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Note

Condensation of benzotriazole with O-alkyl P-(dichloromethyl) chlorophosphonate : Some unusual observations

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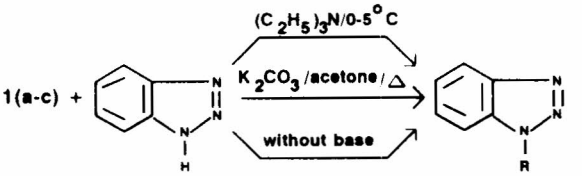
The condensation of benzotriazole with O-alkyl P-(dichloromethyl) chlorophosphonate give corresponding 1-alkylbenzotriazole rather than desired N-(benzotriazol-1-yl) P-(dichloromethyl) O-alkyl phosphonate.

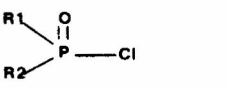
Several organophosphorus pesticides containing heterocyclic moieties[1,2] are successfully employed in crop protection e.g. triazophos [O,O-diethyl O-(1-phenyl- 1H-1,2,4- triazol-3-yl) phosphorothioate]. The broad spectrum activity of such compounds prompted us to synthesise organophosphorus compounds with a triazole moiety. Therefore, a study was undertaken which involved the condensation of benzotriazole with O-alkyl P-(dichloromethyl) chlorophosphonate.

The usual method of synthesising an organophosphorus (phosphonate) compound is by the reaction of phenolic[3], mercapto[4] and amino[5] compounds with chlorophosphonate in a suitable solvent in the presence of a base (triethylamine/ K_2CO_3).

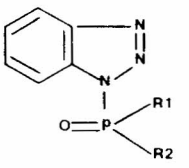
In the present study, the condensation of benzotriazole with O- alkyl P-(dichloromethyl) chlorophosphonate was carried out to synthesise corresponding phosphonate compounds. Surprisingly, the desired products were not obtained. Whereas, different products were obtained under all conditions (i.e. with base triethylamine/K_2CO_3 or without base) in all the cases.

The products obtained by condensation of P-(dichloromethyl) O- methyl chlorophosphonates **1a** with benzotriazole under all the conditions were identical. In ^{1}HNMR spectrum the product showed a





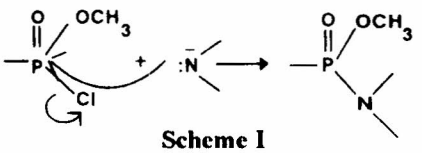
R1	R2		R	
OCH_3	$CHCl_2$	1a	CH_3	2a
OCH_2CH_3	$CHCl_2$	1b	CH_2CH_3	2b
OC_6H_5	$CHCl_2$	1c	C_6H_5	2c



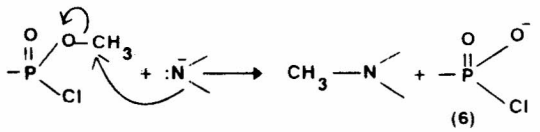
R1	R2	
OCH_3	$CHCl_2$	3
OCH_2CH_3	$CHCl_2$	4
OC_6H_5	$CHCl_2$	5

three proton singlet at δ 4.2 for NCH_3, besides the other signals for benzotriazole. It did not show the presence of signals due to dichloromethyl moiety as expected in the desired compound **3**. Its ^{1}HNMR spectrum was similar to that of 1-methylbenzotriazole[6] **2a**. This shows that during condensation, there is formation of the N-C bond rather than the P-N bond to give 1-methylbenzotriazole **2a**. But, when aniline was used instead of benzotriazole, under similar conditions, the desired product was obtained[5].

Similarly, the condensation of benzotriazole with O-ethyl **1b** or O-phenyl P-(dichloromethyl) chlorophosphonates **1C**, also gave the corresponding ethyl benzotriazole **2b** or phenyl benzotriazole **2c**, respec-



Scheme I



Scheme II

tively rather than the desired products N-(benzotriazolyl) P-(dichloromethyl) O-ethyl phosphonate **4** or N-(benzotriazolyl) P- (dichloromethyl) O-phenyl phosphonate **5**.

Usually, the reaction of chlorophosphonate with primary or secondry amines results in the product -P(O) (O-alkyl) (N) by nucleophilic attack of N^- at the P^+ atom. But, in this study, when benzotriazole is used as substrate, there is alkylation of benzotriazole. Two different types of mechanisms can be postulated for phosphorylation reaction. Initially formed nucleophile (N^-) can attack in two different ways: (i) either at P atom (Scheme I) to give the desired product as in the case of aniline, with the chloride ion as the leaving group or (ii) at carbon atom instead of P atom (Scheme II) to give N-alkyl product with as P- (dichloromethyl) chlorophosphonate **6** as leaving group. Which of the two competing reactions dominate would depend upon the nucleophilicity of the anion towards phosphorus and/or carbon atoms. The formation of N-alkyl benzotriazole in these reactions can be explained on the basis of the fact that the benzotriazole anion formed is less nucleophilic towards P atom as compared to C atom. Benzotriazole is very less basic than aniline and its anion and hence is less nucleophilic than aniline anion. Therefore, because of less nucleophilicity, benzotriazole anion preferably attacks C atom than P atom. Due to the presence of electron withdrawing groups at P atom, it becomes highly electropositive as compared to C atom (which is less electropositive) and benzotriazole anion which is less electronegative, attacks C atom rather than P atom.

Similar results have been reported by Ahluwalia *et al.*[6], when they carried out the condensation of O, O-dimethyl chlorophosphorothioate with different mercaptothiazols. The explanation given for this unusual behaviour is the varying nucleophilicity of thiol anion towards carbon and phosphorus atoms. This observation of Ahluwalia *et al.*[7] is in accordance with the earlier findings of Bernard Miller[8].

When phosphorylation of P-(dichloromethyl) O-alkyl chlorophosphonates was carried out in the absence of base, the 1- alkyl products were obtained. The probable explanation may be that the benzotriazole (acidic $pK_a = 8.2$) behaves more like an acid than as a base. This may be the reason that benzotriazole does not require any base.

Experimental Section

Melting points reported are uncorrected. ^{1}HNMR spectra were recorded on Varian EM-360L 60 MHz spectrometer in $CDCl_3$ (values in δ, ppm) using TMS as internal standard and mass spectra on a JEOL-JMSD-300 mass spectrometer.

Preparation of P-(dichloromethyl) O-alkyl chlorophosphonate. A solution of dichloromethyl phosphonic dichloride[9] (0.01 mol), in dry benzene (20mL) was cooled to 0-5°C and to this was added a solution of dry alcohol or phenol (0.01 mol of methanol/ethanol/phenol) in benzene (10mL) dropwise with stirring. After the addition was complete, triethylamine (0.01 mole) in benzene (5mL) was added dropwise. Stirring was continued for 1 hr. The inorganic precipitate obtained was filtered off and filterate was distilled on a water-bath. The crude product thus obtained was used for further reactions.

Condensation of benzotriazole and O-alkyl P-(dichloromethyl) chlorophosphonates: Condensation was carried out under following conditions:

Condition (i) O-Alkyl P-(dichloromethyl) chlorophosphonate **1a-c**, 0.01 mole was dissolved in dry methylene chloride (20mL) and the solution was cooled to 0-5°C. To this, a solution of benzotriazole (0.01 mole) in methylene chloride (10mL) was added dropwise with constant stirring. Triethylamine (0.01 mole) in methylene chloride (5mL) was then added dropwise and stirring continued for another 1 hr. The inorganic salt obtained was filtered off and the filtrate distilled on a water-bath. The crude product was purified by column chromatography on a silica gel column. On the basis of spectral data (^{1}HNMR and mass) the compounds were identified as 1-methyl/ethyl/phenyl-benzotriazoles and were assigned the structures **2a-c**, respectively.

Condition (ii): Above reaction was repeated in the absence of a base. The compounds obtained were identical to that obtained under condition (i).

Condition (iii): O-Alkyl P-(dichloromethyl) chlorophosphonate **1a- c**, 0.01 mole), benzotriazole (0.01 mole) in the presence of anhydrous K_2CO_3 (2.0 g) in dry acetone (20 mL) was refluxed for 16 hr. K_2CO_3 was removed by filteration and acetone was distilled on a water-bath. The crude products were purified by column chromatography as mentioned above. The compounds obtained were identical to that obtained under condition (i).

2a; m.p. 64-65°C (Lit. m.p. 64-65°C) yield 80% (condition-i), 70% (condition-ii), 75% (condition-iii); ^{1}HNMR: 4.2 (s, 3H, -NCH_3), 7.0-8.2 (m, 4H); Mass : 133 (M^+)

2b, m.p. 67-68°C; yield 75% (condition-i), 69% (condition-ii), 72% (condition-iii); ^{1}HNMR: 3.9 (t, 3H, -CH_3), 4.8 (q, 2H, -NCH_2-), 7.2-8.2 (m, 4H); Mass : 147 (M^+)

2c, m.p. 124-25°C; yield 67% (condition-i), 54% (condition-ii), 59% (condition-iii); ^{1}HNMR: 7.2=8.2 (m, 4H), 8.2- 9.2 (m, 5H); mass : 195 (M^+)

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References

1 Eto M, *Organophosphorus pesticides: Organic and biological chemistry*, (CRC Press Inc., Ohio), **1974**.

2 Fest C & Schmidt K J, *The chemistry of organophosphorus pesticides*, (Springer-Verlag, Berlin, Heidelberg, New York), **1973**.

3 Bedi S & Roy N K, *Indian J Agric Sci*, 48, **1978**, 248.

4 Aries R, *Fr Pat*, 2168182; *Chem Abstr*, 80 **1974**, 47978a.

5 Khazanchi R & Roy N K, *Agricul Bio Chem*, 47, **1983**, 331.

6 Abbott P J, Acheson R M, Foxton M W, Raulins N R & Robinson G E, *J Chem Soc, Perkin-I*, **1972**, 1791.

7 Ahluwalia V K, Arora K K, Kaur G & Mehta B, *Synth Commun*, 17, **1974**, 1441.

8 Miller B, *Tetrahedron*, 20, **1964**, 2069.

9 Roy N K & Mukherjee S K, *Indian J Chem*, 10, **1972**, 1159.