Organometallic and Organometalloidal Fluorine Compounds. Part X. Trifluoromethyl-phosphonous and -phosphonic Acids.†*

By F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine.

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Oxidative hydrolysis of the compounds $CF_3 \cdot PX_2$ or $(CF_3)_2PX$ (X = Cl or I), or controlled hydrolysis of $(CF_3)_3P$ followed by oxidation, yields trifluoromethylphosphonic acid, $CF_3 \cdot PO(OH)_2$. This is a dibasic acid ($K_1 = 6{\cdot}8 \times 10^{-2}$, $K_2 = 1{\cdot}2 \times 10^{-4}$) and is one of the strongest known acids of phosphorus. Salts have been prepared, and their infra-red spectra are discussed.

Trifluoromethylphosphonous acid, $CF_3 \cdot P(OH)_2$, differs considerably from the phosphonic acid, since it is volatile in water vapour at low pressure, is monobasic, and yields fluoroform when its aqueous solutions are heated or treated with alkali. It has been isolated as its monosodium salt, and spectroscopic evidence shows this to be $CF_3 \cdot PH(:O)(ONa)$ rather than $CF_3 \cdot P(OH)(ONa)$. Solutions of the acid are obtained by the aqueous hydrolysis of the compounds $CF_3 \cdot PX_2$ or $(CF_3)_2PX$ or by the controlled stepwise hydrolysis of $(CF_3)_3P$. Oxidation yields trifluoromethylphosphonic acid. Bistrifluoromethylphosphinous acid, $(CF_3)_2P \cdot OH$, is unstable in water and yields trifluoromethylphosphonous acid and fluoroform.

This paper, which records the beginning of a systematic investigation of perfluoroalkyl acids containing phosphorus, is concerned with the synthesis and properties of trifluoromethyl-phosphonous and -phosphonic acids [(I) and (II)]. Trifluoromethylphosphine oxide (III), a third possible acid containing only one trifluoromethyl group, has yet to be

* Part IX, *J.*, 1954, 881, erroneously numbered Part VIII; Part VIII, *J.*, 1953, 2372.

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investigated. The forms containing four-co-ordinated phosphorus are more probable than those containing tervalent phosphorus.

$$CF_3{\cdot}P(OH)_2 \rightleftharpoons CF_3{\cdot}PH(:O){\cdot}OH \qquad CF_3{\cdot}PO(OH)_2 \qquad CF_3{\cdot}PH_2(:O) \rightleftharpoons CF_3{\cdot}PH(OH)$$
(I) (II) (III)

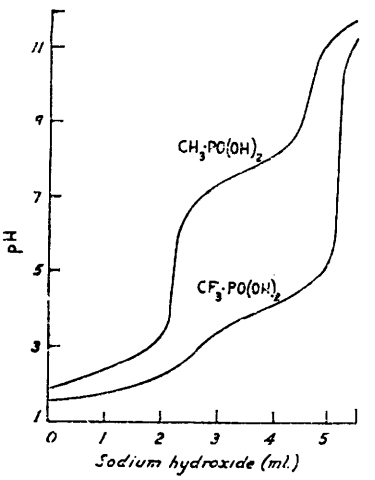
Aqueous hydrolysis of chlorobistrifluoromethylphosphine or dichlorotrifluoromethylphosphine or the corresponding iodo-compounds (Part VII; *J.*, 1953, 1565) gives a solution which, on treatment with hydrogen peroxide followed by evaporation to dryness, yields trifluoromethylphosphonic acid. The oxidative hydrolysis is performed in two stages because of the vigour of the direct oxidation of the halogeno-compounds with hydrogen peroxide:

$$(CF_3)_2PX \xrightarrow{H_2O\text{–}H_2O_2} (II) + CHF_3 + HX$$

$$CF_3{\cdot}PX_2 \xrightarrow{H_2O\text{–}H_2O_2} (II) + 2HX$$

The phosphonic acid is also obtained by oxidation of trifluoromethylphosphine, $CF_3{\cdot}PH_2$.

Trifluoromethylphosphonic acid is dibasic with $K_1 = 6{\cdot}8 \pm 1{\cdot}2 \times 10^{-2}$, $K_2 = 1{\cdot}2 \pm 0{\cdot}1 \times 10^{-4}$, corresponding to values for pK_1 and pK_2 of $1{\cdot}16 \pm 0{\cdot}1$ and $3{\cdot}93 \pm 0{\cdot}03$, respectively. In aqueous solution the acid approximates in strength to dichloroacetic acid, but the slightness of the first inflection point in the titration curve (see Figure) indicates the relatively small ratio of the two dissociation constants (*ca.* 575); in this respect it resembles oxalic and malonic acid. The titration curve for the much weaker methylphosphonic acid ($K_1 = 3{\cdot}3 \times 10^{-3}$, $K_2 = 4{\cdot}6 \times 10^{-8}$) is also shown in the Figure; its shape is typical of those of most dibasic acids, and the K_1/K_2 ratio is $7{\cdot}25 \times 10^4$.



Comparison of the pK values shown in the annexed Table reveals the marked electrophilic nature of the trifluoromethyl group. Trifluoromethylphosphonic acid is, in fact, one of the strongest known phosphorus acids. The pK_2 values for phosphoramidic acid, $H_2N{\cdot}PO(OH)_2$, and aminomethylphosphonic acid, $H_2N{\cdot}CH_2{\cdot}PO(OH)_2$ (3·8 and 5·9, respectively; Rumpf and Chavanne, *loc. cit.*), approach fairly closely the value for trifluoromethylphosphonic acid.

The last acid yields ammonium, barium, and mono- and di-sodium salts. The sparingly soluble barium salt crystallises with 1·5 molecules of water. Since solutions of the acid or its salts fail to give a precipitate with solutions of lead acetate, silver nitrate, mercurous nitrate, or calcium chloride, the corresponding salts are probably soluble. That the same

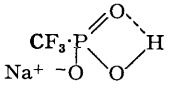
	pK_1	pK_2
Pyrophosphoric acid, $H_4P_2O_7$	0·85	—
Trifluoromethylphosphonic acid (II)	1·16	3·93
Phosphorous acid, H_3PO_3	1·41 [1]	6·7 [1]
Methyl dihydrogen phosphate, $MeO{\cdot}PO(OH)_2$	1·54 [2]	6·31 [2]
Ethyl dihydrogen phosphate, $EtO{\cdot}PO(OH)_2$	1·60 [2]	6·62 [2]
Trichloromethylphosphonic acid, $CCl_3{\cdot}PO(OH)_2$	1·63 [3]	4·81 [3]
Phosphoric acid, H_3PO_4	1·97 [2]	6·82 [2]
Phenylphosphonic acid, $Ph{\cdot}PO(OH)_2$	2·2 [4]	—
Methylphosphonic acid, $Me{\cdot}PO(OH)_2$	2·48	7·34
Ethylphosphonic acid, $Et{\cdot}PO(OH)_2$	2·45 [5]	7·85 [5]

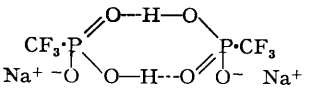
[1] Yost and Russell, "Systematic Inorganic Chemistry," Prentice Hall, New York, 1944. [2] Kumler and Eiler, *J. Amer. Chem. Soc.*, 1943, **65**, 2355. [3] Crofts and Kosolapoff, *ibid.*, 1953, **75**, 5738. [4] Topley, *Chem. and Ind.*, 1950, S 859. [5] Rumpf and Chavanne, *Compt. rend.*, 1947, **224**, 919.

trifluoromethyl acid of phosphorus is obtained by each of the routes described above is shown by comparison of the infra-red spectra of the mono- and di-sodium salts prepared in each case.

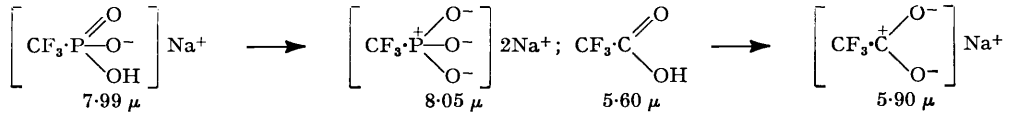
The infra-red spectra of mono- and di-sodium trifluoromethylphosphonates (C.S. Nos. 125 and 126 *) are suitable for characterisation of the acid. The spectrum of the monosodium salt shows no free hydroxyl vibration near 2·76 μ; instead, a broad weak band appears at 4·25 μ and this is assigned to the hydrogen-bonded P–OH group. This vibration is at a much longer wave-length than the bonded P–OH vibration (3·70—3·80 μ) in other phosphonic acids (*e.g.*, phenylphosphonic acid 3·72 μ, Daasch and Smith, *loc. cit.*; *cyclo*-hexylphosphonic acid 3·75 μ, Bellamy and Beecher, *J.*, 1952, 1701), and the very strong hydrogen bonding of type (IV) or (V) so revealed is consistent with the strength of trifluoromethylphosphonic acid. The disodium salt shows no band in the 3·5—5 μ region, thus confirming the assignment for the P–OH vibration.

The presence of the electronegative trifluoromethyl group on the phosphorus atom of monosodium trifluoromethylphosphonate would be expected to cause a shift of the P:O (*i.e.*, $P^+–O^-$) vibration to wave-lengths shorter than those (7·9—8·5 μ) for the corresponding vibration in aliphatic or aromatic phosphonic acids, just as the C:O vibration in aldehydes, acids, esters, ketones, etc., is shifted to shorter wave-lengths when fluorine is present in the molecule (Haszeldine, *Nature*, 1951, **168**, 1028). On the other hand, the strong hydrogen

(IV) 

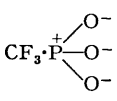
 (V)

bonding will tend to move the P:O vibration to longer wave-lengths, although this shift will be less than the opposing shift caused by the inductive effect. These predictions are borne out, since monosodium trifluoromethylphosphonate shows a strong band in the infra-red at 7·99 μ which is outside the 8·2—8·8 μ region for the strong carbon–fluorine stretching vibrations; these are centred on 8·34 μ. The P:O vibration is thus near to that in phosphoryl chloride (7·81 μ) or dialkyl phosphites (7·70—8·00 μ) (Meyrick and Thompson, *J.*, 1950, 225) which also contain electronegative atoms or groups attached to phosphorus. The P:O vibration in disodium trifluoromethylphosphonate is clearly the strong sharp band at 8·05 μ; the slight shift to longer wave-length compared with the monosodium salt, even though the possibility of hydrogen bonding is now removed, is caused by increase in the ionic character of the P:O bond, analogous to the shift of the C:O band in salts of carboxylic acids, thus:



7·99 μ 8·05 μ 5·60 μ 5·90 μ

The P–OH deformation vibration in the spectrum of monosodium trifluoromethylphosphonate is assigned to the strong 10·64 μ band; this disappears in the spectrum of the disodium salt, and is replaced by a strong band at 10·22 μ which is probably characteristic of the system shown inset. The band at 13·5 or 13·6 μ in the spectra is caused by a trifluoromethyl deformation vibration (see Part VII, *loc. cit.*).



The aqueous hydrolysis of chloro- and iodo-bistrifluoromethylphosphines, and of dichlorotrifluoromethylphosphine, yields trifluoromethylphosphonous acid (I). Di-iodotrifluoromethylphosphine also yields (I), but there is evidence that in this case other products result as the conditions and proportion of reactants are varied. Trifluoromethylphosphonous acid has not been isolated as the free acid, since it is volatile in water vapour at reduced pressure. It behaves as a strong monobasic acid, and differs sharply from trifluoromethylphosphonic acid, since it liberates fluoroform quantitatively at pH >11 or when its solutions are heated at 100°. The monosodium salt is obtained by the controlled hydrolysis of tristrifluoromethylphosphine, iodobistrifluoromethylphosphine, or di-iodotrifluoromethylphosphine with dilute aqueous sodium hydroxide. Sodium trifluoromethyl-

* Spectra thus designated have been deposited with the Society. Photocopies may be obtained, price 3*s.* 0*d.* each by application to the General Secretary, quoting the C.S. No.

phosphonite, which can be isolated as a white solid, yields fluoroform when treated with an excess of aqueous alkali. Treatment of the salt with sulphuric acid yields a solution of trifluoromethylphosphonous acid which is freed from sodium sulphate and excess of sulphuric acid by distillation under reduced pressure.

The infra-red spectrum of sodium trifluoromethylphosphonite (C.S. No. 127) shows C–F absorption at 8·80, 9·00, and 9·25 μ, and a CF_3 deformation at 13·6 μ. There is also a band at 4·2 μ which is much sharper than a P–OH vibration, and is more plausibly assigned to a P–H stretching vibration. Sodium trifluoromethylphosphonite is thus better represented as CF_3·PH(:O)(ONa) than as CF_3·P(OH)(ONa). This conclusion is strongly supported by the presence of a strong band at 8·05 μ, which can be assigned only to the P:O vibration, and by the fact that trifluoromethylphosphonous acid is a strong monobasic acid. It is doubtful if any alkylphosphonous acids have yet been prepared in the stable R·$P(OH)_2$ form. Dialkyl phosphites are similarly best represented by the form $(RO)_2PH(:O)$, since their infra-red spectra show P–H absorption at 4·1 μ [*e.g.*, $(MeO)_2$P·OH 4·11; $(EtO)_2$P·OH 4·11; $(Pr^iO)_2$P·OH 4·11; $(Bu^nO)_2$P·OH 4·15], and P:O absorption at 7·94—8·00 μ; arylphosphonous acids also show P–H and P:O absorption [*e.g.*, Ph·$P(OH)_2$ 4·20; Ph·P(OEt)(OH) 4·25 μ (Meyrick and Thompson; Daasch and Smith, *locc. cit.*)]. Trifluoromethylphosphonous acid and its sodium salt show only weak reducing properties (cf. phosphorous acid).

Oxidation of an aqueous solution of trifluoromethylphosphonous acid yields trifluoromethylphosphonic acid.

The loss of one equivalent of fluoroform during the aqueous hydrolysis of the compounds $(CF_3)_2PX$ points to the instability of bistrifluoromethylphosphinous acid which accords with the general behaviour of other substituted phosphinous acids, although the usual product is the substituted phosphine, $2R_2P{\cdot}OH \longrightarrow R_2PH + R_2PO{\cdot}OH$ (Kosolapoff, "Organo-phosphorus Compounds," Wiley, New York, 1950, p. 137). The preparation of the second possible acid containing two trifluoromethyl groups, *i.e.*, bistrifluoromethylphosphinic acid, is being investigated.

Experimental

The general techniques were similar to those described in Part VII (*loc. cit.*). Products were identified tensimetrically, by molecular-weight determination, and by infra-red spectroscopic examination whenever possible.

Trifluoromethylphosphonic Acid.—(a) *From di-iodotrifluoromethylphosphine.* The iodo-compound (2·61 g.) was kept *in vacuo* with distilled water (5 ml.) at 20° until the mixture became homogeneous (2 hr.). Water (10 ml.) was then added, followed by unstabilised hydrogen peroxide (100-vol.; 5 ml.), dropwise. The precipitated iodine was washed with water (2 ml.), and the combined solution was evaporated by freeze-drying (6 days). The light brown hygroscopic residue was heated at 85°/10^{-3} mm. to give a sublimate of *trifluoromethylphosphonic acid* (0·92 g., 83%) as white hygroscopic crystals, m. p. 81—82° (Found: F, 37·5%; equiv., 74. $CH_2O_3F_3P$ requires F, 38·0%; equiv., 75). A small amount of iodic acid remained in the sublimation apparatus. Direct addition of the oxidising agent to di-iodotrifluoromethylphosphine causes it to ignite explosively. Trifluoromethylphosphonic acid was decomposed by sodium fusion at 600° for analysis.

(b) *From iodobistrifluoromethylphosphine.* The iodo-compound (0·736 g.) had reacted completely with water (2 ml.) at 20° after 30 min. to give fluoroform (0·170 g., 49%). Hydrogen peroxide (100-vol.; 2 ml.) was then added dropwise until liberation of iodine was completed, and after filtration evaporation to dryness by freeze-drying (10 days) gave trifluoromethylphosphonic acid (0·33 g., 88%) which on vacuum-sublimation gave the pure compound (0·278 g., 74%).

(c) *From dichlorotrifluoromethylphosphine.* The reaction of this phosphine (0·692 g.) with water (0·5 ml.), followed by oxidation with hydrogen peroxide (50-vol.; 2 ml.), evaporation (5 days), and sublimation *in vacuo*, gave trifluoromethylphosphonic acid (0·49 g., 82%).

(d) *From chlorobistrifluoromethylphosphine.* The chloro-compound (0·467 g.) on treatment with water (2 ml.) evolved fluoroform (0·157 g., 49%) during 30 min. After 3 hr., water (5 ml.) and then hydrogen peroxide (50-vol.; 2 ml.) were added; freeze-drying (4 days) gave the phosphonic acid (0·283 g., 80%) which was further purified by vacuum-sublimation (0·206 g., 60%).

(e) *From trifluoromethylphosphine.* See Part XI (*J.*, in the press).

Salts of Trifluoromethylphosphonic Acid.—The disodium salt was prepared from the acid (made by each of the above methods) by titration with sodium hydroxide (phenolphthalein) and freeze-drying the product to constant weight. In a typical experiment, trifluoromethylphosphonic acid (0·230 g.) was neutralised with 0·49N-sodium hydroxide (6·305 ml.); freeze-drying (3 days) yielded the white *disodium trifluoromethylphosphonate* (0·291 g., 98%) (Found: Na, 23·7. $CO_3F_3Na_2P$ requires Na, 23·7%). The infra-red spectra of the disodium salts prepared were identical (C.S. No. 126); the weak bands at 2·9 and 6·15 μ are caused by moisture.

Reaction of trifluoromethylphosphonic acid with only one equiv. of sodium hydroxide, followed by freeze-drying, gave the monosodium salt. In a typical experiment, trifluoromethylphosphonic acid (0·168 g.) was treated with 0·49N-sodium hydroxide (2·32 ml.), and the solution freeze-dried to give the white monosodium trifluoromethylphosphonate (0·180 g., 94%). The infra-red spectra of the monosodium salts (C.S. No. 125) were also identical.

To trifluoromethylphosphonic acid (0·556 g.) was added 2·21N-ammonia solution (*ca.* 4 ml.), and the solution was evaporated to dryness first over silica gel, then over calcium oxide to give diammonium trifluoromethylphosphonate (0·635 g., 94%), m. p. 212—216° (decomp.).

Titration of the phosphonic acid (0·195 g.) against 0·342N-barium hydroxide (7·67 ml.) (phenolphthalein) gave an immediate precipitate which after 3 days was filtered off and dried *in vacuo* (0·414 g.). *Barium trifluoromethylphosphonate* is hydrated (Found: Ba, 43·6. $CF_3{\cdot}PO_3Ba,1{\cdot}5H_2O$ requires Ba, 43·7%) as shown by examination of its infra-red spectrum; one molecule of water is lost after 24 hr. at 120° *in vacuo*.

Titration of Trifluoromethylphosphonic Acid and Methylphosphonic Acid.—A Cambridge Instrument Co. portable mains pH meter, sensitive to ±0·01 pH unit, fitted with a glass electrode, was used. Trifluoromethylphosphonic acid (0·0430 g.), dissolved in water (5 ml.), was titrated with 0·1127N-sodium hydroxide with a slow stream of nitrogen passing to stir the solution. The titration curve (see Fig.) shows that complete neutralisation occurs at approximately pH 8, but the dissociation constants cannot be determined accurately from the graph; the method outlined by Britton ("Hydrogen Ions," Vol. I, Chapman and Hall, 1942, p. 197) was therefore used. The titration value for neutralisation occurs at 5·15 ml., whence the equivalent is 74 (Calc. for $CH_2O_3F_3P$: equiv., 75). The dissociation constants are $K_1 = 6{\cdot}81 \pm 1{\cdot}2 \times 10^{-2}$, $K_2 = 1{\cdot}18 \pm 0{\cdot}08 \times 10^{-4}$.

A 5-ml. aliquot portion of a solution of methylphosphonic acid (0·7533 g. in 150 ml.), similarly titrated with the alkali, gave the curve shown in the Fig. The points of inflection are at *ca.* pH 5·2 and 9·8 (titre values 2·26 and 4·65 ml.), and the equivalents of the acid are 98·5 and 47·8 (Calc. for CH_5O_3P: equivs., 96 and 48). Calculation gives $K_1 = 3{\cdot}31 \times 10^{-3}$, $K_2 = 4{\cdot}57 \times 10^{-8}$.

Trifluoromethylphosphonous Acid.—(a) *From tristrifluoromethylphosphine.* Tristrifluoromethylphosphine (0·655 g., 0·00275 mole) and sodium hydroxide (0·1146N; 24·0 ml.; 0·00275 mole) were shaken in a sealed tube for two days, giving unchanged tristrifluoromethylphosphine (0·0545 g., 8%), fluoroform (0·3508 g., 66%), and a neutral solution which, when evaporated to dryness by freeze-drying, gave a white solid. The solid (0·187 g.) was treated with two successive portions of 3N-sulphuric acid (*ca.* 3 ml.) and the liquid was partly evaporated by freeze-drying (2 days). The condensate, which contained the volatile trifluoromethylphosphonous acid, was treated with an excess of sodium hydroxide solution to give fluoroform (0·068 g., 81%) and sodium phosphite but no sodium phosphate (qualitative tests). The residual sulphuric acid solution, treated with an excess of sodium hydroxide, gave fluoroform (0·013 g., 14%), the total of which is thus 95%.

Sodium trifluoromethylphosphonite (C.S. No. 127) was prepared by reaction of a solution of trifluoromethylphosphonous acid with an equivalent of sodium hydroxide followed by evaporation to dryness *in vacuo*. Titration of a solution of the solid (0·087M; 2 ml.) against 0·113N-sodium hydroxide showed that the solution (initially pH 6) evolved fluoroform at pH 11·5 (1·29 ml. of NaOH) [Found: CF_3 (as CHF_3), 44·0. CHO_2F_3NaP requires CF_3, 44·9%].

Sodium trifluoromethylphosphonite (0·087 g.), oxidised by concentrated nitric acid (5 ml.) (8 hr.) gave after evaporation to dryness monosodium trifluoromethylphosphonate (0·095 g., 99%); the salt was identified by comparison of its infra-red spectrum with that of an authentic specimen.

(b) *From dichlorotrifluoromethylphosphine.* This compound (0·233 g.) and water (1 ml.) *in vacuo* formed two layers at lower temperatures, but at 20° a vigorous exothermic reaction occurred and a homogeneous solution was obtained. This was completely volatile when evaporated by freeze-drying. Treatment of the condensate with an excess of sodium hydroxide yielded fluoroform (0·092 g., 90%), thus revealing the presence of the volatile trifluoromethylphosphonous acid.

(c) *From iodobistrifluoromethylphosphine.* The iodo-compound (0·484 g.) and water (2 ml.)

reacted at room temperature to form a homogeneous solution (10 min.) and fluoroform (0·114 g., 48%). The solution was completely volatile when freeze-dried, and liberated fluoroform when treated with an excess of sodium hydroxide.

A solution of trifluoromethylphosphonous acid containing hydrogen iodide prepared as above liberated fluoroform quantitatively when heated at 100° for 16 hr. Fluoroform was also liberated quantitatively if the hydrogen iodide was first exactly neutralised by sodium hydroxide and the solution was then heated.

(d) *From di-iodotrifluoromethylphosphine.* Hydrolysis of this phosphine with the *minimum* amount of water yields a white substance when the solution is evaporated to dryness *in vacuo* (see Part VII). This substance, which is formed by decomposition of trifluoromethylphosphonous acid under these conditions, is being studied further. When an excess of water is used for the hydrolysis, evaporation by freeze-drying leaves no residue.

Di-iodotrifluoromethylphosphine (0·72 g.) and water (2 ml.) were allowed to react at 20°, then 3 equiv. of sodium hydroxide (12·45 ml. of 0·496N) and water (5 ml.) were added slowly; no gas was evolved. An aliquot portion, evaporated by freeze-drying, gave a white solid consisting of sodium iodide and sodium trifluoromethylphosphonite. The infra-red spectrum of the mixture was identical with that recorded as above for sodium trifluoromethylphosphonite (sodium iodide is transparent in this region of the infra-red). Addition of an excess of aqueous sodium hydroxide to a solution of the solid caused quantitative evolution of fluoroform.

Infra-red Spectra.—A Perkin–Elmer Model 21 double-beam instrument with rock-salt optics was used. The weak bands near 3 and 6 μ are caused by traces of moisture.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, March 19th*, 1954.]