first fraction (2.4 g), bp 36–40 °C (0.12 mm), was a mixture of isobutyrophenone and 2-octanol from which the latter was obtained pure by chromatography over alumina (100 g, activity 1). The ketone was eluted by 1:1 hexane/diethyl ether and the alcohol by 1:9 methanol/diethyl ether. The alcohol was distilled to give pure 2-octanol (1.0 g): bp 36.0 °C (0.1 mm); $n^{22.0}_D$ 1.4261° (lit.[15] n^{20}_D 1.4264°); d^{20}_4 0.083°; $[\alpha]^{20.0}_D$ −0.3 ± 0.5° (neat); 3 ± 1% optically pure based on lit.[15] $[\alpha]^{20.4}_D$ −9.72 ± 0.05° (neat). Optically pure 2-octanol was shown to be unaffected by the above acid conditions.

The last fraction from the distillation of the hydrolysis products contained 90–95% of **2** (shown by GLC at 225 °C), bp 105.5–106.5 °C (0.06 mm). This material was redistilled to give the pure product (1.6 g): bp 112–113 °C (0.08 mm); $n^{22.9}_D$ 1.4997°; MS, *m/e* 260; $[\alpha]^{21.0}_D$ +1.5 ± 0.2° (neat); 3.8 ± 0.5% optical purity.

ii. The reaction in dioxolane was carried out on the same scale for 14 weeks and worked up in the same way. The overall yield of substitution products was 5.4% (**2**/**3** = 0.85) by GLC. Distillation afforded two fractions. From the first, bp 45–51 °C (0.3 mm), pure 2-iodooctane, n^{20}_D 1.4874°, was isolated by column chromatography over acidic alumina (activity 1) followed by GLC at 185 °C. It had $[\alpha]^{17}_D$ +26.7° (neat), corresponding to 54.5% optical purity. The second fraction (1.3 g), bp 92–118 °C (0.05 mm), consisting of **2** and **3** was separated into its constituents by preparative GLC at 225 °C. Compound **2** (0.114 g), $n^{21.5}_D$ 1.5011°, *m/e* 260, had $\alpha^{16.5}_D$ +3.8 ± 0.2° (14.9% w/w in ethanol), corresponding to 78 ± 6% optical purity. Compound **3** (0.049), $n^{20.0}_D$ 1.4982°, *m/e* 260, was made up to 1 mL with 1.2 M aqueous methanolic (1:4) hydrochloric acid and allowed to stand for 1 h by which time hydrolysis was complete (GLC). This solution had $\alpha^{18.4}_D$ −0.22 ± 0.02°. The same value was obtained for an equivalent solution of isobutyrophenone and (−)-2(*R*)-octanol, $[\alpha]^{24.0}_D$ −8.9 ± 0.1° (neat), 92% optical purity. The enol ether **3** was therefore 92 ± 9% optical pure.

(15) Coppock, J. B. M.; Goss, F. R. *J. Chem. Soc.* **1939**, 1789.

Acknowledgment. One of us (L.M.J.) greatfully acknowledges Grant No's. CHE-7620879 and CHE-8002426 from the National Science Foundation, which supported this research.

Registry No. **1**, 62416-34-6; (+)-(*R*)-**2**, 87640-37-7; (−)-(*R*)-**3**, 87640-41-3; **6** (isomer 1), 87640-32-2; **6** (isomer 2), 87640-33-3; (+)-(*R*)-**7**, 63707-85-7; (±)-**7**-DNP, 87640-34-4; (*E*)-(*R*)-**8**, 87640-35-5; (*Z*)-(*R*)-**8**, 86414-43-9; (+)-(*R*)-**9** (R = H), 52075-16-8; (−)-(*R*)-**10**, 87640-36-6; (*Z*)-(*R*)-**11**, 87640-38-8; (*R*)-(+)-methyl citronellate, 20425-48-3; *n*-propyltriphenylphosphonium bromide, 6228-47-3; 1-phenyl-2,3-dimethyl-1-nonanone (isomer 1), 87640-39-9; 1-phenyl-2,3-dimethyl-1-nonanone (isomer 2), 87640-40-2; (−)-2(*R*)-octanol, 5978-70-1; (*S*)-(+)-2-iodooctane, 1809-04-7; *O*-(trimethylsilyl)isobutyrophenone, 39158-85-5; isobutyrophenone, 611-70-1.

6,2-Methyl Migration in the Norbornane System

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A synthesis of 2-(6-*exo*-methyl-2-norbornylidene)ethanoic acid (**5**) is described; 2-(2-norbornylidene)ethanoic acid (**3**) and **5** are each treated with trifluoroacetic acid and thereby are rearranged to the respective isomeric lactones of 6-*exo*-hydroxynorbornaneethanoic acid (**4**) and 6-*exo*-hydroxy-6-*endo*-methylnorbornaneethanoic acid (**6**). Both lactones proved to be all but wholly racemic though **3** and **5** were each optically active. Thus it is demonstrated that one may have a 6,2-*endo*-methyl shift analogous to the well-known 6,2-hydride shift in the norbornane system.

In the course of structural and configurational studies in the norbornane system[6] it was discovered that a strongly acidic isomerization of optically active 2-(3,3-dimethyl-2-norbornylidene)ethanoic acid ((−)-**1**) into 7,7-dimethyl-2-*exo*-hydroxynorbornane-1-ethanoic acid (**2**) afforded all but completely racemic product. Extensive investigation led to the conclusion that the only way in which the isomerization–racemization could occur is via the well established 6,2-hydride shift in which the migrating hydride is the endo hydrogen on carbon-6 (R^2). (Scheme I, compound **2**).

Some years later the study of this isomerization–racemization was reopened,[1] the compounds in this instance being rather simpler, lacking the dependent methyl groups of **1** and **2**, i.e., compounds (−)-**3** and (+)-**4**, Scheme I. The behavior of (−)-**3** on treatment with trifluoroacetic acid led to the expected lactone which proved to be all but completely racemic through **3** had been optically active. Thus analogous isomerization–racemization occurred as with (−)-**1** → (±)-**2**.

At this juncture it occurred to the senior author that the foregoing system might be ideal for demonstrating whether or not an alkyl group might experience a 6,2-shift analogous to the 6,2-hydride shift. The only previous instance of a 6,2-alkyl shift in the norbornane system is implicit in Schleyer and Donaldson's first proposed mechanism of adamantane synthesis.[7] But subsequent work[8] no longer had recourse to the 6,2-shift. Thus the problem remained open to investigation. The compound required for study

(1) B. A. Gross, M.S. Dissertation, The University of Connecticut, 1971.

(2) Stephen E. Burkle, Postdoctoral Research Associate, The University of Connecticut, 1973.

(3) Marjorie A. Langell, B.S. Honors Thesis, The University of Connecticut, 1974.

(4) Ronald Caple, vising Professor from The University of Minnesota, Duluth, 1974. The senior author wishes to thank Professor Caple for his contribution to the synthesis of 6-*exo*-methyl-2-norbornanone.

(5) David B. Oakes, B.S. Honors Thesis, The University of Connecticut, 1982, and subsequent research leading to the completion of the problem. He was generously supported by Summer Research Fellowships from The University of Connecticut Foundation in 1981 and 1982.

(6) W. R. Vaughan, J. Wolinsky, R. R. Dueltgen, S. Grey, and F. S. Seichter, *J. Org. Chem.* **35**, 400 (1970).

(7) P. R. Schleyer and M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

(8) E. M. Engler, M. Farcasin, A. Levin, J. M. Cense, and P. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5769 (1973).

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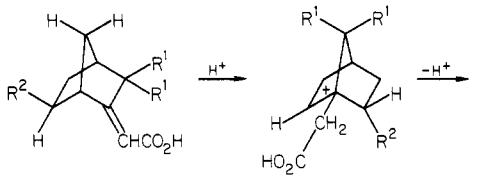
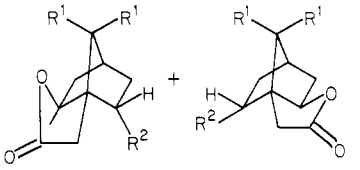
Scheme I



1, $R^1 = CH_3$; $R^2 = H$
3, $R^1 = H$; $R^2 = H$
5, $R^1 = H$; $R^2 = CH_3$



(±)-2, $R^1 = CH_3$; $R^2 = H$
(±)-4, $R^1 = H$; $R^2 = CH_3$
(±)-6, $R^1 = H$; $R^2 = CH_3$

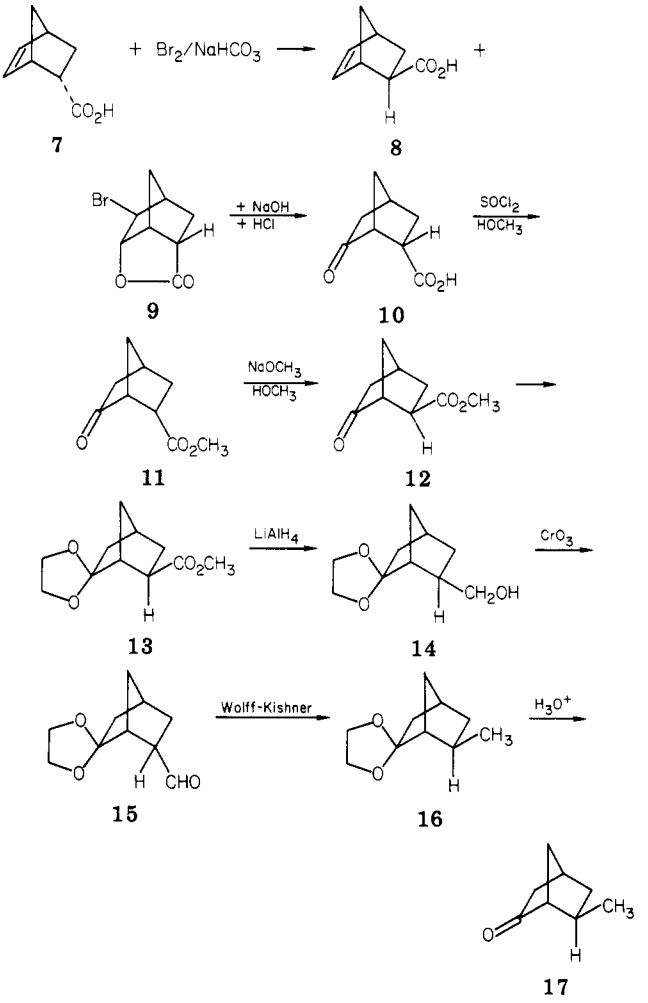
would be 2-(6-*exo*-methyl-2-norbornylidene)ethanoic acid (**5**) which should afford racemic **6** (Scheme I) if the methyl group does shift and optically active **6** if no shift occurs.

If racemization does in fact occur in the reaction **5** → **6** (Scheme I) one may use the same arguments advanced to account for it as were used to prove that only a 6,2-hydride shift can account for racemization in the reactions (−)-**1** → **2**[6] and (−)-**3** → **4**[1] (Scheme I).

Compound **1** has been prepared from an optically active starting material,[6] but both **3** and **5** were prepared as racemates and accordingly required resolution though not necessarily complete resolution. For these two compounds partial resolution was effected by means of cinchonidine, following which each was treated with trifluoroacetic acid, and in each case the resultant lactone (**4** and **6**, Scheme I) proved to be completely racemic. The isomerization–racemization in the case of **5** → **6** (Scheme I) provides the evidence for the existence of a 6,2-methyl shift.[5]

Since we have demonstrated a unique example of a 6,2-methyl shift in the norbornane system, it is now necessary to explain how compounds (−)-**3** and (+)-**5** were obtained. In each case an appropriate Wittig reaction was carried out on a 2-norbornanone, 2-norbornanone itself for **3** and 6-*exo*-methyl-2-norbornanone for **5**. The former ketone is, of course, a known compound, but the latter ketone proved to be rather difficultly accessible. However, a reasonable method of synthesis (Scheme II) was developed,[2-4] and an alternative pathway to **5** by way of norbornane-2,5-dione was investigated. This latter route might have been the route of choice had the preparation of the known dione been more readily achievable.[9-17] Since synthesis of **17**[3-5] in the event proved more convenient (Scheme II), it was the synthesis of choice,[5] and the conversion of **17** to **5** was carried out by treatment of

Scheme II



17 with the Wittig reagent derived from triethyl phosphonoacetate, as indicated above.

While a careful reinvestigation of the individual steps in Scheme II and the comnpletion of the isomerization–racemization of **5** (Scheme I) was in progress,[5] it came to our attention that the synthesis of **17** via Scheme II had been published.[18] In view of this premature and unauthorized publication, there is no point in detailing the specific experimental results in this paper, but the senior author cautions anyone wishing to repeat any of the individual synthetic steps that he may have considerable difficulty as did one of us.[5] However that may be there is no question about the identity of the compounds in Scheme II, because all of those carrying out the reaction sequence obtained the same intermediates and the same final compound (**17**).[2-5,18]

In conclusion (as suggested by one of the referees and the senior editor) there is the possibility of raising the specter that rotations of the lactones are simply very small and that no racemization has occurred. It does *not* arise in the case of **1** in which the lactone **2** is completely inactive.[6] Since **3** is structurally identical to **1** at the crucial

(9) H. Toivonen, *Suom. Kemistil. B.*, **31B**, 354 (1958).
(10) H. B. Henbest and B. Nichols, *J. Chem. Soc.*, 222 (1959).
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(13) J. Meinwald, J. K. Crandal, and P. Gassman, *Tetrahedron*, 18, 815 (1982).
(14) H. Krieger, *Suom. Kemistil. B.*, **35B**, 127 (1962).
(15) K. Heyns, G. Rudiger, and H. Paulsen, *Chem. Ber.*, **105**, 1019 (1972).
(16) R. T. Hawkins, R. S. Hsu, and S. G. Wood, *J. Org. Chem.*, **43**, 24 (1978).
(17) It is unfortunate that an early incomplete synthesis of dimethyl 2,5-dioxonobornane-3,6-dicarboxylate, H. Meerwein and W. Schurmann, *Ann.*, **398**, 241 (1913) apparently could not be confirmed, P. R. Levy and R. Robinson, *J. S. Afr. Chem. Inst.*, **XV**, 55 (1962), as it would be a very useful source of 2,5-norbornanedione.

(18) J. Radhakrishnan, *Z. Naturforsch. B.*, **35B**, 481–487 (1979). The reader will take note of the fact that this individual has published *as sole author* both the ideas and the substance of Scheme II which others[2-4] had completed before he appeared on the scene. Since he was unable to carry the reactions past **17** and since his published version of Scheme II leaves much to be desired (as was noted by the final investigator[5]), it would seem that he has published nothing relative to Scheme II which is original with him and done so in an ethically questionable manner. That this was not a misunderstanding is to be seen in virtually identical circumstances (J. Radhakrishnan, *Tex. J. Sci.*, 31, 295 (1979)).

points it seems most likely that the residual activity reported herein for lactone **4** is attributable to incomplete racemization rather than to a very small intrinsic rotation for **4**. Minor differences in the conditions for rearrangement–lactonization between **1** and **3** would account for minor differences in residual optical activity.

If one accepts this line of reasoning for **3** → **4** with almost complete racemization of **4**, it is not unreasonable to accept the analogous, though structurally somewhat different, situation in **5** → **6**; this situation is the crucial one in the present investigation.

In any case it seems to us most likely that racemization of **4** and **6** is indeed most reasonably attributable to 6,2-migrations of H in the case of **3** → **4** (as with **1** → **2**) and of CH_3 in the case of **5** → **6**. This does not absolutely lay the specter raised above, but we maintain that the specter is a most unlikely participant in the overall process, and that we are dealing with cases of almost but not quite complete racemization involving 6,2-shifts, in one of which we have a methyl group doing the migrating—a new 6,2-shift.

Experimental Section

Melting points were measured with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were observed with a Perkin-Elmer Model 237B grating spectrometer. NMR spectra were measured with a Varian Associates Model EM-360 spectrometer. The spectra were obtained at 60 MHz, and chemical shifts were measured with respect to tetramethylsilane. Mass spectra were obtained and recorded by Marvin R. Thompson using an Associated Electrical Industries Ltd. Model MS 902. GC spectra were obtained with a Perkin-Elmer 3920B programmable gas chromatograph. In all cases initial heating period was 8 min at 150 °C followed by an 8 °C/min increase to 200 °C which was maintained for 32 min.

Purification of Reagents. Cyclopentadiene: cracked and distilled immediately prior to use, boiling range 40–45 °C. Acrylic acid: distilled from its polymeric form immediately prior to use, collected at 35 °C (10 mm). Pyridine: distilled over potassium hydroxide pellets and collected at 113–114 °C. Chromic anhydride: dried for 12 h in an oven at 120 °C. Methylene chloride: stirred for 12 h with concentrated sulfuric acid and then distilled. All other reagents were reagent grade and were not further purified.

Partial Resolution of 2-(2-Norbornylidene)ethanoic Acid (3).[1] To a boiling solution of cinchonidine (0.487 g, 0.0166 mol) in 15 mL of absolute ethanol was added 0.501 g (0.033 mol) of **3** followed by an additional 3 mL of ethanol. The mixture was gently warmed on a steam bath for 10 min, then cooled to −15 °C. No crystals appeared after 12 h so 5 mL of ethanol was distilled off whereupon the solution became cloudy. When cooled to −15 °C, white crystals were obtained, collected by filtration in the cold room, and then oven dried at 105 °C for 1.5 h: 0.4104 g, mp 155–157 °C.

The acid was regenerated by placing the crystals in 50 mL of a 1% potassium hydroxide solution when was then extracted with chloroform. The aqueous layer was acidified with 0.5% hydrochloric acid and then extracted with ether. The ethereal solution was dried and the ether was removed in vacuo. The residual white solid had an mp of 79–82 °C and an infrared spectrum identical with that of the racemate. $[\alpha]^{29}_D$ −14.62°.

Lactonization–Racemization of 2-(2-Norbornylidene)-ethanoic Acid (3).[1] To 15 mL of trifluoroacetic acid was added 2 g (0.0132 mol) and **3** and the mixture was stirred at room temperature for 66 h. The resultant pale yellow solution was twice extracted with ether, and combined ethereal extracts were extracted with 10% sodium bicarbonate, and the remaining ether solution was dried over anhydrous magnesium sulfate. Evaporation left behind a yellow oil which on standing overnight yielded 1.22 g (61%) of white crystals. These were recrystallized (petroleum ether, 65–110 °C) thus affording an oily solid: IR 1770 (C=O lactone), 1680 cm^{-1} (C=O acid).

Approximately 100 mg of this material was dissolved in 6 mL of carbon tetrachloride and then shaken twice with 10 mL of 10% aqueous sodium bicarbonate. The carbon tetrachloride was dried and then removed in a nitrogen stream, and the residue was sublimed: mp 75–76 °C; IR 1785 cm^{-1} (C=O lactone); $[\alpha]^{21}_D$ −0.72° (chloroform).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.05; H, 7.89. Found: C, 71.16; H, 8.01.

2-(6-*exo*-Methyl-2-norbornylidene)ethanoic Acid (5).[5] To 25 mL of benzene (dried with molecular sieves) was added 2.18 g of 50% sodium hydride in mineral oil. The resulting slurry was magnetically stirred and to it was added dropwise 8.75 g (3.90×10^{-2} mol) of triethyl phosphonacetate over a 25 min period. The reaction temperature was kept below 15 °C by means of an ice bath, and at this temperature 4.5 g (3.6×10^{-2} mol) of 6-*exo*-methylnorbornan-2-one (**17**) was added dropwise over a 10 min period. The reaction mixture was then heated at 75 °C for 35 min after which the benzene was removed by distillation. The residual brown gummy product was distilled at 0.7 mm and 1.60 g (22.7%) of colorless liquid was collected at 84 °C. This is the ethyl ester of compound **5**: IR (KBr plates) 2880–2960 (C–H stretch), 1715 (C=O stretch), 1650 (C=C stretch), 1200 cm^{-1} (C–O stretch); NMR ($CDCl_3$) 6.7–5.3 (m, 2 C–H), 4.3–3.8 (m, 2 CH_2), 2.8–0.8 ppm (m).

The saponified ester (90–105 °C) showed the following IR: (NaCl plates) 2800–3600 (O–H stretch), 1690 (C=O stretch), 1650 (C=C stretch), 1240 cm^{-1} (C–O stretch); NMR ($CDCl_3$) 10.7 (s, 1, OH), 5.6 (s, 1, C–H), 1.8–2.0 ppm (d, 3, CH_3); calcd mass, 166.0994; found, 166.1007 ± 1.5 mmu.

Partial Resolution of 2-(6-*exo*-Methyl-2-norbornylidene)ethanoic Acid (5).[5] A solution of 5 mL of absolute ethanol and 0.133 g (4.52×10^{-4} mol) of cinchonidine was prepared and brought to boiling. To this boiling solution was added 0.15 g (9.04×10^{-4} mol) of **5** and mild heating on the steam bath was continued for 10 min. Recrystallization from ethanol by cooling was unsuccessful so most of the ethanol was removed by boiling on the steam bath. The residual solution was treated with ethyl acetate and cooled to −10 °C with scratching to induce crystallization. By this procedure 0.188 g of the cinchonidine salt, mp 164–174 °C, was isolated. The salt was then dissolved in 20 mL of a 1% potassium hydroxide solution and stirred for 5 min. The solution was next extracted with two 20-mL portions of chloroform. The aqueous layer was then acidified with 14 mL of 0.5% hydrochloric acid, and the cloudy solution was extracted with three 40-mL portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate, and the ether was removed with a Roto-Vap. The residual oil (0.188 g) crystallized in the refrigerator, and the crystals proved to have an NMR spectrum virtually identical with that of the racemate, **5**: NMR ($CDCl_3$) 10.7 (s, 1, OH), 5.5 (s, 1, C–H), 1.8–2.0 ppm (d, 3, CH_3); $[\alpha]^{30°}_D$ +22.2.

Lactonization–Racemization of 2-(6-*exo*-Methyl-2-norbornylidene)ethanoic Acid (5).[5] To 0.087 g (5.24×10^{-4} mol) of partially resolved **5** was added 1.4 mL of freshly distilled trifluoroacetic acid. Stirring of the mixture was begun and continued for 47.5 h. At 18 h 0.5 mL of additional trifluoroacetic acid was added, and at the end of stirring the dark brown reaction mixture was added to 14 g of cracked ice. After the ice had melted, the faintly yellow solution was extracted with two 30-mL portions of ether. The combined ethereal extracts were carefully extracted with two 25-mL portions of saturated aqueous sodium bicarbonate solution. The residual ether solution was dried over anhydrous magnesium sulfate, and the ether was removed by a Roto-Vap. The result was 0.116 g of dark yellow-brown liquid: IR (NaCl plates) 2880, 3460 (C–H stretch), 1780 (C=O stretch of lactone), 1670 cm^{-1} (C–O stretch); NMR ($CDCl_3$) 1.1–2.5 ppm (m); $[\alpha]^{26°}_D$ −0.38°; calcd mass, 166.0994; found, 166.0996 ± 0.8 mmu.

Acknowledgment. Studies of various routes to 2,5-norbornanedione were conducted by David Rawn, Postdoctoral Research Associate (1972), Joseph Kozakiewicz, B.S. Honors Thesis, University of Connecticut (1978), William P. Dailey, III, B.S. Honors Thesis, University of Connecticut (1979), Blair Anthony, Senior Thesis, University of Connecticut (1979), and Robert A. Budding, B.S. Honors Thesis, University of Connecticut (1980). Synthesis of 6-*exo*-methyl-2-norbornanone (**17**) was conducted

by J. Radhakrishnan, Postdoctoral Research Associate (1977), Jeffery A. Naus, B.S. Honors Thesis, University of Connecticut (1977), and C. L. Rossiter, IV, B.S. Honors Thesis, University of Connecticut (1982). W.R.V. gratefully acknowledges financial support for several summers in the course of this investigation from the University of Connecticut Research Foundation.

Registry No. (±)-**3**, 87554-07-2; (−)-**3**–cinchonidine, 87583-08-2; (−)-**3**, 87554-08-3; (±)-**4**, 87494-97-1; (±)-**5**, 87494-95-9; (+)-**5**–cinchonidine, 87508-86-9; (+)-**5**, 87494-96-0; (±)-**5** ethyl ester, 87495-00-9; (±)-**6**, 87494-98-2; (±)-**17**, 87494-99-3; triethyl phosphonoacetate, 867-13-0.

Nucleophilic Substitutions of Unactivated Vinyl Halides with Alkanethiolate Anions in Hexamethylphosphoramide[1]

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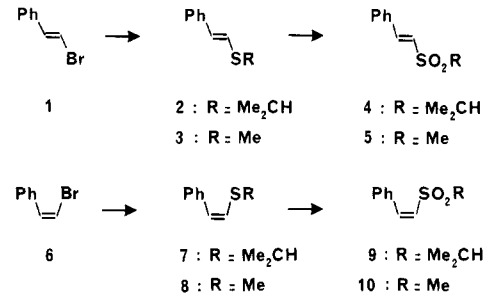
Received March 2, 1983

The reactions of unactivated vinyl halides with the sodium salts of alkanethiols in HMPA gave vinyl alkyl sulfides in high yields. These reactions occur with complete retention of configuration. With di-, tri-, and tetrachloroethylenes all the chlorine atoms are substituted by alkylthio groups. By treatment with alkanethiolates the vinyl sulfides are dealkylated to give the sodium salts of the ene thiols. By reaction with sodium all the alkylthio groups present in the molecule suffer fragmentation to give the sodium salts of the corresponding mercaptoethylenes.

Alkenyl sulfides are valuable synthetic precursors of several organic compounds,[2,3] and various methods have therefore been described for their synthesis. Several procedures, which include Wittig-type reactions,[4] dehydration of β-hydroxy thioacetals,[5] and dehydrochlorination of chloro sulfides,[6] use carbonyl compounds as starting products. Carbonyl compounds can afford alkenyl sulfides also by treatment with the lithium salts of (alkylthio)- or (arylthio)(trimethylsilyl)methane.[7] Another useful synthesis of alkenyl sulfides consists of the addition of thiolate anions to acetylenic compounds.[8] Other systems use alkenyl halides as starting materials. These can be transformed into the alkenylmagnesium halides and treated with methyl sulfinate esters to produce alkenyl sulfoxides, which are then reduced to the sulfides.[9] Direct displacement of vinylic halogens by thiolate anions can be effected in activated substrates,[10,11] i.e., in ethylenic compounds of the type YCH=CHX where Y is an electron-withdrawing group and X the halogen atom. Nucleophilic vinylic substitutions on unactivated substrates do not generally take place. The few examples reported in the literature represent special cases in which mechanisms different from those proposed for activated systems are operating. Thus displacement of vinylic halogens by copper alkane thiolates has been described.[12] This reaction takes place with β-bromostyrene only at 200 °C; however with dibromoethylene the product obtained was the (alkylthio)acetylene deriving from the elimination of HBr. (*Z*)-Dichloroethylene reacts with arenethiolates in ethanol, in the presence of sodium ethoxide, to give the (*Z*)-bis(arylthio)ethylenes; this reaction however proceeds through an elimination–addition mechanism and in fact the (*E*)-dichloroethylene does not give any reaction product under the same experimental conditions.[13] Successful stereospecific substitutions of vinyl halides by the lithium salts of alkane- and arenethiols have been recently described; these reactions however require the use of tetrakis(triphenylphosphine)palladium as catalyst in order to activate the substitution process.[3]

Scheme I



We have recently reported that sodium alkanethiolates easily react with unactivated aryl halides[14] and with polyhalogenoarenes[15] to give aryl alkyl sulfides and poly(alkylthio)arenes in high yields when the reactions are carried out in HMPA. We now report that this procedure can be successfully applied to the vinyl halides to effect a stereospecific and very efficient synthesis of vinyl alkyl sulfides. Owing to the easy availability of the starting compounds and to the extremely simple experimental

(1) Presented in part at the 2nd European Symposium of Organic Chemistry, Stresa, Italy, June 1–5, 1981; Abstract No. 30A.
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