gents; (d) decreasing the volume in order to discourage intramolecular reactions; (e) carrying out the reaction at room temperature for 45 min. (the yield was decreased considerably but the same degree of racemization occurred); and (f) adding only 1 mole of tri-*n*-butylamine to the reaction mixture.

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Nitration with Uranium Nitrate–Nitrogen Tetroxide–Water Complex in the Presence of Acetic Anhydride[1]

JOHN R. LACHER, JEAN SCHWARZ, AND J. D. PARK

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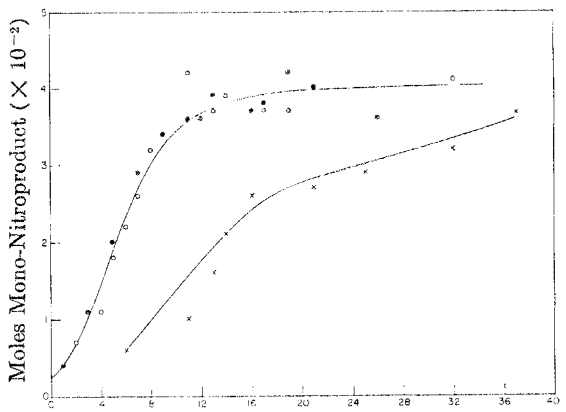
The type of influence which acetic anhydride has on the nitrating ability of nitric acid is not definitely understood. Menke[2] examined the nitrating abilities of inorganic nitrates with acetic anhydride. He found that nitrates of metals such as Fe^{+3}, Cu, Ni, Co, Al, Ce, and UO_2^{++} acted as very strong nitrating agents in acetic anhydride. Menke suggested possibly that acetyl nitrate is formed in the nascent state and this is then decomposed as the temperature rises. Also, he found that the velocity of nitration could be modified by a change in temperature, the choice of inorganic nitrate, and by using mixtures of acetic anhydride and acetic acid in various proportions. Putokhin[3] nitrated thiopene with cupric nitrate–trihydrate in acetic anhydride and obtained good results. He found the reaction quieter with 80% acetic acid in place of acetic anhydride and almost nil with 60% acetic acid. Dewar and Maitlis[4] nitrated quinoline using lithium nitrate with a little copper nitrate in acetic anhydride at 100°. Traverso[5] examined the nitration of tetralin with copper and aluminum nitrates in acetic acid and acetic anhydride. Borewell and Garbisch[6] in a recent study of the behavior of acetic anhydride and 70% nitric acid feel that the exothermic reaction between these compounds forming acetyl nitrate is essential for successful nitrations, and the acetyl nitrate so formed is the nitrating agent.



Moles Acetic Anhydride (× 10^{-2})
Nitrations with I. $UO_2(NO_3)_2 \cdot N_2O_4 \cdot H_2O$. II. $UO_2(NO_3)_2 \cdot 6H_2O$

○ Nitrobenzene I
× Nitrobenzene II
● Nitro-o-xylenes I

We initially intended to nitrate aromatic compounds with uranium nitrate–nitrogen tetroxide–water complex[7] in acetic anhydride. It was noted that as the quantity of acetic anhydride was increased the reaction became increasingly vigorous. We therefore, investigated the influence of increasing amounts of acetic anhydride on the amount of mononitration products of benzene and *o*-oxylene. An excess of aromatic compound was used as a solvent. Nitration with uranyl nitrate hexahydrate was also investigated for comparison to the above uranyl nitrate complex.

EXPERIMENTAL

Benzene, 25 cc. and varying quantities of acetic anhydride (from 0.02 to 0.40 mole) were mixed in a 125 cc. Erlenmeyer flask immersed in an ice bath with a magnetic stirrer. Uranium nitrate–nitrogen tetraoxide-water complex (0.02 mole) was slowly added to this mixture with constant stirring. Approximately 20 min. was taken for addition. A slight exothermic reaction occurred during addition of complex while the reaction flask was in the ice bath. When all the complex had been added and the solution was well stirred, it was removed from the ice bath and stirring was continued at room temperature. A very vigorous exothermic reaction occurred, and a yellow precipitate settled out of the solution. The temperature was kept below 60° until the reaction had subsided. The yellow precipitate has been identified as uranyl acetate. The entire reaction mixture was then washed twice with ice water and once with 5% sodium carbonate solution. The resulting organic layer was vacuum distilled. The nitrobenzene obtained was weighed and the amount in moles was recorded in Fig. 1 as a function of the moles of acetic anhydride used.

Benzene nitrations were also carried out using uranyl nitrate hexahydrate (0.02 mole) in the same manner as above with the exception that addition of the solid nitrate was at room temperature, as the reaction was much less vigorous than that with the complex.

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(1) This work was supported by a grant from the Chemistry Branch of the Division of Research, United States Atomic Energy Commission.

(2) J. B. Menke, *Rec. Trav. Chim.*, **44**, 141 (1925).

(3) N. I. Putokhin, *Sbornik Nauch. Trudov Kuibyshev, Ind. Inst. im. V. V. Kuibyshiva*, No. **5**, 271 (1955).

(4) M. J. S. Dewar, P. M. Maitlis, *Chem. & Ind.*, **48**, 685 (1955).

(5) Georgio Traverso, *Ann. Chim.*, **45**, 706 (1955).

(6) F. G. Bordwell and C. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

(7) J. R. Lacher, Keith Ensley, Anne Tenge, and J. D. Park, *J. Org. Chem.*, **24**, 1347 (1959).

o-Xylene (25 cc.) was mixed with varying quantities of acetic anhydride and the complex was slowly added in a manner similar to that above. When mixed at room temperature, the exothermic reaction was not allowed to exceed 30°.[8] The same yellow precipitate mentioned above formed in this reaction from a dark red-brown solution. Washing and vacuum distillation were carried out in the same manner as previously described. No attempt was made to separate the isomeric mixture obtained. Very large amounts of acetic anhydride (eg. 0.35 mole) could not be used because of increasing amounts of tarry oxidation products coating the distilling flask.

The yield of mononitro products obtained in all cases with the uranium nitrate-nitrogen tetroxide–water complex seemed to increase almost linearly with increasing amounts of acetic anhydride between 0.02 and 0.12 mole and then leveled off to an average of approximately 0.04 mole of nitro product. The yield then became independent of the amount of acetic anhydride used. With uranyl nitrate hexahydrate the yield increased linearly with amounts of acetic anhydride between 0.06 and 0.18 mole and the yield increased slowly.

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[8] A. W. Crossley and N. Renouff, *J. Chem. Soc.*, 95, 202 (1909).

Poly(diphenylvinylphosphine Oxide)[1]

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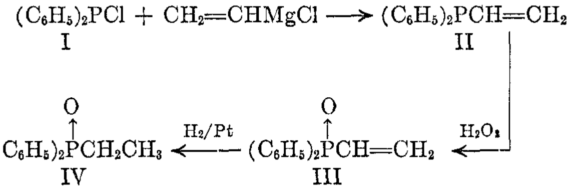
In previous studies concerned with cyclic polymerization involving tertiary phosphine oxides it was postulated that a radical could form on a carbon atom adjacent to a phosphoryl function.[3,4] To our knowledge only one report on the polymerization of a vinyl substituted tertiary phosphine oxide has been recorded.[5] Since the completion of the present work, an investigation of the homopolymerization of several vinylphosphonates has been described; low molecular weight polymers were obtained.[6] We now wish to report the synthesis and results of polymerization of diphenylvinylphosphine oxide. This monomer was specifically selected for the study because: (a) there are no alyllic hydrogen atoms in the molecule which could take part in degradative chain transfer[7] and (b) the vinyl group is in conjugation with the phosphoryl group which would be adjacent to the propagation radical.

RESULTS AND DISCUSSION

Diphenylvinylphosphine oxide (III) was prepared as depicted in the scheme. In the final step the phosphine II was oxidized to give white crystals of diphenylvinylphosphine oxide in a yield of 47.2%. In addition to the elemental analysis and infrared spectrum which support the structure III, the oxide was reduced under low pressure to the known diphenylethylphosphine oxide (IV).

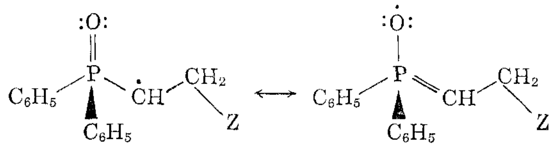


$$\underset{\text{I}}{(C_6H_5)_2PCl} + CH_2{=}CHMgCl \longrightarrow \underset{\text{II}}{(C_6H_5)_2PCH{=}CH_2}$$

$$\underset{\text{IV}}{(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}CH_2CH_3} \xleftarrow{H_2/Pt} \underset{\text{III}}{(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}CH{=}CH_2} \xleftarrow{H_2O_2} \text{II}$$

In contrast to vinyl phenyl ketone which is unstable and polymerizes upon standing,[8] diphenylvinylphosphine oxides (III) is stable in air and does not polymerize in storage for several months. However, in the presence of radical initiators this monomer homopolymerized in bulk or in solution. The polymer is soluble in dimethylformamide and alcohol, and one sample (m.p. 220–242°) in alcohol gave a value of 0.047 for its intrinsic viscosity.

Although the monomer III does not seemingly contain such active hydrogen as were present in the compounds described in the studies mentioned previously,[3,4,6] the intrinsic viscosity measurement obtained on the sample of poly(diphenylvinylphosphine oxide) suggests the polymer is of low molecular weight. The degree of stabilization of the propagation radical through enolic-like structures involving the phosphoryl function may influence chain growth. Since the *d*-orbitals of the phosphorus atom would participate in the stabilization of the radical, such contributing structures as V may have different steric requirements from those of a carbon-carbon double bond composed of only



V

Z = polymer chain

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[3] K. D. Berlin and G. B. Butler, *J. Am. Chem. Soc.*, 82, 2712 (1960).

[4] K. D. Berlin and G. B. Butler, *J. Org. Chem.*, 25, 2006 (1960).

[5] An attempted preparation of di-*n*-propenylphenylphosphine oxide and diisopropenylphenylphosphine oxide *via* Grignard reaction resulted in polymerization of the monomers *in situ*. See C. G. Gebelein and E. Howard, Jr., Abstracts of Papers, Third Delaware Regional Meeting, Philadelphia, February 25, 1960, p. 79.

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[8] For a discussion of vinyl ketone polymers see: C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley & Sons, Inc., New York, 1952, Chap. 14.