Phosphonium Ylides, V.
Wittig Reaction with 2,3,4(1H)-Quinolinetriones

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Quinolinetriones, Phosphonium Ylides, Wittig Reaction

Quinolinetrione (1a) reacts with phosphonium ylides (2a–c) to yield the corresponding ethylenes (3a–c) together with triphenylphosphine oxide. Treatment of trione (1b) with ylides (2a–b) affords, on the other hand, the cyclobuta (c) quinoline derivatives (4a) and (4b), respectively. Structural assignments are based on analytical and spectroscopic evidence.

Introduction

Although the Wittig reaction with various carbonyl systems has been frequently observed [1–4], very little is known [5] regarding the same reaction with 2,3,4(1H)-quinolinetrione (1a).

R = CH
3a:

R = H; R' = COCH
3b:

R = H; R' = COC
3c:

R = R' = Br

This together with our current interest in the chemistry of phosphonium ylides [6–9], has stimulated us to investigate the behaviour of 1a as well as its N-methyl analog 1b towards a number of Wittig reagents of type 2.

Results and Discussion

We have found that carbomethoxymethylenetriphenylphosphorane (2a) reacts with 2,3,4(1H)-quinolinetrione (1a), in boiling benzene, to give a yellow crystalline compound formulated as methyl (1,4-dihydro-2,4-dioxo-3(2H)-quinolinylidene) acetate (3a) for the following reasons: (a) Elemental analysis and molecular weight determination (MS) for 3a corresponds to C12H21NO4. (b) The IR spectrum of 3a (in KBr), lacks the absorption band at 1720 cm⁻¹ recorded for the middle carbonyl group [10, 11] and 3100 cm⁻¹ shows absorption bands at 1650 cm⁻¹ (C=O, amide) [11] and 3200 cm⁻¹ (NH). The aryl and ester carbonyl absorptions [11, 12] lie together as a broad absorption band at 1695 cm⁻¹. (c) The ¹H NMR spectrum of compound 3a shows singlets at δ = 3.90 (3H), and δ = 6.25 (1H) attributable to the carbomethoxy —CH₃ protons and the exocyclic methine proton, respectively [13]. The exchangeable (D₂O) proton (NH) appears as broad singlet at δ = 7.80. The aromatic protons fall in the region δ = 7.10–7.66 as a multiplet. Similarly, the reaction of benzoylmethylenetriphenylphosphorane (2b) and dibromomethylenetriphenylphosphorane (2c) with trione (1a) affords 3-(2-oxo-2-phenylethylidene)-2,4-(1H, 3H) quinolinedione (3b) and 3-(dibromomethylene)-2,4-(1H, 3H) quinolinedione (3c), respectively (cf. Experimental). Triphenylphosphine oxide was also isolated and identified in each case.

The reaction of phosphonium ylides (2a) and (2b) with 1-methyl-2,3,4-quinolinetrione (1b) was also investigated. In benzene, the reaction of 2a with trione 1b was almost complete at room temperature after 24 h. The colourless crystalline compound thus formed was assigned structure 4a as inferred from the following evidences: (a) Elemental analysis and molecular weight determination (MS) confirmed a molecular formula of C16H15NO5. (b) Its IR spectrum, in KBr, revealed the absence of absorption
bands both at 1720 cm$^{-1}$ and 1690 cm$^{-1}$ recorded for the carbonyl groups at positions 3 and 4 in the starting trione (1b). The strong absorption band around 1650 cm$^{-1}$ (C=O, amide) recorded for the amide grouping in trione (1b), is still present in the IR spectrum of compound 4a. Structure 4a is, therefore, likely than 5a to designate the reaction product of phosphonium ylide 2a with trione 1b. Structure 4a finds also support from the inspection of its $^{1}$H NMR spectrum which shows the methine protons (R=H) as two doublets (J$_{HH}$ = 9 Hz) due to the vicinal coupling [14] at $\delta = 7.38$ and $\delta = 7.43$. Structure 4a accommodates these data more adequately, whereas formula like 5a predicts two singlets [14] for the two methine protons. Further, compounds of structure 5 are expected to be deeply colored*. Similarly, the reaction of ylide (2b) with trione (1b), affords a colourless crystalline compound formulated as 1,2-dibenzoxy-2,4-dihydro-4-methylcyclobuta(c)-quinoline-3(1H)-one (4b), since its $^{1}$H NMR spectrum shows the methine protons as two doublets at $\delta = 6.27$ and $\delta = 6.56$ (cf. Experimental).

The results of the present investigation allow certain interesting conclusions to be drawn. While quinolinetrione (1a) reacts with phosphonium ylides (2) to yield the corresponding methylenes (3a–c), a different behaviour is noted with its N-methyl analog 1b. This latter gives with the same reagents the respective cyclobuta(c)quinoline derivatives (4). Worthy to mention is that trione 1a yields only the corresponding monomethylene (3a–c) even when it allowed to react with two equivalents of the ylide reagent. This is equally true, when the formed methylene compound, e.g. 3a was further reacted with a mole of the Wittig ylide reagent 2a under similar conditions. That the reaction of trione 1a with ylides 2a–c terminates at the formation of monomethylene (3a–c), may be ascribed to the possible existance of structure like 3a which does not allow further reactions with Wittig reagent (vide infra).

**Experimental**

All mp’s were uncorrected. The benzene (thiophene-free) was used as dried (Na). The IR spectra were recorded, Kbr, with Perkin Elmer Infracord Model 137 and Beckman Infracord Model 4220. The $^{1}$H NMR spectra were run on Varian Spectrophotometers at 60 MHz and or 90 MHz, using TMS as an internal reference. The mass spectra were recorded at 70 eV with a Varian MAT 112 Mass Spectrometer.

*Methyl(1,4-dihydro-2,4-dioxo-3(2H)-quinolinylidene) acetate (3a)*

To a suspension of trione (1a) [15] (0.17 g, 0.001 mol) in dry benzene (10 ml), was added a solution of ylide 2a [16] (0.33 g, 0.001 mol) in the same solvent (10 ml) and the reaction mixture was refluxed for 6 h. After cooling, the solid product that formed was collected (0.2 g, 86%) recrystallized from chloroform-petroleum ether (b.r. 40–60 °C) to give 3a as yellow crystals m.p. 265 °C.

C$_{12}$H$_{9}$NO$_{4}$


From the benzene filtrate triphenylphosphine oxide was isolated and identified (m.p. and mixed m.p.) [17].

Similarly, the reaction of trione 1a with ylide 2b [18] afforded 3-(2-oxo-2-phenylethylidene)-2,4(1H,3H)-quinolinedione (3b). Compound 3b gave yellow crystals (90%) from chloroform, m.p. 315 °C.

C$_{17}$H$_{11}$NO$_{3}$

Calcd C 73.64 H 4.00 N 5.05 Mol.Wt. 277. Found C 73.25 H 4.12 N 5.30 Mol.Wt. 277.

IR: Bands at 1650 cm$^{-1}$ (C=O, amide), 3160 cm$^{-1}$ (NH). – $^{1}$H NMR (DMSO-d$_{6}$): Signals at $\delta = 5.90$ (s, 1H) and $\delta = 8.25$ (m, 9H).

* The name of compounds described in this work are in line of the current CA index names.

* Quinolinetriones 1 are deep red in color.
3-(Dibromomethylene)-2,4-(1\(H\),3\(H\))quinolinedione (3c)

Triphenylphosphine (0.5 g, 0.1 mol) was added to a well stirred solution of carbontetrabromide (0.3 g, 0.05 ml) in dry methylene chloride (3 ml). When the solution becomes orange (i.e. the dibromomethylene-triphenylphosphorane is formed) [19], trione (1a) (0.17 g, 0.001 mol) was added and the mixture was refluxed on water bath for 4 h. After evaporation of the volatile material, the yellow residual substance was recrystallized from chloroform-petroleum ether (b.r. 40–60 °C) to yield as yellow crystals in (90%) yield, m.p. 110 °C.

\[ C_{10}H_{12}NBr_2O_2 \]
Calcd C36.29 H1.52 N4.23 Mol.Wt.331, Found C36.30 H1.63 N4.30 Mol.Wt.331.

IR: Bands at 1650 cm\(^{-1}\) (C=O, amide), 1680 cm\(^{-1}\) (C=O, at position 4), and 3225 (NH).

Similarly, the reaction of trione 1a (0.01 mol) with ylides 2a–c (0.02 mol), afforded the same ethylene compounds 3a–c in almost quantitative yield (mixture m.p. with no depression).

Reaction of compound 3a with carbomethoxymethylenetriphenylphosphorane (2a)

A mixture of 3a (0.001 mol) and ylide 2a (0.001 mol) in benzene (25 ml) was refluxed for 6 h. After cooling, the substance that separated was collected (97%) and recrystallized from chloroform-petroleum ether (40–60 °C) to give yellow crystals proved to be compound 3a (m.p. and mixed m.p. with no depression). From the benzene filtrate ylide 2a was isolated in an almost quantitative yield (mixture m.p. with no depression).

Under similar conditions, 3b and 3c were recovered almost quantitatively when allowed to react with ylides 2b and 2c, respectively.

Dimethyl-1,2,3,4-tetrahydro-4-methyl-3-oxocyclobuta(c)-quinoline-1,2-dicarboxylate (4a)

To a suspension of trione 1b [20] (1.19 g, 0.001 mol), in dry benzene (15 ml), was added ylide 2a (0.66 g, 0.002 mol) in benzene (10 ml) and the reaction mixture was kept at room temperature for 24 h. The colourless precipitated material was filtered off, crystallized from chloroform to give 4a as colourless crystals m.p. 250 °C (85%).

\[ C_{16}H_{19}NO_3 \]
Calcd C63.63 H5.05 N4.65 Mol.Wt.301, Found C63.63 H5.10 N4.59 Mol.Wt.301.

From the benzene filtrate triphenylphosphine oxide was also isolated and identified (m.p. and mixed m.p.) [17].

In the same manner, the reaction of trione 1b with ylide 2b afforded colourless crystals (yield 95%) m.p. 330 °C from chloroform proved to be 1,2-dibenzo-2,4-dihydro-4-methylcyclobuta(c)quinoline-3(1\(H\))one (4b).