The Chemistry of Acyl Tellurides: Generation and Trapping of Acyl Radicals, Including Aryltellurium Group Transfer

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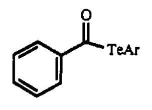
Acyl selenides have been shown in recent years to be excellent precursors for the generation of acyl radicals, when used in conjunction with tributyltin hydride, in radical chain reactions.[2,3] This is overall a reductive process, whatever the radical trap employed, involving hydrogen atom abstraction from the tin hydride as an essential chain propagation step. Alternative chain sequences designed to eliminate this reductive step make use of the phosphite deoxygenation of acyloxy radicals,[4] generated by the *O*-acyl thiohydroxamate method,[5] with chain transfer by attack at the thiocarbonyl sulfur, the photoinitiated cleavage of acylcobalt(III) derivatives,[6] and the photolysis of *S*-acyl xanthate esters, again with propagation by attack at the thiocarbonyl sulfur.[7] In the continuation of our study of the chemistry of acyl radicals, we have investigated the photostimulated reactions of acyl aryl tellurides and report that, at least for aromatic acid derivatives, they are efficient sources of acyl radicals suitable for use in oxidative processes.

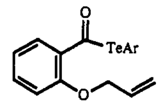
The acyl tellurides **1–6**[8] prepared from the corresponding acyl chlorides by treatment with the appropriate aryl telluride anion, itself generated in situ from the ditellurides[9] by reduction with sodium borohydride in 10:1 THF/MeOH, are mostly orange brown crystalline solids that can be stored at room temperature under a nitrogen atmosphere.[10] The 4-fluoroderivatives **1**, **3**, and **6** are stable in air, presumably due to an increased oxidation potential. White light photolysis[11] of **1** under an inert atmosphere at 8 °C in benzene with 1 equiv of diphenyl diselenide gave, after 1.5 h, the selenoester (**7**)[12] quantitatively. Replacement of diphenyl diselenide with diphenyl disulfide gave the thioester (**8**)[13] in 85% yield, but only after 6.0 h. Irradiation of **1** in the presence of the stable nitroxyl **9** as a radical trap led to the isolation, after 2 h at 8 °C, of the (benzoyloxy)amine **10** in 86% yield. Grossly analogous results were obtained on irradiation of **2** with dichalcogenides and **9** as the radical trap. Thermally, reaction of **1** in benzene at reflux under nitrogen in the dark with diphenyl diselenide gave 80% of **7** after 2 h. With diphenyl disulfide, **8** was obtained but only in 16% yield after 16 h, and with **9** the (benzoyloxy)amine **10** was formed quantitatively after 5 h at 80 °C. These observations are best interpreted in terms of either photochemically and/or thermally initiated homolytic cleavage of the acyl–tellurium bond followed by attack of the acyl radical on the trap, with the possible intervention of an ensuing radical chain mechanism in the case of the disulfide and diselenide.

In order to explain the considerable differences in reaction rate, it is necessary to invoke the reduced efficiency of disulfides over diselenides and nitroxyl radicals as radical traps[14] and, in the case

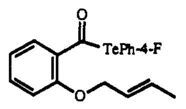
Chart I



1 Ar = 4-F-Ph
2 Ar = 4-MeOPh



3 Ar = 4-F-Ph
4 Ar = 4-MeOPh
5 Ar = 2,4-(MeO)$_2$Ph



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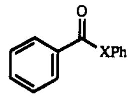
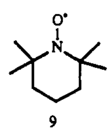


7 X = Se
8 X = S



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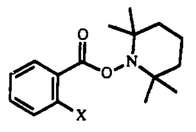
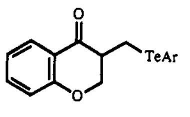
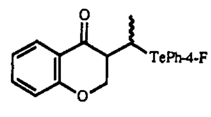


10 X = H
18 X = OCH$_2$CH═CH$_2$



11 Ar = 4-F-Ph
12 Ar = 4-MeOPh
13 Ar = 2,4-(MeO)$_2$Ph



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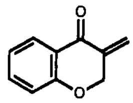

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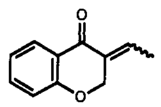

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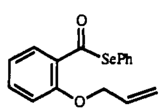

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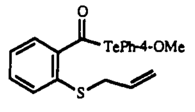

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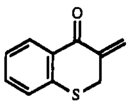

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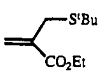

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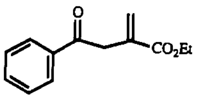

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(1) On study leave from the Department of Chemistry, University College, London, UK.

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(8) (a) **1**, 92%, mp 51–54 °C. (b) **2**, 100% mp 88–89 °C. (c) **3**, 89%, mp 50–51 °C. (d) **4**, 85%, mp 78–79 °C. (e) **5**, 97%, oil. (f) **6**, 76%, mp 60–62 °C.

(9) (a) Bis(4-fluorophenyl) ditelluride (mp 66–67 °C, EtOH) was prepared by reaction of (4-fluorophenyl)magnesium bromide with tellurium powder in THF in 67% yield. (b) Bis(4-methoxyphenyl) ditelluride: Comasseto, V.; Lang, S.; Ferreira, J.; Simmonelli, F. *J. Organomet. Chem.* **1987**, *334*, 369. (c) Bis(2,4-dimethoxyphenyl) ditelluride: Tarbell, D.; McCall, M. *J. Am. Chem. Soc.* **1952**, *74*, 48.

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(11) Photolyses were carried out with a GE 250-W sunlamp at an average distance of 15 cm through Pyrex. The reactions were either cooled in a cold water bath or heated to reflux with the excess heat generated by the lamp.

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of the less efficient radical trap, a degenerate background reaction in which an acyl radical abstracts an aryltelluro group from an additional molecule of acyl telluride.[15] An alternative mechanism, suggested by a referee, in which PhSe$^\bullet$ PhS$^\bullet$, or **9** attacks at the carbonyl carbon of the acyl telluride with formation of a radical tetrahedral intermediate as in ArC(TeAr′)(SPh)O$^\bullet$ followed by expulsion of the aryltelluryl radical is unlikely given the high energy of the proposed intermediate radical with respect to the acyl telluride and attacking radical and given the cyclization results presented below (Chart I).

Irradiation of **3**–**5** in benzene at reflux gave the products of acyl radical cyclization with aryltellurium group transfer, **11**–**13**, in 96, 80, and 86% yields, respectively. The mass balance, in each case, was made up of the elimination product **15**. Photolysis of the acyl telluride **6** resulted in the formation of the cyclization product **14** in 90% yield after only 1.5 h. We view these cyclizations as radical chain reactions, with the two propagation steps being (i) cyclization of the unsaturated acyl radical and (ii) chain transfer by abstraction of an aryltelluryl group from an additional molecule of acyl telluride. The alternative possibility of attack of an aryltelluryl radical on the terminus of the allyl group followed by cyclization of the adduct radical onto the carbonyl group and expulsion of a chain carrying aryltelluryl radical, as has been demonstrated[16] for the superficially similar unsaturated acyltriphenylgermanes,[17] is unlikely. In particular the comparable ease of cyclization of **3** and **6** militates against this mechanism. When **4** was irradiated in the presence of diphenyl diselenide, and **9**, the trapping products **17** and **18** were isolated in 78 and 87% yields, respectively, indicating that trapping by these species competes effectively with cyclization. However, irradiation of **4** in the presence of diphenyl disulfide gave **12** in 90% yield, reinforcing the notion of the disulfide as a much poorer radical trap. Moreover, in none of these last three reactions was there any indication of products formed by attack of PhSe$^\bullet$, **9**, or PhS$^\bullet$ on the alkene terminus followed by cyclization of the adduct radical onto the acyl telluride moiety, reinforcing the notion that the observed chemistry is that of acyl radicals. The tellurium transfer products **11**–**13** were somewhat unstable, undergoing slow elimination to **15** on prolonged photolysis, on standing in air, and on silica gel chromatography. They could also be converted to **15** in excellent yield by simple stirring at room temperature with hydrogen peroxide in THF. Similarly, **14** was unstable decomposing slowly to **16**. Photolysis of the thiosalicylate derivative **19**, followed by chromatography on silica gel, gave the elimination product **20** in 41% yield.

Intermolecular carbon–carbon bond formation was achieved by photolysis of **2** in the presence of the allylic sulfide[18] **21**. The adduct **22**[19] was isolated from this reaction in 52% yield after 26 h at 8 °C. To date, although we have been able to prepare and isolate a number of stable acyl tellurides from aliphatic acids, we have been unable to induce them to undergo any radical chemistry, either thermally, photochemically (W and Hg), or with AIBN initiation. Our chemistry is therefore highly complementary to the acylcobalt chemistry of Pattenden[6] where problems were experienced with aromatic acids. We also anticipate that this facile method for the generation of aryl acyl radicals will be of use to those involved in fundamental spectroscopic studies of such species.[20]

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(15) Precedent for the efficient abstraction of aryltellurium groups from alkyl aryl tellurides by methyl radicals has been provided by the Barton group: (a) Barton, D. H. R.; Ramesh, M. *J. Am. Chem. Soc.* **1990**, *112*, 891. (b) Barton, D. H. R.; Dalko, P. I.; Gēro, S. D. *Tetrahedron Lett.* **1991**, *32*, 4713. (c) Barton, D. H. R.; Jaszberenyi, J. Cs.; Theodorakis, E. A. *J. Am. Chem. Soc.* **1992**, *114*, 5904.

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Radical Cation Photoisomerization of Bicyclo[2.2.2]octa-2,5-diene to Tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octane and Its Thermal Retrogression

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Whereas the efficient photoisomerization of norbornadiene to quadricyclane has attracted interest and possible application as a means of storing solar energy,[1] it is the remarkably facile reverse reaction that has hitherto commanded attention in the radical cation chemistry of these valence isomers.[2–9] Thus, the norbornadiene radical cation product was readily detected following the ionization of quadricyclane in the gas phase,[2] in solution,[7] and in several solid matrices,[3,6,8] while the parent radical cation was not observed. Nevertheless, a discrete quadricyclane radical cation precursor, albeit short-lived, was implicated by pulse radiolysis[7] and CIDNP[4] studies on the one-electron oxidation of quadricyclane. Moreover, the formation of an excited state of the quadricyclane radical cation was recently proposed[9] as the primary photochemical step in the conversion of the norbornadiene radical cation to other bicyclic and monocyclic $C_7H_8^{\bullet+}$ isomers.[6,9] This interest in the intermediacy of the highly-strained quadricyclane radical cation prompted us to study the radical cations derived from the congeneric valence-isomer pair of tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octane[10] (**1**) and bicyclo[2.2.2]octa-2,5-diene[11] (**2**), and here we report the first direct spectroscopic evidence for the interconversion of **1**$^{\bullet+}$ and **2**$^{\bullet+}$.

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(11) (a) Although **1**$^{\bullet+}$ has not previously been identified, its formation was proposed as the first step in one of two alternate mechanisms used to describe the overall photorearrangement of **2**$^{\bullet+}$ to the 1,3,5,7-octatetraene radical cation, a transformation observed by electronic absorption spectroscopy in an argon matrix: Dunkin, I. R.; Andrews, L.; Lurito, J. T.; Kelsall, B. J. *J. Phys. Chem.* **1985**, *89*, 1701. (b) Reaction pathways for the stepwise photoisomerizations of **2**$^{\bullet+}$ and of the bicyclo[4.2.0]octa-2,4-diene radical cation in a Freon glass have also been formulated as proceeding initially through a benzene–ethylene radical cation π-complex assigned by electronic absorption spectroscopy: Fujisaka, Y.; Makino, M.; Takahashi, J.; Shida, T.; Roth, K.; Straub, R.; Bally, T. *J. Phys. Chem.* **1992**, *96*, 2205. Bally, T.; Roth, K.; Straub, R. *J. Am. Chem. Soc.* **1988**, *110*, 1639.

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