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Reaction Of Unsaturated β–Bromo Phosphonite And α–Chloro Phosphonate With DiazoMethane And Its Derivatives

by

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The product 3 g (93 % yield) recrystallised from benzene-petroleum ether (40-60 °C) gave 4-hydro-3,5- diphenyl -3- benzoyl -1, 2- diazo cyclo-4-ene (IV), m. p. 190-192 °C. Anal. Calcd. for $C_{22}H_{16}ON_2$: C, 69.5; H, 5.0. Found: C, 69.3; H, 5.0.

REFERENCES

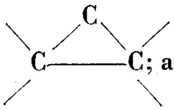
[1] **A. Yu. Platonov, A.S. Kruglov. V. N. Chistokletov,** and **A.V. Dogadina,** Zh. Obshch. Khim., 50, 1269-1273 (1980).

[2] **L. G. Kolokol tseva, V.N. Chistokletov,** and **A.A. Petrov,** Zh. Obshch. Khim., 38, 2819 (1968).

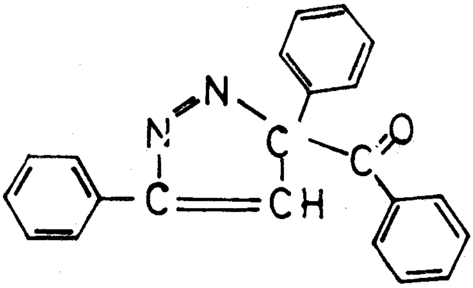
[3] **V. V. Kosovtsev, V.N. Chistokletov,** and **A.A. Petrov,** Zh. Obshch. Khim., 38, 2819 (1968).

[4] **L. A.** Tamm, **V.N. Chistokletov,** and **A.A. Petrov,** Zh. Obshch. Khim., 42, 1864 (1972).

The i.r. spectrum and elemantal analysis were in good agreement with the suggested structure. The reaction goes by 3 + 2 = 5 scheme of dipolar cycloaddition via addition to double bond.

Diethyl (1-chloro -1-phenyl, vinyl) phosphonate reacts with diphenyldiazomethane (1:1 molar ratio) in boiling benzene to give a good yield of a colourless product. It contains no nitrogen, phosphorus nor halogen. The analytical data fit for $C_{21}H_{16}$. The i.r. spectrum showed absorption bands at 3070, 1025 cm^{-1} which can be attributed to ; at 3010 cm^{-1} attributed to νAr_{C-H}; and the absorption bands for monosubstituted aromatic moeity. The reaction seems to undergo cleage of C-P bond accompanied with the elimination of the halogen. The present data is not sufficient for suggesting a structure for this product.

The reaction of (1:1 molar ratio) diethyl (1- chloro -1- phenyl, vinyl) phosphonate and phenylbenzoyldiazomethane in boiling benzene gave rise to a product, its proposed structure is:



(IV)

The structure was confirmed by elemental analysis, and the i.r. spectrum which showed the absorption band due to ν C = C at 1700 cm^{-1}, with the disappearance of ν P-O-C_2H_5, and νC-CI. The reaction took place by 3 + 2 = 5 of 1,3- dipolar cycloaddition.

Experimental

Melting points reported are uncorrected. IR spectra were carried out using Perkin-Elmer Model 398 Infrared Spectrophotometer, and KBr technique, U.V. spectrum was measured in chloroform.

Reaction of Diethyl (2- bromo -1- phenyl, vinyl) phosphonite with diazomethane : To the ethereal solution of diethyl (2- bromo-1-phenyl, vinyl) phosphonite (3.03 g), a solution of diazomethane in ether dried over KOH was added. The reaction mixture was left in an ice-chest overnight. The precipitated solid was filtered off to give 3 g (87 % yield of crude product) recrystallised from ether to give yellow crystals of pure 4-phenyl-4 (diethylphosphonate) -5- bromo pyrazoline (I) m.p. 90-92 °C. Anal. Calcd. for $C_{13}H_{18}O_2\ BrN_2P$: C, 45.20; H, 5.20; P, 8.98. Found: C, 46.02; H, 5.44; P, 9.58.

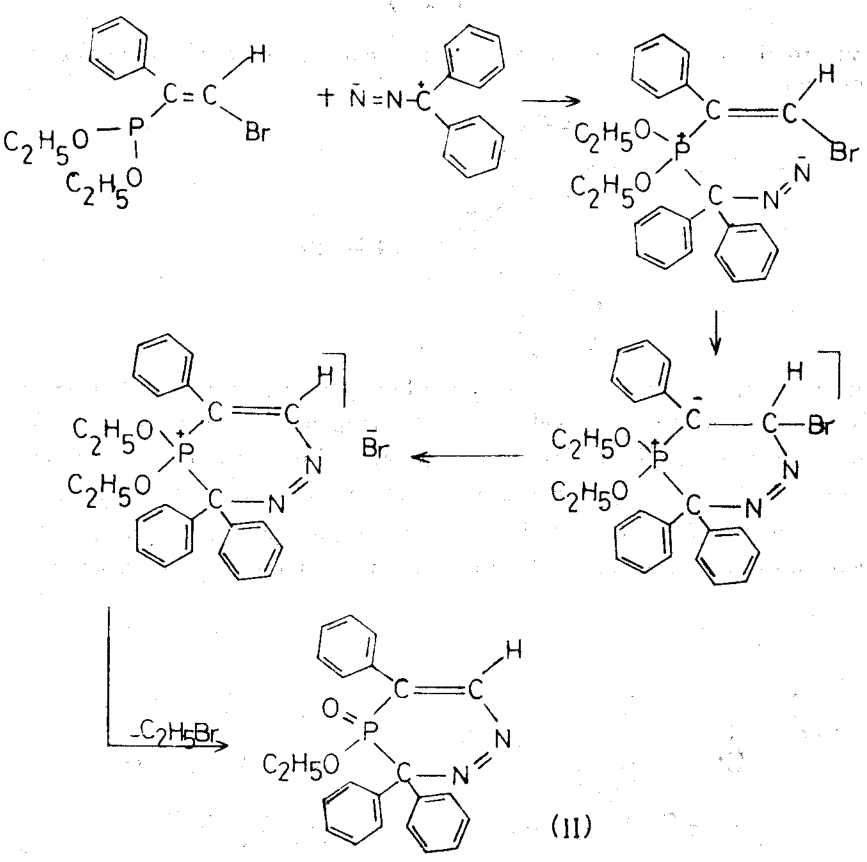
Reaction of Diethyl (2- bromo -1- phenyl, vinyl) phosphonite with diphenyldiazomethane : Diphenyldiazomethane 1.66 g (0.01 mol) was added to a stirred solution of diethyl (2-bromo -1- phenyl, vinyl) phosphonite 3.03 g (0.01 mol) in dry benzene. The reaction mixture was boiled for one hour and left overnight. Petroleum ether was added to give 2.5 g (84 % yield) of recrystalline product. Recrystallisation from benzene-petroleum ether (40-60 °C) gave pure 4-ethoxy -6- hydro -3,3,5- triphenyl-1, 2, 4- diazophosphorine 4-oxide (II), m.p. 150/151 °C. Anal. Calcd. for $C_{23}H_{21}O_2N_2P$: C, 81.1; H, 5.46; N, 7.29. Found: C, 81.7; H, 5.48; N, 7.23.

Reaction of diethyl (1- chloro -1- phenyl, vinyl) phosphonate with diazomethane : The reaction was carried out as described above for compound (I), using (1:1 molar ratio) from the reactants. The product obtained 3.5 g (96 %) on recrystallisation from ether gave pure yellow crystals of 4-chloro -4- phenyl, 5- diethyl phosphate pyrazoline (III), m.p. 98-99 °C. Anal. Calcd. for $C_{13}H_{18}O_3ClN_2P.\ 1\frac{1}{2}\ H_2O$: C, 45.90; H, 6.15. Found: C, 45.03; H, 6.63.

Reaction of diethyl (1- chloro -1- phenyl, vinyl) phosphonate with diphenydiazomethane : The reaction is carried out as described for preparation of compound (II). The solid product on recrystallisation from benzene-petroleum ether (40-60 °C) gave 2.51 g, m.p. 210-211 °C. Anal. Found: C, 90.8; H, 58.

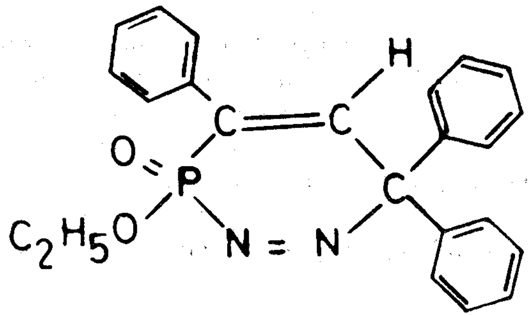
Reaction of diethyl (1- chloro -1- phenyl, vinyl) phosphonate with phenylbenzoyldiazomethane : The reaction was carried out as described above.

The reaction between diethyl (2-bromo-1-phenyl, vinyl) phosphonite (0.01 mol) and diphenyldiazomethane (0.01 mol) in benzene at its boiling point gave a product its structure is deduced from its elemental analysis, i.r. and U.V. spectra The i.r. spectrum showed νP=O at 1320-1295 cm^{-1}; P-O-C_2H_5 at 1030 cm^{-1}; νAr_{C-H} at 3010 cm^{-1}. The u.v. spectrum showed λ_{max} at 315 nm which can be attributed to π-π^* transition. The reaction takes place probably via the 1,3-dipolar cycloaddition.



(II)

The final product may also have the following structure:



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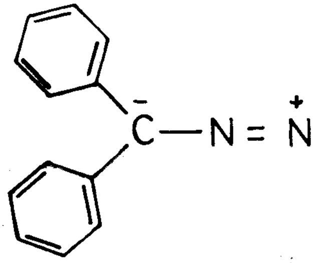
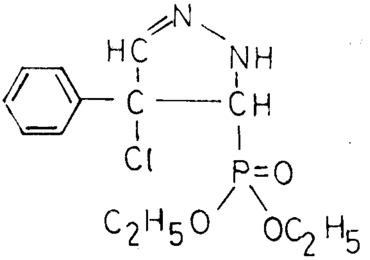
due to the reaction with another canonical structure of diphenyldiazomethane



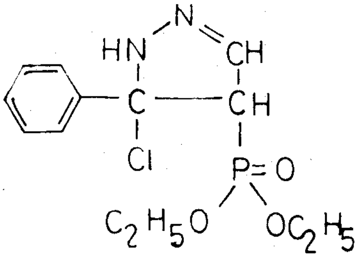
In both cases the attack starts by the lone pair of electrons of the phosphorus atom on the positively charged nitrogen (or carbon) and the formed intermediate is stablized via resonance due to the two phenyl groups, i.e., dissiption of the negative charge on the two phenyl group.

The reaction of diethyl (1-chloro -1- phenyl, vinyl) phosphonate with diazomethane (1:1 molar ratio) in ether at room temperature gave



(III)

or



(IIIa)

Reaction Of Unsaturated β–Bromo Phosphonite And α–Chloro Phosphonate With DiazoMethane And Its Derivatives

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Diethyl (2-bromo-1- phenyl, vinyl) phosphonite and diethyl (1-chloro-1-phenyl, vinyl) phosphonate react with diazomethane, diphenyldiazomethane, and phenylbenzoyldiazomethane. The reaction with diazomethane goes by 3 + 2 = 5 scheme of dipolar cycloaddition. The reaction of the phosphonite with diphenyldiazomethane goes by the 3 + 3 = 6 scheme, while in the case of phosphonate cleavage of C-P bond took place. However, the reaction of phosphonate with phenylbenzoyldiazomethane goes by 3 + 2 = 5 scheme of 1, 3-dipolar cycloaddition with the cleavage of C-P bond.

INTRODUCTION

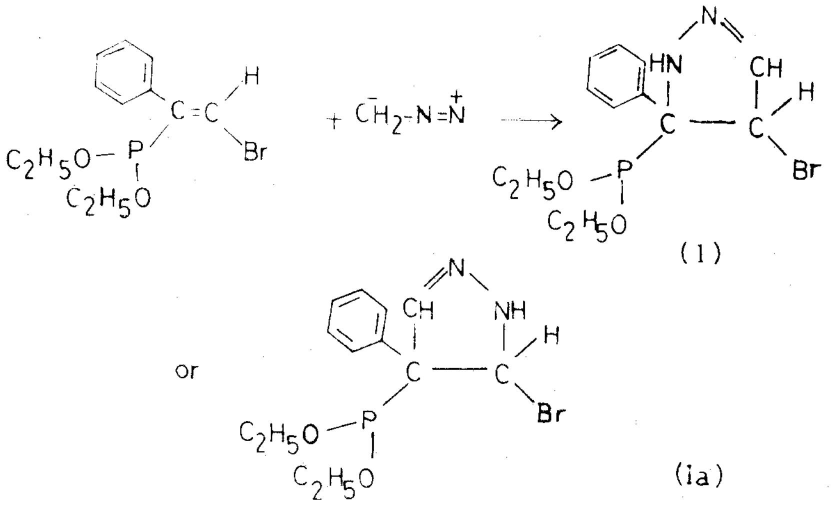
Platonov *et al*[1] reported that the reaction of α, β-unsaturated compounds containing 3- coordinate phosphorus atoms with 1, 3- dipoles proceeds by the 3 + 3 = 6 cycloaddition scheme with the inclusion of a phosphorus atom in the ring.

Kolokol Tseva *et al*[2] showed that unsaturated phosphines react with nitrilimines to from compounds with a six-membered diazophosphorine ring, which in presence of triethylamine hydrochloride are converted into the corresponding phosphonium salts in the case of ethylenic and acetylenic phosphonites the cyclic quasiphosphonium salts formed in the course of the reaction suffer Arbusov rearrangement with the formation of cyclic phosphonites containing a 4-coordinate phosphorus atom[3,4]. The course of the cycloaddition depends on the nature of the substituent at the multiple bond in the β-position relative to phophorus atom.

In the present investigation, diethyl (2-bromo-1-phenyl, vinyl) phosphonite, where the phosphorus atom is in a low oxidation state (3-coordinate phosphorus atom), and diethyl (1-chloro -1- phenyl, vinyl) phosphonate, where the phosphorus atom is in a high oxidation state, were allowed to react with diazomethane, diphenyldiazomethane and phenylbenzoyldiazomethane with the formation of different products some of them due to 3 + 3 = 6 cycloaddition and the other due to 3 + 2 = 5 cycloaddition and some of the reactions proceed with cleavage of P-C bond.

Results and discussion

The reaction of diazomethane with diethyl (2-bromo -1- phenyl, vinyl) phosphonite leads to the formation of a crystalline product. Elemental analysis and i.r. spectrum showed that an addition reaction occurs with the 3 + 2 = 5 scheme of cycloaddition. The absorption bands at 1050-1030 cm^{-1}; 750-500 cm^{-1} and 3400 cm^{-1} are attributed to νP-O-C_2H_5; νC-Br; and νN-H, respectively. The spectrum showed also the absorption bands for the monosubstituted aromatic. The starting attack takes place via the negatively charged carbon on a positive carbon of the double bond to yield at the end the pyrazoline derivative.



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