

Effect of a cobalt(II) complex on the radical reaction of vinyl type sulfides. A 'radico-catalysis'

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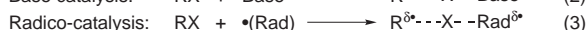
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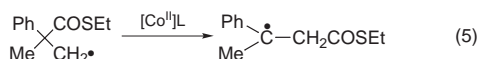
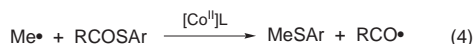
Received (in Cambridge, UK) 4th November 1998, Accepted 27th November 1998

Vinyl type sulfides show increased radicophilicity at the β -position *via* the coordination to a cobalt(II) complex, and hence the balance between Smiles rearrangement and an *ortho*-substitution, in vinyl type sulfides having an intramolecular alkyl radical, is lost to favor the latter reaction.

Acid and base catalysis generates a 'paired electron hole' [eqn. (1)] and a 'paired electron pool' [eqn. (2)], respectively. Likewise radical catalysis can be defined as the generation of 'unpaired electron density' at the reaction center [eqn. (3)].



We have demonstrated that a cobalt(II) complex, cobaloxime(II),^{1†} accelerates the radical substitutions on the sulfur of a thioester group [eqn. (4)]² and the radical 1,2-rearrangement of a thioester group [eqn. (5)].^{2,3} Caddick *et al.*,⁴ Aldabbagh and



Bowman,⁵ and Tada *et al.*⁶ showed the usefulness of the sulfur function in the radical annelation on indole and benzimidazole systems, in which the intramolecular alkyl radicals attack the *ipso*-position to yield indoleno or benzimidazoleno carbocycles by the extrusion of the sulfur function. We have suggested the effect of cobaloxime(II) in the radical annelation of 2-phenylthioindole *via* an intramolecular *N*-alkyl radical.⁶

Here we report another type of radico-catalysis by cobaloxime(II) in the radical annelation of benzothiophene and uracil derivatives. Coordination of a vinyl type sulfide to cobalt(II) generates an unpaired electron (spin) density on the sulfur, which can delocalize to the β -position of the vinyl group as shown in Fig 1. The coordination has been proven *via* an EPR

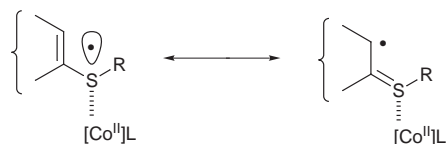
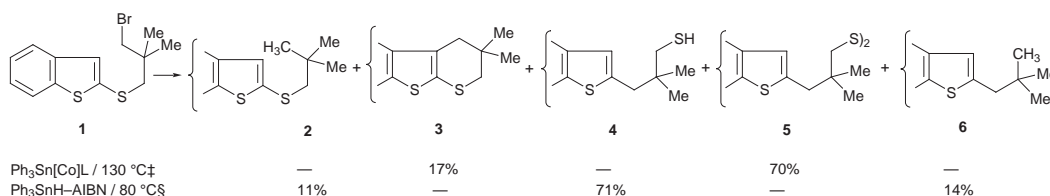


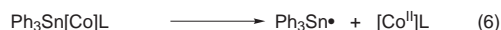
Fig. 1 Resonance expression of spin delocalization in a sulfur-cobalt(II) complex.



Scheme 1

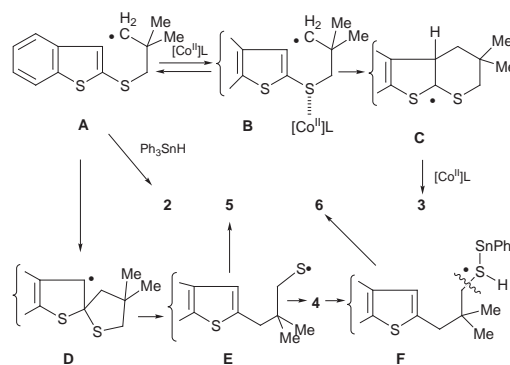
study by us⁷ and characterized by back donation from cobalt(II) to sulfur. The bonding force of this back donation makes the unstable two-centered three electron bond feasible.

Homolysis of triphenyltin cobaloxime produces a triphenyltin radical and cobaloxime(II) [eqn. (6)] but the former dissipates *via* reaction with a halide to leave an organo radical [eqn. (7)]. Thus the organo radical and cobaloxime(II) coexist in the reaction system and associate by the coordinative interaction discussed above [eqn. (8)]. The interaction of the vinyl type



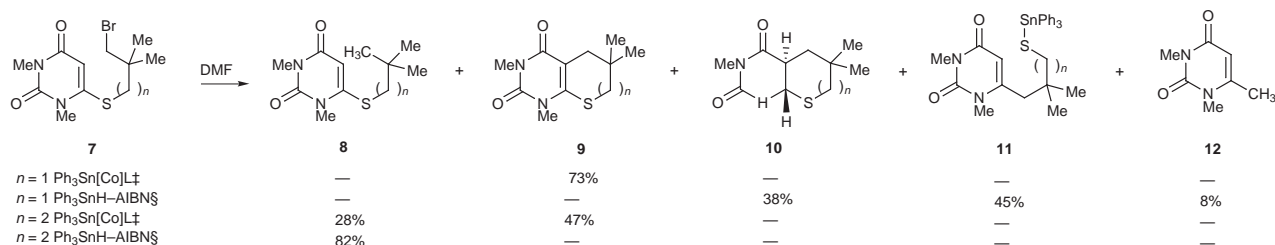
sulfide and the cobalt(II) species may increase the radicophilicity of the vinyl moiety.

Thus 3-(benzothiophen-2-ylthio)-2,2-dimethylpropyl bromide **1** was treated with triphenyltin cobaloxime under heating and the products **3** and **5** were obtained as shown in Scheme 1. The thermolysis gives the cobaloxime(II) radical and the intermediate radical **A** which interact with each other by the coordination discussed above to give radical **B** and thus product **3** (Scheme 2).



Scheme 2

Treatment of bromide **1** with Ph₃SnH-AIBN gave the products **4** and **6** after Smiles rearrangement by an addition-elimination mechanism (**A**→**D**→**E** in Scheme 2)⁸ and the reduction product **2**. Thus the cobaloxime(II) in the reaction system evidently accelerates the radical attack on the 3-position of benzothiophene and *ortho*-substitution becomes competitive with the radical Smiles rearrangement.⁸⁻¹⁰ On the other hand, in

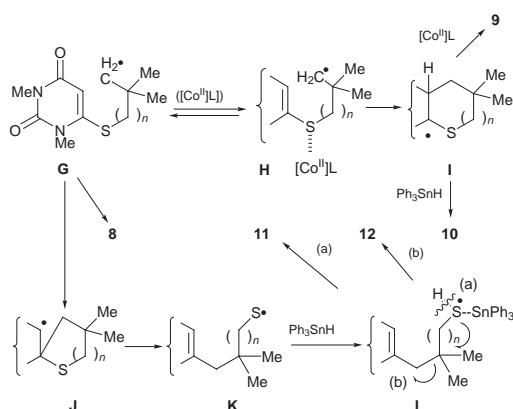


Scheme 3

addition to product **2**, only the products of Smiles rearrangement were obtained without cobaloxime(II). The formation of the product **6** is accounted for by radical substitution on sulfur through the radical intermediate **F**. A reasonable mechanism for formation of these products is shown in Scheme 2.

Next we tested the effect of cobaloxime(II) on the radical from *n*-(1,3-dimethyluracil-5-ylthio)-2,2-dimethylalkyl bromide **7** and a similar acceleration effect was observed for the *ortho*-substitution, as shown in Scheme 3. Bromide **7** (*n* = 1) gave the substitution product **9** in the presence of cobaloxime(II) whereas the reaction with Ph₃SnH gave the addition product **10** and the products **11** and **12** formed *via* Smiles rearrangement (Scheme 4).

Both Smiles rearrangement *via* a six-membered intermediate (**J**) (*n* = 2) and *ortho*-addition *via* a seven-membered intermediate (**I**) (*n* = 2) are slow and the only product from the reaction of Ph₃SnH and bromide **7** (*n* = 2) is the direct reduction product. The reaction with triphenyltin cobaloxime, however, gave the *ortho*-substitution product **9** (*n* = 2) as a major product, however the intramolecular radical addition is still slow and hydrogen abstraction from the solvent to give product **8** (*n* = 2) is the dominant process. A reasonable mechanism for formation of **8–12** is illustrated in Scheme 4. The intermediate radical **I** (*n* = 1) which gives **10** (*n* = 1) is formed even without cobaloxime(II), although with lower efficiency, while radical **I** (*n* = 2) which gives **9** (*n* = 2) is formed only with the assistance by cobaloxime(II). The intermediates **I** (*n* = 1,2) give products **9** (*n* = 1,2) with hydrogen elimination by cobaloxime(II) and the product **10** (*n* = 1) *via* hydrogen abstraction from the tin hydride. Products **11** and **12** derive from the intermediate **L** (*n* = 1) *via* hydrogen elimination [route (a)] and the fragmentation process [route (b)], respectively, after Smiles rearrangement (Scheme 4).



Scheme 4

All the experimental results shown here suggest an acceleration effect of cobalt(II) species on the radical attack of an alkyl radical on a vinyl type sulfide. Thus the coordination of a vinyl sulfide to a paramagnetic cobalt(II) complex generates a spin density at the β -position and makes the β -position more radicophilic. We propose a term 'radico-catalysis' for this effect even though the reaction is stoichiometric and not 'catalytic' in the correct sense.

Experimental details and structural assignments of the products will be reported in a full paper.

The present work was supported by Waseda University and the Ministry of Education, Culture, and Sports of Japan through an Annual Project Program and a Grant-in-Aid for Scientific Research, respectively

Notes and references

[†] Cobaloxime(II) is bis(dimethylglyoximate)(4-*tert*-butylpyridine)cobalt(II) and denoted here by [Co^{II}]L.

[‡] Reaction conditions: **1** or **7** (0.1 mmol), Ph₃Sn[Co]L (0.3 mmol), DMF (5.0 ml), 130 °C, 24 h.

§ Reaction conditions: **1** or **7** (0.1 mmol), Ph₃SnH (0.2 mmol), AIBN (0.1 mmol), benzene (40 ml), 80 °C, 4 h.

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Communication 8/08576E