

(2-TROPONYL)METHYLENETRIPHENYLPHOSPHORANES IV.

WITTIG REACTIONS OF (2-TROPONYL)METHYLENETRIPHENYLPHOSPHORANES

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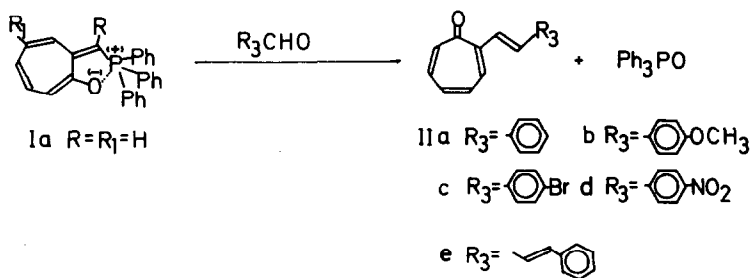
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In an earlier paper, we reported azulene syntheses via cycloaddition reactions¹⁾ of (2-troponyl)methylenetriphenylphosphorane derivatives which were characterized by a "bonding betaine (I)" structure.²⁾ In view of another feasible contribution of the ylide to the phosphorane, we attempted the Wittig type reaction of (2-troponyl)methylenetriphenylphosphorane, and thus if successful, constituting the first example of 2-troponylethylene derivatives.

A mixture of 4.5 g of Ia and 1.26 g of benzaldehyde in 180 ml of dry dioxane was heated under reflux for 30 hours. After evaporation of the solvent, the residue was purified by a silica gel column chromatography to give 1.36 g of 2-styryltropone (IIa) in 55% yield [mp 94-5°C (recrystallization from isopropyl ether); $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ); 225 (4.17), 244 (4.18), 265sh (4.11), 350sh (4.02), 386 (4.16). Found: C, 86.23; H, 5.89%. Calcd for C₁₅H₁₂O: C, 86.51; H, 5.81%]. Analogous reactions with p-substituted benzaldehydes and trans-cinnamaldehyde afforded correspondingly 2-styryltropones (IIb; 45% yield, IIc; 41% yield, IId; 64% yield) and 2-(trans, trans-phenylbutadienyl)troponone (IIe; 34% yield (SCHEME I).



SCHEME I

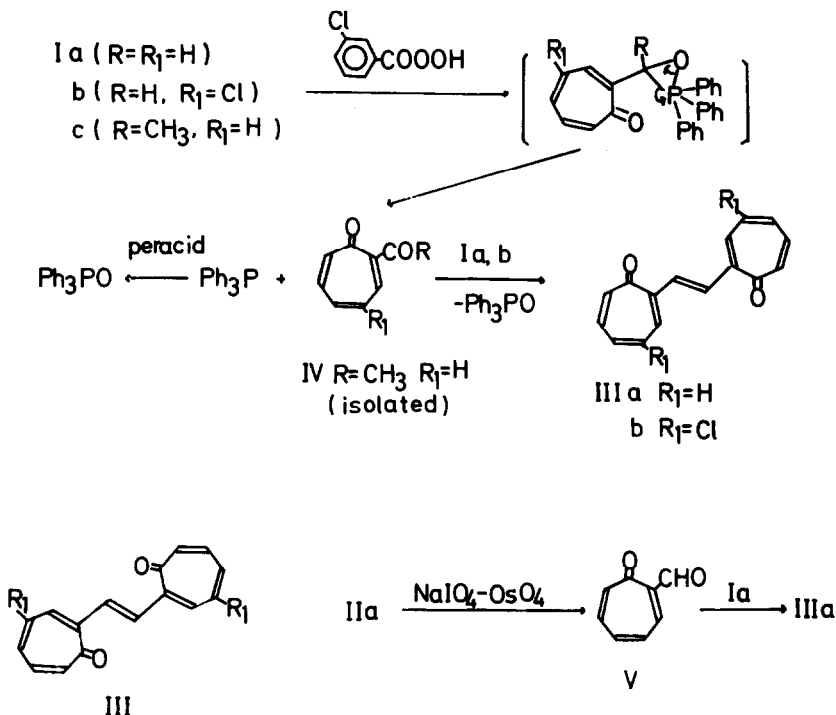
Table 1. Physicochemical data of 2-troponylethylene derivatives.

Comp. no.	mp ($^{\circ}$ C)	$\nu_{\text{C=O}}$	$\nu_{\text{C-H}}$ cm^{-1}	NMR (CDCl_3 , δ ppm)
IIa	94-5	1570,	975	6.86-7.76 (m)
IIb	98	1560,	970	3.83 (3H, s, OCH_3), 6.82-7.70 (11H, m)
IIc	102	1565,	975	6.80-7.80 (m)
IIId	192	1560,	975	6.95-7.23 (4H, m, including d ($J = 13$ Hz) at 7.08), 7.48-7.88 (5H, including A_2 ($J_{AX} = 10$ Hz) of A_2X_2 type of phenyl and d ($J = 13$ Hz) at 7.67, 7.75 respectively), 8.23 (2H, X_2 , $J_{AX} = 10$ Hz)
IIe	99-100	1562,	995	6.50-7.67 (m)
IIIa	166	1570,	970	7.76-7.85 (2H, m), 7.74 (2H, s), 6.93-7.23 (8H, m)
IIIb	250>	1570,	975	7.81 (2H, d, $J = 1.5$ Hz), 7.73 (2H, s), 6.82-7.50 (6H, m)

The IR and NMR data of these compounds are summarized in Table 1. The IR spectra of IIa-e showed absorptions in the neighborhood of 975 cm^{-1} and in the NMR spectra the coupling constant of the ethylenic protons of IIa was determined as 16 Hz using Eu(DPM)_3 and that of IIId was 13 Hz. These evidence suggested that IIa-e possessed a trans double bond. On the other hand, Ia did not react with benzophenone and cyclohexanone.

In order to investigate the ylide character as mentioned before, we conducted the dimerizing oxidation of Ia. There has been few examples in the literature concerning such oxidations of stable ylides.³⁾

For example, to a solution of 1.5 g of Ia in 45 ml of dry benzene was added dropwise a solution of 885 mg of m-chloroperbenzoic acid in 10 ml of methylene chloride and stirred at room temperature overnight. After the usual work-up and purification, 126 mg of IIIa was obtained in 27% yield [mp 166°C (recrystallization from isopropyl ether); $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ); 223 (4.42), 250sh



SCHEME II

(4.24), 318 (3.97), 344sh (3.92), 413 (4.14). Found: C, 81.28; H, 5.05%.
 Calcd for C₁₆H₁₂O: C, 81.34; H, 5.12%.) An analogous reaction of Ib gave the corresponding IIIb. Both IIIa, b showed absorptions at longer wavelengths in the visible region than IIa. Furthermore, the NMR spectra of IIIa, b showed a symmetrical structure, and the H-3 of tropone ring and ethylenic protons⁴⁾ of IIIa, b appeared significantly downfield, as compared with those of IIa. These spectral data suggested a more highly conjugated and thereby planar system. The geometrical structures of IIIa, b seemed more reasonable than III' because the former exhibited fewer electronic repulsions than III' as seen from models. On the other hand, oxidation of Ic with *m*-chloroperbenzoic acid in refluxing methylene chloride gave 2-acetyltropone (IV) [mp 42°C; IR ν (nujol); 1690, 1635, 1585 cm⁻¹. $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ); 231 (4.18), 306 (3.73). NMR (in CDCl₃, δ ppm); 2.48 (3H, s), 7.01-7.24 (4H, m), 7.40-7.64 (1H, m).]

Degradation of IIa by Lemieux-Johnson method⁶⁾ gave 2-formyltropone (V) [mp 63°C; IR ν (nujol); 1696, 1630, 1590sh, 1577 cm^{-1} . NMR (in CDCl_3 , δ ppm); 7.17-7.43 (4H, m), 7.82-8.03 (1H, m), 10.40 (1H, s)]. Under similar conditions for the dimerizing oxidation, Ia reacted with V to give IIIa in 19% yield. Clearly, this suggested that the dimerizing oxidation of Ia proceeded via the Wittig type reaction with the aldehyde as pointed out by Denney, et al.³⁾ (SCHEME II).

All the results described herein indicated proof of the ylide character in this system.

Acknowledgements

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References

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- 4) A pseudo contact shift using Eu(DPM)_3 in the NMR made possible the proton assignment of IIIa comparing to the coupling constant of tropone⁵⁾. The H-3 of tropone ring and ethylenic protons of IIIa appeared at 7.76-7.85 and 7.74, and those of IIIb at 7.81 and 7.73, respectively.
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