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FACILE ROUTE TO 1-PHOSPHORYL- AND 1-SULFONYL-1,3-DIENES VIA PALLADIUM-CATALYZED ELIMINATION OF ALLYLIC ACETATES

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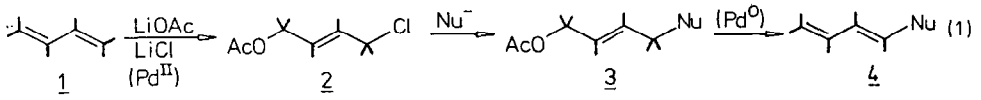
Abstract: The palladium(II)-catalyzed chloroacetoxylation of 1,3-dienes is employed to prepare 1-chloro-4-acetoxy-2-alkenes which are then transformed into 1-phosphoryl- or 1-sulfonyl-4-acetoxy-2-alkenes respectively. Elimination of acetate is promoted by palladium(0)-catalysis or by sodium hydride, producing the useful 1-phosphoryl- or 1-sulfonyl-1,3-dienes.

Metal-catalyzed nucleophilic substitution reactions of allylic acetates are now recognized as important synthetic reactions.[2] Recent work has shown that metal catalysts may also effect the transformation of allylic acetates into 1,3-dienes by elimination of the acetate.[3] Because 4-substituted 1-acetoxy-2-alkenes 3 are readily available from simple dienes 1 by a palladium(II)-catalyzed chloroacetoxylation-nucleophilic substitution sequence (via 2),[4] a potentially general route to specifically 1-functionalized 1,3-dienes 4 is at hand (eq. 1).



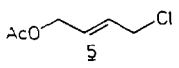
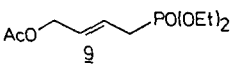
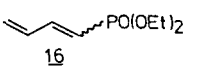
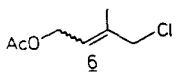
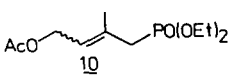
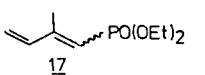
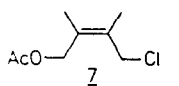
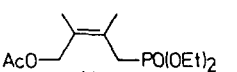
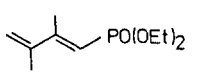
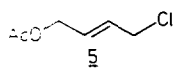
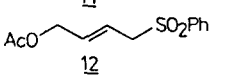
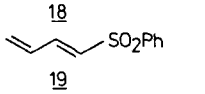
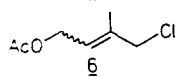
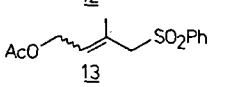
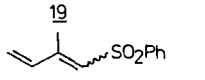
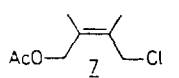
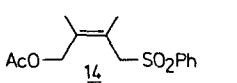
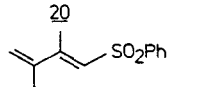
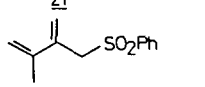
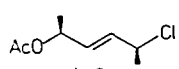
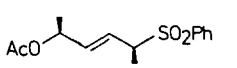
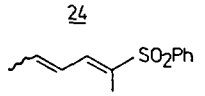
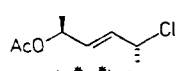
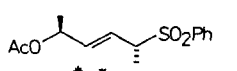
1 2 3 4 (1)

In this account, we report our exploratory studies of this basic strategy which, to date, has permitted us to develop efficient general routes to 1-phosphoryl- and 1-sulfonyl-1,3-dienes, both of which are interesting classes of synthetic intermediates.[5-6]

The five chloroacetates 5-8 were prepared from the corresponding 1,3-dienes as described previously.[4] The chloroacetates 5-7 were smoothly transformed into the phosphoryl acetates 9-11 employing an Arbuzov reaction, whereas the chloroacetate 8 failed to react satisfactorily under a wide range of conditions. The sulfonyl acetates 12-15 were prepared in high yield by utilizing a mild palladium(0)-catalyzed substitution of the allylic chloro group with sodium benzenesulfinate. The double bond in the intermediate compounds 9-15 is formed with retention of configuration. Furthermore, the Pd(0)-catalyzed substitution of the chloro group in 8 occurs with complete retention at carbon.[4a,c,d]

The conversion of the intermediates 9-15 to the dienes 16-22 is generally achieved by treatment with a weak base, e.g. triethylamine, in combination with a palladium(0)-catalyst and acetonitrile as solvent. The phosphoryl dienes 16-18 were isolated in good yield using this method (Table).

Table

Chloroacetate	Conditions[a]	Intermediate, yield[b] (E/Z)		Conditions[a]	Diene products, yield[b] (E/Z)	
 5	A, 5h	 9	70 (9/1)	C, 11h[c]	 16	80 (4/1)
 6	A, 19h	 10	70[d] (3/1)	C, 5h	 17	78[d] (1/1)
				D, 3h	17	90[d] (2/3)
 7	A, 19h	 11	74 (1/9)	C, 72h[e]	 18	79 (30/1)
 5	B, 30min	 12	87[f] (9/1)	C, 30min	 19	53 (>20/1)
 6	B, 3h	 13	92[d,g] (3/1)	C, 3h	 20	16[i] (1/2)
 7	B, 8h	 14	81[h] (1/9)	C, 8h	 21	46[j] (>20/1)
		14		D, 10h	 24	80[k]
 (S*,S*)-8	B, 2h[l]	 (S*,S*)-15	76[m] (99/1)	C, 4h	 22	81 (4/1)
				D, 2h	(E,E)-22	85
 (S*,R*)-8	B, 2h[l]	 (S*,R*)-15	71[m] (99/1)	C, 5h	22	75 (4/1)
				D, 96h	(E,E)-22	80

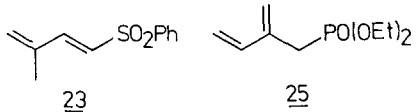
a) A: $P(OEt)_3$, 1,1 eq; NaI, 10 mol%; 125°C. B: $PhSO_2Na$, 4 eq; $Pd(PPh_3)_4$, 3 mol%; THF/DMSO 9/1, 20°C. C: Et_3N, 2 eq; $Pd(PPh_3)_4$, 5 mol%; Diphos, 10 mol%; CH_3CN, 75°C. D: NaH, 1,2 eq; THF, 45°C. b) All yields refer to pure products isolated by chromatography or Kugelrohr distillation. c) THF, 40°C. d) Contains 10% of the 3-methyl regioisomer. e) $Pd(PPh_3)_4$, 10 mol%. f)-h) 1,2-adducts CH_2=CR-CR(SO_2Ph)-CH_2OAc are also formed: f) 9%, g) 6%, h) 13%. i) The main product is 23 (24%). j) 24 is also formed (14%). k) 21 is also formed (11%). l) $Pd(PPh_3)_4$, 5 mol%; 50°C. m) Diastereomeric excess 90%.

In some cases direct treatment of the intermediate phosphoryl- or sulfonylacetate with sodium hydride gave a better result. For instance treatment of 10 with sodium hydride (1.2. eq) in THF at 45° for 3 hrs gives 17 (E/Z = 2/3) in 90% isolated yield. The sodium hydride method (D) is also preferred in the synthesis of (E,E)-22, which was isolated in 85% yield and contained <2% of (E,Z)-22 (HPLC). In contrast, the Pd(0)-catalyzed elimination (method C) gives ~20% of (E,Z)-22. The best conditions for the elimination of acetate from 12-14 were Pd(0)-catalysis and triethylamine in acetonitrile(C). The use of strong base frequently led to polymerization of the

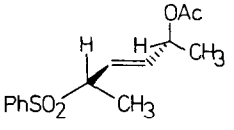
product dienes. Other by-products were also formed, for example dimers from 19, presumably by Pd(0)-catalysis. Elimination from 13 resulted in formation of the rearranged isomer 23 as the major diene product. The expected product 20 was formed to a minor extent.

NMR and HPLC data indicate that the dienes are generally mixtures of E/Z isomers. The unsubstituted dienes 16 and 19 as well as the disubstituted 18 and 21 are predominantly the E-isomers, while isoprene derived compounds 17 and 20 are an essentially equal mixture of the E and Z isomers.[8e] The formation of 21 was always accompanied by the double bond isomer 24. By the use of the sodium hydride method, 24 became the major product, most likely via α-protonation of an intermediate allyl anion. Accordingly, it was observed that (E)- and (Z)-17 could be converted to 25 in good yield by treatment with LDA. Both 24 and 25 should be useful synthetic intermediates.

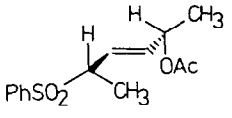
The sodium hydride induced elimination from (S*,S*)-15 and (S*,R*)-15 is noteworthy as both compounds gave the same diene 22 but at very different rates, 2h for (S*,S*)-15 compared with 4 days for (S*,R*)-15. The result can be rationalized by considering the most stable rotamers of compounds 15. In (S*,S*)-15 the proton and the acetoxy group that undergo elimination are predominantly syn to one another, whereas in (S*,R*)-15 they are predominantly anti. The rate difference thus indicates that the 1,4-elimination is syn-stereoselective.



23 25



(S*,S*)-15



(S*,R*)-15

The formation of mixtures of isomers is of course not specific to the present procedures but is also true of the previously developed syntheses of 1-phosphoryl- and 1-sulfonyl-dienes.[5d,e;6a,b;7,8]. A comparison with other methods must be made on an individual basis and will depend largely upon the relative availability of the appropriate substrates. The selectivity of the chloroacetoxylation and the potential generality of the present methodology provide distinct advantages. We are therefore studying in a general fashion the synthesis of dienes from 1-substituted-4-acetoxy-2-alkenes 3 including those with Nu= NR_2, SR, OR, and SiR_3. The corresponding dienes, which should be readily available by the methodoldogy described in this paper, have been well-documented as components in Diels-Alder reactions.[9]

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