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SYNTHESIS OF SOME NEW VIC-TRIAZOLES FROM PHOSPHORUS YLIDS AND ETHYL AZIDOFORMATE.

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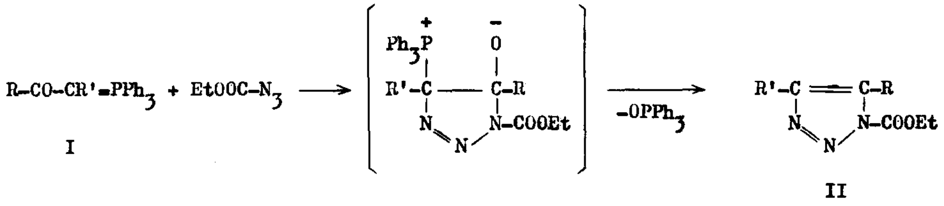
Acylmethylenetriphenylphosphoranes are known to react with azides to give 1,5-disubstituted 1,2,3-triazoles. Harvey (1) studied the reaction with different classes of azides and reported that the reactivity towards α-keto ylids decreases in the order : sulfonyl azides > acyl azides > aryl azides > alkyl azides. Thus most reactions with tosyl azide were complete in a few hours at room temperature, wheras n-dodecyl azide failed to react, even after prolonged heating in chloroform.

We have investigated the reaction of α-keto and α-ester ylids with another class of azides, namely azidoformates, in order to prepare as yet unknown 1-carbethoxy-vic-triazoles.



a) R = CH_3 , R'= H

b) R = p-NO_2-C_6H_4 , R'= H

c) R = OEt , R'= Me

The reactions of ethyl azidoformate with some ylids (I) were carried out in benzene solution. The experimental conditions, recrystalization solvents, yields and melting points of the isolated vic-triazoles are summerized in the table.

TABLE

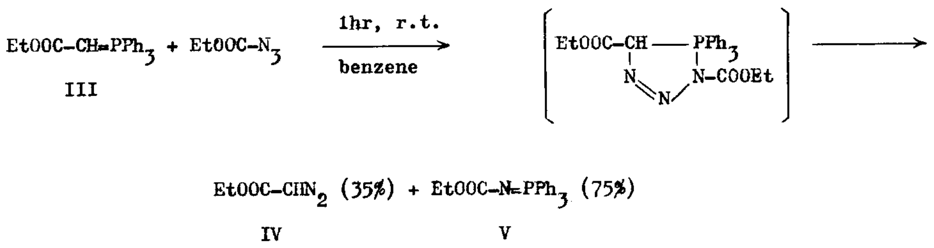
New Vic-Triazoles from Ethyl Azidoformate and Phosphorus Ylids.

Triazole	yield, %	m.p., °C	reaction conditions (reaction time, temp.)	recrystn solvent
IIa	65	liq.	2 hr, room temp.	*
IIb	40	149-150, decompn.	2 hr, reflux	benzene
IIc	100	75-76	5 hr, room temp.	ether

* triazole IIa was purified by distillation at reduced pressure (ca. 70°/ 0.3 mm).

In all cases presented in the table equimolecular mixtures of ylids and azide were used. The rather low yield of triazole IIb is due to the fact that ethyl azidoformate slowly decomposes in refluxing benzene yielding N-carbethoxyazepine (2). This compound indeed was isolated from the reaction mixture. When an excess of azide was used, triazole IIb could be obtained in 80% yield.

The reaction of carbethoxymethylenetriphenylphosphorane (III) with ethyl azidoformate in benzene solution afforded ethyl diazoacetate (IV, 35%) and N-carbethoxyiminotriphenylphosphorane (V) in accordance with the results of Harvey (1).



α-Carbethoxyethylidenetriphenylphosphorane (Ic) however did not react in this way but gave 1-carbethoxy-4-methyl-5-ethoxy-1,2,3-triazole (IIc) in quantitative yield. This is the first reported example of triazole formation from α-ester ylids.

The new triazoles IIa-c were characterized by IR and NMR spectroscopy and by elemental analysis. Triazoles IIb and IIc are crystalline solids which decompose at 149-150° and 180-190° respectively. IIa is a colourless liquid which partially solidifies on standing at room temperature. They exhibited the following NMR spectral data (τ values are given with respect to $SiMe_4$ as internal reference) :

IIa ($CDCl_3$) : H-C=C singlet at 2.35, $-OCH_2$ quartet at 5.4, CH_3-C=C singlet at 7.60 and a methyl triplet at 8.50.

IIb (CD_3NO_2) : H-C=C singlet at 1.65, aromatic quartet at 1.8, methylene quartet at 5.35 and a methyl triplet at 8.50.

IIc ($CDCl_3$) : two methylene quartets in the region 5.3-5.8, CH_3-C=C sharp singlet at 7.75 and two methyl triplets in the region 8.4-8.7.

The integration curves agreed with the number of hydrogen atoms involved.

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