Spontaneous Aromatization of Diels–Alder Adducts in the Reaction of Alkatrienylphosphonates with Dialkyl Esters of Acetylenedicarboxylic Acid

Christo M. Angelov,[*a] **Diana M. Mondeshka,**[b] **and Tschonka N. Tancheva**[b]

[a] *Department of Chemistry, Higher Pedagogical Institute, 9700 Shoumen, Bulgaria*
[b] *Department of Organic Chemistry, Higher Institute of Chemical Technology, 1156 Sofia, Bulgaria*

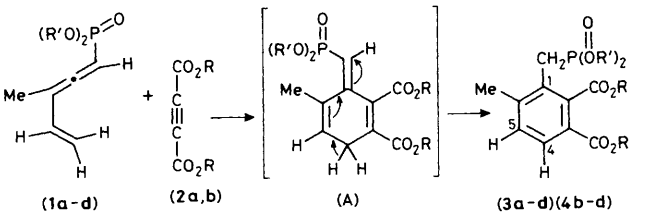
The reaction of dialkyl (3-methylpenta-1,2,4-trienyl)phosphonates with dialkyl esters of acetylenedicarboxylic acid proceeds *via* a novel spontaneous aromatization of the Diels–Alder adducts leading to benzylphosphonic acid derivatives.

Although Diels–Alder reactions are well known in organic chemistry, there is little information concerning this reaction with unsaturated P-containing organic compounds. It has been shown that alka-1,3-dienyl- and alka-1,3,4-trienylphosphonates interact with dienophiles with the formation of six-membered cyclic adducts.[1] The latter when treated with Pd/C–nitrobenzene are transformed into phenylphosphonates.

In the present report we describe the results of the participation of dialkyl (3-methylpenta-1,2,4-trienyl)phosphonates[2] in a Diels–Alder reaction. For this purpose we studied the reaction of the phosphonates (**1a**—**d**) with dialkyl esters of acetylenedicarboxylic acid within the temperature range 65—90 °C, either in chloroform or without solvent. Depending on the alkoxy groups on the phosphorus the reaction proceeded at different rates; (**1a**) reacted most

Table 1. ^{1}H N.m.r. spectroscopic data of the benzylphosphonates (**3a**—**d**) and (**4b**—**d**) (J in Hz).

	R	R′	δH-4 ($^6J_{HP}$,$^3J_{HH}$)	δH-5 ($^5J_{HP}$,$^3J_{HH}$)	δMe ($^5J_{HP}$)	δCH$_2$ ($^2J_{HP}$)
(**3a**)	Me	Me	7.58dd (2.5, 8.0)	7.22dd (0.8, 8.0)	2.50d (1.3)	3.41d (22.6)
(**3b**)	Me	Et	7.48dd (2.4, 8.0)	7.10dd (0.9, 8.0)	2.42d (1.3)	3.34d (22.4)
(**3c**)	Me	Pr^n	7.53dd (2.5, 8.1)	7.13dd (0.7, 8.1)	2.40d (1.1)	3.32d (22.4)
(**3d**)	Me	Pr^i	7.52dd (2.5, 7.8)	7.14dd (0.7, 7.8)	2.42d (1.2)	3.33d (22.7)
(**4b**)	Et	Et	7.52dd (2.4, 8.1)	7.14dd (0.9, 8.1)	2.43d (1.1)	3.37d (22.5)
(**4c**)	Et	Pr^n	7.53dd (2.3, 8.0)	7.14dd(0.8, 8.0)	2.42d (1.2)	3.39d (22.6)
(**4d**)	Et	Pr^i	7.50dd (2.1, 8.1)	7.13dd (0.7, 8.1)	2.43d (1.0)	3.34d (22.5)



rapidly (*ca.* 2 h), while the interaction with (**1c**) as well as with (**1d**) was slow (*ca.* 20 h). It was established by spectroscopic means that the reaction mixtures contained benzylphosphonic acid derivatives (**3a**—**d**), (**4b**—**d**) only; the Diels–Alder adducts (A) were not observed. This means that during the reaction a spontaneous isomerization accompanied by aromatization of the six-membered ring of (A) occurs. Note that at room temperature the two substances still interacted (much more slowly) with the formation of aromatic compounds. The benzene derivatives were isolated from the reaction mixtures as crystals or oils.

The structures of (**3a**—**d**) and (**4b**—**d**) were confirmed by their ^{1}H n.m.r. and i.r. spectra as well as by elemental analyses. In the ^{1}H n.m.r. spectra (see Table 1) the signals for H-4 and H-5 appear as two doublets, characteristic for tetrasubstituted benzenes. A doublet in the range δ 3.32—3.41 was observed for the P–CH$_2$ methylene protons and had a large coupling constant ($^2J_{HP}$ 22.4—22.7 Hz).Furthermore, the signals for the C-6 methyl group and for the alkoxy groups at phosphorus and at the carbonyl C-atoms are seen. In the i.r. spectra of (**3a**—**d**) and (**4b**—**d**), characteristic absorption bands for phosphonyl [1250 (P=O), 950—1100 (P–O–R′)] and carboxy groups (1720—1730) as well as for the benzene ring (750, 840, 890, 1600, 3020) and methyl group (1370—1375 cm^{-1}) appear.

The Diels–Alder reaction described above is a new and original method for the synthesis of benzylphosphonates. It differs considerably from the known methods by the formation of the benzene ring during the reaction.[3]

Received, 23rd November 1984; Com. 1660

References

1 W. M. Daniewski and C. E. Griffin, *J. Org. Chem.*, 1966, **31**, 3236; D. Seyferth and D. H. Paetsch, *ibid.*, 1969, **34**, 1483; C. E. Griffin and W. M. Daniewski, *ibid.*, 1970, **35**, 1691; Y. M. Dangian, G. A. Panosian, M. G. Voskanian, and S. O. Badanian, *Zh. Obshch. Khim.*, 1983, **53**, 61.

2 Ch. M. Angelov, M. Kirilov, and B. I. Ionin, *Zh. Obshch. Khim.*, 1979, **49**, 1960.

3 G. N. Kosolapoff and W. F. Huber, *J. Am. Chem. Soc.*, 1947 **69**, 2020; B. C. Saunders, G. J. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem.Soc.*, 1948, 699; A. Burger and N. D. Dawson, *J. Org. Chem.*, 1951, **16**, 1250.