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THE ROLE OF ORGANIC TELLURIDES AS ACCUMULATORS AND EXCHANGERS OF CARBON RADICALS

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Summary. Primary carbon radicals, generated by photolysis of acyl derivatives of N-hydroxy-2-thiopyridone, exchange efficiently on diisopropyl telluride to give isopropyl radicals which can in turn be trapped by radicophilic olefins.

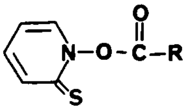
The use of radical reactions in Organic Synthesis is becoming common place.[1] The reason for this is that systems are now available for the generation of disciplined radicals, which give high yields of single products.[2] Carbon radical reactions can also be made stereospecific if there is appropriate functionality near to the radical center.[3]

In the last five years we have shown that the acyl derivatives of thiohydroxamic acids are an excellent source of disciplined radicals.[2] Scheme 1 summaries a typical reaction using derivatives 1 of the readily available and inexpensive[4] N-hydroxy-2-thiopyridone. When the olefin (CH_2=CHE) is not very radicophilic, path A is seen giving the thiopyridines 4, whereas if the E function in the olefin is strongly electron withdrawing, then addition occurs smoothly by path B[5].

The idea of a radical accumulator has been discussed before[4], but without experimental success. Recently, Zard[6] has reexamined the mechanism of the acyl xanthate photolysis reaction that we invented some time ago.[7] The original interpretation has been ingeniously modified by recognition that the acyl radicals produced are degenerate and exchange continuously with the original acyl xanthate. Thus, an accumulation of radicals is ensured.

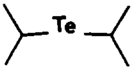
In this article we described a different radical accumulator which serves also as a radical exchanger. Thus, a radical R· derived from 1 could be conceived to add to a compound of type MR'_n to give a radical $R\text{-}\dot{M}R'_n$. If R=R′, then the new radical would be degenerate and act as a radical accumulator. If, on the other hand R≠R′, and if the R′-M bond was weaker than the newly formed R-M bond, then the adduct radical would fragment into a new radical R·′ and $R\text{-}MR'_{n-1}$. Thus there would be radical exchange.

It seemed to us that dialkyl tellurides[8] would be suitable for this role. Thus, methyl radicals generated from acyl derivative 1a underwent an exchange reaction with diisopropyl telluride 2 (1 equiv.) to produce sulfides 4b (40%) and 4a (15%). In addition to its selectivity in the favour of isopropyl radicals, this reaction was regarded as quite efficient in view of the fact that photolysis of 1a gave only 44% of 4a in the absence of 2.



1

a, R=CH_3
b, R=$(CH_3)_2CH$
c, R=$CH_3(CH_2)_{14}$
d, R=$PhCH_2CH_2$



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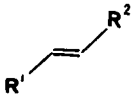
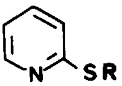


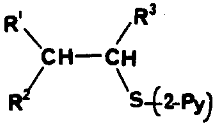
3

a, R^1=H, R^2=SO_2Ph
b, R^1=H, R^2=CO_2CH_3
c, R^1=CH_3, R^2=CN
d, R^1=CH_3, R^2=CO_2CH_3



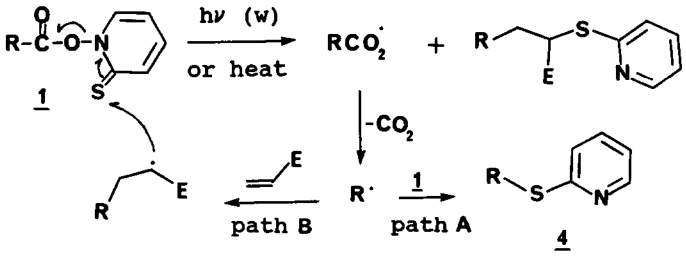
4

a, R=CH_3
b, R=$(CH_3)_2CH$
c, R=$CH_3(CH_2)_{14}$
d, R=$PhCH_2CH_2$



5

a, R^1=H, R^2=$(CH_3)_2CH$, R^3=SO_2Ph
b, R^1=H, R^2=$(CH_3)_2CH$, R^3=CO_2CH_3
c, R^1=H, R^2=$CH_3(CH_2)_{14}$, R^3=SO_2Ph
d, R^1=H, R^2=$PhCH_2CH_2$, R^3=SO_2Ph
e, R^1=CH_3, R^2=$(CH_3)_2CH$, R^3=CO_2CH_3
f, R^1=CH_3, R^2=$(CH_3)_2CH$, R^3=CN



Scheme 1

With this result we were in a position to study the interception of isopropyl radicals formed from 2, with various electron deficient olefins. As shown in Table 1, irradiation of esters 1 in presence of 2 resulted in addition of the isopropyl radical to various olefins in moderate to good yields. In some cases, however, small amounts (<20%) of the adducts of primary radicals with olefins were also detected. As expected, increasing the quantity of diisopropyl telluride 2 favoured the addition of isopropyl radical. Of course, complete inertness of 2 toward the olefin 3a was established in a control experiment.

When the isobutyric acid derivative 1b was used, the intermediate radical $Te(CHMe_2)_3$ was of course degenerate and thus acted as a radical accumulator. There was no obvious favourable effect on the addition to the radicophilic olefin.

The results given in Table 1 demonstrated that the initially foreseen expulsion of isopropyl radical from 2 and its capture by an olefin was a feasible process. Moreover, it appeared to be reasonably efficient without demanding excess of the tellurium compound 2. However, the radical accumulating function of diisopropyl telluride 2 had to be justified before extending this concept to the generation of other radicals (tertiary, benzyl, allyl, etc.). Thus, a series of experiments was run to determine the extent of radical addition to the olefins 3 in the absence of diisopropyl telluride 2 (Table 2). A comparison between entries 3-5 of Table 1 and entries 2-4 of Table 2 leads to the conclusion that there is no enhancement of yield in addition reactions using the telluride 2 as accumulator of radicals.

We have, therefore, demonstrated an efficient exchange of primary radicals into secondary radicals, but we have not shown that this process has meaningful use in synthetic chemistry. Indeed, the iodide exchange reactions of Minisci[9] are of more practical importance.

Table 1[a]

Entry	Ester 1 (mmol)	Diisopropyl Telluride	Alkene 3 (mmol)	Products[b] (% yield)
1	1a (0.07)	(0.07)	3a (0.14)	5a (61)
2	1a (0.08)	(0.16)	3a (0.16)	5a (66)
3	1b (0.14)	(0.14)	3a (0.14)	5a (66), 4b (13)
4	1b (0.16)	(0.16)	3b (0.16)	5b (65), 4b (16)
5	1b (0.13)	(0.13)	3c (0.13)	5f (28), 4b (43)
6	1c (0.08)	(0.08)	3a (0.16)	5a (64), 5c (20)
7	1c (0.07)	(0.14)	3a (0.14)	5a (68), 5c (28)
8	1d (0.08)	(0.16)	3a (0.16)	5a (50), 5d (20)
9	1d (0.09)	(0.45)	3a (0.18)	5a (72)

a) Reactants in $CDCl_3$ are photolyzed (tungsten lamp, 150W) at room temperature.

b) Yields are determined by N.M.R.

Table 2[a]

Entry	Ester 1 (mmol)	Alkene 3 (mmol)	Products[b] (% yield)
1	1b (0.15)	3a (0.30)	5a (85)
2	1b (0.1)	3a (0.1)	5a (75)
3	1b (0.2)	3b (0.2)	5b (65), 4b (16)
4	1b (0.12)	3c (0.12)	5f (22), 4b (49)
5	1b (0.1)	3c (0.5)	5f (43), 4b (21)
6	1b (0.1)	3c (1.0)	5f (60), 4b (12)
7	1b (0.1)	3d (0.5)	5e (30), 4b (32)
8	1b (0.1)	3d (1.0)	5e (50), 4b (18)
9	1c (0.1)	3a (0.2)	5c (90)
10	1d (0.1)	3a (0.2)	5d (70), 4d (25)
11	1d (0.1)	3a (0.5)	5d (82), 4d (15)

a) Reactants in $CDCl_3$ are photolyzed (tungsten lamp, 150W) at room temperature.

b) Yields are determined by N.M.R.

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