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CARBETHOXYALLYLATION USING RADICAL CHEMISTRY

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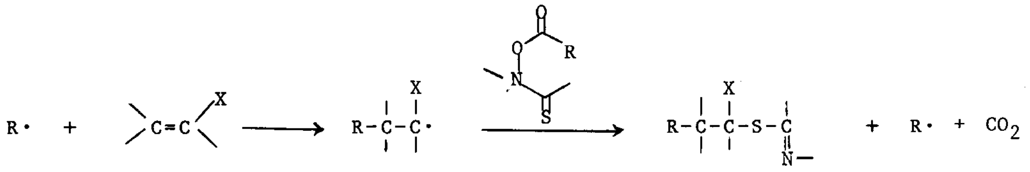
Abstract : Radicals derived from the esters of N-hydroxy-2-thiopyridone react smoothly in a concerted reaction with 2-carbethoxy-3-t-butylthioprop-1-ene to give the corresponding 2-carbethoxyallyl derivatives with shift of the double bond.

We reported recently[1] that the esters of certain thiohydroxamic acids are an excellent source of carbon radicals. Because of the background reaction of decarboxylative rearrangement, radicals produced in this way show controlled behaviour giving selective chemical reactions.

We have already described[2] the addition of such radicals to carbon-carbon double bonds as in Scheme 1. The yields we obtained were comparable with those usually found in such additions.[3]

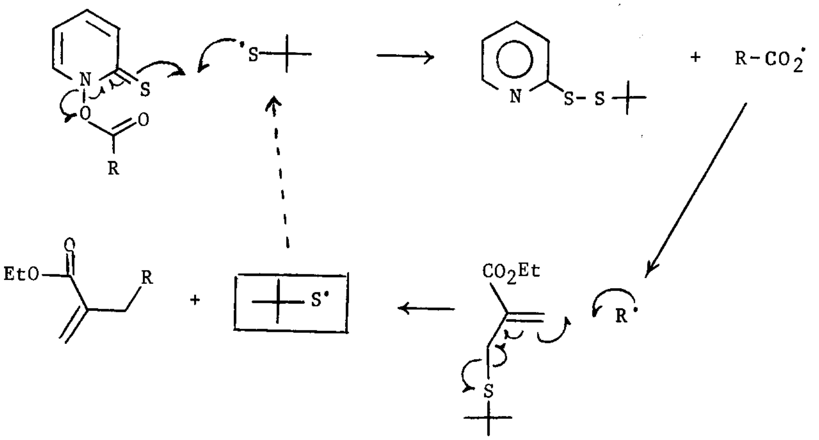


X = electron attracting group

Scheme 1

A related reaction of synthetic utility is allylation.[4] We conceived that improved yields of addition to the olefinic linkage could be secured if the reaction of addition could be concerted with elimination of a thiyl radical, which is an excellent chain carrier in our system.[1] Thus (Scheme 2) using the type of esters easily synthesised from (1) and which react smoothly with thiyl radicals to give disulphides and (eventually) R· radicals, one could imagine addition to (3) concerted with elimination of the thiyl radical. We have reduced this conception to practise.

The ester (3) was readily prepared from dibromide (2)[5] by treatment with a one molar equivalent of t-butylthiol and potassium carbonate in ethanol, followed by extraction and distillation. The disulphide (4) was a by-product of this reaction.



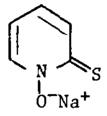
Scheme 2

These radical reactions were easily performed by dropwise addition of the acid chloride in chlorobenzene to (1) and (3) at reflux under nitrogen in chlorobenzene.

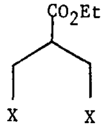
The Table gives the compounds used, the olefins produced and the yields obtained. The yields are, in general, better than those obtained before[2] and the reactions are cleaner with little polymerisation. These facts support the hypothesis that the addition of R· to the olefin and elimination of the thiyl radical are concerted.

In the case of compounds (10) and (12) a mixture (1:1) of the two isomers was obtained. In the case of hederagenin diacetate the derivative (9) was a single isomer of as yet undetermined configuration.

It is particularly gratifying to see that tertiary radicals (as in (9) and (19)) can be added in good yield.

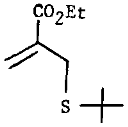


(1)

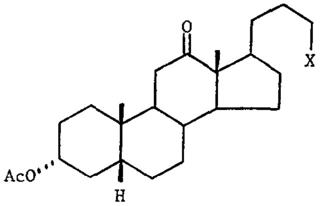


(2) X = Br

(4) X = S 

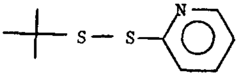


(3)

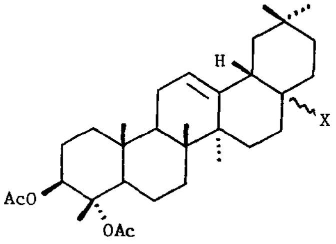


(5) X = COCl

(6) X = $CH_2C(=CH_2)CO_2Et$

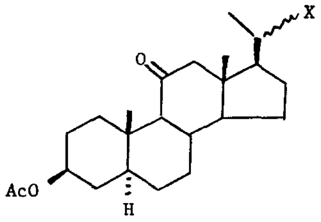


(7)



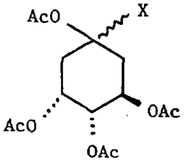
(8) X = β-COCl

(9) X = $CH_2C(=CH_2)CO_2Et$



(10) X = COCl (20 R)

(11) X = $CH_2C(=CH_2)CO_2Et$



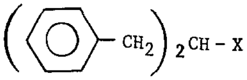
(12) X = β-COCl

(13) X = $CH_2C(=CH_2)CO_2Et$

$CH_3(CH_2)_{14}X$

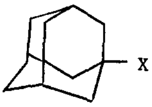
(14) X = COCl

(15) X = $CH_2C(=CH_2)CO_2Et$



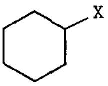
(16) X = COCl

(17) X = $CH_2C(=CH_2)CO_2Et$



(18) X = COCl

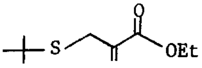
(19) X = $CH_2C(=CH_2)CO_2Et$



(20) X = COCl

(21) X = $CH_2C(=CH_2)CO_2Et$

TABLE

Acid chloride	 (mmoles)	Reaction time (hrs)	Products^a (Isolated Yields %)
(5)^b	5	1 1/2	(6) (49)
(5)^b	1.2	1 1/2	(6) (60)
(5)^b	2	1 1/2	(6) (76), (7) (90)
(8)^b	2	0.5	(9) (74), (7) (64)
(10)^b	2	0.75	(11) (74), (7) (80)
(12)^b	2	0.5	(13) (56), (7) (56)
(14)^c	2	1	(15) (69), (7) (73)
(16)^b	1.5	0.75	(17) (60), (7) (78)
(18)^c	1.5	1	(19) (71), (7) (85)
(20)^c	1.5	0.75	(21) (74), (7) (83)

[a] All new compounds gave satisfactory spectroscopic and microanalytical data.

[b] Prepared in essentially quantitative yield from the corresponding acid with oxalyl chloride and dimethylformamide as catalysts.

[c] Redistilled commercial acid chloride.

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