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Photolyses of 2-(Alkylthio)carbonyl-2-(arylethyl)propyl Cobaloxime(1)

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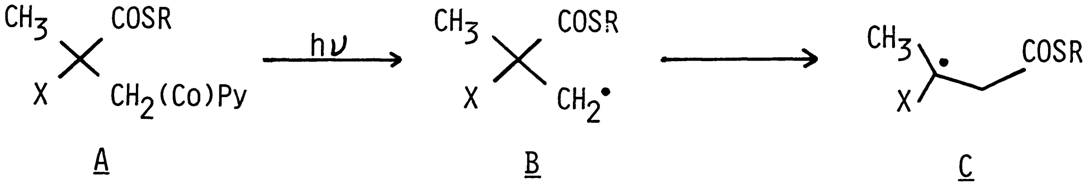
2-(Alkylthio)carbonyl-2-(arylethyl)propyl cobaloximes were photolyzed. When an aryl group is phenyl, a major process is a radical cyclization to give 2-(alkylthio)carbonyl-2-methyltetralin. On the other hand, β-thiolactone is a major product when an aryl group is mesityl and an alkyl group is t-butyl.

We have been concerned with the biomimetic radical rearrangement of a thioester group by using an organocobaloxime, organo(pyridine)-bis-dimethylglyoximatocobalt(III), as a coenzyme model, and have suggested the possible involvement of cobalt in the rearrangement step.(2,3) In the previous study, 2-(alkylthio)carbonyl-2-phenylpropyl cobaloxime A (X=Ph) and 2-(alkylthio)carbonyl-2-methylpropyl cobaloxime A (X=Me) were photolyzed to generate radicals B which rearrange to radicals C.(2) In the former system (A, X=Ph) the formation of of a benzyl radical C (X=Ph) may be a driving force of the thioester rearrangement. In the latter system (A, X=Me) highly volatile products were ignored due to the experimental difficulty.(2) These situations prompted us to investigate the behaviors of 2-(alkylthio)carbonyl-2-(arylethyl)propyl radicals B ($X=PhCH_2CH_2$ and $MesCH_2CH_2$).



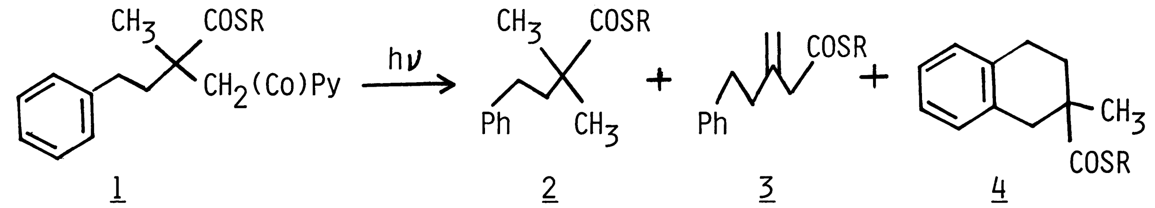
The reactions of 2-(alkylthio)carbonyl-2-phenethylpropyl bromide (alkyl=Et or t-Bu)(4) and 2-(alkylthio)carbonyl-2-mesitylethyl)propyl bromide (alkyl=Et or t-Bu)(4) with 1.2 molar equivalents of tributylstannane (10^{-3} - 10^{-1}M) in benzene gave only 2-(alkylthio)carbonyl-2-phenetylpropane (2) and 2-(alkylthio)carbonyl-2-(mesitylethyl)propane (6). This feature can be explained by the preferential hydrogen transfer from tributylstannane to the radical of type B since the rearrangement of the thioester group is slow compared to the hydrogen transfer.

Photolyses of 2-(alkylthio)carbonyl-2-phenetylpropyl cobaloxime (1)(5) in a variety of solvents gave products 2, 3, and 4 as listed in Table 1.(6) A thioester rearranged product 3 was obtained only from the ethylthioester 1 (R=Et) in minute amount and main products were cyclized ones 4 except for the photolysis in chloroform. To retard the radical cyclization to tetralin derivatives, 2-(alkylthio)-carbonyl-2-(mesitylethyl)propyl cobaloxime (5)(5) was photolyzed in similar solvent systems to give the products 6, 7, and 8, and the results are summarized in Table 2.[6] t-Butylthioester 5 (R=t-Bu) gave a β-thiolactone 8 as a major product and it is in sharp contrast to the formation of the tetralin derivative 4 from the cobaloxime 1.

Products 2 and 6 were identified with authentic samples prepared by α-methylation of the corresponding aralkylthioesters. The structures of rearranged product 3[7] and 7[7] were deduced from the comparison of spectral data with those of the related compounds, S-alkyl 3-methyl-3-butenethioate and S-alkyl 3-phenyl-3-butenethioate.[2] Product 7 (R=Et) shows NMR signals due to the endo-methylene (δ=5.02 and 5.07) and the methylene adjacent to the (alkylthio)carbonyl group (3.31, d, J=0.7). Structures 4 (R=Et)[8] were deduced from an IR absorption for -COSR (1680 cm^{-1}) and NMR signals: a singlet due to the methyl at 1.23 and an AB-quartet at 2.53 and 3.25 (J=16) due to the isolated benzylic methylene. Structure 8[9] was characterized by an IR absorption at 1755 cm^{-1} due to β-thiolactone[10] and NMR signals: a singlet due to the methyl at 1.47, and an AB-quartet at 2.78 and 3.00 (J=8.5). The chemical shift of the quartet is typical for the methylene adjacent to sulfur in β-thiolactone ring. β-Propiothiolactone and α-dimethyl-β-propiothiolactone have signals at 3.05 and 2.73, respectively, due to the β-methylene whereas β-propiothiolactone and its β-substituted derivatives have signals due to the α-methylene at around δ=4.[10] An alternative structure for 8, β-disubstituted β-thiolactone, was eliminated from these spectroscopic features and the analogous formation of α-dimethyl-β-propiothiolactone, which was identified by reported spectroscopic data,[10] on the photolysis of 2-(t-butylthio)carbonyl-2-methylpropyl cobaloxime (A, R=t-Bu, X=Me).

In the photolysis of 1 the radical cyclization to give tetralin derivarives 4 prefers to the hydrogen abstraction to give reduction products 2, which in turn prefers to the radical rearrangement of the thioester group. The ethylthioester 5 (R=Et) gives preferably a reduction product 6 (R=Et) but the t-butylthioester 5 (R=t-Bu) gives a reduction product 6 (R=t-Bu) as a minor product except for the photolysis in chloroform, a strongly hydrogen donating solvent. In less hydrogen donating solvents, formations of the rearranged product 7 (R=Et) from 5 (R=Et) and β-thiolactone from 5 (R=t-Bu), respectively, become more significant.

Three types of collapsing processes exist for the radical intermediate of mesityl derivatives, and both a direct hydrogen abstraction and a thioester rearrangement via 10 are major processes for the radical intermediate 9 (R=Et) but the thiolactone formation is more significant for the radical intermediate 9 (Ar=Mes, R=t-Bu). Thus mesityl group retards the radical cyclization to benzene ring and the rearrangement of the thioester group is rather significant with the ethylthioester. Nevertheless, a thiolactonization by the loss of alkyl group becomes significant with t-butylthioester. This must be due to a facile cleavage of the t-butyl-sulfur bond to result in the radical substitution on sulfur. These results indicate the existence of the equilibrium between the radicals 10 and 11. The formula 11 represents an intermediate of S_H2 reaction on sulfur, which has a trigonal bipyramid geometry.



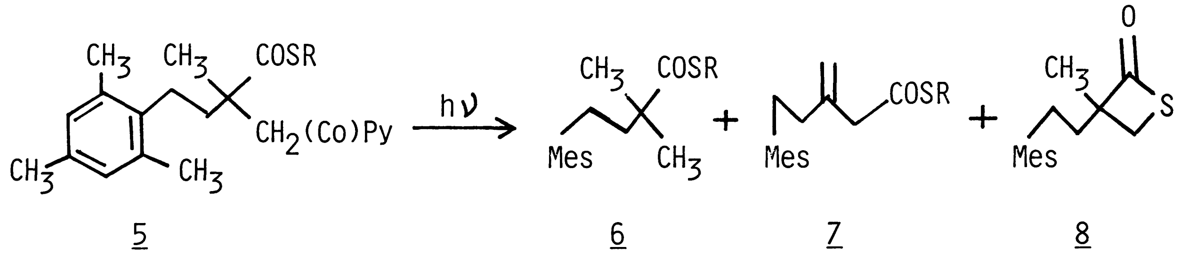
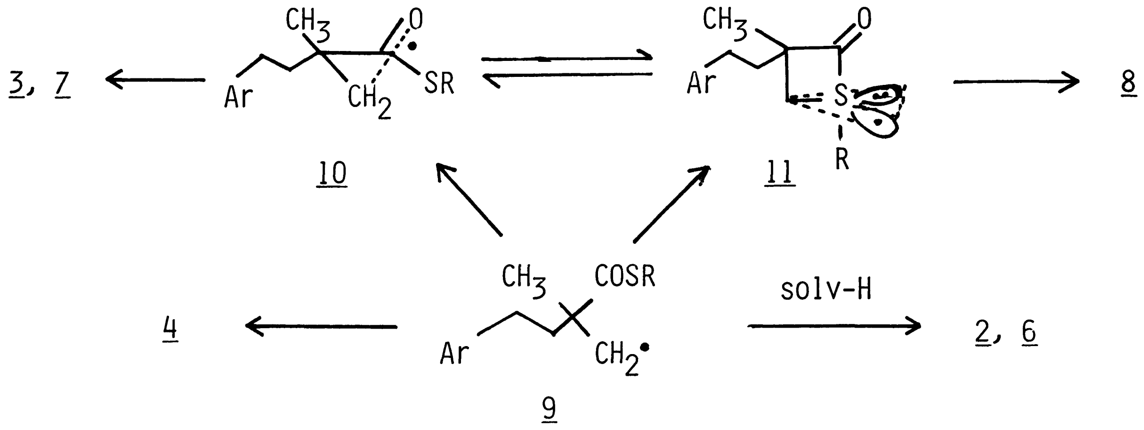


Table 1. Photolyses of cobaloxime 1 [6)]

R	solvent	Product composition/% 2	: 3	: 4
Et	C_6H_6	8	2	90
Et	CH_3OH	13	3	84
Et	CH_2Cl_2	28	2	70
Et	$CHCl_3$	75	0	25
t-Bu	C_6H_6	6	0	94
t-Bu	CH_3OH	19	0	81
t-Bu	CH_2Cl_2	36	0	64
t-Bu	$CHCl_3$	86	0	14

Table 2. Photolyses of cobaloxime 5 [6)]

R	solvent	Product composition/% 6	: 7	: 8
Et	C_6H_6	48	50	2
Et	CH_3CN	66	30	4
Et	CH_3OH	80	16	4
Et	$CHCl_3$	100	0	0
t-Bu	C_6H_6	4	4	92
t-Bu	CH_3CN	18	13	69
t-Bu	CH_3OH	12	4	84
t-Bu	$CHCl_3$	84	0	16



The thioester rearrangement has precedent[2,11)] but the thiolactone formation by S_H2 reaction on sulfur has no precedent, and the present findings disclosed a novel variation of the radical substitution on sulfur atom.[12,13)]

References

1) This study was supported in part by The Annual Project Organized by Waseda University 1986 and The Grant-in-Aid for Science Research 1986, Ministry of Education.

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3) M. Tada, K. Inoue, and M. Okabe, Chem. Lett., 1986, 703.

4) 2-(Alkylthio)carbonyl-2-(arylethyl)propyl bromides were prepared by the bromomethylation of S-alkyl 4-aryl-2-methylbutanothioate in THF using LDA as a base.

5) Cobaloximes 1 and 5 were prepared from the corresponding bromides under the standard conditions recorded in the earlier papers[2,3] and gave the correct elemental analyses (C, H, N) and spectral data (IR and NMR).

6) A solution of 1 or 5 (10 mg) in 10 ml of the solvent was irradiated by a high pressure mercury lamp (400 W) through a Pyrex filter. The reaction mixture was condensed and passed through a short column of silica gel eluted by chloroform, and separated by the preparative TLC on silica gel. Total yields of the products were 80-90% at this stage in the solvents other than benzene and 50-60% in benzene. The product composition was determined by gas chromatographic analyses using SE-30 as a stationary phase.

7) 7 (R=Et): m/z=272(M^+); 1685 cm^{-1}(CCl_4); δ ($CDCl_3$) 1.24(3H, t, J=7.3), 2.23(3H, s), 2.28(6H, s), 2.87(2H, q, J=7.3), 2.70-3.20(4H, m), 3.31(2H, d, J=0.7), 5.02(1H, diff. s), 5.07(1H, diff. s), 6.82(2H, s). The mass spectra of the minor products 3 (R=Et)(M^+=276) and 7 (R=t-Bu) (M^+=304) showed the similar mass-fragmentation pattern to 7 (R=Et).

8) 4 (R=Et): m/z=232; 1680 cm^{-1}(CCl_4); δ ($CDCl_3$) 1.17(3H, t, J=7), 1.23(3H, s), 1.57-2.33(2H, m), 2.53(1H, d, J=16), 2.60-3.00(2H, m), 2.80(2H, q, J=7), 3.25 (1H, d, J=16), 6.98-7.27(4H, m).
4 (R=t-Bu): 1675 cm^{-1}(CCl_4); δ ($CDCl_3$)1.27(3H, s), 1.44(9H, s), 1.80-2.20(2H, m) 2.53(1H, d, J=17), 2.68-2.90(2H, m), 3.24(1H, d, J=17), 7.00-7.28(4H, m).
Mass spectrum of 4 (R=t-Bu) showed the similar fragmentation pattern to 4 (R=Et) except no appearance of the molecular peak.

9) 8, m/z=248(13%, M^+), 187(6.2%, M^+-COS-H), 173(8.4%, M^+-CH_2SCO-H), 147(12%, Mes$CH_2CH_2^+$), 133(100%, MesCH_2^+); 1755 cm^{-1}(CCl_4); δ ($CDCl_3$) 1.47(3H, s), 1.73 (2H, t, J=8.5), 2.24(3H, s), 2.27(6H, s), 2.45-2.80(2H, m), 2.78(1H, d, J=8.5), 3.00(1H, d, J=8.5), 6.82(2H, s).

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