Asian Journal of Chemistry; Vol. 25, No. 11 (2013), 6463-6464

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14249

NOTE

Preparation of High Quality Ethephon Using Domestic Diester *bis*-(2-chloroethyl)-2-chloroethylphosphonate as Substrate

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(*Received*: 30 June 2012; *Accepted*: 14 May 2013) AJC-13498

Ethephon has been widely used globally. However, few companies can manufacture high quality ethephon with content of 90% in China mainland. This work described a practical procedure, which utilizing *bis*-(2-chloroethyl)-2-chloroethylphosphonate **2** produced by local Chinese companies as substrate to prepare ethephon with content of over 90 % and high yield.

Key Words: Ethephon, Preparation, Diester.

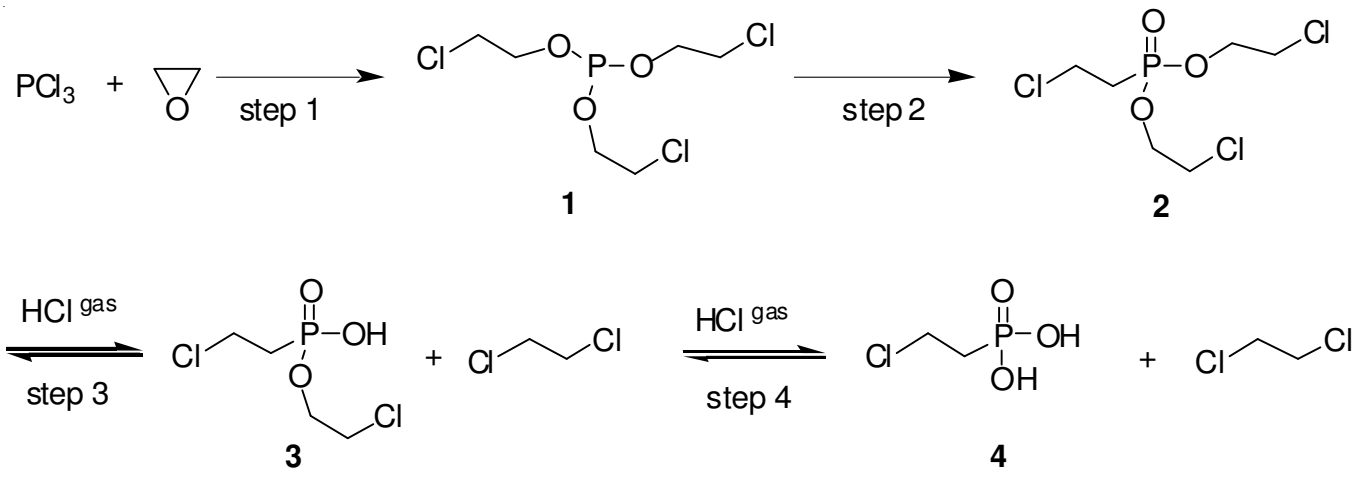
Ethephon **4** is a plant growth regulator and promote plant maturation. As a safe and clean product, it is worldwide used in cotton, rubber, banana, tomato, tobacco, rice and other plants. The Rhodia and The Jiangsu Electric Company Limited China are the two major producers of ethephon. The export of ethephon in China has been limited by low quality of ethephon. The content of most of the ethephon produced in China is lower than 80 %. In spite of some improvements on the basis of old technology made by many enterprises in the 70's, there are still some problems such as low content (60-70 %), low yield and large waste discharge[1]. The common synthetic route employed in preparation of ethephon is described as following (**Scheme-I**).

British patent[2] disclosed a method which can continuously or intermittently manufacture ethephon by increasing pressure from hydrogen chloride. The united states patent[3] described a process to product ethephon by adding concentrated hydrochloric acid to the reaction system and then cooling to separate phases. The united states patent[4] disclosed a procedure to separate and purify the product with benzene based on previous method. All of these preparations actually share the same shortcomings, such as low content in the final products and large amount of wastes. The united states patents[5,6] reported a new strategy which used diester **2** as reaction substrate to produce high quality ethephon (content over 90 %) under high pressure of hydrogen chloride. This reaction requires high-quality substrate **2** (purity = 99 %). Since there is no substrate **2** with content or purity being reached to 99 % in china mainland up to now, therefore, this process is unsuitable for China companies to produce high quality ethephon.

Few researchers in China study how to improve the content of ethephon higher than 90 % *via* domestic technology. We reported our improved preparation by using domestic diester **2** to produce ethephon with content of over 90 % in high yield and furthermore the relationship between the GC content of diester **2** and final product **4** was clarified.

Diester **2** (supplied by Shandong Dacheng pesticide company); and other commercially available materials and solvents were used without further purification. Gas chromatograph (Shimadzu): With FID detector and 2000 mm × 3 mm glass or stainless steel column filled 10 % SE-30/Gas chrom Q150-180 μm (80-100 mesh); NMR spectra were recorded in D_2O at 400 MHz. The chemical shift values are reported on the d scale with respect to TMS (δ 0.00) as internal standards.

Typical preparation of ethephon: Diester **2** (2083 g, GC purity 87 %,1100 mL) was added to 2 L high-pressure reactor (designed pressure: 2 Mpa). The vessel was sealed and then heated with stirring. HCl gas was imported when temperature was reached to 80 ºC. The pressure was set to 0.5 Mpa. The reaction was heated to 150 ºC with efficient stirring. The another part of diester **2** (574 g) was added after 500-600 mL of by-product 1,2-dichloroethane was distillated out. The reaction was finished until no 1,2-dichloroethane could be distillated (totally, about 1200 mL of 1,2-dichloroethane was collected during reaction). Then importing HCl gas was stopped. The reaction mixture was cooled to 120 ºC and concentrated in vacuum for 1 h. The mixture was cooled to



Scheme-I: Synthetic procedure of ethephon

room temperature to give final product ethephon **4** as white solid, 1240 g, yield 100.5 %. The content was 93 % by GC. NMR data were in agreement with published values[7]: ^{1}H NMR (D_2O) δ ppm: 2.13 (d, 2H, CH_2P, $^2J_{H\text{-}P}$ = 18.0, 3.58 (m, CH_2, CH_2Cl, $^2J^{H\text{-}P}$ = 14.12); ^{13}C (D_2O) δ ppm: 30.09 (d, 2H, $J_{P\text{-}C}$ =133.0 Hz), 37.495 ppm (s, 2H). ^{31}P (D_2O) δ ppm: 25.7.

The conversion process of intermediate **2** into final product includings two reversible reactions (step 3 and step 4 in **Scheme-I**). We reasoned that the quality of final product **4** should rely upon both the quality of diester **2** and the conversion of **2** and **3**. The quality of **4** should be improved if both of intermediate **2** and **3** can be converted completely into next product respectively. One important strategy to fulfill this aim is to remove by-product (1,2-dichloroethane) from reaction both in step 3 and step 4 continuously. Another way is to use good quality diester **2**. In our preparation, domestic diester **2** was used as starting reactant, however, the procedure reported in literatures was improved, especially by removing 1,2-dichloroethane from reaction during the process, so that both diester **2** and intermediate **3** could have excellent conversion. Finally, the content and yield of ethephon were achieved over 90 % and nearly quantitative respectively. Furthermore, the relationship between the GC content of diester **2** and final product **4** showed that quality of ethephon would rise with increasing of the GC content of diester **2**. The content of **4** was about 84.0 % to 89.2 % when the GC content of **2** was 78 to 83 % (Table-1, entry 1-4) and it could reach over 90 % while the GC content of diester **2** was 87 % (Table-1, entry 5 and 6).

TABLE-1
INFLUENCE OF GC CONTENT OF DIESTER **2** ON ETHEPHON QUALITY

Entry	GC content (%) of diester 2 [Ref. 8]	Content of ethephon (%) [Ref. 9]
1	78	84.0
2	83	89.2
3	82	87.7
4	78	85.2
5	87	93.1
6	87	92.9

Conclusion

Through the improved process, the good quality ethephon with content of over 90 % were obtained by using domestic diester. The research work showed a clear relationship between GC content of diester and quality of ethephon and this indication could be valuable for production of high quality ethephon.

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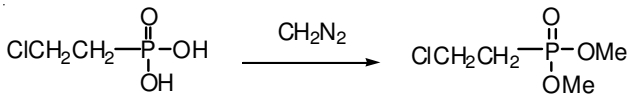
9. GC internal standard method to measure content of ethephon: The ethephon was firstly converted completely into methyl ester by diazonium methane to give dimethyl 2-chloroethyl phosphonate (**5**), which content can be determined by GC through 10%SE-30 / Gas Chrom Q chromatography using *p*-nitrochlorobenzene as internal standard solution Through this way, the content of ethephon could be measured.



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