

[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

## The Unexpected Course of Several Arbuzov–Michaelis Reactions; An Example of the Nucleophilicity of the Phosphoryl Group<sup>1a</sup>

BY H. JAMES HARWOOD<sup>1b</sup> AND DANIEL W. GRISLEY, JR.

RECEIVED MAY 28, 1959

The reaction of dimethyl phenylphosphonite with  $\beta$ -bromoethyl acetate yielded  $\beta$ -acetoxyethyl phenyl-(methyl)-phosphinate and ethylene bis-[phenyl-(methyl)-phosphinate] instead of the expected Arbuzov product, methyl phenyl-( $\beta$ -acetoxyethyl)-phosphinate. Similarly, dimethyl phenylphosphonite and ethylene dibromide reacted to form ethylene bis-[phenyl-(methyl)-phosphinate]. The formation of these unexpected esters occurred *via* isomerization of dimethyl phenylphosphonite to methyl phenyl-(methyl)-phosphinate followed by reaction of this latter ester with alkyl halide. A probable mechanism for this and related reactions is discussed.

### Introduction

A variety of organophosphorus compounds<sup>2</sup> has been prepared by the Arbuzov–Michaelis reaction since it was first reported at the turn of the century.<sup>3</sup> A considerable body of experience has developed confidence in the normal course of reaction which involves the formation of a new carbon–phosphorus bond. However, it has been shown recently that products isomeric with the usual can be obtained in this reaction.<sup>4,5</sup> Thus, the Perkow and Allen reactions yield unsaturated phosphorus esters with a new phosphorus–oxygen linkage instead of forming a carbon–phosphorus bond.

This paper describes new types of isomeric products obtainable from the Arbuzov–Michaelis reaction. These products, in contrast to those from the Perkow or Allen reactions, contain a new carbon–phosphorus bond different from that expected.

### Results

In connection with a study on the Arbuzov–Michaelis reaction, the reaction of dimethyl phenylphosphonite (I) with  $\beta$ -bromoethyl acetate was investigated. Although methyl phenyl-( $\beta$ -acetoxyethyl)-phosphinate (II) was the expected product, it was formed in not greater than 5% yield. An isomer,  $\beta$ -acetoxyethyl phenyl-(methyl)-phosphinate (IV) was obtained in 60% yield instead. The structure of the unexpected ester was established by hydrolysis to phenyl-(methyl)-phosphinic acid and ethylene glycol (isolated as its dibenzoate). In addition, a 25% yield of a mixture of ethylene bis-[phenyl-(methyl)-phosphinate] (VI) and an ester of ethylene bisphenylphosphinic acid (VII)<sup>6,7</sup> was isolated.

(1) (a) Presented before the Division of Organic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958. (b) University of Akron, Akron, Ohio.

(2) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950.

(3) (a) A. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **38**, 687 (1906); *Chem. Zentr.*, **77**, II, 1639 (1906); (b) A. Michaelis, *Ann.*, **326**, 139, 162 (1903).

(4) (a) W. Perkow, *Ber.*, **87**, 755 (1954); (b) W. Perkow, E. W. Krochow and K. Knoevenagel, *ibid.*, **88**, 662 (1955).

(5) J. F. Allen, U. S. Patent 2,816,128 (Dec. 10, 1957).

(6) The exact nature of the ester was not determined due to the small amount present in the mixture. Although the dimethyl ester VIII was probably present in the mixture, the presence of a cyclic pyroester from VII is also a reasonable possibility.

(7) Esters of bisphosphinic acids related to VII have been obtained from similar reactions; see, for example: (a) M. I. Kabachnik and P. A. Rossiiskaya, *Bull. acad. Sci. U.S.S.R., classe sci chim.*, 631 (1947); *C. A.*, **42**, 5845 (1948); (b) J. L. Van Winkle and R. C. Morris, U. S. Patent 2,681,920 (June 22, 1954).

The reaction of ethylene dibromide with dimethyl phenylphosphonite proceeded similarly. In this case, the major products were ethylene bis-[phenyl-(methyl)-phosphinate] (57%) and methyl phenyl-(methyl)-phosphinate (38%). A low yield of the bisphosphinic acid (VII) indicated that an insignificant amount of diesters derivable from the normal Arbuzov reaction was formed. Surprisingly, there was no evidence for the presence of monosubstituted esters<sup>8</sup> among the reaction products.

**Hypothesis of Mechanism.**—Formation of the isomeric esters can be explained by a mechanism involving first the rapid isomerization of dimethyl phenylphosphonite to methyl phenyl-(methyl)-phosphinate (III), followed by nucleophilic reaction is believed to involve the formation of an intermediate dialkoxyphosphonium ion V, which is decomposed by attack of halide ion to yield the isomeric product.

**Evidence for Hypothesis.**—The isolation of III as a reaction product, and the simultaneous disappearance of III and the appearance of IV with increased reaction time provide evidence that methyl phenyl-(methyl)-phosphinate is an intermediate in the formation of the isomeric esters. This conclusion was further substantiated when methyl phenyl-(methyl)-phosphinate was heated with  $\beta$ -bromoethyl acetate using the same conditions used for the attempted Arbuzov reaction. The yields of IV and VI obtained were identical with those from the Arbuzov reaction. As expected, none of the normal Arbuzov esters were obtained in this latter reaction. Several other examples of reactions of pentavalent phosphorus esters with alkyl halides have been reported recently.<sup>9</sup>

The proposed reaction sequence requires that the phosphoryl group behave as a nucleophilic reagent.<sup>10</sup> This is not without precedent, however; Meisen-

(8) The lack of monosubstituted products may indicate that the phosphoryl group of monosubstituted esters activates the residual bromine through a neighboring group effect.

(9) (a) V. V. Korshak, I. A. Gribova and V. K. Shitikov, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk.*, 210 (1958); *C. A.*, **52**, 12804 (1958); (b) H. Maier-Bode and G. Kotz, *Ger. Patent Appln.* 1,014,107 (Aug. 27, 1957).

(10) Similar nucleophilic behavior has been shown with carbonyl (C=O) compounds,<sup>11</sup> amine oxides<sup>12</sup> (N  $\rightarrow$  O) and sulfoxides<sup>13</sup> (S  $\rightarrow$  O).

(11) (a) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 687 (1956); (b) W. Lwowski, *Angew. Chem.*, **70**, 490 (1958).

(12) Several recent examples are quoted: (a) V. J. Traynelis and R. F. Martello, *This Journal*, **80**, 6590 (1958); (b) F. Ramirez and P. V. vonOstwalden, *ibid.*, **81**, 156 (1959).

(13) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).



phenylphosphonite: In their reaction, the starting alkyl halide was more reactive than the halide produced and the isomerization reaction was therefore minimized. Likewise in our work, the higher yields of normal Arbuzov reaction products obtained from the  $\beta$ -bromoethyl acetate reaction as contrasted to the ethylene dibromide reaction reflect the greater reactivity of  $\beta$ -bromoethyl acetate.

In conclusion, the Arbuzov-Michaelis reaction, although a useful synthetic route for the preparation of phosphonic esters, can yield isomeric mixtures when applied to the preparation of phosphinic esters. This will be particularly true when methyl esters of trivalent phosphorus derivatives are used as starting materials but can be expected to apply to some extent with higher esters also.

### Experimental

**Dimethyl Phenylphosphonite.**—A mixture of methanol (225 ml.) and hexane (80 ml.) was added slowly with stirring to a mixture of dichlorophenylphosphine (500 g., 2.8 moles) and dry pyridine (475 ml.) in hexane (1500 ml.) at 0–10° during 2 hr. After stirring an additional hour, pyridine hydrochloride was filtered, the clear filtrate was concentrated on a water-bath and distilled. After a small forerun, there was obtained dimethyl phenylphosphonite (322.5 g., 68% yield), b.p. 98° (17 mm.),  $n_D^{25}$  1.5261 (lit.<sup>26</sup> b.p. 94.5° (13 mm.),  $n_D^{25}$  1.5186).

**$\beta$ -Bromoethyl Acetate.**—Eastman No. 1634 was redistilled under nitrogen, b.p. 155–160°,  $n_D^{25}$  1.4543. Material prepared by acetylation of ethylene bromohydrin was also used, b.p. 79–83° (45 mm.),  $n_D^{25}$  1.4531.

**Reaction of Dimethyl Phenylphosphonite with  $\beta$ -Bromoethyl Acetate (A).**—A mixture of dimethyl phenylphosphonite (85 g., 0.5 mole) and freshly distilled  $\beta$ -bromoethyl acetate (85 g., 0.5 mole) was heated carefully to 120° (in a dry atmosphere) at which temperature a vigorous reaction ensued.<sup>27</sup> The mixture was then heated to 150° for 3 hr. and allowed to stand at room temperature for several days. The mixture was distilled to yield crude  $\beta$ -bromoethyl acetate (21 g., 25% yield), b.p. 52–64° (7 mm.),  $n_D^{25}$  1.4492; methyl phenyl-(methyl)-phosphinate (32 g., 38% yield), b.p. 131–132° (5 mm.),  $n_D^{25}$  1.5123–1.5181<sup>28</sup>; and  $\beta$ -acetoxyethyl phenyl-(methyl)-phosphinate (39.5 g., 34%), b.p. 182–183° (3 mm.),  $n_D^{25}$  1.5045–1.5070.<sup>28</sup> A sample of this latter material was redistilled for analysis, b.p. 176–178° (0.7 mm.),  $n_D^{25}$  1.5107. The infrared spectrum of this ester was identical with that of the ester obtained from the reaction of methyl phenyl-(methyl)-phosphinate with  $\beta$ -bromoethyl acetate.

*Anal.* Calcd. for  $C_{11}H_{16}O_4P$  (242.2): C, 54.54; H, 6.24; P, 12.50; sapon. equiv., 121.1. Found: C, 54.92; H, 6.47; P, 12.23; sapon. equiv., 116.

The light-yellow viscous distillation residue (21 g.),  $n_D^{25}$  1.5555, was treated with 150 ml. of acetone. A white powder separated, 5.0 g., m.p. 237–255°. A sample of this material was dissolved in 5%  $NaHCO_3$  solution and reprecipitated by adding 10% HCl. The solid was washed with water and dried over  $P_2O_5$ , m.p. 266–267°. The infrared spectrum of this acid was identical with that of authentic ethylene bis-(phenylphosphinic acid) obtained from the reaction of dimethyl phenylphosphonite and ethylene dibromide, followed by hydrolysis.

*Anal.* Calcd. for  $C_{14}H_{16}P_2O_4$  (310.5): C, 54.1; H, 5.2; P, 20.0; neut. equiv., 155.2. Found: C, 53.9; H, 5.0; P, 20.0.

(26) A. E. Arbuzov and A. I. Razumov, *Izvest. Akad. Nauk, U.S.S.R. Otdel. Khim. Nauk*, 167 (1945); *C. A.*, 40, 3411 (1946).

(27) This reaction was probably the isomerization of dimethyl phenylphosphonite to methyl phenyl-(methyl)-phosphinate. A similar exothermic reaction was not observed when methyl phenyl-(methyl)-phosphinate was heated with  $\beta$ -bromoethyl acetate.

(28) The refractive indices of these materials fall rapidly on exposure to the atmosphere. For example, the refractive index of IV fell from 1.5080 at 25.8° to 1.5058 during a one-minute exposure to the atmosphere as a thin film on the refractometer prisms. This may account for the spread in refractive index values obtained from fractions of otherwise apparently pure material.

19.5; neut. equiv., 153.9 (after recrystallization from glacial acetic acid).

**Reaction of Dimethyl Phenylphosphonite with  $\beta$ -Bromoethyl Acetate (B).**—Dimethyl phenylphosphonite (40 g., 0.24 mole) was added to freshly distilled  $\beta$ -bromoethyl acetate (40 g., 0.24 mole) at 100° during one-half hour in a nitrogen atmosphere. The temperature of the mixture was raised to 120° where a vigorous reaction of approximately three minutes duration ensued.<sup>27</sup> The stirred mixture was heated for three hours at 160–170°, then for two hours at 175° and was then distilled. Two major fractions were obtained. The first, b.p. 155–160° (1 mm.),  $n_D^{25}$  1.5039–1.5092,<sup>28</sup> was shown by infrared to be  $\beta$ -acetoxyethyl phenyl-(methyl)-phosphinate. Vapor chromatography indicated contamination with about 5% of another substance, probably the isomer II; yield 33.7 g. (59.5%).

The higher boiling fraction, b.p. 204–207° (0.15 mm.),  $n_D^{25}$  1.5624, 10.1 g., was a pale yellow, viscous liquid.

*Anal.* Calcd. for  $C_{16}H_{20}P_2O_4$  (338.3): C, 56.87; H, 5.95. Found: C, 56.86; H, 5.64.

A sample of the higher boiling ester (2.22 g.) was decomposed by heating with distilled water and the solid product formed was filtered. Phenyl-(methyl)-phosphinic acid, 0.93 g. (45%), was extracted from the solid with ethanol. Ethylene bis-(phenylphosphinic acid), 0.45 g. (23%), remained undissolved. The infrared spectrum of a sample of this acid was identical with that of authentic material obtained from the reaction of dimethyl phenylphosphonite with ethylene dibromide.

**Structure Proof for  $\beta$ -Acetoxyethyl Phenyl-(methyl)-phosphinate by Hydrolysis. Isolation of Acid Fragment.**—A solution of  $\beta$ -acetoxyethyl phenyl-(methyl)-phosphinate (1.0 g., 4 mmoles) in 10% NaOH (20 ml.) was refluxed for 2 hr. The solution was acidified with concd. HCl and was allowed to stand at room temperature for two weeks. The fine colorless needles which separated from solution was phenyl-(methyl)-phosphinic acid (0.53 g., 82% yield), m.p. 133–134° (lit.<sup>29</sup> 133–134°). A mixed m.p. with authentic material gave no depression.

**Isolation of Alcohol Fragment.**—A solution of  $\beta$ -acetoxyethyl phenyl-(methyl)-phosphinate (2.00 g., 8.2 mmoles) in 10% NaOH solution (25 ml.) was refluxed for 1.5 hr. The solution was cooled to 0°. Benzoyl chloride (3 ml.) was added with shaking during 45 minutes. The precipitate which formed was filtered and dried. It was ethylene dibenzoate (1.42 g., 63% yield), m.p. 70–72°. A mixed m.p. with authentic ethylene dibenzoate prepared from ethylene glycol and benzoyl chloride gave no depression. The infrared spectra was identical with that of ethylene dibenzoate.

**Methyl Phenyl-(methyl)-phosphinate.**—A small scale experiment following the conditions of Arbuzov and Razumov<sup>28</sup> indicated that a direct scale-up of their procedure would be hazardous due to the vigor with which dimethyl phenylphosphonite isomerizes. Accordingly dimethyl phenylphosphonite (100 g.) was added slowly to a solution of a few drops of methyl iodide in methyl phenyl-(methyl)-phosphinate (9 g.) with stirring at 100–120°. Occasionally a few drops of methyl iodide was added. The reaction mixture was distilled yielding methyl phenyl-(methyl)-phosphinate (100 g., 92%), b.p. 119° (3.5 mm.),  $n_D^{25}$  1.5260.

A variety of values have been reported for the refractive index of this material. This is due to the rapid change of refractive index when the ester is exposed to the atmosphere. For example, the refractive index of a sample, originally  $n_D^{25}$  1.5260, fell to  $n_D^{25}$  1.5190 when it was exposed to the atmosphere for 1.5 minutes as a film on the refractometer prisms. The refractive index of a sample stored in a tightly stoppered bottle remained unchanged over one month.

**Phenyl-(methyl)-phosphinic Acid.**—Methyl phenyl-(methyl)-phosphinate (32.7 g., 0.19 mole) in 3% NaOH solution (400 ml.) was refluxed for 2 hr. The solution was acidified with concd. HCl and white crystals separated. The crystals were filtered, washed with distilled water and dried. The yield of phenyl-(methyl)-phosphinic acid was 32 g. (77%), m.p. 133–134° (lit.<sup>29</sup> m.p. 133–134°).

**Reaction of Methyl Phenyl-(methyl)-phosphinate with  $\beta$ -Bromoethyl Acetate.**—Methyl phenyl-(methyl)-phosphinate (40 g., 0.24 mole) was added to freshly distilled  $\beta$ -bromo-

(29) W. J. Pope and C. S. Gibson, *J. Chem. Soc.*, 101, 740 (1912).

ethyl acetate (40 g., 0.24 mole) with stirring at 100° in a nitrogen atmosphere during 30 minutes. The mixture was slowly heated to 160°. It was then heated at 160–170° for 3 hr. and finally at 175° for two hr. The reaction mixture was distilled to yield  $\beta$ -acetoxyethyl phenyl-(methyl)-phosphinate (33.2 g., 59%), b.p. 155–160° (0.9 mm.),  $n_D^{25}$  1.5073–1.5093.<sup>27</sup> The ester gave a single peak on vapor chromatography.

*Anal.* Calcd. for  $C_{11}H_{15}PO_4$  (242.2): C, 54.54; H, 6.24; P, 12.50. Found: C, 53.94; H, 6.53; P, 12.47.

Further distillation of the reaction mixture yielded a light-yellow viscous liquid (10.5 g.), b.p. 214–217° (0.15 mm.),  $n_D^{25}$  1.5600.

*Anal.* Calcd. for  $C_{16}H_{20}P_2O_4$  (338.3): C, 56.87; H, 5.95; P, 18.24; sapon equiv., 169. Found: C, 56.79; H, 5.85; P, 18.82; sapon. equiv., 167.

A sample of the high boiling ester (2.45 g., 14.9 mmoles) was refluxed for 2 hr. with 10% NaOH (20 ml.). The solution was chilled to 0° and was then shaken with benzoyl chloride (2.7 g., 19.2 mmoles). The precipitate which formed was ethylene dibenzoate, 0.9 g. (50%), m.p. 69–70.5°.

Hydrolysis of a 1.02-g. sample of the high boiling ester with dilute alkali, as described above, followed by acidification yielded 0.76 g. (82%) of phenyl-(methyl)-phosphinic acid. No ethylene bis-(phenylphosphinic acid) was found. The high boiling ester was therefore ethylene bis-[phenyl-(methyl)-phosphinate].

**Reaction of Dimethyl Phenylphosphonite with Ethylene Dibromide.**—Dimethyl phenylphosphonite (54 g., 0.37 mole) was slowly added with stirring to ethylene dibromide (30 g., 0.16 mole) at 130° during 4 hr. After heating for an additional 2 hr. at 150–160°, the mixture was distilled to yield methyl phenyl-(methyl)-phosphinate (20.3 g., 38%), b.p. 123° (5 mm.),  $n_D^{25}$  1.5164–1.5252, and a mixture of the higher boiling bisphosphinic esters VI and VIII (30.7 g., 56%), b.p. 205–220° (0.2–0.4 mm.),  $n_D^{25}$  1.5630.

*Anal.* sapon. equiv., 164.8; Br, 0.38.

Unreacted ethylene dibromide (9.1 g., 30%),  $n_D^{25}$  1.5328, was recovered from the Dry Ice trap.

Vapor chromatography of the methyl phenyl-(methyl)-phosphinate fraction showed that traces of water and alco-

hol were the only impurities present. There was no evidence for the presence of either methyl phenyl-( $\beta$ -bromoethyl)-phosphinate or  $\beta$ -bromoethyl phenyl-(methyl)-phosphinate.

**Composition of Diester Mixture by Hydrolysis.**—A sample of the diester fraction (19.4 g., 0.058 mole) was dissolved in 2.5% NaOH solution (400 ml.) and the solution was acidified with concd. HCl. A mixture (11.7 g.) of phenyl-(methyl)-phosphinic acid and ethylene bis-(phenylphosphinic acid) precipitated, m.p. 128–205°. Extraction with ethanol yielded ethylene bis-(phenylphosphinic acid) (0.74 g., 0.024 mole, 4%), m.p. 252–260°. After recrystallization from glacial acetic acid, the product melted 267–269°.<sup>28</sup>

*Anal.* Calcd. for  $C_{14}H_{16}P_2O_4$  (310.5): C, 54.1; H, 5.2; P, 20.0. Found: C, 53.60; H, 5.85; P, 19.78.

Evaporation of the ethanol extract to dryness yielded phenyl-(methyl)-phosphinic acid, m.p. 132–133.5°, neut. equiv. 157 (calcd. 156).

A sample of the diester mixture (5.1 g., 0.015 mole) in 10% NaOH solution (50 ml.) was boiled to distil off methanol. The solution was chilled and then treated with four 1-ml. portions of benzoyl chloride. There was obtained ethylene dibenzoate (1.97 g., 0.0073 mole, 48.7%), m.p. 70–72°. The infrared spectrum was identical with that of ethylene dibenzoate. A mixed m.p. was undepressed.

**Acknowledgments.**—Spectroscopic and vapor chromatography analyses were made by Messrs. D. R. Beasecker, R. B. Coffey, J. W. Cooper, J. V. Pustinger, J. M. Schlater and W. D. Ross of our instrumental laboratory; chemical analyses were made by Messrs. R. Knotts, A. Wheeler and Mrs. W. Harden of our analytical department and by Galbraith Microanalytical Laboratories.

(30) This reaction is regarded as an independent synthesis of ethylene bis-(phenylphosphinic acid) even though the product was obtained in very low yield. An alternate procedure for preparing this acid in high yield will be published subsequently.

DAYTON, OHIO

[CONTRIBUTION NO. 16 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD.]

## Ionic Polymerization. I. Reaction Mechanism Investigation of the Cationic Polymerization of $\alpha$ -Olefins through Intermediate Carbonium Ion Complexes<sup>1</sup>

BY G. A. OLAH, H. W. QUINN AND S. J. KUHN

RECEIVED MAY 1, 1959

The reaction mechanism of the ionic polymerization of  $\alpha$ -olefins was investigated in the olefin:HF:BF<sub>3</sub>, olefin:DF:BF<sub>3</sub>, olefin:alkyl fluoride:BF<sub>3</sub>, olefin:acyl fluoride:BF<sub>3</sub> and olefin:nitril fluoride:BF<sub>3</sub> systems. Olefin:anhydrous silver tetrafluoroborate:organic chloride or bromide systems were similarly used. Electrophilic aromatic alkylation and cationic polymerization of olefins as consecutive and concurrent reactions were investigated by treating protonated alkylbenzene tetrafluoroborates with olefins.

The polymerization of  $\alpha$ -olefins and certain vinyl monomers with small amounts of catalyst of the Friedel-Crafts type is well known.<sup>2</sup> Effective polymerization catalysts in this class include AlCl<sub>3</sub>, AlBr<sub>3</sub>, BF<sub>3</sub>, TiCl<sub>4</sub>, SnCl<sub>4</sub>, etc. All of them are strong acids in the terminology of G. N. Lewis, *i.e.*, they are strong electron acceptors. Isobutylene, styrene,  $\alpha$ -methylstyrene, butadiene and vinyl alkyl ethers are representatives of the monomer types readily converted to polymers of high molec-

ular weight by catalysts among those mentioned. However, these reactions are generally too fast to be suitable to follow. Propylene, butenes and other olefins may also be polymerized, but the products tend to be relatively low in molecular weight. The formation of these liquid polymers is however more easily followed in reaction mechanism investigations.

The mechanism of the Friedel-Crafts polymerization of  $\alpha$ -olefins was originally proposed<sup>3</sup> as the direct interaction of the Lewis acid-type catalyst with the corresponding olefin.

The inactivity of a pure Friedel-Crafts catalyst for polymerization was first reported by Ipatieff

(1) Presented partly as a paper at the 8th Canadian High Polymer Forum, St. Anne de Bellevue (Quebec), Canada, May 13, 1958.

(2) D. C. Pepper, *Sci. Proc. Roy. Dublin Soc.*, **25**, 131 (1950) (a discussion ed. by D. C. Pepper); P. H. Plesch, "Cationic Polymerization and Related Complexes," W. Heffer and Sons, Cambridge, England, 1953; P. H. Plesch, *Research (London)*, **2**, 267 (1949).

(3) W. Chalmers, *Can. J. Research*, **7**, 113, 472 (1932); *This Journal*, **56**, 912 (1934).