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Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 63–66

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photosensitized (2+2) cycloadditions of 2,3-dimethylmaleic anhydride to 3,4-dimethyl-1-phenylphosphole

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Received 13 May 2003; received in revised form 10 June 2003; accepted 18 June 2003

Abstract

As a continuation of studies carried out in this laboratory on the properties of five-membered heterocycles such as furan, thiophene, selenophene and pyrrole as substrates for excited carbonyl compounds and for methylmaleic anhydride derivatives in photosensitized reactions, a less common substrate namely 3,4-dimethyl-1-phenylphosphole was chosen this time. The results obtained, a (2+2) cycloadduct formed between 2,3-dimethylmaleic anhydride and the heterocycle indicate that phosphole derivatives could be used as well, to initiate a new series of adducts of synthetic interest.

Keywords: 3,4-Dimethyl-1-phenylphosphole; 2,3-Dimethylmaleic anhydride; Oxetane; Photocycloaddition; (2+2) Cycloadduct

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1. Introduction

Direct irradiation of ketones in the presence of heterocycles such as furan [1–3], pyrrole [4], thiophene [5] and selenophene [6] derivatives to yield oxetanes as well as photosensitized cycloaddition reactions between maleic anhydride derivatives and the five-membered heterocycles mentioned above to yield cyclobutane containing adducts has been an important field of research in this laboratory. Considering the synthetic aspects [7,8] as well as the photochemical kinetics [9,10] approach to these reactions it has been possible to have a well round knowledge of these processes. Nevertheless, since in contrast to the common heterocycles mentioned above which are routinely used in the organic chemistry laboratory, phosphole and its derivatives are rather uncommon in the sense that they are not commercially available and their syntheses are cumbersome perhaps due to the nature of phosphorus as the heteroatom, all this contributes to make it an interesting substrate and deserves to be presented as such. That will be done in the discussion for the sake of coherence in the text.

It is important at this point to mention that Mathey and co-workers [11] and Li et al. [12] have reported intramolecular $[2 + 2]$ and $[4 + 2]$ photodimerizations of phospholes albeit as ligands in coordination complexes when exposed to sunlight.

Anyhow, interest aroused to attempt the direct irradiation of benzophenone in the presence of 3,4-dimethyl-1-phenylphosphole and also the photosensitized cycloaddition of 2,3-dimethylmaleic anhydride to the just mentioned heterocycle. The former was not successful, the latter yielded a $(2 + 2)$ adduct which was identified by spectroscopic methods. This result stimulates further investigation on the synthesis of other adducts to start a new family of compounds as has been done before with the other heterocycles, as well as attaining the photoadditions with phospholes free of the coordination spheres of transition metal carbonyl complexes.

2. Experimental details

2.1. Chemicals

Benzophenone and 2,3-dimethylmaleic anhydride were purchased from Aldrich (Steinheim, Germany). All analytical or HPLC grade solvents were obtained from Merck (Darmstadt, Germany). The preparation of 3,4-dimethyl-1-phenylphosphole was carried out following the procedure of

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doi:10.1016/S1010-6030(03)00292-2

Breque et al. [13]. The product was identical to that synthesized by Breque et al. [13].

2.2. Photochemical reactions

A solution of 4.8 g (0.01 mol) of 3,4-dimethyl-1-phenylphosphole, 1.8 g (0.01 mol) of benzophenone and 1.26 g (0.01 mol) of 2,3-dimethylmaleic anhydride in 200 ml of dry benzene was placed in a 250 ml reaction vessel. A quartz immersion well containing a Pyrex filter sleeve and a Hanovia 250 W lamp was fitted into the reaction vessel. The lamp was cooled at 10 °C (Colora Kälte thermostat) and nitrogen was bubbled through the solution before and during the irradiation. At the end of 8 h (optimum time on the basis of product isolated), the irradiation was stopped and the liquid portion was evaporated under reduced pressure (14 Torr) at room temperature. The residue was purified by column chromatography (silica gel) using dichloromethane–methanol mixture (1:1 (v/v)) as elutant and the photoproduct was isolated by preparative TLC chromatography (silica gel, Merck 60 F_{254}) or alternatively by preparative high-performance liquid chromatograph (HPLC). The high-performance liquid chromatograph (HPLC) used in all experiments described herein was a Waters Delta Prep 4000 equipped with a 3.9 mm × 300 mm Porasil 10 μm column using a CH_2Cl_2–MeOH binary solvent system. The isolated product **7** was analyzed by ^{1}H-NMR and ^{13}C-NMR spectroscopy (Bruker Aspect 3000, 300 MHz), FT IR (Nicolet DX V 5.07) and GC–MS (HP-5890 (series II)–HP-5972, DB5-column, 25 m).

The experimental procedure for the direct irradiation of benzophenone in the presence of 3,4-dimethyl-1-phenylphosphole was as follow: a solution of 1.8 g (0.01 mol) of benzophenone and 4.8 g (0.01 mol) 3,4-dimethyl-1-phenylphosphole in 200 ml of dry benzene was irradiated in the photoreactor described for the previous experiment. After 8 h irradiation, the solvent was evaporated under reduced pressure (14 Torr) and the work up of the residue was carried out as in the previous experiment. The isolated photoproduct was not the expected oxetane; instead a polymeric compound was formed.

3. Results

3.1. Photocycloaddition products: (2 + 2) adduct **7**

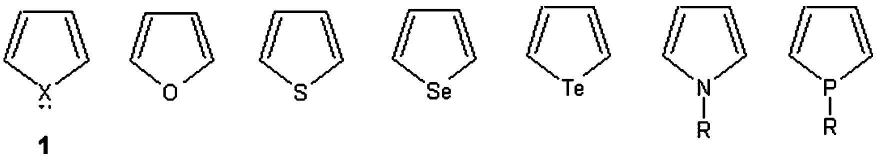
Yield: 80%. d.p.: 206–208 °C, $R_f = 0.40$. IR (KBr; cm^{-1}): $\upsilon = 3095, 3075, 2960, 1700, 1392, 1375, 850$. ^{1}H NMR ($CD_3OD$, 300 MHz): $\delta = 7.14$ (m, 2H, aromatic-H), 6.95 (m, 3H, aromatic-H), 5.96 (q, 1H, $J = 1.3$ Hz, P–CH=C), 4.59 (s, 1H, P–CH–C), 1.78 (d, 3H, $J = 1.3$ Hz, –C=C–CH_3), 1.41 (s, 3H, –C–C–CH_3), 1.37 and 1.34 (s, 3H each, maleic ring–CH_3). ^{13}C NMR (CD_3OD, 100 MHz): $\delta =$ 173 (s, C=O), 172 (s, C=O), 134 (s, aromatic-C–P), 132 (d, 2C, aromatic-CH), 131 (s, –CH=$\underline{C}$–CH_3), 129 (d, P–$\underline{C}$H=C), 124 (d, 2C, aromatic-CH), 120 (d, aromatic-CH), 67 (d, P–$\underline{C}$H–C), 58 (s, CH–$\underline{C}$–CH_3), 56 (s, maleic ring–$\underline{C}$–CH_3), 50 (s, maleic ring–$\underline{C}$–CH_3), 20 (q, CH=C–$\underline{C}H_3$), 14 (q, CH–C–$\underline{C}H_3$), 10 (q, maleic ring–$\underline{C}H_3$), 8 (q, maleic ring–$\underline{C}H_3$). MS: m/z (%): retro Diels–Alder 188 ($C_{12}H_{13}P$, 10), 127 (90), 126 ($C_6H_6O_3$, 40), 149 (25), 108 (80), 83 (60), 67 (100), 52 (10), 39 (60).

4. Discussions

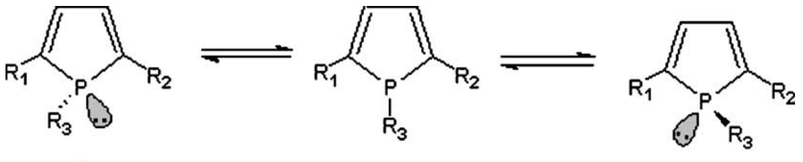
First of all it is interesting to note that in group six of the periodic table the series of compounds (**1**, X = O, S, Se and Te, Scheme 1) and their methyl derivatives have been studied in this laboratory as substrates both for excited carbonyl compounds under direct irradiation with UV light and for maleic anhydride derivatives in benzophenone photosensitized reactions. In addition to the synthetic work, photochemical kinetics haven been used to elucidate the mechanism of the reaction.

In group five of the periodic table, the compound **1**, X= N–R has been partially studied and now hopefully compounds **1**, X = P–R starts a new series of compounds beginning with above mentioned derivative, 3,4-dimethyl-1-phosphole (**5**).

On the other hand, it is important to describe phosphole to understand its chemical behavior [14]. Phosphole is a five-membered heterocycle where the lone pair of electrons on phosphorus exhibits a pyramidal configuration and as a result the third valence of the heteroatom is not coplanar with the ring. Therefore, phospholes may not be aromatic and presumably this property facilitates the (2 + 2) cycloaddition reactions since the two double bonds in the ring are not interacting with each other as much as they would if the compound were aromatic. However, the fact that phospholes have been shown by variable temperature NMR determinations to require less energy for interconversion of the isomer **2** (Scheme 2) to the isomer **4** than would for a saturated analogue may indicate that the SP^2 hybrid transition state **3** is aromatic. Nevertheless, this character is probably very weak.

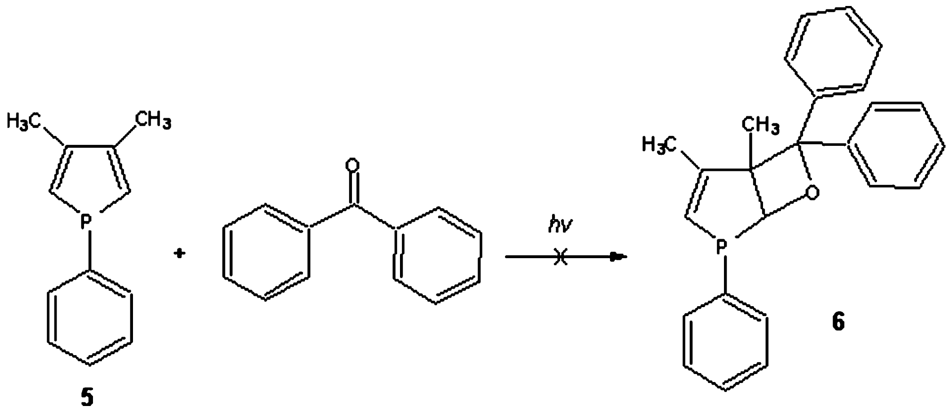


Scheme 1.



2 **3** **4**

Scheme 2.



5 **6**

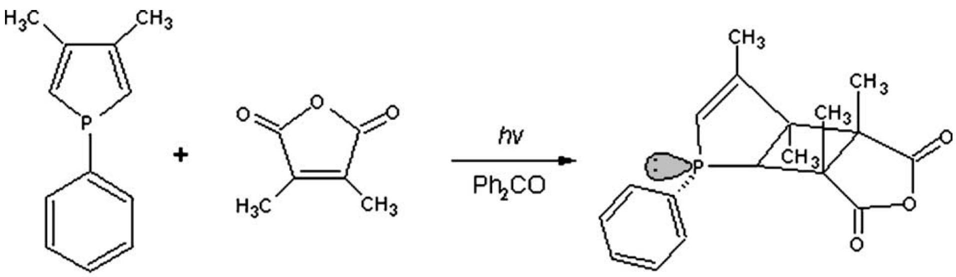
Scheme 3.

Actually, for a long time controversial arguments supporting and opposing delocalization have been going on. However, the most accepted viewpoint is that the P atom in simple phospholes retains its pyramidal character [15]. Recent investigations on planarization of phospholes has shown that significant flattening of the pyramid is attained by substituting very bulky groups, such as 2,4,6-$But_3C_6H_2$ on the P atom with the concomitant delocalization [16].

Irradiation of **5** in the presence of benzophenone was carried out for different lengths of time reaching in one of the experiments up to 70 h, different solvents, including hexane, benzene, dichloromethane, methanol, were used as well as different temperatures but it was not possible to isolate the expected oxetane **6**. This result is not entirely discouraging for it is possible that substituting the methyl groups in other positions in the ring or substituting only one methyl group the oxetane may be obtained. There are examples in our research where 3,4-dimethyl substitution does not favor oxetane formation; that is the case of 3,4-dimethylthiophene [17] and 3,4-dimethylselenophene [18]; the reason for this behavior is not very obvious because it has been observed that in methyl-substituted furans, thiophenes and selenophenes the excited carbonyl compound reacts preferably with the double bond with a higher degree of substitution as in the case of 2,3-dimethylfuran and 2,3-dimethylthiophene; therefore the argument in favor of steric hindrance is not valid. Scheme 3.

Irradiation of 2,3-dimethylmaleic anhydride in the presence of 3,4-dimethyl-1-phenylphosphole using benzophenone as a photosensitizer yielded as expected the (2 + 2) cycloadduct **7** (80% yield) which was isolated and identified by spectroscopic methods.

Regarding the stereochemistry of adduct **7**, it can be described as *anti* as depicted in Scheme 4 on the basis of an



5 **7**

Scheme 4.

analogy to several other adducts with the carbon skeleton whose stereochemistry was elucidated by means of homonuclear [19] ^{1}H {^{1}H} and heteronuclear ^{1}H {^{13}C}NOE [20].

5. Conclusions

After the isolation and characterization of compound **7** a cycloadduct from 3,4-dimethyl-1-phenylphosphole and 2,3-dimethylmaleic anhydride, other derivatives of phosphole will be tested as substrates both for excited carbonyl compounds and maleic anhydride derivatives in photosensitized reactions. It is expected that substitution of the methyl groups in positions in the ring other than 3 and 4 will favor formation of oxetanes.

Acknowledgements

This research was supported by a grant from the German Embassy in Venezuela and Fundación Polar.

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