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SYNTHESIS OF NORBORNENE EPISULFIDES USING ARENETHIOSULFENYL CHLORIDES

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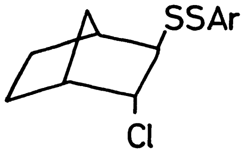
Preparation of new kinds of norbornene episulfides by use of arenethiosulfenyl chlorides has been investigated. Norbornene and 7,7-dimethylnorbornene afforded exo and endo epithio derivatives, respectively. Norbornadiene gave a mixture of exo and endo mono-epithio compounds. The structure of the episulfides and of the intermediately formed adducts of the norbornenes with the chlorides is discussed on the basis of nmr spectra.

We wish to report a method for preparing new kinds of norbornene episulfides. Although epoxides of norbornenes are well known, the corresponding episulfide reported so far is only endo-2,3-epithio-5-norbornene (**8**),1a) which was obtained by the treatment of exo,exo-3,5-dichloro-8-thiatricyclo[2.2.1.1^{2,6}]octane with potassium cyanide. The reaction of these epoxides with thiourea or potassium thiocyanate, which is the most commonly used route for episulfide synthesis,2) could not take place and the starting materials were recovered, because norbornene system compounds are tightly rigid olefins.3) Thus, we applied the episulfidation procedure using arenethiosulfenyl chlorides4) to the synthesis of highly strained norbornene system episulfides.

o-Nitrobenzenethiosulfenyl chloride reacted with norbornene to give a crude disulfide adduct5) quantitatively, when the chloride was dropped into a solution of norbornene in methylene chloride at refluxing temperature. The adduct was confirmed to be exo-2-o-nitrophenyldithio-endo-3-chloronorbornane (**1**) because the splitting patterns in the nmr spectrum resemble those of exo-2-phenylthio-endo-3-chloronorbornane.6) The observed splitting patterns and coupling constants indicate a trans relationship with the chemical shifts of the endo proton at δ 2.71 and the exo proton at δ 4.02 (J = 4.6Hz). When the crude adduct was slowly added to sodium amide at the temperature of 90-95°C under reduced pressure (3mmHg), an oily product was collected in a cold trap. Distillation of the product at 30-31°C/5mmHg yielded 2,3-epithionorbornane (**2**): mp 30-32°C, MS: m/e 126 (M^+). The chemical shifts and coupling constants of **2** (anti 7-H, δ 0.85 and syn 7-H, δ1.24) suggest the exo orientation of the epithio group by comparison with those of the exo epoxide[7] (δ 0.07 and 1.35) and the exo aziridine[8] (δ 0.85 and 1.22) derivatives.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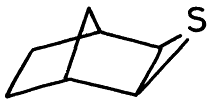
Ar = o-$NO_2C_6H_4$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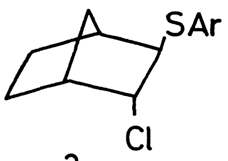
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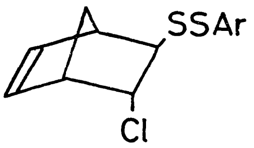
It is noteworthy that **2** was also obtained in 20 % yield by the treatment of monosulfide adduct (**3**), prepared from norbornene and o-nitrobenzenesulfenyl chloride, with sodium amide.

It is difficult to prepare norbornadiene monoepoxide from the corresponding diene by peracid oxidation.[9] However, the corresponding monoepisulfide of norbornadiene could be obtained from norbornadiene by the episulfidation. Although o-nitrobenzenethiosulfenyl chloride formed an adduct, it reacted explosively with sodium amide to yield only 8 % of the expected episulfide. On the other hand, the episulfidation of norbornadiene proceeded smoothly with the use of p-toluenethiosulfenyl chloride to give the corresponding episulfide in 63 % yield. The reaction between the reagents occurred at 0-5°C to give a crude adduct in quantitative yield. A mixture of exo-2-p-tolyldithio-endo-3-chloro-5-norbornene (**4**) and endo-2-p-tolyldithio-exo-3-chloro isomer (**5**) was isolated by column chromatography. The structure of the isomers can be confirmed by nmr spectrum: an exo proton at δ 4.05 and endo proton at δ 2.76 suggested the existence of **4**, and the chemical shift at δ 3.45 was assigned to the exo and endo protons of **5**. The disulfide adducts are considerably unstable and decompose to the corresponding monosulfides in glpc at 200°C. The nortricyclene type of adduct (**6**) was also isolated as a monosulfide[10] by preparative glpc. The crude mixture of adducts was treated with sodium amide to give 2,3-epithio-5-norbornene, MS: m/e 124 (M^+). The episulfide consisted of two components in a ratio of 70:30, which could be isolated by preparative column chromatography. The major product was confirmed to be exo-episulfide (**7**) by its nmr spectrum, which displays a doublet at δ 1.27 (1H) characteristic of an anti-7-proton, a doublet at δ 1.83 (1H) for a syn-7-proton and a triplet at δ 6.34 (2H) for olefinic protons. The minor product showed identical glpc retention time, ir and nmr with those of endo-2,3-epithio-5-norbornene (**8**) of authentic sample.[1a] The behavior of chemical shifts of the exo and endo compounds is identical with that of exo- and endo-tricyclo[3.2.1.0^{2,4}]oct-6-enes.[11)]



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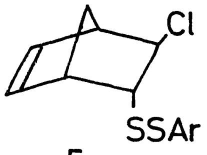

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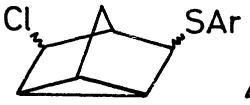
Ar = p-$CH_3C_6H_4$



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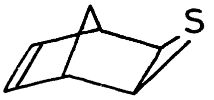

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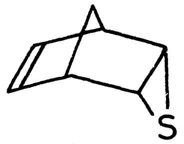

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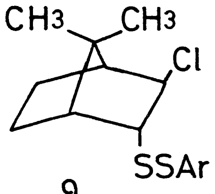
For the stereochemistry of additions to 7,7-dimethylnorbornene, these substituents has been proposed to direct the reaction to proceed preferentially endo when it proceeds through a cyclic intermediate.[12)] Addition of p-toluenethiosulfenyl chloride to 7,7-dimethylnorbornene took place slowly and an adduct (9) was obtained quantitatively. The adduct 9 was confirmed to be exclusively one component by nmr data. The observed splitting patterns and coupling constants indicate a trans relationship with an exo proton at δ 3.96 and an endo proton at δ 3.67. The nmr data resembling that of endo-2-phenylthio-exo-3-chloro-7,7-dimethylnorbornane[12)] suggest that 9 has an exo-chloro and endo-p-tolyldithio orientation. Treatment of the crude adduct 9 with sodium amide yielded an episulfide (10), mp 57-58°C, MS: m/e 154 (M^+). The difference in the chemical shifts of the two methyl singlets (δ 1.04 and 1.33) indicates the endo orientation of the epithio group, through identification with the difference of those for endo-epoxy-7,7-dimethylnorbornane (δ 0.91 and 1.21) prepared from the corresponding norbornene by oxidation with m-chloroperbenzoic acid.[13)]

Episulfidation was also successful in the treatment of adducts with sodium sulfide[14)] instead of sodium amide as listed in Table. These episulfides are stable and neither decompose nor isomerize even in glpc at 130°C

Table. Episulfidation of Norbornenes Using Arenethiosulfenyl Chlorides

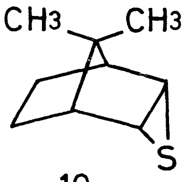
Starting Norbornene	Ar in ArSSCl	Product	Orientation	mp °C, or (bp °C/mmHg)	Yield[a,b)] % $NaNH_2$	Na_2S
Norbornene[c)]	o-$NO_2C_6H_4$	2	exo	30-32	65	84
Norbornadiene	o-$NO_2C_6H_4$	7, 8	exo, endo	(27-28/1)[d)]	8	63 (79:21)
	p-$CH_3C_6H_4$	7, 8	exo, endo		63 (70:30)	78 (77:23)
7,7-dimethyl-norbornene	o-$NO_2C_6H_4$	10	endo	57-58	32	44
	p-$CH_3C_6H_4$	10	endo		30	50

a) Isolated yield based on arenethiosulfenyl chloride used. b) The ratio of exo and endo isomers by glpc is given in parentheses. c) p-Toluenethiosulfenyl chloride reacted with norbornene even at -78°C to give only monosulfide adduct, exo-2-p-tolylthio-endo-3-chloronorbornane, which could not yield the episulfide. d) Bp of the mixture of exo and endo isomers. Lit mp of endo isomer, 45-47°C(Ref. 1a).



9

Ar= p-$CH_3C_6H_4$ or o-$NO_2C_6H_4$



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The present results therefor reveal that the stable orientation of the episulfonium salt as an intermediate in the addition stage[4] exerts steric control on this episulfidation reaction. Thus, norbornene and 7,7-dimethylnorbornene give exclusively exo and endo episulfides, respectively. Norbornadiene can be attacked from both exo and endo sides by a thiosulfenium cation, exo and endo episulfides are obtained.

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