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FORMATION OF CARBON-CARBON BONDS WITH RADICALS DERIVED FROM THE ESTERS OF THIOHYDROXAMIC ACIDS

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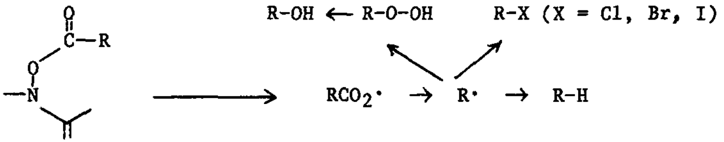
ABSTRACT - Radicals formed from the esters of thiohydroxamic acids readily add to electron deficient olefins to give adducts of potential synthetic value in variable yield. In certain cases the added sulphur function is easily eliminated with reformation of olefin.

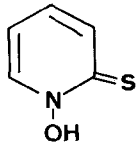
Functional group manipulation in complexe natural products can often be carried out advantageously using radical reactions[1]. We recently reported that the esters of thiohydroxamic acids readily participate in efficient radical chain sequences generating R-CO_2· radicals which furnish a good source of R· radicals.[2] Thus acids can be decarboxylated to nor-hydrocarbons, nor-halides and nor-hydroperoxides and alcohols in high yield (Scheme).



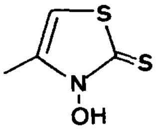
Scheme

The formation of carbon-carbon bonds in radical chemistry has been much discussed from the theoretical point of view.[3] It is, however, only recently that such reactions have been used in selective additions to the carbon-carbon double bond.[4] Following the pioneering work on cyclisation reactions of Julia and his colleagues,[5] using peroxide generated radicals and where the yields were variable, considerable progress has recently been made with the cyclisation of radicals generated from tin hydride reagents.[6]

We now report that radicals from the esters[2] of thiohydroxamic acids (1) and (2) add with variable efficiency to electron-deficient carbon-carbon double bonds. The results are given in the Table. Addition to singly activated olefins affords adducts where the



(1)



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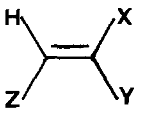
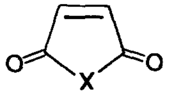
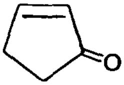


	X	Y	Z
(3)	CN	H	H
(4)	CO_2CH_3	H	H
(5)	NO_2	H	H
(6)	$COCH_3$	H	H
(7)	CN	Cl	H
(8)	CN	H	CN

terminal containing the sulphur function permits further synthetic manipulation. Addition to two acetylenes [(15) and (16)] gives products (31) and (32). Addition to a number of olefins with α,β-double activation gives products [(33), (34) etc.] which result from elimination on work up. In certain cases (e.g. (29) and (30)] the stereochemistry of the addition is well defined. In the other examples, where stereoisomers are possible, mixtures of isomers were obtained. These were not separated but the mixtures were characterised.



(9) X = CMe_2
(10) X = O
(11) X = NMe



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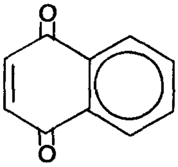

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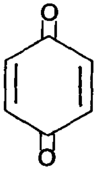
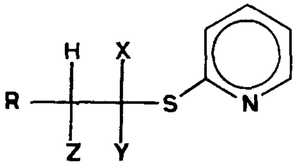


(14)

$X-\equiv-CO_2CH_3$

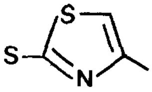
(15) X = H
(16) X = CO_2Me

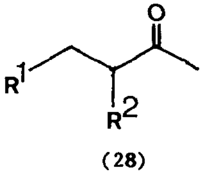


(17) R = $C_{15}H_{31}$, X = CN, Y = Z = H
(18) R = $C_{15}H_{31}$, X = CO_2CH_3, Y = Z = H
(19) R = $C_{15}H_{31}$, X = NO_2, Y = Z = H
(20) R = $C_{15}H_{31}$, X = $COCH_3$, Y = Z = H

(21) R = $C_{15}H_{31}$, X = CN, Y = Cl, Z = H
(22) R = $C_{15}H_{31}$, X = Z = CN, Y = H
(23) R = C_6H_{11}, X = Z = CN, Y = H
(24) R = C_6H_{11}, X = NO_2, Y = Z = H
(25) R = 1-adamantyl, X = CO_2CH_3, Y = Z = H
(26) R = $(CH_3)_3C$, X = NO_2, Y = Z = H
(27) R = $(CH_3)_3C$, X = Z = CN, Y = H

For formulae (28) through (39) $R^1 = C_{15}H_{31}$, $R^2 =$





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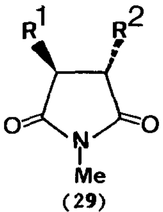

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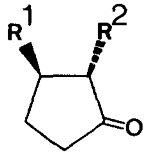

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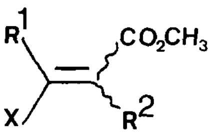
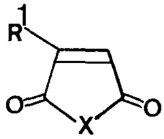
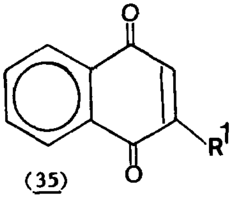


(31) X = H
(32) X = CO_2Me



(33) X = CMe_2
(34) X = O



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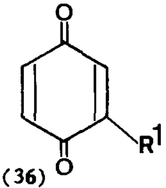

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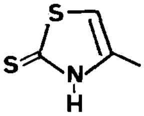

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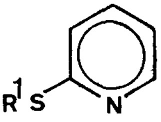

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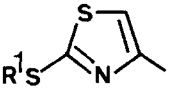

(39)

Table*

Radical	Thiohydroxamic Acid	Olefin (equivs)	Temp. (°C)	Conditions	Products (% yield)
$C_{15}H_{31}$	(1)	(3) (5)	R.T.	hν$^{a)}$, 15 mn	(17) (59), (38) (10)
$C_{15}H_{31}$	(1)	(4) (2)	R.T.	hν$^{a)}$, 10 mn	(18) (83)
$C_{15}H_{31}$	(1)	(4) (5)	R.T.	hν$^{a)}$, 15 mn	(18) (63)
1-adamantyl	(1)	(4) (2)	R.T.	hν$^{a)}$, 15 mn	(25) (35)
$C_{15}H_{31}$	(1)	(5) (1.1)	R.T.	hν$^{a)}$, 15 mn	(19) (53)
C_6H_{11}	(1)	(5) (1.2)	R.T.	hν$^{a)}$, 1 h	(24) (45)
$(CH_3)_3C$	(1)	(5) (1.2)	R.T.	hν$^{a)}$, 15 mn	(26) (52)
$C_{15}H_{31}$	(2)	(6) (5)	110°	1 h $^{c)}$	(28) (43), (39) (6)
$C_{15}H_{31}$	(1)	(7) (1.1)	R.T.	hν$^{a)}$, 30 mn	(21) (40)
$C_{15}H_{31}$	(1)	(8) (1.2)	110°	rapid addition of ester, 30 mn$^{c)}$	(22) (60)
C_6H_{11}	(1)	(8) (1.2)	110°	10 mn$^{c)}$	(23) (56)
$(CH_3)_3C$	(1)	(8) (1.2)	80°	10 mn	(27) (57)
$C_{15}H_{31}$	(2)	(9) (1.5)	R.T.	hν$^{b)}$	(33) (70), (39) (7)
$C_{15}H_{31}$	(2)	(10) (1.5)	R.T.	hν$^{b)}$	(34) (69); (37) (93)
$C_{15}H_{31}$	(2)	(11) (1.5)	R.T.	hν$^{b)}$	(29) (93), (39) (2)
$C_{15}H_{31}$	(2)	(12) (2)	110°	1h $^{c)}$	(30) (30), (39) (58)
$C_{15}H_{31}$	(2)	(13) (2)	110°	1.5 h$^{c)}$	(35) (26), (39) (28)
$C_{15}H_{31}$	(2)	(14) (5)	110°	1.5 h$^{c)}$	(36) (27), (39) (18)
$C_{15}H_{31}$	(2)	(15) (5)	110°	1 h$^{c)}$	(31) (38), (39) (33)
$C_{15}H_{31}$	(2)	(16) (2.5)	110°	1 h$^{c)}$	(32) (50)

* The results given represent the best conditions that we could develop. The variation of the olefin in equivs. is needed where there is a competing polymerisation of the olefin monomer.

a) : 300 W tungsten lamp, in benzene under N_2.

b) : 100 W medium pressure mercury lamp, in benzene under N_2.

c) : reflux in toluene under N_2.

Acknowledgments

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