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NEW STEREOSPECIFIC SYNTHESIS OF VINYL SULFIDES VIA CIS-TRANS OLEFIN INVERSION

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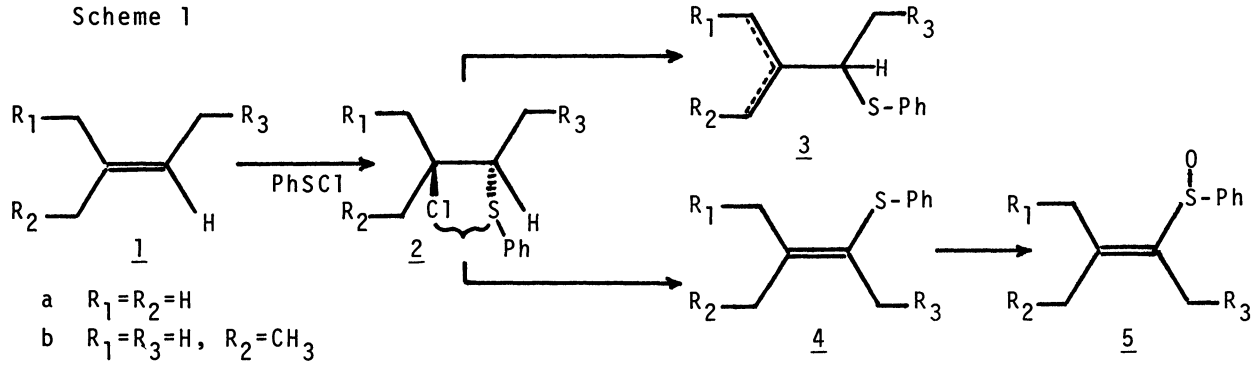
A new stereospecific synthesis of vinyl sulfides (4) was achieved via complete cis-trans olefin inversion in which benzenesulfenyl chloride addition to olefins (1) and trans elimination of hydrogen chloride are involved.

Substituted vinyl sulfides which have clear cis or trans geometry are useful for highly stereoselective syntheses of substituted olefins by reductive desulfurization[1] or by substitution of aryl or alkyl group for arylthio group with Grignard reagents.[2] Now we report that trisubstituted olefins (1) gave corresponding vinyl sulfides (4) with complete inversion of olefin geometry via benzenesulfenyl chloride (PhSCl) addition followed by dehydrochlorination with t-BuOK (Scheme 1).

Sulfenyl halide addition to olefins is well known to proceed through complete trans addition.[3] We have observed that PhSCl-adducts (2a) of gem-dimethyl olefins (1a) are dehydrochlorinated exclusively to give terminal allylic sulfides (3a) and trisubstituted vinyl sulfides (4a) respectively by treatment with Et_3N in DMF (60°, 20 hr) and t-BuOK in DMSO (r.t, 20 hr).[4] Allylic sulfides (3a) have been reported to isomerize readily to vinyl sulfides (4a) by treatment with t-BuOK in DMSO at

Scheme 1



a $R_1=R_2=H$
b $R_1=R_3=H$, $R_2=CH_3$
c $R_1=CH_3$, $R_2=R_3=H$

room temperature.[5] We have been interested in investigating the mechanisms in the formation of vinyl sulfides (4) from adducts (2) on treatment with t-BuOK. If vinyl sulfides (4) are formed via allylic sulfides (3), stereospecific introduction of olefinic bond would not be expected. On the other hand, if direct trans HCl-elimination occurs with removal of the more acidic proton H_a shown in (2i)(Scheme 2), stereospecific inversion of olefinic bond is expected.

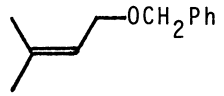
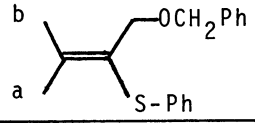
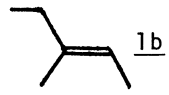
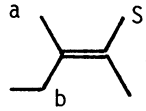
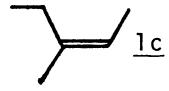
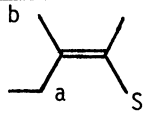
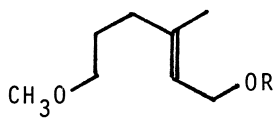
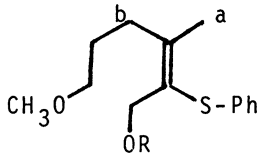
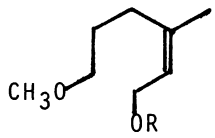
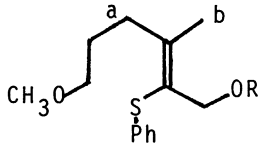
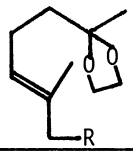
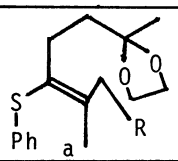
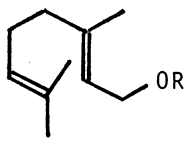
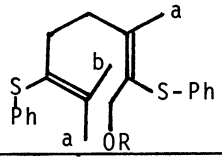
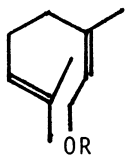
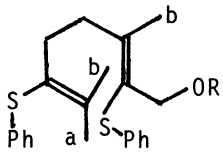
Trans and cis 3-methyl-2-pentene (1b and 1c) were individually treated with an equivalent of PhSCl at -20° to give quantitatively corresponding regioisomeric mixture of adducts (2b) and that of adducts (2c) respectively. Stereospecific dehydrochlorination was accomplished by treating the adducts (2b) with 1.0-1.2 equivalent of t-BuOK in DMSO at room temperature for 20 hr to give single vinyl sulfide (4b) in 88% yield, which was readily oxidized to afford vinyl sulfoxide (5b) by usual manner ($NaIO_4$ or 30% H_2O_2). Also from the adducts (2c) vinyl sulfide (4c)(82%) and vinyl sulfoxide (5c) were obtained by the same procedure.

The vinyl sulfide (4b) and the sulfoxide (5b) were stereochemically pure and completely without contamination with the other isomers (4c) and (5c), and vice versa in the NMR analysis. Mikolajczyk[6] and Uda[7] reported that the NMR signals of allylic methyl or methylene protons cis to sulfur are markedly shifted downfield (ca. 0.2 ppm) upon conversion of vinyl sulfide into the corresponding vinyl sulfoxide. The excellent agreement between the observed downfield shift of one of the allylic methyl signals (see Table) in conversion of the vinyl sulfide (4b) into the sulfoxide (5b) and that reported enabled us to assign the configuration of geometry as cis, and also trans geometry was assigned to the other ones (4c) and (5c) on the basis of the observed significant downfield shift (0.23 ppm) of the allylic methylene signal.

Generality of the cis-trans stereospecific inversion[8] was demonstrated in the transformation of various trisubstituted olefins into the corresponding vinyl sulfides (Table).

It should be noted about dehydrochlorination mechanism of PhSCl-adduct (2) that the thermodynamically favored regioisomer (2i)[3] would exclusively take part in the reactions because no isolable products that are anticipated to come from the other regioisomer (2ii) were obtained and that in the substantially thermal condition (solvent only (toluene or DMF) or Et_3N in DMF)[4] the proton H_b is eliminated to provide allylic sulfide (3) and in the strongly basic condition studied in this paper concerted trans dehydrochlorination takes place with removal of the proton H_a

Table. Preparation of Vinyl Sulfides and Chemical Shifts of Allylic Methyl or Methylene Signals of Vinyl Sulfides and Sulfoxides.

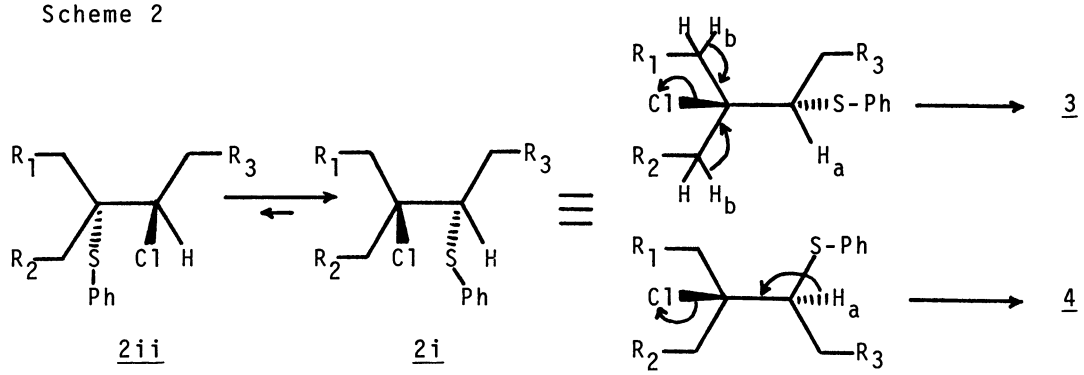
Olefin	Vinyl Sulfide*1	R*2	Yield (%)		Chemical Shift*3 Sulfide	Sulfoxide
			67	a	2.04	2.22
				b	1.95	1.93
 1b	 4b		88	a	1.97 or 1.93	2.23
				b	2.23	2.18
 1c	 4c		82	a	2.47	2.70
				b	1.88 or 1.85	1.86
		CH_2Ph	69	a	2.03	2.26
				b	2.35	2.32
		CH_2OCH_3	62	a	2.02	2.28
				b	2.37	2.34
		H	72	a	2.00	2.24
				b	2.39	2.35
		CH_2Ph	77	a	2.48	2.76
				b	1.93	1.98
		CH_2OCH_3	65	a	2.48	2.75
				b	1.98	2.00
		H	77	a	2.47	2.71
				b	1.99	2.00
		CH_3	64	a	1.97	2.22
		n-Bu	64	a	1.95	2.21
		CH_2Ph	70	a	2.00, 1.92	2.20, 2.15
				b	1.82	1.80
		CH_2OCH_3	66	a	2.03	2.27, 2.22
				b	1.94	1.93
		H	62	a	2.03	2.24, 2.21
				b	1.92	1.96
		CH_2Ph	67	a	1.97	2.22
				b	1.87, 1.82	1.95, 1.88
		CH_2OCH_3	69	a	1.99	2.29
				b	1.89	2.01, 1.94
		H	50	a	1.99	2.29
				b	1.88	2.01, 1.97

*1 Preparation of vinyl sulfides from geraniol and nerol derivatives was achieved by addition of 2 equivalents of PhSCl followed by dehydrochlorination with 2.5 equivalents of t-BuOK in DMF or DMSO at 45° for 20 hr.

*2 Hydroxy vinyl sulfides (R=H) were prepared by removing the protective methoxymethyl group with p-TsOH in MeOH at 45° for 2 days.

*3 NMR spectra were recorded in CCl_4 at 60 MHz and chemical shifts are reported in δ. Values presented by 'a' indicate the chemical shifts of allylic methyl or methylene proton signals cis to sulfur, and values 'b' stand for those trans to sulfur as shown in formulae.

Scheme 2



to give vinyl sulfide (4) with overall stereospecific inversion of olefin geometry as illustrated in Scheme 2.

The following procedure for the preparation of vinyl sulfides is representative for stereospecific inversion of olefin geometry. To a solution of trans 3-methyl-2-pentene (1b)(200mg, 2.4 mmol) in CH_2Cl_2 (2.0 ml) was added dropwise over a period of 5 min a CH_2Cl_2 solution (1.0 ml) of PhSCl (350 mg, 2.4 mmol) at -20°. After stirring the mixture for 10 min at -20° the solvent was evaporated under reduced pressure to give a crude adducts (2b)(530 mg). t-BuOK (300 mg, 2.7 mmol) was added in portions into the solution of (2b) in DMSO (10 ml) at room temperature, and the mixture was stirred for 20 hr at the ambient temperature. The reaction mixture was extracted with Et_2O, washed with water, dried, and evaporated to give a crude oil. Columun chromatography on silica gel (hexane) gave cis vinyl sulfide (4b)(405 mg) in 88% yield.

References and Notes

1 W. E. Truce and J. J. Breiter, J. Am. Chem. Soc., 84, 1623 (1962).

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6 M. Mikolajczyk, S. Grzejszczak and A. Zatorski, J. Org. Chem., 40, 1979 (1975).

7 S. Yamagiwa, N. Hoshi, H. Sato, H. Kosugi and H. Uda, J. Chem. Soc. Perkin I, 1978, 214.

8 Cis-trans inversion of olefinic bond was also confirmed by highly stereoselective reductive desulfurization that will be reported elsewhere.

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