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LEWIS ACID INITIATED OR HIGH PRESSURE PROMOTED REACTIONS OF ISOPRENE WITH PHENYLSULPHINYL CHLORIDE

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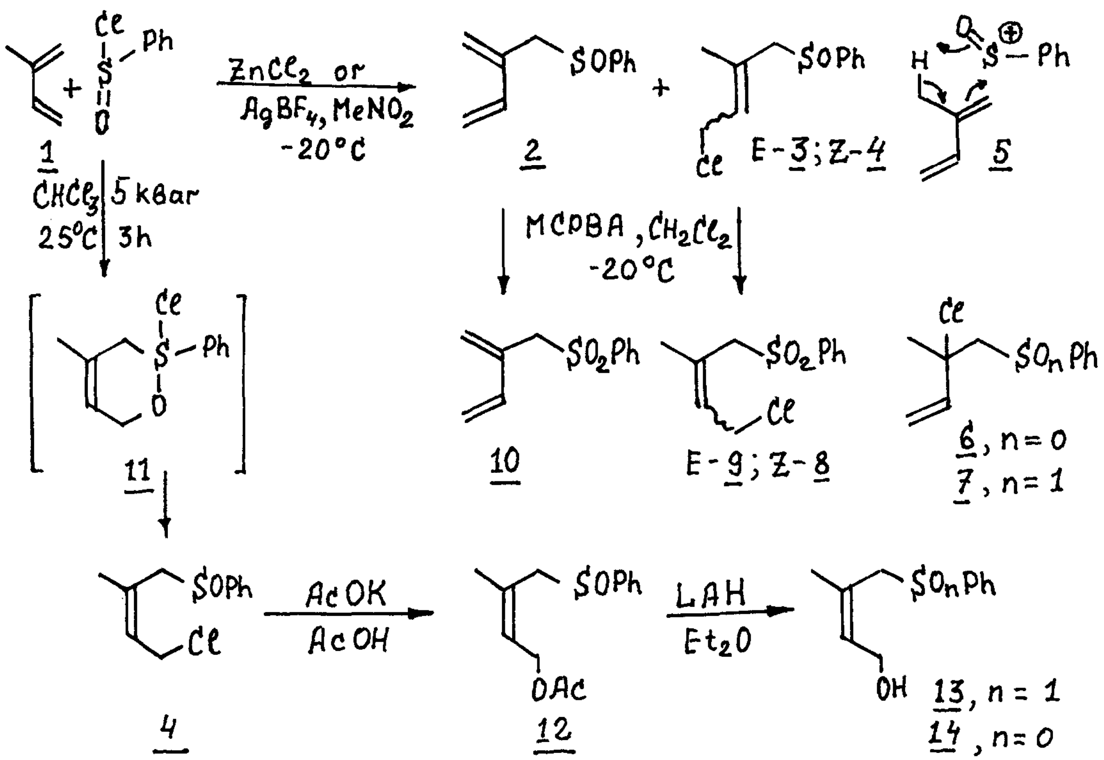
Summary. Lewis acid initiated reaction of isoprene with PhSOCl proceeds in a ene fashion with the formation of 2-phenylsulphinylmethyl-1,3-butadiene. High pressure promoted addition produces Z-1-phenylsulphinyl-4-chloroadduct presumably *via* [4+2] cycloaddition.

According to existing scarce reports,[1] Ad_E-reaction of ArSOCl with alkenes proceeds only in the presence of Lewis acids and yields respective 1, 2-arylsulphinyl chloroadducts. No data are available on the reactivity pattern of 1,3-dienes in this reaction. In the search of novel methods for the regiospecific isoprene (1) functionalization we have studied the interaction of 1 with PhSOCl under various conditions.

The addition of PhSOCl to 1 was found to proceed smoothly in the presence of Lewis acids (e.g. $ZnCl_2$, $SnCl_4$, $TiCl_4$, $BF_3 \cdot Et_2O$) in CH_2Cl_2 or $MeNO_2$ at $-20 \div 0^{o}C$ producing the mixture of diene 2 and E,Z-chloroolefins 3,4 (Scheme) their separation being easily achieved by flash chromatography (SiO_2, gradient elution from hexane to ether). Under optimal conditions ($-20^{o}C$, $MeNO_2$, 1 : PhSOCl:$ZnCL_2$ = 3:1:1) 2 is formed as a major product (2:3:4 ≃ 15:5:1, total yield 80%). Similar reaction performed with $AgBF_4$ instead of $ZnCl_2$ gave 2 as a single product[2] with *ca.* 75% isolated yield (b.p. $100-103^{o}C/0.05$ torr; n_D^{20} 1.5873; PMR, 250 MHz, $\delta^{CDCl_3}_{TMS}$: 3.69 ppm,q, AB, CH_2S). Sulphoxide 2 was transformed with MCPBA into the known[3] sulphone 10 (m.p.65-65.5°C, from ether-hexane; δ 4.00 s, CH_2S).[2,4] E-Configuration of the main isomer of 1,4-adduct 3 (m.p. 65-66°C from ether-hexane; δ 3.50 bs, CH_2S, 4.11 d, J=7.8 Hz, CH_2Cl)[2] was checked by its MCPBA oxidation to the

Scheme



known[5] E-sulphone 9. The structure of the minor isomer 4 will be discussed below.

To account for the exclusive formation of 2 in AgBF$_4$ initiated reaction it can be suggested that the addition of incipient phenylsulphinyl cation to 1,2-double bond of 1 proceeds in an ene-like fashion *via* six-membered transition state 5. Similar mechanism is evidently operating in ZnCl$_2$ induced reaction. Adducts 3 and 4 formed in the latter case probably arose due to secondary process involving the initial formation of 1,2-adduct 7 followed by its non-stereospecific isomerization into the mixture of 1,4-adducts in the presence of Lewis acid (*c.f.*[6] similar 1,2 → 1,4 isomerisation of ArSCl -isoprene adducts 6).

An ever increasing number of heterodienic reactions involving various O,N, and S containing dienophiles[7] and ene-like reactivity of PhSOCl observed made it very tempting to look for the conditions of its [4+2] reaction with 1. It turned out however that in the abscence of Lewis acids the interaction of 1 and PhSOCl in various solvents (CH$_2$Cl$_2$, Et$_2$O, THF, glyme, etc.)

proceeds very slowly at ambient temperature ($\leqslant$ 25% of conversion after one week) giving rise rather complicate product mixture. Our attempts to carry out the reaction under more drastic conditions (up to 100°C) failed due to thermolability of PhSOCl.

The benefitial effects of high pressure on the rate and selectivity of [4+2] cycloadditions are well-known.[8] These data encouraged us to test the effect of high pressure on the reaction under study. The result observed was rather unexpected and truly rewarding.

We have found that the application of high pressure (3-5 kbar) to the solution of 2:1 mixture of 1 and PhSOCl in $CHCl_3$ resulted in ca. 75% yield formation of Z-chlorosulphoxide 4 uncontaminated by the admixture of 3 or 2 (250 MHz PMR data). In all runs PMR data revealed the presence of 7-15% of unknown impurity; fortunately, the latter is unstable and is easily removed in the course of further chemical transformation of 4 (vide infra).

The structure of 4 was supported by its PMR spectrum (δ 3.59, AB-quartet, CH_2S and 3.87 ppm, AB-part of ABX system, CH_2Cl). The comparison of CMR spectrum (62.08 MHz, $CDCl_3$) of 4 with that of E-isomer 3 revealed the substantial upfield shift of CH_2S signals in the former (δ 60.6 for 4 and 67.7 ppm for 3). Both $\Delta\delta$ sign and its magnitude are in a well accord with the stereochemistry ascribed to these compounds.[9] MCPBA oxidation of 4 yields the known[3] Z-sulphone 8, m.p. 88-89°C (from ether-hexane).[2,4] The same shift, $\Delta\delta \simeq 7$ ppm, was observed for CH_2S signals within the pair 9 and 8.

The mechanism of high pressure promoted formation of 4 is at present unclear. We believe however that the observed Z-stereospecificity of its formation is certainly indicative of some kind of cycloaddition process involved. One may suggest that the addition of PhSOCl to 1 proceeds in a [4+2] fashion via six-membered σ-sulphurane intermediate 11. Intrinsic instability of the latter precludes its isolation; the proposed isomerization 11 → 4 has some analogy with the chemical transformations observed for the stabilized σ-sulphuranes.[10]

Easily accessible chlorosulphoxide 4 represents a novel Z-isoprenoid synthon which could be converted to a series of related functionalized derivatives. For example, acetolysis of 4 yields (~75%) oily sulphoxide 12

(δ 3.65, AB-quartet, CH_2S, and 4.32 ppm, AB-part of ABX system, CH_2O).[2] Reduction of 12 with LAH at -20°C proceeds selectively to give 70% yield of hydroxy sulphoxide 13 as an oil; its spectral data matched those reported earlier[11] for this compound. Similar reduction at 25°C produces (~ 75%) oily hydroxy sulphide 14 (b.p. 96-98°C/0.07 torr; n_D^{20} 1.5840; δ 1.88 bs, CH_3, 3.50 s, CH_2S, 3.78 bd, J=7.0 Hz, CH_2O, 5.48 bt, HC=C).[2]

Thus, the reaction of 1 with PhSOCl could serve as the selective preparative method for the synthesis of either diene 2 or Z-adduct 4. Both products and derived diene 10 and Z-1,4 -bifunctional compounds 12-14 are well suited for their further use as the isoprenoid synthons. Preliminary studies also indicated that diene 10 is able to react with typical dienophyles (e.g. maleimides) and hence could be used for the synthesis of cyclic isoprenoids *via* [4+2] reaction with suitable substrates.

Our further work is aimed at the evaluation of applicability of the disclosed 1,2-ene and Z-1,4-stereoselective additions to other 1,3-dienic systems.

References and Notes

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