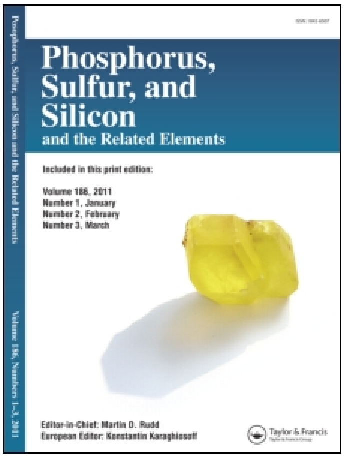

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REACTIONS WITH PHOSPHACUMULENES: SYNTHESIS OF PYRAN DERIVATIVES FROM THE REACTION OF *N*-PHENYLIMINOKETENYLIDENE TRIPHENYL-PHOSPHORANE WITH α,β-UNSATURATED CARBONYL COMPOUNDS

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REACTIONS WITH PHOSPHACUMULENES: SYNTHESIS OF PYRAN DERIVATIVES FROM THE REACTION OF *N*-PHENYLIMINOKETENYLIDENE TRIPHENYLPHOSPHORANE WITH α,β-UNSATURATED CARBONYL COMPOUNDS

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Dedicated to Professor Dr. Hans Jürgen Bestmann on the occasion of his 60th birthday

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2-Benzylidene-1,3-indanedione (**2**), 4-benzylidene-1,2-diphenyl-3,5-pyrazolidenedione (**4**) and/or 5-benzylidenebarbituric acid (**6**) can be converted by reaction with *N*-phenyliminoketenylidene triphenylphosphorane (**1**) into pyransubstituted phosphoranes **3**, **5** and **7**. The structure of the new cyclic imino-phosphoranes **3**, **5** and **7** was confirmed on the basis of elemental analysis and spectral studies. Moreover, when Wittig reaction was carried out on the pyran compound **7**, using p-nitrobenzaldehyde, the new olefin **8** was isolated.

INTRODUCTION

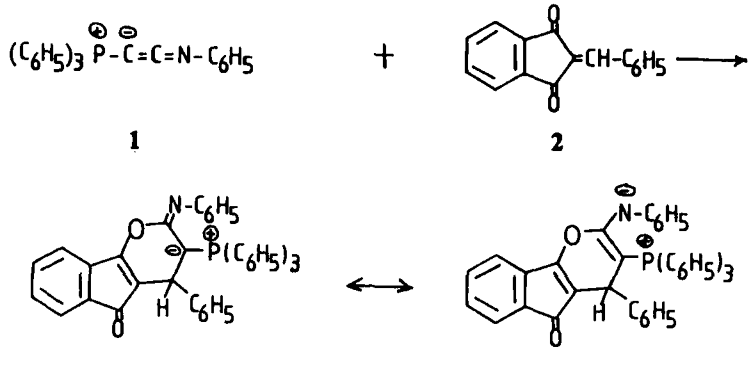
Phosphacumulene ylids are nucleophilic reagents, which are interesting building blocks for the synthesis of heterocycles.[1] We have now investigated the reaction of *N*-phenyliminoketenylidene triphenylphosphorane (**1**) with some α,β-unsaturated carbonyl compounds to prepare new pyrano-derivatives.

RESULTS AND DISCUSSIONS

The phosphacumulene ylid **1** reacted with 2-benzylidene-1,3-indandione (**2**), in dry THF at 20°C for 4 hours by [4 + 2]-cycloaddition to the corresponding pyran-substituted phosphorane which can be represented by the resonance structures **3a** and **3b**.

The elemental microanalysis, IR, ^{1}H-, ^{31}P-NMR and MS data agree with the structure of the cyclic imino-phosphorane **3**. The ^{31}P-NMR spectrum of **3** is of particular interest. A signal at $\delta = +26.479$ ppm was observed which supports structure **3** and excludes 4-membered ring-structure by [2 + 2]-cycloaddition which would have a signal from $+5$ till -5 ppm.[2] In the MS of **3** the m/e = 611 (M$^+$).

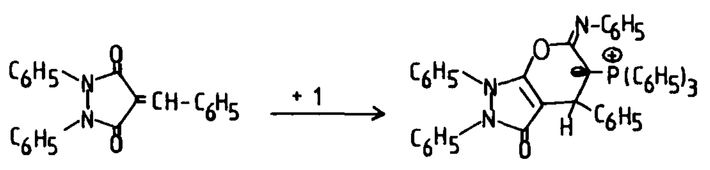
When 1,2-diphenyl-3,4-pyrazolidenedione (**4**) was allowed to react with the phosphacumulene **1**, under the same previous experimental conditions, the new



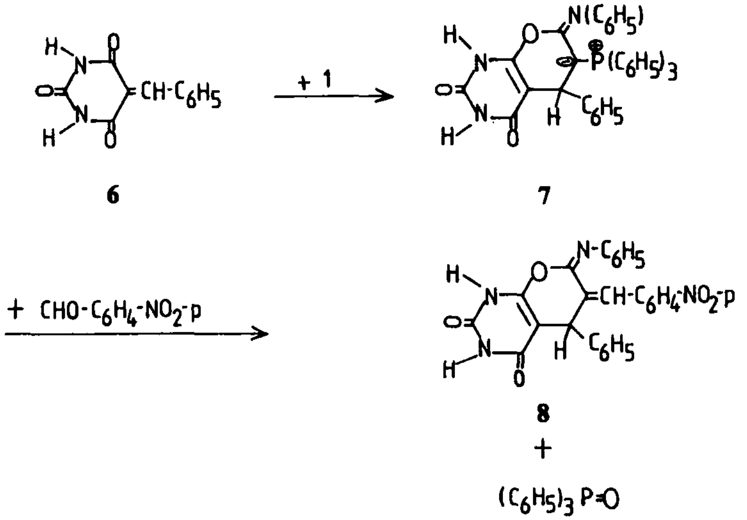
1 **2**

3a **3b**

pyran-derivative **5** was isolated. ^{31}P-NMR: $\delta = 26.687$ ppm, m/e = 717 (M^+). In a similar manner the phosphorane **7** was produced from the reaction of 5-benzylidenebarbituric acid (**6**) and the ylide **1**. ^{31}P-NMR: $\delta = 26.763$ ppm, m/e = 593 (M^+). When Wittig reaction was carried on the pyran-compound **7**, using p-nitro benzaldehyde, the new exocyclic olefin **8** m/e = 466 (M^+), together with triphenylphosphine oxide, were isolated.



4 **5**



6 **7**

8

EXPERIMENTAL

All melting points are uncorrected. THF was peroxide-free and absolutely dry. All reactions were carried out under N_2 atmosphere. ^{31}P-NMR spectra were run on Spectrometer JNM-PS 100 Jeol Tokio, in $CDCl_3$, using H_3PO_4 as external standard. MS were carried on Varian MAT CH-4B.

Reaction of N-Phenyliminoketenylidenetriphenylphosphorane (**1**) *with 2-Benzylidene-1,3-indandione* (**2**). To a solution of the phosphacumulene ylid (**1**)[3] (3.7 g, 0.01 mole) in 30 ml tetrahydrofuran, was added drop by drop with stirring at room temperature, a solution of the α,β-unsaturated compound (**2**)[4] (2.3 g, 0.01 mole) in 30 ml THF. The reaction mixture was left for 24 hrs during which yellow crystals precipitated. After THF was distilled under reduced pressure, the residue that left behind was crystallized from dry ethyl acetate to give the pyran-substituted phosphorane **3**, as yellow crystals, m.p. 200°C (decomp.) (5.6 g, 93%). Calcd. for $C_{42}H_{30}NO_2P$: C, 82.48; H, 4.90; N, 2.29; P, 5.07. Found: C, 82.20; H, 4.72; N, 2.32; P, 4.89.

In a similar manner, the pyran-substituted phosphorane (**5**) was obtained from the reaction of *N*-phenyliminoketenylidenetriphenylphosphorane (**1**) (3.7 g, 0.01 mole) and 1,2-diphenyl-3,5-pyrazolidenedione (**4**)[5] (3.4 g, 0.01 mole), as yellow crystals, m.p. 236°C (decomp.) from ethyl acetate (6.4 g, 90%), Calcd. for $C_{48}H_{36}N_3O_2P$: C, 80.33; H, 5.02; N, 5.85 P, 4.32. Found: C, 80.01; H, 4.92; N, 5.83; P 4.19.

The pyran-substituted phosphorane (**7**) was isolated from the reaction of the cumulated ylid (**1**) (3.7 g, 0.01 mole) and 5-benzylidene barbituric acid (**7**)[6] (2.1 g, 0.01 mole), as yellow crystals, m.p. 210°C (decomp.), from ethyl acetate (5.5 g, 95%). Calcd. for $C_{37}H_{28}N_3O_3P$: C, 74.87; H, 4.72 N, 7.08; P, 5.22. Found: C, 74.63; H, 4.51; N, 6.98; P, 4.97.

The Reaction of Pyran-substituted Phosphorane (**7**) *with p-Nitro benzaldehyde*. A mixture of the phosphorane (**7**) (0.7 g, 0.001 mole) and *p*-nitrobenzaldehyde (0.15 g, 0.001 mole) and ethyl acetate (20 ml) was refluxed for four hours. After the reaction mixture was concentrated to half its volume, it was left overnight in the refrigerator. The precipitate that formed was filtered off and crystallized from ethyl acetate/*n*-hexane, to give the olefin **8** as yellow crystals m.p. 224°C (0.36 g, 77%). Calcd. for $C_{26}H_{18}N_4O_5$: C, 66.95; H, 3.86; N, 12.01. Found: C, 66.73; H, 3.70; N, 11.93.

The ethyl acetate filtrate, afforded upon concentration and addition of *n*-hexane, a colourless precipitate, which upon recrystallization from benzene gave triphenylphosphine oxide, m.p. and mixed m.p. 151°C[7] (0.23 g, 82%).

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