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DEOXYGENATION OF OXIRAN COMPOUNDS TO OLEFINS BY $[Fe_4S_4(SC_6H_5)_4]^{2-}$ IN THE PRESENCE OF $NaBH_4$

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Abstract: The dianion complex $[Fe_4S_4(SC_6H_5)_4]^{2-}$ caused deoxygenation reaction of oxiran compounds to olefins in the presence of $NaBH_4$. The reduced form $[Fe_4S_4(SR)_4]^{3-}$ was suggested as an active reductant in this reaction.

Comparison of physicochemical properties between the active sites of non heme iron-sulfur proteins[2)] and the synthetic polynuclear complexes $[Fe_4S_4(SR)_4]^{n-}$ has revealed n = 1, 2 and 3[3)] to be excellent analogs of the active sites of super-oxidized form, oxidized form[4)] and reduced form[5)] of the proteins, respectively. Holm has reported[6)] that anaerobic electrochemical reduction of dianions $[Fe_4S_4(SR)_4]^{2-}$ allows generation of the corresponding trianions $[Fe_4S_4(SR)_4]^{3-}$. Also, the trianions have been prepared by Na/Hg or sodium acenaphthylenide employed as the reducing agent.[6)] We have already reported[7)] the following reductions by the dianion complex and reductant systems; the formation reactions of *cis*-stilbene,[8)] amines,[9)] aromatic amines and hydroquinones,[10)] from diphenylacetylene, imines, aromatic nitro compounds and quinones, respectively. Inoue et al. have also reported some organic reactions by the dianion complex and reductant system.[11)]

We found the formation of the trianion complex $[Fe_4S_4(SR)_4]^{3-}$ in the reaction of the dianion complex $[Fe_4S_4(SR)_4]^{2-}$ and $NaBH_4$. This paper shows the deoxygenation of oxiran compounds to the corresponding olefins by the trianion complex generated from the dianion complex and $NaBH_4$. In a typical experiment, the complex $(nBu_4N)_2[Fe_4S_4(SC_6H_5)_4]$ (0.1 mmol) was added under an Ar atmosphere to the CH_3CN (10 ml)/C_2H_5OH (10 ml) solution of the *trans*-stilbene oxide (0.5 mmol) and $NaBH_4$ (10.0 mmol) and the reaction mixture was stirred at 25°C. After stirring for 3 hr, *trans*-stilbene was obtained in a 75% yield. *cis*-Stilbene oxide was deoxygenated to *trans*-stilbene (65%) and *cis*-stilbene (28%). β-Methylstyrene oxide, styrene oxide and 2-octene oxide were also deoxygenated to β-methylstyrene, styrene and 2-octene, respectively, as shown in Table I. The maximal yield was obtained after stirring for 3 hr. The complex was essential for the deoxygenation, because the yields were extremely low (0~8 %) even in the presence of $NaBH_4$ when, instead of the complex, $FeCl_2$, $FeCl_3$, C_6H_5SH, Na_2S, $FeCl_3$ + C_6H_5SH or $FeCl_3$ + Na_2S + C_6H_5SH was used. Using EPR spectroscopy, the complex $[Fe_4S_4(SC_6H_5)_4]^{2-}$ was shown to be reduced to $[Fe_4S_4(SC_6H_5)_4]^{3-}$ by $NaBH_4$. When the complex $(nBu_4N)_2[Fe_4S_4(SC_6H_5)_4]$ was allowed to react with excess amounts of $NaBH_4$ in CH_3CN/CH_3OH, the axial EPR signal was observed in the reaction solution (Fig. 1), whereas the dianion complex was EPR-inactive in the absence of $NaBH_4$. The formation of the reduced state was confirmed by comparison with the EPR spectral data reported by Holm.[12)] As shown in Fig. 1, the peak intensity increased with lowering temperature for the measurement of EPR spectra, which is in accord with the data reported by Holm. In addition, the signal of the EPR spectra depended on the solvent. Using CH_3CN only as solvent, the dianion complex was EPR-inactive

Chart 1

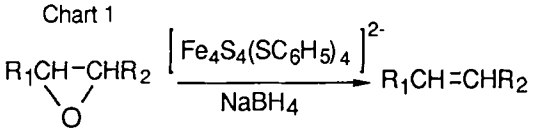

Table I Deoxygenation of oxiran compounds by $(nBu_4N)_2[Fe_4S_4(SC_6H_5)_4]$ and $NaBH_4$

run	substrate	product(s) (%)
1	*trans*-stilbene oxide	*trans*-stilbene (75)
2	*cis*-stilbene oxide	*cis*-stilbene (28) *trans*-stilbene (65)
3	β-methylstyrene oxide[a]	β-methylstyrene (70)
4	styrene oxide	styrene (35)
5	2-octene oxide[a]	2-octene (30)

The reaction conditions are shown in the text.
[a] mixture of *cis*- and *trans*-forms.

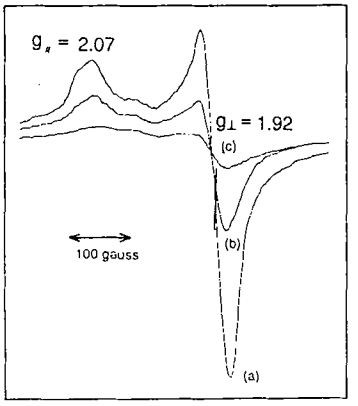

Fig. 1 Temperature dependence of EPR spectra of CH_3CN/CH_3OH solution of $(nBu_4N)_2[Fe_4S_4(SPh)_4]$ and $NaBH_4$. Spectrometer settings: microwave power, 5 mW; frequency, 9.03 GHz; modulation amplitude, 5 G. (a) 39 K, (b) 49 K, (c) 61 K.

even in the presence of $NaBH_4$. We examined the effect of alcohol on the yield in the deoxygenation of *cis*-stilbene oxide to stilbene. When CH_3OH, C_2H_5OH, n-C_3H_7OH or iso-C_3H_7OH was added to the CH_3CN reaction solution, the yield was 73, 93, 90 or 68 %, respectively. However, in CH_3CN only, the dianion complex-$NaBH_4$ system carried out the deoxygenation of oxiran compounds in an extremely low yield. Protic solvents such as CH_3OH, C_2H_5OH, n-C_3H_7OH and iso-C_3H_7OH were shown to be essential for the formation of the trianion complex and for the deoxygenation of oxiran compounds. Though the mechanism of this solvent effect is unclear yet, it is noteworthy that the dianion complex can not be reduced to the trianion complex in the absence of protic solvents.

Since $NaBH_4$ can be easily handled as a reductant even by a biochemist, the dianion complex-$NaBH_4$ system should be useful not only for the development of novel reductants for use in organic reduction but also for the elucidation of the enzymatic mechanism of HP or Fd proteins.

References and Note

1) Present address: School of Pharmaceutical Sciences, Showa University, Hatanodai, Shinagawa-ku, Tokyo 142, Japan. 2)a) W. Lovenberg (ed.), *"Iron-Sulfur Proteins"* Vol. 1-3, Academic Press, New York (1973-1977). b) R. Cammack, D. P. E. Dickson and C. E. Johnson, *ibid*, pp283 (1977). c) C. W. Carter, J. Kraut, S. T. Freer, R. A. Alden, L. C. Sieker, E. Adman and L. H. Jensen, *Proc. Natl. Acad. Sci., U.S.A.*, **69**, 3526 (1972). d) D. P. E. Dickson, C. E. Johnson, R. Cammack, M. C. W. Evans, D. O. Hall and K. K. Rao, *Biochem. J.*, **139**, 105 (1974). e) T. G. Spiro (ed.), *"Iron-Sulfur Proteins"* Vol. 4, Wiley, New York (1982). f) R. C. Prince, M. W. W. Adams, *J. Biol. Chem.*, **262**, 5125 (1987). g) K. Fukuyama, Y. Nagahara, T. Tsukihara, Y. Katsube, T. Hase and H. Matsubara, *J. Mol. Biol.*, **199**, 183 (1988). 3)a) R. H. Holm, *Acc. Chem. Res.*, **10**, 427 (1977). b) R. H. Holm, *Endeavour*, **34**, 38 (1975). 4)a) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips and J. F. Weiher, *Proc. Natl. Acad. Sci., U.S.A.*, **69**, 2437 (1972). b) B. A. Averill, T. Herskovitz, R. H. Holm and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3523 (1973). c) C. L. Hill, J. Renaud, R. H. Holm and L. E. Mortenson, *J. Am. Chem. Soc.*, **99**, 2549 (1977). 5)a) E. J. Laskowski, J. G. Reynolds, R. B. Frankel, S. Foner, G. C. Papaefthymiou and R. H. Holm, *J. Am. Soc. Chem.*, **101**, 6562 (1979). b) M. J. Carney, G. C. Papaefthymiou, K. Spartalian, R. B. Frankel and R. H. Holm, *J. Am. Chem. Soc.*, **110**, 6084 (1988). 6) R. B. Frankel, T. Herskovitz, B. A. Averill, R. H. Holm, P. J. Krusic and W. D. Phillips, *Biochem. Biophys. Res. Commun.*, **58**, 974 (1974). 7) M. Hirobe, *J. Synth. Org. Chem. Japan*, **45**, 755 (1987). 8) T. Itoh, T. Nagano and M. Hirobe, *Tetrahedron Lett.*, **21**, 1343 (1980). 9) T. Mashino, T. Nagano and M. Hirobe, *Tetrahedron Lett.*, **24**, 5113 (1983). 10)a) T. Itoh, T. Nagano and M. Hirobe, *Chem. Pharm. Bull.*, **34**, 2013 (1986). b) T. Nagano, K. Yoshikawa and M. Hirobe, *Tetrahedron Lett.*, **21**, 297 (1980). 11)a) H. Inoue and T. Nagata, *J. Chem. Soc., Chem. Commun.*, (1986) 1177. b) H. Inoue, M. Suzuki and N. Fujimoto, *J. Org. Chem.*, **44**, 1722 (1979). c) H. Inoue and M. Sato, *J. Chem. Soc., Chem. Commun.*, (1982) 1014. 12) J. A. Ibers and R. H. Holm, *J. Am. Chem. Soc.*, **100**, 5322 (1978).

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