required for stabilization of the intermediate carbanion (VI).[3]

## EXPERIMENTAL

*Alkaline epoxidation of diethyl ethylidenemalonate.* To a 1-l., five-neck, round-bottom flask equipped with stirrer, thermometer, *p*H electrodes and dropping funnel, were charged 400 ml. of methanol, 122 g. (0.656 mol.) of diethyl ethylidenemalonate[4] and 49 g. (0.72 mol.) of 50% hydrogen peroxide. To the dropping funnel was charged *N* sodium hydroxide.

The mixture was held at 35–40° by periodic cooling with an ice bath as alkali was added as needed to maintain a *meter p*H of 8.5–9.0; the true *p*H by indicator paper was about 7.5. At the end of 1 hr., 85% of the peroxide had been consumed (iodometric titration) along with 37 ml. of caustic. After an additional hour at meter *p*H 9–9.5, the reaction was essentially complete; 81 ml. of caustic had been consumed.

After dilution of the colorless reaction mixture with 1-l. of water, three 250-ml. portions of chloroform were used for extraction. The combined extract was washed, dried over anhydrous magnesium sulfate, and concentrated on the steam bath to a colorless residue. Distillation of the latter through a 0.7 × 50 cm. glass spiral packed column afforded 5 g. of pre-cut, b.p. 70–80° (1 mm.) and 99 ml., 109 g. (82% yield) of ethyl 2-carbethoxy-2,3-epoxybutyrate, b.p. 80–81° (1 mm.); $n_D^{20}$ 1.4294.

*Anal.* Calcd. for $C_9H_{14}O_5$: C, 53.4; H, 7.0; O, 39.6; sapon. equiv., 101; mol. wt., 202. Found: C, 53.2; H, 6.9; O, 39.0; sapon. equiv., 100; mol. wt., 195 ± 10.

*Hydrogenation of ethyl 2-carbethoxy-2,3-epoxybutyrate.* To a 300-ml. capacity autoclave were charged 116 g. (0.57 mol.) of epoxy diester, 50 ml. of ethanol, and 2 teaspoons of Raney nickel catalyst. Hydrogenation was compete in 6 hr. at 100° and 300–900 lb. pressure; it was necessary to repressure three times. Exactly 2 mol. equiv. of hydrogen were consumed.

After cooling, venting, and filtration, the filtrate was distilled through the small spiral column to give 83 g. (77% yield) of diethyl ethylmalonate, b.p. 58–59° (2 mm.); $n_D^{20}$ 1.4147 (lit.[5] b.p. 94–96° (13 mm.); $n_D^{20}$ 1.4170).

*Anal.* Calcd. for $C_9H_{16}O_4$: C, 57.4; H, 8.6; sapon. equiv., 94.1. Found: C, 56.9; H, 8.5; sapon. equiv., 93.5.

Saponification of 17 g. of this ester afforded 10 g. (83% yield) of ethylmalonic acid, m.p. 109–111°. Recrystallization from benzene gave 6 g. of pure acid, m.p. 112–113°; mixed m.p. with an authentic sample[6] of ethylmalonic acid (m.p. 112–113°) was not depressed.

*Anal.* Calcd. for $C_5H_8O_4$: equiv. wt., 66. Found: equiv. wt., 66.

*Ethanolysis of ethyl 2-carbethoxy-2,3-epoxybutyrate.* A solution of 16 g. (0.08 mol.) of epoxy diester in 100 ml. of ethanol containing 2 ml. of concentrated sulfuric acid was allowed to reflux overnight. The cooled solution was treated with 10 ml. of water and 10 g. of calcium carbonate to neutralize the catalyst. After filtration and concentration, the resulting residue was taken up in warm ether and filtered to remove 4.5 g. of insoluble material. Distillation of the filtrate through a 0.7 × 50 cm. spiral packed column gave 14.9 g. of material, b.p. 85–87° (0.3 mm.), $n_D^{20}$ 1.4323, having an analysis in substantial agreement for ethyl 2-carbethoxy-2-hydroxy-3-ethoxybutyrate or its isomer, ethyl 2-carbethoxy-2-ethoxy-3-hydroxybutyrate.

*Anal.* Calcd. for $C_{11}H_{20}O_6$: C, 53.2; H, 8.1; sapon. equiv., 124; hydroxyl value, 0.40 equiv./100 g. Found: C, 52.6; H, 8.0; sapon. equiv., 116; hydroxyl value, 0.42 equiv./100 g.

SHELL DEVELOPMENT CO.
EMERYVILLE, CAL.

---

(3) See H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959) for a recent discussion of the stereochemistry of alkaline epoxidation.

(4) F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, 3343 (1923).

(5) V. H. Wallingford, A. H. Homeyer, and D. M. Jones, *J. Am. Chem. Soc.*, **63**, 2056 (1941).

(6) From diethyl ethylidenemalonate by hydrogenation followed by saponification.

---

# Phosphonic Acids and Esters. I. Radical Initiated Addition of Phosphorous Acid to Olefins

CLAIBOURNE E. GRIFFIN AND HENRY J. WELLS

*Received July 6, 1959*

The generation of carbon-phosphorus bonds by addition to olefins of radicals produced by homolysis of phosphorus-hydrogen bonds has been investigated by a number of workers during the past decade. The following phosphorus compounds have been utilized: phosphine and alkyl phosphines, hypophosphorus acid, dialkyl phosphonates, alkyl and aryl phosphinates.[1,2] In conjunction with studies in progress on phosphonic acids containing acid labile groupings, it became important to investigate methods which would lead to the direct synthesis of free phosphonic acids, avoiding the hydrolytic step necessary in conventional synthetic methods. Toward this end, the reaction of phosphorous acid (I) with olefins was investigated. In analogy with previously investigated systems, it was expected that homolysis of the phosphorus-hydrogen bond in I would lead to a chain reaction with the over-all result:

$$RCH{=}CH_2 + HP(O)(OH)_2 \longrightarrow RCH_2CH_2P(O)(OH)_2$$

This expectation is borne out by the experimental results; however, the reaction does not constitute a practical approach to alkylphosphonic acids because of the meager yields obtained.

The reactions of three representative olefins (1-octene, cyclohexene, and indene) with I were investigated; in the absence of peroxides, no reaction occurred at reflux temperature in either aqueous dioxane or acetic acid. When the reactions were conducted in the presence of either dibenzoyl peroxide or di-*t*-butyl peroxide at 90° or ultraviolet irradiation at room temperature, the expected products were obtained. Reactant ratios, reaction conditions, and yields of the purified products are presented in Table I.

---

(1) P. C. Crofts, *Quarterly Revs.*, **12**, 363 (1958).

(2) L. A. Hamilton, paper presented at the 134th meeting of the American Chemical Society, Chicago, Ill., September 11, 1958; Abstracts, p. 69P.

TABLE I

REACTION OF PHOSPHOROUS ACID WITH OLEFINS

| Olefin[a] | Initiator[b] | Temp., °C. | Time, Hr. | Product Phosphonic Acid | Yield,[c] % |
|---|---|---|---|---|---|
| 1-Octene | | | | | |
| (0.33) | DBP | 90 | 6 | *n*-Octyl | 23 |
| (1.0) | DBP | 90 | 6 | | 18 |
| (3.0) | DBP | 90 | 6 | | 8 |
| (0.33) | DTBP | 90 | 6 | | 28 |
| (0.33) | UV | 25 | 18 | | 18 |
| Cyclohexene | | | | | |
| (0.33) | DBP | 90 | 6 | Cyclohexyl | 26 |
| (1.0) | DBP | 90 | 6 | | 20 |
| (0.5)[d] | DBP | 90 | 6 | | 25 |
| (0.5)[e] | DBP | 90 | 6 | | 14 |
| (0.33) | DTBP | 90 | 7 | | 24 |
| (0.33) | UV | 25 | 18 | | 20 |
| Indene | | | | | |
| (0.30) | DBP | 90 | 5 | 2-Indanyl | 23 |
| (0.30) | DTBP | 90 | 4 | | 20 |
| (0.30) | UV | 25 | 18 | | 18 |

[a] Mol. olefin/mol. phosphorous acid in parentheses. [b] DBP = dibenzoyl peroxide, DTBP = di-*t*-butyl peroxide (5 mol. % based on phosphorous acid); UV = ultraviolet irradiation (Hanova ultraviolet lamp). [c] Based on minor component of reaction mixture. [d] 0.5 mol. cyclohexane/mol. phosphorous acid added. [e] 0.5 mol. cumene/mol. phosphorous acid added.

An excess of phosphorous acid was generally employed in order to minimize telomerization and obtain a maximum yield of the 1:1 adduct. The following phosphonic acids were obtained in yields of 18–28%: *n*-octylphosphonic acid, cyclohexylphosphonic acid and 2-indanylphosphonic acid. In no case was an appreciable amount of olefin recovered; the major reaction product in each experiment was an intractable oil of high molecular weight. In reactions with 1-octene, basic extraction of the oil and ion exchange chromatography of the extract led to the isolation of a fraction which analysis indicated to be the 2:1 adduct, 2-hexyldecylphosphonic acid.[3] Fractionation of the oil from the indene reaction led to the isolation of 3-isochromanone and 2 - (1 - indanyl) - indene. The former substance has been demonstrated to be a degradation product of the polymeric peroxide formed on autooxidation of indene[4,5] and the latter has been shown to arise from acid catalyzed reactions of indene.[6] When the addition to indene was performed in the absence of oxygen, no 3-isochromanone could be detected.

The results of this study parallel those of other investigators in the field.[7,8] The diminished yields effected by increases in olefin concentration indicate an inhibition by the olefin itself as observed in the addition of dialkyl phosphonates to olefins.[7] Abstraction of an allylic hydrogen from the olefin would give a relatively unreactive allyl radical which effectively interrupts the chain reaction. This inhibition by allylic abstraction was substantiated by the experiments with cyclohexene indicated in Table I: Dilution with cyclohexane led to increased phosphonic acid yield, while the addition of cumene produced a marked lowering of yield. The tendency toward formation of telomers and polymers derived from the monomer olefin indicates the kinetic chain length for the reaction to be quite low. By comparison of 1:1 adduct yields with both phosphine and dialkyl phosphonate additions, it is to be concluded that the transfer constant for phosphorous acid is quite low and dimerization, telomerization, and allylic abstraction become dominant processes.

## EXPERIMENTAL

The experimental procedure was comparatively simple. The reactants were dissolved in either 50% aqueous dioxane or 50% aqueous acetic acid; because of better solubility characteristics, aqueous dioxane was preferred. Peroxide was added and the solution heated at the desired temperature; irradiation experiments were conducted at room temperature in quartz flasks employing a Hanovia quartz ultraviolet lamp (140 watts) as radiation source. Upon completion of reaction, all volatiles were stripped off at 50°/1 mm.; the residual dark oil was treated as below to yield the products. Normally 0.12 mol. of phosphorous acid was employed; the ratio of olefin to acid is given in Table I.

*1-Octene reactions.* The dark oil from a typical run was repeatedly extracted with ligroin. Vacuum evaporation of the extracts gave a semicrystalline mass which was recrystallized from *n*-hexane to yield *n*-octylphosphonic acid, m.p. 99–100° (reported[9] m.p. 99.5–100.5°). A mixture melting point of this material with an authentic sample was not depressed.

The ligroin-insoluble material was extracted with 10% aqueous potassium hydroxide; the basic extract was washed with ether and chromatographed on a 30-cm. column of Amberlite IRA-400 (chloride form). Fractions (10 ml.) were eluted with 0.1*M* hydrochloric acid. Unreacted phosphorous acid was eluted in fractions 3–11; identity was established by reduction of potassium iodate to iodine. Fractions 17–25 were collected and evaporated to dryness to yield a colorless crystalline material. Recrystallization from ligroin gave *2-hexyldecylphosphonic acid* (10–14%), m.p. 100.5–101.5°. A mixture melting point of this material with an authentic sample[3] was not depressed.

*Anal.* Calcd. for $C_{16}H_{35}O_3P$: C, 62.71; H, 11.51; P, 10.11; mol. wt., 306; neut. equiv., 153.2. Found: C, 62.48; H, 11.40; P, 9.80; mol. wt. (Rast), 321; neut. equiv., 152.7.

*Cyclohexene reactions.* The dark oil from a typical run was extracted with 0.1*N* sodium hydroxide. The basic extract was acidified with sulfuric acid and thoroughly extracted with ether. Evaporation of the ethereal solution gave a crystalline mass which was recrystallized from water to yield *cyclohexylphosphonic acid*, m.p. 166–167° (reported m.p.

---

(3) 2-Hexyldecylphosphonic acid has been synthesized independently and has been shown to be identical to the material isolated in this study. Experimental results will be reported elsewhere.

(4) H. Hock, S. Lang, and G. Knauel, *Chem. Ber.*, **83**, 227 (1950).

(5) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1035 (1956).

(6) H. Stobbe and E. Farber, *Ber.*, **57**, 1838 (1924).

(7) A. R. Stiles, W. E. Vaughan, and F. F. Rust, *J. Am. Chem. Soc.*, **80**, 714 (1958).

(8) A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74**, 3282 (1952).

(9) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67**, 1180 (1945).

166–167°,[10] 167–168°[11]). A mixture melting point of this material with an authentic sample was not depressed.

*Indene reactions.* The dark oil from a typical run was extracted with hot glacial acetic acid; upon cooling a colorless crystalline material separated from the acetic acid solution. The solid was washed with a mixture of acetic acid and methanol and recrystallized from glacial acetic acid to yield *2-indanylphosphonic acid,* m.p. 195–196° (reported[12] m.p. 196°). The infrared spectrum (Nujol mull) of this material was identical to that of an authentic sample of 2-indanylphosphonic acid.

The dark material remaining after acetic acid extraction was further extracted with ether. Evaporation of the ethereal solution yielded a solid which was recrystallized from ether to yield *2-(1-indanyl)-indene* (14–31%), m.p. 56–57° (reported[5] m.p. 57–58°). The identity of this material was confirmed by comparison of infrared spectra and lack of mixture melting point depression with an authentic sample of 2-(1-indanyl)-indene.

The ether insoluble material remaining after the isolation of 2-(1-indanyl)-indene was extracted with 20% aqueous potassium hydroxide. The basic extract was acidified with sulfuric acid and filtered (60°); upon cooling, a crystalline material precipitated. Recrystallization of this material from a mixture of benzene and petroleum ether gave *3-isochromanone* (8–21%), m.p. 81–83° (reported m.p. 81–83°,[4] 83°[3]). The identity of this product was confirmed by infrared and mixture melting point methods. No 3-isochromanone was detected when an indene/phosphorous acid reaction was conducted in a nitrogen atmosphere.

Department of Chemistry
University of Pittsburgh
Pittsburgh 13, Pa.

---

(10) J. O. Clayton and W. L. Jensen, *J. Am. Chem. Soc.,* **70,** 3880 (1948).

(11) R. Graf, *Chem. Ber.,* **85,** 9 (1952).

(12) E. Bergmann and A. Bondi, *Ber.,* **63,** 1158 (1930).

---

## 4-Fluoro- and 3,4-Difluorobenzoic Acids: An Isomorphic Pair

Dale N. Robertson

*Received July 8, 1959*

We recently had occasion to prepare 3,4-difluorotoluene (I). As a proof of structure, the material was oxidized to the known 3,4-difluorobenzoic acid (II). We should like to record our observations with this acid and 4-fluorobenzoic (III).

The product obtained on oxidation of I, when crystallized from toluene, melted at 184–185°.[1] The melting point of III is 184–186°. The melting point of a mixture of the oxidation product with an authentic sample of III was 183–184°. The neutral equivalent of the oxidation product was determined to be 158 (theory for II, 158). The neutral equivalent of the authentic sample of III was determined to be 142.8 (theory, 140). A fluorine analysis of the oxidation product gave a value consistent with its formulation as 3,4-difluorobenzoic acid. These data suggested an isomorphic relationship between II and III.

J. W. Turley of Dow's Spectroscopy Laboratory obtained single-crystal x-ray diffraction photographs of the two acids and indicated them to be isomorphic crystals with the following unit cell constants:

| 4-Fluorobenzoic | 3,4-Difluorobenzoic |
|---|---|
| a = 26.64 Å | a = 26.96 Å |
| b = 6.421 Å | b = 6.529 Å |
| c = 3.835 Å | c = 3.795 Å |
| B = 109.9° | B = 101.5° |
| Space group Pz/N | Space group Pz/N |

### EXPERIMENTAL

*2-Fluoro-5-methylaniline.* 3-Bromo-4-fluorotoluene (75.6 g.), ammonium hydroxide (220 g., 27.5% $NH_3$) and cuprous oxide (6.5 g.) were charged to a stainless steel bomb. The bomb was agitated by rocking and heated at 175–180° for a period of 5 hr. The cooled reaction mixture was filtered through a supercel filter pad to remove catalyst and sludge. The sludge was washed with ether and the filtrate extracted with ether. The combined ether layers were extracted with dilute hydrochloric acid until no more color went into the aqueous phase. Unreacted 3-bromo-4-fluorotoluene was recovered from the ether. The aqueous phase was made alkaline with 20% sodium hydroxide. The dark oil which separated was taken up in ether and the aqueous phase was extracted with ether several times. The combined ether extracts was dried over anhydrous magnesium sulfate overnight. The solvent was removed by distillation and the residual liquid was distilled under reduced pressure. The fraction boiling 80–86°/11 was collected. This amounted to 30.9 g. or 61.8% of the theoretical. The literature reports a b.p. of 88–90/17 mm.[2]

*2-Fluoro-5-methylbenzenediazonium fluoborate.* 2-Fluoro-5-methylaniline (37.1 g.) was dissolved in a mixture of 100 ml. of fluoboric acid (48–50%) and 100 g. of ice. With stirring and while maintaining the temperature below 10°, a solution of 21.0 g. of sodium nitrite in 35 ml. of water was added slowly. A precipitate formed as the reaction proceeded. The mixture was stirred at 0° for 0.5 hr. after the nitrite solution had been added. The salt was collected by filtration, washed with 50 ml. of 5% fluoboric acid, 50 ml. of ice-cold absolute methanol and then with several portions of anhydrous ether. The product was air dried for several hours and finally kept in a vacuum desiccator over calcium chloride overnight. There was obtained 60.0 g. of pale tan solid, decomposing at 140–145° (vigorous evolution of gas). Yield, 90.2%.

*3,4-Difluorotoluene.* 2-Fluoro-5-methylbenzenediazonium fluoborate (60.0 g.) was placed in a 500 ml. three necked flask, fitted with a thermocouple, stirrer, and air condenser. The air condenser was connected downward to a cold water condenser by means of an adapter carrying a thermometer. 1,2,4-Trichlorobenzene (250 ml.) was added to the reaction flask and, with vigorous stirring, heating was begun. A white gas began to evolve at 100°. As this initial reaction subsided, the temperature was again raised slowly and evolution of gas was again apparent at 140°. The temperature was slowly raised as the reaction proceeded until the temperature at the top of the air condenser had reached 195°. The reaction was stopped by cooling. The material which had collected in the receiver connected to the cold water condenser was dried over calcium chloride overnight and distilled through a short Vigreaux column. The fraction

---

(1) J. T. Minor and C. A. Vanderwerf, *J. Org. Chem.,* **17,** 1429 (1952) report a m.p. of 119.2–120.1 for the hydrate of this compound (0.5 $H_2O$).

(2) Ng. Ph. Buu-Hoï and Ng. D. Xuong, *J. Chem. Soc.,* 386 (1953).