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PUMMERER REARRANGEMENT PROMOTED BY POLYPHOSPHORIC ACID TRIMETHYLSILYL ESTER (PPSE)

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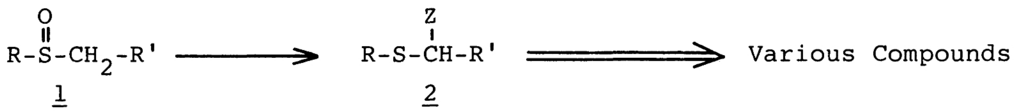
It was found that PPSE catalyzed Pummerer rearrangement of various types of sulfoxides. When α-(phenylsulfinyl)acetophenone was used as sulfoxide, unusual product, phenyl phenylthioglyoxylate was isolated. The reaction seems to proceed via phosphorylation of oxygen of sulfoxides.

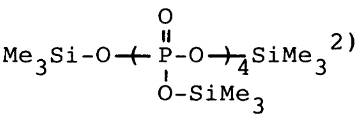
It is well known that sulfoxides 1 which possess hydrogen atom in α-position rearrange to α-substituted sulfides 2, and the rearrangement is catalyzed by electrophilic reagents such as acid anhydrides and acids. This Pummerer rearrangement has been developed as synthetic methods by an ingenious conversion of sulfides 2 into various compounds such as carbonyl compounds, heterocyclic compounds, and α,β-unsaturated sulfides etc.[1)]



$$\underset{\underline{1}}{R\text{-}\overset{O}{\overset{\|}{S}}\text{-}CH_2\text{-}R'} \longrightarrow \underset{\underline{2}}{R\text{-}S\text{-}\overset{Z}{\overset{|}{C}}H\text{-}R'} \Longrightarrow \text{Various Compounds} \qquad (1)$$

Z= OAc, Cl, OR, etc.

Recently, polyphosphoric acid trimethylsilyl ester (PPSE)[2)] has been utilized extensively for the synthesis of heterocyclic compounds,[3)] nitriles from amides,[4)] iodides from alcohols,[5)] and amidines from carboxylic acids and amines,[6)] and for the unusual aldol reaction.[7)] It is also known that PPSE promotes Beckmann rearrangement[8)] and pinacol-pinacolone rearrangement.[9)] In this paper, we describe Pummerer rearrangement of some sulfoxides in the presence of PPSE.

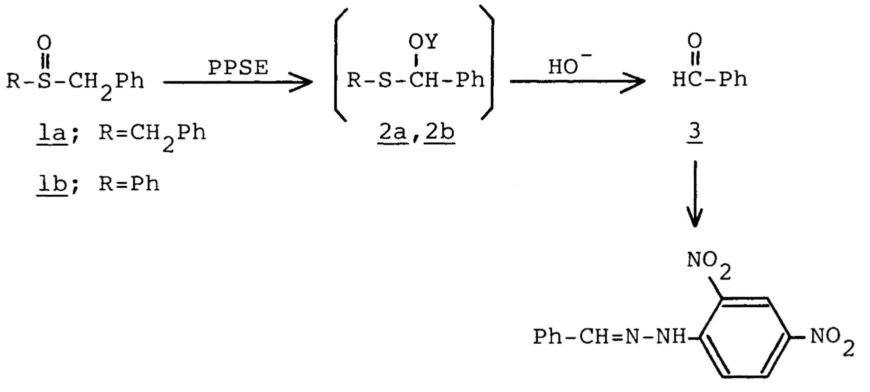


$$Me_3Si\text{-}O\text{-}\!\!\left(\!\overset{O}{\overset{\|}{\underset{\underset{O\text{-}SiMe_3}{|}}{P}}}\text{-}O\!\right)_{\!4}\!SiMe_3{}^{2)}$$

PPSE

The reactions of dibenzyl sulfoxide 1a and benzyl phenyl sulfoxide 1b[10)] with PPSE were examined first. As depicted in Eq. 2, benzaldehyde 3 was the major product when the reaction mixtures were worked-up by treating with an alkaline solution.

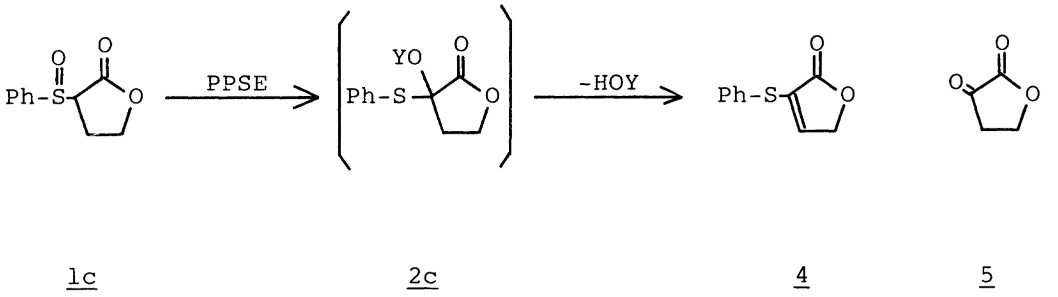
The typical example is as follows: PPSE was prepared as described in the previous



(2)11)

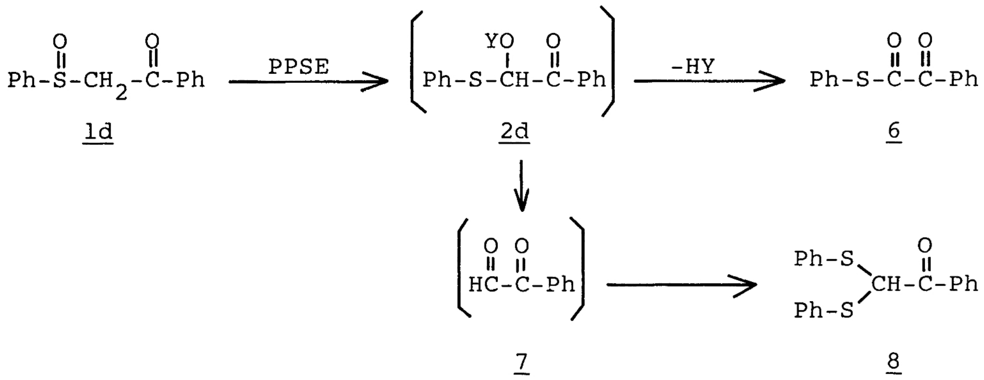
report;3c) thus P_4O_{10} (1.63 g, 5.7 mmol) and hexamethyldisiloxane (2.79 g, 17.2 mmol) in 5 ml of 1,2-dichloroethane were heated at 80 °C for 30 min under nitrogen. Dibenzyl sulfoxide 1a (920 mg, 4 mmol) was added to the solution, and the mixture was kept at 80 °C for 3 h. On cooling, the solution was poured into 1 M NaOH solution. The aqueous solution was extracted with dichloromethane. After the solvent was evaporated, the residue was treated with 2,4-dinitrophenylhydrazine in phosphoric acid and ethanol.12) The product isolated was benzaldehyde 2,4-dinitrophenylhydrazone (1.04 g, 91%) whose structure was confirmed by the comparison of melting point and the IR spectrum with those of an authentic sample. In the case of benzyl phenyl sulfoxide 1b, the same product was isolated in 72% yield.

Next, 2-phenylsulfinyl-4-butanolide 1c afforded 2-phenylthio-2-butene-4-olide 413) in 93% yield under the same conditions, whereas 2-oxo-4-butanolide 5 was not detected. In this case, β-elimination of HOY from the intermediate 2c affording butenolide 4 was predominant over hydrolysis producing 5. The same conversion from 1c to 4 was also achieved using trifluoroacetic anhydride in high yield.14)



(3)11)

When α-(phenylsulfinyl)acetophenone 1d was treated with PPSE in a similar manner as described above, phenyl phenylthioglyoxylate 615) and bis(phenylthio)-acetophenone 816) were isolated in 22% and 30% yields,respectively. In the higher temperature reaction (150 °C), 6 was obtained in 36% yield and the yield of 8 was 8%. Kenney described that dithioacetal 8 which was produced via phenylglyoxal 7 was the major product in the reaction of the acid catalyzed cleavage of 1d.17) In the present reaction, the novel oxidation reaction can be explained by the elimination of HY from the intermediate 2d to produce thioester 6. It is reported that Pummerer rearrangement of higher oxidation state sulfoxides such as α-diazo and α-halo sulfoxides afforded thioesters.[18] To our knowledge, this is the first example of the synthesis of thioesters from the simple sulfoxides via Pummerer rearrangement and oxidation.



1d 2d 6 7 8

(4)[11]

PPSE possesses the migratory trimethylsilyl group and reactive phosphoric anhydride function in the molecule. When one discusses the mechanism of this rearrangement, there are tow possible ways, where PPSE acts as silylating agent (Y= trimethylsilyl), and phosphorylating agent (Y= phosphoric function), repectively. In the present reaction, phosphorylation mechanism is more likely due to the following observations. 1) Tris(trimethylsilyl)orthophosphate whose trimethylsilyl function seems to possess almost the same reactivity as PPSE was found to be ineffective for Pummerer rearrangement of dibenzyl sulfoxide 1a. 2) Polyphosphoric acid ethyl ester was able to catalyze the rearrangement, thus 1a was converted to benzaldehyde in 31% yield under the same conditions as those in the case of PPSE. 3) In the reaction of sulfoxide 1d, the elimination of HY from 2d is possible if Y is reducible phosphoric function. On the contrary, suppose Y is silyl function, the eliminating group should be trimethylsilane, and the formation of this compound is quite difficult.

References

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2) Although the structure of PPSE was confirmed as a mixture of cyclotetraphosphate, isocyclotetraphosphate, and linear tetraphosphate, only the linear structure is presented in the figure. See Ref. 3b.
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8) T. Imamoto, H. Yokoyama, and M. Yokoyama, Tetrahedron Lett., 22, 1803 (1981).

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11) 'Y' means trimethylsilyl function or phosphoric function, *vide infra*.

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13) Butenolide 4 has the following spectra: IR(KBr) νcm^{-1}; 1760. 1595, 1435, 1330, 1050. ^{1}H-NMR, δppm (CDCl$_3$); 4.72 (d, 2H), 6.63 (t, 1H), 7.37 (m, 5H).

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15) Thioester 6 has the following spectra: IR (NaCl film) νcm^{-1}; 1675, 1655, 1595, 1260, 815. Mass; 242 (M^{+}). Furthermore the structure of 6 was confirmed by the conversion into N-(p-methoxyphenyl)phenylglyoxamide, mp 118-120 °C (lit., 123 °C),19) whose spectra: IR (KBr) νcm^{-1}; 3320, 1665, 1655, 1500, 1240, 830. ^{1}H-NMR, δppm (CDCl$_3$); 3.71 (s, 3H), 6.77-8.97 (m, 10H).

16) Dithioacetal 8, mp 101-103 °C (lit., 98.5-100 °C),17) has the following spectra: IR (KBr) νcm^{-1}; 1670, 1260, 990, 805, 750. ^{1}H-NMR, δppm (CDCl$_3$); 5.45 (s, 1H), 7.30 (m, 15H).

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