A New Phosphorylation Reaction of Olefins. III. Derivatives of Some Unsaturated Fatty Materials[1]

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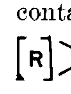
Abstract

The reaction of olefins with phosphorus trichloride in the presence of aluminum chloride was recently reported to result in phosphorus-containing acids or acid chlorides of the type  $[R]>P(\rightarrow O)X$ where X = OH or Cl.

This new phosphorylation reaction was extended to fatty acid derivatives containing olefinic double bonds, such as methyl oleate, oleonitrile, oleamide, N,N-dimethyloleamide, olive oil, oleylacetamide and oleyl alcohol. Phosphorylated fatty derivatives were obtained in good yield in all cases.

Introduction

We recently reported a new general method for preparing organophosphorus compounds by the reaction of olefins with phosphorus trichloride in the presence of a Friedel-Crafts catalyst (Fig. 1) (1,2,3).

$$\text{OLEFIN} + PCl_3 + AlCl_3 \longrightarrow [R]>P(\rightarrow O)X$$

where X = OH and/or CL

FIG. 1.

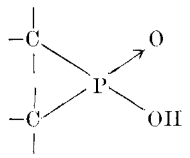
The following steps are involved in the new phosphorylation procedure:

(1) Formation of the $PCl_3 \cdot AlCl_3$ complex in methylene chloride.
(2) Addition of the olefin at 0C.
(3) Treatment of the reaction complex with methyl alcohol at room temperature.
(4) Decomposition with water and subsequent work-up of the sample.

The reaction was found to be very general and applicable to a large number of olefins. They include *alpha*-olefins, compounds with a centrally located double bond such as tricosene-11, and compounds with highly hindered double bonds. The latter gave the phosphorus acid chlorides in very high yield. Commercial propylene trimers and tetramers which are complex mixtures of highly branched olefins were phosphorylated quantitatively by this procedure.

The phosphorylated derivatives undergo the typical reactions expected of phosphorus acid chlorides and phosphorus acids. Thus the acid chlorides react with alcohol in the presence of the corresponding sodium alcoholate to yield the ester. The esters are readily hydrolyzed by base to the corresponding acid. The acid is also obtained directly by the hydrolysis of the acid chloride, and reaction of the acid with thionyl chloride yields the acid chloride.

While the existence of the functional groups was well established by these reactions and by elemental and instrument analysis, some difficulties were encountered in determining how these groups were attached to the carbon chain. The best fit for the data obtained is a disubstituted phosphinic acid:

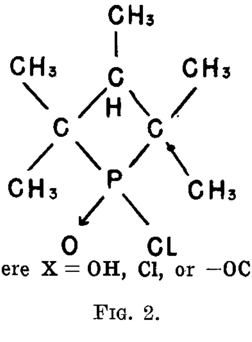


Working with the highly branched 2,4,4-trimethylpentene-2, we were able to establish the existence of a 4-membered phosphorus-containing cyclic structure (Fig. 2) for the acid, acid chloride, and methyl ester derivative obtained from this olefin (3).

While no claims are made that all the phosphorylated derivatives reported by us have such cyclic structures, the evidence for the 4-membered ring is excellent when working with hindered olefins. In the case of the less branched olefins, the existence of the disubstituted phosphinic acid group is established without doubt, though the exact attachment of this group to the carbon chain needs further confirmation.

It is the purpose of this paper to describe application of the new phosphorylation reaction to fatty acid derivatives containing olefinic double bonds. The effect of reaction conditions on the products obtained with methyl oleate have been reported previously (2). In this publication, variations in the terminal functional group are examined while the unsaturated hydrocarbon moiety (oleyl) is being phosphorylated by the new procedure.

Several techniques have been reported in the literature for the formation of phosphorus derivatives from unsaturated fatty materials. Sasin et al. (4) and Stiles et al. (5) reported preparation of dialkyl alkyl phosphonates by the free radical addition of dialkyl phosphites to the olefins using a peroxide catalyst. The free radical catalyzed addition of phosphorus trichloride to *alpha*-olefins had been reported by Kharasch (6), and the direct addition of yellow phosphorus in the presence of oxygen has also been described (7,8). These procedures have several shortcomings, in particular low yields, limited reactivity or utilization of expensive raw materials.



where X = OH, Cl, or $-OCH_3$

FIG. 2.

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[1] Presented at the AOCS meeting in New Orleans, La., 1962.

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Experimental

Raw Materials

(1) Unsaturated fatty materials. In all cases, commercially available raw materials were used without purification. Sources and analysis are shown below:

   (a) Oleonitrile (Arneel OD[3]). *Anal* Calcd.: Iodine Value (I.V.) 96.4. Found: I.V., 83.5.

   (b) Methyl oleate. Oleic acid (Neofat 90–04[3]) was refluxed with excess of methanol and a trace of acid, followed by distillation. *Anal.* Calcd.: I.V., 85.6; sap. equiv., 296. Found: I.V., 87; sap. equiv., 288.

   (c) Oleamide (Armid O[3]). *Anal.* Calcd.: I.V. 90.1. Found: I.V., 84.4.

   (d) N,N-Dimethyloleamide from C. P. Hall Co. *Anal.* Calcd.: I.V., 82.2. Found: I.V., 84.8.

   (e) Oleyl alcohol from Croda, Inc. *Anal.* Calcd.: I.V., 94.6. Found: I.V., 75.5.

   (f) Commercial olive oil. *Anal.* Specific Gravity 20C/20C. 0.9122.

   (g) Oleylacetamide. Oleylamine (Armeen OD[3]) was refluxed with acetic anhydride and triethylamine, the reaction mixture poured onto ice and the organic layer was dried and purified. *Anal.* Calcd.: I.V., 62.8. Found: I.V., 66.7.

   (h) Methyl linoleate. Pharmafat 858[4] (consisting of about 75% linoleic acid, 13% oleic acid, and 12% saturated acids) was esterified by refluxing with an excess of methanol followed by distillation. *Anal.* Calcd.: I.V., 144. Found: I.V., 141.

(2) Other reagents:

   (a) Phosphorus trichloride, reagent grade, from J. T. Baker Chem. Co.

   (b) Aluminum chloride, anhydrous, technical grade from Fisher Scientific Co.

   (c) Methylene chloride, certified reagent grade from Fisher Scientific Co.

Procedure

Three typical examples of the general phosphorylation procedure are shown:

(1) *Methyl Oleate:* The reaction was run in a round bottom flask with a stirrer, thermometer, dropping funnel, and a condenser with a drying tube. To the reaction flask was added 125 ml of methylene chloride, 42.8 g (0.316 mole) of phosphorus trichloride, and 41.6 g (0.316 mole) of aluminum chloride. The mixture was cooled to 0C and 46.2 g (0.158 mole) of methyl oleate in 62.5 ml of methylene chloride was added over a 45 min period. During the addition, the temperature was kept at 0C. After the addition was completed, stirring was continued at room temperature for 1.5 hr. Anhydrous methanol (250 ml) was then added over a half-hour period, allowing the temperature to rise to 40C. The reaction mixture was then stirred for 2 hr at room temperature. Excess water was carefully added with stirring. The organic layer was then separated, washed with water until neutral, and dried over anhydrous sodium sulfate. The methylene chloride was taken off *in vacuo* and 61 g of a light yellow oil was obtained. *Anal.* Calcd, for $C_{19}H_{38}PO_3Cl$: P, 8.2; Cl, 9.4; sap. equiv., 189. Found: P. 8.3; Cl, 3.6; sap. equiv., 210. The low values for Cl indicated that extensive hydrolysis of the acid chloride to the acid form had occurred.

(2) *Oleonitrile:* Using the same procedure as above, oleonitrile was phosphorylated using the following quantities. 30.4 g (0.10 mole) of oleonitrile dissolved in 75 ml of methylene chloride, 27.6 g (0.20 mole) of aluminum chloride in 125 ml of methylene chloride, and 160 ml of methanol. The yield was 31 g [85% based on $C_{17}H_{33}CN(PO_2H)$]. *Anal.* Calcd. for $C_{17}H_{33}(PO_2H)CN$: P, 8.4; Cl, 0. Found: P, 8.0; Cl, 3.9.

(3) *N,N-Dimethyloleamide:* In the same manner N,N-dimethyloleamide was reacted using the following quantities: 31 g (0.10 mole) of N,N-dimethyloleamide dissolved in 75 ml of methylene chloride, 40.4 g (0.30 mole) of phosphorus trichloride and 40.1 g (0.30 mole) of aluminum chloride in 200 ml of methylene chloride, and 240 ml of methanol. The yield was 33 g [88% based on $C_{17}H_{33}CON(CH_3)_2(POOH)$]. *Anal.* Calcd. for $C_{17}H_{33}CON(CH_3)_2(POOH)$: P, 8.3; Cl, 0.0. Found: P, 8.7; Cl, 3.6.

Results and Discussion

The new phosphorylation reaction was extended to the following unsaturated fatty derivatives: oleyl alcohol, oleonitrile, oleamide, N,N-dimethyloleamide, oleylacetamide, methyl linoleate and olive oil. All reactions were carried out in methylene chloride using at least 100% molar excess of the $PCl_3 \cdot AlCl_3$ reagent. The excess was used in order to overcome possible interference by the terminal group. In all cases, the phosphorylated products were obtained in good yields. The results obtained are shown in Table I.

The reduction of the I.V. and phosphorus analyses are in good agreement with the proposed formation of a phosphinic acid derivative by addition at the carbon-carbon double bond. The presence of less than the theoretical amounts of chlorine for the acid chloride form indicates that hydrolysis to the free acid occurred during work-up of the samples. This was confirmed by titrations and infrared spectra. The I.V. of all the products indicated that a small amount of residual unsaturation always remained. This was believed to be due to some polyunsaturation in the starting material. To investigate this point, a sample containing a high amount of methyl linoleate was phosphorylated with excess of the $AlCl_3 \cdot PCl_3$ reagent. It was found that only one phosphorus group added when two double bonds were available in the same molecule. A correspondingly high I.V. was found.

Under the reaction conditions used, the terminal

TABLE I

Fatty derivative RX [d]	Iodine value		%P found/ calcd.[c]	Yield %
	Starting material	Phosphorylated product		
Methyl oleate	87.0	7.8	8.3/ 8.6	95
Oleyl nitrile	83.5	7.6	8.0/ 8.4	84
Oleamide	84.4	7.9	8.3/ 8.5	87
N,N-dimethyloleamide	84.8	16.5	8.7/ 8.3	88
Oleylacetamide	66.7	7.7	7.6/ 8.1	81
Oleyl alcohol	75.5	13.4	10.2/10.7 [a]	90
Stearyl alcohol	2.2	......	5.7/ 5.3 [b]	52
Olive oil	81.3	7.8	5.4/ 8.2	80
Methyl linoleate	141.0	22.4	9.4/ 9.0	98

[a] Calcd. for $[R(POOH)O]_2PH \rightarrow O$

[b] Calcd. for $(RO)_2PH \rightarrow O$.

[c] Calcd. for R(POOH)X, where

R = $C_{17}H_{33}$, $C_{18}H_{35}$, $C_{17}H_{31}$ or $C_{18}H_{37}$

X = $COOCH_3$, CN, $CONH_2$, $CON(CH_3)_2$, $NHCOCH_3$, or OH.

[d] All products were isolated as mixtures of the acid chloride, R(POCl)X and the free acid, R(POOH)X.

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[3] Trade name: Armour and Co.

[4] Trade name: Archer Daniels Midland.

functional groups did not react under the phosphorylation conditions used, except in the case of oleyl alcohol. This was confirmed by functional group analyses and infrared spectra. In the case of oleyl alcohol, in addition to reaction of the double bond, the terminal group also reacted to form a dialkylphosphite. To confirm the general course of this reaction, the corresponding saturated fatty alcohol, stearyl alcohol was reacted under the general conditions of the phosphorylation reaction. Distearylphosphite was obtained in high yield; acidic hydrolysis yielded the starting fatty alcohol.

Considerable work is in progress to extend the scope of this reaction to other fatty unsaturated materials, as well as to additional olefinic structures. Related phosphorylating agents, such as phenylphosphorus dichloride, are also being studied. The chemistry of the reaction is quite complex and further basic studies are required. In addition, there exists a tremendous potential for doing creative application research.

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Nitration of Methyl Oleate with Acetyl Nitrate: A Synthesis of Methyl Aminostearate[1]

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Abstract

Acetyl nitrate, an effective reagent for the nitration of simple alkenes, provided a convenient means of introducing nitrogen into unsaturated fatty acids. This nitrating agent was found to react quantitatively under mild conditions with methyl oleate forming isomeric nitro, acetoxy-nitro, and nitro-nitrate derivatives. These nitro derivatives were isolated by column and thin-layer adsorption chromatography, and their structures were elucidated by infrared spectroscopy.

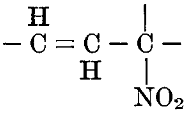
In addition, the isomeric nitro derivative was reduced by catalytic hydrogenation to give methyl aminostearate.

Introduction

IN THE PREPARATION of fatty nitrogen derivatives, nitrogen is usually introduced into the fatty acid molecule by reactions of the carboxyl group with ammonia or amines. Such reactions yield high-molecular-weight nitriles and amides that are convenient intermediates for preparing amino and quaternary ammonium compounds.

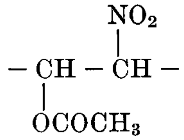
Relatively few methods have been described for introducing nitrogen into the fatty acid chain at the sites of unsaturation. Nevertheless, reactions of this type may be expected to yield derivatives that have useful and interesting properties. Fatty acid derivatives containing nitrogen are important industrially as surfactants, germicides, and fungicides (1).

The present communication reports that acetyl nitrate, an effective reagent for nitrating simple alkenes (2), reacts quantitatively with methyl oleate forming isomeric nitro (I), acetoxy-nitro (II), and nitro-nitrate (III) derivatives.



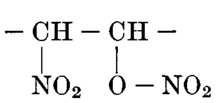
$$-\overset{H}{C}=\underset{H}{C}-\underset{\underset{NO_2}{|}}{\overset{|}{C}}-$$

I



$$-\underset{\underset{OCOCH_3}{|}}{CH}-\overset{\overset{NO_2}{|}}{CH}-$$

II



$$-\underset{\underset{NO_2}{|}}{CH}-\underset{\underset{O-NO_2}{|}}{CH}-$$

III

These derivatives were isolated from the nitration mixture by column and thin-layer chromatography (TLC), and their structures were elucidated by infrared spectroscopy. Structures of isomers of derivative I were determined *via* oxidative degradation of the double bonds. In addition, methyl aminostearate was synthesized from derivative I by catalytic hydrogenation.

Experimental

Nitro Derivatives: Analysis and Structure

Nitration of Methyl Oleate. The reaction of acetyl nitrate with methyl oleate (obtained from the Hormel Foundation, Austin, Minn.) was conducted as follows: 5 ml (0.08 mole) of colorless 70% nitric acid was added slowly to 70 ml of acetic anhydride at 15C. The temperature of the reaction was maintained between 20 and 25C by controlling the rate of addition of nitric acid. Methyl oleate (3.6 g, 0.012 mole) was added to the acetyl nitrate solution, and the reaction was continued at about 25C for 1 hr. The reaction was terminated by adding 150 ml of ice water, and the products were extracted from the resulting mixture with diethyl ether. The extract was washed with distilled water until the washings were neutral and then was dried over anhydrous Na_2SO_4. The product (3.7 g) was recovered after evaporation of the solvent.

Analysis and Isolation of Nitro Derivatives by TLC. The product from the nitration of methyl oleate was resolved into its components by TLC on silicic acid (4) using 85:15 petroleum ether-diethyl ether as the eluent. Individual spots were charred with 50% H_2SO_4 and then analyzed with a densitometer as previously described (5). Small amounts (50–100 mg) of derivatives I, II, and III were obtained by chromatography on 1 mm layers of silicic acid using 85:15 petroleum ether-diethyl ether as the eluent. The purity of each fraction eluted from the silicic acid was confirmed by analytical TLC (4). The identity of each fraction was verified by infrared analysis. The presence of the acetoxy group in II was established by the infrared absorbance characteristic of hydroxyl groups in the corresponding nitro alcohol derivative (2). Characteristic infrared absorbancies of the derivatives were as follows: I, 6.43 μ (unconjugated

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[1] Presented at the AOCS meeting in Toronto, Canada, 1962.

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