On the Reaction of *N*-Vinyliminophosphoranes. Part 7.[1] A Short New 1-Aza-azulene Synthesis

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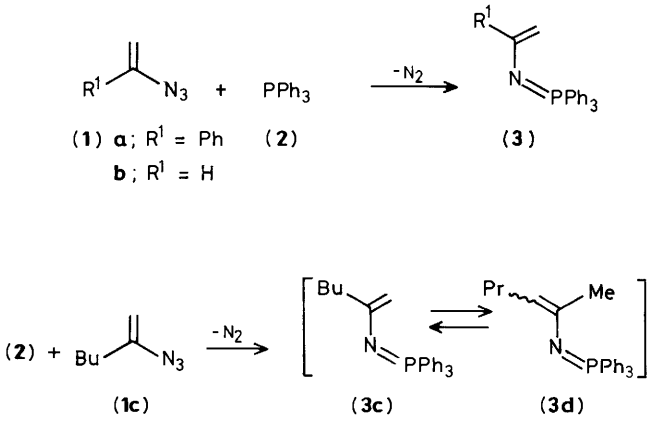
Thermal reaction of triphenyl(vinylimino)phosphorane derivatives with several tropones have been studied to provide a short new route to the 1-aza-azulene ring system. (1-Phenylvinylimino)-, vinylimino-, and a mixture of (1-butylvinylimino)- and (1-methylpent-1-enylimino)-triphenylphosphorane were treated with tropone and alkylated tropones in an enamine alkylation process, and the subsequent aza-Wittig reaction resulted in the formation of 1,8-dihydrocyclohepta[*b*]pyrroles. The pyrrole derivatives were easily dehydrogenated by nickel peroxide or manganese dioxide to give 1-aza-azulene derivatives. In a similar fashion, the iminophosphoranes were treated with 2-bromotropone or with 2-chlorotropone in the presence of triethylamine to give 1-aza-azulenes in a single step. The 1-aza-azulenes, which were halogenated on the seven-membered ring, were also prepared conveniently by the reaction of triphenyl(1-phenylvinylimino)phosphorane with 2,7-dibromo-, 2,4,7-tribromo-, and 2,3,5,7-tetrachlorotropone, albeit in modest yields.

The reaction of a tertiary phosphine with an organic azide to produce an iminophosphorane after nitrogen evolution is known as the Staudinger reaction.[2] Recently, much attention has been focused on the synthetic utilities of iminophosphoranes, and their hydrolysis to amines or ketones,[3] oxidation to nitro compounds,[4] and intermolecular[5] and intramolecular[6] Wittig type (aza-Wittig) reactions with carbonyl groups have been reported. However, the synthetic versatility of iminophosphoranes is not fully explored compared with that of methylenephosphoranes.[7] This fact can be ascribed in part to the poor variation of substituent on the nitrogen atom of iminophosphoranes. Recently, we have demonstrated the simple preparation of *N*-(1-phenylvinyl)iminophosphoranes,[8] which were found to react with α-bromo ketones, α,β-unsaturated ketones, and tropone derivatives in an enamine alkylation process followed by aza-Wittig reaction to provide convenient routes to phenyl-substituted pyrroles,[9,10] pyridines,[10,11] and 1-aza-azulenes.[12]

Aza-azulenes[13] have received considerable interest, particularly in companion with the chemistry of non-benzenoid aromatic azulene hydrocarbons, and have played a major role in the advancement of our understanding of cyclic conjugation.[14] Owing to our interest in the synthesis and chemistry of polycyclic systems containing the 1-aza-azulene nucleus, we have embarked on a study of a convenient synthesis of 1-aza-azulenes. This paper describes our findings regarding a new general synthesis of 1-aza-azulenes, utilizing several *N*-vinyliminophosphoranes (**3a**—**d**).

Results and Discussion

Our synthetic strategy for 1-aza-azulenes (cyclohepta[*b*]pyrroles) was, first, to obtain the iminophosphoranes (**3a**—**d**) bearing vinyl groups on the nitrogen atom. Triphenyl-(1-phenylvinylimino)phosphorane (**3a**) was prepared easily by the reaction of α-azidostyrene (**1a**) with triphenylphosphine (**2**).[8] Similarly, the new triphenyl(vinylimino)phosphorane (**3b**) was prepared in high yield by the reaction of azidoethylene (**1b**)[15] with compound (**2**). On the other hand, reaction of 2-azidohex-1-ene (**1c**)[16] with (**2**) in benzene at room temperature gave a mixture of iminophosphoranes, 1-butylvinylimino(triphenyl)-phosphorane (**3c**) and 1-methylpent-1-enylimino(triphenyl)-phosphorane (**3d**) (see Scheme 1).[1] Since compounds (**3c**) and



Scheme 1.

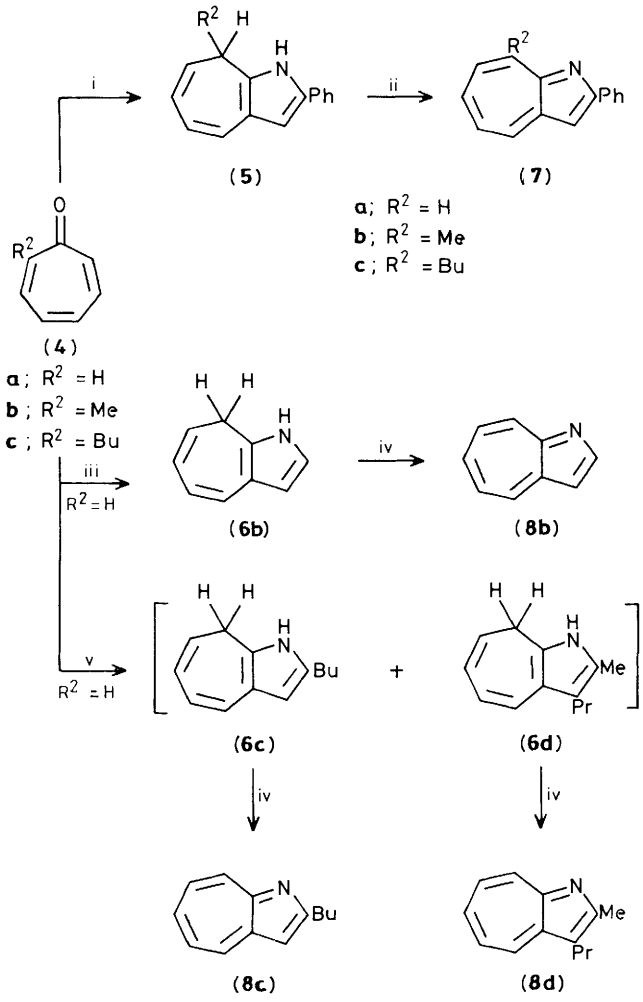
(**3d**) seemed to be unstable we were not able to separate them in pure form. However, preparation of a mixture of (**3c**) and (**3d**) in CD_3CN and the ensuing ^1H n.m.r. spectral study showed that the initial ratio (1:2) of (**3c**):(**3d**) was changed to 1:4 after heating of the mixture at 80 °C for 10 min. The ratio was fixed at 1:6 after 30 min or after prolonged heating at 80 °C. Thus, thermal isomerization was suggested to occur, and the equilibrium between (**3c**) and (**3d**) is considered to lie towards (**3d**). The iminophosphorane (**3b**), and a mixture of (**3c**) and (**3d**), were very labile toward water, as in the case of (**3a**),[8] to give acetaldehyde and hexan-2-one in quantitative yields.[1]

The reaction of the iminophosphorane (**3a**) with tropones (**4a**—**c**) in anhydrous benzene under reflux resulted in the formation of 1,8-dihydrocyclohepta[*b*]pyrrole derivatives (**5a**—**c**) and triphenylphosphine oxide. Similarly, the reaction of (**3b**) with (**4a**) afforded 1,8-dihydrocyclohepta[*b*]pyrrole (**6b**) in modest yield (Scheme 2). The results are summarized in Table 1 (entries 1—4). The structural assignment of new compounds (**5a**, **b**) and (**6b**) was made on the basis of elemental analyses, and high-resolution mass, i.r., and ^1H n.m.r. spectra, all of which are summarized in the Experimental section. Although compound (**5c**) was contaminated with acetophenone, which derived from (**3a**), the ^1H n.m.r. spectrum and the following chemical transformation could confirm the structure of compound (**5c**).

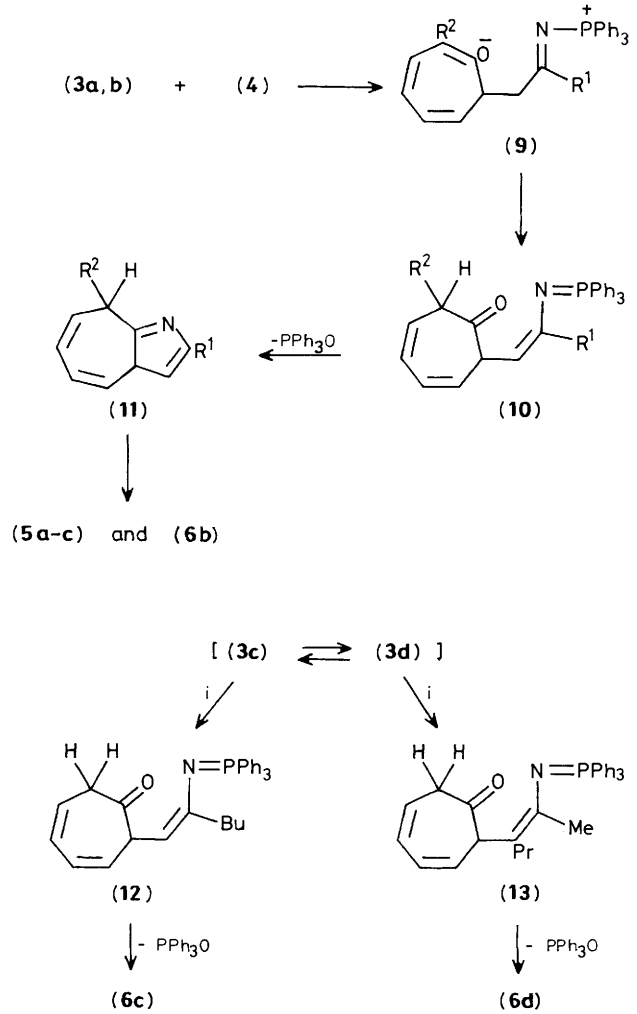
Table 1. Results for the annelation reaction of tropones (**4a—c**) with iminophosphoranes (**3a—d**), and the dehydrogenation of aza-azulenes (**5a—c**) and (**6b—d**)[a]

	Annelation reaction			Dehydrogenation of (5) and (6)		
Entry	(3)	(4)	Product yield (%)	(5) or (6)	Reagent	Product yield (%)
1	(3a)	(4a)	(5a) (84)	(5a)	NiO_2	(7a) (85)
2	(3a)	(4b)	(5b) (54)	(5b)	NiO_2	(7b) (74)
3	(3a)	(4c)	(5c) (34)	(5c)	NiO_2	(7c) (77)
4	(3b)	(4a)	(6b) (32)	(6b) *b*	MnO_2	(8b) (85)
5	{(3c) (3d)}	(4a)	{(6c) (6d)} *c*	{(6c) (6d)} *b*	MnO_2	{(8c) (18) (8d) (42)} *d*

[a] Unless stated otherwise, all the reactions were carried out in anhydrous benzene under reflux. [b] The reaction was carried out at room temperature. [c] The mixture was not isolated, and it was subsequently dehydrogenated to give compounds (**8c**) and (**8d**). [d] The yields are based on (**4a**) used.



Scheme 2. *Reagents:* i, (**3a**); ii, NiO_2; iii, (**3b**); iv, MnO_2; v, (**3c**) + (**3d**)



Scheme 3. *Reagent:* i, (**4a**)

The oxidation of compounds (**5a—c**) with nickel peroxide[17] in benzene under reflux gave the red-coloured 1-aza-azulenes (**7a—c**) in good yields. Manganese dioxide[18] could also act as dehydrogenating reagent, and compound (**6b**) was oxidized to give 1-aza-azulene (**8b**) in good yield. The results are also summarized in Table 1. The compounds (**7b** and **c**), with the exception of (**7a**)[19] and (**8b**),[20] are new and have been characterized by comparison of their physical data with those of known derivatives.[19,21]

On the other hand, the *in situ* preparation of a mixture of phosphoranes (**3c**) and (**3d**) and reaction with (**4a**) afforded a mixture of dihydroaza-azulenes (**6c**) and (**6d**). The mixture was difficult to separate, but was purified and subsequently oxidized with manganese dioxide to give aza-azulenes (**8c**) and (**8d**) (Scheme 2 and Table 1). The structures of the products were also determined unequivocally on the basis of their physical data.

The formation of compounds (**5a—c**) and (**6b**) is best explained by the mechanism in Scheme 3. Nucleophilic addition

Table 2. Results for the reaction of iminophosphoranes (**3a**—**d**) with tropones (**14a** and **b**) or with (**20a**—**c**)[a]

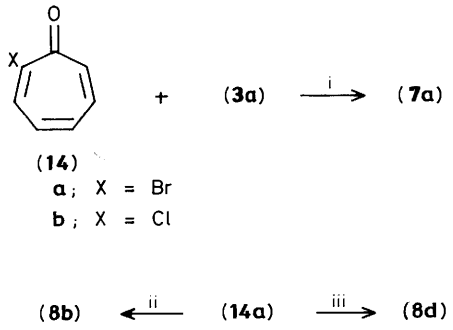
Entry	(3)	Tropone	Reaction time (h)	Product yield (%)
1	(**3a**)	(**14a**)	24	(**7a**) (77)
2	(**3a**)	(**14b**)	24	(**7a**) (44)
3	(**3b**)	(**14a**)	5	(**8b**) (56)
4	(**3c**) + (**3d**)	(**14a**)	3	(**8d**) (43)
5	(**3a**)	(**20a**)	6	(**22**) (32)
6	(**3a**)	(**20b**)	7	(**23**) (31) + (**24**) (16)
7[b]	(**3a**)	(**20c**)	5	(**25**) (25)

[a] All the reactions were carried out in anhydrous benzene under reflux. [b] The reaction was carried out at room temperature.

onto a tropone nucleus is generally known to take place onto the α-position. On the analogy of the reaction of tropone with *N*-ylides,[22] the initial step is the enamine alkylation of phosphoranes (**3a** and **b**) onto a tropone (**4**) to give the intermediate (**9**), which undergoes hydrogen migration to give ketone (**10**). The following intramolecular aza-Wittig reaction to give the 3a,8-dihydroaza-azulene (**11**) and subsequent aromatization to construct the pyrrole ring gives products (**5a**—**c**) and (**6b**). Reaction of the mixture of (**3c**) and (**3d**) with (**4a**) is expected to give intermediates (**12**) and (**13**), respectively, in similar fashion. It is reasonable to assume that intramolecular aza-Wittig reaction of intermediates (**13**) and (**14**), followed by aromatization for construction of pyrrole rings, gives products (**6c**) and (**6d**). The reaction of 2-alkyltropones (**4b**) and (**4c**) gives products (**5b**) and (**5c**), respectively, in rather low yields (Table 1, entries 2 and 3). This fact is attributable to the steric hindrance between the alkyl group and the triphenylphosphine moiety during the aza-Wittig reaction.

The iminophosphorane (**3b**) seemed to be thermally unstable and it decomposed gradually in benzene under prolonged heating. Therefore, the yield of 1,8-dihydroaza-azulene (**6b**) is rather low (Table 1).

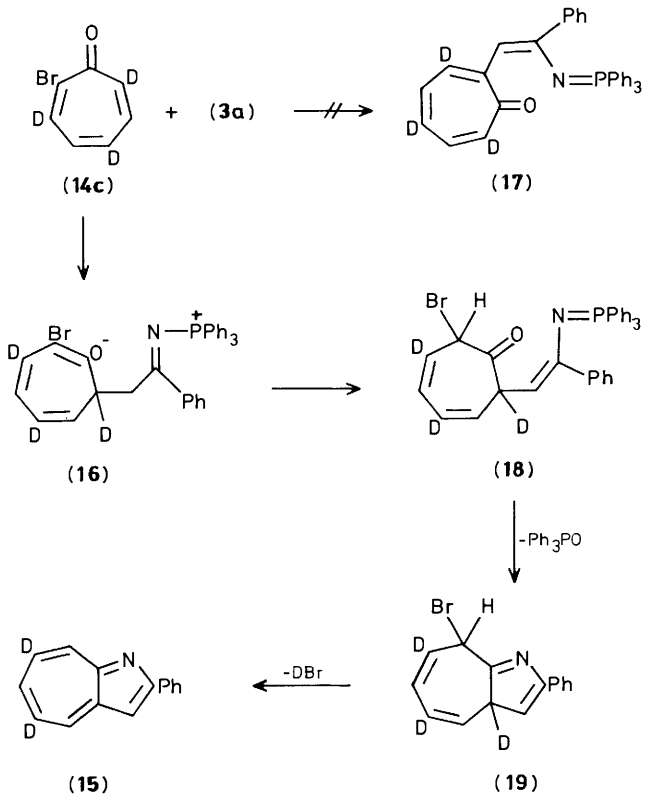
We next observed that phosphorane (**3a**) reacts with 2-bromotropone (**14a**) and with 2-chlorotropone (**14b**) in the presence of triethylamine to give 2-phenyl-1-aza-azulene (**7a**) in good or modest yield in a single step (Scheme 4, Table 2, entries



Scheme 4. *Reagents and conditions:* i, NEt_3, heat; ii, (**3b**); iii, (**3c**) + (**3d**)

1 and 2). Similarly, reaction of phosphorane (**3b**) with (**14a**) gave (**8b**) (Table 2, entry 3). In the reaction of a mixture of phosphoranes (**3c**) and (**3d**) with (**14a**), only the product (**8d**), which derived from the isomer (**3d**), was obtained (Table 2, entry 4). The product (**8c**), which derives from the isomer (**3c**), was not detected. The reason for this is unclear at this stage.

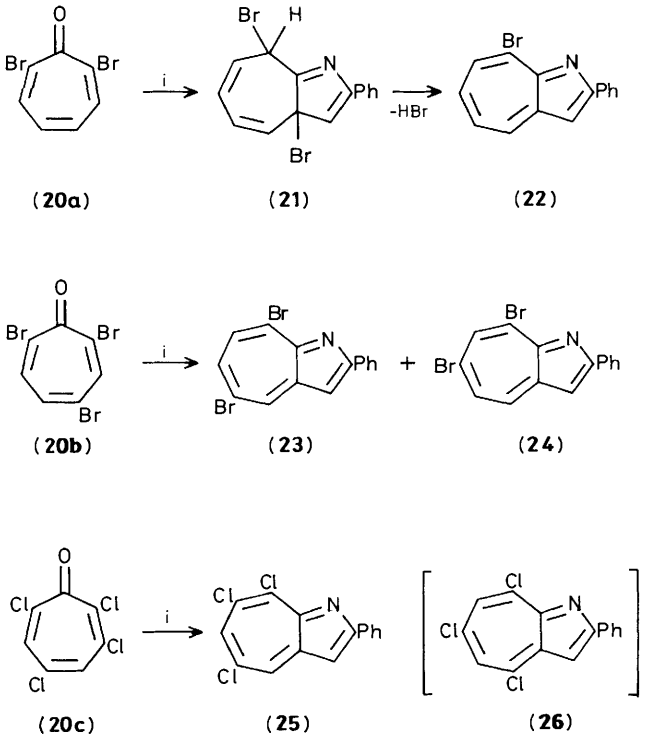
Nucleophilic substitution onto a tropone carrying a mobile substituent is known to take place at C-2 (usual substitution) or at C-7 (abnormal substitution) to give 2-substituted tropones.[22] The present reaction of phosphorane (**3a**) with (**14a** and **b**), as well as of (**3b**—**d**) with (**14a**), does not seem to involve a straightforward displacement of halide ion by the enamine alkylation. This was proved by labelling the troponoid ring with deuterium. Thus, reaction of 2-bromo-3,5,7-trideuteriotropone (**14c**) with (**3a**) gave a product to which we assigned the structure (**15**) (Scheme 5). This structural assignment was based on high-



Scheme 5.

resolution mass and ^1H n.m.r. spectral data. The h.r.m.s. showed a peak for $C_{15}H_9D_2N$, indicating that enamine alkylation occurred at C-7. The ^1H n.m.r. spectrum unequivocally showed, besides a phenyl group, four other signals, at δ_H 7.74 (s, 1 H), 7.76 (br s, 1 H), 8.50 (br s, 1 H), and 8.67 (br s, 1 H). These signals are assigned to the C-3, C-6, C-4, and C-8 protons, respectively. Therefore the mechanistic pathway for the reaction of the tropone (**14c**) with phosphorane (**3a**) was deduced as shown in Scheme 5. The initial enamine alkylation process takes place at C-7 to give intermediate (**16**), and not at C-2 to give (**17**). The intermediate (**16**) then rearranges to give ketone (**18**), aza-Wittig reaction of which gives compound (**19**). Elimination of DBr easily gives the final product (**15**). Compound (**14b**) is expected to react in a similar way. Thus, the reaction of (**3b**) and (**3c** and **d**) with the tropone (**14a**) seems to follow this pathway also.

Furthermore, the reaction of the phosphorane (**3a**) with polyhalogenated tropones (**20a**—**c**) was shown to give 1-aza-azulene derivatives in the presence of triethylamine in a single step. The results are also summarized in Table 2 (entries 5—7). The enamine alkylation of (**3a**) onto C-2 (or onto C-7) of (**20a**) and following reactions give the intermediate (**21**), which derives easily from the analogous pathways shown in Scheme 3 and



Scheme 6. *Reagents: i,* (**3a**) and NEt_3

Scheme 5. It then undergoes dehydrobromination to give compound (**22**) in the presence of triethylamine. In a similar manner, attack of (**3a**) onto both C-2 and C-7 of (**20b**) occurred to give the isomers (**23**) and (**24**), respectively. The formation of 5,8-dibromide (**23**) is favoured over that of 6,8-dibromide (**24**). In the reaction of (**20c**), however, enamine alkylation of (**3a**) took place only onto C-7 to give product (**25**). The expected isomer (**26**), which derives from enamine alkylation onto C-2, was not obtained (Scheme 6). The lack of C-2-attack may be ascribed to the large steric hindrance at C-2 as compared with C-7, because of the adjacent chlorine atom on C-3.

In a prelude to synthesis of polycyclic aromatic compounds incorporating the 1-aza-azulene unit, the *N*-vinyliminophosphoranes (**3a**—**d**) are confirmed to react generally with tropones, 2-halogenated tropones, and polyhalogenated tropones. The present reactions could serve as a convenient route to 1-aza-azulene derivatives. The preparation and synthetic applications of *N*-vinyliminophosphoranes involved in several cyclic systems are in progress.

Experimental

I.r. spectra were recorded on a Shimadzu IR-400 spectrometer. ^1H N.m.r. and ^{13}C n.m.r. spectra were recorded on Hitachi R-24 and Hitachi R-90H spectrometers and the chemical shifts are given relative to internal $SiMe_4$ standard. Mass spectra or high-resolution mass spectra were run on a Shimadzu GCMS-QP-1000 or a JEOL DX-300 spectrometer. M.p.s were measured on a Büchi apparatus and are uncorrected. The desired tropones, 2-methyltropone (**4b**),[23] 2-butyltropone (**4c**),[23] 2-bromotropone (**14a**),[23] 2-chlorotropone (**14b**),[23] 2-bromo-3,5,7-trideuteriotropone (**14c**),[24] 2,7-dibromotropone (**20a**),[25] 2,4,7-tribromotropone (**20b**),[26] and 2,3,5,7-tetrachlorotropone (**20c**),[26] were prepared by the methods described in the literature.

General Procedure for the Reaction of Triphenyl (1-*Phenylvinylimino*)*phosphorane* (**3a**) *with Tropones* (**4a**—**c**).—A solution of compound (**3a**) (1 mmol) and a tropone (**4a**—**c**) (1 mmol) in anhydrous benzene (5 ml) was heated under reflux for 24 h. After the benzene had been evaporated off, the resulting residue was chromatographed on Florisil. The fractions eluted with CCl_4 afforded a compound (**5a**—**c**). The fractions eluted with CH_2Cl_2 afforded triphenylphosphine oxide (80—90%). The results are summarized in Table 1 (entries 1—3).

For 2-phenyl-1,8-dihydrocyclohepta[*b*]pyrrole (**5a**): m.p. 112—114 °C (from CCl_4); δ_H ([$^2H_6$]acetone) 3.27 (2 H, d, *J* 6.0 Hz), 5.30—5.50 (1 H, m), 5.77—6.05 (2 H, m), 6.42 (1 H, d, *J* 2.7 Hz), 6.66 (1 H, dt, *J* 10.2 and 2.4 Hz), and 6.95—7.60 (5 H, m); $\nu_{max.}$($CHCl_3$) 3 448 cm^{-1} (NH) (Found: M^+, 207.1035. Calc. for $C_{15}H_{13}N$: *M*, 207.1047).

For 8-*methyl*-2-*phenyl*-1,8-*dihydrocyclohepta*[b]*pyrrole* (**5b**): oil, δ_H(CCl_4) 1.20 (3 H, d, *J* 7.1 Hz), 3.25 (1 H, m), 5.10—5.45 (1 H, m), 5.70—6.20 (2 H, m), 6.35 (1 H, d, *J* 2.4 Hz), 6.50—6.80 (1 H, m), 7.00—7.50 (5 H, m), and 7.70—8.10 (1 H, m); $\nu_{max.}$($CHCl_3$) 3 472 cm^{-1} (NH) (Found: M^+, 221.1184. $C_{16}H_{15}N$ requires *M*, 221.1205).

For 8-butyl-2-phenyl-1,8-dihydrocyclohepta[*b*]pyrrole (**5c**) was contaminated with acetophenone and the ^1H n.m.r. spectrum was assigned as follows: δ_H($CDCl_3$) 0.80—1.85 (7 H, m), 2.10—2.50 (2 H, m), 3.05—3.45 (1 H, m), 5.40—6.80 (4 H, m), 6.46 (1 H, d, *J* 2.5 Hz), 7.00—7.70 (5 H, m).

General Procedure for the Dehydrogenation of Compounds (**5a**—**c**) *with* NiO_2.—A solution of a compound (**5a**—**c**) (1 mmol) and NiO_2[17] (540 mg, 6 mmol) in anhydrous benzene (10 ml) was heated under reflux for 20 h. After the reaction mixture had been filtered through Celite to remove insoluble materials, the filtrate was purified by t.l.c. on silica gel with CH_2Cl_2 as developer to give the corresponding 1-aza-azulene derivative (**7a**—**c**) in the yield indicated in Table 1.

For 2-phenyl-1-aza-azulene (**7a**): m.p. 148—149.5 °C (from EtOH) (lit.,[19] 157—159 °C); δ_H($CDCl_3$) 7.35—7.80 (6 H, m), 7.68 (1 H, s), and 8.20—8.80 (4 H, m); $\nu_{max.}$ 1 583, 1 517, 1 469, 1 441, and 1 412 cm^{-1}; $\lambda_{max.}$(EtOH) 237, 285, 310, 365, 371, 497, and 531sh nm (log ε 4.28, 4.67, 4.53, 4.16. 4.12, 3.52, and 3.19) (Found: M^+, 205.0918. $C_{15}H_{11}N$ requires *M*, 205.0891).

For 8-*methyl*-2-*phenyl*-1-*aza-azulene* (**7b**): oil, b.p. 110 °C (bath temp.)/0.5 Torr; δ_H($CDCl_3$) 3.20 (3 H, s), 7.30—7.70 (6 H, m), 7.60 (1 H, s), and 8.20—8.45 (3 H, m); $\nu_{max.}$($CHCl_3$) 1 562, 1 466, and 1 439 cm^{-1}; $\lambda_{max.}$(EtOH) 240, 291, 309sh, 357, 375, 482, and 526sh nm (log ε 4.51, 4.75, 4.58, 4.24, 4.15, 3.50, and 3.20) (Found: M^+, 219.1056. $C_{16}H_{13}N$ requires *M*, 219.1048).

For 8-*butyl*-2-*phenyl*-1-*aza-azulene* (**7c**): oil, b.p. 130 °C (bath temp.)/0.5 Torr.; δ_H(CCl_4) 0.80—2.00 (7 H, m), 3.72 (2 H, t, *J* 8.2 Hz), 7.10—7.62 (6 H, m), 7.60 (1 H, s), and 8.15—8.40 (3 H, m); $\nu_{max.}$($CHCl_3$) 1 545, 1 470, 1 434, and 1 385 cm^{-1}; $\lambda_{max.}$(EtOH) 241, 290, 311sh, 358, 387, and 484 nm (log ε 4.24, 4.40, 4.25, 3.92, 3.86, and 3.09) (Found: M^+, 261.1517. $C_{19}H_{19}N$ requires *M*, 261.1518).

Reaction of Compound (**3b**) *with Tropone* (**4a**).—A solution of compound (**3b**) (606 mg, 2 mmol) and tropone (**4a**) (106 mg, 1 mmol) in anhydrous benzene (5 ml) was heated under reflux for 6 h. The reaction mixture was then chromatographed on Florisil. The fractions eluted with benzene gave 1,8-dihydrocyclohepta[*b*]pyrrole (**6b**) (42 mg, 32%). The fractions eluted with AcOEt gave triphenylphosphine oxide (167 mg, 60%). For (**6b**): δ_H(CCl_4) 3.07 (2 H, d, *J* 5.8 Hz), 5.05—5.45 (1 H, m), 5.70—5.85 (1 H, m), 5.90—6.17 (2 H, m), and 6.35—6.70 (2 H, m); $\nu_{max.}$($CHCl_3$) 3 460 cm^{-1} (NH).

Dehydrogenation of Compound (**6b**) *with Manganese Dioxide.*—A solution of compound (**6b**) (42 mg, 0.32 mmol) and activated MnO_2[18] (500 mg, 6 mmol) in anhydrous benzene (20 ml) was stirred for 45 min at room temperature. After the

reaction mixture was filtered through Celite to remove insoluble materials, the filtrate was then concentrated and the residue was purified by t.l.c. to give 1-aza-azulene (**8b**) (35 mg, 85%), $\delta_H(CDCl_3)$ 7.30—7.95 (4 H, m) and 8.45—8.90 (3 H, m); picrate: m.p. 195—197 °C (lit.,[21] m.p. 197—198 °C).

Reaction of a Mixture of Phosphoranes (**3c**) *and* (**3d**) *with Tropone* (**4a**), *and Subsequent Dehydrogenation of the Products* (**6c**) *and* (**6d**).—A solution of a mixture of phosphoranes (**3c**) and (**3d**) was prepared by the reaction of 2-azidohex-1-ene (**1c**) (375 mg, 3 mmol) with triphenylphosphine (**2**) (786 mg, 3 mmol) in anhydrous benzene (10 ml). To this reaction mixture was added tropone (**4a**) (106 mg, 1 mmol), and the mixture was heated under reflux for 6 h. After the benzene had been evaporated off, the residue was purified by chromatography on Florisil. The fractions eluted with benzene gave a mixture of adducts (**6c**) and (**6d**). The fractions eluted with CH_2Cl_2 gave triphenylphosphine oxide (80%). The mixture of products (**6c**) and (**6d**) and activated MnO_2 (1.3 g, 15 mmol) in anhydrous benzene (10 ml) was stirred at room temperature for 6 h. After the reaction mixture had been filtered through Celite to remove insoluble materials, and the filtrate had been evaporated, the resulting residue was separated by t.l.c. on silica gel with AcOEt as developer to give 2-butyl-1-aza-azulene (**8c**) (33 mg, 18%) and 2-methyl-3-propyl-1-aza-azulene (**8d**) (78 mg, 42%).

For compound (**8c**): picrate: m.p. 174—175 °C (from methanol) (decomp.); the *free base* had δ_H 0.98 (3 H, t, *J* 5.8 Hz), 1.20—2.10 (4 H, m), 3.08 (2 H, t, *J* 7.4 Hz), 7.06 (1 H, s), 7.30—7.75 (3 H, m), 8.15—8.57 (2 H, m); $\nu_{max.}(CHCl_3)$ 1 587, 1 481, 1 449, and 1 407 cm^{-1} (Found: M^+, 185.1160. $C_{13}H_{15}N$ requires *M*, 185.1206).

For compound (**8d**): picrate: m.p. 180—190 °C (from methanol) (decomp.); the *free base* had δ_H 0.93 (3 H, t, *J* 6.5 Hz), 1.30—1.95 (2 H, m), 2.67 (3 H, s), 2.80 (2 H, t, *J* 6.8 Hz), 7.20—7.60 (3 H, m), and 7.90—8.40 (2 H, m); $\nu_{max.}(CHCl_3)$ 1 582, 1 466, 1 441, and 1 400 cm^{-1} (Found: M^+, 185.1188. $C_{13}H_{15}N$ requires *M*, 185.1206).

General Procedure for the Reaction of the Phosphorane (**3a**) *with the Halogenated Tropones* (**14a**, **b**) *and* (**20a**—**c**).—A solution of compound (**3a**) (379 mg, 1 mmol), a tropone (**14a**, **b**) or (**20a**—**c**) (1 mmol), and triethylamine (202 mg, 2 mmol) in anhydrous benzene (5 ml) was heated under reflux for the period indicated in Table 2, until the tropone completely disappeared. The reaction mixture was filtered, the filtrate was concentrated, and the resulting residue was separated by t.l.c. on silica gel to give 1-aza-azulene derivatives (**7a**) and (**22**)—(**25**), and triphenylphosphine oxide (80%). The results are summarized in Table 2 (entries 1, 2, and 5—7). The new 1-aza-azulene derivatives were identified on the basis of the following physical data.

For 8-*bromo*-2-*phenyl*-1-*aza-azulene* (**22**): m.p. 102—105 °C (from EtOH); $\delta_H(CDCl_3)$ 7.20—7.68 (6 H, m) and 7.92—8.42 (4 H, m); $\nu_{max.}(CHCl_3)$ 1 566, 1 468, 1 440, and 1 308 cm^{-1}; $\lambda_{max.}$(EtOH) 258, 295, 315, 366, 373, 492, and 550sh nm (log ε 4.42, 4.42, 4.26, 3.99, 3.99, 3.30, and 2.94); *m/z* 285 (M^+, 82%), 284 (88), 283 (M^+, 72), and 282 (100) (Found: C, 63.1; H, 3.4; N, 4.95. $C_{15}H_{10}BrN$ requires C, 63.40; H, 3.55; N, 4.93%).

For 5,8-*dibromo*-2-*phenyl*-1-*aza-azulene* (**23**): m.p. 143—145 °C (from EtOH); $\delta_H(CDCl_3)$ 7.41—7.84 (6 H, m), 8.22—8.43 (2 H, m), and 8.56 (1 H, d, *J* 1.2 Hz); $\nu_{max.}(CHCl_3)$ 1 554, 1 482, 1 414, and 1 359 cm^{-1}; $\lambda_{max.}$(EtOH) 264, 306, 375, 394, 506, 520, and 562sh (log ε 4.59, 4.65, 4.15, 4.14, 3.40, 3.40, and 3.07); *m/z* 365 (M^+, 66%), 363 (M^+, 93), 361 (M^+, 75), and 203 (100) (Found: C, 49.5; H, 2.5; N, 3.8. $C_{15}H_9Br_2N$ requires C, 49.63; H, 2.50; N, 3.86%).

For 6,8-*dibromo*-2-*phenyl*-1-*aza-azulene* (**24**): m.p. 143—145 °C (from EtOH); $\delta_H(CDCl_3)$ 7.34—7.77 (6 H, m), 8.13—8.35 (2 H, m), and 8.35—8.48 (1 H, m); $\nu_{max.}(CHCl_3)$ 1 547, 1 452, 1 439, and 1 380 cm^{-1}; $\lambda_{max.}$(EtOH) 267, 302, 330, 377, 397, 492, 503, and 550sh nm (log ε 4.67, 4.63, 4.43, 4.28, 4.32, 3.53, 3.53, and 3.12); *m/z* 365 (M^+, 68%), 363 (M^+, 100), and 361 (M^+, 71) (Found: C, 49.8; H, 2.55; N, 3.9%).

For 5,7,8-*trichloro*-2-*phenyl*-1-*aza-azulene* (**25**): m.p. 148—149 °C (from hexane); $\delta_H(CDCl_3)$ 7.35—7.65 (4 H, m) and 8.15—8.42 (4 H, m); $\nu_{max.}(CHCl_3)$ 1 580, 1 448, 1 399, and 1 357 cm^{-1}; $\lambda_{max.}$(EtOH) 267, 312, 328, 363, 398, 524, and 557sh nm (log ε 4.40, 4.47, 4.40, 4.18, 3.84, 3.00, and 2.85); *m/z* 313 (M^+, 5%), 311 (M^+, 35), 309 (M^+, 99), and 307 (M^+, 100) (Found: C, 58.5; H, 2.7; N, 4.6. $C_{15}H_8Cl_3N$ requires C, 58.38; H, 2.61; N, 4.54%).

Reaction of the Phosphorane (**3a**) *with* 2-*Bromo*-3,5,7-*trideuteriotropone* (**14c**).—A solution of compound (**3a**) (114 mg, 0.3 mmol), the tropone (**14c**) (56 mg, 0.3 mmol), and triethylamine (61 mg, 0.6 mmol) in anhydrous benzene (3 ml) was heated under reflux for 24 h. After the reaction mixture had been concentrated, the residue was separated by t.l.c. on silica gel with hexane–AcOEt (1:1) as developer to give 5,7-*dideuterio*-2-*phenyl*-1-*aza-azulene* (**15**) (70%): m.p. 149—151 °C (from EtOH); $\delta_H(CDCl_3)$ 7.42—7.58 (3 H, m), 7.74 (1 H, s), 7.76 (1 H, br s), 8.27—8.38 (2 H, m), 8.50 (1 H, br s), and 8.67 (1 H, br s); $\nu_{max.}(CHCl_3)$ 1 581, 1 517, 1 454, 1 449, 1 407, and 1 396 cm^{-1} (Found: M^+, 207.1007. $C_{15}H_9D_2N$ requires *M*, 207.1018).

Reaction of the Phosphorane (**3b**) *with* 2-*Bromotropone* (**14a**).—A solution of compound (**3b**) (460 mg, 1.5 mmol), the tropone (**14a**) (93 mg, 0.5 mmol), and triethylamine (101 mg, 1 mmol) in anhydrous benzene (3 ml) was heated under reflux for 5 h. After the reaction mixture had been filtered, the filtrate was concentrated, and the residue was separated by t.l.c. on silica gel with AcOEt as developer. The first band from the t.l.c. plates gave 1-aza-azulene (**8b**) (36 mg, 56%). The second band gave triphenylphosphine oxide (80%).

Reaction of a Mixture of Compounds (**3c**) *and* (**3d**) *with* 2-*Bromotropone* (**14a**).—A solution of the phosphoranes (**3c**) and (**3d**) was prepared by treatment of 2-azidohex-1-ene (**1c**) (146 mg, 1.17 mmol) and triphenylphosphine (**2**) (306 mg, 1.17 mmol) in anhydrous benzene (3 ml) at room temperature for 2 h. To this solution were added 2-bromotropone (**14a**) (152 mg, 0.82 mmol) and triethylamine (202 mg, 2 mmol), and the mixture was heated under reflux for 3 h. After the benzene had been evaporated off, the residue was separated by t.l.c. on alumina with hexane–AcOEt (3:1) as developer to give 2-methyl-3-propyl-1-aza-azulene (**8d**) (65 mg, 43%) and triphenylphosphine oxide (80%).

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References

1 Part 6, Y. Iino and M. Nitta, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2235.
2 Yu. G. Gololobov, I. N. Zhmurova, and L. F. Kasukhin, *Tetrahedron*, 1981, **37**, 437.
3 J. B. Hendrickson, K. W. Bair, and P. M. Keehn, *J. Org. Chem.*, 1977, **42**, 2935; N. Knouzi, M. Vaultier, and R. Carrié, *Bull. Soc. Chim. Fr.*, 1985, 815; A. Koziara, K. Osowska-Pacewicka, S. Zawadzki, and A. Zwierzak, *Synthesis*, 1985, 202.
4 E. J. Corey, B. Samuelson, and F. A. Luzzio, *J. Am. Chem. Soc.*, 1984, **106**, 3682.
5 J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, 1978, **43**, 1460; O. Tsuge, S. Kanemasa, and K. Matsuda, *ibid.*, 1984, **49**, 2688.
6 P. H. Lambert, M. Vaultier, and R. Carrié, *J. Chem. Soc., Chem. Commun.*, 1982, 1224; T. Sasaki, S. Eguchi, and T. Okano, *J. Am.*

Chem. Soc., 1983, **105**, 5912; D. M. B. Hickey, A. R. MacKenzie, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1984, 776; L. Bruché, L. Garanti, and G. Zecchi, *Synthesis*, 1985, 304; H. R. Stegmann, D. Klotz, and J. E. Weiss, *Chem. Ber.*, 1985, **118**, 4632.
7 K. B. Becker, *Tetrahedron*, 1980, **36**, 1717, and references cited therein.
8 T. Kobayashi and M. Nitta, *Chem. Lett.*, 1985, 1459.
9 Y. Iino, T. Kobayashi, and M. Nitta, *Heterocycles*, 1986, **24**, 2437.
10 T. Kobayashi, Y. Iino, and M. Nitta, *J. Chem. Soc. Jpn.*, 1987, 1237.
11 T. Kobayashi and M. Nitta, *Chem. Lett.*, 1986, 1549.
12 Preliminary accounts of this paper: M. Nitta and T. Kobayashi, *Chem. Lett.*, 1986, 463.
13 For a recent review, see T. Nishiwaki and N. Abe, *Heterocycles*, 1981, **15**, 547.
14 D. Lewis and D. Peters, 'Facts and Theories of Aromaticity,' Macmillan Press, London, 1975; L. T. Scott, M. A. Minton, and M. A. Kirms, *J. Am. Chem. Soc.*, 1980, **102**, 6311, and references cited therein.
15 R. H. Wiley and J. Moffat, *J. Org. Chem.*, 1957, **22**, 995.
16 F. W. Fowler, A. Hassner, and L. A. Levy, *J. Am. Chem. Soc.*, 1967, **89**, 2077.
17 K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, 1962, **27**, 1597.
18 R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **8**, 194.
19 Y. Sugimura, N. Soma, and Y. Kishida, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3174.
20 T. Nozoe, S. Seto, S. Matsumura, and T. Terasawa, *Chem. Ind. (London)*, 1954, 1357.
21 K. Yamane, K. Fujimori, J.-K. Sin, and T. Nozoe, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1184.
22 G. Biggi, F. Del Cima, and F. Pietra, *J. Am. Chem. Soc.*, 1973, **95**, 7101; F. Pietra, *J. Chem. Soc., Chem. Commun.*, 1974, 544, and references cited therein.
23 W. von E. Doering and C. F. Hiskey, *J. Am. Chem. Soc.*, 1952, **74**, 5688.
24 F. Pietra and F. Del Cima, *J. Chem. Soc. B*, 1971, 2224.
25 T. Mukai, *Bull. Chem. Soc. Jpn.*, 1958, **31**, 846.
26 W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 1952, **74**, 5683.

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