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CATALYTIC OXIDATION OF THIOCARBONYL COMPOUNDS INVOLVING THE USE OF 1,2-DIBROMOTETRACHLOROETHANE AS A BROMINATING REAGENT FOR DIARYL TE^{II} SPECIES

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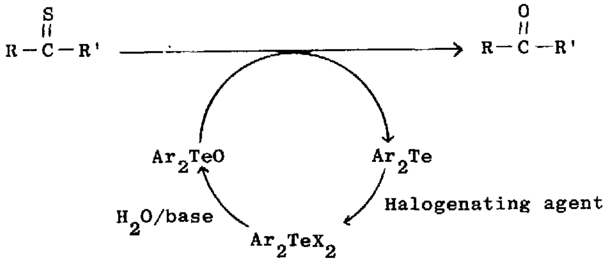
Summary: 1,2-Dibromotetrachloroethane acts as a useful brominating reagent for diaryl Te^{II} species in the establishment of a room temperature catalytic cycle for the conversion of thiocarbonyl compounds to their oxo analogues.

We have recently shown the bis-p-(methoxyphenyl) telluoxide (1a) is a very mild and selective oxidant for certain organic substrates.[1] As catalytic oxidative processes are of prime importance in synthesis[2] we have sought to develop such a procedure for the thiocarbonyl-carbonyl transformation. A room temperature catalytic cycle for this conversion using organotellurium (IV) species is shown in the Scheme.

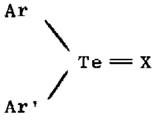


Scheme

Clearly, the cycle can be entered at the telluride, telluroxide, or tellurium dihalide stage.

The cycle requires that the telluride is readily halogenated and subsequently converted to the telluroxide by a suitable aqueous base. Whilst vicinal halides have been used to effect halogenation they often require high temperatures.[3] We have found that the inexpensive 1,2-dibromotetrachloroethane is an excellent brominating agent for tellurides at room temperature. Other reagents that we studied, hexachloroacetone, carbon tetrabromide or Meldrum's acid dibromide, were much less effective in the catalytic cycle. For the reaction to work well aqueous potassium carbonate was the most satisfactory base although aqueous Et_3N can also be used.

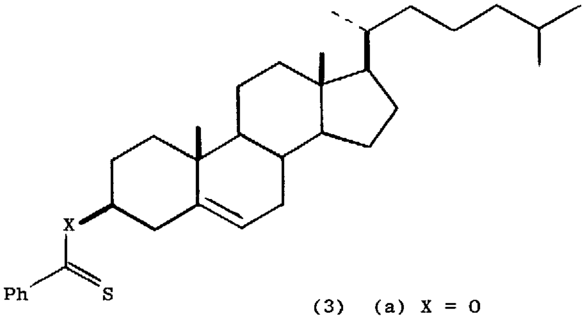
Under optimum conditions the thiocarbonyl derivative is dissolved in chloroform together with 1.5% of the tellurium species. To this mixture is added an excess of 1,2-dibromotetrachloroethane and aqueous K_2CO_3 and the reaction stirred rapidly until complete (Table). Our study has largely focused on the conversion of the thiobenzoate (3a) to the benzoate although other derivatives (3b), (4) and (5) were also investigated.



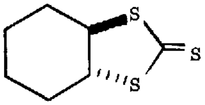
(1) (a) Ar = Ar' = *p*-MeO-phenyl; X = O
    (b) Ar = Ar' = *p*MeO-phenyl; X = Cl, Cl
    (c) Ar = *p*MeO-phenyl; Ar' = *p*-Me_2N-phenyl; X=Cl,Cl
    (d) Ar = Ar' = *p*-Me_2N-phenyl; X = Cl, Cl
    (e) Ar = Ar' = *p*-HO_2C-CH_2-O-phenyl; X = O

(*p*-MeO-phenyl)$_2$Te

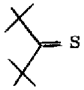
(2)



(3) (a) X = O
    (b) X = S



(4)



(5)

TABLE *

Oxidation of Thiocarbonyl Compounds at Room Temperature using 1,2-Dibromotetrachloroethane as Halogenating Agent

Substrate	Eq. of halogenating agent	Eq. of tellurium species		Aqueous Base	Time h	Yield %
(3a)	1.1	(2)	0.1	10% K_2CO_3	116	88
"	3	"	0.1	"	23	90
"	5	"	0.015	"	88	75
"	5	"	"	20% K_2CO_3	20	70
"	3	"	"	"	80	70
"	5	(1b)	0.1	"	26	87
"	5	(2)	1	Et_3N	15	85
"	5	(2)	0.01	"	48	41
"	5	(1c)	0.1	20% K_2CO_3	20	88
"	5	(1d)	0.1	"	2	88
(3b)	10	(2)	0.015	"	72	70
"	5	"	"	"	114	70
(4)	5	"	"	"	72	60
(5)	5	"	"	"	15	Quant.

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* In the absence of the diaryltellurium species no reaction was observed.

In an effort to improve the cycle tellurium containing species in which the aromatic group was substituted by stronger electron donating group (1c) and (1d) were briefly examined. Preliminary data suggests that the *bis*-dimethylamino derivatives undergo a more rapid reaction. On the other hand potential water soluble oxidants derivated from (1e) are considerably less reactive.

1,2-Dibromotetrachloroethane should find further use as a mild oxidant and source of bromine. It has been used once before in radical chemistry[4].

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