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AMINIUM RADICAL SALT CATALYZED DESULPHURIZATION OF THIIRANES: AN EFFICIENT PREPARATION OF ARYLSUBSTITUTED OLEFINS

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Summary: Arylsubstituted olefins are obtained from corresponding thiiranes in high yields under mild conditions by using catalytic amount of tris-(p-bromophenyl)aminium hexachloroantimonate (**1**) as a single electron transfer (SET) oxidant.

Desulphurization of thiiranes is a useful method for the preparation of olefins. A wide variety of desulphurization reagents are utilized, e.g. phosphorous compounds,[1] organolithium compounds,[2] Grignard reagents,[3] and iron carbonyl complexes.[4] Those reactions require more than equivalent amount of reagents to thiiranes. However, so far the catalytic desulphurization of thiiranes has never been reported. We now report an efficient conversion of arylsubstituted thiiranes to corresponding olefins catalyzed by tris-(p-bromophenyl)aminium hexachloroantimonate (**1**)[5], which is well known as an effective SET oxidant.[6]

We conducted the reaction of 2,2,3,3-tetraarylthiiranes (**2a-e**)[7] and 2,2,3-triarylthiiranes (**2f-j**) with aminium radical salt (**1**). Thiiranes (**2a-j**) were easily prepared by the reaction of corresponding thiobenzophenone derivatives with diaryldiazomethanes or aryldiazomethanes. A typical experimental procedure is as follows. Aminium radical salt (**1**) [0.30 mmol, 0.1 equiv. to (**2a**)] was added to a stirred solution of (**2a**) (3.00 mmol) in dry dichloromethane (60 ml) and the mixture was stirred for 1 h at 0°C under nitrogen atmosphere. Subsequently, the reaction was quenched by addition of 1,4-diazabicyclo[2,2,2]octane (0.30 mmol). Column separation (silica gel, n-hexane-dichloromethane) afforded (**3a**)[8] in 98% yield. Similarly, thiiranes (**2b-j**) were found to undergo an efficient conversion to olefins (**3b-j**).[8] The results are summarized in Table 1.

Detailed mechanistic studies further provided the following results: i) addition of 1,2,4,5-tetramethoxybenzene[9] [TMB, 5 equiv. to (**1**)], which

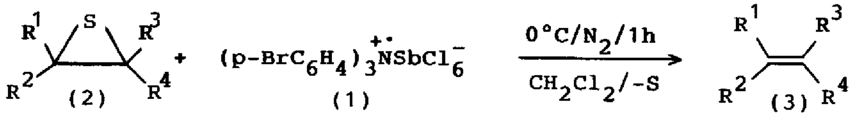


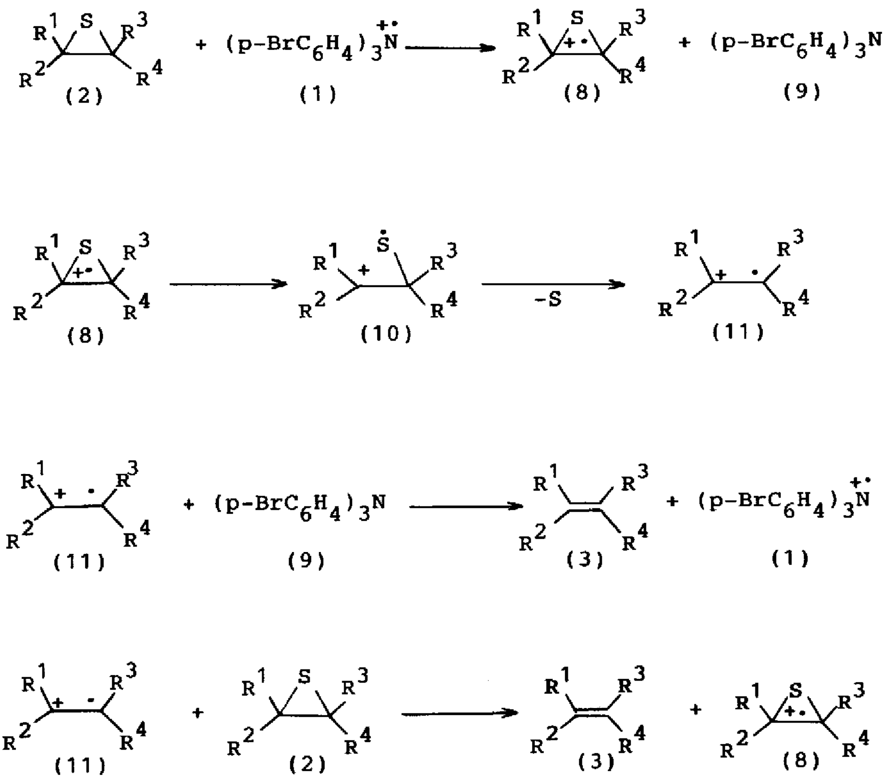
Table 1. Preparation of arylsubstituted olefins (3) by catalytic desulphurization of (2) with (1).

$(2)^a$	$E^{ox}_{1/2}/V^b$ vs. SCE	yield of (3)/%^{c}	m.p. of (3)/°C (lit. m.p.)
2a; $R^1=R^2=p\text{-}MeOC_6H_4$, $R^3=R^4=Ph$	1.44	98	157-158(154)^d
2b; $R^1=R^2=p\text{-}MeOC_6H_4$, $R^3=R^4=p\text{-}ClC_6H_4$	1.50	98	196-197
2c; $R^1=p\text{-}MeOC_6H_4$, $R^2=R^3=R^4=Ph$	1.51	90	132-133
2d; $R^1=R^2=p\text{-}MeC_6H_4$, $R^3=R^4=Ph$	1.74	98	166-167
2e; $R^1=R^2=R^3=R^4=Ph$	1.84	98	220-222(223-224)^e
2f; $R^1=R^2=R^3=p\text{-}MeOC_6H_4$, $R^4=H$	1.45	93	69-70(100-101)^f
2g; $R^1=R^2=p\text{-}MeOC_6H_4$, $R^3=p\text{-}MeC_6H_4$, $R^4=H$	1.50	95	97-98(87)^g
2h; $R^1=R^2=p\text{-}MeOC_6H_4$, $R^3=Ph$, $R^4=H$	1.50	94	78-79(62-64)^f
2i; $R^1=R^2=p\text{-}MeOC_6H_4$, $R^3=p\text{-}ClC_6H_4$, $R^4=H$	1.50	98	94-95
2j; $R^1=R^2=Ph$, $R^3=p\text{-}MeOC_6H_4$, $R^4=H$	1.55	98	83-84

[a] (2) = 3.00 mmol, (1)=0.30 mmol, CH_2Cl_2=60 ml. [b] Measured by cyclic voltammetry at a platinum electrode in CH_3CN with 0.10 M tetraethylammonium perchlorate as a supporting electrolyte, SCE = saturated calomel electrode. [c] Isolated yields. [d] Reference 14. [e] Reference 15. [f] Reference 16. [g] Reference 17.

is known as an efficient quencher for SET processes,[6d, 6e] supressed the desulphurization of (2a), while no quenching was observed when anisole[9] [AN, 5 equiv. to (2a)] was added; ii) treatment of cis-2,3-diphenylthiirane (4a) with (1) afforded both cis-stilbene (5a) (29%) and trans-stilbene (5b) (40%), while trans-2,3-diphenylthiirane (4b) afforded only (5b) (84%); iii) tris-(2,4-dibromophenyl)aminium hexachloroantimonate (6)[10] which is a stronger catalyst than (1) also resulted in the desulphurization of (2a), while triphenylcarbenium hexachloroantimonate (7)[12] could not catalyze the reaction. These results indicated that this reaction is initiated by SET from thiiranes (2) to aminium radical salt (1). A plausible mechanism taking all above observations into account is proposed in Scheme 1.

Scheme 1



The first step is the formation of thiirane radical cations (8) and tris-(p-bromophenyl)amine (9). The next step is the C-S bond cleavage of (8) to give radical cations (10) which undergo desulphurization to give radical cations (11). The SET from (9) to (11) reproduces (1) accompanied by the formation of (3). Also, (3) can be formed by the SET from (2) to (11).

References and Notes

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8) Satisfactory elemental analysis and spectroscopic data were obtained for all olefins (**3a-j**).

9) The calculated ΔG value for SET from TMB to (**1**) is -3.5 kcal/mol in CH_2Cl_2 employing the equation $\Delta G = 23.06[E^{ox}_{1/2}(TMB) - E^{red}_{1/2}(\mathbf{1}) + 0.16]$ kcal/mol, where $E^{ox}_{1/2}(TMB)$ is 0.74 V and $E^{red}_{1/2}(\mathbf{1})$ is 1.05 V vs. SCE. That from AN ($E^{ox}_{1/2}$ = 1.74 V vs. SCE in CH_3CN) to (**1**) is 19.6 kcal/mol in CH_2Cl_2.

10) $E^{red}_{1/2}(\mathbf{6})$ = 1.49 V (vs. SCE in CH_3CN) estimated from the oxidation potential of tris-(2,4-dibromophenyl)amine.[11]

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