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ON THE REACTION OF N-VINYLIMINOPHOSPHORANES. A NOVEL ROUTE TO 1-AZAAZULENE RING SYSTEM UTILIZING AZA-WITTIG REACTION

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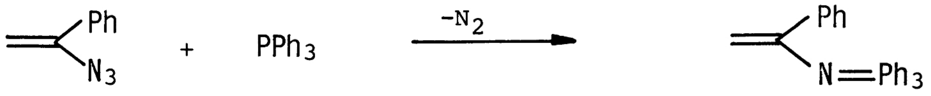
N-(1-Phenyl)vinyliminotriphenylphosphorane, conveniently prepared from α-azidostyrene and triphenylphosphine, readily undergoes an annelation reaction with tropone derivatives to result in the formation of 1-azaazulene ring system.

The reaction of tertiary phosphine with an organic azide to produce an iminophosphorane after nitrogen evolution is known as the Staudinger reaction.$^{1)}$ The iminophosphorane is known to react with carbonyl compounds to give the corresponding Shiff bases in a Wittig-type (aza-Wittig) reaction.$^{2)}$ However, it is only recently that the synthetic application based on the intramolecular$^{3)}$ and intermolecular$^{4)}$ aza-Wittig reaction has appeared. Although no vinyliminophosphorane had been isolated,$^{5)}$ we have reported that N-(1-phenyl)vinyliminotriphenylphosphorane (1) (Scheme 1) or N-(1-phenyl)vinyltrimethoxyphosphorane are conveniently prepared in very good yield by the reaction of α-azidostyrene with triphenylphosphine or with trimethyl phosphite in benzene at room temperature.$^{6)}$ N-Vinyliminophosphorane has also been shown to undergo cycloaddition reaction with acetylenic esters.

We report hereon a construction of 1-azaazulene skeleton$^{7)}$ based on the aza-Wittig reaction utilizing the tropone (2a-e) (Scheme 2) and N-vinyliminotriphenylphosphorane 1. Reaction of 1 (1 mmol) with tropones 2a-c (1 mmol) in anhydrous

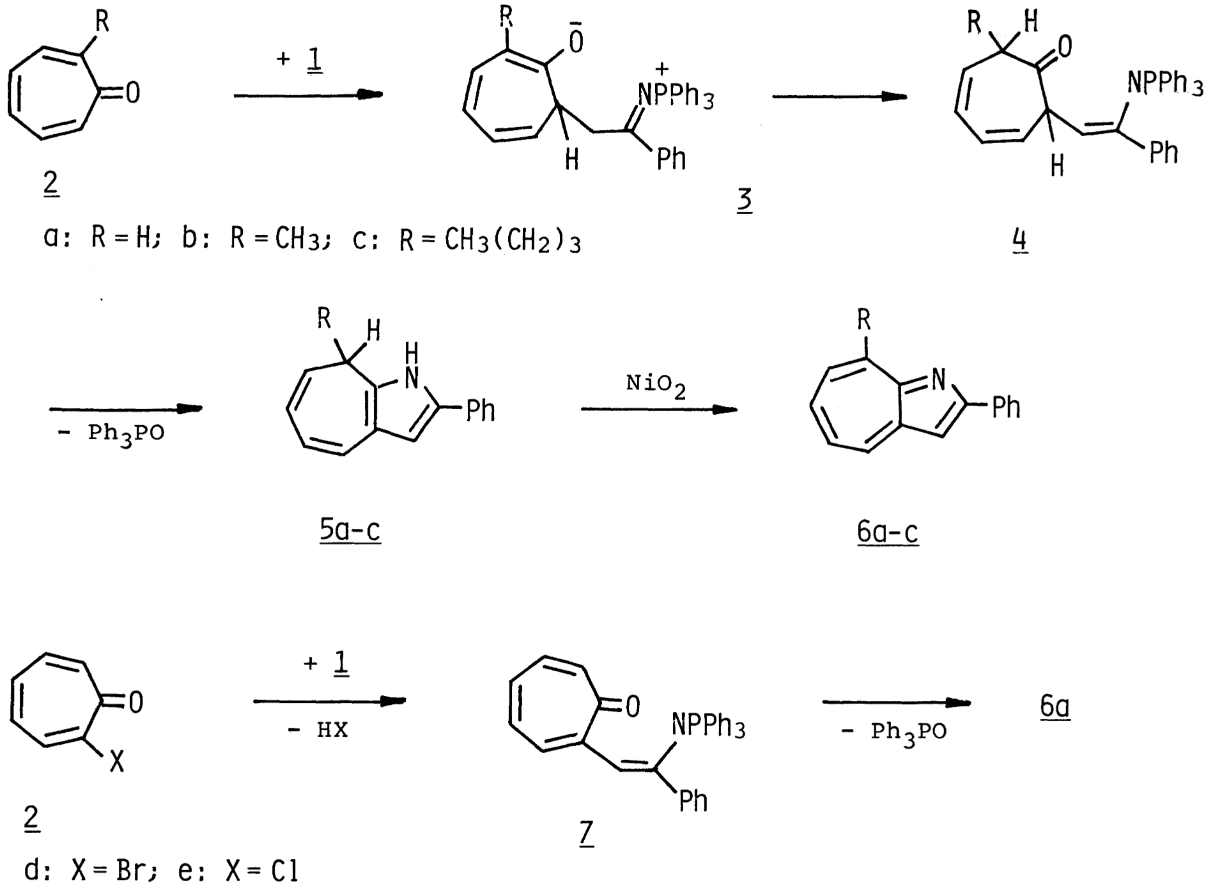


Scheme 1.

benzene (5 cm^3) under reflux for 24 h resulted in the complete consumption of 2a-c. A purification of a mixture in the reaction of 2a and 1 through column chromatography on silica gel caused hydrogen migration of the cycloheptatriene moiety of 5a to give three isomers, which are hardly separable. Therefore, the general purification was carried out through column chromatography on Florisil to afford triphenylphosphine oxide (80-90%) and 2-phenyl-8H-cycloheptapyrrole derivatives 5a-c.[8,9] The results are summarized in Table 1.

The formation of 5a-c is best explained by the mechanism shown in Scheme 2. On the analogy of the reaction of tropone with N-ylides,[10] the initial step seems to be the formation of a C-C bond between 1 and 2a-c to give the intermediate 3, which undergoes the hydrogen migration to give 4. The following intramolecular aza-Wittig reaction of 4 followed by hydrogen migration constructing a pyrrole ring would give 5a-c and triphenylphosphine oxide. Rather low yields of 5b and 5c would be attributable to the steric factor on the stage of the aza-Wittig reaction.

Oxidation of 5a-c with selenium dioxide or with DDQ followed by treatment



Scheme 2.

Table 1. Annelation Reaction of Tropone 2a-e with 1 and Dehydrogenation of 5a-c[a)]

Annelation reaction[b)]			Dehydrogenation of 5a-c		
Tropone	Product	Yield/%	Product	Mp or Bp	Yield/%
2a	5a	84	6a	mp 148-149 °C	85
2b	5b	54	6b	bp 110 °C/67 Pa[c)]	74
2c	5c[d)]	34	6c	bp 130 °C/67 Pa[c)]	77
2d	6a	77			
2e	6a[d)]	44			

a) With exception of 6a, (Ref. 10), all the compounds are new and have been characterized by the physical data[9)] in comparison with those of known derivatives (Ref. 7, 10, and 12). b) No tropone or 1 was recovered. c) Denote bath temperature. d) Acetophenone, derived from hydrolysis of 1, was obtained in 5-20% yields.

with aqueous NaOH gave red-colored 1-azaazulene derivatives 6a-c[8,9)] in rather low yields. However, the best yields were obtained on the oxidation of 5a-c (1 mmol) with nickel peroxide[11)] (10 mmol) in benzene (5 cm^3) under reflux for 2 h followed by purification through TLC on silica gel. The results are listed in Table 1.

Furthermore, one-step preparation of 6a was accomplished (Scheme 2). Thus, the reaction of 2-halotropone (2d and 2e) (1 mmol) with 1 (1 mmol) and triethylamine (1 mmol) in anhydrous benzene (5 cm^3) under reflux for 24 h afforded 6a and triphenylphosphine oxide (85%) (Table 1). In this reaction, the C-C bond formation of 1 with 2d or 2e results in an elimination of hydrogen halide to give 7, the aza-Wittig reaction of which gives 6a.

The present reactions might serve as a convenient route to the 2-phenyl-1-azaazulene and its alkyl derivatives. Further studies concerning preparation of unsubstituted 1-azaazulene ring system are now in progress.

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8) With exception of 5c, which is contaminated with acetophenone and is not separable, analytical and mass spectral data are satisfactory for all new compounds described in this paper.

9) 5a: mp 112-114 °C (from CCl_4); ^{1}H-NMR (acetone-d_6) δ 3.27 (2H, d, J=6.0 Hz), 5.30-5.55 (1H, m), 5.77-6.05 (2H, m), 6.42 (1H, d, J=2.7 Hz), 6.66 (1H, dxt, J=10.2, 2.4 Hz), 6.95-7.60 (5H, m). 5b: oil; ^{1}H-NMR (CCl_4) δ 1.20 (3H, d, J=7.1 Hz), 3.25 (1H, m), 5.10-5.45 (1H, m), 5.70-6.20 (2H, m), 6.35 (1H, d, J=2.4 Hz), 6.50-6.80 (1H, m), 7.00-7.50 (5H, m), 7.70-8.10 (1H, m). 5c: ^{1}H-NMR ($CDCl_3$) δ 0.80-1.85 (7H, m), 2.10-2.50 (2H, m), 3.05-3.45 (1H, m), 5.40-6.80 (4H, m), 6.46 (1H, d, J=2.5 Hz), 7.00-7.70 (5H). 6b: ^{1}H-NMR ($CDCl_3$) δ 3.20 (3H, s), 7.30-7.70 (6H, m), 7.60 (1H, s), 8.20-8.45 (3H, m); UV (EtOH) λ_{max} (log ε) 240 (4.15), 291 (4.75), 309 (4.58, sh), 357 (4.24), 375 (4.15), 482 (3.50), 526 (3.20, sh) nm. 6c: ^{1}H-NMR ($CDCl_3$) δ 0.80-2.00 (7H, m), 3.72 (2H, t, J=8.2 Hz), 7.10-7.62 (6H, m), 7.60 (1H, s), 8.15-8.40 (3H, m); UV (EtOH) λ_{max} (log ε) 241 (4.24), 290 (4.40), 311 (4.25, sh), 358 (3.92), 387 (3.86), 484 (3.09) nm.

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