# On the reaction of prop-2-enylidenetriphenylphosphorane derivatives. Novel synthesis of the azulene ring system

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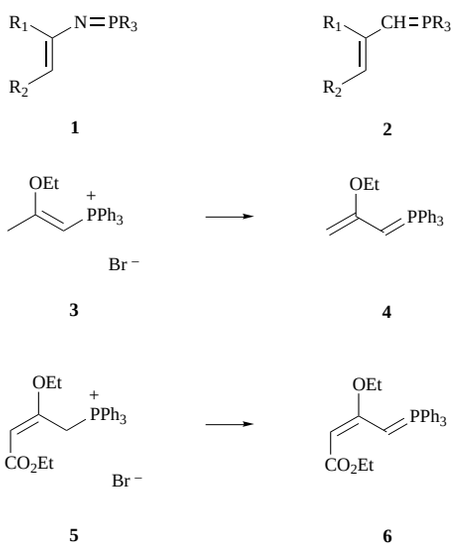
**Reaction of prop-2-enylidenetriphenylphosphorane derivatives with several tropones has been studied in an attempt to provide a short new route to the azulene ring system. (2-Ethoxyprop-2-enylidene)triphenylphosphorane 4 reacts with 2-chloro-, 2-methoxy- and 2,3,5,7-tetrachlorotropones 7a–c to give azulene derivatives 8 and 9 in moderate yields. On the other hand, reaction of [2-ethoxy-3-(ethoxycarbonyl)prop-2-enylidene]triphenylphosphorane 6 with tropones 7a,c results in the formation of azulene esters 10 and 11 in low yields, whilst that with tropone 7b gives no azulene and substrate 7b is recovered. In order to gain insight into the mechanistic pathways, reaction of phosphoranes 4 and 6 with deuteriated tropones 14a,b which are the corresponding trideuteriated derivatives of compounds 7a,b, have also been studied. Furthermore, compound 4 reacts also with 5-(dimethylaminomethylene)cyclopenta-1,3-dienecarbaldehyde 33 to give 6-ethoxyazulene 37 in moderate yield.**

## Introduction

Previously, we have demonstrated a simple preparation of (vinylimino)phosphoranes **1**, which have two nucleophilic centres at the α- and β-positions.[1] (Vinylimino)phosphoranes are found to react with compounds bearing two electrophilic centres or Michael acceptors [*e.g.* α-bromo ketones,[2] α,β-unsaturated ketones or aldehydes,[3] tropone derivatives,[4] methano-[11]annulenones[5] and 5-(dimethylaminomethylene)cyclopenta-1,3-dienecarbaldehyde[6,7]] in an enamine alkylation process followed by an aza-Wittig reaction. This provides efficient routes to pyrroles, pyridines, 1-azaazulenes, methanocycloundeca[*b*-]pyrrole and 5-azaazulenes. On the other hand, it was shown that prop-2-enylidenephosphoranes **2** also have two nucleophilic centres, at the α- and γ-positions. Although there are several reports demonstrating substitution at both the α- and γ-position,[8] aldehydes and ketones usually react at the α-position in a normal Wittig reaction.[9] Acylation occurs predominantly at the γ-position,[10] whilst the regioselectivity of the alkylation is uncertain because of a paucity of examples.[11] It was shown that prop-2-enylidenephosphoranes react with compounds containing two electrophilic centres, (*e.g.* α,β-unsaturated aldehydes, ketones[12,13] and α-halogeno ketones[14]) to give cyclohexadienes and cyclopentadienes, respectively, bearing a variety of substituents. However, the synthetic utility of the prop-2-enylidenephosphoranes in various annulation reactions is still unexplored. In this context, we planned to take advantage of the above methodology for the preparation of the azulene ring system by using the reaction of (2-ethoxyprop-2-enylidene)-triphenylphosphorane **4**,[15] which is prepared *in situ* by base treatment of phosphonium salt **3**,[16] and the isolated analogue [2-ethoxy-3-(ethoxycarbonyl)prop-2-enylidene]triphenylphosphorane **6**[14] (see Scheme 1) with 2-chloro-, 2-methoxy- and 2,3,5,7-tetrachloro-tropones **7a–c** and 5-(dimethylamino-methylene)cyclopenta-1,3-dienecarbaldehyde **33**. In order to gain insight into the reaction pathways, 2-chloro-3,5,7-trideuteriotropone **14a**[17] and 3,5,7-trideuterio-2-methoxytropone **14b**[18] were also studied. We describe here our results in detail.




**Scheme 1**

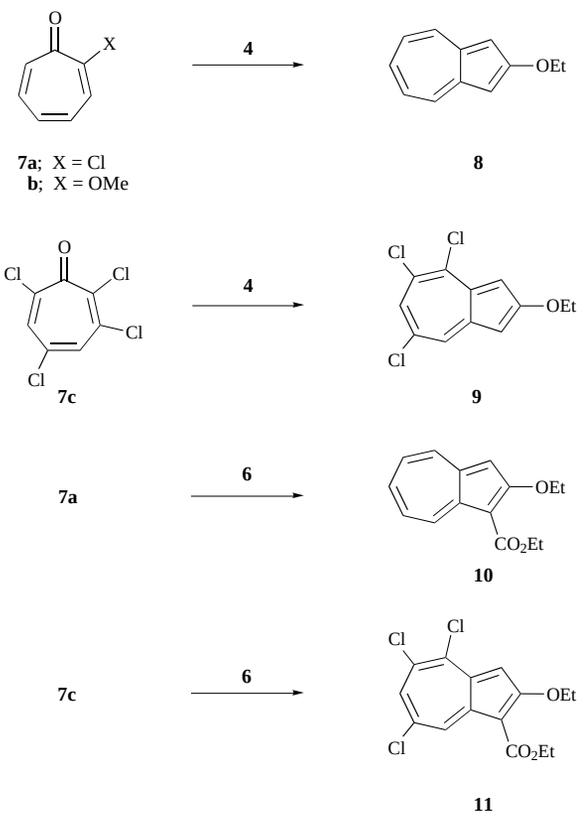
## Results and discussion

Reaction of prop-2-enylidenephosphoranes **4** and **6** with tropones **7a–c** was carried out to give azulene derivatives (Scheme 2). The reaction conditions and the yields of the products are summarized in Table 1. The reaction is considered to proceed *via* a Michael addition from the γ-position of phosphoranes **4** and **6** onto the tropone nucleus as in the case of the reaction of compounds **1** with tropones.[4] The reaction of phosphorane **4** with tropones **7a** and **7b** proceeded under mild conditions to give 2-ethoxyazulene **8**[19] in moderate yield (entries 1–3). The reaction of phosphorane **4** with tetrachlorotropone **7c**, which has four electron-withdrawing chlorine atoms, did not proceed at room temperature, but was successful at 70 °C to give 4,5,7-trichloro-2-ethoxyazulene **9** in modest yield (entry 4). On the other hand, reaction of ester phosphorane **6**, which has an additional electron-withdrawing $CO_2Et$ group on the parent structure **4**, did not react with the tropone **7a** at room temperature, and tropone **7a** was recovered. However, compound **6** reacted with the tropone **7a** to give 2-ethoxy-1-ethoxycarbonylazulene **10**[20] under forcing conditions (entry 5). Similarly, the reaction of compound **6** with the tropone **7c** afforded azulene derivative **13** in low yield (entry 7). Compound **6** did not react with tropone **7b**, and the starting material **7b** was recovered (entry 6). It is clear that the phosphorane **4**, which has an electron-donating substituent, reacts smoothly under mild conditions to result in moderate yields of the products. The phos-

**Table 1** Reaction of phosphoranes **4** and/or **6** with tropones **7a–c**, **14a**,**b** and carbaldehyde **33**

| | | | Reaction conditions | | | | |
|---|---|---|---|---|---|---|---|
| Entry | Phosphorane | Tropone | Solvent | *T*/°C | *t*/h | Product | Yield (%) |
| 1 | **4**[a] | **7a** | DMSO | r.t.[c] | 12 | **8** | 60 |
| 2 | **4**[a] | **7b** | DMSO | r.t. | 12 | **8** | 55 |
| 3 | **4**[b] | **7b** | DMF | r.t. | 10 | **8** | 55 |
| 4 | **4**[b] | **7c** | DMF | 70 | 1 | **9** | 21 |
| 5 | **6** | **7a** | DMSO | 140 | 12 | **10** | 27 |
| 6 | **6** | **7b** | DMF | 145 | 12 | none | |
| 7 | **6** | **7c** | DMF | 90 | 12 | **11** | 4 |
| 8 | **4**[b] | **14a** | DMSO | r.t. | 2 | **24** | 50 |
| 9 | **4**[b] | **14b** | DMSO | r.t. | 2 | **24**/**28**[d] | 54 |
| 10 | **6** | **14a** | DMSO | 120 | 12 | **29**/**30**[e] | 27 |
| 11 | **4**[b] | **33** | DMF | 95 | 12 | **37** | 66 |

[a] Bu$^t$OK was used to generate phosphorane **4**. [b] $KN(SiMe_3)_2$ was used to generate phosphorane **4**. [c] Room temp. [d] A mixture of products **24** and **28** in the ratio 1:3. [e] A mixture of products **29** and **30** in the ratio 1:6.



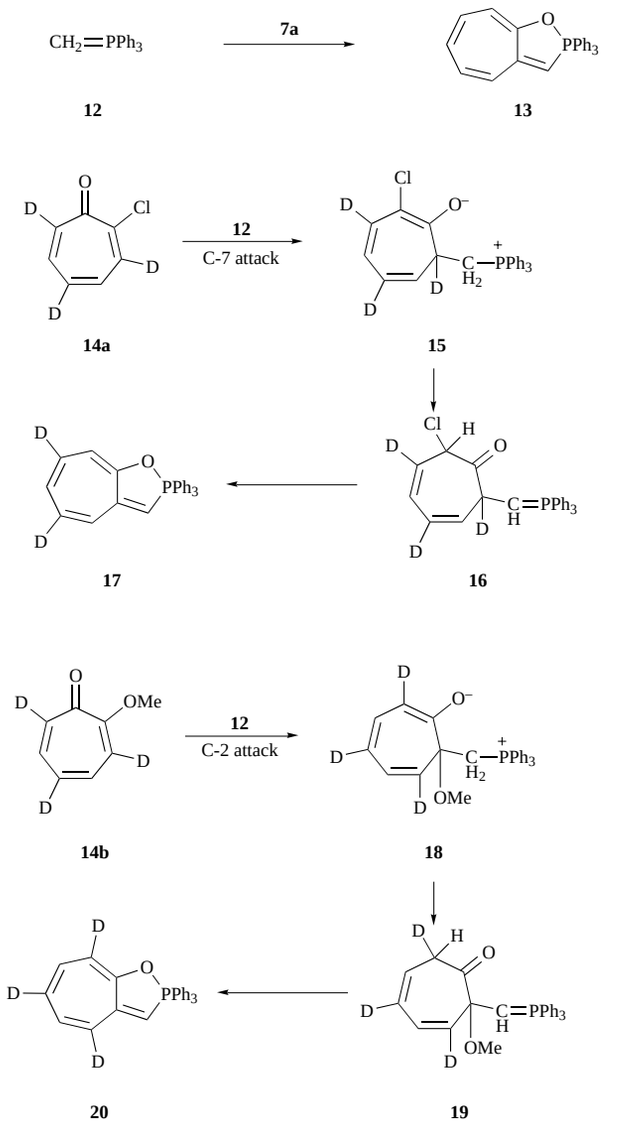

**Scheme 2**

phorane **6**, which has an additional $CO_2Et$ group, is considered to be less reactive. 2-Chlorotropone **7a** seems to be more effective than 2-methoxytropone **7b** for the preparation of the azulene ring system (*cf.* entries 5 and 6).

The structures of known compounds **8** and **10** were unequivocally assigned on the basis of a comparison of their physical data with those reported in the literature.[19,20] The $^1$H and $^{13}$C NMR spectra clearly suggest that compound **9** does not have a symmetrical structure; the proton signal at $\delta$ 8.03 is typical for azulene and is assigned to 8-H. The structure of compound **9** was deduced from this. The spectral data of compounds **10** and **11** can be considered consistent with their structures. The proton signals of 8-H of compounds **10** and **11** appear at $\delta$ 9.37 and 9.50, respectively, suggesting that each 8-H proton of compounds **10** and **11** is located very close to the $CO_2Et$ group: thus the structure **11** was deduced. The results suggest that the Michael addition of phosphoranes **4** and **6** onto the tropone **7c** takes place mainly at C-7 of tropone **7c** (*vide infra*).

Nucleophilic substitution onto 2-chlorotropone **7a** is known to take place at C-7 (abnormal substitution), while that onto 2-methoxytropone **7b** occurs at C-2 (normal substitution) to give 2-substituted tropones.[21] It was shown that methylenetriphenylphosphorane **12** does not undergo Wittig reaction with tropone **7a** but it does react with this tropone to give oxaphosphole derivative **13**, the structure of which was assigned by X-ray crystallographic analysis.[22] Since mechanistic aspects of the reaction are unclear,[18] the pathways for the formation of compound **13** are confirmed here by labelling the troponoid ring with deuterium (Scheme 3). Thus, the attempted reaction of phosphorane **12** with compound **14a** afforded compound **17**. The structural assignment of **17** was based on high-resolution mass spectral data as well as on a comparison of the $^1$H NMR spectral data with those of the parent compound **13**. Thus it is clear that compound **12** attacks at C-7 of tropone **14a** to give intermediate **15**, which undergoes proton migration, regenerating a phosphorane compound, **16**. The elimination of DCl, followed by cyclization, gives bicycle **17**. On the other hand, methylenephosphorane **12** attacks at C-2 in the reaction with 2-methoxytropone **14b** to give the intermediate **18**, which undergoes proton transfer to regenerate a phosphorane, compound **19**. The elimination of HOMe in compound **19** occurs readily, and the subsequent cyclization gives the oxaphosphole **20**. The structure **20** was assigned unequivocally on the basis of high-resolution mass and $^1$H NMR data. The formation of oxaphospholes **17** and **20** suggests that reaction of phosphorane **12** with tropones **14a** and **14b** proceeds in a different way to give the products, and the results are in good accord with the reactivity observed in usual nucleophilic substitutions of tropones **7a**,**b**.[21]

On the other hand, the reaction of the phosphorane **4** with tropone **14a** gave compound **24** (Scheme 4, Table 1). The $^1$H NMR spectrum unequivocally showed, besides an ethyl group, three signals. These signals are assigned to the C-1/3, C-4/8 and C-6 protons, respectively. This fact suggests that initial $\gamma$-alkylation of compound **4** onto tropone **14a** (**7a**) occurred at C-7 to give the intermediate **21**, which regenerates a phosphorane **22** as suggested also in Scheme 3. The subsequent Wittig reaction leading to the azulene derivative **23** followed by elimination of DCl results in the formation of final product **24** (**8**). The regioselectivity observed in **14a** (**7a**) is similar to that observed for methylenephosphorane **12** in Scheme 3. In the reaction of the phosphorane **4** with methoxytropone **14b**, the dideuterioazulene **24** and trideuterioazulene **28** were obtained in the ratio 1:3 (Scheme 5, Table 1). The compound **24** is clearly derived from $\gamma$-alkylation of compound **4** at C-7 of tropone **14b** (*cf.* Scheme 4). An alternative pathway is observed here. The phosphorane **4** attacks at C-2 of tropone **14b** to give the intermediate **25**, which regenerates a phosphorane, **26**. The intermediate **26** undergoes an intramolecular Wittig reaction to give the dihydroazulene **27**, which eliminates HOMe readily to give the azulene **28**. Unexpectedly, alkylation by compound **4** occurs

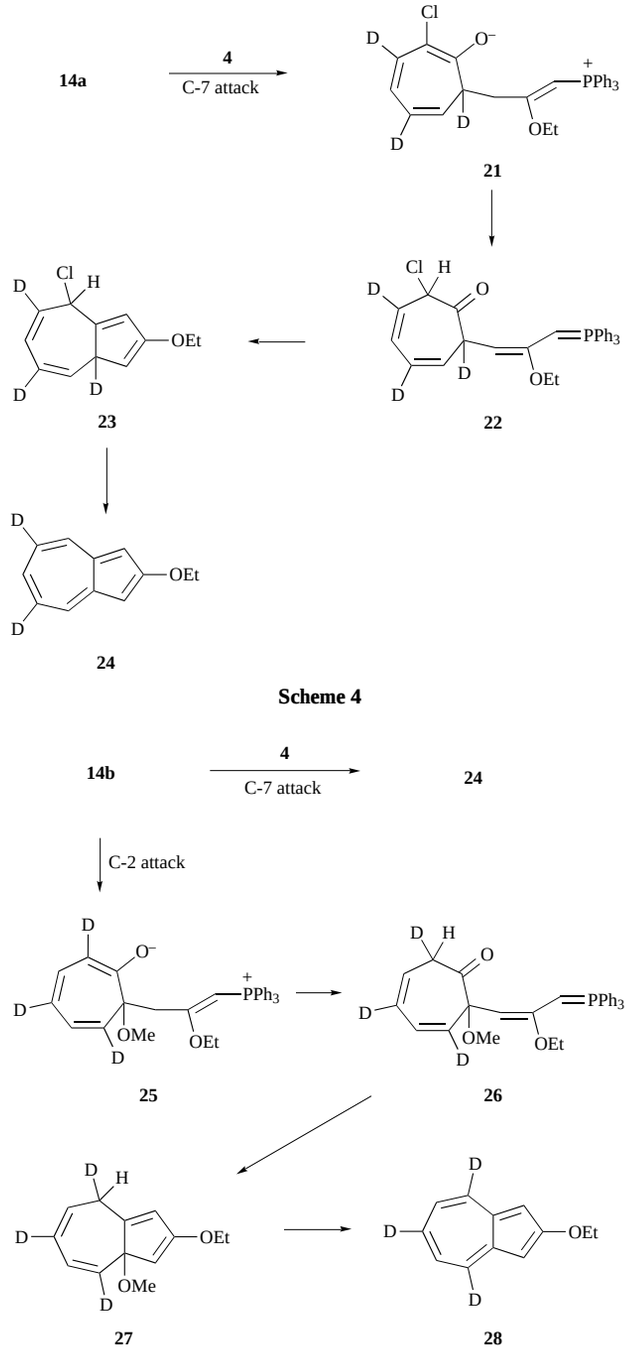


Scheme 3

on tropone **14b** (**7b**) at both C-7 and C-2, with preference for C-2 attack. In the reaction of phosphorane **6** with tropone **14a**, the dideuterioazulene **29** and the trideuterioazulene **30** were obtained in the ratio 1:6 (Scheme 6, Table 1). It is clear that alkylation of compound **6** occurs at C-7 as well as C-2, with preference for C-2, as in the case of the reaction of phosphorane **4** with tropone **14b**.

In the reaction of phosphoranes **4** and **6** with tropone **7c**, alkylation on **7c** ocurs at C-7, leading to intermediate **31**, and finally to formation of the products **9** and **11**. No C-2 attack is observed here, and this is probably due to the large steric hindrance preventing formation of intermediate **32**: the presence of the adjacent chlorine substituents at C-2 and C-3 probably prevents C-2 attack of phosphoranes **4** and **6** onto the tropone nucleus **7c**. As observed above the regioselectivity of the nucleophilic γ-attack of compounds **4** and **6** onto tropone **14a** (**7a**) and **14b** (**7b**) does not follow the pathway observed in the reactions of compound **12** with **14a** (**7a**) and **14b** or that of nucleophiles with compounds **7a**,**b**.[21] Furthermore, α-attack (carbon atom bearing the $PPh_3$ group) of phosphoranes **4** and **6** leading to the intermediates, such as that in the reactions of phosphorane **12** with tropones **14a**,**b**, may occur in the present reactions. However, we could not isolate any product expected from α-attack of substrates **4** and **6**. One may consider that such an attack on the tropone nucleus would reduce the yield of the products. This point is unclear at this stage.

Regarding carbaldehyde **33**, it reacts with both nucleophilic



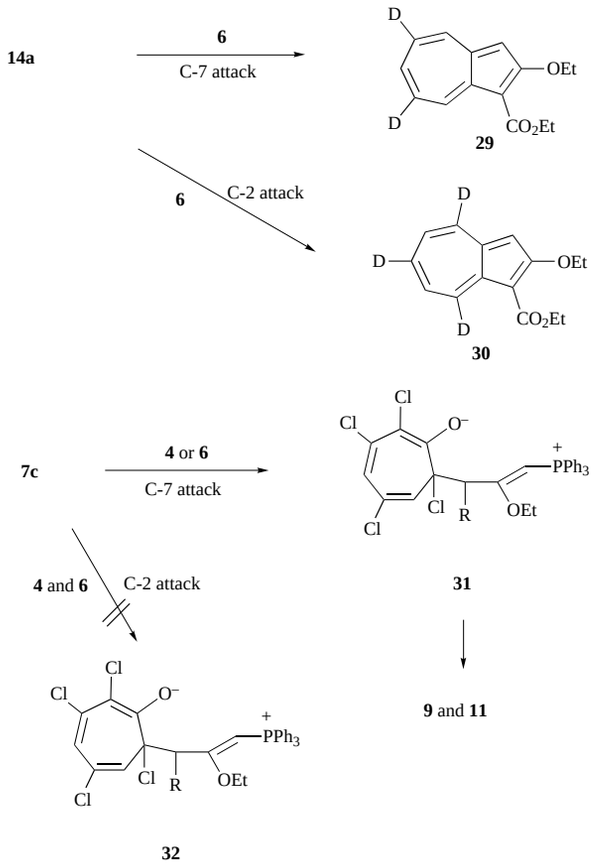
Scheme 4



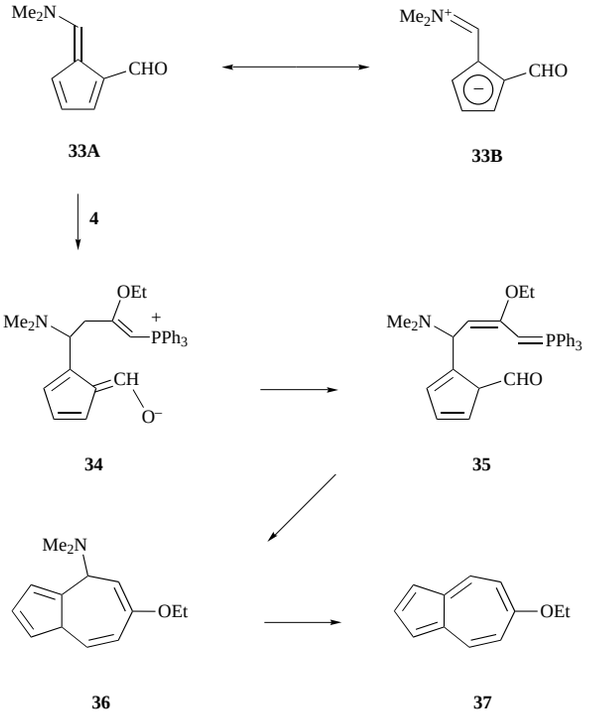
Scheme 5

and electrophilic reagents, indicating a participation of the polar structure **33B**.[23] Previously, we have prepared 5-aza-azulene derivatives by the reaction of (vinylimino)phosphoranes **1** with aldehyde **33**.[7] The results prompted us to investigate the reaction of phosphoranes **4** with aldehyde **33**. As expected, compound **4** reacted with aldehyde **33** to give 6-ethoxyazulene **37**[24] (Scheme 7). The physical data of compound **37** are consistent with its assigned structure.[24] Similar to the reaction of aldehyde **33** with (vinylimino)phosphoranes **1**, we propose the reaction pathways outlined in Scheme 7. Michael addition of substrate **4** occurs at the C-6 position of aldehyde **33** to give the intermediate **34**. The following proton transfer and ketonization of intermediate **34** regenerates a phosphorane **35**, which then undergoes an intramolecular Wittig reaction to give bicycle **36**, which eliminates $HNMe_2$ to afford the azulene **37** in moderate yield (Table 1, entry 11).

In conclusion, the utility of substituted prop-2-enylidene-phosphoranes **4** and **6** for the preparation of the azulene ring system having substituents on either the five-membered ring or




**Scheme 6**




**Scheme 7**

the seven-membered ring has been demonstrated. Phosphorane **4** is more efficient than its analogue **6**, but the parent prop-2-enylidenetriphenylphosphorane does not react with carbonyl compounds **7a** or **33** to give any product except for tarry materials (see Experimental section). Detailed reasons for this are not given here. Further applications of prop-2-enylidenephosphoranes and related compounds toward the preparation of theoretically interesting compounds are now in progress in our laboratory.

## Experimental

IR Spectra were recorded on a Shimadzu IR-400 spectrometer. Mass spectra and high-resolution mass spectra were run on a JEOL Automass 150 and a DX-300 spectrometer. Unless otherwise specified, $^1$H NMR spectra at 90, 270 and 400 MHz were recorded on a Hitachi R-90, a JEOL EX-270 and a JNM-GSX-400 spectrometer, and $^{13}$C NMR spectra at 100.6 MHz were recorded on a JNM-GSX-400 spectrometer. All spectra were recorded in $CDCl_3$, and the chemical shifts are given relative to internal $SiMe_4$ standard. *J* Values are given in Hz. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. All reactions were carried out under anhydrous conditions and dry nitrogen. Samples were dried over $P_2O_5$ *in vacuo*.

### Preparation of phosphonium bromide 3

To stirred aq. acetonyltriphenylphosphonium chloride (8.85 g, 25 mmol in 30 ml) was added aq. $Na_2CO_3$ (2.00 g, 19 mmol in 20 ml) over a period of 20 min at 0 °C. The resulting precipitates were collected by filtration, washed with water and dried *in vacuo* at 60 °C to give acetonylidenetriphenylphosphorane (6.64 g, 89%). The dried crystals were then dissolved in EtBr (100 ml) at room temperature, and the mixture was stirred at room temperature for 24 h. The precipitate was collected by filtration and dried *in vacuo* at 60 °C to give title compound **3** (3.98 g, 46%) as crystals, mp 161–162 °C (decomp.) (from MeCN–AcOEt) [lit.,[16] 173 °C (decomp.)]; $\delta_H$(90 MHz) 0.71 (3 H, t, *J* 7.0), 2.61 (3 H, s), 4.05 (2 H, q, *J* 7.0), 5.75 (1 H, br d, *J* 19.9) and 7.52–7.88 (15 H, m).

### Preparation of phosphorane 6

To stirred aq. (2-ethoxy-3-ethoxycarbonylprop-2-enyl)triphenylphosphonium bromide **5** (8.99 g, 18 mmol in 200 ml) was added dropwise aq. NaOH (790 mg, 20 mmol in 50 mol) over a period of 1 h at 0 °C. Then the resulting precipitate was collected by filtration, washed with water and dried *in vacuo* at 60 °C to give compound **6** (7.17 g, 95%) as a yellow powder, mp 162–164 °C (from MeCN–AcOEt) (lit.,[14] 164–167 °C); $\delta_H$(90 MHz) 0.58 (3 H, t, *J* 7.0), 1.31 (3 H, t, *J* 7.0), 3.69 (2 H, q, *J* 7.0), 4.12 (2 H, q, *J* 7.0), 4.41 (1 H, d, *J* 5.7), 4.86 (1 H, br d, *J* 15.4) and 7.27–7.77 (15 H, m).

### General procedure for the reaction of phosphorane 4 with tropones 7a–c

To a stirred solution of $KN(SiMe_3)_2$ (2 ml of a 0.5 M solution in toluene, 1 mmol) or Bu$^t$OK (112 mg, 1 mmol) was added a solution of phosphonium bromide **3** (427 mg, 1 mmol) in anhydrous dimethylformamide (DMF) (1 ml) or in dimethyl sulfoxide (DMSO) (1 ml), and the mixture was stirred at room temperature for 30 min. To this was added solution of a tropone **7a–c** (0.5 mmol) in DMF (1 ml) or DMSO (1 ml) at room temperature, and the mixture was stirred at room temperature or with heating for periods indicated in Table 1. After the reaction was complete, the solvent was removed *in vacuo*, and the residue was separated by TLC on alumina [hexane–AcOEt (10 : 1)] to give azulenes **8** and **9**. The reaction conditions and the yields of the products are summarized in Table 1.

For compound **8**: violet prisms, mp 76–77 °C (from EtOH) (lit.,[19] 76–77 °C); $\delta_H$(90 MHz) 1.41 (3 H, t, *J* 7.0), 4.20 (2 H, q, *J* 7.0), 6.73 (2 H, s), 7.21–7.45 (3 H, m) and 7.97 (2 H, d, *J* 9.9).

For 4,5,7-*trichloro*-2-*ethoxyazulene* **9**: light violet needles, mp 133–135 °C (from EtOH); $\delta_H$(90 MHz) 1.52 (3 H, t, *J* 7.35, $CH_3$), 4.33 (2 H, q, *J* 7.3, $CH_2$), 6.69 (1 H, d, *J* 2.0, 1- or 3-H), 7.16 (1 H, d, *J* 2.0, 3- or 1-H), 7.91 (1 H, d, *J* 2.0, 6-H) and 8.03 (1 H, d, *J* 2.0, 8-H); $\delta_C$(100.6 MHz) 14.7, 66.8, 102.5, 107.6, 128.1, 128.2, 129.9, 130.2, 133.9, 134.1, 137.9 and 170.9;

$\nu_{max}(CHCl_3)/cm^{-1}$ 2976, 2915, 1515, 1439, 1389, 1364, 1317, 1288, 1171, 1129, 1111, 1021, 935, 925, 873 and 847; *m*/*z* (rel. int.) 278, 276 and 274 ($M^+$, 13, 49 and 50%) and 246 (100) (Found: $M^+$, 273.9709; C, 52.4; H, 2.9. $C_{12}H_9Cl_3O$ requires *M*, 273.9719; C, 52.31; H, 3.29%).

### General procedure for the reaction of phosphorane 6 with tropones 7a–c

To a stirred solution of $K_2CO_3$ (83 mg, 0.6 mmol) and phosphorane **6** (418 mg, 1 mmol) in anhydrous solvent (1 ml) was added a solution of tropone **7a–c** (0.5 mmol) at room temperature, and the mixture was heated for periods indicated in Table 1. After the reaction was complete, the solvent was removed *in vacuo* and the residue was chromatographed on alumina [hexane–AcOEt (5:1)]. The fractions were collected and concentrated, and the residue was further purified by TLC on alumina [hexane–AcOEt (5:1)] to give azulenes **10** and **11**. The reaction conditions and the yields of the products are summarized in Table 1.

For compound **10**: pink needles, mp 80–81 °C (from EtOH) (lit.,[20] 84–85 °C); $\delta_H$(90 MHz) 1.44 (3 H, t, *J* 7.0, Me), 1.55 (3 H, t, *J* 7.0, Me), 4.33 (2 H, q, *J* 7.0, $CH_2$), 4.36 (2 H, q, *J* 7.0, $CH_2$), 6.73 (1 H, s, 3-H), 7.30–7.61 (3 H, m, 5-, 6- and 7-H), 8.13 (1 H, d, *J* 7.0, 4-H) and 9.37 (1 H, d, *J* 11.2, 8-H).

For compound **11**: mp 134–136 °C (decomp.) (from EtOH); $\delta_H$(90 MHz) 1.26–1.59 (6 H, m, $CH_3$ × 2), 4.19–4.56 (4 H, m, $CH_2$ × 2), 7.13 (1 H, s, 3-H), 8.05 (1 H, d, *J* 1.5, 6-H) and 9.50 (1 H, d, *J* 1.5, 8-H); $\delta_C$(100.6 MHz) 14.2, 14.4, 59.7, 65.7, 93.4, 95.2, 109.2, 120.9, 126.5, 131.6, 132.3, 132.4, 164.9 and 172.1; $\nu_{max}(CHCl_3)/cm^{-1}$ 1724 and 1686; *m*/*z* (rel. int.) 348 and 346 ($M^+$, 29 and 33%) and 139 (100) (Found: $M^+$, 345.9907. $C_{15}H_{13}Cl_3O_3$ requires *M*, 345.9932).

### General procedure for the reaction of methylenephosphorane 12 with tropone 7a and deuteriotropones 14a,b

To a stirred solution of phosphorane **12**, which was prepared by the reaction of $CH_3PPh_3Br$ (357 mg, 1 mmol) and $KN(SiMe_3)_2$ (2 ml of a 0.5 M solution in toluene, 1 mmol) in DMSO (1 ml), was added a tropone **7a** (0.5 mmol) or **14a**,**b** (0.5 mmol), and the mixture was stirred at room temperature for 1 h. After evaporation of the mixture *in vacuo*, the resulting residue was chromatographed on alumina. The fractions eluted with hexane–AcOEt (5:1) were collected and concentrated, and the residual solids were crystallized from benzene–hexane (1:1) to give products **13**,[18] **17** and **20**, respectively, in quantitative yields.

For compound **13**: mp 87–88 °C [from PhH–hexane (1:1)]; $\delta_H$(90 MHz) 4.29 (1 H, br d, *J* 37.8, 3-H), 6.17 (2 H, m, 4- and 6-H), 6.70 (2 H, m, 5- and 7-H), 7.06 (1 H, d, *J* 9.9, 8-H) and 7.36–7.70 (15 H, m, Ph); *m*/*z* (rel. int.) 380 ($M^+$, 77%), 277 (19), 262 (100) and 183 (93).

For compound **17**: $\delta_H$(270 MHz) 4.30 (1 H, br d, *J* 36.0, 3-H), 6.15 (2 H, br s, 4- and 6-H), 7.04 (1 H, br s, 8-H) and 7.36–7.59 (15 H, m, Ph); *m*/*z* (rel. int.) 382 ($M^+$, 5%), 277 (28), 262 (83) and 183 (100) (Found: $M^+$, 382.1497. $C_{26}H_{19}D_2OP$ requires *M*, 382.1457).

For compound **20**: $\delta_H$(90 MHz) 4.28 (1 H, br d, *J* 37.8, 3-H), 6.70 (2 H, br s, 5- and 7-H) and 7.36–7.70 (15 H, m, Ph); *m*/*z* (rel. int.) 383 ($M^+$, 61%), 277 (100), 262 (67), 184 (61) and 181 (29) (Found: $M^+$, 383.1508. $C_{26}H_{18}D_3OP$ requires *M*, 383.1519).

### Reaction of phosphorane 4 with deuteriotropones 14a,b

A solution of phosphonium bromide **3** (427mg, 1 mmol) and $KN(SiMe_3)_2$ (2 ml of a 0.5 M solution in toluene, 1 mmol) in DMSO (1 ml) was stirred at room temperature for 10 min. To this solution was added a tropone **14a** (73 mg, 0.5 mmol) or **14b** (70 mg, 0.5 mmol) and the mixture was stirred at room temperature for 2 h. The reaction mixture was then poured into water, extracted with diethyl ether and the extract was dried over $MgSO_4$. After the diethyl ether had been evaporated off *in vacuo*, the resulting residue was purified by TLC on alumina [hexane–AcOEt (5:1)] to give dideuterioazulene **24** or a mixture of **24** and trideuterioazulene **28** in the ratio ~1:3, which was deduced from the following $^1$H NMR spectral data. The results are also summarized in Table 1.

For compound **24**: $\delta_H$(270 MHz) 1.51 (3 H, t, *J* 7.2, $CH_3$), 4.31 (2 H, q, *J* 7.2, $CH_2$), 6.82 (2 H, s, 1- and 3-H), 7.39 (1 H, s, 6-H) and 8.08 (2 H, s, 4- and 8-H); *m*/*z* (rel. int.) 174 ($M^+$, 33%) and 146 (100).

For a mixture of **24** and **28**: $\delta_H$(270 MHz) 1.44 (3 H, t, *J* 7.2, $CH_3$), 4.23 (2 H, q, *J* 7.2, $CH_2$), 6.82 (2 H, s, 1- and 3-H), 7.25–7.40 (1.8 H, m, 5-, 6- and 7-H) and 8.08 (0.5 H, br s, 4- and 8-H); *m*/*z* (rel. int.) 175 ($M^+$, 38%), 174 ($M^+$, 41) and 117 (100).

### Reaction of phosphorane 6 with deuteriotropone 14a

A solution of phosphorane **6** (418 mg, 1 mmol) and tropone **14a** (73 mg, 0.5 mmol) in DMSO (1 ml) was heated at 120 °C for 12 h. The reaction mixture was then poured into water, extracted with diethyl ether, and the extract was dried over $MgSO_4$. After the solvent had been removed *in vacuo*, the residue was separated by TLC on alumina [hexane–AcOEt (5:1)] to give a mixture of dideuterioazulene **29** and trideuterioazulene **30** in the ratio ~1:6, which was determined by the following $^1$H NMR spectral data. The results are summarized in Table 1.

For a mixture of **29** and **30**: $\delta_H$(270 MHz) 1.44 (3 H, t, *J* 7.0, $CH_3$), 1.55 (3 H, t, *J* 7.0, $CH_3$), 4.33 (2 H, q, *J* 7.0, $CH_2$), 4.36 (2 H, q, *J* 7.0, $CH_2$), 6.73 (1 H, s, 3-H), 7.38 (0.86 H, br s, 5- or 7-H), 7.50 (0.86 H, br s, 7- or 5-H), 7.55 (0.14 H, br s, 6-H), 8.13 (0.14 H, br s, 4-H) and 9.37 (0.22 H, br s, 8-H); *m*/*z* (rel. int.) 247 ($M^+$, 100%) and 246 ($M^+$, 26).

### Reaction of phosphorane 4 with compound 33

To a stirred solution of $KN(SiMe_3)_2$ (2 ml of a 0.5 M solution in toluene, 1 mmol) was added a solution of phosphonium salt **3** (427 mg, 1 mmol) in DMF (1 ml). To this mixture was added a solution of aldehyde **33** (75 mg, 0.5 mmol) in DMF (2 ml), and the mixture was heated at 95 °C for 12 h. After the reaction was complete the solvent was removed *in vacuo*, and the residue was purified by TLC on alumina [hexane–AcOEt (5:1)] to give 6-ethoxyazulene **37**, as purple needles, mp 79–81 °C (from EtOH) (lit.,[24] 80–81 °C); $\delta_H$(90 MHz) 1.44 (3 H, t, *J* 7.0), 4.10 (2 H, q, *J* 7.0), 6.75 (2 H, d, *J* 11.0, 5- and 7-H), 7.26 (2 H, d, *J* 3.7, 1- and 3-H), 7.60 (1 H, t, *J* 3.7, 2-H) and 8.16 (2 H, d, *J* 11.0, 4- and 8-H); *m*/*z* (rel. int.) 172 ($M^+$, 50%) and 144 (100) (Found: C, 83.9; H, 7.3. Calc. for $C_{12}H_{12}O$: C, 83.69; H, 7.20%).

### Reaction of prop-2-enylidenetriphenylphosphorane with carbonyl compounds 7a and 33

To a stirred solution of $KN(SiMe_3)_2$ (2 ml of a 0.5 M solution in toluene, 1 mmol) was added dropwise a solution of prop-2-enyltriphenylphosphonium bromide (383 mg, 1 mmol) in DMSO (1 ml) at 0 °C, and the solution was stirred for 30 min until the solution turned a red–orange colour. To this solution was added a solution of carbonyl compound **7a** or **33** (0.5 mmol) in DMSO (2 ml), and the mixture was stirred at room temperature for another 30 min until the reagent **7a** or **33** had been consumed. The reaction mixture was extracted with diethyl ether, and the extract was washed with brine and dried over $MgSO_4$. After evaporation of the mixture, the residue was purified by TLC on silica gel [hexane–AcOEt (3:1)] to give no identified products except triphenylphosphine oxide and tarry materials.

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