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SYNTHESIS AND FRAGMENTATION-CONDENSATION REACTIONS OF 1,3-DIETHOXYCARBONYLALLYLIDENETRIPHENYLPHOSPHONIUM YLIDE

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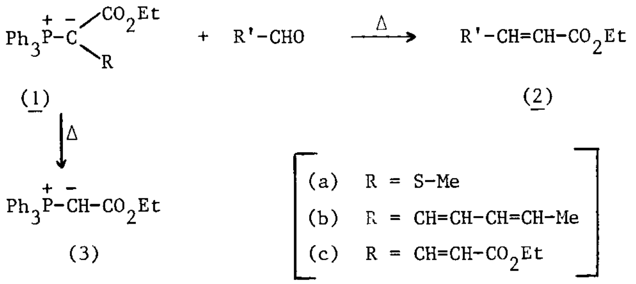
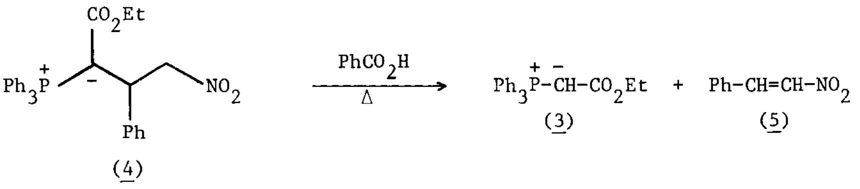
Abstract Alkylidenephosphonium ylides with ethoxycarbonyl substituents in the α-position fragment in a *retro*-Michael fashion during condensation with aldehydes.

During our efforts aimed at the synthesis of cross-conjugated systems, we observed that α-ethoxy carbonylated alkylidenephosphonium ylides (1) condensed with aldehydes to produce the esters (2) as major reaction products [1] The formation of the esters (2) under these circumstances can be ascribed to fragmentation of the α-substituted phosphonium ylides (1) to yield ethoxycarbonylmethylenetriphenylphosphonium ylide (3), followed by a Wittig condensation of (3) with the corresponding aldehydes



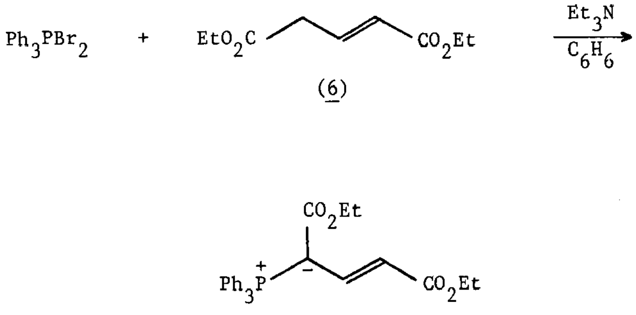
(a) R = S-Me
(b) R = CH=CH-CH=CH-Me
(c) R = $CH=CH-CO_2Et$

In this context, it was previously found by Connor and von Strandtmann[2] that the phosphonium ylide (4), during an attempted Wittig condensation with p-chlorobenzaldehyde in the presence of benzoic acid as catalyst,[3] decomposed *via* a protonation-elimination mechanism with the concomitant generation of the nitrostyrene (5) and ylide (3), but no Wittig condensation products could be detected



In order to shed more light on these unusual ylide reactions, we have undertaken a detailed investigation of the fragmentation-condensation reaction of the cross-conjugated phosphonium ylide (1c) with p-chlorobenzaldehyde

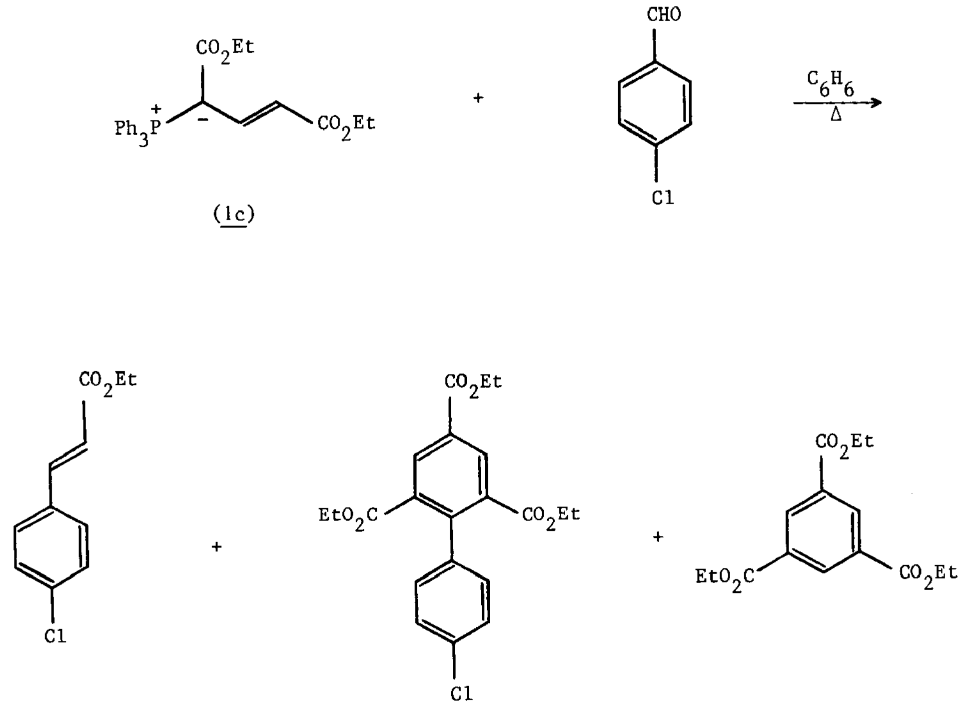
The phosphonium ylide (1c),[4] m.p. 148° (from benzene), ^{1}H n.m.r. ($CDCl_3$) δ 6.31 (1 H, d, J 14.8 Hz) and 7.07 (1 H, dd, J_{PH} 16.8 and J_{HH} 14.8 Hz), was very conveniently synthesized in 80% recrystallized yield[5] *via* condensation of triphenylphosphine dibromide with the diester (6) in the presence of triethyl amine.[6]



(6)

(1c)

Condensation of the cross-conjugated phosphonium ylide (1c) with p-chlorobenzaldehyde produced ethyl p-chlorocinnamate (7) (40%) as the major reaction product, while the triesters (8) (11%) and (9) (1%) were formed in smaller quantities.



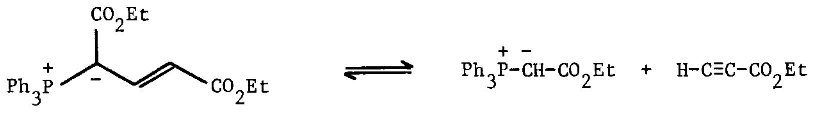
(1c)

(7)

(8)

(9)

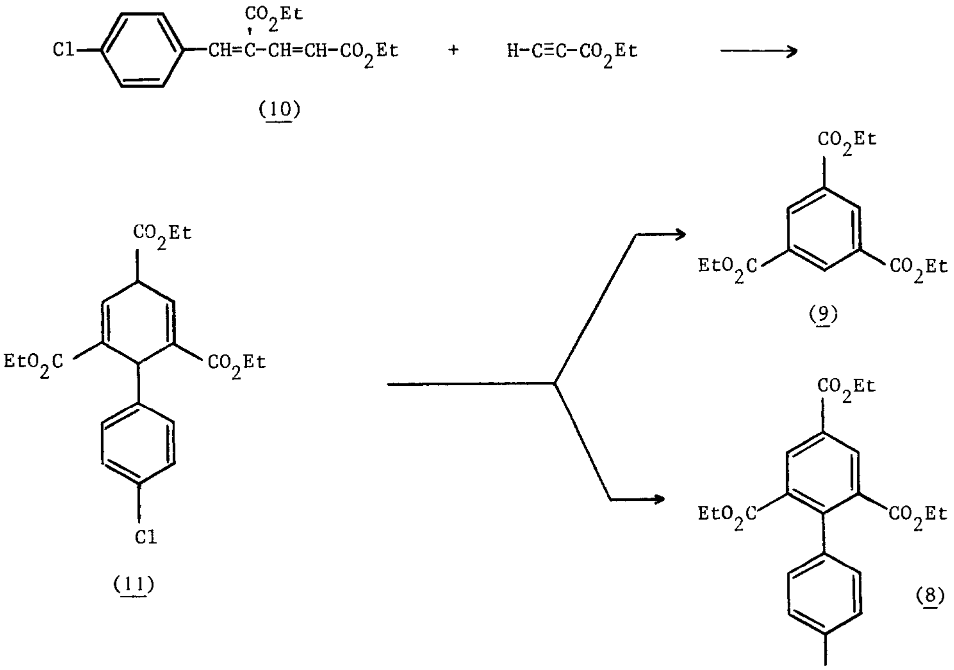
The production of ethyl p-chlorocinnamate (7) under these reaction conditions evidently resulted from fragmentation of the ylide (1c) in a *retro*-Michael reaction to produce the ylide (3) and ethyl propynoate.



(1c) (3)

In full accord with our expectations, it was found that the corresponding Michael addition of the phosphonium ylide (3) to ethyl propynoate took place in a totally stereospecific fashion to produce the cross-conjugated phosphonium ylide (1c) in 90% recrystallized yield This ylide fragmentation reaction is furthermore substantiated by the formation of the triesters (8) and (9)

The formation of the aromatic triester (8) can be rationalized as being the result of a Diels-Alder addition of ethyl propynoate to the cross-conjugated diester (10), which resulted from a Wittig condensation between p-chlorobenzaldehyde and the phosphonium ylide (1c) prior to its fragmentation Spontaneous aromatization of the intermediate Diels-Alder adduct (11) according to two competing modes can finally account for the formation of the triesters (8) as well as (9)



(10) (11) (9) (8)

ACKNOWLEDGEMENT

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REFERENCES AND NOTES

1. C.J. Meyer, T.B.A. Rutherford, and D.F. Schneider, unpublished results.

2. D.T. Connor and M. von Strandtmann, *J. Org. Chem.*, 1973, 38, 1047.

3. C. Rüchardt, P. Panse, and S. Eichler, *Chem. Ber.*, 1967, 100, 1144.

4. All new compounds exhibited satisfactory analytical and spectrometric data.

5. Yields were not optimized.

6. L. Horner and H. Oediger, *Chem. Ber.*, 1958, 91, 437.

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