Reactions of Pentavalent Phosphorus Esters with *gem*-Dihalides. A New Synthesis of Phosphinic Anhydrides[1]

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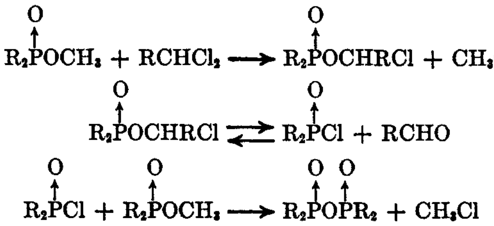
Alkyl esters of phosphinic acids react at elevated temperatures with *gem*-dihalides to form alkyl halides, aldehydes, and phosphinic anhydrides in high yield. The reaction is believed to involve the following steps. The



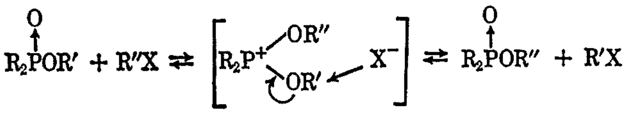
$$R_2\overset{O}{\overset{\uparrow}{P}}OCH_3 + RCHCl_2 \longrightarrow R_2\overset{O}{\overset{\uparrow}{P}}OCHRCl + CH_3Cl$$

$$R_2\overset{O}{\overset{\uparrow}{P}}OCHRCl \rightleftarrows R_2\overset{O}{\overset{\uparrow}{P}}Cl + RCHO$$

$$R_2\overset{O}{\overset{\uparrow}{P}}Cl + R_2\overset{O}{\overset{\uparrow}{P}}OCH_3 \longrightarrow R_2\overset{O}{\overset{\uparrow}{P}}O\overset{O}{\overset{\uparrow}{P}}R_2 + CH_3Cl$$

reaction of dialkyl alkylphosphonates with benzal chloride appears to proceed similarly, except that the bis-(alkylalkylphosphonic) anhydrides formed in these reactions equilibrate to form dialkyl alkylphosphonate and a polymeric phosphonic anhydride.

Alkyl esters of pentavalent phosphorus acids react with a variety of halogen compounds, including alkyl, acyl, phosphoryl, and metal halides, to yield alkyl halides and derivatives of the original phosphorus compounds. A reasonable body of evidence supports the contention[2,3] that such conversions proceed by displacement reactions in which phosphoryl or thiophosphoryl groups behave as nucleophiles. The reactions are believed to involve intermediate alkoxyphosphonium ions analogous to those occurring in Arbuzov–Michaelis reactions. Thus, electron-releasing groups substituted on phosphorus facilitate such reactions,[2–5,7] the relative reactivities of alkyl halides with pentavalent phosphorus esters are in the same order as are their relative reactivities toward nucleophilic substitution,[3,4] and the presence of electronegative substituents on phosphorus halides facilitates their reactivity toward phosphorus esters.[6] Furthermore, studies[8,9] with O^{18}-labeled pentavalent phosphorus esters definitely indicate that their reactions with halogen compounds and isocyanates involve the phosphoryl oxygen atom.

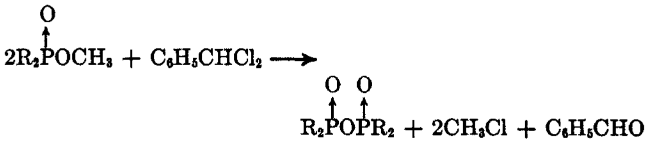


$$R_2\overset{O}{\overset{\uparrow}{P}}OR' + R''X \rightleftarrows \left[R_2P^{+}\begin{matrix}OR''\\ OR'\end{matrix}\; X^{-}\right] \rightleftarrows R_2\overset{O}{\overset{\uparrow}{P}}OR'' + R'X$$

In recent years, the reactions of alkyl halides with pentavalent phosphorus esters have been studied by a number of workers. These reactions have been responsible for the formation of unexpected isomeric[2,3] or cyclic[10–12] products in Arbuzov–Michaelis reactions. They have caused cross linking in attempts to prepare polymers *via* the Arbuzov–Michaelis reaction[13] and have been utilized for the preparation of phosphonate polyesters.[14] In addition, the activity of phosphine oxides and of pentavalent phosphorus esters as catalysts for the isomerization of phosphites[15] has been attributed to the nucleophilic activity of phosphoryl groups in the compounds.

Results

In the present work, the reactions of pentavalent phosphorus esters with *gem*-dihalides were investigated. Methyl esters of phosphinic acids were found to react with benzal chloride to yield methyl chloride, benzaldehyde, and phosphinic anhydrides in high yield, as is illustrated by the following general equation.



$$2R_2\overset{O}{\overset{\uparrow}{P}}OCH_3 + C_6H_5CHCl_2 \longrightarrow R_2\overset{O}{\overset{\uparrow}{P}}O\overset{O}{\overset{\uparrow}{P}}R_2 + 2CH_3Cl + C_6H_5CHO$$

Thus, methyl dimethylphosphinate ($R = CH_3$) reacted with benzal chloride to form methyl chloride, benzaldehyde, and dimethylphosphinic anhydride in 87, 86, and 77% yields, respectively. The reaction of methyl methylphenylphosphinate ($R = CH_3$, C_6H_5) with benzal chloride yielded methyl chloride, benzaldehyde and methylphenylphosphinic anhydride in 81, 72, and 62% yields, respectively. Similarly, the reaction of methyl diphenylphosphinate with benzal chloride afforded methyl chloride, benzaldehyde, and diphenylphosphinic anhydride in 83, 74, and 73% yields, respectively.

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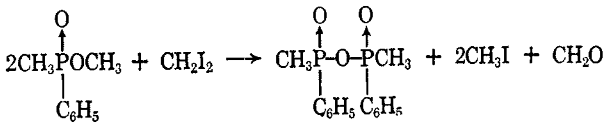
[15] V. Mark, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 29L.

When methyl methylphenylphosphinate was treated with methylene diiodide, methyl iodide, and methyl phenylphosphinic anhydride were obtained in 63 and 68% yields, respectively. Formaldehyde was shown to be a product of the reaction, and its yield was approximately 75%. Previously, Pudovik and co-workers[4] reported isolating diesters of methylene glycol from reactions of methylene iodide with alkyl phosphonates. No evidence for the presence of such esters among our products was obtained, however; the high boiling products obtained from our reaction were hydrolyzed and tested for formaldehyde, but none was found.



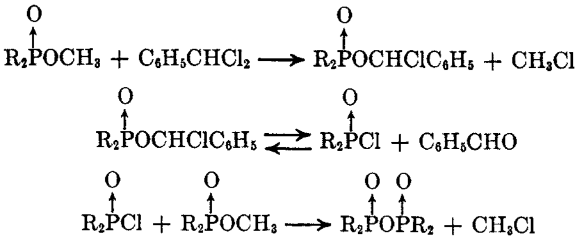
$$2CH_3\underset{C_6H_5}{\overset{\overset{O}{\uparrow}}{P}}OCH_3 + CH_2I_2 \longrightarrow CH_3\underset{C_6H_5}{\overset{\overset{O}{\uparrow}}{P}}{-}O{-}\underset{C_6H_5}{\overset{\overset{O}{\uparrow}}{P}}CH_3 + 2CH_3I + CH_2O$$

The reaction of excess dimethyl methylphosphonate with benzal chloride was also investigated, in an attempt to extend the above reaction to the synthesis of bis(alkylalkylphosphonic) anhydrides. Methyl chloride was formed in 85% yield in this reaction. Benzaldehyde was also formed but could not be separated from unreacted dimethyl methylphosphonate by distillation. Vapor phase chromatography (vpc) of the benzaldehyde–dimethyl methylphosphonate mixtures recovered from the reaction indicated that 94% of the theoretical amount of benzaldehyde had been formed. Although distillation of the reaction mixture yielded a small amount of material whose boiling point was close to that previously reported[15] for bis(methylmethylphosphonic) anhydride, the expected product, this material was shown by vpc to contain about 50% dimethyl methylphosphonate. The principal phosphorus-containing product obtained was a glassy, amber-colored, water-soluble resin which was considered to be the polyanhydride $(CH_3PO_2)_n$. Similar polymeric products have been obtained by the thermal decomposition of alkyl alkylphosphonochloridates[17,18] and by the controlled hydrolysis[18] of phosphonic dihalides.

One concludes, then, that the reactions of phosphonic esters with benzal chloride proceed in the same way as do the reactions of benzal chloride and methylene diiodide with phosphinic esters, except that anhydrides formed in the phosphonic reactions are unstable. On distillation these anhydrides equilibrate to yield starting material and a polymeric anhydride. Petrov and Neimysheva[16] have discussed the thermal instability of bis(alkylalkylphosphonic) anhydrides. They obtained results similar to ours when attempting the distillation of bis(methylmethylphosphonic) anhydride.

Discussion

The products obtained in this study are believed to be formed *via* the series of reactions 1–3. There is ample precedent for each of the reactions proposed. The first reaction in the scheme below (reaction 1) may be considered to be simply another example of a thermal reaction between a pentavalent phosphorus ester and an alkyl halide. It should be entirely analogous to the reactions described by Harwood and Grisley,[2] Laughlin,[3] and Pudovik, *et al.*[4]



$$R_2\overset{\overset{O}{\uparrow}}{P}OCH_3 + C_6H_5CHCl_2 \longrightarrow R_2\overset{\overset{O}{\uparrow}}{P}OCHClC_6H_5 + CH_3Cl \quad (1)$$

$$R_2\overset{\overset{O}{\uparrow}}{P}OCHClC_6H_5 \rightleftharpoons R_2\overset{\overset{O}{\uparrow}}{P}Cl + C_6H_5CHO \quad (2)$$

$$R_2\overset{\overset{O}{\uparrow}}{P}Cl + R_2\overset{\overset{O}{\uparrow}}{P}OCH_3 \longrightarrow R_2\overset{\overset{O}{\uparrow}}{P}O\overset{\overset{O}{\uparrow}}{P}R_2 + CH_3Cl \quad (3)$$

The second reaction in the proposed scheme (reaction 2) involves the reversible dissociation of an α-haloalkyl phosphinate (or phosphonate) to yield a phosphinic (or phosphonic) halide and benzaldehyde. The facile decompositions of α-halo ethers or α-halo esters to yield alkyl or acyl halides and carbonyl compounds have been frequently described. Such materials have been suggested as intermediates in the hydrolysis of benzal chloride[19] and in the reactions of α,α-dichloroalkyl ethers with acids,[20] alcohols,[21] and esters.[21] In addition, 2,2,3,3-tetrachloro-1,4-dioxane has been reported to decompose at 190°, yielding ethylene dichloride and oxalyl chloride.[22] Also, benzoyl bromide and benzaldehyde have been reported to form a crystalline adduct which dissociates into reactants at elevated temperatures.[23]

Experimental support for the participation of phosphinic chlorides as intermediates in these reactions was obtained by treating methyl methylphenylphosphinate with a large excess of benzal chloride. Methylphenylphosphinic chloride was obtained from this reaction in 39% yield, in addition to a 28% yield of the anhydride. In addition, almost 1 mole of benzaldehyde was recovered from this reaction/mole of original phosphinate. When equimolar amounts of phosphinate and halide are allowed to react, 1 mole of benzaldehyde is formed for every 2 moles of phosphinate.

The third reaction in our proposed scheme (reaction 3) is well established and is commonly employed for the synthesis of phosphinic, phosphonic, etc., anhydrides.[24] In fact, phosphinic anhydrides have been prepared in the past almost entirely by this very reaction.[24c]

An interesting reaction described by Moedritzer[25] provides a convenient route for preparing phosphinic anhydrides from the corresponding *phosphinic halides.* Our reactions provide a route to phosphinic anhydrides which complements that of Moedritzer, in that *phosphinic esters* are used as starting materials. It is therefore not necessary to have *both*[18c] phosphinic esters and phosphinic halides available for the preparation of phosphinic anhydrides. Our synthesis should be particularly useful for synthesizing phosphinic anhydrides from those phosphinic esters that are conveniently prepared *via* Arbuzov–Michaelis reactions. The yields

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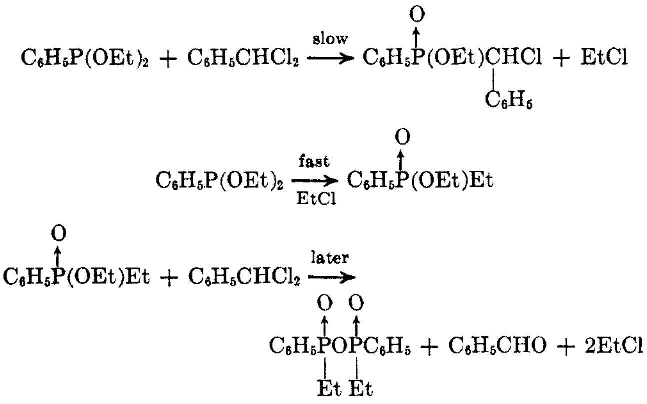
(25) K. Moedritzer, *J. Am. Chem. Soc.*, **83**, 4381 (1961).

of anhydrides obtained in this study are good, but but they will undoubtedly be better when large-scale preparations are attempted. In the present work, residues resulting from anhydride distillations were an appreciable fraction of the high boiling products encountered.

Finally, it seems reasonable to assume that reactions similar to those described herein were encountered by Henning[26] in studies on the reactions of dialkyl phenylphosphonites with *gem*-dihalides. For example, the reaction of equimolar quantities of diethyl phenylphosphonite and benzal chloride yielded ethyl chloride (~1.5 moles/mole of phosphonite), benzaldehyde, and a viscous uncharacterized product. This latter product probably contained ethylphenylphosphinic anhydride, formed by the following series of reactions.



$$C_6H_5P(OEt)_2 + C_6H_5CHCl_2 \xrightarrow{\text{slow}} C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)\underset{\underset{C_6H_5}{|}}{C}HCl + EtCl$$

$$C_6H_5P(OEt)_2 \xrightarrow[\text{EtCl}]{\text{fast}} C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)Et$$

$$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)Et + C_6H_5CHCl_2 \xrightarrow{\text{later}} C_6H_5\underset{\underset{Et}{|}}{\overset{\overset{O}{\uparrow}}{P}}O\underset{\underset{Et}{|}}{\overset{\overset{O}{\uparrow}}{P}}C_6H_5 + C_6H_5CHO + 2EtCl$$

Experimental Section

Reaction of Methyl Dimethylphosphinate with Benzal Chloride.—A mixture of methyl dimethylphosphinate (7.6 g, 0.07 mole) and benzal chloride (5.6 g, 0.035 mole) was heated at 210–238° for 2.5 hr. Methyl chloride which evolved was collected (3.1 g, 87%) in a Dry Ice cooled trap and identified by its infrared spectrum. The mixture was distilled to yield benzaldehyde [(3.2 g, 86%), bp 50–60° (5 mm)], dimethylphosphinic anhydride [(4.6 g, 77%), mp 118–120° (lit.[25] mp 120°), neut equiv 87.6 (calcd 85.0)], and 0.7 g of residue (mp 124–126°).

The identification of benzaldehyde was established by preparation of the 2,4-dinitrophenylhydrazone [mp 236–238° (lit.[27] mp 237°)], and *p*-nitrophenylhydrazone [mp 189–192° (lit.[27] mp 192°)] derivatives. The anhydride was converted into dimethylphosphinic acid [mp 88–90° (lit.[28] mp 89–90°)] by hydrolysis in aqueous acetone.

Reaction of Methyl Methylphenylphosphinate with Benzal Chloride.—A mixture of methyl methylphenylphosphinate[2] (17 g, 0.10 mole) and benzal chloride (8 g, 0.05 mole) was heated gradually for 2.5 hr to a final temperature of 215°. Methyl chloride which formed in the reaction was collected in a trap cooled to −78°. It was identified by its infrared spectrum, yield 4.1 g (81%). Distillation of the reaction mixture yielded benzaldehyde [(3.8 g, 72% yield), bp 47–60° (5 mm)], unreacted methyl methylphenylphosphinate [(1.3 g, 8% of charge), bp 110° (2 mm)], methylphenylphosphinic anhydride [(9.1 g, 62% yield), bp 200–210° (1 mm)], and 2.1 g of a dark viscous residue.

Vpc indicated that there was no more than a trace of unreacted benzal chloride in the benzaldehyde or methyl methylphenylphosphinate fractions.

Methylphenylphosphinic anhydride crystallized on standing, mp 89–92° (lit.[25] mp 94°). Its equivalent weight was determined to be 147.4 (calcd 147.1). The infrared spectrum of this material contained absorption bands at 1235 (P=O), 968 (POP), and 695 (POP) cm^{-1}. Hydrolysis of the anhydride yielded methylphenylphosphinic acid, mp and mmp 134–135.5° (lit.[2] mp 133–134°).

As in the previous experiment, the identification of benzaldehyde was confirmed by preparing the 2,4-dinitrophenylhydrazone (mp 236–238°) and *p*-nitrophenylhydrazone (mp 189–192°) derivatives.

Reaction of Methyl Methyl(phenyl)phosphinate with Excess Benzal Chloride.—Under an atmosphere of nitrogen, methyl methyl(phenyl)phosphinate (27.4 g, 0.16 mole) was added dropwise over a period of 2.5 hr to a stirred sample of benzal chloride (129 g, 0.80 mole) at 220–225°. After the addition was complete, the reaction mixture was heated, with stirring, at 225° for an additional hour. Methyl chloride (6.0 g, 74%) evolved during the reaction was collected in a trap cooled to −78°, and was identified by gas chromatography. The reaction mixture was then separated into five fractions by distillation. The first fraction [98.8 g, bp 70–80° (10 mm)] was found by gas chromatography to contain 15.5 g of benzaldehyde and 81.2 g of benzal chloride. The second fraction [24.0 g, bp 60–74° (2 mm)] was shown by gas chromatography to be essentially pure benzal chloride. The other volatile fractions consisted of methylphenylphosphinic chloride [(7.4 g, 28%), bp 102–107° (1 mm)] and methylphenylphosphinic anhydride [(9.3 g 39%), bp 190–215° (0.1 mm), mp 90–92° (lit.[25] mp 94°)]. Neutralization equivalents determined for the methylphenylphosphinic chloride and methylphenylphosphinic anhydride fractions were 88.0 (calcd 87.3) and 146.5 (calcd 147.1), respectively. Both fractions yielded methylphenylphosphinic acid [mp and mmp 134–135.5° (lit.[2] mp 133–134°)] on hydrolysis.

In addition to these volatile products, a dark viscous distillation residue (3.5 g) was obtained. This residue probably contained a mixture of the anhydride and its corresponding acid. Crystals that separated from a benzene solution of the residue melted at 120–123°.

Reaction of Methyl Diphenylphosphinate with Benzal Chloride.—A mixture of methyl diphenylphosphinate[29] (23.2 g, 0.10 mole) and benzal chloride (8.3 g, 0.05 mole) was heated for 4.5 hr under nitrogen at 200–220°. Methyl chloride (4.2 g, 83%), which evolved during this reaction, was collected in a trap cooled to −70° and was identified by gas chromatography. The reaction mixture was distilled to obtain benzaldehyde (3.9 g, 74%), bp 62–70° (15 mm). Examination of the aldehyde by gas chromatography indicated it to contain only a trace of benzal chloride.

The distillation residue (17.3 g) was recrystallized from a benzene–hexane mixture to obtain diphenylphosphinic anhydride (15.2 g, 73%), mp 140–143° (lit.[25] mp 143°). The product absorbed in the infrared region at 1234 (P=O), 968 (POP) and 695 (POP) cm^{-1}.

Reaction of Methyl Methylphenylphosphinate with 2,6-Dichlorobenzal Chloride.—A mixture of methyl methylphenylphosphinate (25.9 g, 0.15 mole) and 2,6-dichlorobenzal chloride (17.3 g, 0.075 mole) was heated in 30 min to a bath temperature of 210–220°. Since no methyl chloride was evolved at this temperature, the temperature was increased to 240–260° for another 30 min. Only a trace of material was collected in the Dry Ice trap. This material was not analyzed but it responded like methyl chloride when warmed to room temperature.

Reaction of Methyl Methyl(phenyl)phosphinate with Methylene Iodide.—A mixture of methyl methylphenylphosphinate (35.6 g, 0.21 mole) and methylene iodide (29.4 g, 0.11 mole) was heated under nitrogen, with stirring, for 6 hr at 175–185°. During the course of the reaction, methyl iodide (19.5 g, 63%) and formaldehyde (2.5 g, 75%) escaped from the reaction mixture and were collected in a trap cooled to −78°. Methyl iodide was identified and determined by gas chromatography. Formaldehyde was identified by formation of its 2,4-dinitrophenylhydrazone derivative [mp 162–164° (lit.[30] mp 166°)] and the amount formed was calculated from the difference between the total yield of gaseous products and the yield of methyl iodide obtained.

Distillation of the reaction mixture yielded unreacted methyl methylphenylphosphinate [(5.1 g, 14% recovered), bp 122° (6 mm)], methylphenylphosphinic anhydride [(21.2 g, 68%), bp 205° (0.25 mm), mp 92–94°], and 3.2 g of distillation residue. The neutralization equivalent determined for the anhydride was 149.5 (calcd 147.1). The hydrolyzed anhydride gave a negative result when tested for aldehyde with 2,4-dinitrophenylhydrazine.

Reaction of Dimethyl Methylphosphonate with Benzal Chloride.—A mixture of dimethyl methylphosphonate (32.2 g, 0.25 mole) and benzal chloride (13.9 g, 0.086 mole) was heated at

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[28] H. Reinhardt, O. Bianchi, and O. Mölle, *Chem. Ber.*, **90**, 1656 (1957).

[29] K. D. Berlin, T. H. Austin, and K. L. Stone, *J. Am. Chem. Soc.*, **86**, 1787 (1964).

[30] Reference 27, p 229.

TABLE I

Fraction	Wt, g	Bp, °C (4 mm)	Formula (g)
1	9.3	51	$CH_3P(O)(OCH_3)_2$ (4.8) C_6H_5CHO (4.5)
2	12.6	55–60	$CH_3P(O)(OCH_3)_2$ (8.6) C_6H_5CHO (4.0)
3	1.6	65–130	$CH_3P(O)(OCH_3)_2$ (1.0) C_6H_5CHO (0.1)
4	6.6	130–138	$CH_3P(O)(OCH_3)_2$ (3.1)
5	1.2	50–90	$CH_3P(O)(OCH_3)_2$ (1.1)
6	5.9	Residue	...

250–260° (bath temperature) for 6 hr. Methyl chloride evolved from the reaction and was collected (7.4 g, 85%) in a Dry Ice cooled trap. The reaction mixture was distilled to yield five fractions which were analyzed by vpc (Apiezon L on firebrick at 215° using helium as the carrier gas). The results of the distillation and subsequent chromatographic analysis are summarized in Table I.

On the basis of the results shown in Table I, the total amount of benzaldehyde formed in the reaction was 8.6 g (94%). The material not accounted for in fractions 3–5 was presumed to be bis(methylmethylphosphonic) anhydride [lit.[16] bp 137.5–138° (4 mm)]. The residue (fraction 6) from the distillation was a glassy, amber-colored, water-soluble solid.

Registry No.—Methyl dimethylphosphinate, 14337-77-0; methyl methylphenylphosphinate, 6389-79-3; methylphenylphosphinic chloride, 5761-97-7; methyl diphenylphosphinate, 1706-90-7; dimethyl methylphosphonate, 756-79-6; 2,6-dichlorobenzal chloride, 81-19-6; methylene iodide, 75-11-6; benzal chloride, 98-87-3; dimethylphosphinic anhydride, 14337-82-7; methylphenylphosphinic anhydride, 14337-83-8; diphenylphosphinic anhydride, 5849-36-5.

Acknowledgments.—The authors are indebted to Mr. Robert A. Coburn and Mr. Fred A. Miller for preparing samples of methyl dimethylphosphinate and dimethyl methylphosphonate used in this investigation. We are grateful to Mr. Natvarlal K. Patel for experimental assistance.

Peroxynitrates. The Unstable Products of Olefin Nitration with Dinitrogen Tetroxide in the Presence of Oxygen. A New Route to α-Nitro Ketones

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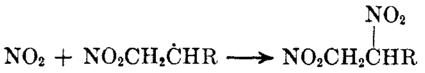
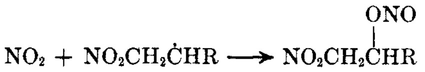
The reaction of olefins with dinitrogen tetroxide in the presence of oxygen has been investiged in nonpolar media at 0° and has been found to result in the formation of β-nitroalkyl peroxynitrates. These materials are moderately stable at 0° but rapidly decompose at room temperature. The structure of the peroxynitrate compound has been ascertained for the first time by its spectral properties and by a novel reaction with dimethylformamide or dimethyl sulfoxide which converts it into the corresponding α-nitro ketone and nitric acid. The nature of this latter reaction has been investigated and its general utility has been shown for the preparation of 1-nitro-2-alkanones.

Considerable investigation[2] has shown that the reaction of dinitrogen tetroxide[3] with olefins in nonpolar media below room temperature results in the formation of mixtures of β-substituted nitroalkanes, particularly vicinal dinitro compounds and β-nitroalkyl nitrites. The reaction is generally considered to proceed by a free-radical mechanism involving initial formation of a nitroalkyl radical and subsequent addition of a nitrogen dioxide molecule (eq 1–3).

$$NO_2 + CH_2{=}CHR \longrightarrow NO_2CH_2\dot{C}HR \quad (1)$$



$$NO_2 + NO_2CH_2\dot{C}HR \longrightarrow NO_2CH_2\overset{\overset{\textstyle NO_2}{|}}{C}HR \quad (2)$$



$$NO_2 + NO_2CH_2\dot{C}HR \longrightarrow NO_2CH_2\overset{\overset{\textstyle ONO}{|}}{C}HR \quad (3)$$

Addition to the olefin is such that a nitro function always becomes attached to the olefinic carbon atom bearing the most hydrogens.

The results of several previous studies indicate that the presence of molecular oxygen alters the course of the olefin–dinitrogen tetroxide reaction. Thus it has been reported[4-9] that oxygen greatly increases the yields of β-nitroalkyl nitrates (minor products in the absence of oxygen) and concurrently reduces the yields of dinitro adducts. The effect increases with increasing oxygen concentration.[10] Oxygen was found to be absorbed at a measurable rate by an olefin solution only when nitrogen dioxide was present.[11]

Baryshnikova and Titov[11] and Stevens[7-9] have reported that the use of molecular oxygen also results in the formation of oxidation products, including α-nitro ketones, which are not otherwise produced and have suggested that the effect of oxygen may be due to the intermediate formation of a β-nitroalkylperoxy free radical or the corresponding peroxynitrate *via* the nitroalkyl radical. The products finally obtained from the low-temperature, olefin–dinitrogen tetroxide reaction in the presence of oxygen were believed to result from the thermal or hydrolytic decomposition of the β-nitroalkyl peroxynitrate, which was never isolated or characterized (eq 4–6).

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(1) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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