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FREE RADICAL ADDITIONS OF α-IODOALKYLPHENYL SULFONES TO ALKENES

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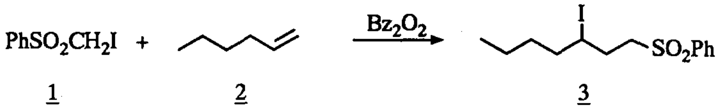
Summary: Atom-transfer free radical additions of α-iodoalkylphenyl sulfones to alkenes are described.

In recent years, atom-transfer free radical additions to C-C multiple bonds have emerged as a powerful synthetic method for formation of new C-C bonds$^{1)}$. Particular attention has been given to additions involving halogens as the transferred atoms. Various classes of compounds, including iodofluoro derivatives, α-haloesters and α-haloketones have been successfully applied in these reactions$^{2)}$. In 1986 Fields and Shechter reported the atom-transfer free radical addition of tribromomethylphenyl sulfone to alkenes$^{3)}$. Attempts to extend this reaction to the synthetically more useful dibromomethylphenyl sulfone, leading to 1-sulfonyl-3-bromo derivatives with α-sulfonyl hydrogen atom have, however, failed. Assuming that the iodine atom is much easier transferred in free radical processes than any other halogen, we decided to investigate an analogous reaction with iodomethylphenyl sulfone (1)$^{4)}$. This communication presents the preliminary results of this work.

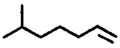
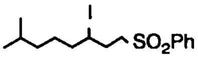
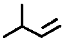
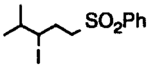
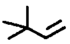
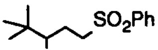
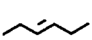
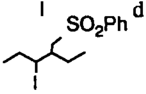
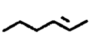
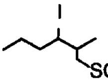
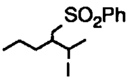
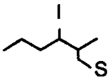
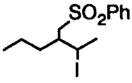
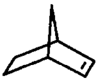
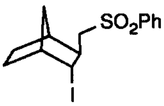
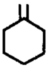
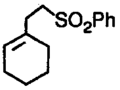
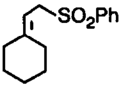
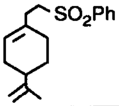
It was found that iodomethylphenyl sulfone (1) reacts regioselectively with an excess of 1-hexene (2) (10 equiv) in the presence of catalytic amount of benzoyl peroxide$^{5)}$ (0.05 equiv) in benzene solution, within 5 h, at 100°C in a sealed tube, affording adduct 3 in 70% yield, according to Scheme 1.



Scheme 1

The results of other eleven reactions, collected in Table 1, ilustrate the scope and limitations of this method.

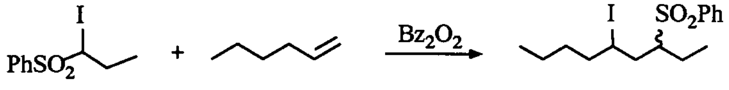
Table 1

Entry	Alkenes	Reaction time (h)	Products [a]	Regio-selectivity	Yield (%) [b]
1		5		>99:1	66
2		5		>99:1	70
3		5		>99:1	73
4		10[c]	 [d]	–	23
5		10[c]	 e  [d]	6:1	36
6		10[c]	 e  [d]	6:1	36
7		10[c]	no reaction	–	–
8		10[c]	no reaction	–	–
9		5		–	50
10		10[c]	 	>99:1[f]	58[g]
11		5		>99:1[f]	50

a) Satisfactory ^{1}H NMR, ^{13}C NMR and MS were obtained for all compounds.
b) Yields after purification by silica gel chromatography.
c) After 5 h an additional portion of Bz_2O_2 (0.05 equiv) was added.
d) A mixture of two diastereomers in a 1:1 ratio.
e) A mixture of two diastereomers in a 3:2 ratio; at this point we do not know, however, the exact stereochemical relationship at two chiral centres
f) Estimated regioselectivity of the addition step of the reaction.
g) A mixture of olefins in a 1:1 ratio.

Presented examples show that the described procedure seems to be a convenient way for one step preparation of 1-sulfonyl-3-iodo derivatives, however, only monosubstituted alkenes ensure good yields and high regioselectivity (Entries 1-3). In contrast, the reactions with 1,2-disubstituted alkenes are sluggish. Acyclic alkenes as (E) 3-hexene, (E) 2-hexene and (Z) 2-hexene (Entries 4-6) afford addition products in low yield, whereas cyclohexene and cyclooctene (Entries 7-8) do not react at all. Apparently the reactivity of alkenes towards α-sulfonyl radicals6) depends on steric factors. In the case of (E) and (Z) 2-hexenes (Entries 5-6), apart from low yield of the reactions, moderate regioselectivity (6:1), reflecting a preferred attack of α-sulfonyl radical on the less hindered side of the double bond, was observed. Interestingly, the major products of these reactions are the same mixtures of diastereomers in a 3:2 ratio. In an analogous reaction, symmetric (E) 3-hexene (Entry 4) affords the addition product as the expected mixture of diastereomers in a 1:1 ratio. Under these circumstances, the relatively high reactivity of norbornene (Entry 9) can be rationalized by assuming that an internal strain in norbornene molecule is a driving force for the reaction. In the case of 1,1-disubstituted alkenes, e.g. methylenecyclohexane (Entry 10), the initially formed addition product, bearing iodine at the tertiary carbon atom, is spontaneously subjected to nonselective hydrogen iodide abstraction, leading to a mixture of alkenes. Under the same conditions, β-pinene (Entry 11) undergoes a typical rearrangement, followed by hydrogen iodide elimination.

After getting insight into the additions of iodomethylphenyl sulfone (1) to alkenes, we tried to extend the described procedure to other α-iodoalkylphenyl sulfones. We investigated an analogous reaction with α-iodopropylphenyl sulfone (4)7), a representative of secondary alkylphenylsulfonyl iodides. It was found that iodide 4 reacts with 1-hexene (2) under the above-described conditions , within 5 h, affording adduct 5 as a mixture of diastereomers in a 1:1 ratio, in 60% yield (Scheme 2).



4 2 5

Scheme 2

Further investigations on the atom-transfer mediated reactions of secondary α-iodoalkylphenyl sulfones with alkenes are in progress.

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