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NEW DECARBOXYLATIVE CHALCOGENATION OF ALIPHATIC AND ALICYCLIC CARBOXYLIC ACIDS.

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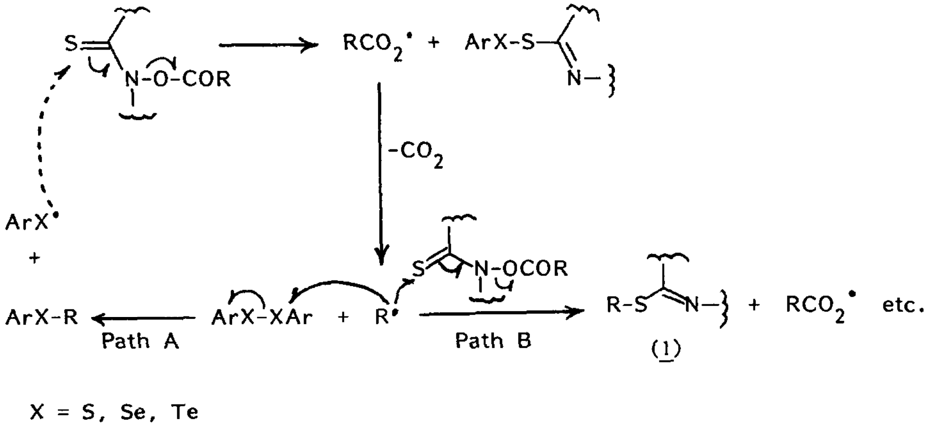
Summary: Thiohydroxamic-carboxylic mixed anhydrides can be decarboxylated in the presence of diaryl disulphides, diselenides and ditellurides to give sulphides, selenides and tellurides respectively in reasonable to good yield.

We have recently described a novel decarboxylation of carboxylic acids via their mixed anhydrides with suitable thiohydroxamic acids. The reaction proceeds under mild conditions by way of carbon radicals which can be intercepted to give a variety of products often in high yield.[1] In order to extend further the scope of this method we have explored the possibility of trapping these radicals with disulphides, diselenides and ditellurides. This would result in an overall decarboxylative chalcogenation of carboxylic acids.

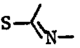
Radical substitution (S_H2) on disulphides (or diselenides) is known to give a sulphide (or selenide) and a thiyl (or selenyl) radical. In our system this radical can propagate the chain reaction in the desired direction (Scheme 1, Path A). An extension to ditellurides can be conceived too (Scheme 1).

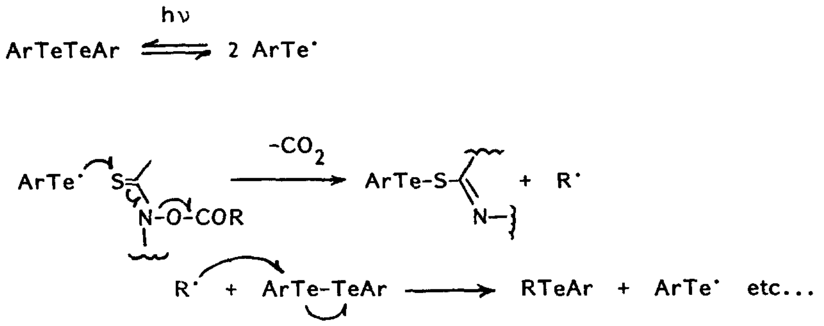


Scheme 1

However, in order to prevail, the substitution reaction has to compete successfully against the back-ground addition[1] of the radical R$^{\cdot}$ to another mixed anhydride molecule (Path B) to give sulphide (1).

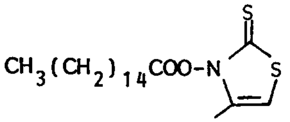
We have been able to reduce this concept to practice. Thus heating anhydride (2), easily obtained from palmitoyl chloride and thiohydroxamic acid (3), in excess diphenyl disulphide gave phenyl pentadecyl sulphide (6) in 74% yield. In a similar way, various selenides were prepared using diphenyl diselenide (Table). A promising experimental variation is the slow addition of the acid chloride to a mixture of diphenyl diselenide and the sodium salt of 2-pyridine thiol N-oxide (4) in refluxing toluene (entry 6). Although this procedure could be successfully applied to the synthesis of tellurides (16) and (17), most of the other tellurides were thermally unstable and decomposed at the reaction temperature. In order to lower the reaction temperature we took advantage of the fact that ditellurides are easily dissociated by light to give two telluriyl radicals. These initiated the radical decarboxylation efficiently and gave the desired tellurides. (Scheme 2). Good yields of tellurides (Table) were thus simply obtained by operating at 35°C under laboratory lighting. In the dark the reaction was very slow.

As implied in path A (Scheme 1), dichalcogenides of type ArX-S- are also produced. Although these could, if wished, be isolated when X = S or Se, the tellurium analogs suffered "disproportionation" to give the corresponding ditelluride and dipyridyl disulphide.

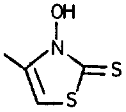


Scheme 2

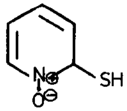
This simple decarboxylative chalcogenation provides an expedient entry to otherwise not readily accessible compounds, and in particular to the increasingly important organotellurium derivatives.[3] Tellurides for example have been used recently as myocardial imaging agents.[4]



(2)



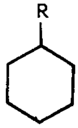
(3)



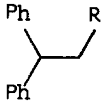
(4)

$CH_3(CH_2)_{14}$-R

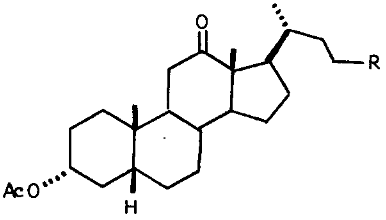
(5) R = CO_2H
(6) R = SPh
(7) R = SePh
(8) R = Te-p-C_6H_4OPh



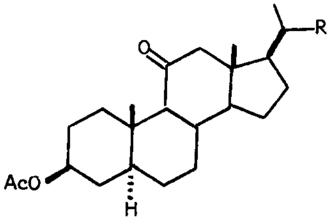
(9) R = CO_2H
(10) R = SePh



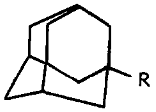
(11) R = CO_2H
(12) R = SePh
(13) R = Te-p-C_6H_4OPh



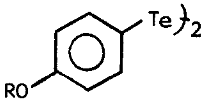
(14) R = CO_2H
(15) R = SePh
(16) R = Te-β-$C_{10}H_7$



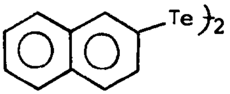
(18) R = CO_2H (20αMe)
(19) R = Te-p-C_6H_4OPh



(20) R = CO_2H
(21) R = Te-p-C_6H_4OPh
(22) R = Te-β-$C_{10}H_7$
(23) R = Te-p-C_6H_4OMe



(24) R = Ph
(25) R = Me



(26)

Entry	Acid	Method[a]	Temperature °C (Reaction time, hrs)	ArXXAr (equivalents)	Products[b] (isolated yields %)
1	(5)	A	120 (1.5)	PhSSPh (30)	(6) (74)
2	(5)	B	110 (1.5)	PhSeSePh (10)	(7) (75)
3	(9)	B	110 (5)	PhSeSePh (10)	(10) (75)
4	(9)	A	120 (2)	PhSeSePH (20)	(10) (73)
5	(11)	A	120 (2)	PhSeSePh (20)	(12) (72)
6	(14)	C	110 (5.5)	PhSeSePh (10)	(15) (80)
7	(14)	C	110 (2.5)	(24) (2)	(16) (56)
8	(14)	C	110 (6)	(26) (2)	(17) (65)
9	(5)	C[c]	35 (1.5)	(24) (2)	(8) (65)
10	(11)	C[c]	35 (1.5)	(24) (2)	(13) (55)
11	(18)	C[c]	35 (1.5)	(24) (2)	(19) (55)
12	(20)	C[c]	35 (2)	(24) (2)	(21) (75)
13	(20)	C[c]	50-60 (2)	(26) (2)	(22) (65)
14	(20)	C[c]	35 (2)	(25) (2)	(23) (70)

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a) Method A : Mixed anhydride prepared from the acid chloride and thiohydroxamic acid (3) was heated with neat PhSSPh or PhSeSePh under N$_2$.
Method B : Mixed anhydride with (3) was added slowly to a refluxing solution of PhSeSePh in toluene under N$_2$.
Method C : Acid chloride, prepared in quantitative yield from the acid using oxalyl chloride and a trace of DMF, was added slowly (motor driven syringe) to a mixture of the sodium salt of (4) and ArXXAr heated to the specified temperature under N$_2$.

b) All new compounds were satisfactorily analysed.

c) Under laboratory lighting.

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