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THE INVENTION OF NEW RADICAL CHAIN REACTIONS. PART XIII. HIGH YIELDING DECARBOXYLATIVE CHALCOGENATION OF ALIPHATIC AND ALICYCLIC ACIDS[†]

Derek H.R. Barton, Dominique Bridon, and Samir Z. Zard[*]
Institut de Chimie des Substances Naturelles, C.N.R.S.
91190 Gif-sur-Yvette, France

Abstract —— Irradiation with a tungsten lamp of mixed anhydrides (e.g. 8) derived from aliphatic or alicyclic carboxylic acids and N-hydroxy-2-pyridine thione 3 in the presence of a disulphide, diselenide or ditelluride gives the corresponding chalcogenide (e.g. 9, 10, or 11) in high yield. The process involves a radical decarboxylation followed by S_H2 reaction of the intermediate carbon radical on the dichalcogenide.

Access to organic chalcogenides, especially selenides and tellurides, has generally been through ionic reactions such as, for example, nucleophilic substitution by a chalcogen containing nucleophile or addition to a nucleophilic organochalcogen species.[1] Radical processes, in contrast, have not enjoyed a similar popularity, partly because of the relatively limited number of preparatively useful sources of carbon radicals compatible with the various chalcogenating agents.[2]

We have recently invented a mild method for generating carbon radicals from aliphatic and alicyclic carboxylic acids through a novel decarboxylation reaction.[3a] Thus, mixed anhydrides 1 derived from suitable thiohydroxamic acids such as 2 or 3 undergo a thermally or photochemically induced decarboxylative rearrangement to give the corresponding sulphides 4. The reaction follows a simple radical chain mechanism as depicted in Scheme 1 (path A). The intermediate carbon radical produced is easily captured by a variety of reagents allowing

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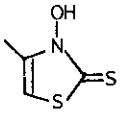
[†] Dedicated with admiration and affection to Professor Gilbert Stork on the occasion of his first sixtyfifth birthday.

synthetically useful modifications of the basic process.[3] Specifically we could perform an S_H2 type reaction[4] on a number of dichalcogenides which led to the synthesis of sulphides, selenides and tellurides 6 in preparatively acceptable yields. In this overall decarboxylative chalcogenation, the co-produced chalcogenyl radical 5 acts as an efficient chain carrier (Scheme 1, path B).[5]



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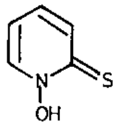

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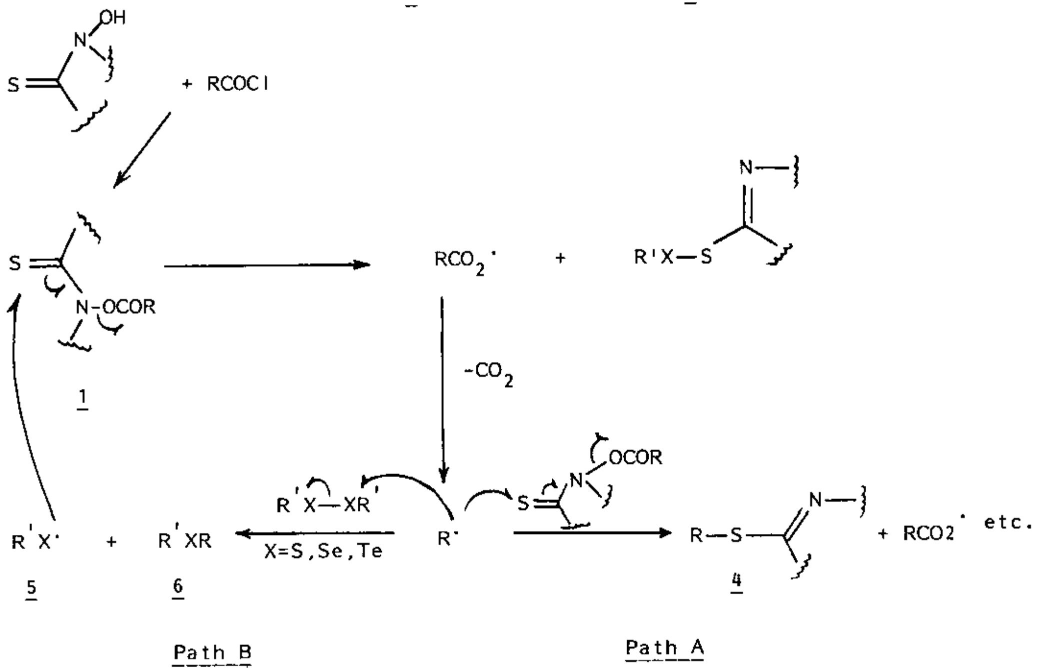


Scheme 1

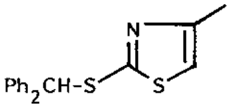
These early experiments were carried out using thermal decomposition of the esters of 2 as radical source. However, large amounts of diphenyl disulphide and diphenyldiselenide had to be employed for the desired reaction to prevail over the background decarboxylative rearrangement which produces sulphide 4 through path A. This made work-up and purification quite tedious especially when the product and the reagent had similar polarities. Thus, to raise the yield of phenyl sulphide 9a to 74%, the reaction had to be conducted in 30 equiv. of molten diphenyl disulphide (cf. Table 1, entries 1-3). In the case of selenides, smaller but nevertheless substantial, amounts of the more reactive diphenyl diselenide were necessary (cf. Table 2, entries 1-6). These conditions were too drastic for the preparation of the somewhat thermally unstable tellurides, exception being made for the steroid tellurides 11f and 11g (Table 3, entries 1 and 2). This difficulty was circumvented by taking advantage of the dissociation of ditellurides by visible light to initiate the chain reaction and thus operate at the lower temperature of 35°C under laboratory lighting (Table 3, entries 3-8).

Table 1[a]

Entry	Mixed Anhydride	Temperature (°C)	R'SSR' (eq.)	Products (isolated yields,%)
1	7a	110	PhSSPh (2)	9a (30)
2	7a	110	PhSSPh (10)	9a (48)
3	7a	120	PhSSPh (30)	9a (74)
4	8a	0	PhSSPh (2)	9a (82)
5	8a	0	MeSSMe (45)	9b (64)
6	8a	0	MeSSMe (neat)	9b (83)

a) Entries 1-3 are from Ref. 5.

In all cases, the main side product was the corresponding sulphide 4. However, a simple way to suppress this competing pathway to a large extent emerged following observations made during a study of the decarboxylative rearrangement of anhydride 7d derived from diphenylacetic acid. We noted that in addition to the expected sulphide 15, substantial amounts of 1,1,2,2 tetraphenylethane 16 were formed. More importantly, however, the yield of 16 decreased considerably when the reaction temperature was raised from 80°C to 110°C. Furthermore, when the corresponding anhydride 8l was irradiated with a tungsten lamp at 0°C, the dimer 16 became the major product and could be isolated in about 70% yield. These observations strongly suggested that the addition of the carbon radical is reversible and that the rate limiting step is in fact the breaking of the N-O bond (Scheme 2). Thus, at lower temperatures, this fragmentation becomes slow enough to allow a build-up of carbon radicals leading eventually to dimerisation. At higher temperatures, the irreversible cleavage of the N-O bond is fast, promoting the formation of sulphide 4.[5]



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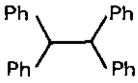

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Table 2[a]

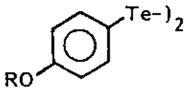
Entry	Mixed Anhydride	Temperature (°C)	PhSeSePh (eq.)	Products (isolated yields, %)
1	7a	110	(2)	10a (60)
2	7a	110	(10)	10a (75)
3	7b	110	(10)	10b (75)
4	7b	120	(20)	10b (73)
5	7c	120	(20)	10c (72)
6	8h	110	(10)	10h (80)
7	8a	0	(2)	10a (85)
8	8b	0	(2)	10b (91)
9	8c	0	(2)	10c (89)
10	8d	0	(2)	10d (97)
11	8e	0	(2)	10e (88)
12	8f	0	(2)	10f (90)
13	8g	0	(2)	10g (84)
14	8i	0	(2)	10i (92)
15	8j	0	(2)	10j (93)

a) Entries 1-6 are from Ref. 5.

Table 3

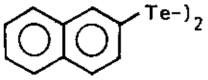
Entry	Mixed Anhydride	Temperature (°C)	ArTeTeAr (eq.)	Products (isolated yields, %)
1	8h	110	12 (2)	11f (56)
2	8h	110	14 (2)	11g (65)
3	8a	35	12 (2)	11a (65)
4	8c	35	12 (2)	11b (55)
5	8j	35	12 (2)	11c (75)
6	8j	50-60	14 (2)	11d (65)
7	8j	35	13 (2)	11e (70)
8	8k	35	12 (2)	11h (55)
9	8a	0	14 (2)	11i (82)
10	8c	0	12 (2)	11b (88)[b]
11	8j	0	13 (2)	11e (94)

a) Entries 1-8 are from Ref. 5. b) Yield determined by NMR.



12 R = Ph

13 R = Me



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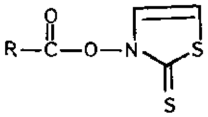
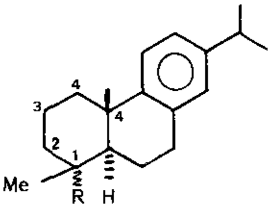
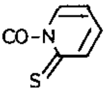
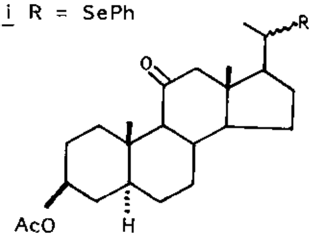
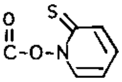


7a R = $CH_3(CH_2)_{14}$-
7b R = cyclohexyl-
7c R = Ph_2CHCH_2-
7d R = Ph_2CH-



8i R = α-CO-N 
10i R = SePh



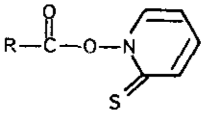
8k R =  (20-S)
11h R = Te-p-C_6H_4-OPh

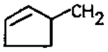
R—S—R'

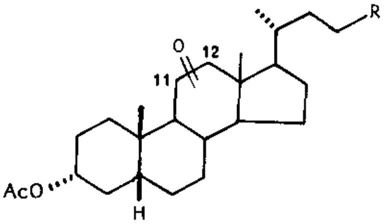
9a R = $CH_3(CH_2)_{14}$; R' = Ph
9b R = $CH_3(CH_2)_{14}$; R' = Me

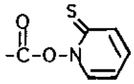
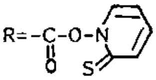
R—Te—Ar

11a R = $CH_3(CH_2)_{14}$-; Ar = p-C_6H_4OPh
11b R = Ph_2CHCH_2-; Ar = p-C_6H_4OPh
11c R = 1-adamantyl; Ar = p-C_6H_4OPh
11d R = A-adamantyl; Ar = β-naphthyl-
11e R = 1-adamantyl; Ar = p-C_6H_4OMe
11i R = $CH_3(CH_2)_{14}$; Ar = β-naphthyl-

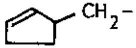


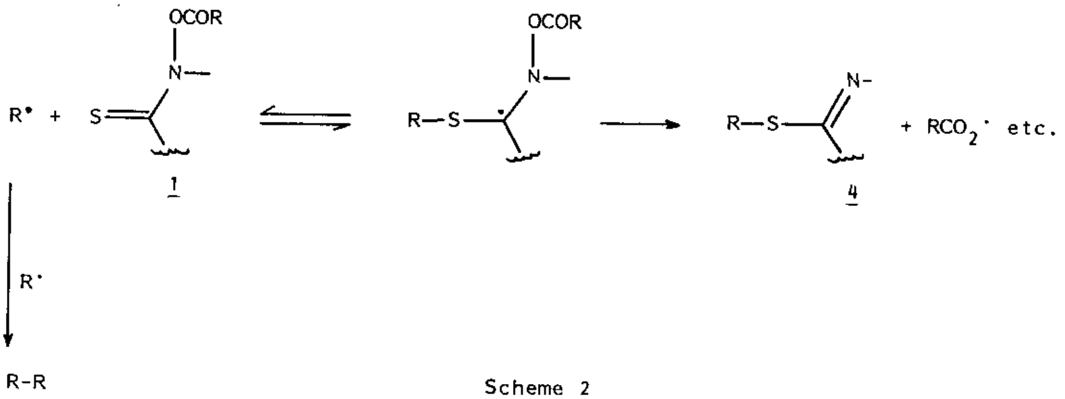
8a R = $CH_3(CH_2)_{14}$-
8b R = cyclohexyl-
8c R = Ph_2CHCH_2
8d R = $(PhCH_2)_2CH$
8e R = 1-methylcyclohexyl-
8f R = 
8j R = 1-adamantyl
8l R = Ph_2CH-



8g R =  ; 11-oxo
10g R = SePh; 11-oxo
8h R = R= ; 12-oxo
10h R = SePh; 12-oxo
11f R = Te-β-$C_{10}H_7$; 12-oxo
11g R = Te-p-CH_6H_5OPh; 12-oxo

R—SePh

10a R = $CH_3(CH_2)_{14}$-
10b R = cyclohexyl
10c R = Ph_2CHCH_2-
10d R = $(PhCH_2)_2CH$-
10e R = 1-methylcyclohexyl
10f R = 
10j R = 1-adamantyl



Scheme 2

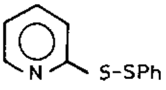
Although the benzylic nature of the radical in this case would particularly favour the reverse process, the same situation should nevertheless prevail, perhaps to a lesser extent, with other aliphatic or alicyclic carbon radicals.[6] If this were true, lowering the reaction temperature should favour the desired irreversible S_H2 process (Scheme 1, path B) at the expense of the competing decarboxylative rearrangement (path A). This would also explain, in retrospect, the relatively good yields originally obtained with only 2 equiv. of ditelluride at 35°C and which were initially ascribed to the higher reactivity of ditellurides as compared with diselenides or disulphides.[7]

Indeed, by operating at 0°C a dramatic improvement in the yield of chalcogenides was observed. Furthermore, much smaller amounts of disulphides or diselenides were required, which simplified considerably the purification. Anhydrides 8 derived from thiohydroxamic acid 3 were used since they could be photolysed by a tungsten lamp at low temperature. The corresponding derivatives 7 require U.V. irradiation.

Thus, with only 2 equivalents of diphenyl disulphide at 0°C and after irradiation with an ordinary projector lamp for a few minutes, an 82% yield of sulphide 9a was obtained as compared with 74% using 30 equivalents of molten reagent under thermal conditions (cf. Table 1, entries 3 and 4). Even the much less reactive dimethyl disulphide produced the desired adduct 9b in 64% yield. Given the volatility of this reagent, we could use it neat to raise the yield of 9b to 83% without complicating the purification procedure (Table 1, entries 5, 6).

In the case of diphenyl diselenide, yields were practically quantitative with only two equivalents of reagent. This allows a ready access to a variety of primary, secondary and even tertiary phenyl selenides (Table 2, entries 7-15) some of which are not easily obtainable. Since the discovery of the mild selenoxide elimination reaction, selenides have found extensive use as olefin precursors.[8]

Lowering the temperature also increased significantly the yield of tellurides as can be judged by inspecting Table 3 (entries 3-5 and 9-11). As in the previous study, the expected tellurosulphide co-product 19 is not observed. It disproportionates under the reaction conditions to give back the ditelluride and 2,2'-dipyridyldisulphide 20. In contrast, the corresponding mixed disulphide 17 and selenosulphide 18 can be isolated.



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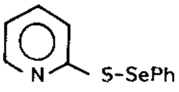

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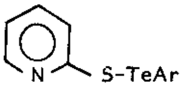

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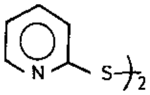

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The efficiency of this decarboxylative chalcogenation, as well as the mildness of the experimental conditions should make this method attractive for the obtention of otherwise inaccessible selenides and especially tellurides which are becoming increasingly important not only as synthetic intermediates[9] but also as myocardial imaging agents.[10]

In our preliminary Communication[5] we unintentionally overlooked the prior publication[11] by Professor Perkins (University of London) of the reaction of the 1-adamantyl radical with diphenyl diselenide to give the 1-phenylseleno- derivative. The yield was low (<20%) but this was due to the difficulties of radical generation. The 1-phenylseleno- derivative was better prepared on that occasion by nucleophilic displacement (80%).

EXPERIMENTAL

Mp's were determined with a Köfler hot stage apparatus. ^{1}H-NMR spectra are for deuteriochloroform solutions with tetramethylsilane as internal standard, unless otherwise stated. Optical rotations are for chloroform solutions. I.R. spectra are of nujol mulls for solid samples or neat in the case of liquids, unless stated to the contrary. Irradiations were performed with a 300 W projector lamp placed close to the reaction vessel.

Preparation of the Acid Chlorides

The acid chlorides used in the following preparations of the mixed anhydrides 8 were prepared immediately before use and were not purified. Thus to a solution of the corresponding carboxylic acid (1 mmole) in benzene (5 ml) was added oxalyl chloride (3 mmole) and a drop of dimethyl formamide. After stirring for 2 h at room temperature with protection from moisture, the solvent and excess oxalyl chloride were evaporated and the residual acid chloride used as such.

General Procedure for the Synthesis of Mixed Anhydrides 8

(Note: These compounds are sensitive to light. The reaction vessel, chromatography column etc.. should therefore be covered with aluminium foil). To a solution of the carboxylic acid chloride (10 mmole) in dry, degassed dichloromethane (50 ml) was added the sodium salt of N-hydroxy-2-thiopyridone 3 (10.5 mmole). After stirring at room temperature in the absence of light and under an inert atmosphere for 1-2 h, the reaction mixture was rapidly filtered and the solvent evaporated without heating. The yellow residue may be used as such or further purified by filtration on a short silica column. In some cases the mixed anhydrides were completely characterised. These are listed below.

N-Palmitoyloxypyridine-2-thione 8a

Purified by flash chromatography on silica (pentane-dichloromethane 1:1) and by crystallisation from dichloromethane pentane (yield 82%); mp: 48-55°C (dec.); $\nu_{max.}$: 1810 cm^{-1}; δ_H: 6.40-8.40 (4H, m), 2.68 (2H, t), 0.85-1.26 (29H); Ms m/z: 365 (M^+), 321 ($M^+ - CO_2$). (Found: C, 68.96; H, 9.63; N, 4.13; S, 8.58. Calc. for $C_{21}H_{35}NO_2S$: C, 68.99; H, 9.65; N, 3.83; S, 8.77%).

N-(3,3-Diphenylpropionyloxy)-pyridine-2-thione 8d

Purified by flash chromatography on silica (dichloromethane-pentane 1:1) and by recrystallisation from dichloromethane-pentane; yellow crystalline solid (yield 77%); mp 118-120 (dec.); $\nu_{max.}$: 1790 cm^{-1}; δ_H: 6.35-7.75 (4H, m), 7.40 (10H, broad s), 4.68 (1H, t), 3.46 (2H, d); Ms m/z: 335 (M^+), 291 ($M^+ - CO_2$). (Found: C, 71.40; H, 5.17; N, 4.42; S, 9.84. Calc. for $C_{20}H_{17}NO_2S$: C, 71.61; H, 5.11; N, 4.18; S, 9.56%).

N-(1-Methylcyclohexylcarbonyloxy)-pyridine-2-thione 8e

Purified by flash chromatography on silica (dichloromethane-pentane 3:2) and by crystallisation from dichloromethane-pentane; yellow crystalline solid (yield 76%); mp 92-94°C (dec.); $\nu_{max.}$: 1800 cm^{-1}; δ_H: 6.40-7.82 (4H, m), 1.47 (3H, s), 1.00-2.32 (10H, m); Ms m/z 251 (M^+). (Found: C, 61.96; H, 6.71; N, 5.84; S, 12.63. Calc. for $C_{13}H_{17}O_2NS$: C, 62.12; H, 6.82; N, 5.57; S, 12.76%).

n-Pentadecylmethyl Sulphide 9b

An ice-cold solution of anhydride 8a (187.4 mg, 0.51 mmole) in dimethyl disulphide (10 ml) was irradiated for 30 min under argon. The excess dimethyl disulphide was distilled off and the residue purified by chromatography on silica (dichloromethane-pentane 1:9) to give the sulphide 9b as an oil (110 mg, 83%); δ_H: 2.45 (2H, t), 2.07 (3H, s), 0.88-1.28 (29H). (Found: C, 74.48; H, 13.37. Calc. for $C_{16}H_{34}S$: C, 74.34; H, 13.26%).

General Procedure for the Synthesis of Sulphide 9a; Selenides 10a-j and Tellurides 11b, 11e, 11i

The mixed anhydride 8 (1 mmole) was added to an ice-cold, degassed solution of the dichalcogenide (2 mmole) (See Tables 1-3) in dichloromethane (20 ml) under argon. Irradiation for 20 minutes with a 300 W tungsten lamp placed near the reaction vessel followed by concentration and chromatography of the residue on silica afforded the desired product. In some cases, involving diphenyldiselenide, treatment with aqueous sodium borohydride removed the excess diphenyldiselenide and simplified the purification. Yields are given in Tables 1-3.

Pentadecylphenyl Sulphide 9a

Eluted with dichloromethane-pentane (1:4); mp: 49-50°C (methanol); (lit.[12] mp 51°C).

1-Phenylselenopentadecane 10a

Eluted with dichloromethane-pentane (1:4); mp: 40-41°C (methanol); δ_H: 7.35 (5H, broad s), 2.95 (2H, t), 0.88-1.28 (29H); Ms m/z: 368, 366 (M^+). (Found: C, 68.32; H, 9.77. Calc. for $C_{21}H_{36}Se$: C, 68.63; H, 9.87%).

Phenylselenocyclohexane 10b

Eluted with dichloromethane-pentane (1:4); low melting solid; δ_H: 7.28 (5H, broad s), 3.28 (1H, m), 1.45 (10H, m); Ms m/z: 240, 238 (M^+). (Found: C, 60.49; H, 6.56. Calc. for $C_{12}H_{16}Se$: C, 60.25; H, 6.74%).

1-Phenylseleno-2,2-diphenylethane 10c

Eluted with dichloromethane-pentane (1:4); mp 32°C (methanol); δ_H: 7.20-7.70 (5H, m), 7.37 (10H, broad s), 4.30 (1H, t, J = 8 Hz), 3.60 (2H, d, J = 8 Hz); Ms m/z 336, 334 (M^+). (Found: C, 71.28; H, 5.28. Calc. for $C_{20}H_{18}Se$: C, 71.21; H, 5.38%).

2-Phenylseleno-1,3-diphenylpropane 10d

Eluted with dichloromethane-pentane (1:1); colourless oil; δ_H: 7.45 (2H, m), 7.20 (3H, m), 7.08 (10H, broad s), 3.46 (1H, qn, J = 8 Hz), 2.84 (4H, d, J = 8 Hz); Ms m/z 349, 351 (M^+). (Found: C, 72.04; H, 5.96. Calc. for $C_{21}H_{20}Se$: C, 71.79; H, 5.74%).

1-Phenylseleno-1-methylcyclohexane 10e

Eluted with dichloromethane-pentane (1:4); colourless oil; δ_H: 7.45 (2H, m), 7.25 (3H, m), 1.52 (10H, m), 1.34 (3H, s); Ms m/z: 252, 254 (M^+). (Found: C, 61.76; H, 7.37. Calc. for $C_{13}H_{18}Se$: C, 61.66; H, 7.16%).

3-(Phenylselenomethyl)-cyclopent-1-ene 10f

Eluted with dichloromethane-pentane (1:9); colourless oil; δ_H: 7.45 (2H, m), 7.25 (3H, m), 5.70 (2H, broad s), 2.92 (2H, s), 1.50-2.50 (4H, m); Ms m/z: 238, 236 (M^+). (Found: C, 61.05; H, 5.70. Calc. for $C_{12}H_{14}Se$: C, 60.76; H, 5.95%).

3α-Acetoxy-23-Phenylseleno-11-oxo-24-norcholane 10g

Eluted with dichloromethane-ethylacetate (9:1); mp 90-92°C (hexane); $[\alpha]_D$ = +61° (c = 1); $\nu_{max.}$ ($CHCl_3$): 1720, 1700 cm^{-1}; δ_H: 7.60 (2H, m), 7.45 (3H, m), 4.80 (1H, broad), 2.92 (2H, t), 2.05 (3H, s), 1.20 (3H, s), 0.94 (3H, d), 0.61 (3H, s); Ms m/z: 544, 542 (M^+). (Found: C, 68.25; H, 8.11. Calc. for $C_{31}H_{44}O_3Se$: C, 68.49; H, 8.16%).

3α-Acetoxy-23-Phenylseleno-12-oxo-24-norcholane 10h

Eluted with dichloromethane-ethylacetate (9:1); mp 173-176°C (hexane); $[\alpha]_D$ = +112° (c = 1); $\nu_{max.}$ ($CHCl_3$): 1720, 1700 cm^{-1}; δ_H: 7.70 (2H, m), 7.42 (3H, m), 4.78 (1H, broad), 2.97 (2H, t), 2.09 (3H, s), 1.08 (6H, s), 0.87 (3H, d); Ms m/z: 544, 542 (M^+). (Found: C, 68.49; H, 8.16. Calc. for $C_{31}H_{44}O_3Se$: C, 68.49; H, 8.16%).

1-(Phenylseleno)-7-(1-methylethyl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene 10i

Eluted with dichloromethane-pentane (1:4). Two epimers at C-1 were obtained in approximately 3:1 ratio. The more polar and major epimer is a solid with a mp 65-68°C (methanol); $[\alpha]_D$ = -165° (c = 0.36); δ_H (200 MHz): 6.90-7.80 (8H, m), 1.22 (6H, d, J = 6 Hz), 1.21 (3H, s, 4a-Me), 1.19 (3H, s, 1-Me); Ms m/z 412, 410 (M^+). (Found: C, 73.41; H, 7.83. Calc. for $C_{25}H_{32}Se$: C, 72.97; H, 7.84). Comparison of the NMR with that of the starting dehydroabietic acid and especially the chemical shifts of the 1- and 4a-methyl groups indicates a 1α-orientation for the phenylseleno group. This is in accord with results in the related steroid field[13] as well as with the expected favoured attack from the least hindered α-side.

1-Phenylselenoadamantane 10j

Eluted with dichloromethane-pentane (1:4); mp 34-35°C (methanol) (lit.[11] mp 35°C).

1-(4-Phenoxyphenyltelluro)-2,2-diphenylethane 11b

Eluted with dichloromethane-pentane (1:1); the product obtained was contaminated with small amounts of di-(4-phenoxylphenyl)-telluride and could not be completely purified; δ_H: 7.08-7.95 (9H, m), 7.51 (10H, broad s), 4.52 (1H, t, J = 8 Hz), 3.66 (2H, d, J = 8 Hz); Ms m/z 476, 478, 480 (M^+).

1-(4'-Methoxyphenyltelluro)-adamantane 11e

Eluted with dichloromethane-pentane (1:1); mp: 54-56°C (methanol); δ_H: 8.08 (2H, d, J = 9 Hz), 7.05 (2H, d, J = 9 Hz), 3.93 (3H, s), 2.26 (6H), 1.97 (3H), 1.80 (6H); Ms m/z: 368, 370, 372 (M^+). (Found: C, 54.76; H, 6.03. Calc. for $C_{17}H_{22}OTe$: C, 55.04; H, 6.25%).

1-(2-Naphthyltelluro)-pentadecane 11i

Eluted with dichloromethane-pentane (1:4); mp 57°C (methanol); δ_H: 7.10-8.00 (7H, m), 2.90 (2H, t), 0.86-1.25 (29H); Ms m/z: 464, 466, 468 (M^+). (Found: C, 64.09; H, 8.09. Calc. for $C_{25}H_{38}Te$: C, 64.41; H, 8.21%).

General Procedure for the Synthesis of Tellurides 11a, 11c, 11d, 11h

A mixture of the acid chloride (1 mmole), the sodium salt of N-hydroxy-2-pyridine thione (1.1 mmole) and the ditelluride (2 mmoles) in dry, degassed toluene (20 ml) was stirred at 35°C

(50-60°C in the case of 11d) under nitrogen for about 2 h and without protection from laboratory lighting. The solvent was removed using a rotary evaporator and the residue purified by chromatography on silica.

1-(4-Phenoxyphenyltelluro)-pentadecane 11a

Eluted with pentane; mp: 52-53°C (methanol); δ_H: 7.88 (2H, d, J = 8.5 Hz), 7.15-7.40 (5H, m), 6.97 (2H, d, J = 8.5 Hz), 2.93 (2H, t), 0.88-1.34 (26 H); Ms m/z: 505, 507, 509 (M^+). (Found: C, 63.58; H, 7.92. Calc. for $C_{27}H_{40}OTe$: C, 63.81; H, 7.93%).

1-(2-naphthyltelluro)-adamantane 11d

Eluted with dichloromethane-pentane (1:9); mp 119-120°C (methanol); δ_H: 7.15-8.00 (7H, m), 2.33 (6H, d), 1.92 (3H, m), 1.76 (6H, d); Ms m/z: 388, 390, 392 (M^+). (Found: C, 61.42; H, 5.84. Calc. for $C_{20}H_{33}Te$: C, 61.59; H, 5.69%).

1-(4-Phenoxyphenyltelluro)-adamantane 11c

Eluted with dichloromethane-pentane (5:95); mp: 102-104°C (methanol); δ_H: 8.00 (2H, d, J = 8.5 Hz), 7.20-7.60 (5H, m), 7.02 (2H, d, J = 8.5 Hz), 2.66 (6H, m), 1.95 (3H, m), 1.83 (6H, m); Ms m/z: 430, 432, 434 (M^+). (Found: C, 61.22; H, 5.55. Calc. for $C_{22}H_{24}OTe$: C, 61.16; H, 5.60%).

3β-Acetoxy-20-(4'-phenoxyphenyltelluro)-pregnan-11-one 11h

Eluted with dichloromethane-ethyl acetate (9:1) (mixture of epimers at C-20); mp: 128-135°C (hexane); $[\alpha]_D$ = +5° (c = 0.57); $\nu_{max.}$($CHCl_3$): 1720, 1700 cm^{-1}; δ_H: 6.92-8.05 (9H, m), 2.08 (3H, s), 1.07 (3H, s), 0.66 (3H, s); Ms m/z: 654, 656, 658 (M^+). (Found: C, 63.86; H, 6.83. Calc. for $C_{35}H_{44}O_4Te$: C, 64.05; H, 6.76%).

3α-Acetoxy-23-(4'-phenoxyphenyltelluro)-24-nor-cholan-12-one 11g

The mixed anhydride 8h was formed *in situ* by adding slowly (5 h) a solution of the corresponding carboxylic acid chloride (0.45 mmole) in toluene (10 ml) to a mixture of the sodium salt of N-hydroxy-2-thiopyridone (3) (70.4 mg, 0.47 mmole) and ditelluride 12 (527 mg, 0.88 mmole) in refluxing toluene (5 ml) under an innert atmosphere. After additional heating for 2 h, the toluene is evaporated and the residue purified by chromatography on silica (dichloromethane-ethyl acetate 9:1) to give telluride 11g (171 mg, 56%); mp 132-135°C (hexane); $[\alpha]_D$ +98° (c = 1.2); $\nu_{max.}$($CHCl_3$): 1720, 1700 cm^{-1}; δ_H: 7.90 (2H, d, J = 8.5

Hz), 7.20-7.60 (5H, m), 7.00 (2H, d, J = 8.5 Hz), 4.80 (1H, m), 2.94 (2H, m), 2.06 (3H, s), 1.05 (3H, s), 0.85 (3H, s); Ms m/z: 682, 684, 686 (M^+). (Found: C, 65.10; H, 7.04. Calc. for $C_{32}H_{48}O_4Te$: C, 64.94; H, 7.07%).

3α-Acetoxy-23-(2'-naphthyltelluro)-24-nor-cholan-12-one 11f

Prepared by the same procedure as for 11g but using di-β-naphthyl ditelluride 14 instead of 12. The yield of telluride 11f was 65%; mp 115-120°C (hexane); $[\alpha]_D$ = +97° (c = 1.1); $\nu_{max.}(CHCl_3)$: 1720, 1700 cm^{-1}; δ_H: 7.12-8.40 (7H, m), 4.82 (1H, m), 3.03 (2H, m), 2.02 (3H, s), 1.02 (3H, s), 0.90 (3H, s); Ms m/z: 640, 642, 644 (M^+). (Found: C, 65.20; H, 7.14. Calc. for $C_{35}H_{46}O_3Te$: C, 65.44; H, 7.22%).

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