

Synthesis and Structure of 2-(Triphenylphosphoranylideneamino)tropone and its Utility in the Preparation of New Cyclohepta-annulated Heterocycles¹

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2-(Triphenylphosphoranylideneamino)tropone is synthesized for the first time and treated with heterocumulenes to give novel cyclohepta-annulated heterocycles in good yields.

The utility of (imino)phosphoranes as useful building blocks for the synthesis of azaheterocycles has been demonstrated convincingly.² With the expectation of a novel reaction and the formation of new cyclohepta-annulated five-membered heterocycles, we investigated the synthesis, structure and reactions of 2-(triphenylphosphoranylideneamino)tropone (**8**) with heterocumulenes such as phenyl isocyanate, phenyl isothiocyanate, diphenylketene and carbon disulfide. The reaction of compound **8** with dimethyl acetylenedicarboxylate (DMAD) was also studied.

Compound **8** was synthesized by several methods, and X-ray crystallographic analysis revealed that it exists as an (imino)phosphorane structure (**8**) but not as a P–O bonded oxazaphosphole structure (**8'**). The reaction of (imino)phosphorane **8** with phenyl isocyanate or phenyl isothiocyanate in benzene or toluene under reflux occurred in an aza-Wittig/electrocyclization manner to give 2*H*-cyclohepta[2',1'-b:2',3'-b']pyrrolo[1,2-*a*]pyrrole-1,2,4,5-tetracarboxylate (**26**) was obtained, probably *via* 2,3-bis-methoxycarbonyl-1-azaazulene.



On the other hand, when compound **8** was allowed to react with DMAD in bromobenzene under reflux, tetramethyl 2*H*-cyclohepta[2',1'-b:2',3'-b']pyrrolo[1,2-*a*]pyrrole-1,2,4,5-tetracarboxylate (**26**) was obtained, probably *via* 2,3-bis-methoxycarbonyl-1-azaazulene.

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Techniques used: IR, UV, ¹H, ¹³C and ³¹P NMR, mass spectro-metry and X-ray diffraction

References: 32

Schemes: 6

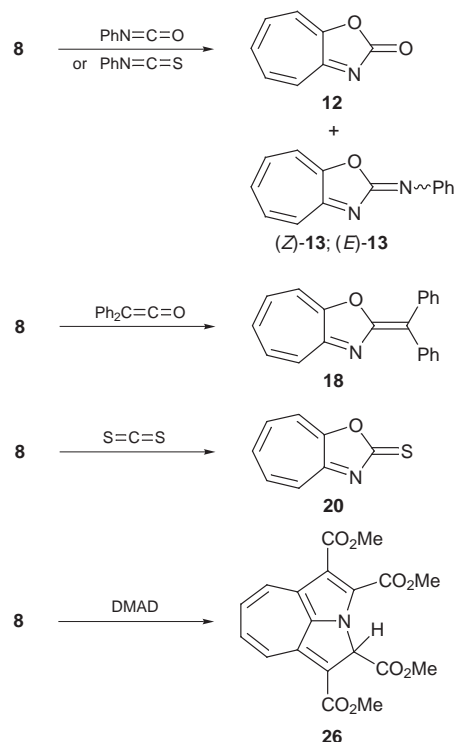


Table 1: Results for the reaction of compound **8** with heterocumulenes **9a–d** and DMAD (**21**)

Table 2: ¹H NMR spectral data (400 MHz) of compounds **8**, **12**, (Z)- and (E)-**13**, **18**, **20** and **16**

Table 3: UV–VIS spectral data of compounds **8**, **12**, (Z, E)-**13**, **18** and **20**

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