Tetrahedron Letters,Vol.28,No.29,pp 3391-3392,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

INTRAMOLECULAR DIELS-ALDER REACTION OF ARYL ALLENE PHOSPHONATES

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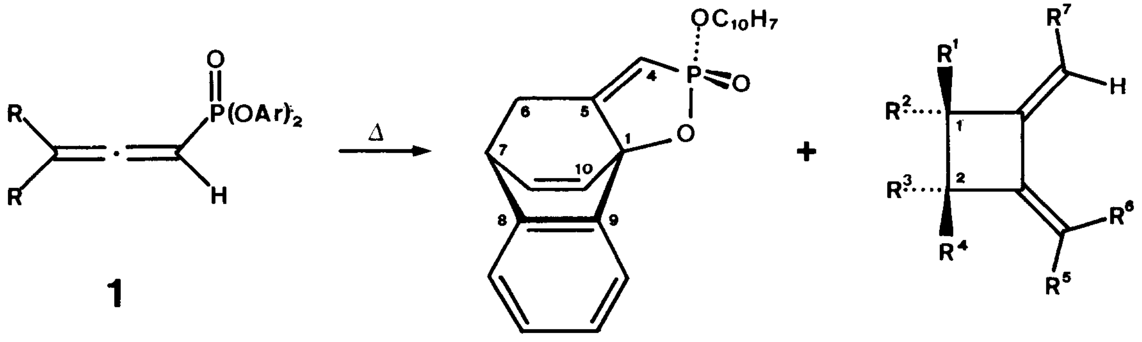
Abstract: Intramolecular Diels-Alder cyclization in aryl allene phosphonates leads only in 1c to the tricyclic 2,3-oxaphospholene 2, 2+2 dimerization being observed in the remaining cases.

Several examples have been recently reported describing intramolecular Diels-Alder reaction with allenes[1-5] proceeding in some cases even spontaneously in the absence of a catalyst.[6] In an attempt to define the scope and limitations of these reactions we presently report the synthesis of a 2,3-oxaphosphatricyclo[5.2.2.0^{1,5}]undecatriene, i.e. compound 2.

The starting aryl allene phosphonates 1[7] afforded the cyclization product 2(20% yield) on prolonged reflux in xylene only in the case of 1c, i.e. of a non-substituted at C(3) 1-naphthyl allene phosphonate. The structure of 2 was easily established on the basis of the very characteristic chemical shifts for H-C(4)(dt, $^2J_{PH}$=36.0, $^4J_{HH}$=1.9 at 5.95 ppm), for H-C(6)(AB system centered at 2.63 and at 2.48 ppm, J=17.0) and for H-C(7)(m at 4.25 ppm) in the ^{1}H NMR spectrum and also for C(1)(d, J_{PC}=11.9 at 89.5 ppm) and for C(7)



1 2 3

	R	Ar
1a	H	Ph
b	CH_3	Ph
c	H	1-Naphthyl
d	CH_3	1-Naphthyl

	R^1&R^2	R^3	R^4	R^5	R^6	R^7	%
3a	H	H	H	X	H	X	6
b	CH_3	CH_3	CH_3	X	H	X	17
c	CH_3	H	X	CH_3	CH_3	X	38
d	CH_3	H	Y	CH_3	CH_3	Y	42

X=$P(O)(OPh)_2$, Y=$P(O)(OC_{10}H_7)_2$

(at 40.3 ppm) in the ^{13}C NMR spectrum.

Of the two possible diastereomers of 2 only one was isolated as shown by the NMR spectra. Assuming least steric interactions this is the isomer depicted in the scheme possessing trans-situated 1-naphthyloxy group at the phosphorus atom and C(9).

The intramolecular cyclization only of the ester 1c, and not of the other esters, is in agreement with observations of Himbert and co-authors showing that the intramolecular 4+2 cyclization is facilitated by lack of substitution at C(3) of the allene and the use of a 1-naphthyl instead of a phenyl group as diene.[4] In the case of the remaining examined esters 1a,b,d were observed only the 2+2 head-to-head and head-to-tail dimers 3. The structures of the dimers 3a-d were deduced mainly from the ^{1}H and ^{13}C NMR spectra and NOE experiments as well as from the MS data.[8]

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7. The esters 1a,b were prepared according to H.F.Schuster; G.M.Coppola, "Allenes in Organic Synthesis", Wiley, New York, 1984, p. 247; 1c,d according to K.K.Shtengel; L.N.Mashlyakovski; I.S.Okhrimanko, Zh.Obshch. Khim., 1976, 46, 434 (Chem.Abstr. 85, 33128) and V.M.Ignat'ev; B.I.Ionin; A.A.Petrov, Zh.Obshch.Khim., 1967, 37, 1898.
8. The structure elucidation of 3 will be published elsewhere.

(Received in UK 26 May 1987)