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The Reaction of Vicinal Triketones with Cumulative Phosphorus Ylides. Synthesis of Phosphoranylidenecyclobutanes[1]

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ABSTRACT

*1,2,3-Indantrione (**1**), diphenylpropanetrione (**6**), and alloxan (**8**) can be converted by reactions with ketenylidene-(**2a**) and thioketenylidenetriphenylphosphorane (**2b**) into phosphoranylidenecyclobutanes (**5**, **7**, and **9**). The structures of the new cyclic compounds were confirmed on the basis of elemental analysis and spectral studies.*

INTRODUCTION

Phosphacumulenes (**2a** and **b**) are some of the most important phosphorane compounds, and they have been used recently by Bestmann and co-workers [2] in organic syntheses. However, no information is available about the reaction of these reagents with vicinal triketones. Therefore, it was of interest to study the reactions of the cumulative phosphorus ylides, ketenylidene- (**2a**), and thioketenylidenetriphenylphosphorane (**2b**) with some vicinal triketones, namely, 1,2,3-indantrione (**1**), diphenylpropanetrione (**6**), and alloxan (**8**) and to compare the reactivities of these reactive cumulative ylides (**2**) with those of known stabilized ylides (**10**) toward the aforementioned vicinal triones.

RESULTS AND DISCUSSION

When the red 1,2,3-indantrione (**1**) was treated with one equivalent of ketenylidenetriphenylphosphorane (**2a**) in THF at room temperature for 1 hour, the corresponding brownish phosphoranylidenecyclobutane derivative (**5a**), triphenylphosphine oxide, and some unchanged 1,2,3-indantrione (**1**) were isolated. Carrying out the reaction using two moles of the phosphorane (**2a**) instead of one led to the formation of **5a** in good yield. The structure of compound **5a** was verified through elemental analysis and spectroscopic results. The IR spectrum showed bands at 1695 cm^{-1} (C=O, indandione) [3], 1630 (C=O, cyclobutandione) [4], and 1440 (P-phenyl) [5]. The ^{31}P NMR shift recorded for the product **5a** was $\delta = +20.7$. In the mass spectra, the $m/e = 486$ (M^+).

The reaction of 1,2,3-indantrione (**1**), with thioketenylidenetriphenylphosphorane (**2b**), is of particular interest. When **1** was allowed to react with **2b** in THF at ambient temperature for 2 hours, the corresponding dithioxophosphoranylidenecyclobutane (**5b**) and triphenylphosphine oxide were obtained. The structure of **5b** was elucidated by a study of its IR, ^{31}P NMR, and mass spectra as well as by elemental analyses. The IR spectrum of **5b** showed bands at 1705, 1440, and 1250 cm^{-1} characteristic of C=O (indandione), P-phenyl, and C=S, respectively. In the MS of **5b** the $m/e = 518$ (M^+) and the ylidic phosphorus gave rise to a signal at $\delta = +14$ in its ^{31}P NMR spectrum. This value lies in the known range of phosphoranylidene shifts [6].

When diphenylpropanetrione (**6**) was allowed to react with the phosphacumulene **2a** or **2b**, under the same conditions, the new phosphoranyli-

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[1] Dedicated to Prof. Hans Jürgen Bestmann on the occasion of his sixty-seventh birthday.

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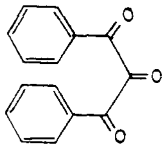
denecyclobutanes **7a** and **7b**, respectively, were isolated.

The reactive phosphacumulene ylides **2a** and **2b** reacted with alloxan (**8**) to give the corresponding cyclobutanedione **9a** and the dithioxocyclobutane **9b**, respectively.



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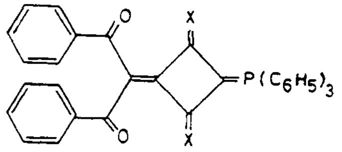
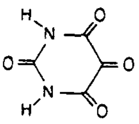


7 a, X = O
b, X = S



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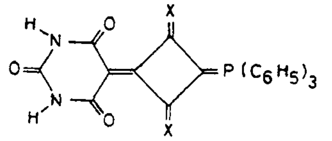


9 a, X = O
b, X = S

It can be rationalized that the formation of phosphoranylidenecyclobutanes (**5**) by the reaction of the phosphacumulene ylides (**2**) with the trione (**1**) occurs by [2 + 2]-cycloaddition of the reactive carbonyl group [3,7] in the trione to the ylidic C–P of the phosphacumulenes to give the oxaphosphetanes (**3**) as intermediates [8]. Triphenylphosphine oxide is eliminated with the formation of the unstable ketenes (**4**) [9]. The intermediates (**4**) add a second molecule of the reactive ylide (**2**) by a [2 + 2]-cycloaddition to give the phosphoranylidenecyclobutanes (**5**). On the other hand, it was found by us [7] that stabilized 2-oxoalkylidenephosphoranes (**10**) behave differently toward the trione (**1**). Wittig reactions give the reactive intermediates (**11**), and then dimerizations afford the spiro compounds (**12**). These reactions represent a convenient preparation of the cyclobutandiones (**5a**, **7a**, and **9a**), dithioxocyclobutanes (**5b**, **7b**, and **9b**) and the six-membered dihydroaromatic ring compounds (**12a** and **b**) (Scheme 1).

EXPERIMENTAL

Melting points are uncorrected. Solvents were dried and distilled using common methods. Reactions were carried out under a nitrogen atmosphere. Analyses were performed by the National Research Centre Microlab. IR spectra were obtained using a Carl Zeiss Infracord Spectrometer Model UR 10. ^{31}P NMR spectra were recorded on a spectrometer JNM-PS 100 Jeol Tokio, in $CDCl_3$, using H_3PO_4 as external standard. Mass spectra were obtained on a Varian MAT CH-4B instrument.

The Reaction of Vicinal Triketones (**1**, **6**, *and* **8**) *with Cumulative Phosphorus Ylides* (**2a** *and* **b**). *Preparation of the new Phosphoranylidenecyclobutane Derivatives* (**5**, **7**, *and* **9**)

General Procedure. To a solution of 1,2,3-indantrione (**1**) [10], diphenylpropanetrione (**6**) [11], or dry alloxan (**8**) [12] (0.01 mol) in 20 mL of tetrahydrofuran was added dropwise, with stirring at room temperature, a solution of the ketenylidene- (**2a**) [13] or thioketenylidenetriphenylphosphorane (**2b**) [13] (0.02 mol) in 30 mL of THF. The reaction mixture was left for 1 hour when **2a** was used and for two hours with **2b**. After THF had been distilled off under reduced pressure, the residue was dissolved in 20 mL of chloroform, followed by addition of 20 mL of *n*-hexane, and the new solution was left overnight in the refrigerator. The precipitate that had formed was filtered off and crystallized from an appropriate solvent.

The chloroform/*n*-hexane filtrate was chromatographed on alumina, affording triphenylphosphine oxide, mp and mixed mp 151°C [14].

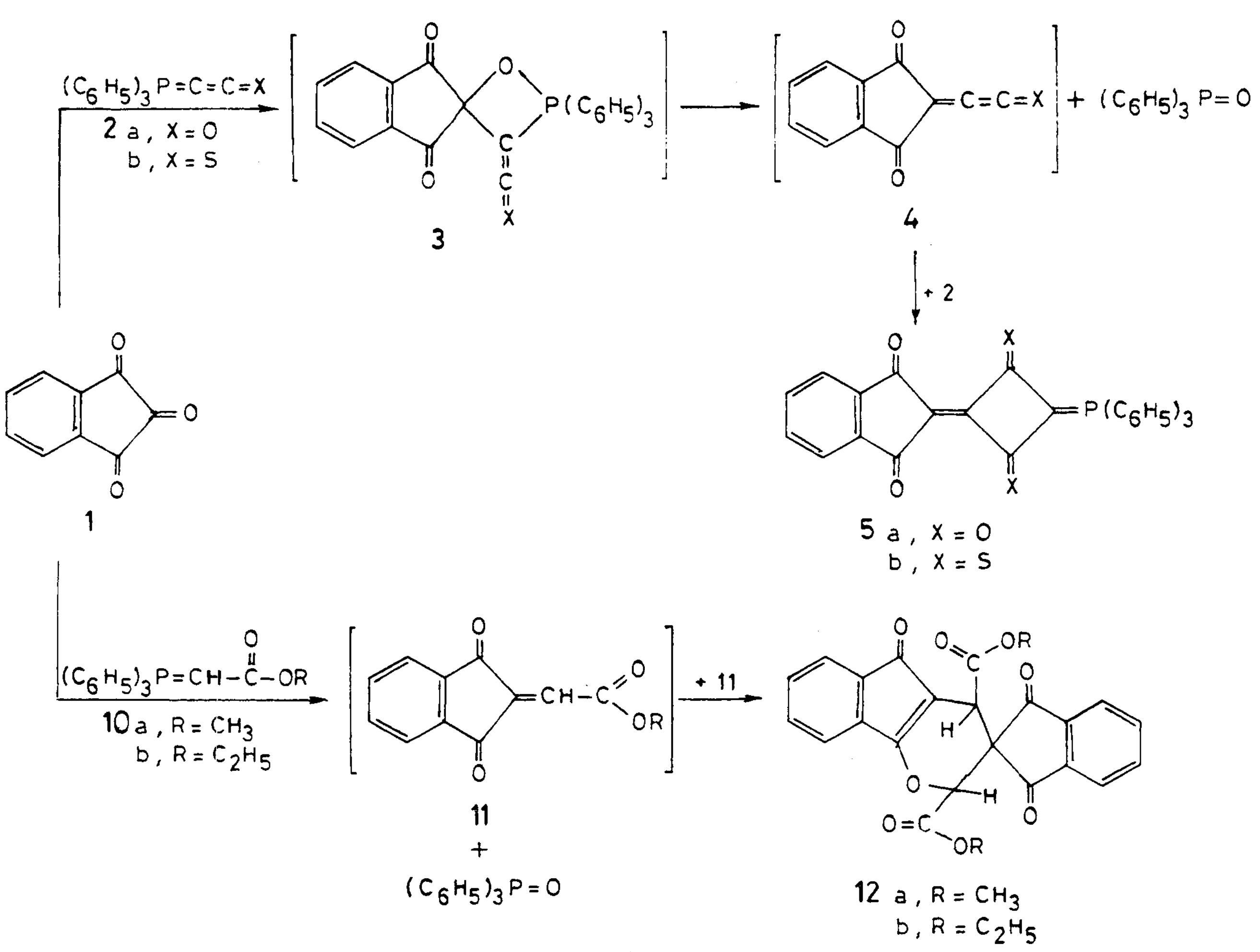
When the reaction was performed using equimolar amounts of the cumulative phosphorus ylides (**2a** and **b**) and the vicinal triketones (**1**, **6**, and **8**), the corresponding phosphoranylidenecyclobutane derivatives (**5**, **7**, and **9**) and triphenylphosphine oxide were obtained together with some unchanged vicinal triketone.

The phosphoranylidenecyclobutanedione derivative (**5a**) was obtained by the reaction of 1,2,3-indantrione (**1**) (0.01 mol) with the ketenylidene triphenyl phosphorane (**2a**) (0.02 mol) as brown crystals, mp 208°C (from chloroform/light petroleum) (70%). Anal. calcd for $C_{31}H_{19}O_4P$: C, 76.53; H, 3.93; P, 6.36. Found: C, 76.31; H, 4.01; P, 6.06.

The dithioxophosphoranylidenecyclobutane (**5b**) was isolated from the reaction mixture of 1,2,3-indantrione (**1**) (0.01 mol) and thioketenylidenetriphenylphosphorane (**2b**) (0.02 mol) as brown crystals, mp 180°C from chloroform/light petroleum (66%). Anal. calcd for $C_{31}H_{19}O_2PS_2$: C, 71.79; H, 3.69; P, 5.97; S, 12.38. Found: C, 71.52; H, 3.61; P, 5.70; S, 12.07.

The phosphoranyldienecyclobutanedione derivative (**7a**) was similarly obtained (65%) by the reaction of diphenylpropanetrione (**6**) (0.01 mol) with the phosphorane (**2a**) (0.02 mol). Compound (**7a**) was crystallized from benzene/light petroleum as yellow crystals, mp 100°C. Anal. calcd for $C_{37}H_{25}O_4P$: C, 78.13; H, 4.46; P, 5.48. Found: C, 78.03; H, 4.25; P, 5.83. IR: 1640 cm^{-1} (C=O), 1440 (P-phenyl). ^{31}P NMR $\delta = +21.7$.

The dithioxocyclobutane (**7b**) was obtained by the reaction of diphenylpropanetrione (**6**) (0.01 mol) with the thiophosphorane (**2b**) (0.02 mol) as yellow crystals, mp 180°C. (from chloroform/light petro-



SCHEME 1

leum). Anal. calcd for $C_{37}H_{25}O_2PS_2$: C, 74, 47; H, 4.22; S, 10.74; P, 5.19. Found: C, 74.21; H, 4.12; S, 10.40; P, 5.00, IR: 1650 cm^{-1} (C=O); 1440 (P-phenyl), 1240 (C=S). ^{31}P NMR $\delta = +14$.

Under similar conditions, the phosphoranylidene derivative (**9a**) was obtained by the reaction of dry alloxan (**8**) (0.01 mol) with the phosphorane (**2a**) (0.02 mol) as pale brown crystals, mp 200°C from chloroform/light petroleum (72%). Anal. calcd for $C_{26}H_{17}N_2O_5P$: C, 66.66; H, 3.65; N, 5.98; P, 6.61. Found: C, 66.56; H, 3.45; N, 5.58; P, 6.60. IR: 3200 cm^{-1} (NH), 1690, 1630 (C=O), 1440 (P-phenyl). ^{31}P NMR $\delta = +21.5$.

The dithioxocyclobutane (**9b**) was isolated from the reaction mixture of dry alloxan (**8**) (0.01 mol) and the thiophosphorane (**2b**) (0.02 mol) as brown crystals, mp 210°C from chloroform/light petroleum (69%). Anal. calcd for $C_{26}H_{17}N_2O_3S_2P$: C, 62.09; H, 3.31; N, 5.48; S, 12.61; P, 6.09. Found: C, 62.11; H, 3.31; N, 5.49; S, 12.63; P, 6.07. IR: 3200 cm^{-1} (NH), 1690, 1630 (C=O), 1440 (P-phenyl), 1240 (C=S). ^{31}P NMR $\delta = +15.5$.

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