

Reaction of 2,2,2-Triphenyl-2*H*-6,11-methanocycloundec[*d*]-1,2λ⁵-oxaphosphole (2-Triphenylphosphoranylidene-methyl-5,10-methano[11]-annulenone) and its related Compounds with Heterocumulenes

Makoto Nitta* and Shin-ichi Naya

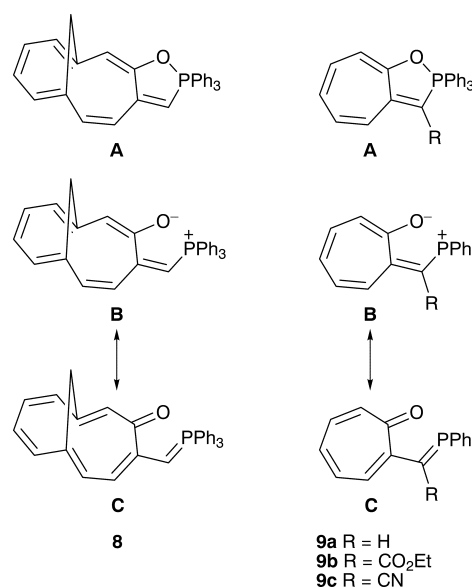
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

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Reactions of 2,2,2-triphenyl-2*H*-6,11-methanocycloundec[*d*]-1,2λ⁵-oxaphosphole (2-triphenylphosphoranylidene-methyl-5,10-methano[11]annulenone) and 2-triphenylphosphoranylidene-methyltropones with heterocumulenes have been studied to provide evidence for a P–O bonding oxaphosphole structure and to explore a preparative method for annulated heterocycles.

Reactions of phosphonium ylides with heterocumulenes have been reported in a few papers.¹ Previously, we have reported the synthesis of 2-triphenylphosphoranylidene-methyl-5,10-methano[11]annulenone **8** by the reaction of 2-chloro-5,10-methano[11]annulenone with triphenylphosphonium methylide.⁹ The ³¹P NMR spectrum of **8** exhibited a signal at δ_P –36.3. Although the structure was assigned previously as a resonance hybrid of **8B** and **8C**,⁹ compound **8** is considered to exist as 2,2,2-triphenyl-2*H*-6,11-methanocycloundec[*d*]-1,2λ⁵-oxaphosphole (**8A**) on the basis of the ³¹P NMR data.¹⁰ In relation to compound **8**, the structures^{11a,b} and reactivities¹² of 2-triphenylphosphoranylidene-methyltropones **9a–c** are of interest. X-Ray crystallographic analyses^{11a,b} of compounds **9b,c** revealed that the phosphorus atom is involved in a near trigonal bipyramidal structure but the intramolecular P–O distances (2.36 Å for **9b**, and 2.14 Å for **9c**) are significantly longer than that found in oxyphosphoranes (1.76–1.79 Å),¹⁴ and lies below the sum of the van der Waals radii (3.32 Å).¹⁵ Evidently compounds **9b,c** do not form a P–O bond, but there is appreciable interaction between the phosphorus and the oxygen atoms in these compounds. Thus the compounds **9a–c** could be characterized by a ‘bonding betaine’ structure and a resonance hybrid of **9A–C**.^{11a,b} The ³¹P NMR spectra of **9a–c** were recorded and found to exhibit signals at δ_P –3.6, –2.3 and 7.8, respectively; values that are different from the reported data^{11b} and are rather close to the values of simple methylene phosphoranes. To provide evidence for a P–O bonding oxaphosphole structure as well as to explore the methodology of synthesizing annulated heterocycles, the

reactions of **8** and **9a–c** with heterocumulenes are now reported.



Reaction of oxaphosphole **8** with phenyl isocyanate **2** occurred to give the *N*-phenyl-2*H*-6,11-methanocycloundeca[*b*]pyrrol-2-one **10**. Similarly, the reaction of **8** with phenyl isothiocyanate (**4**) afforded the *N*-phenyl-6,11-cycloundeca[*b*]pyrrole-2-thione **11** and 2-(*N*-phenylamino)-6,11-methanocycloundeca[*b*]thiophen-4-one **12**. The reaction

Table 1 Results for the reaction of compounds **8** and **9a–c** with heterocumulenes **2–4**

Entry	Compound	Cumulene	Ratio of 2–4 : 8 or 9	Reaction conditions ^a		
				Solvent	Time (<i>t</i> /h)	Product (yield (%)) ^b
1	8	2	2.0	PhH	24	10 (88)
2	8	4	2.0	PhH	24	11 (37) 12 (53)
3	9a	2	2.0	PhH	24	17a (88) (Z)- 18a /(E)- 18a (12) ^c
4	9b	2	5.0	Xylene	22	17b (77) (Z)- 18b (19)
5	9b	2	5.0	Anisole	3	17b (76) (Z)- 18b (21)
6	9c	2	5.0	Anisole	24	17c (47) (Z)- 18c (26)
7	9a	3	1.0	PhH	26	(Z)- 18a /(E)- 18a (81) ^c
8	9b	3	5.0	Xylene	77	(Z)- 18b (14)
9	9c	3	5.0	Anisole	24	(Z)- 18c (0) ^d
10	9a	4	1.5	PhH	24	27 (76) (Z)- 18a /(E)- 18a (5) ^c
11	9b	4	5.0	Anisole	10	28b (12) (Z)- 18b (4)
12	9c	4	5.0	Anisole	24	28c (8) (Z)- 18c (55)

^aReactions carried out under reflux. ^bYields based on compounds **8** and **9a–c** used. ^cObtained in a ratio of 1.4:1. ^d71% of the starting material **9c** was recovered.

*To receive any correspondence.

