in quantitative crude yield was immediately dehydrobrominated (1.2 equiv of KOBu-*t*, benzene, 5 °C for 1 h and then 65 °C for 10 min)[12] to afford after MPLC $\Delta^{9(11)}$-THC (<5% yield) and the required (−)-Δ^9-THC (**1**) containing <10% (−)-Δ^8-THC in 75% overall yield from the diether **4**. This product had the required ^1H NMR, MS, and CH analysis and $[\alpha]^{17}_D$ −161° (*c* 0.087, EtOH) in agreement with literature[13] [$[\alpha]^{20}_D$ −156° (*c* 0.34, EtOH)].

Earlier addition of boron tribromide to the hydrobromination reaction, at the stage when only the dihydrobromide **5** was present, also gave the cyclized and fully demethylated bromide **6b** in high yield. However, the Δ^9-THC (**1**) obtained from this material was extensively racemized, showing that in order to preserve chirality the pyran ring system of the ether **6a** must be formed before treatment with Lewis acid. Presumably carbocations developed from **5** with boron tribromide are not trapped immediately by pyranyl ether formation as with hydrogen bromide alone but instead survive to cause isomerization at the two adjacent tertiary centres.

The present carbanionoid approach to (−)-Δ^9-THC (**1**) proceeds via two isolated intermediates **4** and **6b** in 59% overall yield from the menthadienyl acetate **3b** and offers advantages over the previous cationic routes[2-4] in terms of simplicity of reaction mixtures and yield of isolated product. The route is equally applicable to the synthesis of the less-studied enantiomeric (+)-Δ^9-THC (*ent*-**1**),[2] since (1*R*,4*S*)-*p*-mentha-2,8-dien-1-yl acetate (*ent*-**3b**) is readily available from (−)-(*S*)-limonene.[5]

Acknowledgment. We thank Mr. A. J. Herlt for expert technical assistance.

(13) "Dictionary of Organic Compounds"; Chapman and Hall: New York, 1982; Vol. 5, p 5178.

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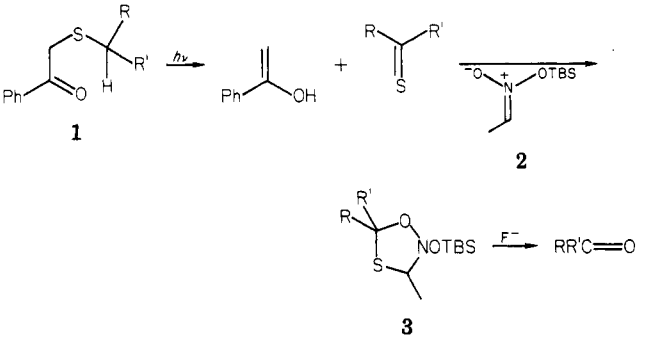
A Method for Mild Photochemical Oxidation; Conversion of Phenacyl Sulfides into Carbonyl Compounds

Summary: Sunlamp irradiation of phenacyl sulfides $PhCOCH_2SCHRR'$ affords thiocarbonyl compounds S=CRR' that can be trapped in high yield by using the nitronate $CH_3CH{=}N^+(OTBS)O^-$; the heterocycle **3** resulting from 1,3-dipolar cycloaddition is cleaved rapidly by fluoride ion to give ketones or aldehydes.

Sir: We have been interested in mild methods for oxidation α to sulfur.[1] This transformation is of general importance in syntheses using organosulfur intermediates and becomes especially significant as a tool for removal of sulfur from large ring sulfides or their transformation products.[1c,2] In this paper, we report several examples of mercaptan oxidation via the photochemical fragmentation of phenacyl sulfides **1** to thiocarbonyl compounds.[3,4] The optimum oxidation sequence involves 1,3-dipolar trapping of thiocarbonyl intermediates in situ with *tert*-butyldimethylsilyl nitronate ester **2**,[5] followed by cleavage of the intermediate heterocycle **3** with $Bu_4N^+F^-$. The starting



phenacyl sulfides are most easily prepared by treatment of mercaptans with phenacyl chloride/Et_3N in THF (method A). Michael addition of phenacyl mercaptan[6] to enones, method B (Table I; entries f and g) or alkylation of phenacyl mercaptan with alkyl halides (method C) can also be used.[4] Irradiation of a 0.05 M benzene solution of **1** and approximately 1.5 equiv of **2** using a simple sunlamp apparatus[7] affords the cycloadducts **3**. It is possible to

(1) (a) Vedejs, E.; Mullins, M. *Tetrahedron Lett.* **1975**, 2017. (b) Vedejs, E.; Mastalerz, H.; Meier, G. P.; Powell, D. W. *J. Org. Chem.* **1981**, *46*, 5253. (c) Vedejs, E.; Dolphin, J. M.; Mastalerz, H. *J. Am. Chem. Soc.* **1983**, *105*, 127.

(2) Vedejs, E.; Powell, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 2046.

(3) (a) Hogeveen, H.; Smit, J. J. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 489. (b) Trost, B. M. *J. Am. Chem. Soc.* **1967**, *89*, 138. (c) Fish, R. H.; Chow, L. C.; Caserio, M. C. *Tetrahedron Lett.* **1969**, 1259. (d) Caserio, M. C.; Cauer, W.; Novinson, T. *J. Am. Chem. Soc.* **1970**, *92*, 6082. (e) Cheney, J.; Mores, C. J.; Raleigh, J. A.; Scott, A. I.; Young, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, *47*. (f) Brandt, A.; Bassignani, L.; Re, L. *Tetrahedron Lett.* **1976**, 3975. (g) Padwa, A.; Pashayan, D. *J. Org. Chem.* **1971**, *36*, 3550.

(4) Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445.

(5) Calvin, E. W.; Beck, A. K.; Bastani, B.; Seebach, D.; Kai, Y.; Dunitz, J. D. *Helv. Chim. Acta* **1980**, *63*, 697.

(6) (a) Asinger, F.; Thiel, M.; Schafer, W. *Liebigs Ann. Chem.* **1960**, *637*, 146. (b) Asinger, F.; Thiel, M.; Püchel, P.; Haaf, F.; Schäfer, W. *Ibid.* **1962**, *660*, 85. We use an improved procedure to make $PhCOCH_2SH$ from $PhCOCH_2SCOCH_3$, available in >98% yield from $PhCOCH_2Cl$ + thiolacetate. A 10% solution of $PhCOCH_2SCOCH_3$ in ether is stirred vigorously with 10% NaOH/H_2O (equal volumes) for 20 min at room temperature. The intensely yellow aqueous layer is separated and acidified with 10% H_2SO_4; and the mercaptan is extracted into CH_2Cl. After drying and solvent removal, the product is distilled bp 90–100 °C (0.2 mmHg); 91%.

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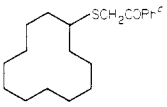
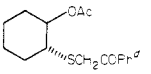
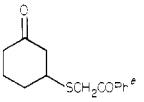
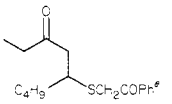
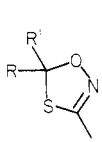
Table I. Conversion of Phenacyl Sulfides into Carbonyl Compounds via 3

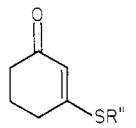
	1 (phenacyl sulfide)	yield of 3, %	carbonyl product (% yield)
a		90[a]	cyclododecanone (96)
b		*b*	2-acetoxycyclohexanone (78)
c	$Ph(CH_2)_3SCH_2COPh$[c]	91[a]	$PhCH_2CH_2CHO$ (94)
d	$PhCH(OAc)CH_2SCH_2COPh$[d]	*b*	$PhC(O)CH_2OAc$[f] (98)
e	$CH_3CH(OBn)CH(OAc)CH_2SCH_2COPh$[d]	*b*	$CH_3CH(OBn)CH(Ac)CHO$ (54)
f		34[a]	cyclohexane-1,3-dione (>98)
g		70	2-methylnonane-3,5-dione (58)

[a] 3 isolated by chromatography. [b] 3 cleaved without isolation; carbonyl yield is based on 1. [c] Made by method A. [d] Thiol generated in situ from thiolacetate in CH_3OH/K_2CO_3 in the presence of $PhCOCH_2Cl$. [e] Made by method B. [f] Derived from enolization and acyl shift from unstable PhCH(OAc)CHO.

isolate 3 as a mixture of diastereomers[8] by chromatography over silica gel, but it is usually more convenient to cleave the crude product with $Bu_4N^+F^-$ in THF. Cleavage is accompanied by a characteristic transient green color, presumably due to an unstable nitroso intermediate. The sulfur- or nitrogen-containing decomposition products are removed by simple aqueous workup, and the carbonyl compound may be purified by conventional means. Other cleavage methods may be used if desired,[9] but simple acid hydrolysis is complicated by the formation of a byproduct. Thus, treatment of **3c** (R = H; R′ = CH_2CH_2Ph) with $TsOH{\cdot}H_2O/C_6H_6$ affords hydrocinnamaldehyde and the unsaturated heterocycle **4**[10] in an 8:1 ratio. Aqueous HCl/THF gives **4** as the major product.



4



5, R″ = H
6, R″ = CH_3

Inspection of Table I shows that thiocarbonyl trapping by the nitronate **2** is usually very efficient. We have employed the same technique to prepare several other cycloadducts **3** (R′ = H; R = H, 73%; R = *t*-Bu, 93%; R = $CH{=}CH_2$, 92%) to help characterize transient thioaldehydes.[11] Among the examples studied, only **3f** is formed in poor yield. This appears due to the very rapid tautomerization of the 3-oxocyclohexanethione intermediate, resulting in vinyl mercaptan **5**. Efficient formation of **5** can be demonstrated by performing the photolysis of **1f** in the absence of nitronate trap, followed by methylation with $CH_3I/Et_3N–CH_2Cl_2$ to give **6** in 87% overall yield. The sequence leading to **6** begins with cyclohexenone (1,4 addition of $PhCOCH_2SH$, 91%) and therefore constitutes a method for the net oxidation of the enone to an unsymmetrical 1,3-dione equivalent. More importantly, vinyl sulfides related to **6** may be used for enone transposition via 1,2-reduction and acid hydrolysis.[12]

We have also examined the conversion of phenacyl sulfides into carbonyl compounds by photolysis in the presence of oxygen. In certain cases, this process works fairly well: cyclododecanone (68%), deoxybenzoin (52%), $PhCH_2CH_2C(SPh){=}O$ (49%), fluorenone (72%); but the reaction is less general ($PhCH_2CH_2CHO$, <10%) than nitronate trapping. Presumably, the overall conversion involves the known photooxidation of a thiocarbonyl intermediate.[13,14]

In summary, the Norrish cleavage of phenacyl sulfides constitutes a mild technique for photochemical oxidation using no special apparatus other than a sunlamp. The variation involving nitronate trapping and fluoride cleavage (Table I) allows the efficient synthesis of ketones or aldehydes. The only other reasonably general photochemical oxidation method is the analogous photofragmentation of oxalate or pyruvate esters reported by Binkley et al. using a mercury vapor lamp.[15]

(7) The apparatus consists of a simple Pyrex flask sealed with a septum cap and flushed with nitrogen. Photolysis is performed by using a 275-W sunlamp, dry benzene, and a room-temperature water bath. About 2 h are required to convert 0.5 mmol of phenacyl sulfide. Volatiles, including unreacted **2** and acetophenone, are removed under vacuum, and the residue of crude **3** can be cleaved with $Bu_4N^+F^-$/THF or purified by chromatography (silica gel) for isolation of **3**.[4]

(8) Inversion at nitrogen is slow at room temperature. Thus, **3a** from in situ trapping of cyclododecanethione is a single diastereomer: 200-MHz NMR (partial, $CDCl_3$, ppm) 0.15 (3 H, s), 0.23 (3 H, s), 0.93 (9 H, s), 1.46 (3 H, d, *J* = 6.4 Hz), 4.86 (1 H, q, *J* = 6.4 Hz). Upon heating **4** h at 75–80 °C in benzene, a second diastereomer is formed in equal amounts: 200-MHz NMR (partial, $CDCl_3$, ppm) 0.18 (6 H, s), 0.91 (9 H, s), 1.42 (3 H, d, *J* = 6.9 Hz), 4.75 (1 H, q, *J* = 6.9 Hz).

(9) $Et_3NH^+F^-/CH_3OH$ is recommended for sensitive carbonyl compounds. Good conversion to ketones is also obtained by using *N*-chlorosuccinimide in $THF–H_2O$.

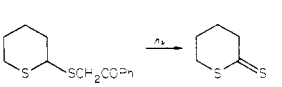
(10) 200-MHz NMR of **4** ($CDCl_3$, ppm): 7.35–7.10 (5 H, m), 6.02 (1 H, t, *J* = 6.2 Hz), 2.76 (2 H, m), 2.31 (1 H, m), 2.10 (1 H, m), 2.19 (3 H, s); correct exact mass.

(11) Vedejs, E.; Perry, D. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1983**, *105*, 6999.

(12) Nishio, T.; Omote, Y. *Chem. Lett.* **1979**, 365.

(13) For example, see: Ramamurthy, V.; Rajes, R. *Tetrahedron Lett.* **1978**, 5127. Campaigne, E. In "The Chemistry of the Carbonyl Group"; Patai, S., Ed.; Interscience: New York, 1966; Chapter 17.

(14) In the following example, the relatively stable thiocarbonyl compound can be isolated if photolysis is performed in the absence of oxygen:



(15) Binkley, R. W.; Hehemann, D. G.; Binkley, R. W. *J. Org. Chem.* **1978**, *43*, 2573. Binkley, R. W. *Ibid.* **1976**, *41*, 3030 and references therein.

Acknowledgment. This work was supported by NIH Grant CA17918.

Registry No. **1a**, 88358-41-2; **1b**, 88358-42-3; **1c**, 87598-28-5; **1d**, 88358-43-4; **1e**, 88358-44-5; **1f**, 88358-45-6; **1g**, 88358-46-7; **2**, 77242-15-0; **3** (R′ = H; R = H), 88358-59-2; **3** (R′ = H; R = *t*-Bu), 84850-27-1; **3** (R′ = H; R = CH=CH_2), 88358-60-5; **3a**, 88358-52-5; **3b**, 88358-53-6; **3c**, 88358-54-7; **3d**, 88358-55-8; **3e**, 88358-56-9; **3f**, 88358-57-0; **3g**, 88358-58-1; **4**, 88358-61-6; **5** (R″ = H), 88358-62-7; **6** (R″ = CH_3), 5682-78-0; $PhCH_2CH_2CHO$, 104-53-0; $PhC(O)CH_2OAc$, 2243-35-8; $CH_3CH(OBr)CH(Ac)CHO$, 88358-47-8; $PhCOCH_2Cl$, 532-27-4; $PhCH_2CH_2C(SPh)$=O, 53573-33-4; cyclohexenone, 25512-62-3; cyclododecanone, 830-13-7; 2-acetoxycyclohexanone, 17472-04-7; cyclohexane-1,3-dione, 504-02-9; 2-methylnonane-3,5-dione, 88358-48-9; cyclododecanethiol, 7447-11-2; 2-(acetyloxy)cyclohexanethiol, 73921-29-6; 3-phenylpropanethiol, 24734-68-7; 2-(acetyloxy)-2-phenylethanethiol, 88358-49-0; 2-(acetyloxy)-3-(benzyloxy)butanethiol, 88358-50-3; 3-mercaptocyclohexanone, 33449-52-4; 5-mercapto-1-methylnonan-3-one, 88358-51-4; deoxybenzoin, 451-40-1; fluorenone, 486-25-9.

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Stable Vinyl Cations. 2.[1] Carbon-13 NMR Spectroscopic Observation of a Substituted Cyclopropylidenemethyl Cation

Summary: ^{13}C NMR spectroscopic data show the effective stabilization of the 1-cyclopropylidene-3-methyl-2-butenyl cation in solution.

Sir: The stabilizing ability of a cyclopropyl ring is well-known in trisubstituted as well as in disubstituted carbenium ions.[2] However, for vinyl cations there is a unique opportunity for stabilization by a cyclopropyl group, when one carbon of the cyclopropane ring is part of the vinyl cation, as in the cyclopropylidenemethyl cation 1.[3]

1

Cations 1 were first postulated as intermediates in the homopropargyl rearrangement.[4] The rapid solvolysis of cyclopropylidenemethyl bromide has been attributed to the high stability of the intermediate vinyl cation.[5] This conclusion is supported by ab initio and MINDO/3 calculations[6] and by experimental evidence for 1 in the gas phase.[7]

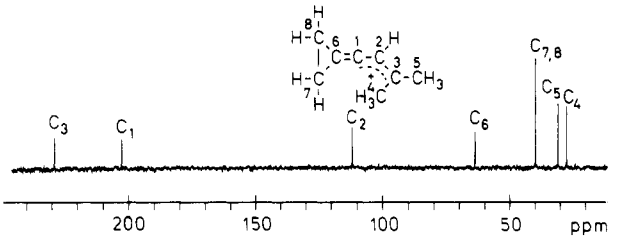
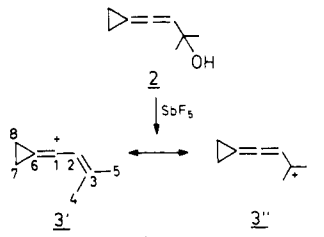


Figure 1. 100.62-MHz ^{13}C NMR spectrum of cation **3** in SO_2ClF/SO_2F_2 (2:1) at −100 °C.

Vinyl cations have been rather elusive toward direct ^{13}C NMR spectroscopic observation;[8] however, we have shown recently that α-vinyl-substituted vinyl cations can be generated from tertiary α-allenyl alcohols as stable species in solution.[1] We report here the first successful generation and NMR spectroscopic observation of the 1-cyclopropylidene-3-methyl-2-butenyl cation **3**.[9]

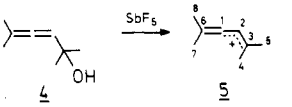
A clean yellow solution of **3** in SO_2ClF/SO_2F_2 was obtained by reaction of **2**[10] with SbF_5 by using the method already described.[11] The ^{13}C NMR spectrum (Figure 1) was recorded at −100 °C. Assignments were made by using proton-coupled spectra. Single-frequency proton-decoupled spectra were used to confirm these assignments.[12] C_3 shows long-range couplings to six methyl protons and thus could be distinguished from C_1.

Cation **3** can be considered either as a α-vinyl-β-cyclopropyl-stabilized vinyl cation (**3′**) or as a cyclopropylidene-substituted allyl cation (**3″**). The downfield



2 3′ 3″

shifts of C_1 (202.66 ppm) and C_3 (228.92 ppm)[9] indicate extensive charge delocalization between these two positions. Comparison of **3** with the analogous C_1-isopropylidene-substituted cation **5**[1] (Table I) reveals sig-



4 5

nificant differences. The corresponding allyl carbons in **5**, C_3 (257.64 ppm) and especially C_1 (245.39 ppm), are much more deshielded than those in **3**. The C_3 carbons in **3** and **5** have almost identical chemical shift values in the precursor alcohols **2** and **4**. The problem of neighboring group effects is minimized for C_3 since the substituent change is occuring at C_1, which is effectively screened from C_3.[13] We attribute the 29-ppm shielding of C_3 in **3** to the superior electron-donating capability of the β-cyclopropyl ring compared to the effect of two β-methyl groups in vinyl cation **5**. Calculations (STO-3G) have shown that a β-cyclopropyl ring stabilizes a primary

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(2) (a) le Noble, W. J. "Highlights of Organic Chemistry"; Marcel Dekker: New York, 1974; Chapter 20. (b) Olah, G. A., Schleyer, P. v. R., Eds. "Carbonium Ions"; Wiley-Interscience: New York, 1972; Vol. 3, Chapters 25 and 26.
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(7) Franke, W.; Schwarz, H.; Stahl, D. *J. Org. Chem.* **1980**, *45*, 3493.
(8) See ref 3, Chapter 8.
(9) For clarity we use here a different carbon numbering sceme from that given in ref 1.
(10) Details of the synthesis of **2** will be reported in a full paper.
(11) Saunders, M.; Cox, D.; Lloyd, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 6656.
(12) ^1H NMR spectra will be discussed in a full paper.
(13) For a detailed study of allyl cations, see: Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1539.

0022-3263/84/1949-0575$01.50/0