Table I. Second-Order Rate Constants for Nucleophilic Substitutions of Methanesulfonate by Anions Y^- Associated with $[H^+\subset(1.1.1,C_{14})]$, $[K^+\subset(2.2.2,C_{14})]$, $(C_8H_{17})_4N^+$, or $C_{16}H_{33}P^+Bu_3$, in Anhydrous Chlorobenzene at 60 °C

	10^2k,[a] M^{-1} s^{-1}			
Y^-	$[H^+\subset(1.1.1,C_{14})]$ Y^-[b]	$[K^+\subset(2.2.2,C_{14})]$ Y^-[c]	$(C_8H_{17})_4N^+Y^-$[b]	$C_{16}H_{33}P^+Bu_3Y^-$[d]
Cl^-	1.9	5.1	3.7	2.0
Br^-	1.1	3.7	2.0	0.81
I^-	0.60	0.87	0.68	0.30
N_3^-	7.0	15.0	15.6	7.0

[a] The rate constants are computer generated by using a least-square analysis and are the average of at least two runs. [b] [substrate] = 2–6 × 10^{-2} M; [nucleophile] = 0.8–2.4 × 10^{-2} M. [c] Data from ref 3. [d] Data from ref 7.

allow a stronger cation–anion interaction within the ion pair, hence a lower reactivity of **1** compared with those of **3** and **4**. In any case, anion activation by cryptates **1** is roughly comparable with that of the largely used quaternary phosphonium salts **5**.

As a conclusion, attachment of an aliphatic chain to $[H^+\subset(1.1.1)]$ cryptate results in a "unique example" of protonated tertiary amine, which behaves, in all of the essential aspects, like a tetralkylammonium or -phosphonium cation, and it is capable to impart to the anions a high nucleophilic reactivity.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian EM-390 90-MHz spectrometer with tetramethylsilane as internal standard. Potentiometric titrations were carried out with a Metrohm Titroprocessor E636 using silver and calomel electrodes, the latter isolated with a potassium sulfate bridge.

Materials and Solvents. *n*-Octyl methanesulfonate, bp 112–114 °C (2 mm), n^{20}_D 1.4398, was prepared according to the literature [lit.[12] bp 110–114 °C (2 mm), n^{20}_D 1.4392]. Quaternary ammonium salts **4a–d** were obtained from the commercially available tetraoctylammonium perchlorate (**4e**) by exchange with the appropriate anion, according to a previously described procedure.[13] Many of these salts are hygroscopic and must be stored in a desiccator. The $[H^+\subset(1.1.1,C_{14})]I^-$ cryptate (**1c**), mp 65–67 °C, was synthetized as previously reported.[11a] Cryptates **1a,b,d** were prepared from the corresponding perchlorate **1e** by exchange with the appropriate anion as follows: to a solution of **1e** (1 mmol) in methanol (15 mL) a solution of potassium salt (1.1 mmol) in methanol (100 mL) was added and stirred for 15 min. The precipitated $KClO_4$ was filtered and the solvent evaporated. The residue was taken up in CH_2Cl_2 and filtered again to remove traces of inorganic salts, and the solvent was evaporated. The overall sequence was repeated (at least 2 times), until a ≥95% exchange value was reached (potentiometric titration with 0.01 N silver nitrate of the nucleophile). The cryptates **1a,b,d** were carefully dried under vacuum at 1 mm at 50 °C and used for kinetic measurements without further purification. The $[H^+\subset(1.1.1,C_{14})]ClO_4^-$ cryptate (**1e**) was obtained by stirring a CH_2Cl_2 solution (100 mL) of the corresponding iodide **1c** (5 mmol) with an aqueous solution (50 mL) of $NaClO_4$ (20 mmol) for 30 min. The aqueous phase was substituted by a fresh solution of $NaClO_4$ and the procedure was repeated (at least 3 times) until the I^-/ClO_4^- exchange was complete (potentiometric titration of iodide). The organic phase was evaporated to give **1e**, mp 66–68 °C (hexane). Anal. Calcd for $C_{26}H_{53}ClN_2O_7$: C, 57.70; H, 9.87; N, 5.17. Found: C, 57.55; H, 10.00; N, 5.03. Chlorobenzene was carefully purified and dried by standard methods[14] and stored over molecular sieves. Karl Fischer titration showed a water content ≤40 ppm.

Kinetic Measurements. At zero time a standardized solution (10 mL) of substrate [(10–30) × 10^{-2} M] was added to a standardized solution (40 mL) of cryptate $[H^+\subset(1.1.1,C_{14})]Y^-$ or quaternary salt [(1–3) × 10^{-2} M] in a 100-mL flask thermostated at 60 ± 0.1 °C. Samples (2–5 mL) withdrawn periodically were quenched in ice-cold MeOH (50 mL), and the unreacted nucleophile was determined by potentiometric titration with 0.01 N silver nitrate. From the equation $1/([B_0] - [A_0])\ \ln([BA_0]/[AB_0]) = kt$, where [A] = [substrate] and [B] = [nucleophile] or vice versa, the second-order rate constants were calculated by using a least-squares computer program. All rates involved at least nine samplings and gave correlation coefficients ≥0.996.

Attempt at Deprotonation of $[H^+\subset(1.1.1,C_{14})]I^-$ (1c). A heterogeneous mixture of a deuteriotoluene solution (3 mL) of **1c** (300 mg) and 50% aqueous NaOH (1 mL) was stirred at room temperature for 5 days. ^1H NMR (C_7D_8) analysis of the organic phase showed that **1c** was unchanged: δ 8.8 (br s, 1 H, $>N^+-H$).

Registry No. **1a**, 92958-32-2; **1b**, 92958-33-3; **1c**, 92958-34-4; **1d**, 92958-35-5; **1e**, 92958-36-6; $(n\text{-}C_8H_{17})OSO_2CH_3$, 16156-52-8; $(n\text{-}C_8H_{17})_4N^+Cl^-$, 3125-07-3; $(n\text{-}C_8H_{17})_4N^+Br^-$, 14866-33-2; $(n\text{-}C_8H_{17})_4N^+I^-$, 16829-91-7; $(n\text{-}C_8H_{17})_4N^+N_3^-$, 81389-83-5.

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Synthesis and Photolysis of *S*-Methyl *S*-Alkenyl Dithiocarbonates in the Monoterpene Series

Faroudja Chatzopoulos-Ouar and Gérard Descotes*

Laroratoire de Chimie Organique II, Université de Lyon I, Villeurbanne 69622 Cedex, France

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The use of xanthate derivatives in organic synthesis continues to provoke interest particularly in carbohydrate chemistry as reflected in the recent reports on reductive,[1,2] thermal,[3-6] and photolytic reactions.[5,7-9] Surprisingly, the literature provides few examples of transformations of dithiocarbonates and particularly of unsaturated ones.[10] In connection with our preceding investigations into the allylic rearrangements of terpenic substrates,[11] we herein report the synthesis and photolysis of dithiocarbonates derived from myrtenol (**1**). *trans*-Pinocarveol (**2**) and perillyl alcohol (**3**).

Xanthation of **1**, **2**, and **3** in Me_2SO gave the crude xanthates **4**, **5**, and **6**, respectively. Xanthate **5** was spontaneously transformed into dithiocarbonate **8**, whereas xanthates **4** and **6** required silica gel chromatography or thermolysis at 85 °C in Me_2SO for their [3.3] sigmatropic rearrangement into dithiocarbonates **7** and **9**.[12-15] Pho-

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Table I. Synthesis and Spectral Data of Compounds 7–9

no.	yield, %	$[\alpha]^{20}_D$ (ethanol)	selective ^1H NMR ($CDCl_3$), δ[a]	selective ^{13}C NMR ($CDCl_3$), δ[a]
7	80	+33°	0.75 (s, 3 H, CH_3-9), 5.08 and 4.88 (2 s, 2 H, CH_2-10), 4.73 (d, J = 8 Hz, 1 H, CH-3), 2.45 (s, 3 H, CH_3-12)	150.15 (s, C-2), 51.57 (d, C-3), 112.74 (t, C-10), 189.26 (s, C-11), 12.86 (q, C-2)
8	80	−33.5°	0.80 (s, 3 H, CH_3-9), 3.65 (s, 2 H, CH_2-10), 5.55 (m, 1 H, CH-3), 2.45 (s, 3 H, CH_3-12)	141.86 (s, C-2), 121.20 (d, C-3), 36.53 (t, C-10), 189.12 (s, C-11), 12.96 (q, C-12)
9	65	+9.2°	5.00 (m, 1 H, CH-2), 4.82 (s large, 1 H, CH_2-7), 2.43 and 2.45 (2 s, 3 H, CH_3-12)	146.05 (s, C-1), 49.31 (d, C-2), 110.92 (t, C-7), 188.54 (s, C-11), 13.02 (q, C-12)

[a] Only the most significant values are given.

Table II. Synthesis and Spectral Data of Compounds 10–13

	λ 254 nm		λ ≥313 nm				
no.	irradn time, h	yield, %	irradn time, h	yield, %	$[\alpha]^{20}_D$ (ethanol)	selective ^1H NMR ($CDCl_3$), δ[c]	selective ^{13}C NMR ($CDCl_3$), δ[c]
10	3.30,[a] 6[b]	67,[a] 10[b]	8[a]	70[a]	−16.5°	3.00 (s, 2 H, CH_2-10), 5.40 (m, 1 H, CH-3), 1.83 (s, 3 H, CH_3-11)	143.18 (s, C-2), 119.40 (d, C-3), 40.33 (t, C-10), 14.59 (q, C-11)
11	3.30,[a] 6[b]	28,[a] 80[b]			−28°	3.35 (s large, CH_2-10), 5.52 (m, 1 H, CH-3), 2.45 (s, 3 H, CH_3-11)	142.62 (s, C-2), 121.22 (d, C-3), 44.97 (t, C-10), 21.23 (q, C-11)
12	4	85	10	85	−71.2°	5.60 (m, 1 H, CH-2), 3.08 (s large, 2 H, CH_2-7), 2.00 (s, 3 H, CH_3-11)	132.86 (s, C-1), 124.11 (d, C-2), 41.13 (t, C-7), 14.16 (q, C-11)
13	4	10	10	5	−88.4°	5.78 (m, 1 H, CH-2), 3.28 (s large, 2 H, CH_2-7), 2.40 (s, 3 H, CH_3-11)	132.57 (s, C-1), 125.70 (d, C-2), 46.16 (t, C-7), 23.20 (q, C-11)

[a] Obtained from 7. [b] Obtained from 8. [c] Only significant values are given.

Table III

						Anal.		
no.	IR (film, ν cm^{-1})	mol form	mol wt	MS, m/e (rel int)		C	H	S
7	1640 (SC=O + C=C) (s), 860 (CS) (s)	$C_{12}H_{18}OS_2$	242.39	242 (2), 182 (4), 167 (10), 134 (100), 119 (43), 91 (85)	calcd	59.49	7.49	26.42
					found	59.21	7.49	26.69
8	1640 (SC=O + C=C) (s), 860 (CS) (s)	$C_{12}H_{18}OS_2$	242.39	242 (4), 182 (4), 167 (3), 134 (27), 91 (100)	calcd	59.49	7.49	26.42
					found	59.21	7.60	26.39
9	1650 (SC=O + C=C) (s), 860 (CS) (s)	$C_{12}H_{18}OS_2$	242.39	242 (18), 182 (14), 167 (16), 134 (60), 105 (100), 93 (59)	calcd	59.49	7.49	26.42
					found	59.16	7.75	26.00
10	1640 (C=C) (w), 730 (CS) (w)	$C_{11}H_{18}S$	182.32	182 (54), 134 (52), 119 (70), 91 (100), 79 (24)	calcd	72.49	9.96	17.56
					found	72.10	9.97	17.76
11	1640 (C=C) (w), 880 (CS) (w)	$C_{11}H_{18}S_2$	214.38	214 (33), 167 (11), 135 (70), 119 (13), 93 (100), 79 (87)	calcd	61.66	8.47	29.87
					found	63.25[a]	8.58	27.68
12	1640 (C=C) (w), 720 (CS) (w)	$C_{11}H_{18}S$	182.32	182 (100), 167 (8), 134 (60), 119 (60), 93 (80), 79 (64)	calcd	72.49	9.96	17.56
					found	72.71	10.13	17.48
13	1640 (C=C) (w), 860 (CS) (w)	$C_{11}H_{18}S_2$	214.38	214 (34), 167 (30), 135 (80), 107 (62), 93 (100), 79 (66)	calcd	61.66	8.47	29.87
					found			29.69

[a] With traces of impurities.

tolysis of **7** and **8** in methanol at 254 nm gave a mixture of sulfide **10** and disulfide **11**. The primary dithiocarbonate **8** mainly gives disulfide **11** (80%), whereas the secondary dithiocarbonate **7** is primarily converted to sulfide **10** (67%). Photolysis of **9** at 254 nm affords a mixture of sulfide **12** and disulfide **13**. Like its bicyclic analogue **7**, the major product from the photolysis of **9** is sulfide **12** (85%).

Dithiocarbonate **9** yields the same mixture of **12** and **13** on photolysis at 313 nm, while **7** affords sulfide **10** (70%), as the exclusive product. Dithiocarbonate **8** is recovered unchanged even after irradiation for 40 h. A change in solvent does not appear to have an effect on the course of these photolyses (Scheme I), Tables I–III).

In summary, photolysis of terpenic allylic dithiocarbonates gives in good yields regioselective thioethers and disulfides according to competitive cleavages depending on the primary or secondary position of initial xanthates.

Experimental Section

General Methods. Optical rotations were obtained with a Perkin-Elmer 141 polarimeter. Infrared spectra were recorded on a Perkin-Elmer 683 spectrometer, ultraviolet spectra on a Varian 634 UV–vis spectrophotometer, and ^1H NMR spectra on a Brucker WP 80 spectrometer in $CDCl_3$ as solvent. ^{13}C NMR spectra were obtained ($CDCl_3$) on a Varian XL 100 A instrument. Chemical shifts are expressed in parts per million downfield from internal Me_4Si and coupling constants (J values) are given in hertz. Mass spectra (EI) were recorded on a Varian Mat CH 7 spectrometer. Gas chromatographic analyses were performed on an IGC 112 M Intersmat chromatograph, column packed with 10% SE-30 on Chromosorb PAW/80, heated at 140 °C. Column chromatography was performed on silica gel Kieselgel 60 (230–400 mesh). Elemental microanalyses were performed by Service Central de Microanalyse du CNRS, F.69390 Vernaison, France.

Solutions were irradiated with a Hanovia 688 A 45-W low pressure mercury lamp (for λ 254 nm) and a Hanovia 450-W medium pressure mercury lamp in a water-cooled Pyrex jacket

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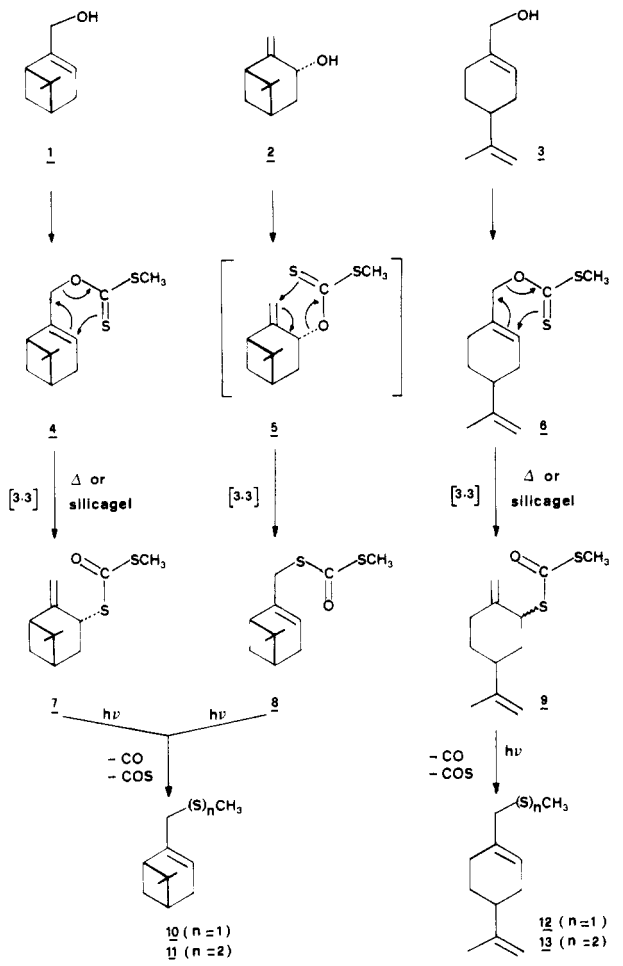
Scheme I



(for $\lambda > 313$ nm). The Me_2SO was freshly distilled from sodium hydride.

Xanthation or Alcohols 1, 2, and 3. Myrtenol (1) is a Fluka commercial product (purity 99%). *trans*-Pinocarveol (2) was prepared following a described method[16] from commercial pinene epoxide (Aldrich; purity 95%). Perillyl alcohol (3) was an EGA-CHEMIE commercial product (purity 90%).

Ethylenic alcohol (1.7 g, 11 mmol) was stirred for 30 min between 10 and 15 °C with a suspension of 1.65 g of powdered KOH in 30 mL of dry Me_2SO. Then 1.98 g (or 1.56 mL) of dry CS_2 were added dropwise such that the temperature never rised above 10 °C. After 30 min of stirring, 3.3 g (1.45 mL) of ICH_3 were added to the orange solution. The mixture was stirred at about 5 °C for 4.5 h for **1** and **2** and 1 h for **3** to limit aromatization reaction.[17] The solution was poured onto a small amount of ice water to avoid emulsion. The organic phase was extracted with ether. The etheric layer was washed with a saturated NaCl solution until pH 7 was obtained and then dried. The solvent was removed under reduced pressure. The yellow liquid residue (2.3 g, yield 85%) was subjected to column chromatography on silica gel with gradual eluting: (1) Hexane, afforded 100 mg of $(CH_3S)_2C{=}S$; NMR (CCl_4) 2.70 ppm; (2) 90 hexane/10 methylene chloride afforded 1.8 g of dithiocarbonate **7** or **8** (yield 80%), and 1.2 of g dithiocarbonate **9** (yield 65%) (IR, NMR, MS, molecular centesimal formulae; analyses of **7**, **8**, and **9**, see Tables I and III).

***S*-Methyl *O*-α-pinenyl dithiocarbonate (4) (crude)**: IR (film) ν 1120 and 1250 cm^{-1} (COC + C=S), 1650 (C=C); ^1H NMR ($CDCl_3$) δ 5.00 (s, 2 H, CH_2-10), 5.70 (m, 1 H, H-3), 2.45 (s, 3 H, CH_3-12).

***S*-Methyl *O*-dithiocarbonate (6) (crude)**: IR (film) ν 1200 and 1060 cm^{-1} (COC + C=S), 1640 (C=C); ^1H NMR ($CDCl_3$) δ 5.90 (m, 1 H, CH-2), 4.90 (s large, 2 H, CH_2-7), 4.70 (s large, 2 H, CH_2-9), 1.70 (s large, 3 H, CH_3-10), 2.40 (s, 3 H, CH_3-11).

Thermolysis of Xanthates 4 and 6. The crude product (2.3 g) obtained by xanthation of **1** and **3** was heated in 40 mL of dry Me_2SO at 85 °C under a nitrogen atmosphere for 2.5 h. Me_2SO was removed by etheric extraction. After drying and solvent removal under reduced pressure, 2 g of dithiocarbonate **7** or **9** were obtained and subjected to column chromatography of silica gel with gradual eluting (hexane, 90 hexane/10 methylene chloride): 1.8 g of **7** (yield 80%) and 1.2 g of **9** (yield 50% after two necessary consecutive elutions on silica gel) were isolated.

Photolysis of Dithiocarbonates 7-9. A sample of 40 mL of 5×10^{-2} M **7**, **8**, or **9** (484 mg) in methanol was poured into a quartz tube under a nitrogen stream. The whole solution was irradiated $\lambda = 254$ nm or $\lambda > 313$ nm. The reaction was followed by gas chromatography and stopped when the percentage of starting product did not vary.

***S*-Methyl *S*-β-pinenyl dithiocarbonate (7)**: λ_{max_1} 251 nm (ϵ_1 7200) and λ_{max_2} 203 nm (ϵ_2 12400) (ethanol). (1) λ 254 nm; time of irradiation 3.5 h in methanol. After removal of the solvent under reduced pressure, 350 mg of crude product was obtained and subjected to column chromatography on silica gel (eluent 95 hexane/5 methylene chloride), 80 mg of disulfide **11** (28%), 200 mg of thioether **10** (67%), and 15 mg of dithiocarbonate **7** (5%) were separated in this order. (2) For $\lambda > 313$ nm; time of irradiation 8 h in methanol. The solvent was removed under reduced pressure: 356 mg of crude product were obtained and subjected to column chromatography as described previously; 220 mg of thioether **10** (70%) and dithiocarbonate **7** (30%) were separated.

***S*-Methyl *S*-α-pinenyl dithiocarbonate (8)**: λ_{max_1} 249 nm, ϵ_1 6000; λ_{max_2} 206 nm, ϵ_2 10400 (ethanol). For λ 254 nm; time of irradiation 6 h in methanol. The solvent was removed under reduced pressure: 320 mg of crude product was obtained and subjected to column chromatography on silica gel (eluent 95 hexane/5 methylene chloride); 200 mg of disulfide **11** (80%), 46 mg of thioether **10** (10%), and 50 mg of dithiocarbonate **8** (10%) were separated. For $\lambda > 313$ nm; no reaction after 40 h of irradiation.

***S*-Methyl *S*-isocarveyl dithiocarbonate (9)**: λ_{max_1} 250 nm, ϵ_1 2600; λ_{max_2} 203 nm, ϵ_2 6000 (ethanol). (1) λ 254 nm (solvent methanol, time of irradiation 4 h). 425 mg of irradiated compound **9** afforded 330 mg of crude product. The mixture was subjected to successive column chromatographies on silica gel (eluent, 95 hexane/5 methylene chloride). Finally, 160 mg of thioether **12** (85%), 20 mg of disulfide **13** (10%), and 20 mg of dithiocarbonate **9** (5%) were separated without further purification. (2) $\lambda > 313$ nm. The results were analogous to those obtained with λ 254 nm, and with cyclohexane as solvent, longer irradiation times were necessary.

Registry No. 1, 515-00-4; 2, 1674-08-4; 3, 536-59-4; 4, 93040-75-6; 5, 93040-76-7; 6, 93040-77-8; 7, 93040-78-9; 8, 93040-79-0; 9, 74940-37-7; 10, 93040-80-3; 11, 93040-81-4; 12, 93040-82-5; 13, 93040-83-6; CS_2, 75-15-0; CH_3I, 74-88-4.

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(2*R*,5*R*)-(-)-2,5-Dimethylcyclopentanone and (5*S*)-(+)-2,5-Dimethyl-2-cyclopenten-1-one by Microbiological Reduction of Racemic 2,5-Dimethyl-2-cyclopenten-1-one

Jean-Claude Gramain, Alain Kergomard,* Michel F. Renard, and Henri Veschambre

ERA 392 du CNRS, Université de Clermont II, B.P. 45, 63170 Aubiere, France

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We reported in a previous work[1] that microbiological reduction of an α-substituted α,β-unsaturated ketone such as **1** gives the corresponding optically active saturated

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