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### STUDIES ON PHOSPHONIUM YLIDES-XII. THE REACTION OF STABLE PHOSPHORANES WITH HEXAHYDRO-1,3-PHTHALANDIONE

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## STUDIES ON PHOSPHONIUM YLIDES-XII. THE REACTION OF STABLE PHOSPHORANES WITH HEXAHYDRO-1,3-PHTHALANDIONE

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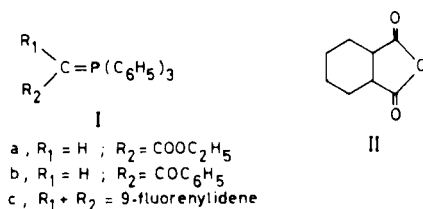
*(Received November 28, 1989)*

Wittig reagents (Ia–c) react with hexahydro-1,3-phthalandione (II) yielding the new adducts (IIIa–e). The structure of these products were established by analytical and spectroscopic methods. A mechanism is proposed to explain the formation of the new ylid-phosphorane adduct IIIa.

**Key words:** Wittig reagents I; Hexahydro-1,3-phthalandione II; Hexahydro-3-[(triphenylphosphoranylidene) methylene] phthalide IIIa; Ethyl 3a,4,5,6,7,7a-hexahydro-3-oxo- $\Delta^{1,\alpha}$ -phthalanacetate IIIb; Hexahydro-3-phenacylidene-phthalide IIIc; and Fluoren-9-ylidenehexahydrophthalide derivatives IIId, IIIe.

### INTRODUCTION

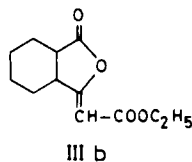
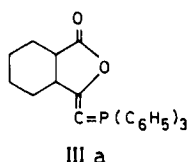
Our continuing interest in the reaction of phosphonium ylides for the production of novel, synthetically useful ylides and new heterocyclic systems,<sup>1–11</sup> led us to investigate the reaction of (carbethoxymethylene)-(Ia), (benzoylmethylene)-(Ib), and (9-fluorenylidene)-(Ic)-triphenylphosphoranes with hexahydro-1,3-phthalandione (II).



### RESULTS AND DISCUSSION

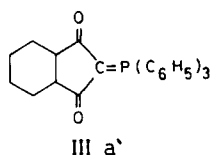
We have found that the reaction of carbethoxymethylene-triphenylphosphorane (Ia) with hexahydro-1,3-phthalandione (II) proceeds in boiling toluene to give two chromatographically pure products assigned structures IIIa and IIIb, respectively. Triphenylphosphine oxide (TPPO) was also isolated from the reaction medium.

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Elemental and mass spectral analyses for compound IIIa corresponded to an empirical formula of  $C_{27}H_{25}PO_2$ . Its IR spectrum, in KBr, revealed the presence of lactone-carbonyl absorption band appearing at  $1790\text{ cm}^{-1}$ . Strong bands at  $1630\text{ cm}^{-1}$  ( $C=C$ , ethylenic) and at  $1235\text{ cm}^{-1}$  ( $C-O$ , stretching) were also present in the IR spectrum of IIIa. Moreover, the IR spectrum of adduct IIIa exhibits strong absorption bands at  $1680$  and  $1505\text{ cm}^{-1}$  characteristic for the  $>C=P$  group absorption,<sup>12</sup> at  $1410\text{ cm}^{-1}$  denoting the  $>P-C$  (phenyl) absorption.<sup>13</sup> Hexahydro-3-[(triphenylphosphoranylidene)methylene] phthalide (IIIa) possesses ylid-phosphorane structure since it exhibits a positive shift in its  $^{31}\text{P}$  NMR (vs, 85%  $\text{H}_3\text{PO}_4$ ) and absorbs in the region characteristic for this class of compounds.<sup>12,14-16</sup>  $^1\text{H}$  NMR spectrum of IIIa showed signals at  $\delta = 1.2-2.03$  (m, 8H; methylene protons),  $2.6-2.87$  (m, 2H;  $>CH-CH<$ ), and at  $7.33-7.97$  (m, 15H, aromatic protons).

These data are most adequately accommodated in structure IIIa since in the alternative structure IIIa' (having the same empirical formula), the IR spectrum would have given a strong absorption bands at  $1600$  ( $\nu\text{CO}$ ), and  $1725\text{ cm}^{-1}$  characteristic for  $\beta$ -diketone.<sup>17</sup> Moreover, the IR spectrum of IIIa' would have lacked both lactone carbonyl absorption band and the ethylenic  $C=C$  band present in the spectrum of IIIa.

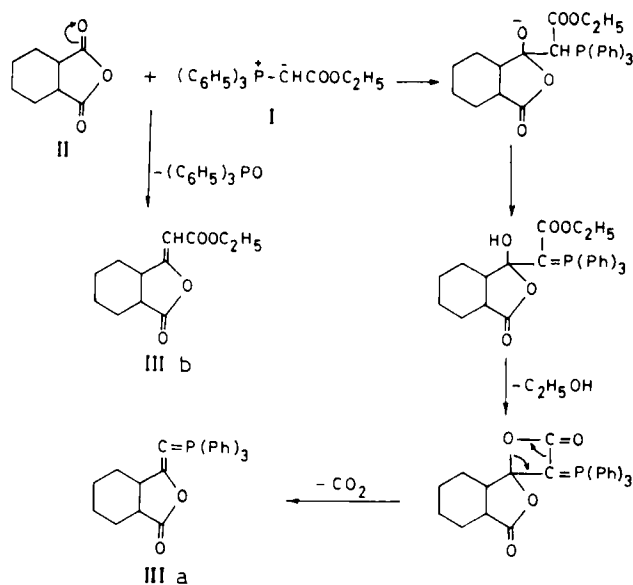


A possible explanation for the course of the reaction of ethoxymethylenetriphenylphosphorane (Ia) with hexahydro-1,3-phthalandione (II) is shown in "Scheme I".

Hexahydro-3-[(triphenylphosphoranylidene)methylene] phthalide (IIIa) can be obtained by addition of one mole ylide (Ia) to hexahydro-1,3-phthalandione (II), affording the stable ylid-phosphorane adduct IIIa, possibly through loss of both ethanol and carbon dioxide.

Although stabilised ylides of type I react with cyclic anhydrides according to the Wittig mechanisms,<sup>6,18</sup> yielding the respective ethylene and TPPO, a different course is observed in the reaction of the same reagent Ia with hexahydro-1,3-phthalandione (II) where addition reaction takes place to form a new type of ylid-phosphorane IIIa.

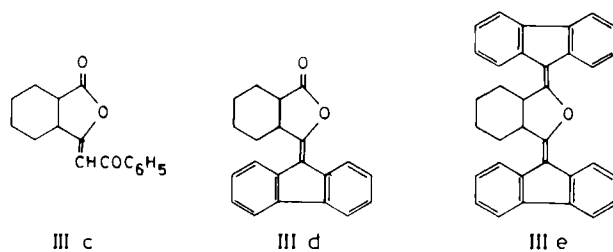
The identity of the other isolated product IIIb was inferred from its correct analytical, mass spectroscopic analyses, and IR spectrum which reveal both the lactone carbonyl absorption band at  $1790\text{ cm}^{-1}$  and the ethylenic ( $C=C$ ) band at  $1630\text{ cm}^{-1}$ .  $^1\text{H}$  NMR spectrum of ethyl 3a,4,5,6,7,7a-hexahydro-3-oxo- $\Delta^{1,\alpha}$ -phthalanacetate (IIIb) showed signals at  $\delta = 1.1$  (3H, ethoxy- $\text{CH}_3$ , t),  $4.19$  (2H,



SCHEME I

ethoxy-CH<sub>2</sub>, q), 1.25–2.03 (m, 8H, methylene protons), 2.6–2.87 (m, 2H, >CH—CH<) and at 5.25 (s, 2H, CHCOOEt).

Benzoylmethylenetriphenylphosphorane Ib reacts with hexahydro-1,3-phthalandione in boiling toluene to give the corresponding ethylenic compound IIIc. Triphenylphosphine oxide (TPPO) was also isolated from the reaction medium. Hexahydro-3-phenacylidene-phthalide IIIc is chromatographically pure and possesses a sharp melting point. Structure IIIc was attested by compatible analytical and mass spectroscopic results (IR, NMR, and MS) (c.f. Experimental).



Fluorenylidetriphenylphosphorane (FTP, Ic) was found to react with hexahydro-1,3-phthalandione (II), in boiling toluene, yielding two coloured products assigned structures III d and III e, respectively. TPPO was also isolated from the reaction medium. Elemental and mass spectral analysis for 1,3-difluorenyl-9-ylidenehexahydrophthalan III e corresponded to an empirical formula of C<sub>34</sub>H<sub>26</sub>O. Its IR spectrum lacked both the carbonyl and lactone-carbonyl absorption bands appearing in the starting anhydride at 1600, and 1790 cm<sup>-1</sup>, respectively, but showed strong bands at 1630, 1635 (C=C, ethylenic), and at

1235  $\text{cm}^{-1}$  (C—O, stretching). The identity of 3-fluoren-9-ylidenehexahydrophthalide IIIId was inferred from analytical, MS, IR, and NMR spectral data (c.f. Experimental).

The findings of the present investigation are of particular interest since they represent a novel application of the Wittig reaction. Moreover, a new method for the preparation of hexahydro-3-[(triphenylphosphoranylidene) methylene] phthalide IIIa by the utilization of Wittig reagents (Ia) is developed.

## EXPERIMENTAL†

All melting points are uncorrected. The toluene used was dried over Na. Carbethoxymethylene-,<sup>19</sup> benzoylmethylene-,<sup>20</sup> and 9-fluorenylidene-triphenylphosphoranes,<sup>21</sup> were prepared according to established procedures. The IR spectra were recorded in KBr, with Perkin-Elmer Infracord Model 137 and Beckman Infracord Model 4220. The  $^1\text{H}$  NMR spectra were run on Varian Spectrophotomers at 60 MHz and/or 90 MHz, using TMS as an internal reference. The  $^{31}\text{P}$  NMR spectra were measured in  $\text{CDCl}_3$  (vs.  $\text{H}_3\text{PO}_4$  as external standard) on Varian CFT 20, 32 MHz Spectrometer. The mass spectra were recorded at 70 eV with Varian MAT 112 mass spectrometer.

*General procedure for the reaction of hexahydro-1,3-phthalandione II with Wittig reagents (Ia-c):* A mixture of 0.01 mole of the anhydride (II) and 0.01 mole of the ylides (I) was heated in 25 ml of dry toluene under reflux with stirring until no more of the starting materials could be detected (TLC). After cooling to room temperature, the reaction mixture was evaporated on a rotavapor under reduced pressure and the residue applied to silica gel column using the eluent stated below. The reaction conditions and yields are also given.

*Compound IIIa:* Hexahydro-3-[(triphenylphosphoranylidene) methylene] phthalide, reaction temperature  $110^\circ$ , reaction time 12 hrs, eluent: ethyl acetate/pet. ether (3:7, V:V) yield 41%, m.p.  $145^\circ$ . Anal. Calcd. for  $\text{C}_{27}\text{H}_{25}\text{PO}_2$  (412.497) C, 78.62; H, 6.11; P, 7.51. Found: C, 78.5; H, 6.15; P, 7.58.  $^{31}\text{P}$  NMR (in  $\text{CDCl}_3$ , vs. 85%  $\text{H}_3\text{PO}_4$ ): +10.74 ppm. (MS): 412  $\text{M}^+$ , 301 ( $\text{M}^+ - \text{C}_7\text{H}_6\text{O}$ ), 262 (TPP).

*Compound IIIb:* Ethyl 3a,4,5,6,7,7a-hexahydro-3-oxo- $\Delta^1$ , $\alpha$ -phthalanacetate, reac. temp.  $110^\circ$ , reac. time 12 hrs, eluent: ethyl acetate/pet. ether (3:7, V:V), yield 45%, m. p.  $155^\circ$ . Anal. Calcd. for  $\text{C}_{12}\text{H}_{16}\text{O}_4$  (224.26) C, 64.27; H, 7.19. Found: C, 64.3; H, 7.2. (MS): 224  $\text{M}^+$ , 179 ( $\text{M}^+ - \text{OC}_2\text{H}_5$ ), 151 ( $\text{M}^+ - \text{COOC}_2\text{H}_5$ ).

*Compound IIIc:* Hexahydro-3-phenacylidene phthalide, react. temp.  $110^\circ$ , reaction time 12 hrs, eluent: chloroform/pet. ether 3:7, V:V) pale yellow crystals m.p.  $135^\circ$ , yield 75%. Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_3$  (256.304) C, 74.97; H, 6.29. Found: C, 74.9; H, 6.3. (MS): 256  $\text{M}^+$ , 188 ( $\text{M}^+ - \text{C}_6\text{H}_5$ ), 160 ( $\text{M}^+ - \text{COC}_6\text{H}_5$ ). IR: bands at 1785 (C=O, lactone), 1635 (C=C, ethylenic)  $^1\text{H}$  NMR: signal at 5.8 ppm (s, 1H,  $\text{CH}$   $\text{COC}_6\text{H}_5$ ).

*Compound IIId:* 3 Fluoren-9-ylidenehexahydrophthalide, react. temp.  $110^\circ$ , reaction time 24 hrs, eluent: ether/pet. ether 1:1, pale yellow crystals m.p.  $188^\circ$  yield 40%. Anal. Calcd. for  $\text{C}_{21}\text{H}_{18}\text{O}_2$  (302.375). C, 83.42; H, 6.00. Found: C, 83.5; H, 6.1%. (MS): 302  $\text{M}^+$ , 138 ( $\text{M}^+ - \text{C}_{13}\text{H}_8$ ). IR: bands at 1780 (C=O, lactone), 1630 (C=C), ethylenic.

*Compound IIIf:* 1,3-Difluoren-9-ylidenehexahydrophthalan. eluent: ether/pet. ether 1:1, yellow crystals, m.p.  $190^\circ$  yield 45% from 0.01 mole of the anhydride II and 0.015 mole of the ylide Ic. Anal. Calcd. for  $\text{C}_{34}\text{H}_{26}\text{O}_2$  (466.582) C, 87.58; H, 5.62. Found: C, 87.6; H, 5.7%. (MS): 466 ( $\text{M}^+$ ), 302 ( $\text{M}^+ - \text{C}_{13}\text{H}_8$ ), 138 ( $\text{M}^+ - \text{C}_{13}\text{H}_{18} - \text{C}_{13}\text{H}_8$ ).

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† Nomenclature is in the line of recent Chemical Abstract Index Names.

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