phosphine sulfide (IV), mp 194.5–197°. A second crystallization from benzene afforded 0.98 g (38.6%) of acid, mp 196.5–198.5°. Work-up of the mother liquors gave an additional 0.52 g (21%) of product, mp 190–196°.

Anal. Calcd for $C_{13}H_{23}O_2PS$: C, 65.89; H, 6.65; mol wt, 346. Found: C, 66.4; H, 7.5; mol wt, 346.

The Reaction of *n*-Butyllithium with Di-*n*-Butylvinylphosphine.—To 4.5 g (0.026 mole) of di-*n*-butylvinylphosphine dissolved in 25 ml of ether, and contained in a metalation tube,[1b] 30 ml (1.6 *M* in hexane, 0.05 mole) of *n*-butyllithium was added rapidly. After stirring for 24 hr at room temperature, the reaction mixture was carbonated,[1b] treated with 1.28 g (0.04 mole) of sulfur, and extracted thoroughly with water. The organic layer was concentrated and distilled, bp 30–85° (0.5 mm), to give 0.57 g of a mixture of di-*n*-butyl ketone and tri-*n*-butyl alcohol, as evidenced by gas phase chromatographic retention times and infrared spectral analysis. An infrared spectrum of the distillation residue had an absorption band at 6.2 μ characteristic of a carboxylic acid salt.[11] The residue was dissolved in ether and acidified with dilute sulfuric acid. The organic layer was separated, dried over sodium sulfate, and concentrated. An infrared spectrum of the concentrate, 4.6 g, did not exhibit the 6.2-μ band and did have an absorption band at 5.87 μ characteristic of a carboxylic acid.[11] A portion of the amorphous acid, 2.5 g, was esterified with diazomethane in the usual manner. An infrared spectrum of the ester had a carbonyl absorption at 5.77 μ. An nmr spectrum of the material in $CDCl_3$ exhibited proton absorptions at τ 6.26 (3), 8.56 (65), and 9.04 (26), assigned to methoxy, methylene, and methyl groups, respectively. The polymeric acid contained 59.3% carbon and 10.4% hydrogen by analysis.

The original aqueous layer was acidified with dilute sulfuric acid and thoroughly extracted with ether. Concentration afforded 0.76 g of material that was distilled under reduced pressure to give 0.12 g of valeric acid, bp 30–50° (0.5 mm), n^{20}_D 1.4094. The distillation residue was esterified in the usual manner. An nmr spectrum of the esterified material was essentially identical with the spectrum of the ester described above.

Acknowledgment.—The author is indebted to Dr. J. McLeskey for the detailed proton nmr analysis of one of the compounds.

[11] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, New York, N. Y., 1958, p. 174.

The Reaction of Aryl Chloroformates with Silver Nitrate

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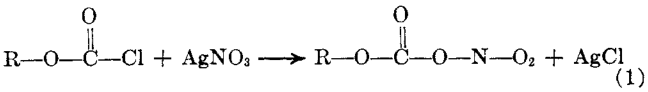
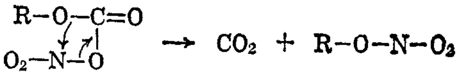
The reaction of silver nitrate with chloroformates has not been extensively investigated. However, during the past several years a few publications have emerged. Boschan[1] and, slightly later, Mortimer[2] reported on the reactions of alkyl chloroformates and presented a facile synthesis of alkyl nitrate esters. Each gave evidence that the major reaction pathway involved initial formation of an alkyl nitratoformate.



$$R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl + AgNO_3 \longrightarrow R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}N{-}O_2 + AgCl \qquad (1)$$

More recently, confirming kinetic proof has been presented by Kevill and Johnson.[3] Boschan suggested that the next step was a concerted SNi rearrangement with loss of carbon dioxide to form the product nitrate.



$$\begin{matrix} R{-}O{-}C{=}O \\ O_2{-}N{-}O \end{matrix} \longrightarrow CO_2 + R{-}O{-}N{-}O_2 \qquad (2)$$

At about the same time, Chaney and Wolfrom[4] reported that the reaction of phenyl chloroformate with silver nitrate yields *o*-nitrophenol. By analogy with the above reactions, they suggested that phenyl nitrate might be a primary intermediate which subsequently rearranged internally to the more stable isolated product.

We have repeated and extended the latter work and have obtained results that lead to further speculation with regard to some of these mechanisms. Experiments were carried out in essentially the same manner used by previous workers. An acetonitrile solution of silver nitrate and aryl chloroformate was stirred at 0–10° for several hours. After removing silver chloride precipitate by filtration, the reaction mixture was examined by vpc and the products were isolated and identified by standard methods. A summary of pertinent experiments and results are presented in Table I.

TABLE I
REACTIONS BETWEEN ARYL CHLOROFORMATES AND SILVER NITRATE

Substrate	Moles of $AgNO_3$	Product(s) (%)
p-Cresyl chloroformate[a]	2.0	*o*-Nitro-*p*-cresol (44)
Phenyl chloroformate[a,b]	1.0	*o*-Nitrophenol (34) *p*-Nitrophenol (28)
Phenyl chloroformate and *p*-cresol[c]	1.3	*o*-Nitrophenol (3.6) *p*-Nitrophenol (2.9) *o*-Nitro-*p*-cresol (43)

[a] Isolated yields. [b] In a similar reaction, vpc analysis of the crude reaction product showed 19% *o*-nitrophenol, 33% *p*-nitrophenol, and less than 0.01% *m*-nitrophenol. [c] Values shown were obtained by vpc. Because of difficulty with tailing, the analysis for *p*-nitrophenol is inaccurate. However, the values shown are qualitatively correct.

As shown, the reaction of phenyl chloroformate with silver nitrate yields not only *o*-nitrophenol but also large amounts of the *para* isomer. This mixture does not result from secondary rearrangement of a primarily formed *o*-nitrophenol as shown by the stability of that material under the reaction conditions (see Experimental Section). In addition, the exchange experiment wherein *p*-cresol was extensively nitrated in the presence of reacting phenyl chloroformate and silver nitrate suggests that the reaction is intermolecular.[5]

The lack of positional specificity and the intermolecular nature of the reaction are consistent with the following sequence (3). The first step is identical with that suggested by previous workers[1-4] and is predicated on their work and on the known reaction of silver nitrate with benzoyl chloride to form benzoyl nitrate.[6] We have described the subsequent ionization as yielding nitronium and phenolate ions that recombine to the

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[1] R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

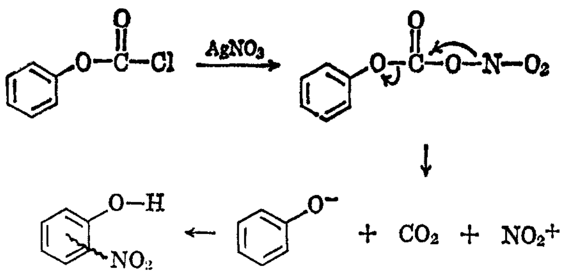
[2] G. A. Mortimer, *J. Org. Chem.*, **27**, 1876 (1962).

[3] D. N. Kevill and G. H. Johnson, *J. Am. Chem. Soc.*, **87**, 928 (1965).

[4] A. Chaney and M. L. Wolfrom, *J. Org. Chem.*, **26**, 2998 (1961).

[5] This result might also be explained by transesterification of the *p*-cresol and subsequent intramolecular reaction of the *p*-cresyl chloroformate with silver nitrate. However, when 1 mole of *p*-cresol and 1 mole of phenyl chloroformate were treated with a deficiency (0.5 mole) of silver nitrate, the product mixture contained 0.5 mole of phenyl chloroformate and no *p*-cresyl chloroformate, suggesting that there was little or no transesterification under the reaction conditions.

[6] (a) A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press Ltd., London, 1959, Chapter 6; (b) F. Francis, *J. Chem. Soc.*, **89**, 1 (1906).



(3)

product nitrophenols. This is probably a gross oversimplification of the process, considering the complications in the thoroughly studied acyl nitrate nitrations.[7] However, the data presented herein and the attractive analogy with the reactions of acyl and aroyl nitrates suggests that there is an ionic dissociation in which substrate and nitrating agent are both generated from an intermediate nitratoformate ester. When an alternate substrate is available, this will also be nitrated depending on its reactivity. There seems to be little evidence for a concerted S$_N$i rearrangement. This reaction scheme is also similar to the suggestion put forth by Kevill and Johnson[3] for the alkyl chloroformates.

Experimental Section[8]

Nitrophenols.—All of the nitrophenols used as infrared and vpc standards were commercially available and were used as received.

Aryl Chloroformates.—These materials were prepared by reaction of the corresponding phenol with *ca.* 10% excess phosgene in toluene solution and cold aqueous base. After washing the product solution with water and drying over sodium sulfate, the product was distilled through an efficient column.

A. **Phenyl chloroformate** was obtained in 52% yield: bp 84–87° (22 mm), n^{25}D 1.5101 [lit.[9] bp 80° (22 mm)].

B. ***p*-Cresyl chloroformate** was obtained in 73% yield: bp 93–96° (15 mm), n^{25}D 1.5020 [lit.[10] bp 108° (30 mm)].

Reactions with Silver Nitrate. A. Phenyl Chloroformate.—A solution of 31.4 g (0.20 mole) of phenyl chloroformate and 34.0 g (0.20 mole) of silver nitrate in 450 ml of acetonitrile (cooled to 0° before mixing) was stirred for 1 hr at 0°, then for 2 hr at room temperature. Precipitated silver chloride was removed by filtration, and the dark filtrate was diluted with water and made basic. Acetonitrile was removed by distillation, and the product solution was acidified and steam distilled to yield 9.4 g (34%) of *o*-nitrophenol melting at 42–45°. The infrared spectrum of this material was identical with that of an authentic sample of that material. The pot residue from the steam distillation was refluxed shortly with hydrochloric acid (to coagulate tars), treated with decolorizing carbon, and extracted with ether. The residue from solvent evaporation was treated with 50% sodium hydroxide solution to obtain the solid salt of *p*-nitrophenol. This was slurried with water and acidified to yield 7.8 g (28%) of *p*-nitrophenol melting at 112–115° (from benzene). The infrared spectrum of this material was identical with that of an authentic sample of that material.

In a similar experiment on one-half the above scale, vpc analysis of the crude reaction mixture showed the yields to be 19% *o*-nitrophenol, 33% *p*-nitrophenol, and less than 0.01% *m*-nitrophenol.

B. Reaction of Phenyl Chloroformate with Silver Nitrate in the Presence of *p*-Cresol.—A mixture of 21.3 g (0.13 mole) of silver nitrate, 15.7 g (0.10 mole) of phenyl chloroformate, and 10.8 g (0.10 mole) of *p*-cresol in acetonitrile solution were stirred for 1 hr at 0°. Vpc analysis of the crude reaction mixture showed it to contain 3.6% *o*-nitrophenol, 2.9% *p*-nitrophenol, and 43% *o*-nitro-*p*-cresol (based on silver nitrate). Steam distillation of the product yielded 10.2 g of yellow oil, the infrared spectrum of which was essentially identical with that of an authentic sample of *o*-nitro-*p*-cresol. Distillation gave one cut, bp 100° (4 mm), that crystallized and melts at 32–35°.

C. Reaction of Phenyl Chloroformate and *p*-Cresol with a Deficiency of Silver Nitrate.—A solution of 15.7 g (0.10 mole) of phenyl chloroformate, 10.8 g (0.10 mole) of *p*-cresol, and 8.5 g (0.050 mole) of silver nitrate in acetonitrile was stirred for 1 hr at 0° and *ca.* 2 hr at room temperature. The silver chloride (7.0 g, 98%) was removed by filtration. Vpc analysis of the crude product solution showed it to contain 8.7 g (55%) of phenyl chloroformate and less than 0.1% *p*-cresyl chloroformate. No attempt was made to analyze for other products.

D. Attempted Reaction of *o*-Nitrophenol with Silver Nitrate.—A mixture of 2.8 g (0.020 mole) of *o*-nitrophenol and 6.8 g (0.040 mole) of silver nitrate was stirred in acetonitrile solution for 3 hr at room temperature. Vpc analysis of the reaction product showed that it contained only starting material and there was no *p*-nitrophenol present.

E. *p*-Cresyl Chloroformate.—An acetonitrile solution of 34 g (0.20 mole) of *p*-cresyl chloroformate and 68 g (0.40 mole) of silver nitrate was stirred for *ca.* 1 hr at 0° and 2 hr at room temperature. Distillation of the crude product from filtration of the silver chloride yielded 12.5 g (44%) of *o*-nitro-*p*-cresol melting at 34–35° (from cold hexane). The infrared spectrum of this material was identical with that of an authentic sample of material.

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[7] (a) G. Drefahl and H. Cramer, *Chem. Ber.*, **91**, 745 (1958); (b) M. A. Paul, *J. Am. Chem. Soc.*, **80**, 5332 (1958); (c) H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 729 (1955); (d) V. Gold, F. D. Hughes, and C. K. Ingold, *ibid.*, 2467 (1950); F. G. Bordwell and E. W. Garbisch, *J. Am. Chem. Soc.*, **82**, 3588 (1960).

[8] Infrared spectra were obtained as Nujol mulls or neat smears using a Perkin-Elmer Model 337 spectrophotometer. Vpc analyses were performed using a column comprised of SE 30 silicone oil on Anakrom ABS support. An internal standard was 1,2,3,4-tetrachlorobenzene.

[9] Y. Iwakura and A. Nobeya, *J. Org. Chem.*, **25**, 1118 (1960).

[10] M. Capisarow, *J. Chem. Soc.*, 251 (1929).

Fluoride Ion Initiated Reactions of Perfluoro α-Olefins. I. Reaction of the Pentafluoroethyl Carbanion with Tetrafluoroethylene

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The polymerization of tetrafluoroethylene (TFE) has usually followed a free-radical mechanism and yielded solid polymers. Anionic catalysis has been successfully used in the limited polymerization of other fluoro olefins to produce liquids, but TFE has been unreactive, presumably owing to its symmetry. This suggested a possible advantage in the use of a solid catalyst. Cesium fluoride on an active-carbon support did catalyze the reaction of TFE with itself, but the products were so tightly bound to the catalyst that elevated temperatures (exceeding 100°) were required for their removal. The product was an extensive mixture of saturated compounds, olefins, and diolefins. Some of the compounds formed contained an uneven number of carbon atoms, indicating rupture of the carbon-to-carbon bond. A milder reaction, avoiding rupture of the bond between carbon atoms, was obtained with a catalyst system comprising cesium fluoride suspended in an activating solvent such as di-, tri-, or tetraethylene glycol dimethyl ether (hereinafter called di-, tri-, or tetraglyme).

The condensation of TFE with itself in the presence of solvent-activated cesium fluoride presumably follows a cycle comprising the following steps: (1) formation