

유기 티오엔아민 포스포네이트와 산화스티렌과의 반응

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The Reaction between Organothioenamine Posphonate and Styrene Oxide

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요 약. Organothioenamine phosphonate 와 styrene oxide 와의 반응에서 얻어진 생성물의 구조를 규명한 결과 그것이 cyclopropane 유도체임을 알았다. 이것은 반응이 styrene oxide에 대한 thioenamine phosphonate의 친핵공격에 의해서 생긴 산소 음이온이 다시 인 원자를 공격함으로써 중간체로 betaine이 형성 된다음 이어서 약한 P—C 결합이 끊어지면서 생성물로 이끌어져 감을 가리켜 주고있다. 또한 생성물의 광학활성을 조사한 결과는 우회전성 이어서 이 반응은 중간체에서 생긴 benzyl carbon의 입체적 효과를 받으며 어디까지나 안정한 경로를 거쳐서 이끌어져 감을 알 수 있었다.

ABSTRACT. The fact that a reaction between organothioenamine phosphonate and styrene oxide produces a derivative of cyclopropane has been proved by structural identification. This suggests that an anionic oxygen atom from the ring opening of the styrene oxide by nucleophilic attack of thioenamine phosphonate links to the phosphorous atom to form a betaine as an intermediate which is followed by cleavage of the weak P—C bond. The dextrorotatory optical activity of the product showed that the reaction was under the control of steric stability of the benzyl carbon in styrene which leads to the product through a sterically stable pathway.

INTRODUCTION

New synthetic methods, reactions and geometrical isomerism of organophorous enamine have been extensively studied by Auguiar's group and others¹. Not only these reactions, but their further usage in the preparation of β -ethylenic

ketone were also reported by many workers. For example, it is known that cyclopropylketimine is obtained as a product of the reaction between diphenylenamine phosphonate and styrene oxide, and cyclopropylketone being produced upon hydrolysis of the ketimine². This illustrates that a betaine formed as an intermediate during

the reaction disappears by breaking of the weak P—C bond between phosphorus and carbon atoms in the betaine structure. At this point, we have speculated as to how the reaction would proceed when the sulphur atom is linked to the phosphorous atom in the structure of organophosphorous enamine in place of the oxygen atom. Thus, in order to discern any difference from the case of diethylenamine phosphonate, we have examined the reaction between diethylenamine thiophosphonate and styrene oxide.

EXPERIMENTAL

Butylacetylene. This compound was prepared by using a slightly modified Campbell's method.³ Into a three necked flask containing 800 ml of liquid ammonia were added, dried and purified acetylene gas and then, slowly, small pieces of sodium metal. Whenever a piece of the metal was added to the medium, a blue color appeared for a moment. In this way a total of 23 g of sodium metal was added in an hour. Into this reaction mixture, were added 200 ml of *n*-butyl bromide, and then the mixture was stirred for two hours. Using an ice bath the whole system was cooled and maintained at 0°C while 100 ml of saturated ammonium hydroxide was added. The upper layer was separated using a funnel, dried with potassium carbonate, and then distilled under vacuum. A fraction of b.p. 72~3°C was collected, yield 90%; $\text{ir } 2212 \text{ cm}^{-1} (\text{C}\equiv\text{C})$.

Diethyl Alkanyl-thiophosphonate⁴. All reactions for the preparation of this compound were run under a stream of nitrogen. Hexyne (0.005 mol) was dissolved in a mixture of 50 ml of THF and cooled to 0°C. A hexane solution of *n*-butyl lithium (0.005 mol, 32.5 ml) was slowly added with continuous stirring to obtain a fine suspension of lithium alkynylide. After five drops of pyridine were added, this suspension

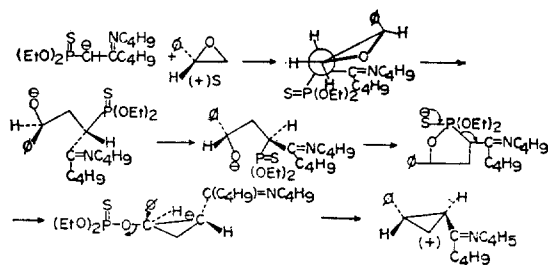
was slowly added to a solution of diethyl phosphochlorido thionate (0.005 mol) dissolved in 50 ml of ether at 0°C. The mixture was stirred for one hour keeping the temperature at 0°C. Then the temperature was raised to room temperature, stirred for 5~6 hours, and 100 ml of saturated aqueous ammonium chloride was slowly added. An oily phase was separated and dried with magnesium sulfate. It was distilled under vacuum b.p. 75~7°C (3 mm), 70% yield. $n_D^{25} 1.3984\sim 1.3900$, $\text{ir } 2212 (\text{C}\equiv\text{C})$, $650\sim 670 \text{ cm}^{-1} (\text{P}=\text{S})$.

Diethylenamine Thiophosphonate⁵. A mixture of the above described alkynyl-1-thiophosphonate (0.05 mol) and an excess amount (10~12 mol) *n*-butylamine was refluxed for two days. The completion of the reaction was checked by disappearance of their absorption band at $2212 \text{ cm}^{-1} (\text{C}\equiv\text{C})$. The excess amine was evaporated and the resulting oily product was dried with magnesium sulfate and distilled under vacuum, b.p. 126.7°C (mm), 76% yield. $n_D^{25} 1.3590\sim 2$, $\text{ir } 1600 (\text{C}=\text{C})$, $1640\sim 2 (\text{C}=\text{N}) \text{ cm}^{-1}$.

The Reaction between Organoenamine Thiophosphonate and Styrene Oxide. Diethyl enamine thiophosphonate (0.5 mol) was added to a mixed solution of 80 ml THF and 30 ml of *n*-butyllithium. The solution was warmed at 30~40°C for one hour and 6 g of styrene oxide (dextro rotation of +15) in 100 ml THF was added to the solution. The reaction mixture was warmed to 60~70°C and stirred for 4 hrs. Upon completion of the stirring the solvent was evaporated. The crude product was washed with distilled water and extracted with ether twice, dried with MgSO_4 and distilled under reduced pressure. The yield was 50% (yellowish oily liquid). b.p. 136~7°C. $n_D^{23} 1.5250$, $\text{ir } 1640\sim 2 (\text{C}=\text{N})$, 1020 cm^{-1} (characteristic cyclopropane skeletal vibrational band) $[\alpha]_D^{25} = +15$.

RESULTS AND DISCUSSION

The product of the reaction between diethyl thioenamine phosphonate and styrene oxide having dextro rotation (+12) was characterized by the appearance of infrared absorption bands of a double bond between the carbon and nitrogen atoms at 1640 cm^{-1} and of a characteristic cyclopropane skeletal vibration band at 1020 cm^{-1} . In addition to these, a boiling point at $136\sim 7^\circ\text{C}$ at 3 mmHg and a refractive index of 1.5250 value are just the same as Agui's² experimental results. Especially the appearance of optical rotation of the product strongly suggests that the reaction product was a derivative of cyclopropane. Therefore, it is proposed that an anionic oxygen atom would make a nucleophilic attack upon the phosphorus atom to form a betaine and then a bond between the phosphorus and carbon atom would cleave to form a cyclopropane ring, which is in accordance with Denny's mechanism.⁶ It would seem that a sulfur atom attached to a phosphorous atom does not greatly affect the mechanism of the reaction as when an oxygen atom is attached, as in enamine phosphonate. the fact that the product possesses a dextro rotatory optical activity of +15 suggests that the sequence of the reaction would be as follows:



The above mechanism is in good agreement with Tömösközi's sterically favorable pathway⁷. It can be readily seen from the above sequence that an inversion has to occur at the two asym-

metric centers for the formation of a bond between the phosphorus and oxygen atoms associated with the anionic oxygen atom which is formed by ring opening of styrene oxide when levo styrene oxide was used. However, in this case, it is obvious that the levo product is unfavorable because of the steric hinderance due to bulky groups. On the other hand, when dextro rotatory styrene oxide was used, it seems apparent that a sterically favorable pathway would allow the reaction to yield the more sterically favorable dextro rotatory product. Experimental results in this work yielded a dextro rotatory product thus showing that the above proposed mechanism is plausible. It can be concluded that substitution of a less electronegative sulfur atom than oxygen atom which are attached to the phosphorus atom does not affect the reaction mechanism between organophosphorus thioenamine and styrene oxide; rather it confirms the idea that steric effects dominate the reaction mechanism as described above. Finally, although another mechanism has been proposed by McEween⁸ in which an anionic oxygen atom would attack a benzyl carbon to form benzyl acetophenone it is not applicable in this reaction based upon the results obtained. The cyclopropane resulting in this reaction means that this reaction path must follow the route as described by Denny's mechanism, and not the route given in McEween's mechanism⁸, which states that the oxygen anion attacks the benzyl carbon and not the phosphorous atom. The fact that optically active products were obtained means that the above reaction also passed through a sterically stable route just as in Tömösközi's reaction.

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