

REACTION OF ALKENES WITH IODINE (I) THIOCYANATE

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Although reactions of a variety of alkenes with iodine(I) thiocyanate have been reported,¹ and kinetic data² support an ionic pathway involving an open carbonium ion, little conclusive identification of products has been made.^{1,2} With one exception³ ISCN has been generated by treatment of thermally unstable thiocyanogen, (SCN)₂, with iodine: limited spectroscopic data⁴ indicate partial reaction in this system to form ISCN which has reasonable stability^{1f} in solution (HOAc, Et₂O, C₆H₆). An investigation of alternative syntheses of vicinal iodothiocyanates and iodoisothiocyanates has resulted in experimentally simple procedures which do not involve prior formation of (SCN)₂. Thus, reaction of ICl (1.5 mmol) with KSCN (2.5 mmol) in CHCl₃-sulpholane (1:1, 10 ml) at 0° for 2 h gave a blood-red solution to which cyclohexene (1.25 mmol) was added. After 4 h at 0° in the dark work-up gave trans-1-iodo-2-thiocyanatocyclohexane (67%),⁵ trans-1-iodo-2-isothiocyanatocyclohexane (1%)⁶ and a trace of trans-1-chloro-2-iodocyclohexane. Use of sulpholane or CHCl₃-sulpholane (2:1) as solvents with ICl (1.50 mmol)-KSCN (1.25 mmol) at ambient temperature resulted in increased yields of the iodochloride at the expense of the iodothiocyanate, while CHCl₃-DMSO (1:1) or CHCl₃-HMPT (1:1) decreased the crude yield significantly. However, I₂ (3 mmol)-KSCN (3.75 mmol) and cyclohexene (1.25 mmol) in CHCl₃-sulpholane (1:1, 10 ml) at 0° in the dark for 21 h gave 96% of the trans-iodothiocyanate: the yield from this reaction was unchanged in the presence of galvinoxyl under nitrogen. Use of TlSCN instead of KSCN also gave a crude yield of 96%, but in this case the iodoisothiocyanate (60%)⁵ predominated over the iodothiocyanate (15%). When CHCl₃ (15 ml) was used as solvent with TlSCN the crude product (92%) contained the iodoisothiocyanate and the thiocyanate in the ratio 2:1 (53% and 25% respectively).⁵ Thus simple variation of the metal thiocyanate allows formation of either the iodothiocyanate or the iodoisothiocyanate as the major product. The enhanced yield of iodoisothiocyanate from TlSCN is presumably due to

retention of thallium-sulphur bonding⁷ resulting in increased availability of nucleophilic nitrogen in the potential ambident anion, via a pathway similar to that postulated⁸ for the iodocarboxylation of alkenes using $\text{TlO}_2\text{CR-I}_2$.

Reaction of ICl (2.5 mmol)- KSCN (5 mmol) in CHCl_3 -sulpholane (1:9, 10 ml) gave the cleanest conversion of styrene (1.25 mmol) to the Markownikoff adduct, $\text{PhCH}(\text{SCN})\text{CH}_2\text{I}$ (65%) after 22 h. I_2 (3 mmol)- KSCN (3.75 mmol) in CHCl_3 -sulpholane (1:1, 10 ml) gave only 50% conversion after 68 h and the regioisomer, $\text{PhCH}(\text{I})\text{CH}_2\text{SCN}$, was also isolated (3%), suggesting that the cationic intermediate may be iodonium-like when I_2 is used, but carbonium-like when ICl is used. I_2 (3 mmol)- TlSCN (3.75 mmol) in CHCl_3 (15 ml) gave $\text{PhCH}(\text{SCN})\text{CH}_2\text{I}$ (47%), $\text{PhCH}(\text{NCS})\text{CH}_2\text{I}$ (22%), $\text{PhCHICH}_2\text{SCN}$ (7%), $\text{PhCH}(\text{SCN})\text{CH}_2\text{SCN}$ (1%) and $\text{PhCH}(\text{NCS})\text{CH}_2\text{SCN}$ (<1%). No anti-Markownikoff products were formed from I_2 (2.5 mmol)- TlSCN (3.75 mmol) in CHCl_3 -sulpholane (1:9, 10 ml). The expected iodothiocyanate (29%) and iodoisothiocyanate (12%), $\text{PhCH}(\text{SCN})\text{CH}_2\text{SCN}$ (11%) and $\text{PhCH}(\text{NCS})\text{CH}_2\text{SCN}$ (8%) were isolated, indicating that under more polar homogeneous conditions the iodine-containing adducts react further.

As expected,² the reactions of both 1-phenylpropene and 2-phenylpropene were much slower than those of cyclohexene. Consequently, extended reaction times were needed to achieve appreciable conversions of these alkenes, resulting in the formation of mixtures of products from secondary reactions. The majority of the products (Table 1) from 2-phenylpropene arise via Markownikoff attack of electrophilic iodine followed by elimination or by capture of the anion: further substitution of the iodine then occurs. In only one case [conditions B, Table 1] was an anti-Markownikoff product isolated: the benzylic iodide would be expected to be labile towards further elimination or substitution. For 1-phenylpropene I_2 - TlSCN - CHCl_3 (conditions D, Table 1) gave a good conversion (86% crude) to $\text{PhCH}(\text{NCS})\text{CHICH}_3$ (threo only, 39%),⁵ $\text{PhCHICH}(\text{SCN})\text{CH}_3$ (erythro and threo ca. 1:1, 7%, unstable), $\text{PhCH}(\text{NCS})\text{CH}(\text{SCN})\text{CH}_3$ (mainly threo, trace erythro, 12%) and $\text{PhCH}(\text{SCN})\text{CH}(\text{SCN})\text{CH}_3$ (erythro and threo, ca. 1:1, 4%). Use of CHCl_3 -sulpholane (conditions C, Table 1) resulted in an increase in yield of the latter two compounds (26% and 10%, respectively) at the expense of $\text{PhCH}(\text{NCS})\text{CHICH}_3$ (23%). Under the same conditions (C) indene gave a similar result, the products⁵ being trans-2-iodo-3-isothiocyanatoindane (9%), 2-thiocyanatoindene (3%), trans-3-isothiocyanatoindane (13%), trans-2-isothiocyanato-3-thiocyanatoindane (6%), trans-2-iodo-3-thiocyanatoindane (1%) and cis-2-iodo-3-thiocyanatoindane (2%).

Thus, conditions are now available which allow isolation of the iodothiocyanates or

Table 1
Products^a from 2-phenylpropene/ISCN

Compound	Conditions ^b			
	A ^c	B ^d	C ^e	D ^e
CH ₃ C(Ph)(NCS)CH ₂ I	10	7	19	53
CH ₃ C(Ph)ICH ₂ NCS	0	2	0	0
CH ₃ C(Ph)=CHSCN	2	1	3	0
CH ₂ =C(Ph)CH ₂ SCN	17	2	15	0
CH ₃ C(Ph)(NCS)CH ₂ SCN	9	15	27	14
CH ₃ C(Ph)(SCN)CH ₂ SCN	7	2	12	6
CH ₃ C(Ph)(OH)CH ₂ I ^f	11	1	0	0

- (a) Isolated yields were low because of product instability on p.l.c.
- (b) A, B, C were carried out with 2-phenylpropene (1.25 mmol) in CHCl₃-sulpholane (1:9, 10 ml) at 0°; CHCl₃ (15 ml) was used for D.
- (c) ICl (2.5 mmol)-KSCN (2.75 mmol), 20 h.
- (d) I₂ (3 mmol)-KSCN (3.75 mmol), 48 h.
- (e) I₂ (3 mmol)-TlSCN (3.75 mmol), 48 h.
- (f) From traces of moisture in hygroscopic solvent.

iodoisothiocyanates in good yield from both simple alkenes and arylalkenes. Moreover, these results suggest that the use of I₂-(SCN)₂¹ probably does not yield simply a vicinal iodothiocyanate. Detailed analysis of the products from this system is in progress.

References

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5. Isolated (p.l.c.) yields. Some compounds were unstable but all gave satisfactory infrared, ¹H n.m.r. and mass spectra.
6. Correct analysis, m.p. 35.5-35.8°. The product, m.p. 33°, reported^{1f} as the iodothiocyanate is probably the iodoisothiocyanate. Independent experiments showed no interconversion of C-SCN to C-NCS products under the conditions used for the addition reactions.
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