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(2-TROPONYL)METHYLENETRIPHENYLPHOSPHORANES. III.[1]

NOVEL SYNTHESES OF AZULENES VIA CYCLOADDITION REACTIONS

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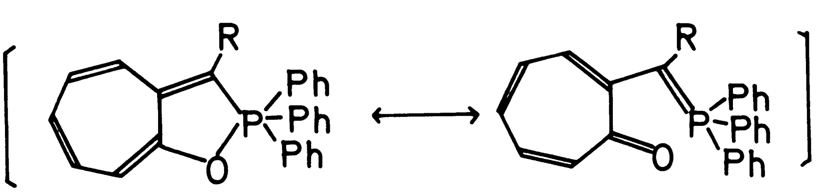
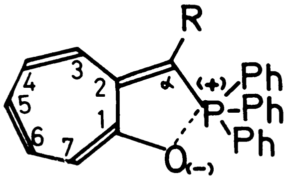
The cycloaddition reactions of (2-troponyl)methylenetriphenylphosphoranes (I), which were characterized as the "bonding betaine", were investigated. Some azulene derivatives were synthesized via [8 + 2] cycloaddition of I with acetylenic esters.

We reported the syntheses of (2-troponyl)methylenetriphenylphosphorane derivatives by the reaction of 2-chlorotropone with phosphonium ylides. Structure determination by X-ray analyses suggested that these derivatives were regarded as "bonding betaine (I)".[1] On the other hand, it is known that heptafulvene[2] and monocyanoheptafulvene[3] react with acetylenedicarboxylate and successive dehydrogenations gave the corresponding azulene derivatives. In addition, Burger and Fehn[4] reported [3 + 2] cycloaddition of 4,5-dihydro-1,3,5-oxazaphospholes.



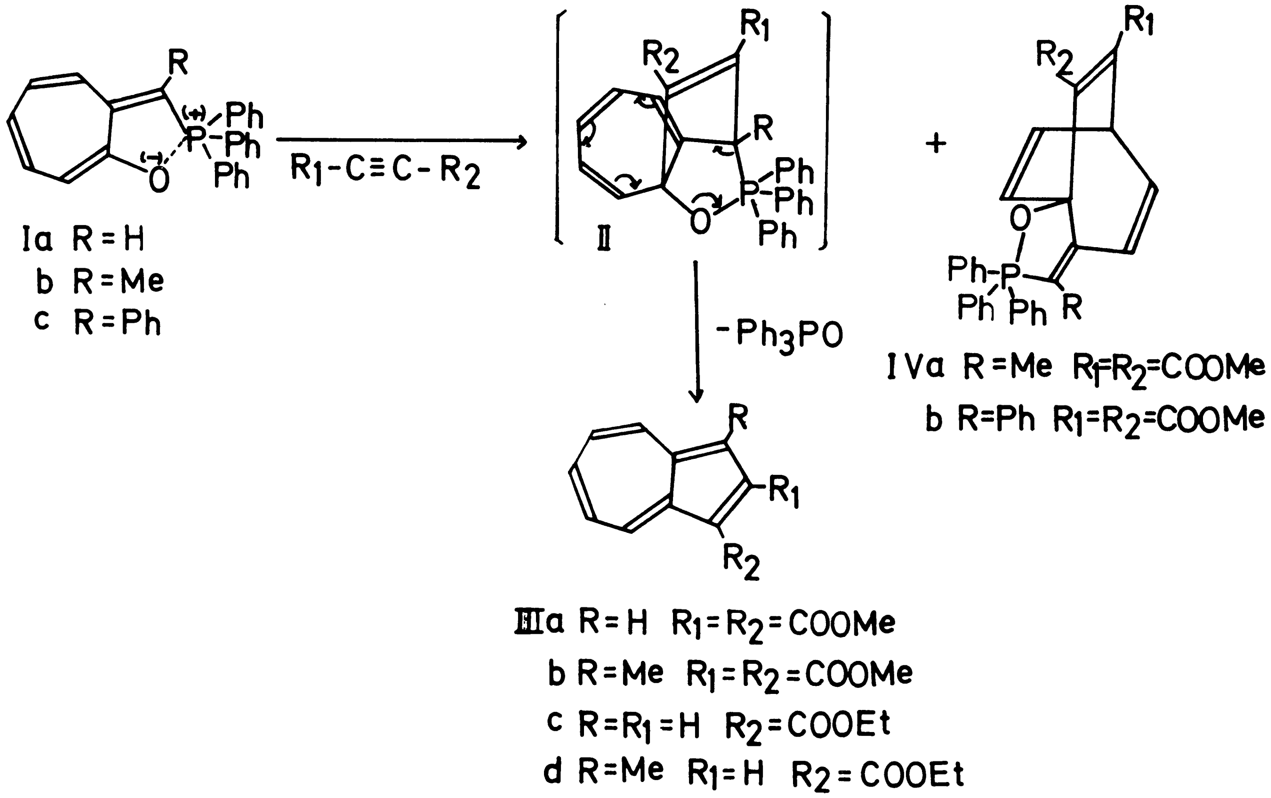


I

In estimating the extent of the contribution of the heptafulvene character to I, we have found a novel method of azulene synthesis.

On refluxing in dioxane or in xylene I and acetylenic esters gave azulenes III and/or Diels-Alder adducts IV. For example, on refluxing (2-troponyl)-methylenetriphenylphosphorane (Ia) with dimethyl acetylenedicarboxylate in dioxane for 8 hours, only dimethyl 1,2-azulenedicarboxylate (IIIa)[2] was produced. The crude IIIa chromatographed on a silica gel column to give dark violet needles of mp 45°C in 44% yield [$C_{14}H_{12}O_4$ (based on mass spectrum and analytical data); IR ν (nujol), 1730, 1690 cm^{-1}; UV (isoöctane) λ max (log ε), 237 (4.30), 288.5

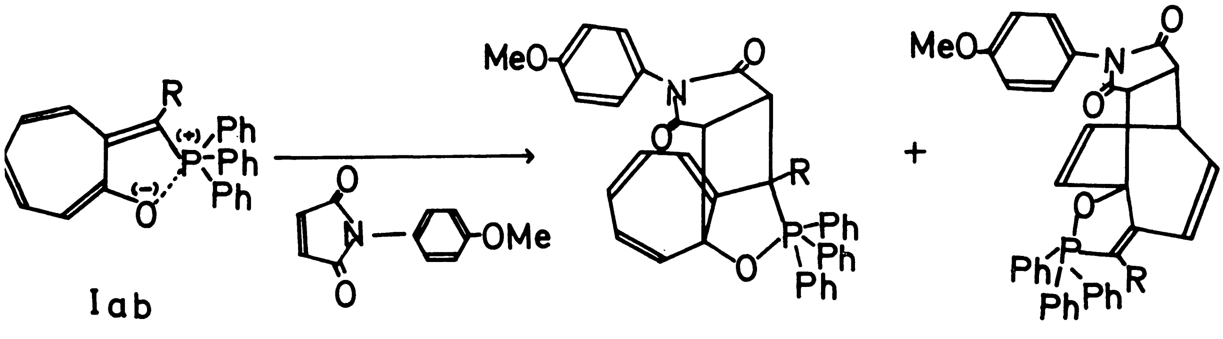
(4.66), 299(4.77), 347(3.81), 365(3.64), 570(2.66)nm; NMR (in CCl_4, 60 MHz), δ ppm, 3.89(s, OCH_3), 3.92(s, OCH_3), 7.10-7.61(m, H-5) and H-7), 7.33(s, H-3), 7.73 tt, H-6, $J_{56} = J_{67} = 9.5$ Hz, $J_{64} = J_{68} = 1.5$ Hz), 8.33(dd, H-4, $J_{45} = 9.5$ Hz, $J_{64} = 1.5$ Hz), 9.31 (dd, H-8, $J_{78} = 9.5$ Hz, $J_{68} = 1.5$ Hz) .



SCHEME I

While the same treatment of α-(2-troponyl)ethylidenetriphenylphosphorane (Ib) gave dimethyl 1-methyl-2,3-azulenedicarboxylate (IIIb) of mp 85°C(trace) and Diels-Alder adduct (IVa) of mp 235-236°C in 69% yield, and further the reaction of (2-troponyl)bezylidenetriphenylphosphorane(Ic) gave only Diels-Alder adduct (IVb) of mp 128-129°C in 61% yield. The NMR spectra (in $CDCl_3$) of IVa showed peaks at δ 1.43 (3H, d, J = 16.0 Hz), 3.57 (3H, s), 3.70 (3H, s), 4.12 (1H, ddt, J = 7.5, 6.5, ca. 1.0 Hz), 5.54 (1H, dd, J = 8.0, ca. 1.0 Hz), 6.27 (1H, dd, J = 8.0, 6.5 Hz), 6.37 (1H, ddd, J = 10.7, 7.5, 3.2 Hz), 6.97 (1H, ddd, J = 10.7, 1.7, 1.0 Hz), 7.03-7.49 (15H, m)ppm, and further the cyclic structure of IVa was suggested by the IR and P^{31} NMR spectra.[5] Analogous reactions of Ia and Ib with ethyl propiolate gave only corresponding azulenes, (IIIc) and (IIId) (oily products, in 11% and 9% yield, respectively). We confirmed the structures of these azulenes on the basis of the spectral data and elemental analyses. These cycloaddition reactions suggested that the azulenes would be formed through the [8 + 2] intermediate (II) and that the Diels-Alder adducts were the products of [4 + 2] cycloaddition, both of which involved P - O bond formation.

Then, the reaction of (2-troponyl)methylenetriphenylphosphoranes (Ia, b) with N-p-methoxyphenylmaleimide was carried out with the intention of isolating [8 + 2] intermediate.



Iab

Va R=H
b R=Me

VIa R=H
b R=Me

The reaction of Ia, b with N-p-methoxyphenylmaleimide in tetrahydrofuran at room temperature for 48 hours gave both [8 + 2] and [4 + 2] adducts (V and VI). The ratio of Va : VIa was determined from the NMR to be about 3 : 2 and that of Vb : VIb was about 2 : 5, respectively. The NMR (in $CDCl_3$) of isolated [8 + 2] adduct, Vb (mp 98-99°C), shows peaks at δ 1.52 (3H, d, J = 16.0 Hz), 2.98 (1H, d, J = 8.0 Hz), 3.44 (1H, dd, J = 8.0, 2.0 Hz), 3.75 (3H, s), 5.61 (1H, d, J = 9.0 Hz), 6.12 (1H, dd, J = 9.0, 7.0 Hz), 6.49 (1H, dd, J = 5.0, 3.5 Hz), 6.52 (1H, d, J = 3.5 Hz), 6.73 (1H, dd, J = 7.0, 5.0 Hz), 6.90-7.62 (19H, m)ppm. In contrast, the NMR (in $CDCl_3$) of [4 + 2] adduct, VIb (mp 213°C), shows peaks at δ 1.49 (3H, d, J = 16.5 Hz), 3.22 (1H, dd, J = 9.5, 4.5 Hz), 3.49 (1H, d, J = 9.5 Hz), 3.5-3.8 (1H, m), 3.83 (3H, s), 4.87 (1H, d, J = 9.0 Hz), 6.03 (1H, dd, J = 9.0, 7.0 Hz), 6.28 (1H, ddd, J = ca. 11, 7.0, 3.5 Hz), 6.54 (1H, dm, J = ca. 11 Hz), 6.9-7.7 (19H, m) ppm. Analogous results were also obtained on Va (mp (110-112°C) and VIa (mp 140°C).

On these cycloaddition reactions, substituent group (R) seems to exert the steric hindrance at α-position of (2-troponyl)methylenetriphenylphosphoranes (I).

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References

The NMR spectra were determined with a Varian A-60 or HA-100 spectrometer, using tetramethylsilane as an internal standard.

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4. K. Burger and J. Fehn, Angew. Chem. internat. Edit., 10, 728, 729 (1971); Tetrahedron Letters, 1972, 1263.
5. In the IR spectra of IVa, the ν c=o absorption (1491-1508 cm^{-1}) which was characterized by "bonding betaine" was disappeared, and the chemical shift in P^{31} NMR spectrum (in $CHCl_3$) was + 44.0 ppm relative to 85% H_3PO_4.

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