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1,2-Disulphenylation of Alkenes Induced by a Hypervalent Iodine(III) Reagent [PhIO–TfOH]

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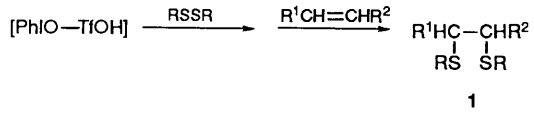
Addition of diphenyl disulphide and dimethyl disulphide to alkenes successfully proceeded with [PhIO–TfOH] to give high yields of 1,2-bis(phenylthio)alkanes and 1,2-bis(methylthio)alkanes, respectively.

Recent development of hypervalent iodine(III) chemistry has provided much interest in organic synthesis.[1] Our recent result showed that iodosylbenzene (PhIO) activated by trifluoromethanesulphonic acid (TfOH) easily added to alkynes to give (*E*)-β-(trifluoromethylsulphonyloxy)vinyliodonium triflates.[2] However, there are no reports on activation of disulphides by use of hypervalent iodine species as far as we know. The high reactivity of the reagent [PhIO–TfOH] compared with Koser reagent [Ph(OH)OTs][3] allows us to use it for activation of disulphides. This paper reports a novel method for the activation of disulphides to allow 1,2-addition of RSSR (R = Ph and Me) to alkenes with [PhIO–TfOH].



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The reagent [PhIO–TfOH] was prepared by mixing PhIO (10 mmol) and TfOH (10 mmol) in CH_2Cl_2 (20 ml) and then stirring the mixture for 2 h.[2] PhSSPh (5 mmol) was added at 0 °C to the mixture which was then stirred at room temperature for 1–3 h. Finally, alkene (5 mmol) was added to the mixture and stirring continued for 12 h. After work-up of the reaction mixture the product was separated by Chromatotron after removal of PhI under reduced pressure. The results are given in Table 1. High yields of 1,2-bis(phenylthio)alkanes **1** were obtained by this method. However, no 1,2-bis(phenylthio)cyclohexane **1b** (R = Ph) was formed when PhIO, PhSSPh and TfOH were mixed together and cyclohexene was added. This result means that initial formation of [PhIO–TfOH] is essential. Next, we examined the catalytic action of [PhIO–TfOH]. PhSSPh was added to a solution of 40 or 10% mol equiv. of [PhIO–TfOH] in CH_2Cl_2 and this was followed by addition of alkenes. The same procedure was also conducted for dimethyl disulphide. The results showed that catalytic 1,2-bisphenylthiolation and 1,2-bismethylthiolation worked very well. *trans*-Addition of RSSR to alkenes was confirmed by comparison of the product **1b** (R = Me) obtained from cyclohexene and dimethyl disulphide with an authentic sample,†[4] Furthermore, formation of only a small amount of PhI after work-up makes the purification procedure easy.

† Chemical shift (δ 2.64–2.70) of the protons on the carbon substituted by sulphur in **1b** (R = Me) also supports the *trans* stereochemistry because the value of the chemical shift is accord with an axial proton, δ 2.57 (R = SH).[5]

As has been recognized in the reaction of organoiodine(III) species,[1] [PhI^+–OH] generated from PhIO and TfOH acts as a Lewis acid and activates RSSR. Accordingly, [PhI^+–OH] adds to RSSR to form the activated species [PhI(OH)–S^+(R)–SR] which reacts with alkenes either directly or indirectly *via* dithiosulphonium ion [RS^+(SR)–SR]. The latter path has been observed previously.[4] Finally, the resulting episulphonium ion reacts with a disulphide or Ph(OH)SR to give 1,2-bis(phenylthio)alkanes **1** (R = Ph) or 1,2-bis(methylthio)-alkanes **1** (R = Me).

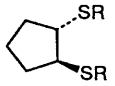
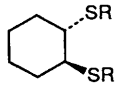
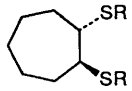
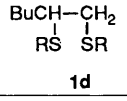
In summary, hypervalent iodine species [PhIO–TfOH] acted as an effective reagent for disulphenylation of alkenes. This one-pot reaction is shown to be useful, in addition to the previous reported reaction with BF_3–OEt_2.[4]

Experimental

Typical Procedure.—To a suspension of PhIO (0.11 g, 0.5 mmol) in CH_2Cl_2 (20 ml) was added TfOH (0.044 ml, 0.5 mmol) at 0 °C. After 2 h at room temperature, a solution of PhSSPh (1.09 g, 5 mmol) in CH_2Cl_2 (6 ml) was added dropwise at 0 °C. After 2 h at room temperature, cyclohexene (0.51 ml, 5 mmol) was added at 0 °C and the mixture was stirred for 12 h. The whole was poured into water and extracted with ether. The organic layer was washed, dried and concentrated under reduced pressure and the residual PhI removed from the product *in vacuo* at 70–80 °C. The product was subjected to preparative centrifugal thin-layer chromatography (Chromatotron) on silica gel with CH_2Cl_2–hexane (1:1). Conveniently, in the cases of catalytic reactions, direct separation could be conducted without pre-removal of PhI under reduced pressure because of the small amount of the latter present.

Selected Spectral Data.—**1a** (R = Ph): δ_H(60 MHz; $CDCl_3$) 1.40–2.48 (6 H, m, $CH_2CH_2CH_2$), 3.35–3.64 (2 H, m, CHCH) and 6.90–7.27 (10 H, m, Ph); δ_C(250 MHz; $CDCl_3$) 23.12, 30.88, 52.65, 126.57, 128.79, 131.12 and 135.45; *m/z* 286 (M^+, 8%), 177 (94), 123 (15), 68 (100) and 66 (20). **1a** (R = Me): δ_H(60 MHz; $CDCl_3$) 1.55–1.80 (6 H, m, $CH_2CH_2CH_2$), 2.14 (6 H, s, Me) and 2.89–3.00 (2 H, m, CHCH); δ_C(250 MHz; $CDCl_3$) 15.05, 23.70, 32.45 and 51.88; *m/z* 162 (M^+, 13%), 148 (100) and 104 (13). **1b** (R = Ph): δ_H(60 MHz; $CDCl_3$) 1.20–2.50 (8 H, m, $CH_2CH_2CH_2CH_2$), 3.10–3.45 (2 H, m, CHCH) and 6.93–7.40 (10 H, m, Ph); δ_C(250 MHz; $CDCl_3$) 23.17, 29.38, 49.36, 126.62, 128.74, 132.12 and 134.73; *m/z* 300 (M^+, 9%), 123 (30), 109 (17), 82 (100), 79 (16) and 65 (13). **1b** (R = Me): δ_H(60 MHz; $CDCl_3$) 1.31–1.75 (8 H, m, $CH_2CH_2CH_2CH_2$), 2.11 (6 H, s, Me) and 2.64–2.70 (2 H, m,

Table 1 (PhIO–TfOH)-induced addition of RSSR to alkenes

Alkene	Disulphide	[PhIO–TfOH] (mol equiv.)	Adduct	Isolated yield (%)
	PhSSPh	2	 **1a**	84 (R = Ph)
		0.4		92 (R = Ph)
	MeSSMe	0.4		94 (R = Me)
	PhSSPh	2	 **1b**	74 (R = Ph)
		0.4		85 (R = Ph)
		0.1		92 (R = Ph)
	MeSSMe	0.4		77 (R = Me)
	PhSSPh	2	 **1c**	92 (R = Ph)
		0.4		90 (R = Ph)
		0.1		98 (R = Ph)
$BuCH{=}CH_2$	PhSSPh	2	 **1d**	83 (R = Ph)
		0.4		88 (R = Ph)
		0.1		92 (R = Ph)

CHCH); δ_C(250 MHz; $CDCl_3$) 14.06, 24.61, 31.57 and 49.21; *m/z* 176 (M^+, 10%), 162 (24), 148 (100) and 82 (29). **1c** (R = Ph): δ_H(60 MHz; $CDCl_3$) 1.40–2.30 (10 H, m, $CH_2CH_2CH_2CH_2CH_2$), 3.30–3.57 (2 H, m, CHCH) and 6.90–7.35 (10 H, m, Ph); δ_C(250 MHz; $CDCl_3$) 23.79, 28.45, 30.29, 53.15, 126.80, 128.91, 131.83 and 135.40: *m/z* 314 (M^+, 10%), 205 (75), 123 (46), 109 (19), 96 (100) and 67 (23). **1d** (R = Ph): δ_H(60 MHz; $CDCl_3$) 0.70–2.10 (9 H, m, Bu), 2.90–3.70 (3 H, m, $CHCH_2$) and 6.90–7.56 (10 H, m, Ph); δ_C(250 MHz, $CDCl_3$) 14.12, 22.63, 29.08, 32.46, 39.61, 48.49, 126.34, 127.29, 129.03, 129.06, 129.91, 132.64, 134.61 and 136.11; *m/z* 302 (M^+, 13%), 193 (93), 123 (100), 109 (40) and 84 (47).

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