Anal. Calcd. for C_8H_4BrNO: Br, 38.10; N, 6.67. Found: Br, 38.20; N, 6.63.

The **oxime of 3-bromoterephthalaldehydonitrile** was prepared, m.p. 151° (from 50% ethanol).

Anal. Calcd. for $C_8H_5BrN_2O$: Br, 35.56; N, 12.44. Found: Br, 35.20; N, 12.53.

3-Bromoterephthalaldehydamide.—The nitrile (2 g., 0.00952 mole) was hydrolyzed by warming it with 20 ml. of concentrated sulfuric acid on a steam bath for 1 hr. The resulting solution was poured into 100 ml. of water, and the amide was purified by crystallization from water, yielding 2.1 g. (97%), m.p. 173°.

Anal. Calcd. for $C_8H_6BrNO_2$: Br, 35.09; N, 6.14. Found: Br, 34.99; N, 6.22.

3-Bromoterephthalaldehydic Acid.—The amide (2 g., 0.00877 mole) was dissolved in 20 ml. of concentrated sulfuric acid, and saturated sodium nitrite solution (containing 2.6 g.) was added slowly below the surface of the liquid.[11] The mixture was cooled and stirred; then it was warmed on a steam bath for a short time; finally it was poured into 100 ml. of water, yielding 1.93 g. (96%), m.p. 236° (from water).

Anal. Calcd. for $C_8H_5BrO_3$: C, 41.92; H, 2.18; neut. equiv., 229. Found: C, 41.83; H, 2.32; neut. equiv., 228.

The **methyl ester of 3-bromoterephthalaldehydic acid** was prepared (with diazomethane), m.p. 77° (from 25% ethanol).

Anal. Calcd. for $C_9H_7BrO_3$: C, 44.44; H, 2.88; Br, 32.92. Found: C, 44.85; H, 3.14; Br, 32.79.

The **oxime** of the methyl ester (above) was prepared, m.p. 131° (from 50% ethanol).

Anal. Calcd. for $C_9H_8BrNO_3$: Br, 31.01; N, 5.43. Found: Br, 30.78; N, 5.43.

Analysis of 3-Bromo-4-hydroxymethylbenzoic Acid–Bromoterephthalic Acid Mixtures.—By experiment it was shown that the volume of standard alkali solution required to neutralize mixtures of these acids was a linear function of weight–percentage composition. A graph[13] representing these data was constructed. Samples of the acid mixtures from the Cannizzaro reaction of bromoterephthalaldehyde (below) were titrated; from the graph, the compositions were determined.

Cannizzaro Reactions. A. Terephthalaldehyde and Formaldehyde.—A mixture of 45 g. (0.6 mole) of 40% formaldehyde solution and 10 g. (0.0746 mole) of terephthalaldehyde was placed in a flask fitted with a stirrer, a dropping funnel, and a thermometer. Methanol (50 ml.) was added, and the mixture was stirred until solution was effected. Sodium hydroxide solution (30 g. in 30 ml. of water) was added in small portions at such a rate that the temperature of the reaction mixture did not exceed 60°. In turn, the mixture was cooled to room temperature and poured into four volumes of water.

Crystals of α,α′-*p*-xylenediol formed and were collected by filtration. The filtrate was extracted with two 150-ml. portions of ether. From the ether solution, additional diol was obtained. The total yield was 7 g. (68%), m.p. 119° (from water).

The aqueous alkaline solution from which the diol had been extracted was acidified with 50% sulfuric acid, and two extractions with 150-ml. portions of ether were made. From the ether solution, *p*-hydroxymethylbenzoic acid was recovered. The yield was 1 g. (9%), m.p. 181° (from water).

B. Bromoterephthalaldehyde and Formaldehyde.—Bromoterephthalaldehyde (10.6 g., 0.05 mole) and formaldehyde (45 g. of 40% solution, 0.6 mole) were dissolved in methanol and treated with sodium hydroxide solution as in A immediately above.

Bromo-α,α′-*p*-xylenediol was isolated in a total yield of 8.25 g. (76%), m.p. 113° (from water).

The acidic product, which was recovered as in A above, was 3-bromo-4-hydroxymethylbenzoic acid, 2.5 g. (22% yield), m.p. 176° (from water).

C. Bromoterephthalaldehyde.—Bromoterephthalaldehyde (10.6 g., 0.05 mole) was dissolved in 100 ml. of methanol. This solution was cooled in an ice bath, and sodium hydroxide solution (40 g. in 60 ml. of water) was added in small portions at such a rate that the reaction temperature did not exceed 60°. After the alkali had been added, the ice bath was removed, and the reaction mixture was maintained at 60° for 1 hr.; then it was poured into three volumes of water, and this solution was warmed on a steam bath to remove methanol.

The aqueous alkaline solution was extracted with two 150-ml. portions of ether, and from the ether solution, 2 g. (19% yield) of bromo-α,α′-*p*-xylenediol was recovered, m.p. 113° (from water).

The aqueous alkaline solution was acidified with hydrochloric acid, and the acidic organic material (7 g.) which precipitated was collected by filtration. The filtrate was extracted with two 150-ml. portions of ether. From the ether solution, more acidic organic material (2 g.) was obtained. The total weight of acidic material was 9 g. Fractional crystallization of a portion of the acid mixture[14] from water resulted in the isolation of two components, bromoterephthalic acid which sublimes at 299° and 3-bromo-4-hydroxymethylbenzoic acid, m.p. 176°. Analysis of the acid mixture by the procedure described above gave bromoterephthalic acid (20%) and 3-bromo-4-hydroxymethylbenzoic acid (80%). This corresponds to 1.8 g. (15% yield) of the dibasic acid and 7.2 g. (63% yield) of the alcohol acid.

The total yield of products—diol and acids—corresponded to 97% of the aldehyde used in the reaction.

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(13) S. E. Hazlet and R. B. Callison, *J. Am. Chem. Soc.*, **66**, 1248 (1944).

(14) The melting behavior of this mixture was studied carefully. Melting started at 169°, and the major portion of the sample was converted to a clear liquid at *ca.* 175°; suspended in the liquid was a solid phase which persisted until the temperature was 235–240°; between 240 and 255° this last solid portion melted. Because melting was not observed below 169°, it was concluded that 2-bromo-4-hydroxymethylbenzoic acid (m.p. 147–148°) was not present in the mixture.

Mixtures were prepared [(a) 10:1, (b) 10:3, and (c) 10:10, respectively] from 3-bromo-4-hydroxymethylbenzoic and bromoterephthalic acids. Melting points were (a) major portion, 165–170°, suspended solid persisted to *ca.* 230°; (b) major portion, 161–170°, suspended solid remained to *ca.* 235°; (c) partial melting, 173°, second component melted at *ca.* 275°.

The Preparation of Organic Phosphorus Compounds by Ivanov Reactions. II

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It has been found, contrary to a statement in the literature,[1] that the Ivanov-like reagent diethyl α-chloromagnesiobenzylphosphonate (I), prepared by the action of isopropylmagnesium chloride on diethyl benzylphosphonate, does behave like a Grignard reagent.

Interaction of I with carbon dioxide yielded an oily acid, diethyl α-carboxybenzylphosphonate (II) which could not be purified; by the use of diazomethane the pure ester, diethyl α-carbomethoxybenzylphosphonate (III), was obtained.

Reagent I reacted with ethylene oxide and with diphenylchlorophosphine oxide to produce diethyl α-(β-hydroxyethyl)benzylphosphonate (IV) and diethyl α-(diphenylphosphinyl)benzylphosphonate (V), respectively.

It was shown that after reaction of I with formaldehyde, acidification of the reaction mixture, and distillation of the crude product (an oil), diethyl α-methylenebenzylphosphonate (VI) was formed; this product may have been formed by spontaneous loss of water from the α-hydroxymethyl derivative which had been produced after acidification of the reaction mixture or possibly during distillation.

The product isolated after the reaction of I with benzophenone was also an unsaturated phosphorus compound, diethyl α-(diphenylmethylene)benzylphosphonate (VIII), which may have been produced by

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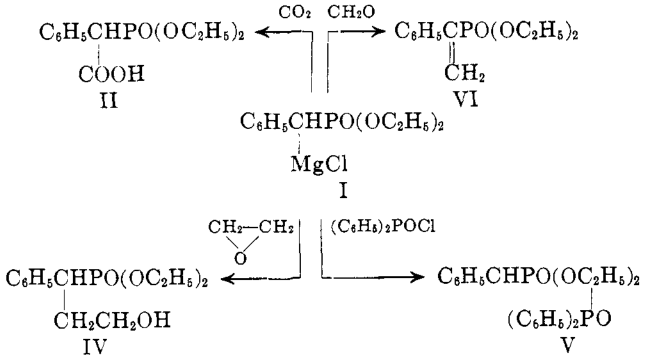
(1) D. Ivanov and G. Borissoff, *Naturwissenschaften*, **46**, 171 (1959).

TABLE I

Compound no.	M.p. or b.p. (mm.), °C.	Yield, %	Formula	% C Calcd.	% C Found	% H Calcd.	% H Found	% P Calcd.	% P Found
III	125–130 (1)	75	$C_{13}H_{19}O_5P$	54.54	54.36	6.69	6.77	10.81	10.70
IV	135 (0.5)	13	$C_{13}H_{21}O_4P$	57.33	56.94	7.77	7.39	11.37	11.44
V[d]	161–162[a]	15	$C_{23}H_{26}O_4P_2$	64.49	64.17	6.12	6.24	14.46	14.66
VI	127 (0.3)	21	$C_{12}H_{17}O_3P$	59.99	59.72	7.13	7.31	12.89	12.77
VIII[d]	183–185[a]	10	$C_{24}H_{25}O_3P$	73.45	73.17	6.42	6.10	7.89	8.02
X	181–183[a,b]	95	$C_{24}H_{27}O_3P$	73.08	73.04	6.90	6.79	7.85	7.82
XI[d]	186–188[a,c]	23	$C_{20}H_{19}O_3P$	71.00	71.22	5.66	5.91	9.16	8.87
XII	130 (0.3)	28	$C_{13}H_{19}O_3P$	61.42	61.17	7.53	7.62	12.18	12.06
XIV	150–155 (0.5)		$C_{15}H_{21}O_5P$	57.69	57.74	6.78	7.18	9.92	9.65

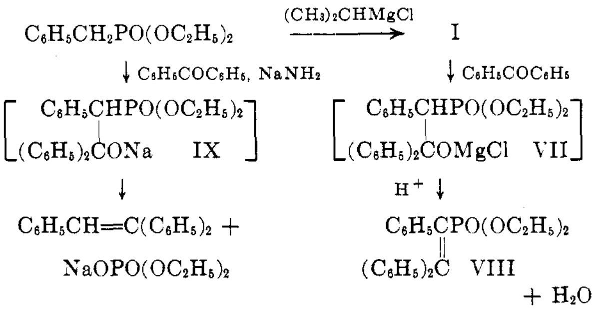
[a] Melting point. [b] The mixture melting point with VIII was 167–175°. [c] The mixture melting point with X was 175–182°. [d] Compound VIII was recrystallized from nitromethane; XI, from absolute ethanol; V, from ethyl acetate.



loss of water from the diphenylhydroxymethyl derivative after the reaction mixture, which contained VII, had been acidified.

An intermediate IX, analogous to VII, was postulated by Horner, *et al.*,[2] as the initial product formed when a mixture of diethyl benzylphosphonate, benzophenone, and sodamide was heated. Cleavage of the intermediate took place with the formation of triphenylethylene in 88% yield.[3]

In view of the fact that VIII was isolated in only 10% yield, it is possible that some triphenylethylene may have been present in the reaction mixture.



Compound VIII was hydrogenated to form diethyl α-(benzohydryl)benzylphosphonate (X), and this ester was hydrolyzed to yield α-(benzohydryl)benzylphosphonic acid (XI).

An Ivanov-like reagent, $C_6H_5CH{=}CHCH(MgCl)$-$PO(OC_2H_5)_2$, was prepared from diethyl cinnamylphosphonate (XII), a substance which was synthesized from the sodium derivative of diethyl phosphite and cinnamyl chloride. The reagent was allowed to react with carbon dioxide whereby diethyl α-carboxycinnamylphosphonate (XIII) was formed. Since this acid could not be purified, it was converted by the use of diazomethane into diethyl α-carbomethoxycinnamylphosphonate (XIV) which was obtained in pure form.

An allylic rearrangement might have taken place during the preparation of XII and the Ivanov-like reagent.[4] However, based on statements in the literature[5] and on the following data, obtained from XII and XIV, it seems that this was not the case: the ultraviolet spectra showed the presence of a double bond conjugated with a benzene ring (styrene group), and the infrared spectrum of XII indicated a *trans* configuration about an internal double bond.

Experimental

The yields and physical properties of the products obtained are listed in Table I.

Preparation of Diethyl α-Chloromagnesiobenzylphosphonate (I).—Diethyl benzylphosphonate[6] (22.8 g., 0.1 mole), dissolved in 25 ml. of sodium-dried benzene, was added dropwise to a stirred solution of isopropylmagnesium chloride which had been prepared from 8.4 g. (0.11 mole) of isopropyl chloride, 2.7 g. (0.11 g.-atom) of magnesium, 1 ml. of ethyl bromide, and 100 ml. of ether. The mixture was stirred and refluxed for 12 hr.

Diethyl α-Carboxybenzylphosphonate (II) and Diethyl α-Carbomethoxybenzylphosphonate (III).—Dry Ice (about 25 g.) was added to a stirred suspension of I. After 1 hr. the mixture was stirred and hydrolyzed by the dropwise addition of a mixture of 10 ml. of concentrated hydrochloric acid and 200 ml. of water. The organic layer was extracted with aqueous sodium bicarbonate; the alkaline layer was acidified and extracted with benzene. After removal of the solvent from the dried benzene layer, the oily residue weighed 9.4 g. (35%). This product (II) could not be purified. The pure ester (III) was obtained by the use of diazomethane.

Diethyl α-(β-Hydroxyethyl)benzylphosphonate (IV).—Ethylene oxide (44.0 g., 1 mole) was added, dropwise, to a stirred suspension of I; the mixture was stirred for 10 hr. and hydrolyzed in the manner mentioned above. The organic layer was separated and dried, the solvent was removed, and the product was distilled.

Diethyl α-(Diphenylphosphinyl)benzylphosphonate (V).—Diphenylchlorophosphine oxide (23.7 g., 0.1 mole) was added dropwise to a stirred suspension of I. The mixture was stirred and refluxed for 4 hr., stirred for 12 hr., and then hydrolyzed. The mixture was filtered to remove diphenylphosphinic acid. The organic layer in the filtrate was separated and dried, and the solvent was removed. The residue, a mixture of an oil and a solid, was filtered with the use of a sintered-glass funnel. The solid material was washed with a small amount of ether and then triturated with hot petroleum ether (b.p. 90–100°).

Diethyl α-Methylenebenzylphosphonate (VI).—After 150 ml. of ether had been added to a suspension of I, the mixture was stirred and formaldehyde, obtained from 45 g. of paraformalde-

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[2] L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, **91**, 64 (1958); see also W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

[3] Cleavage of complex compounds analogous to IX, with the formation of phosphorus-free olefins, has been reported by H. Pommer [*Angew. Chem.*, **72**, 811 (1960)].

[4] See F. F. Blicke and H. Zinnes, *J. Am. Chem. Soc.*, **77**, 5399 (1955).

[5] G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., p. 536; see also A. G. Catchpole and E. D. Hughes, *J. Chem. Soc.*, 4 (1948).

[6] B. C. Saunders, G. J. Stacey, F. Wild, and I. G. E. Wilding, *ibid.*, 699 (1948).

hyde, was introduced in a manner described previously.[7] The material was stirred for 10 hr. and then hydrolyzed. The organic layer was washed with water and dried, the solvent was removed, and the residue was distilled. The product decolorized permanganate rapidly.

Diethyl α-(Diphenylmethylene)benzylphosphonate (VIII).—Benzophenone (18.2 g., 0.1 mole), dissolved in 250 ml. of ether, was added dropwise to a stirred suspension of I. The mixture was stirred and refluxed for 1 hr., stirred for 12 hr., and hydrolyzed. The solvent was removed from the dried organic layer. The oily residue solidified when it was triturated with petroleum ether (b.p. 30–40°). It was triturated again with petroleum ether (b.p. 90–100°).

Diethyl α-(Benzohydryl)benzylphosphonate (X).—A mixture of 2.0 g. of VIII, dissolved in 100 ml. of warm absolute ethanol, and 0.2 g. of 5% palladium on carbon was hydrogenated for 18 hr. under an initial pressure of 40 lb. After filtration, with the use of Celite, water was added to the hot filtrate until it became turbid. The product separated from the cold mixture.

α-(Benzohydryl)benzylphosphonic Acid (XI).—A mixture of 1.0 g. of X and 20 ml. of concentrated hydrochloric acid was refluxed for 24 hr., and the inorganic acid was then removed in a stream of air. The residue was treated with aqueous sodium bicarbonate, and the mixture was extracted with benzene. The alkaline layer was acidified and extracted with benzene. After removal of the solvent from the dried benzene layer, the residue was recrystallized.

Diethyl Cinnamylphosphonate (XII).—To a stirred, refluxing suspension of 11.5 g. (0.5 g.-atom) of sodium and 500 ml. of xylene there was added dropwise 72.5 g. (0.52 mole) of diethyl phosphite.[8] The mixture was refluxed for 5 hr. and 76.0 g. (0.5 mole) of cinnamyl chloride[9] was added dropwise to the stirred refluxing mixture. After the material had been refluxed for 8 hr., it was cooled, the liquid was decanted from the sodium chloride, and the salt was washed with xylene. The solvent was removed and the residue was distilled. The product decolorized permanganate.

Diethyl α-Carboxycinnamylphosphonate (XIII) and Diethyl α-Carbomethoxycinnamylphosphonate (XIV).—The Ivanov-like reagent was prepared, in the usual manner, from 12.7 g. (0.05 mole) of diethyl cinnamylphosphonate dissolved in 25 ml. of benzene. After the addition of about 25 g. of Dry Ice, the mixture was stirred for 3 hr. and then hydrolyzed with dilute hydrochloric acid. The organic layer was shaken with aqueous sodium bicarbonate whereupon three layers were obtained. The alkaline layer and the oil were separated and the mixture was acidified with dilute hydrochloric acid. After extraction with benzene, the solvent was removed from the dried extract and the oily product XIII (6 g., 40%), which decolorized permanganate instantly, was treated with diazomethane to yield XIV.

Acknowledgment.—This investigation was supported by grants from The Wm. S. Merrell Company and from the American Foundation or Pharmaceutical Education.

(7) F. F. Blicke, H. Raffelson, and B. Barna, *J. Am. Chem. Soc.*, **74**, 253 (1952).

(8) Purchased from the Victor Chemical Works.

(9) J. F. Norris, M. Watt, and R. Thomas, *J. Am. Chem. Soc.*, **38**, 1078 (1916).

Preparation of Acyl Halides and Esters from Salts of Perfluoroalkanoic Acids[1]

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It is quite well known that perfluoroacyl chlorides,[2] fluorides,[3] and esters[4] may be prepared from the corresponding free perfluoroalkanoic acids. While acyl chlorides have been prepared from salts by means of inorganic chlorides,[5] the use of organic acyl chlorides[5c] normally produces mixed anhydrides; in certain cases, partially fluorinated acyl chlorides have been obtained by the latter procedure,[6] albeit only in fair yield.

The use of benzenesulfonyl fluoride to convert sodium benzoate to benzoyl fluoride (plus benzoic anhydride) has been reported,[7] though the reaction was not offered as a useful synthetic procedure.

The purpose of this Note is to call attention to several synthetic advantages which may be gained by the use of the salts, rather than the free perfluoroalkanoic acids, in exchange reactions with certain acyl halides and esters. These are (1) high yields, (2) simplicity of procedure, (3) applicability to small scale, (4) freedom from evolution of hydrogen chloride or other volatile species, (5) as a corollary, fractional distillation of the product in good purity directly from the reaction mixture. For large-scale preparations the procedure is somewhat inconvenient owing to the formation of a caked solid phase, and to the relatively high reaction temperatures usually required to achieve a suitable rate of production. In certain cases, as for example perfluorocyclohexanecarboxylic acid,[8] the salt is too unstable to permit such procedures, but this is not the usual case.[9]

It is probable that the greatest value of the salt reactions lies in small-scale analytical applications, as for example in the characterization of fluorocarbon materials by alkaline cleavage or by permanganate oxidation. Normally the sodium or potassium salts are separated from inorganic contaminants by virtue of the relative insolubility of the latter in warm absolute ethanol. Acyl halides and methyl esters are especially desired for nuclear magnetic resonance spectroscopy and for retention time measurement by gas–liquid chromatography, as well as for molecular weight and saponification number determinations. Analytical purity of product is often obtained on a 1- to 5-g. scale without recourse to refractionation.

Experimental

The reactions were conveniently carried out by treating the powdered well-dried salt (usually the sodium salt) with a two- to threefold excess (*i.e.*, about an equal weight) of the organic exchange agent, in a flask of such size as to be about half filled therewith, and which was fitted with a short fractionating column of perhaps five to ten theoretical plates. An intermittent take-off head was desirable for boiling point determination, as well as

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(1) Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., 1955, p. 27M.

(2) (a) CF_3COCl *via* PCl_5: R. G. Jones, *J. Am. Chem. Soc.*, **70**, 143 (1948); and A. L. Henne, R. M. Alm, and M. Smook, *ibid.*, **70**, 1968 (1948). (b) C_3F_7COCl and higher homologs *via* PCl_5: M. Hauptschein, J. F. O'Brien, C. S. Stokes, and R. Filler, *ibid.*, **75**, 87 (1953); J. H. Simons, W. T. Black, and R. F. Clark, *ibid.*, **75**, 5621 (1953); and R. Filler, J. F. O'Brien, J. V. Fenner, and M. Hauptschein, *ibid.*, **75**, 966 (1953); (c) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 549.

(3) G. Olah, I. Kuhn, and I. Beke, *Chem. Ber.*, **89**, 862 (1956).

(4) (a) F. Swarts, *Bull. classe sci. acad. roy. Belg.*, **6**, 300 (1920); (b) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 480.

(5) (a) J. H. Simons and E. O. Ramler, *J. Am. Chem. Soc.*, **65**, 389 (1943); (b) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 547; (c) p. 559.

(6) (a) M. Prober, *J. Am. Chem. Soc.*, **75**, 968 (1953); (b) **77**, 910 (1955).

(7) W. Steinkopf and P. Jaeger, *J. prakt. Chem.*, [2]**128**, 65 (1930).

(8) T. J. Brice and J. H. Simons, *J. Am. Chem. Soc.*, **73**, 4017 (1951).

(9) L. J. Hals, T. S. Reid, and G. H. Smith, *ibid.*, **75**, 4595 (1953).