

Reaction of Alkylidenetriphenylphosphoranes with Nitric Oxide

By KIN-YA AKIBA, MAKOTO IMANARI, and NAOKI INAMOTO*

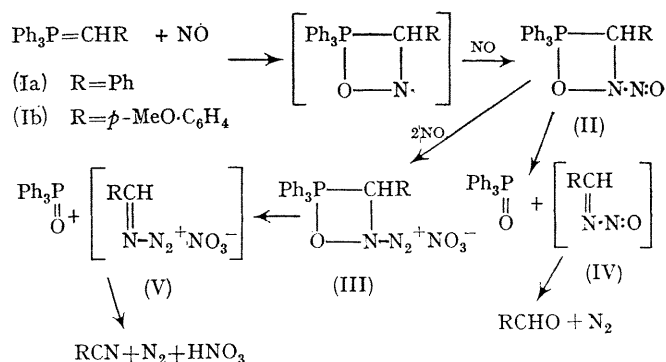
(Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo, Japan)

THE reactions of alkylidenetriphenylphosphoranes with free radicals (other than oxygen¹) have not been studied. We report the reaction of alkylidenetriphenylphosphoranes with nitric oxide; the reaction is more complex than that with nitrosyl chloride.²

The phosphoranes were prepared from the corresponding phosphonium bromides and NaNH_2 -liquid NH_3 .³

Reaction of an excess of nitric oxide (20 mol.) with benzylidenetriphenylphosphorane (Ia) in toluene at -7° under a nitrogen atmosphere gave benzonitrile (24.3), benzaldehyde (17.0), triphenylphosphine oxide (84.6), *cis*- (1.1) and *trans*-stilbenes (1.7), benzene (8.0%), and precipitate. Crystallisation of the precipitate from chloroform-benzene and then water gave benzyltriphenylphosphonium nitrate (ca. 5%). Similar results were obtained for the reaction in ethylbenzene at -20° with a 40 mol. excess of nitric oxide; toluene (5.8%) was also present as a product.

We suggest the following scheme for the reaction:



The conversion of the nitroso-group of (II) to the

TABLE 1

Decomposition of the precipitates formed in the reaction of (Ia) and (Ib) with nitric oxide

(I) (mmoles)	Solvent	Temp.	RCN (%)	RCHO (%)	$\text{Ph}_3\text{P}=\text{O}$ (%)
(Ia) 23.1	PhEt (360 ml.)	-40°	7.1	6.7	12.4
(Ib) 50.2	PhMe (680 ml.)	-20 to -30	16.1	5.4	21.0

TABLE 2

Reactions of alkylidenetriphenylphosphoranes (I) with nitric oxide (toluene, -10°)

(I) (mmoles)	RCN (%)	PhH (%)	$(\text{RCH}=\text{})_2$ (%)	$\text{Ph}_3\text{P}=\text{O}$ † (%)
$\text{R} = \text{Pr}^n$ 50.0	34.0	21.5	~30	55.0
$\text{R} = \text{Pr}^i$ * 38.0	19.0	33.3	—	55.0
$\text{R} = \text{cyclohexyl}$ 34.0	34.0	19.0	~12	76.5

* $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Pr}^i$ (9.7%) was determined by g.l.c.

† Obtained by column chromatography.

diazonium nitrate (III) is analogous to the conversion of nitrosobenzene to benzenediazonium nitrate.⁴ Benzaldehyde probably results from the partial decomposition of (II) *via* the *N*-nitrosoaldimine (IV).⁵ The formation of *cis*- and *trans*-stilbenes is attributed to Wittig reaction between (Ia) and benzaldehyde thus formed.

A further reaction was carried out in ethylbenzene at -40° , the resulting precipitate was washed with ethylbenzene at *ca.* -70° , and then allowed to decompose in the same solvent at room temperature; evolution of gas (N_2) was observed. *p*-Methoxybenzylidetriphenylphosphorane (Ib) behaved similarly. The decomposition

products of these precipitates were determined by g.l.c. (Table 1).

The sum of the amounts of nitrile and aldehyde is almost equal to that of triphenylphosphine oxide which indicates the presence of two kinds of precipitates, (II) and (III), each containing a triphenylphosphine group. The mechanism of formation of benzene and toluene has not been elucidated.

The results for other alkylidetriphenylphosphoranes are shown in Table 2. Only small amounts of aliphatic aldehydes were observed with these and this is probably due to rapid olefin formation by a Wittig reaction.

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