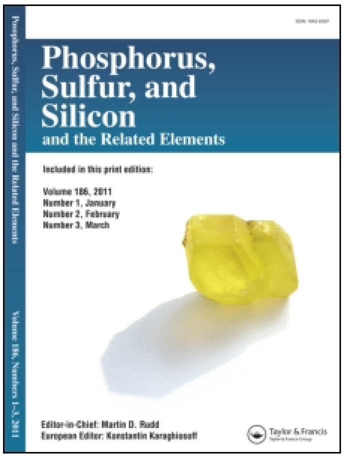

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STUDIES ON PHOSPHONIUM YLIDES-XVI. THE REACTION OF WITTIG REAGENTS WITH 4-CYCLOHEXENE-1,2-DICARBOXYLIC ANHYDRIDE AND ITS N-HYDROXY IMIDE

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STUDIES ON PHOSPHONIUM YLIDES-XVI.† THE REACTION OF WITTIG REAGENTS WITH 4-CYCLOHEXENE-1,2-DICARBOXYLIC ANHYDRIDE AND ITS N-HYDROXY IMIDE

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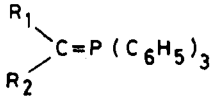
Wittig reagents (**Ia-d**)) react with 4-cyclohexene-1,2-dicarboxylic anhydride (**IIa**) to give the new ethylenic adducts (**IIIa-f**). On the other hand, methylenetriphenylphosphorane (**Id**) reacts with N-hydroxy-4-cyclohexene-1,2-dicarboxy-imide (**IIb**) affording the new spiro ylid-phosphorane adduct (**IV**). Structural reasoning for the new adducts (**IIIa-f**) and (**IV**) was based on compatible analytical and spectral data. A mechanism is proposed to explain the formation of the new ylid-phosphorane adduct (**IV**).

Key words: Wittig reagents (**I**); 4-cyclohexene-1,2-dicarboxylic anhydride and its N-hydroxy-imide (**IIa,b**); ethyl 3a,4,7,7a-tetrahydro-3-oxo-$\Delta^{1,\alpha}$-phthalanacetate (**IIIa**); diethyl 3a,4,7,7a-tetrahydro-$\Delta^{1,3,\alpha}$-1,3-phthalanacetate (**IIIb**); 3a,4,7,7a-tetrahydro-3-phenacylidenephthalide (**IIIc**); 3a,4,7,7a-tetrahydro-1,3-phenacylidenephthalane (**IIId**) and the new spiro-phosphorane adduct (**IV**).

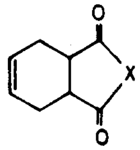
INTRODUCTION

The action of Wittig reagents (**I**) on cyclic anhydrides has been extensively studied.[1–6] However, to the best of our knowledge, there appears no information in the literature regarding the behaviour of these reagents towards 4-cyclohexene-1,2-dicarboxylic anhydride (**IIa**) and its N-hydroxy-imide (**IIb**).



$$R_1R_2C{=}P(C_6H_5)_3$$

I a, $R_1 = H$; $R_2 = COOC_2H_5$
b, $R_1 = H$; $R_2 = COC_6H_5$
c, $R_1 + R_2$ = 9-fluorenylidene
d, $R_1 = H$; $R_2 = COCH_3$



II a, X = O
b, X = NOH

RESULTS AND DISCUSSION

We have found that the reaction of carbethoxymethylene triphenylphosphorane (**Ia**) with 4-cyclohexene-1,2-dicarboxylic anhydride (**IIa**) proceeds in boiling toluene to give two chromatographically pure products assigned structures **IIIa** and **IIIb**,

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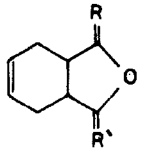
†For part **XV** in this series, cf. A. A. El-Kateb, L. S. Boulos, I. T. Hennawy and H. A. Abdel-Malek, Phosphorus, Sulfur and Silicon (1990) in press.

respectively. Triphenylphosphine oxide (TPPO) was also isolated from the reaction medium.



III a, R = O ; R' = $CHCOOC_2H_5$
b, R = R' = $CHCOOC_2H_5$
c, R = O ; R' = $CHCOC_6H_5$
d, R = R' = $CHCOC_6H_5$
e, R = O ; R' = 9-fluorenylidene
f, R = R' = 9-fluorenylidene

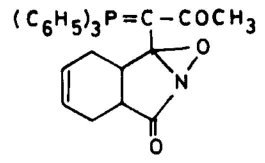
The IR spectrum of ethyl 3a,4,7,7a-tetrahydro-3-oxo-$\Delta^{1,\alpha}$-phthalanacetate **(IIIa)**, taken as an example, revealed the presence of a lactone-carbonyl absorption band appearing[7] at 1785 cm^{-1}. Strong bands at 1740 (C=O, ester), 1630 (C=C, ethylenic) and at 1235 cm^{-1} (C—O, stretching)[7] were also present in the IR spectrum of **IIIa**. In the ^1H-NMR spectrum of **IIIa**, (in $CDCl_3$), signals at δ = 1.18 (3H, ethoxy-CH_3, t); 4.1 (2H, ethoxy-CH_2, q); 6.18 (1H, =CH, s). The four protons of the two chemically equivalent (CH_2) in cyclic structure appear as multiplet centered at 2.3 ppm. The two C$\underline{H}$ protons of the cyclic ring appear as a sextet at 3.1 ppm and the two olefinic protons appear as a sextet centered at δ = 5.9. The mass spectrum of compound **IIIa** gives a promenent ion peak at m/e 222 (M^+, 8%), 177 (M^+-OC_2H_5 30%), 149 (M^+-$COOC_2H_5$, 60%), 105 (M^+-$COOC_2H_5$-CO_2, 90%).

The identity of the other isolated product **IIIb** was inferred from its correct analytical, mass spectroscopic analyses (cf. Experimental) and IR spectrum which lacked both the carbonyl and the lactone-carbonyl absorption bands appearing in the starting anhydride at 1600 and 1790 cm^{-1}, respectively. Moreover, the IR spectrum of **IIIb** showed strong bands at 1630, 1635 (C=C, ethylenic),[7] and at 1235 cm^{-1} (C—O, stretching).

Benzoylmethylenetriphenylphosphorane **(Ib)** and fluorenylidenetriphenylphosphorane **(Ic)** react with **IIa** in boiling toluene to give the corresponding ethylenic compounds **IIIc-f**, respectively. Triphenylphosphine oxide was also isolated from the reaction medium in each case. The structure of the new compounds **IIIc-f** has been established by microanalyses, IR, ^1H-NMR and mass spectra (MS) (cf. Experimental).

Compounds **IIIa-f** are equally obtained, irrespective whether one or two equivalents of the Wittig reagents **Ia-c** were used with respect to one mole equivalent of compound **IIa**.

Next, the reaction of N-hydroxy-4-cyclohexene-1,2-dicarboxyimide **(IIb)** with ylide **Id** was performed in refluxing toluene in 1:1 molar ratio to give adduct **IV**. Triphenylphosphine and/or triphenylphosphine oxide were neither isolated nor identified in the reaction medium by TLC. Compound **IV** is chromatographically pure and possesses a sharp melting point.



IV

Elemental and mass spectral analyses for compound **IV** corresponded to an empirical formula of $C_{29}H_{26}NO_3P$. Its IR spectrum, in KBr, reveals the presence of a strong absorption band at 1710 cm^{-1} corresponding to the carbonyl band of the cyclic imide.[8,9] Moreover, its IR spectrum lacked both the carbonyl (C=O, cyclic imide) and the -OH absorption bands appearing in the starting N-hydroxy-imide at 1770 and 3450 cm^{-1}, respectively. The IR spectrum of adduct **IV** exhibits strong absorption bands at 1680 and 1505 cm^{-1} characteristic for the $\rangle C{=}P$ group absorption,[10] and at 1410 cm^{-1} denoting the $\rangle P{-}C{\equiv}$ (phenyl absorption)[11] and around 1645 cm^{-1} which corresponds to the shifted acyl ylid.[12] The ^{31}P-NMR measurement supports structure **IV**, since it exhibits a sharp signal at $\delta = 14.85$ (vs. H_3PO_4).[13–15] The ^1H-NMR spectrum of **IV** showed signals at $\delta = 2.15$ (3H, $COCH_3$, s), 2.3 (4H, CH_2, m), 3.1 (2H, sextet) and at 5.9 ppm for the two olefinic protons (2H, sextet). The ^1H-NMR spectrum of compound **IV** lacked the hydroxylic proton which appeared at 8.7 ppm in the starting **IIb**. The aromatic protons appeared as multiplet at 7.4–7.7 ppm (15H, m). Actually, the mass spectrum of the spiro-adduct **IV** by Field Ionization Method yielded a prominent ion peak M^+ at 467 which supports structure **IV**.

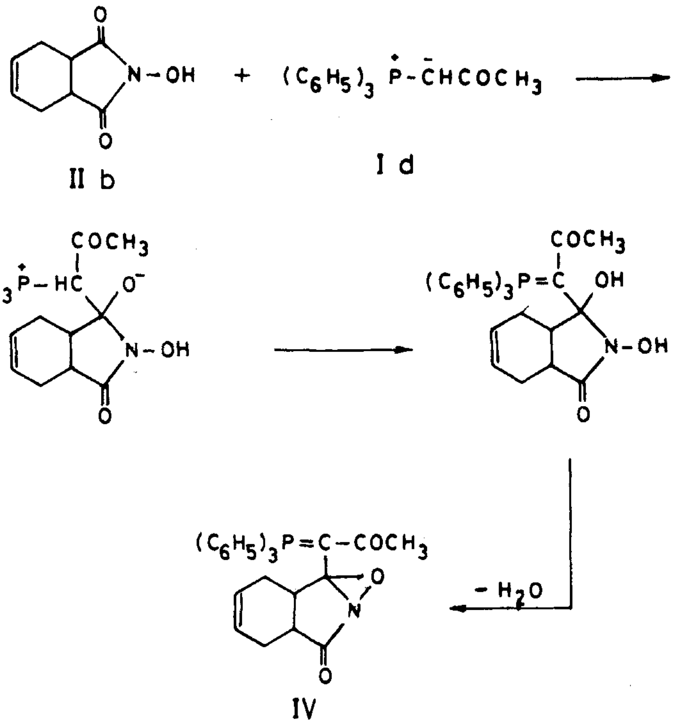
A possible explanation for the course of the reaction of acetylmethylenetriphenylphosphorane (**Id**) with N-hydroxy-4-cyclohexene-1,2-dicarboxy-imide (**IIb**) is shown in "Scheme I." Adduct **IV** can be obtained by addition of one mole ylide (**Id**) to N-hydroxy-4-cyclohexene-1,2-dicarboxy-imide (**IIb**) affording the stable ylid-phosphorane adduct **IV**, possibly through loss of water.

Although stabilized ylides of type I react with tetrahydrophthalic anhydride (**IIa**) according to the Wittig mechanisms,[3,5,6] yielding the respective ethylenes **III** and TPPO, a different course is observed in the reaction of ylid (**Id**) with N-hydroxy-4-cyclohexene-1,2-dicarboxy-imide (**IIb**) where addition reaction takes place to form a new type of ylid-phosphorane **IV**.

This finding, which represents a novel route to **IV**, supplements to the expanded utility of Wittig reagents for the production of new spiro-phosphorane adducts.

EXPERIMENTAL

All melting points are uncorrected. The toluene used was dried over Na. Carb-ethoxymethylene-,[16] benzoylmethylene-,[17] 9-fluorenylidene-,[18] and acetylmethylene-triphenylphosphoranes,[19] 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 ^1H-NMR spectra were run on Varian Spectrophotometers at 60 MHz and/or 90 MHz, using TMS as an internal reference. The ^{31}P-NMR spectra were measured in $CDCl_3$ (vs H_3PO_4 as external standard) on Varian CFT 20, 32 MHz Spectrometer. The mass spectra were run at 70 eV on Kratos MS equipment or Varian Mat 311 A Spectrometer.



" Scheme I "

General procedure for the reaction of cyclohexene-1,2-dicarboxylic anhydride **IIa** *with Wittig reagents* **(Ia-c)**. A mixture of 0.01 mole of anhydride (**IIa**) and 0.01 mole of the ylides (**Ia-c**) 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 eluent stated below. The reaction conditions and yields are also given.

Compound **IIIa**. Ethyl 3a,4,7,7a-tetrahydro-3-oxo-$\Delta^{1,\alpha}$-phthalanacetate, reaction temperature 110°, reaction time 9 hrs, eluent pet-ether/ether (5:15, v:v), yield 41%, m.p. 55°. Anal. Calcd for $C_{12}H_{14}O_4$ (222.244) C, 64.85; H, 6.35. Found: C, 64.71; H, 6.40%. (MS): 222 (M^+).

Compound **IIIb**. Diethyl 3a,4,7,7a-tetrahydro$\Delta^{1,3\alpha}$-1,3-phthalanacetate, reaction temp. 110°, reaction time 9 hrs, eluent pet. ether/ether (5:15, v:v), yield 37%, m.p. 45°. Anal. Calcd for $C_{16}H_{20}O_5$ (292.336) C, 65.73; H, 6.89. Found: C, 65.70; H, 6.90%. ^{1}H-NMR of **IIIb**, 1.35 (6H, ethoxy-CH_3, t), 4.3 ppm (4H, ethoxy-CH_2, q) and 6.05 (2H, =CH, s), (MS): 292 (M^+).

Compound **IIIc**. 3a,4,7,7a-tetrahydro-3-phenacylidenephthalide, reaction temp. 110°, reaction time 9 hrs, eluent chloroform/pet. ether (5:7, v:v), yield 45%, m.p. 110°, Anal Calcd for $C_{16}H_{14}O_3$ (254.288) C, 75.57; H, 5.55. Found: 75.43; H, 5.65%. (MS): 254 (M^+), 177 (M^+-C_6H_5), 149 (M^+-COC_6H_5). IR: bands at 1785 (C=O, lactone), 1635 (C=C, ethylenic). ^{1}H-NMR: signals at 5.9 ppm (1H, $\underline{C}\underline{H}COC_6H_5$).

Compound **IIId**. 3a,4,7,7a-tetrahydro-1,3-phenacylidenephthalane, reaction temp. 110°, reaction time 9 hrs, eluent chloroform. yield 35%, m.p. 130°, Anal. Calcd for $C_{24}H_{20}O_3$ (356.424): C, 80.91; H, 5.65. Found: C, 80.87; H, 5.70%. (MS): 356 (M^+). ^{1}H-NMR: signals at 5.93 ppm (2H, $\underline{C}\underline{H}COC_6H_5$).

Compound **IIIe**. 3-Fluoren-9-ylidene-3a,4,7,7a-tetrahydrophthalide, reaction temp. 110°, reaction time 12 hrs, eluent methylene chloride/pet.ether (4:6, v:v). yield 42%, m.p. 140°, Anal. Calcd for $C_{21}H_{16}O_2$ (300.359): C, 83.97; H, 5.36. Found: C, 83.98; H, 5.37. (MS): 300 (M^+), 136 (M^+-$C_{13}H_8$). IR (bands at 1780) (C=O, lactone), 1630 (C=C, ethylenic).

Compound **IIIf**. 3-Difluoren-9-ylidene-3a,4,7,7a-tetrahydrophthalan, reaction temp. 110°, reaction time 12 hrs, eluent methylene chloride/pet.ether (2:8, v:v), yield 30%, m.p. 78°, Anal. Calcd for: $C_{34}H_{24}O$ (448.566), C, 91.03; H, 5.39. Found: C, 91.1; H, 5.4%. (MS): 448 (M^+), 284 (M^+-$C_{13}H_8$), 120 (M^+-$C_{13}H_8$-$C_{13}H_8$).

Reaction of acetylmethylenetriphenylphosphorane (**Id**) *with N-hydroxy-9-cyclohexene-1,2-dicarboxy-imide* **IIb**. A mixture of **IIb**[20] (0.01 mole) and ylide Id (0.01 mole) was refluxed in dry toluene (30 ml) for 4 hrs. After concentration of the reaction mixture and cooling, the colourless precipitated material was filtered off, washed with benzene and recrystallized from benzene to give **IV** as colourless crystals in 92% yield, m.p. 158°. Anal. Calcd for $C_{29}H_{26}NO_3P$ (467.543) C, 74.49; H, 5.60; N, 2.90; P, 6.63. Found: C, 74.50; H, 5.65; N, 2.90; P, 6.70%. (MS): 467 (M^+).

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