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

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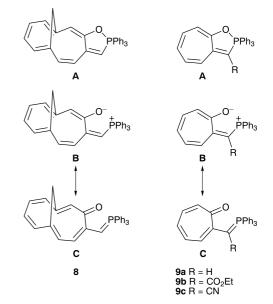
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Reactions of 2,2,2-triphenyl-2*H*-6,11-methanocycloundec[*d*]-1,2 λ^5 -oxaphosphole (2-triphenylphosphoranylidenemethyl-5,10-methano[11]annulenone) and 2-triphenylphosphoranylidenemethyltropones with heterocumulenes have been studied to provide evidence 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-triphenylphosphoranylidenemethyl-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 $\delta_{\rm P}$ -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-2H-6,11methanocycloundec[d]-1,2 λ^5 oxaphosphole (**8A**) on the basis of the ³¹P NMR data.¹⁰ In relation to compound **8**, the structures^{11*a,b*} and reactivities¹² of 2-triphenylphosphoranylidenemethyltropones 9a-c are of interest. X-Ray crystallo-graphic analyses^{11*a,b*} of compounds **9b,c** revealed that the phosphorus atom is involved in a near trigonal bipyramidal structure but the intamolecular 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**.^{11*a,b*} The ³¹P NMR spectra of **9a–c** were recorded and found to exhibit signals at $\delta_{\rm P}$ -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-6,11cycloundeca[*b*]pyrrole-2-thione **11** and 2-(N-phenylamino)-6,11-methanocycloundeca[*b*]thiophen-4-one**12**. The reaction

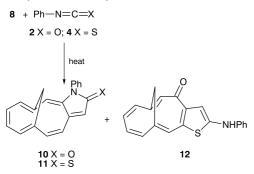
Table 1	Results for the reaction of compounds 8 and 9a-c with heterocumulenes 2-4
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Entry	Compound	Cumulene	Ratio of 2–4:8 or 9	Reaction conditions ^a		
				Solvent	Time (t/h)	Product (yield (%)) ^b
1	8	2	2.0	PhH	24	10 (88)
2	8	4	2.0	PhH	24	11 (37) 12 (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	$(Z) - \mathbf{\hat{18a}} / (E) - \mathbf{18a} (\mathbf{\hat{81}})^c$
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 /(<i>E</i>)- 18a (5) ^{<i>c</i>}
11	9b	4	5.0	Anisole	10	28b (12) (Z)- 18b (4)
12	9c	4	5.0	Anisole	24	28c (8) (Z)- 18c (55)

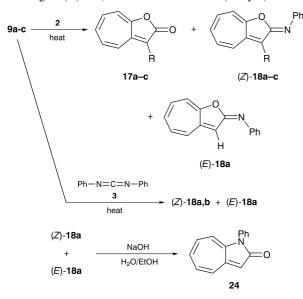
^aReactions carried out under reflux. ^bYields based on compounds 8 and 9a-c used. ^cObtained in a ratio of 1.4:1. ^d71% of the starting material 9c was recovered.

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conditions and the yields of the products are summarized in Table 1 (entries 1 and 2).



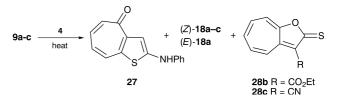
On the other hand, the reaction of compound 9a-c with the isocyanate 2 was carried out to give the cyclohepta[b]furan-2-ones 17a-c and their imines (E)-18a and (Z)-18a-c (entries 3-6). Reaction of compound 9a with the isocyanate 2 proceeded under mild conditions, whilst the reaction of compounds 9b,c, which have an additional electronwithdrawing substituent (CO2Et and CN group, respectively) and hence are classified as more stabilized ylides, proceed very slowly in benzene when boiled under reflux, and required forcing conditions (entries 4–6). A mixture of (Z)-18a and (E)-18a as well as (Z)-18b,c were not hydrolysed over SiO₂, but a mixture of (Z)-18a and (E)-18a was hydrolysed in alkaline solution to give compound 24. The reaction of 9a with diphenylcarbodiimide 3 proceeded smoothly to give a mixture of (Z)-18a and (E)-18a (entry 7), whilst compounds 9b.c did not react with 3 in refluxing benzene. Although compound 9b reacted with the carbodiimide 3 in refluxing xylene to afford (Z)-18b (entry 8), compound 9c did not give (Z)-18c, and 9c was recovered (entry 9).



Compound 9a reacted with the isothiocyanate 4 under mild conditions to give 2-(*N*-phenylamino)cyclohepta[b]-

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thiophen-4-one 27 in addition to a mixture of (Z)-18a and (E)-18a in a ratio of 1.4:1 (entry 10). On the other hand, the reaction of 9b with compound 4 did not proceed under refluxing in benzene, but only under forcing conditions of refluxing anisole to give 3-ethoxycarbonylcyclohepta[b]-furan-2-thione 28b, (Z)-18b, and significant amounts of tar-like materials (entry 11). Similarly the reaction of compound 9c with the isothiocyanate 4 gave 3-cyanocyclohepta[b]furan-2-thione 28c along with (Z)-18c in moderate combined yield (entry 12). Thus, the reaction of 8 proceeded via P–O bonding structure 8A, whilst the reaction of 9 seemed to occur via 9B and 9C.



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Techniques used: IR, $^1\mathrm{H},\ ^{13}\mathrm{C}$ and $^{31}\mathrm{P}$ NMR, mass spectrometry, elemental analysis

References: 21

Schemes: 8

Tables: 1

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