CHEMISTRY LETTERS, pp. 967-968, 1986.

ASYMMETRIC OXIDATION OF SULFIDES TO SULFOXIDES WITH TRIVALENT IODINE REAGENTS

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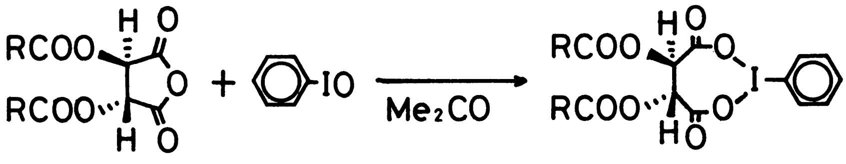
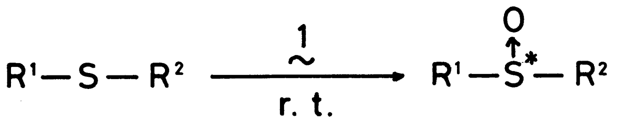
New trivalent iodine reagents possessing chiral center were generated by the reaction of iodosylbenzene with the derivatives of L-tartaric anhydride. The reagents cleanly oxidize prochiral sulfides to optically active sulfoxides with substantial asymmetric induction.

Polyvalent organoiodine compounds have characteristic reactivities[1)] and hence they are often utilized in synthetic organic chemistry.[2)] However, despite their unique oxidizing abilities, asymmetric oxidation with them has not yet been reported. We wish to describe herein generation of new trivalent iodine reagents possessing chiral center and their use in an asymmetric oxidation of prochiral sulfides to optically active sulfoxides.

New chiral oxidizing reagents (1a-c) were generated in situ by the reaction of iodosylbenzene with the derivatives of L-tartaric anhydride in acetone at room temperature. The reagents were allowed to react with sulfides. The reaction proceeded smoothly at room temperature to give the corresponding sulfoxides in high chemical yields.[3)] The optical purities of the products were estimated by comparison of the optical rotations with reported values. Some representative results are summarized in Table 1.



1a : R = Me
1b : R = Ph
1c : R = t-Bu



A substantial asymmetric induction up to 53% optical yield was observed in the oxidation of aryl methyl sulfides.[4)] Unfortunately, however, the reaction of an aliphatic sulfide, benzyl t-butyl sulfide, resulted in poor optical yield (entry 6).

Next, another trivalent iodine reagent, prepared from acetyl-L-lactic acid and iodosylbenzene, was employed for the oxidation of methyl p-tolyl sulfide under the same conditions as employed for entries 1~3. The product sulfoxide was obtained in

Table 1. Asymmetric Oxidation of Sulfides to Sulfoxides[a)]

Entry	Sulfide	Reagent	Product	Yield/%	$[\alpha]_D^{20}$/°[b)]	O.Y./%[c)] (Config.)
1	$p\text{-}CH_3C_6H_4SCH_3$	**1a**	$p\text{-}CH_3C_6H_4\text{-}\overset{O}{\overset{\uparrow *}{S}}\text{-}CH_3$	95	-44	30 (S)
2	"	**1b**	"	73	-52	36 (S)
3	"	**1c**	"	80	-58	40 (S)
4	$o\text{-}CH_3OC_6H_4SCH_3$	**1a**	$o\text{-}CH_3OC_6H_4\text{-}\overset{O}{\overset{\uparrow *}{S}}\text{-}CH_3$	75	-155	53 (S)
5	$o\text{-}CH_3C_6H_4SCH_3$	**1a**	$o\text{-}CH_3C_6H_4\text{-}\overset{O}{\overset{\uparrow *}{S}}\text{-}CH_3$	76	-122	43 (S)
6	$C_6H_5CH_2SC_4H_9\text{-}t$	**1a**	$C_6H_5CH_2\text{-}\overset{O}{\overset{\uparrow *}{S}}\text{-}C_4H_9\text{-}t$	71	+11.3[d)]	5 (R)
7	$p\text{-}CH_3C_6H_4SCH_3$	**2**[e)]	$p\text{-}CH_3C_6H_4\text{-}\overset{O}{\overset{\uparrow *}{S}}\text{-}CH_3$	91	-1.7	1 (S)

a) All reactions were carried out in acetone at room temperature for 3 h. See Ref. 3. b) In acetone, c 2.0, unless otherwise stated. c) Measured by the specific rotation of isolated sulfoxides with use of the maximum specific rotations given in Refs. 4, 5, and 6. d) In $CHCl_3$, c 2.1. e) **2**: $C_6H_5I[OCO\overset{*}{C}H(OCOCH_3)CH_3]_2$

91% yield, but its optical yield was only 1% (entry 7). This result is in sharp contrast to those obtained by the use of reagents **1a-c**; it is clearly indicated that C_2-symmetric seven-membered ring system of oxidizing reagent is an important factor for the efficient asymmetric oxidation of sulfides.

References

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3) A typical experimental procedure: Iodosylbenzene (440 mg, 2 mmol), diacetyltartaric anhydride (432 mg, 2 mmol), and dry acetone (4 ml) were placed in a two-necked flask which was completely dried before use. The mixture was stirred under nitrogen for 30 min at room temperature, and methyl p-tolyl sulfide (138 mg, 1 mmol) was added. After stirring for 3 h, the mixture was worked up in the usual manner to afford methyl p-tolyl sulfoxide (146 mg, 95%).

4) For recent notable examples for the asymmetric oxidation of sulfides, P. Pitchen, E. Duñach, M. N. Desmukh, and H. B. Kagan, J. Am. Chem. Soc., 106, 8188 (1984); T. Komori and T. Nonaka, ibid., 106, 2656 (1984); T. Takata, M. Yamazaki, K. Fujimori, Y. H. Kim, T. Iyanagi, and S. Oae, Bull. Chem. Soc. Jpn., 56, 2300 (1983).

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(Received March 28, 1986)