

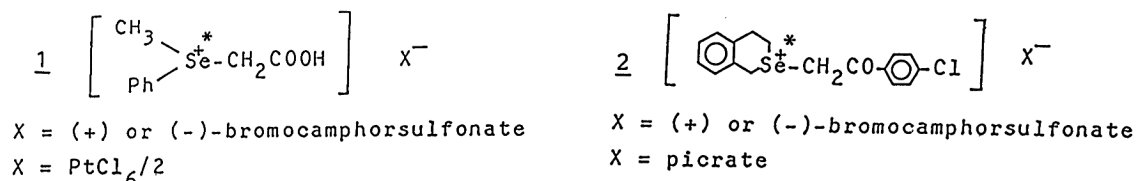
Asymmetric Induction in the Alkylation of Enolate Anion with the Optically Active Selenonium Ions

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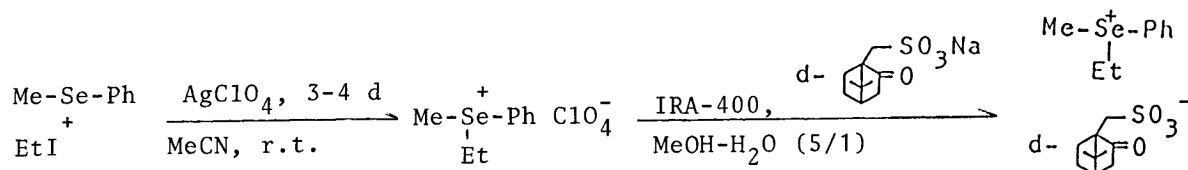
Alkylation of the enolate anion of 2-methoxycarbonyl-1-indanone with optically active dialkylphenyl selenonium salt resulted in the formation of optically active C-alkylated products. Absolute configuration of the optically active selenonium ion was estimated on the basis of the asymmetric alkylation and CD spectra.

Selenonium ions have the pyramidal configuration and those with three different substituents can exist as a pair of the optically active isomers. Several optically active selenonium salts such as 1¹⁾ and 2²⁾ have been described in the literature, but their absolute configuration has not been determined as yet.

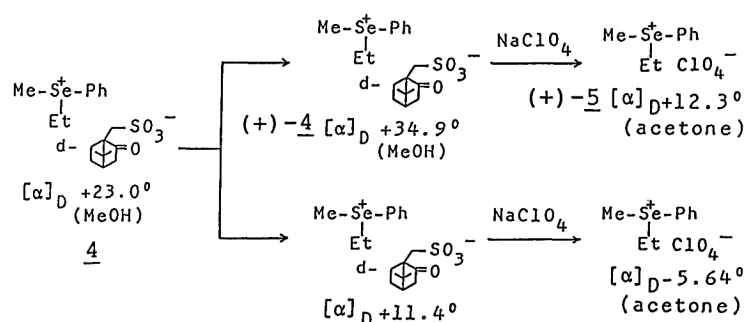


There has been little study on the use of the selenonium salts as the alkylating reagents. Formation of methyl t-butyl ether and benzyl t-butyl ether in the reaction of methylbenzylphenylselenonium salt with potassium t-butoxide was mentioned.³⁾ Recently we have reported an asymmetric induction observed in the alkylation of the enolate anion with the optically active sulfonium salts.⁴⁾ In these reactions, the configuration of the C-alkylated products were found to be related with the absolute configuration of the sulfonium salts used. This result suggested us the possibility of the estimation of the absolute configuration of the optically active selenonium ion by means of the asymmetric alkylation with selenonium salts, if occurred.

Chiral ethylmethylphenylselenonium perchlorate (5) was prepared by optical resolution of racemic selenonium d-camphorsulfonate (4). Racemic salt was obtained by the reaction of ethyl phenyl selenide with methyl iodide in the presence of silver perchlorate in acetonitrile, and subsequent conversion of selenonium perchlorate(3) into d-camphorsulfonate ([α]_D+ 23.0; c 1.01, MeOH) by ion exchange resin.



Fractional recrystallization of the racemic salt 4 from a mixture of methanol-acetone-ether gave the dextro rotatory diastereomer (+)(4)([α]_D +34.9; c 1.10, MeOH) in pure state, and levo diastereomer (-)(4)([α]_D -11.4; c 1.03, MeOH) in about 45% optical purity. Optically active ethylmethylphenylselenonium perchlorate (5) was obtained by ion exchange.



When 2-Methoxycarbonyl-1-indanone (6) was treated with optically active (+) ethylmethylphenylselenonium perchlorate (+)-5 in the presence of potassium carbonate in dichloromethane, 2-methylated product 7 and 2-ethylated product 8 were obtained in 41% and 36% respectively. Both C-alkylated products were optically active. More interestingly, configuration of C-methylated product (7) was found to be (S), and that of C-ethylated product (8) was (R), on the basis of sign of their optical rotation.⁴ When levo rotatory selenonium salt (-)-5 was used in place of d-isomer, optical rotation of the resulted C-alkylated products were reversed. (Table 1).

Table 1. Alkylation of 6 with optical active selenonium salts 5^{a)}

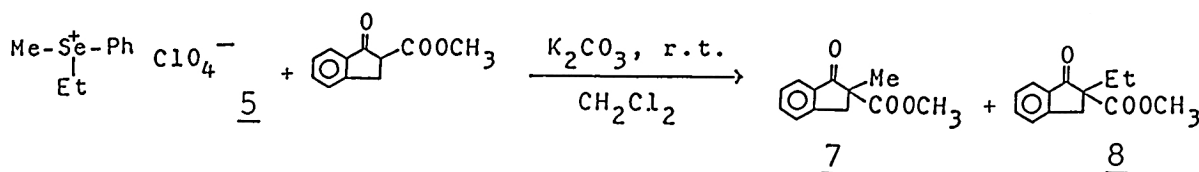
Entry	Selenonium salt (<u>5</u>) (confn)	[α] _D /deg	isolated yield/%	[α] _D /deg ^{b)} (CHCl ₃)	e.e/% ^{c)}	(confn) ^{d)}	CD spectra [α](CHCl ₃)
1	+ <u>5</u>	+12.31	<u>7</u> 41.2	-0.88	2.4	(S)	-19
			<u>8</u> 36.3	+4.58	6.2	(R)	+44
2	- <u>5</u>	-5.67	<u>7</u> 38.8	+0.20	0.55	(R)	+12
			<u>8</u> 35.4	-5.21	7.0	(S)	-71

a) A mixture of selenonium salt 5 (1.50 mmol), β -ketoester 6 (0.75 mmol), and potassium carbonate (1.12 mmol) was stirred at room temperature for 5 days.

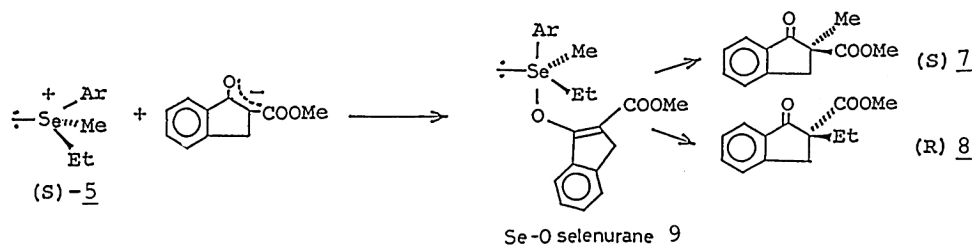
b) Optical rotations were taken in chloroform at 26 °C.

c) Enantiomeric excess was calculated in comparison with the optical rotation of pure 7.

d) Absolute configuration was estimated by correlating 7 and 8 with (-)-(2S)-2-methoxycarbonyl-2-(3-oxobutyl)-1-indanone; Ref. 5.



Formation of C-methyl derivative (7) and C-ethyl derivative (8) in nearly equal yields, and with opposite optical rotations were very difficult to be explained by usual S_N2 reaction mechanism. Above asymmetric alkylation may be understood by assuming Se-O-selenurane (9) as an intermediate which was formed by the attack of enolate anion of α -ketoester on the cationic selenium atom of 5. In the transition state, methyl group may attack the re face of the enolate pi face from the bottom side to give S-(-)-6. C-ethylation will take place preferentially from the top side to si face of the enolate plane of 6 to afford R-(+)-7. If this assumption is valid, absolute configuration of (+)-5 can be deduced as (S).



In the alkylation of the same enolate anion with the optically active sulfonium salts, similar asymmetric induction has been observed.⁴⁾ When (S)(+)-methylethylphenylsulfonium salt was treated with 2-methoxycarbonyl-1-indanone (6) in the presence of base, C-methyl derivative (S)(-)-7 and C-ethyl derivative (R)(+)-8 were obtained. If the analogy will be held between the stereochemical course of the alkylation reactions of sulfonium salt and that of corresponding selenonium salt, the absolute configuration of selenonium salt (+)-5 should be (S).

Above estimation of the configuration of the optically active selenonium salt was supported by study on their CD spectra. (S)(+)Methylethylphenylsulfonium perchlorate exhibited positive Cotton effect in 230 nm region and negative one in 260 nm region (Fig.1). Since the observed CD absorptions can be attributed to the L_a and L_b transition of benzene pi electrons respectively, sign of the Cotton effects may be explained by aromatic quadrant rule⁶⁾ as shown in Fig. 2. (+) Methylethylphenylselenonium perchlorate (5) was found to possess positive Cotton effect in 230 nm region and negative one in 260 nm region (Fig.3), just as in the corresponding sulfonium salts. Study on CD spectra thus justified the assumption on the absolute configuration (Fig. 4) of the selenonium salt (5) from the results of the asymmetric alkylation.

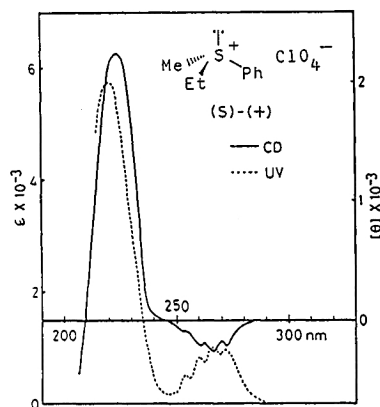


Fig. 1.

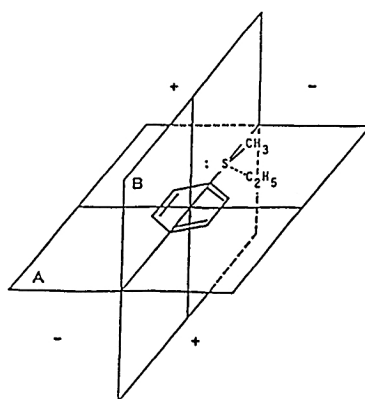
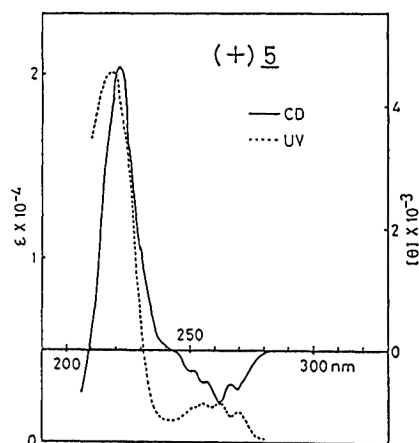


Fig. 2. Quadrant rule applied to (S)(+)-ethylmethylphenylsulfonium ion.

Fig. 4. CD spectrum of (+)-5.

$\begin{array}{c} \text{Me} \quad \text{Et} \quad \text{Ph} \\ \diagup \quad \diagdown \quad \\ \text{Se}^+ \\ \\ \text{ClO}_4^- \end{array}$	
(S)	
$[\alpha]_D$ (acetone)	+12.3°
CD[θ] (MeOH) 262 nm	- 854

Fig. 4. Configuration of (+)-5.

Asymmetric induction was also observed in the alkylation of 2-methoxycarbonyl-1-indanone (6) with optical active selenonium salt 1¹). When 6 was treated with 1 ($[\alpha]_D +62.6$) in the presence of potassium carbonate at room temperature, optical active C-methylated product (S)(-)-7 was obtained in 70% yield. $[\alpha]_D -8.91$ (c 0.91, CHCl_3), e.e. 24.4%.

References

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