CH_2P). ^{31}P NMR, δ: 31.1 ($J_{P,H}$ = 453 Hz). IR, ν/cm^{-1}: 2290 (P—H); 1140 (P=O). Found (%): C, 74.49; H, 7.48; P, 11.60. $C_{16}H_{19}OP$. Calculated (%): C, 74.40; H, 7.41; P, 11.99.

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Formation of cyclic compounds in the reaction of benzoyl peroxide with thioacetals

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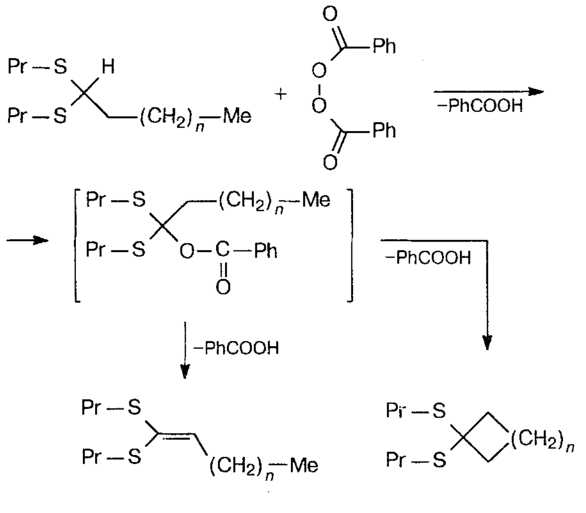
Previously[1] we have reported that the reactions of benzoyl peroxide with thioacetals do not afford products of the oxidation of the S atoms. In the case of formaldehyde thioacetal, the methylene group is mostly transformed,[2] while the reaction of acetaldehyde thioacetal predominantly involves dehydrogenation to give a ketene thioacetal.[3]

We showed that the reactions of *n*-pentanal or *n*-hexanal dipropyldithioacetals with benzoyl peroxide occur *via* α,β- or α,ω-dehydrogenation, probably by the scheme presented below: dipropyldithioacetals of cyclopentanone and cyclohexanone are formed in addition to 1,1-bis(alkylthio)-1-alkenes.



n = 2, 3

The reaction was carried out according to the known procedure;[1] the products were isolated and purified chromatographically (silica gel, hexane—chloroform as the eluent). NMR spectra were recorded in $CDCl_3$.

Cyclopentanone dipropyldithioacetal. Yield 60 %. Found (%): C, 58.98; H, 10.75; S, 30.12. $C_{11}H_{22}S_2$. Calculated (%): C, 60.55; H, 10.09; S, 29.36. ^1H NMR, δ: 0.85 (t, 6 H, Me); 1.4—1.5 (m, 8 H, $-CH_2-$); 1.3 (m, 4 H, $-CH_2-$); 2.45 (t, 4 H, $-CH_2S-$). ^{13}C NMR, δ: 13.95 (q, Me, *J* = 124.42 Hz); 22.76 (t, $-CH_2-$, *J* = 122.89 Hz); 32.78 (t, $-CH_2S-$, *J* = 136.8 Hz); 65.71 (s, C(1)); 41.74 (t, α-*cyclo*-CH_2, *J* = 132.91 Hz); 24.27 (t, β-*cyclo*-CH_2, *J* = 131.82 Hz). MS, *m/z*: 218 $[M]^+$.

1,1-Bis(propylthio)-1-pentene. Yield 30 %. Found (%): C, 59.70; H, 9.97; S, 30.06. $C_{11}H_{22}S_2$. Calculated (%): C, 60.55; H, 10.09; S, 29.36. ^1H NMR, δ: 0.7—0.9 (m, 9 H, Me); 1.32 (m, 2 H, $-CH_2-$); 2.4 (t, 4 H, $-CH_2S-$); 4.0 (m, 2 H, $-CH_2CH=$); 6.0 (t, 1 H, $-CH=$). IR (CCl_4), ν/cm^{-1}: 1685 (C=C). ^{13}C NMR, δ: 13.12 (Me); 22.17 (CH_2); 35.28 (CH_2S); 112.38 (=CH); 107.6 (C(1)).

Cyclohexanone dipropyldithioacetal. Yield 47 %. Found (%): C, 61.98; H, 10.55; S, 27.12. $C_{12}H_{24}S_2$. Calculated (%): C, 62.07; H, 10.34; S, 27.59. ^1H NMR, δ: 0.85 (t, 6 H, Me); 1.4—1.5 (m, 10 H, $-CH_2-$); 1.25 (m, 4 H, $-CH_2-$); 2.45 (t, 4 H, $-CH_2S-$). ^{13}C NMR, δ: 13.98 (q, Me, *J* = 124.30 Hz); 22.91 (t, $-CH_2-$, *J* = 124.6 Hz); 30.58 (t, $-CH_2S-$, *J* = 138.3 Hz); 61.58 (s, C(1)); 38.32 (t, α-*cyclo*-CH_2, *J* = 129.2 Hz); 22.59 (t, β-*cyclo*-CH_2, *J* = 127.8 Hz); 26.08 (t, γ-*cyclo*-CH_2, *J* = 126.4 Hz). MS, *m/z*: 232 $[M]^+$.

1,1-Bis(propylthio)-1-hexene. Yield 39 %. Found (%): C, 62.97; H, 9.95; S, 28.01. $C_{12}H_{24}S_2$. Calculated (%): C, 62.07; H, 10.34; S, 27.59. ^1H NMR, δ: 0.7—0.9 (m, 9 H, Me); 1.32 (m, 2 H, $-CH_2-$); 2.4 (t, 4 H, $-CH_2S-$);

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3.7 (m, 2 H, $-CH_2CH=$); 5.8 (t, 1 H, $-CH=$). IR (CCl_4), ν/cm^{-1}: 1690 (C=C). ^{13}C NMR, δ: 13.52 (Me); 22.37 (CH_2); 35.40 (CH_2S); 112.24 ($=CH-$); 107.2 (C(1)).

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Chemiluminescence and photoluminescence of Tb^{III} in the $TbCl_3 \cdot 3Bu_3PO—Bu^i{}_3Al—C_5H_8$ catalytic system in toluene

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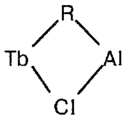
Luminescence of organolanthanide compounds has been reported only for ytterbium(III),[1] terbium(III),[2] europium(II,III),[3] and samarium(II,III)[3] cyclopentadienides.

The present communication reports the first example of photoluminescence (PL) and chemiluminescence (CL) of complex bridged alkyl derivatives of terbium of the general formula **1** obtained by the interaction of $TbCl_3 \cdot 3TBP$ (**2**), R_3Al (**3**), and piperylene (C_5H_8) (**4**) in toluene (TBP is tributyl phosphate; the **2** : **3** : **4** ratio is 1 : 15 : 5).[4] Systems analogous to **2**—**3**—**4** are well known as catalysts of the polymerization of dienes,[5] and PL methods combined with CL methods seem to be promising for studying these systems.



1

$R = Bu^i$

When oxygen (or air) is bubbled through solutions of compound **1** in toluene ([Tb] = $4.1 \cdot 10^{-2}$ mol L^{-1}, 298 K), chemilumiscence occurs ($I_{max} = 5 \cdot 10^7$ photons s^{-1} per mole Tb). The spectrum of this CL correlates well with the PL spectrum of a solution of compound **2** and with the PL spectrum of an oxidized solution of compound **1** (λ_{max} = 490, 445, and 585 nm, respectively).

The analysis of the spectra shows that in all of the cases the radiation is caused by f—f transitions of Tb^{III}, while emissions from the oxide and peroxide forms of Tb^{III} are responsible for the CL of compound **1** and the PL of the oxidized solution of compound **1**.

The formation of organoterbium peroxides during the oxidation of compound **1** is confirmed by the sharp increase in the intensity of the CL (with the same emitter, Tb) following the addition of water to a solution of **1** subjected to oxidation, *i.e.*, in the "aqueous CL-test" used by us previously.[3]

The comparison of the CL that appears during the air-induced oxidation of solutions of compound **1**, a solution of compound **3**, and a $NdCl_3 \cdot 3TBP$—**2**—**3** mixture allowed us to conclude that the excitation of the CL emitter, *viz.*, Tb^{III}, occurs both when the Tb—Alk bonds are oxidized and when energy is transferred to the Tb^{III} atom from the primary emitter, which is excited due to the oxidation of the Al—Alk bonds in the molecules of **1**.

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