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Palladium-catalysed Synthesis of α-Diallylated Ketosulphides of Benzothiazole and their Transformation into Diallyl Thiiranes and Trienes

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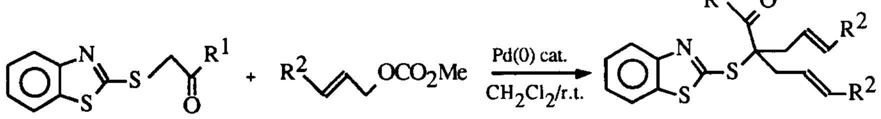
Abstract. α-Ketosulphides of benzothiazole **1** react with allylic carbonates in the presence of palladium acetate in dichloromethane under mild conditions affording α,α-diallylated ketosulphides **2** in high yields. Reduction of **2** with sodium borohydride in isopropanol gives episulphides which in turn can be transformed almost quantitatively into trienes.

Palladium catalysed allylic substitution is a versatile process encompassing a wide range of allyl systems and their nucleophilic partners[1-4]. Among allylic systems, the use of carbonates as leaving groups has gained in popularity since the development of these reagents by Tsuji.[3] The initially displaced carbonate loses carbon dioxide generating an alkoxide which is sufficiently basic to deprotonate active methylene compounds as malonates or β-ketoesters. Contrary to silyl enol ethers or enamines,[5] simple ketones cannot be allylated satisfactorily with allylic carbonates. On the other hand the introduction of two allylic groups at the α-position of ketones, which can be done in principle by regioselective consecutive allylation is generally difficult since the generation of an anion at the same carbon after the first allylation is inhibited and as a consequence α,α'-dialkylated products are obtained.[6]

We wish to report that α-ketosulphides of benzothiazole[7] **1** react with allylic carbonates in the presence of palladium acetate and triphenylphosphine in dichloromethane under mild conditions to afford α,α-diallylated ketosulphides **2** in high yields. (Scheme 1).

Scheme 1



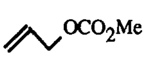
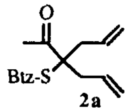
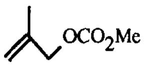
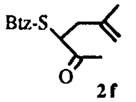
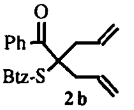
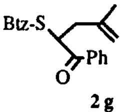
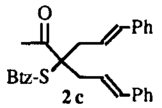
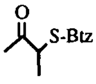
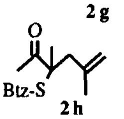
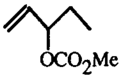
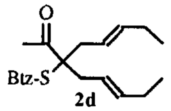
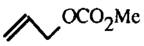
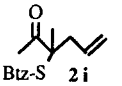
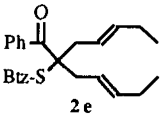
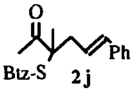
1a,b

2a-e

a, R^1=Me; **b**, R^1=Ph

As reported in table 1, stereoselective allylic rearrangement are observed in the reactions of **1a,b** with some allylic carbonates to give only the E isomers (products **2c-e**). Allylation of these ketosulphides with β-methallyl carbonate afforded only monoallylation products (**2f,g**) even in the presence of large excess of the carbonate. This is probably due to the steric hindrance of the monoallylated ketosulphide. α–Substituted ketone **1c** gave monoallylated products (**2h-j**) as expected.

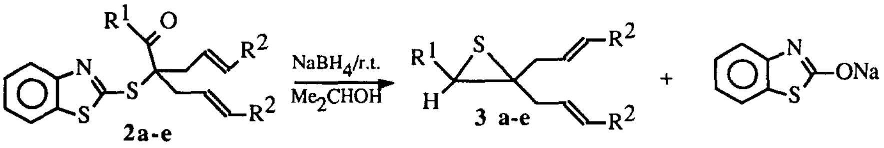
Table 1. Pd^0-Mediated Allylation of Ketosulphides of benzothiazole by Allylic Carbonates.[a]

Carbonate	Ketone	Product[b]	Yield(%)[c]	Carbonate	Ketone	Product[b]	Yield(%)
	1a	 2a	85		1a	 2f	88
"	1b	 2b	86	"	1b	 2g	91
	1a	 2c	78[d]	"	 1c	 2h	93
	1a	 2d	77[d]		1c	 2i	96
"	1b	 2e	82[d]		1c	 2j	71

[a] All reactions were run under nitrogen at r.t. in dichloromethane during 1-3 h. [carbonate]: [ketone]: [Pd]: [phosphine] =3: 1: 0.05: 0.25. [b] All products gave the expected ^{1}H, ^{13}C NMR, IR and mass spectra. [c] Isolated yields. [d] E-isomer.

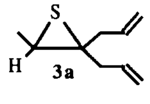
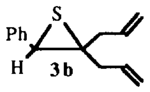
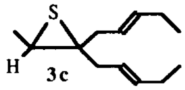
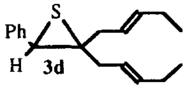
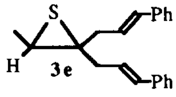
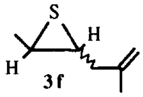
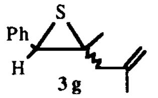
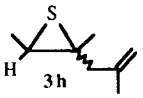
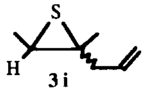
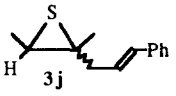
The carbonyl reduction of these compounds with sodium borohydride in isopropanol (Scheme 2) gave directly diallylated episulphides together with 2-hydroxybenzothiazole as byproduct, which can be separated by washing the ethereal extract with sodium carbonate solution.

Scheme 2



This reaction is characteristic for β-hydroxy sulphides of benzothiazole as reported previously by us[7] whereas other different β-hydroxy sulphides did not react under the same reaction conditions. The results are reported in table 2.

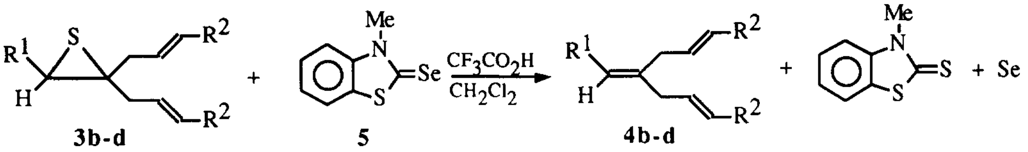
Table 2. Synthesis of episulphides from allylated ketosulphides of benzothiazole.[a]

Ketone	Episulphide[b]	Yield(%)[c] (E:Z ratio)[d]	Ketone	Episulphide	Yield(%)[c] (E:Z ratio)[d]
2a	 **3a**	88	**2b**	 **3b**	85
2c	 **3c**	78	**2d**	 **3d**	90
2e	 **3e**	85	**2f**	 **3f**	70 (60:40)
2g	 **3g**	75 (87:13)	**2h**	 **3h**	60 (59:41)
2i	 **3i**	40 (57:43)	**2j**	 **3j**	65 (85:15)

[a] All reactions were run at r.t. in isopropanol during 5h. [Ketone]: [$NaBH_4$]= 1: 1. [b] All products gave the expected ^1H, ^{13}C NMR, IR and mass spectra. [c] Isolated yields. [d] Evaluated by ^1H NMR.

Reaction of dienyl episulphides with 3-methyl-2-selenoxobenzothiazole[8,9] **5** in dichloromethane or with triphenyl phosphine in boiling THF afforded trienes almost quantitatively (Scheme 3).

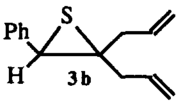
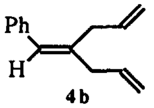
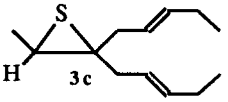
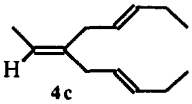
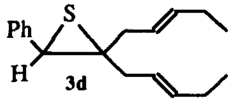
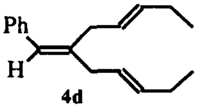
Scheme 3



Some results are reported in table 3.

Beside the synthesis of trienes or dienes which can be further elaborated, the allylated ketones (**2a-j**) can be conveniently desulfurized by reaction with tributyltin hydride in boiling toluene[10,11] to γ,δ-unsaturated ketones which are important intermediates for example for the synthesis of spiro ketals upon peracid oxidation of the double bond.

Table 3. Conversion of allylic episulphides into trienes^a.

Entry	Episulphide	Triene	Yield(%)^b
1	 3b	 4b	95
2	 3c	 4c	97
3	 3d	 4d	98

^{a}All reactions were run in dichlorometane at r.t. [Episulphide]: **5**: Trifluoroacetic acid]: 1: 1: 2. ^{b}Yields evaluated by GC. All products gave the expected ^{1}H, ^{13}C NMR, IR and mass spectra.

General procedure

(a) Allylation of ketosulphides. A mixture of palladium acetate (0.05 mmol), triphenylphosphine (0.25 mmol) carbonate (3 mmol) and ketosulphide (1 mmol) in CH_2Cl_2 (15 ml) was stirred under a nitrogen atmosphere at r.t. until the disappearence of the sulphide (TLC). Concentration in vacuo and chromatographic purification (SiO_2) of the residue provided the diallylated ketone(s). **(b) Synthesis of episulphides.** To the allylated ketone (0.9 mmol) dissolved in isopropanol (10 ml) was added portionwise $NaBH_4$ (0.9 mmol) under stirring at r.t. After the disappearence of the ketone, the solution was evaporated and the residue dissolved in ether was washed with a 5% Na_2CO_3 solution and dried on Na_2SO_4 . Evaporation of the solvent leaves almost pure episulphide. **(c) Synthesis of trienes.** The episulphide (0.9 mmol), 2-selenoxobenzothiazole **5** (0.9 mmol) and trifluoroacetic acid (1.8 mmol) dissolved in 5 ml of dichloromethane were stirred at r.t. until the disappearence of the episulphide (TLC). After the filtration of selenium, concentration in vacuo and chromatography (SiO_2) provided the triene.

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References and notes

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