

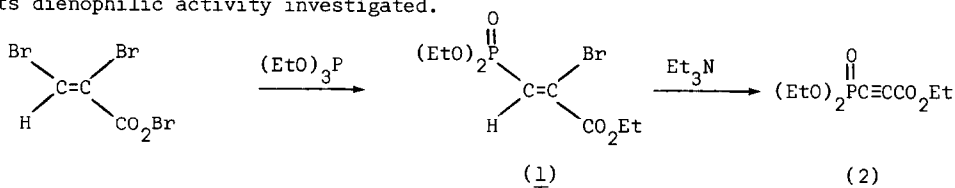
THE PREPARATION AND DIELS-ALDER REACTIVITY OF
ETHYL (DIETHOXYPHOSPHINYL)PROPENOATE

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Summary Ethyl (diethoxyphosphinyl)propynoate has been prepared. It is a highly reactive and regiospecific dienophile.

We are interested in the synthesis of aromatic and heterocyclic phosphonates by cycloaddition reactions. To this end ethyl (diethoxyphosphinyl)propynoate (2) has been prepared and its dienophilic activity investigated.

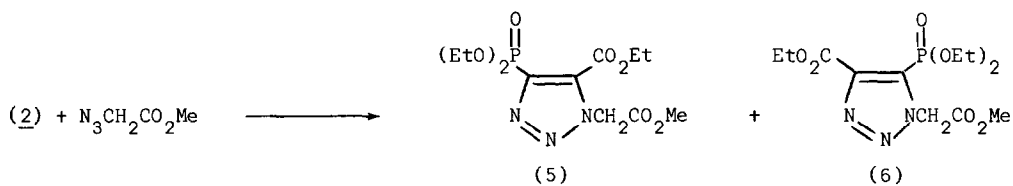


Triethyl phosphite and ethyl Z-2,3-dibromopropenoate¹ at 100 °C gave the phosphonate (1; 58%); this with triethylamine in refluxing ether gave (2; 73%), b.p. 128-130 °C at 0.1 mmHg ³¹P -10.9 ppm, which showed no acetylenic absorption in the infra-red but absorption at 2213 cm⁻¹ in the Raman spectrum.

Ethyl (diethoxyphosphinyl)propynoate is stable in refluxing toluene. It undergoes essentially quantitative Diels-Alder additions to a variety of dienes (Table) as monitored by ³¹P nmr. For example, reaction of (2; 1.0 g) with cyclohexa-1,3-diene (1.73 g) under reflux was complete after 2 h. Distillation then gave the adduct (4), b.p. 160 °C at 0.05 mmHg (76%). Competition experiments for 1,3-diphenylisobenzofuran showed (2) to be less reactive than dimethyl acetylenedicarboxylate by a factor of about 5.

Reaction of (2) with 2-substituted butadienes, e.g. isoprene and 2-chlorobutadiene, gave equal amounts of the possible isomeric adducts, but the regioselectivity of Diels-Alder additions to 1-substituted butadienes was high. As shown by ³¹P and ¹H nmr, piperylene and trans-1-phenylbutadiene gave only one isomer, the adducts (3; R=Me) and (3; R=Ph) respectively. This high regioselectivity is analogous to that reported for methyl propynoate² and for ethyl phenylsulphonylpropynoate.³

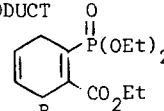
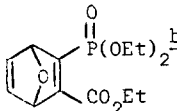
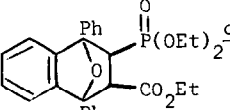
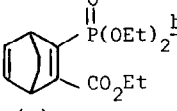
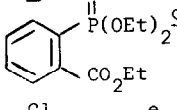
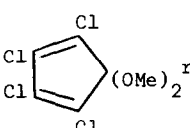
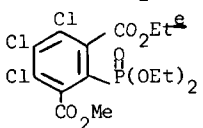
As expected, (2) undergoes addition to a range of 1,3-dipoles, e.g. methyl azidoacetate gave a 4:7 ratio of the triazoles (5) and (6).



We thank S.E.R.C. for a studentship.

1. Addition of bromine to ethyl propynoate in CCl_4 at $60-70^\circ\text{C}$ gives entirely the *Z*-isomer.
2. A.S. Onishchenko, "Diene Synthesis". Israel Program for Scientific Translations Ltd., Jerusalem, 1964, p137-138.
3. Ming Shen and A.G. Schultz, *Tetrahedron Letters*, 1981, 22, 3347.
4. J. Diekmann, *J. Org. Chem.*, 1963, 28, 2880; D.M. Lemal, E.P. Gosselink, and S.D. McGregor, *J. Amer. Chem. Soc.*, 1966, 88, 582.

TABLE Diels-Alder Reactions of Ethyl (Diethoxyphosphinyl)propynoate ^a

DIENE	Molar Ratio Diene: (2)	Conditions	ADDUCT
1. <u>trans</u> -1-phenylbuta-1,3-diene	5:1	125° ; 1h	 (3; R=Ph)
2. furan	5:1	reflux; 6d	 (3) ^b
3. 1,3-diphenylisobenzofuran (ether)	1:1	reflux; 4h	 (3) ^c
4. cyclohexa-1,3-diene	5:1	100° ; 2h	 (4) ^b
5. <u>trans</u> -1-acetoxy-1,3-butadiene	5:1	120° ; 1.5h	 (4) ^d
6.  ref. 4	1:1	150° ; 3d	 (4) ^e

^a Without solvent except in 3. ^b Isolated after silica gel chromatography.

^c Crystallised from EtOAc-petrol. ^d Initial adduct not detected. ^e Structure based on symmetry of product from $(\text{EtO})_2\text{P}(\text{C}\equiv\text{C})\text{CO}_2\text{Me}$ as shown by ^{13}C and ^1H nmr.

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