

## LITERATURE CITED

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REACTION OF C,N-DIPHENYLNITRONE WITH  
N,N-DIMETHYLAMINOMETHYLENE-P-PHENYLPHOSPHINE

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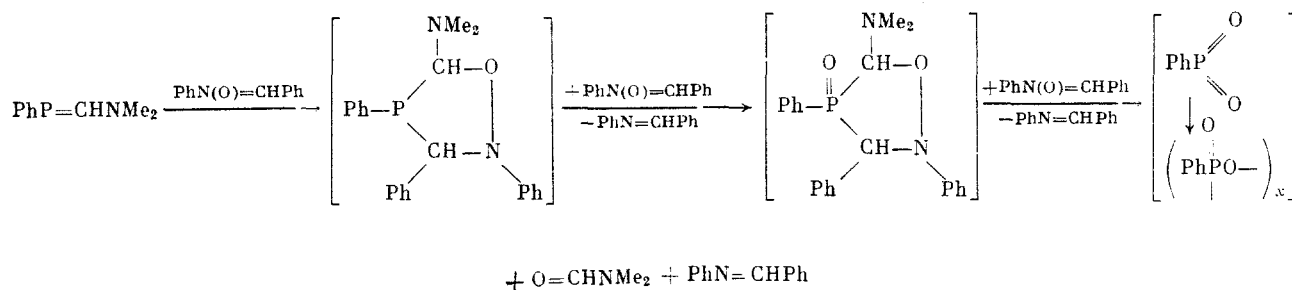
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C,N-Diphenylnitrone oxidizes N,N-dimethylaminomethylene-P-phenylphosphine to give dioxophenylphosphorane and dimethylformamide and is reduced to benzalaniline.

Examples have been reported for the reactions of nitrones as 1,3-dipolar reagents in [3 + 2] cycloaddition with monocoordinated phosphorus compounds [1] and dicoordinated arsenic compounds [2]. The reaction of nitrones with dicoordinated phosphorus compounds have not yet been reported.

A study of the reaction of nitrones with phosphalkenes containing the P=C-N structural elements was indicated since such phosphalkenes have high specific reactivity [3].

We studied the reaction of N,N-dimethylaminomethylene-P-phenylphosphine with C,N-diphenylnitrone. The completion of this reaction requires a 1:3 mole ratio of the starting reagents.



The only phosphorus-containing product of this reaction is a dioxophenylphosphorane, which proved unstable to polymerization [4]. The IR spectrum of the product of the polymerization of dioxophenylphosphorane lacks bands for OH and P(O)OH groups, while the  $^{31}\text{P}$  NMR spectrum shows signals at from 30 to 6 ppm, which is in accord with the literature data [5]. Attempts to detect reaction intermediates using low-temperature  $^{31}\text{P}$  NMR spectroscopy were unsuccessful. Methylene phosphine oxides, in contrast to methylenephosphine sulfides, are not trapped by 2,3-dimethylbutadiene in a Diels-Alder reaction [6]. Trapping with methanol [7] is unsuitable in this case since the starting phosphalkene reacts with alcohols [8].

Benzalaniline and dimethylformamide were isolated and characterized from the products of this reaction. These compounds are formed upon the decomposition of the cycloaddition adducts. A similar type of decomposition leading to azomethine was observed for the adduct of a phosphalkyne and nitrone [1]. The oxygen atom of the nitrone likely adds to the carbon

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atom of the phosphalkene in accord with the polarization of the P-C-N structural fragment [3]. In addition, the adducts with nitrones undergo decomposition specifically in this direction [1].

#### EXPERIMENTAL

The  $^{31}\text{P}$  NMR spectra were measured on a Bruker M-250 spectrometer. The IR spectra were taken on a UR-20 spectrometer. The PMR spectra were taken on a Varian T-60 spectrometer at  $34.6^\circ\text{C}$ . All the operations were carried out in argon.

A sample of 10.09 g (0.051 mole) C,N-diphenylnitrone was added to 2.82 g (0.017 mole) N,N-dimethylaminomethylene-P-phenylphosphine in 15 ml THF and a vigorous exothermal reaction was observed. After completion of the reaction in about 15 min, THF was distilled off at ordinary pressure. Distillation gave 1.13 g (91%) dimethylformamide, bp  $36^\circ\text{C}$  (1 mm). [PMR spectrum (TMS,  $\delta$ , ppm): 2.6 and 2.77 d (6H,  $\text{N}(\text{CH}_3)_2$ ), 7.76 s (1H,  $\text{HC}(\text{O})$ ). At  $105^\circ\text{C}$  8.06 g (87%) benzalaniline, mp  $52^\circ\text{C}$  (from ethanol) was distilled off. Found: C, 85.90; H, 6.07; N, 8.12%. Calculated for  $\text{C}_{13}\text{H}_{11}\text{N}$ : C, 86.19; H, 6.08; N, 7.74%. The  $^{31}\text{P}$  NMR spectrum of the vat residue in  $\text{CHCl}_3$  displayed signals at 30, 28, 14, 11, and 6 ppm with integral intensity ratio 1.7:3:5:3:15.

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