

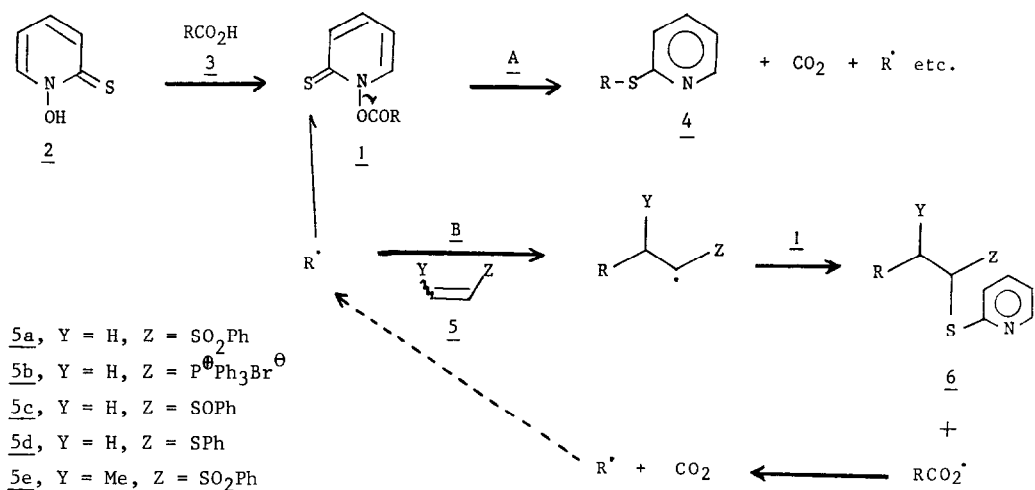
RADICAL ADDITION TO VINYL SULPHONES AND VINYL PHOSPHONIUM SALTS

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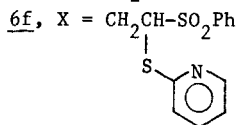
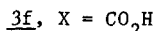
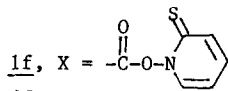
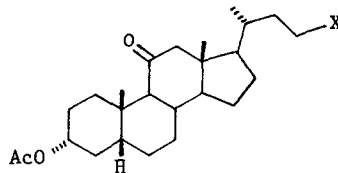
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*Summary* : Alkyl radicals, derived from decarboxylation of carboxylic acids, add readily to phenyl vinyl sulphone and vinyl phosphonium bromide. The adducts may be further converted into a variety of useful synthetic intermediates.

Not long ago we developed a novel and general decarboxylation reaction for aliphatic and alicyclic carboxylic acids involving esters 1 (mixed anhydrides) of thiohydroxamic acids such as 2.<sup>1</sup> The basic reaction is a simple thermally or photochemically initiated radical chain reaction leading, in the absence of external traps, to the sulphide 4 (Scheme 1, path A). The intermediate radical R<sup>•</sup> may be captured by a variety of reagents to give alkyl halides, alcohols etc. An important feature of the method is the easy formation of a carbon-carbon bond by simply incorporating an activated olefin into the system as shown in Scheme 1, path B (Z = electron withdrawing group).



Scheme 1

1 ; 3 ; 4a, R = 1-adamantylb, R = 1-methylcyclohexylc, R = cyclohexyld, R = (PhCH<sub>2</sub>)<sub>2</sub>CH-e, R = Ph<sub>2</sub>CHCH<sub>2</sub>-6a, R = 1-adamantyl; Y = H; Z = SO<sub>2</sub>Ph6b, R = 1-methylcyclohexyl; Y = H; Z = SO<sub>2</sub>Ph6c, R = cyclohexyl; Y = H; Z = SO<sub>2</sub>Ph6d, R = (PhCH<sub>2</sub>)<sub>2</sub>CH-; Y = H; Z = SO<sub>2</sub>Ph6e, R = Ph<sub>2</sub>CHCH<sub>2</sub>-; Y = H; Z = SO<sub>2</sub>Ph6g, R = 1-adamantyl; Y = H; Z = SOPh6h, R = 1-Adamantyl; Y = Me; Z = SO<sub>2</sub>Ph6i, R = adamantyl; Y = Z = H6j, R = cyclohexyl; Y = Z = H6k, R = Ph<sub>2</sub>CHCH<sub>2</sub>; Y = Z = H

Recently<sup>2</sup> we showed that strongly electrophilic olefins like nitroethylene did not polymerise under radical conditions in the presence of a strong acid. However, such nitroolefins showed strong radicophilicity and gave good yields of addition products 6, without the complication of polymerisation as seen with less polarised monomers.

We conceived, therefore, that other highly electrophilic olefins like phenylvinylsulphone 5a and vinyltriphenylphosphonium bromide 5b should also show good radicophilicity and give high yields of addition products.

Irradiation with a 250W projector lamp of a solution of adamantyl ester 1a and phenylvinylsulphone 5a in dichloromethane-benzene (1:1) for ca. 10 min. at room temperature gave the corresponding addition product 6a in quantitative yield. Other primary, secondary and tertiary carboxylic acids also afforded high yields of sulphone derivatives (Table). In the work up procedure the excess of monomer was destroyed by a slight excess of hydrazine.

Table

Further transformation of these adducts into a plethora of useful synthetic intermediates is readily accomplished by exploiting the rich chemistry of the sulphone group as revealed by the extensive work of Julia and others<sup>3</sup> (Scheme 2). Noteworthy is the conversion of 6e via the corresponding disulphone into the homologous acid. Considered from the starting acid 3e, this sequence is another equivalent<sup>2</sup> of the Arndt-Eistert<sup>4</sup> homologation of carboxylic acids. All transformations in Scheme 2 refer to 6e unless indicated to the contrary.

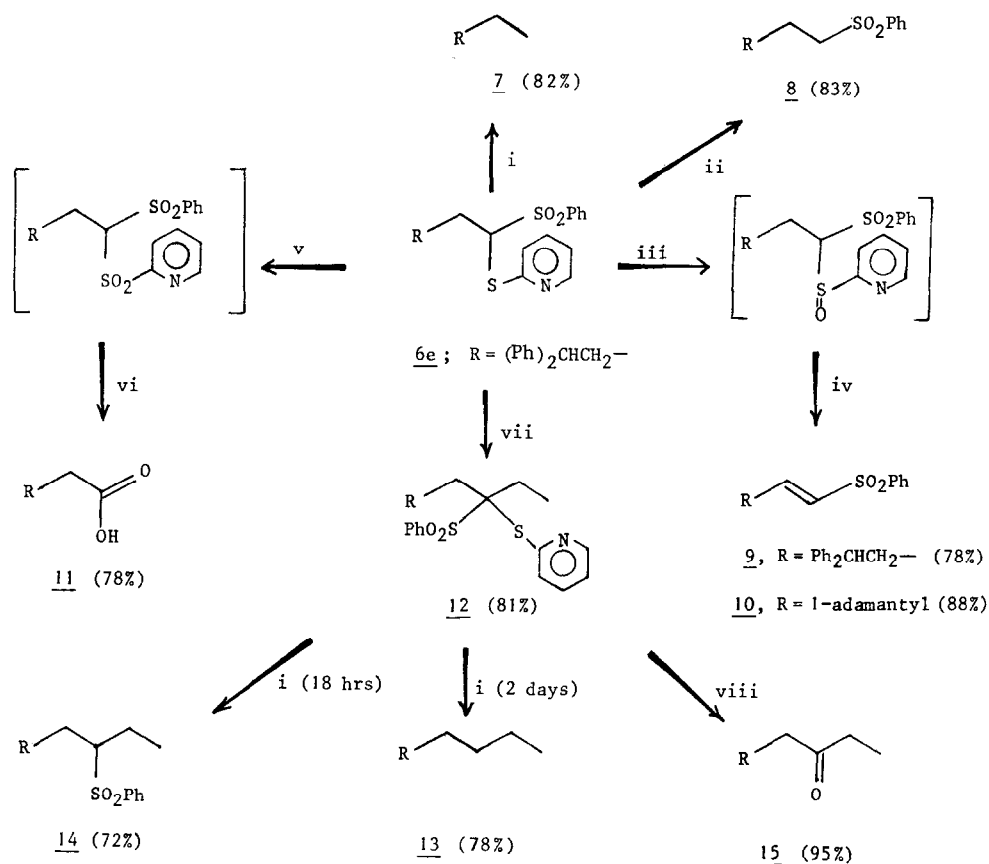
Entry	Ester <sup>a)</sup> <u>1</u>	Olefin <u>5</u> (equiv.)	Adduct <u>6</u> (Yield %)
1	<u>1a</u>	<u>5a</u> (5)	<u>6a</u> (100)
2	<u>1b</u>	<u>5a</u> (5)	<u>6b</u> (87)
3	<u>1c</u>	<u>5a</u> (4.8)	<u>6c</u> (89)
4	<u>1d</u>	<u>5a</u> (5)	<u>6d</u> (57)
5	<u>1e</u>	<u>5a</u> (6)	<u>6e</u> (75)
6	<u>1f</u>	<u>5a</u> (5.4)	<u>6f</u> (70)
7	<u>1a</u>	<u>5c</u> (10)	<u>6g</u> (43)
8	<u>1a</u>	<u>5e</u> (10)	<u>6h</u> (27)
9	<u>1a</u>	<u>5b</u> (2.0)	<u>6i</u> (88)
10	<u>1c</u>	<u>5b</u> (2.5)	<u>6j</u> (71)
11	<u>1e</u>	<u>5b</u> (5)	<u>6k</u> (82)

a) Except for 1a, which was isolated and purified, the esters were prepared *in situ* by treating the acid chloride with thiohydroxamic acid 2 in the presence of 2.5 equivalents of pyridine.

As anticipated on the basis of related radical additions to olefins,<sup>5</sup> the less electrophilic vinyl sulphoxide 5c and vinyl sulphide 5d behaved poorly. In the case of the former, additions were not clean, the best yield from ester 1a of the corresponding adduct 6g being 43%. The latter showed hardly any addition. As implied in Scheme 1, if the trap is not sufficiently reactive, the radical reacts with the ester 1 (path A) to give the sulphide 4. This "decarboxylative rearrangement" also predominates when the vinyl sulphone is substituted in the  $\beta$ -position 6 as in 5e which gave at best a yield of 27% of addition product 6h, the major product being the sulphide 4a (50%).

The highly electrophilic but radical non polymerisable vinylphosphonium salt 5b underwent additions quite readily to give the expected adducts 6 (Y=H, Z=P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup>). These were not isolated but exposed to dilute sodium hydroxide in methanol-water to form the higher sulphides 6i, 6j, 6k (Y=Z=H) with concomitant loss of triphenylphosphine oxide. Radicals derived from primary, secondary and tertiary acids thus afforded good yields of sulphides (Table, entries 9-11). Thus our novel method for generating alkyl radicals is compatible with highly electrophilic olefins providing access to a wide variety of useful synthetic intermediates. Noteworthy, from a practical standpoint is the commercial availability of thiohydroxamic acid 2 and its sodium salt, as well as of olefins 5a and 5b.

We suggest that other vinyl onium salts will also be non-polymerisable under radical conditions, but will be radicophilic. We are currently working on vinylsulphonium, vinylammonium and other onium salts.



- i) R-Nickel, ethanol-water, reflux. ii) Nickel boride, ethanol-water, reflux.  
 iii) MCPBA (1 eq.), 0°C. iv) HCl, 100°C. v) MCPBA, excess, room temp.  
 vi) K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, methanol-THF. vii) NaH, DMF then EtBr. viii) HCl, MeOH-H<sub>2</sub>O, reflux.

Scheme 2

## References

- a) D.H.R. Barton, D. Crich and W.B. Motherwell, *J. Chem. Soc., Chem. Commun.*, 939 (1983); b) *idem*, *Tetrahedron Lett.*, **24**, 4979 (1983); c) D.H.R. Barton and G. Kretzschmar, *ibid.*, **24**, 5887 (1983); d) D.H.R. Barton, D. Bridon and S.Z. Zard, *ibid.*, **25**, 5777 (1984); e) D.H.R. Barton, D. Bridon and S.Z. Zard, *J. Chem. Soc. Chem. Commun.*, 1066 (1985) and references there cited.
- D.H.R. Barton, H. Togo and S.Z. Zard, *Tetrahedron*, accepted for publication.
- See *inter alia*: J. Cuvigny, C. Hervé de Penhoat, J.L. Fabre and M. Julia, *Tetrahedron Lett.*, **24**, 4319 (1983) and references therein; J.L. Fabre and M. Julia, *Tetrahedron Lett.*, **24**, 4311 (1983); J. Cuvigny, C. Hervé de Penhoat and M. Julia, *Tetrahedron Lett.*, **24**, 4315 (1983) and references therein. For recent reviews on the Chemistry of Sulphones, see: P.D. Magnus, *Tetrahedron*, **33**, 2019 (1977); T. Durst in "Comprehensive Organic Chemistry", Vol. 3, D.H.R. Barton, D.N. Jones and W.D. Ollis Eds., Pergamon Press, 1979, Oxford.
- W.E. Bachmann, *Org. React.*, **1**, 39 (1942).
- For a recent review on Radical Additions to Olefins, see: B. Giese, *Angew. Chem. Int. Ed.*, **22**, 753 (1983).

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