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THIOACYLSULFENYL BROMIDES: ELECTROPHILIC DITHIOCARBOXYLATING REAGENTS

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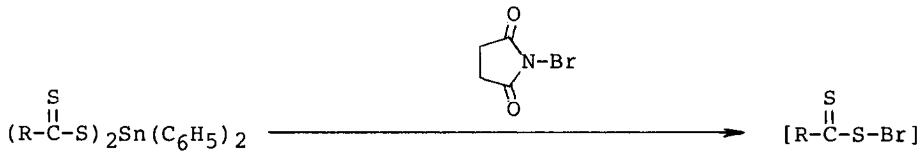
Summary: The reaction of diphenyltin bis(dithiocarboxylates) with N-bromosuccinimide yielded thioacylsulfenyl bromides, which reacted with alcohols and sodium dithiocarboxylates etc. to afford novel O-alkyl thioacylsulfenates and unsymmetrical disulfides.

The chemistry of dithiocarboxylic acids and their derivatives has recently received considerable attention.[1] Dithiocarboxylation has been generally effected by the use of nucleophilic reagents such as alkali[2] or alkali earth metal[3] and ammonium dithiocarboxylates.[4] In contrast, thioacylsulfenyl halides [RC(S)SX, R = alkyl, aryl, X = halogen] are potential electrophilic thiocarboxylating reagents (umpolung synthon). However, due to their extreme instability these compounds have never been described in literature so far, despite their considerable synthetic utility. Recently the isolation of several crystalline acylsulfenyl halides has been realized.[5] Herein we report the synthesis and properties of thioacylsulfenyl bromides **2**, the first thioacylsulfenyl halides, from the reaction of diphenyltin bis(dithiocarboxylates) **1** with N-bromosuccinimide, as well as an approach to novel O-alkyl thioacylsulfenates, thioacylsulfenamide **7**, and unsymmetrical bis(thioacyl) disulfides **9** - **12**, etc.

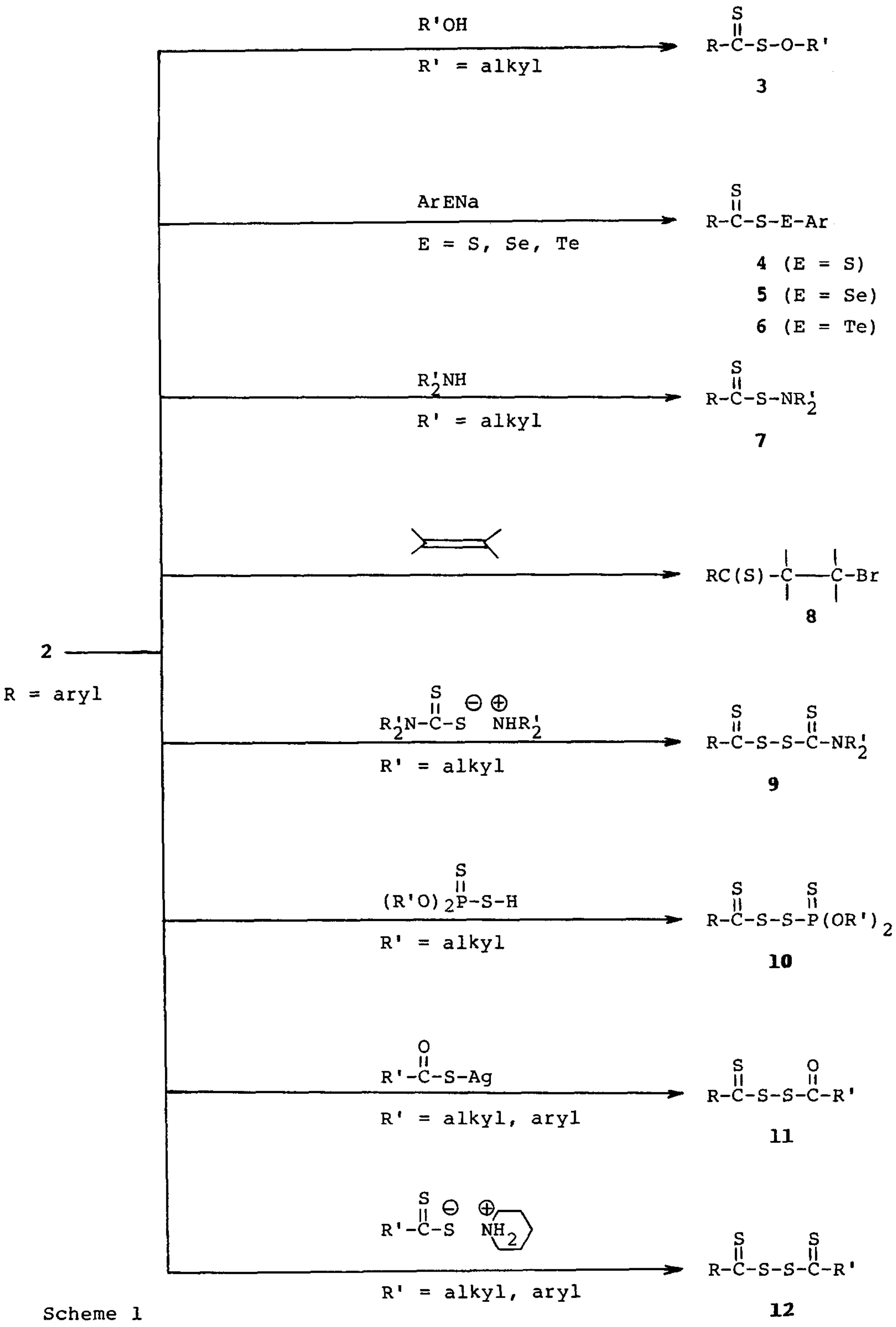
When N-bromosuccinimide was added to a solution of diphenyltin bis[4-(methyl)dithiobenzoate] **1b**[6] in dichloromethane at -15°C, the λmax at 460 nm due



$$(R\text{-}\overset{\overset{S}{\|}}{C}\text{-}S)_2Sn(C_6H_5)_2 \longrightarrow [R\text{-}\overset{\overset{S}{\|}}{C}\text{-}S\text{-}Br]$$

1 **2**

	R	λmax/nm
2a	C_6H_5	504
2b	$4\text{-}CH_3C_6H_4$	504
2c	$4\text{-}CH_3OC_6H_4$	490 sh
2d	$4\text{-}ClC_6H_4$	503


R'OH
R' = alkyl
R-C(=S)-S-O-R'
3
ArENa
E = S, Se, Te
R-C(=S)-S-E-Ar
4 (E = S)
5 (E = Se)
6 (E = Te)
R'2NH
R' = alkyl
R-C(=S)-S-NR'2
7
RC(S)-C—C-Br
8
2
R = aryl
R'2N-C(=S)-S⊖ ⊕NHR'2
R' = alkyl
R-C(=S)-S-S-C(=S)-NR'2
9
(R'O)2P(=S)-S-H
R' = alkyl
R-C(=S)-S-S-P(=S)(OR')2
10
R'-C(=O)-S-Ag
R' = alkyl, aryl
R-C(=S)-S-S-C(=O)-R'
11
R'-C(=S)-S⊖ ⊕NH2
R' = alkyl, aryl
R-C(=S)-S-S-C(=S)-R'
12

Scheme 1

to the n → π* transitions of the thiocarbonyl group quickly disappeared and a new absorption maximum appears at 504 nm, which is attributable to that of the expected 4-(methyl)thiobenzoylsulfenyl bromide **2b**. Similarly, bromination of the diphenyltin esters **1a, c, d** of other aromatic dithiocarboxylic acid produced the corresponding thioacylsulfenyl bromides **2a, c, d**, showing a characteristic absorption maximum at 490 - 505 nm, respectively. The thioacylsulfenyl bromides **2** obtained were oily substance and too unstable to allow purification by thin layer or column chromatography.[7] Therefore, their constitutions were established by conversion into the acyl thioacyl disulfides **11**.[8]

The possibility of preparing novel O-alkyl thioacylsulfenates **3**, S-thioacylsulfenamides **7**, the addition products **8** to alkene, and unsymmetrical disulfides **9** - **12** which are difficult to obtain otherwise was explored (Scheme 1). For example, the in situ formed thiobenzoylsulfenyl bromide **2a** readily reacted with methanol at -20°C to give O-methyl thiobenzoylsulfenate **3a**[9] in moderate isolated yield. Under the similar conditions the reaction with sodium thio-, seleno- and tellurophenolate led to good yields of the corresponding chalcogeno derivatives **4** - **6**.[10] Analogous one pot reactions of **2a** with piperidinium N-pentamethylenedithiocarbamate, O,O'-(diisopropyl)dithiophosphoric acid, silver thiobenzoate, and piperidinium 4-(methyl)dithiobenzoate afforded N-pentamethylenethiocarbamoyl thiobenzoyl **9a**,[11] O,O'-(diisopropyl)thiophosphoryl thiobenzoyl **10a**,[12] benzoyl thiobenzoyl **11a**,[13] and 4-(methyl)thiobenzoyl thiobenzoyl disulfide **12a**[14] in 50 - 70 % yields. In addition, thiobenzoylsulfenyl bromide **2a** reacted with amines such as piperidine and morpholine to give the corresponding S-thioacylsulfenamides **7a** and **a'** in 47 and 55 % yields, respectively.[15] Moreover, **2a** reacted with cyclopentene to afford the addition product, 2-bromocyclopentyl dithiobenzoate **8a**.[16]

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7. At -10°C, **2** decomposed completely within 5 min. to give the corresponding symmetrical bis(thioacyl)disulfide in almost quantitative yield.
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9. **3a**: Yield 47 %; Red liquid; ^{1}H-NMR (CCl_4): δ = 3.86 (s, 3H, CH_3), 7.0-7.8 (m, 5H, Ar); MS (70 eV/110°C): *m/e* 184 (M^+); IR (neat): ν = 1244 cm^{-1} (C=S).
10. $4-CH_3C_6H_4C(S)SSC_6H_5$ (**4**): Yield 71 %, m.p. 32 - 35°C; $4-CH_3C_6H_4C(S)SSeC_6H_5$ (**5**): Yield 68 %, m.p. 105 - 107°C; $4-CH_3C_6H_4C(S)STeC_6H_5$ (**6**) : Yield 75 %, m.p. 110 - 112°C.
11. **9a**: Yield 58 %; m.p. 89-90°C; ^{1}H-NMR ($CDCl_3$): δ = 1.4-2.1 (m, 6H, CH_2), 4.0 -4.5 (m, 4H, CH_2), 7.2-8.3 (m, 5H, Ar); IR (KBr): ν = 1224, 1238 cm^{-1}(C=S); UV/Vis (CH_2Cl_2): λmax(log ε) = 293 (4.24), 522 (2.08) nm.
12. **10a**: Yield 65 %; Red oil; ^{1}H-NMR ($CDCl_3$): δ = 1.2-1.6 (m, 12H, CH_2), 4.87 (m, 2H, CH), 7.2-8.2 (m, 5H, Ar); IR (neat): ν = 1250 (C=S), 647 cm^{-1} (P=S); UV/Vis (cyclo-C_6H_{12}): λmax (log ε) = 303 (4.06), 524 (1.96) nm.
13. **11a**: Yield 43 %; m.p. 66-68°C Lit.[5c] 63-67°C; MS (20 eV, 150°C): *m/e* 290 (M^+); The IR and UV/Vis spectra were exactly consistent with those of the authentic samples.
14. **12a**: Yield 44 %; m.p. 89-91°C; ^{1}H-NMR ($CDCl_3$): δ = 2.33 (s, 3H, CH_3), 7.0-8.2 (m, 9H, Ar); IR (KBr): ν = 1255 cm^{-1} (C=S); UV/Vis (CH_2Cl_2): λmax (log ε) = 319 (4.42), 522 (2.42) nm.
15. **7a**: Yield 47 % Red liquid; ^{1}H-NMR (CCl_4) δ = 1.1-2.0 (m, 6H, CH_2), 2.7-3.8 (b, 4H, CH_2), 7.0-8.1 (m, 5H, Ar); MS (20 eV, 150°C): *m/e* 233 (M^+); IR (neat): ν = 1230 cm^{-1} (C=S); UV/Vis (cyclo-C_6H_{12}): λmax = 294, 318 sh, 530 nm.

    7b: Yield 55 %; m.p. 68-79°C; ^{1}H-NMR (CCl_4): δ = 3.2-3.8 (m, 8H, CH_2), 7.1-7.9 (m, 5H, Ar); IR (KBr): ν = 1230 cm^{-1} (C=S); UV/Vis (cyclo-C_6H_{12}): λmax (log ε) = 286 (4.17), 323 (3.87), 532 (1.89) nm.
16. **8a**: Yield 67 %; Red liquid; ^{1}H-NMR ($CDCl_3$): δ = 1.0-2.8 (m, 6H, CH_2), 3.2-4.1 (m, 1H, CH), 4.1-4.7 (m, 1H, CH), 7.1-8.2 (m, 5H, Ar); MS (70 eV, 110 °C): *m/e* 301 (M^+); IR (neat): ν = 1245 cm^{-1} (C=S).

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