Sulphonic Acid-induced Fragmentation of Dialkyl Acylphosphonates, Formation of Alkyl Carboxylates and Alkyl Sulphonates[1]

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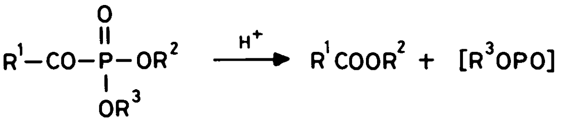
Heating of dialkyl acylphosphonates with sulphonic acids under anhydrous conditions leads to the formation of alkyl sulphonates and alkyl carboxylates. ^{31}P N.m.r. spectroscopy revealed that the reaction of equimolar amounts of dimethyl benzoylphosphonate (**1**) and toluene-*p*-sulphonic acid at room temperature gives dimethyl phosphonate (**6**) in 50% yield. It is proposed that the by-product of this reaction, benzoic toluene-*p*-sulphonic anhydride (**8**), reacts with the excess of toluene-*p*-sulphonic acid, to yield toluene-*p*-sulphonic anhydride (**9**) and benzoic acid. Heating of these two compounds with dimethyl phosphonate was shown to yield methyl toluene-*p*-sulphonate and methyl benzoate, respectively. A postulated by-product of these reactions is phosphenous acid (HPO_2). Quantum mechanical calculations by the MNDO/H method carried out on dimethyl benzoylphosphonate and its protonation products show that the preferred site of protonation of dimethyl benzoylphosphonate is the P=O oxygen, and that protonation at this site is followed by C–P bond breaking, with zero energy of activation, leading to dimethyl phosphite and benzoylium cation.

Phosphonic acid analogues of naturally occurring phosphonates and of carboxylic acids attract considerable interest as potential regulators and inhibitors of metabolic processes.[2] Among these phosphonates the number of acylphosphonic derivatives is rather small.[3] Examination of the literature dealing with acylphosphonates revealed that, although dialkyl acylphosphonates have been known for 40 years[4] the chemical properties of the corresponding acylphosphonic acids (**A**) and alkyl hydrogen acylphosphonates (**B**) have never been examined. As a consequence we considered it of interest to initiate a systematic study of the chemistry of acylphosphonic acid derivatives. In the course of this study we have found that acylphosphonic acids (**A**) and alkyl hydrogen acylphosphonates (**B**) undergo acid-catalysed and thermal fragmentation to the corresponding carboxylic derivatives (Scheme 1), with the putative formation of dico-ordinated phosphorus species.[1,5]



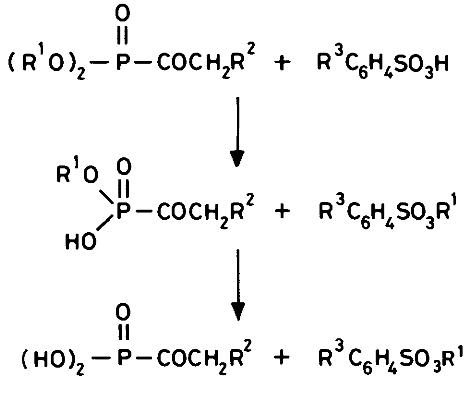
$$R^1{-}CO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR^3}{|}}{P}}{-}OR^2 \xrightarrow{H^+} R^1COOR^2 + [R^3OPO] \quad (1)$$

(**A**) $R^2 = R^3 = H$
(**B**) $R^2 =$ alkyl, $R^3 = H$
(**C**) $R^2 = R^3 =$ alkyl $\quad R^1 =$ Ph or n-C_6H_{13}

Scheme 1.

Following this discovery we found that dialkyl acylphosphonates (**C**), which are thermally stable, also undergo the same type of fragmentation reaction under the influence of catalytic amounts of protic and Lewis acids.[5]

On the other hand Golborn reported some years ago, 'a new synthesis of sulfonate esters based upon the transesterification reaction between a dialkyl acylphosphonate and a sulfonic acid'.[6] The reaction was claimed to proceed in two steps shown in Scheme 2 and was claimed to yield acylphosphonic acids as by-products '... about 80% yield' that 'were characterized by elemental analysis' (not reported).



R^2 = H or Me

Scheme 2.

We were puzzled to read this report since (a) we found in our work that alkyl hydrogen acylphosphonates (**B**) and acylphosphonic acids (**A**), claimed as reaction intermediates and products in Scheme 2, are not expected to survive Golborn's reaction conditions (8 h reflux in benzene or toluene), (b) we suspected that the carboxylic esters formed in Golborn's work would not have been noticed during work-up, because of their volatility, and (c) acylphosphonic acids have never been characterized before and therefore it seemed to us that the evidence for their formation as end-products in this reaction (based solely on elemental analysis) is insufficient. As we are engaged in a systematic study of acylphosphonic derivatives, the clarification of this controversy seemed to us to be of importance. Consequently we undertook to examine more thoroughly the behaviour of dialkyl acylphosphonates in anhydrous acidic conditions.*

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* The behaviour of diethyl benzoylphosphonate under aqueous acidic conditions was studied by Narayanan and Berlin.[7]

Table. Results from the reactions of dialkyl acylphosphonates with toluene-*p*-sulphonic acid[a] in refluxing benzene

	Starting material $R^1COPO_3R^2_2$				TsOH		Products yields	
Exp.	R^1	R^2		Quantity (M)	TsOH quantity (M)	Reaction time (h)	$R^1CO_2R^2$ (M)	$TsOR^2$ (M)
1	Ph	Me	(1)	0.05	0.05	12	0.035	0.036
2	Ph	Me	(1)	0.02	0.04	12	0.017	0.016
3	Ph	Me	(1)	0.01	0.001	12	0.001	0.001
4	Ph	Et	(2)	0.1	0.1	12	0.06	0.07
5	n-C_6H_{13}	Et	(4)	0.05	0.05	12	0.035	0.035
6	n-C_6H_{13}	Me	(3)	0.1	0.1	12	0.08	0.075
7	Me	Bu^n	(5)	0.07	0.07	8	0.042	0.03
8	Ph	Me	(1)	0.01	0.001	12	0.009	
9	n-C_6H_{13}	Me	(3)	0.01	0.001	12	0.008	

[a] Toluene-*p*-sulphonic acid was predried by azeotropic distillation with benzene for experiments 1—7, but used as the commercially obtained monohydrate in experiments 8 and 9.

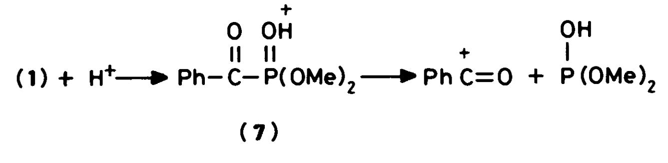
Results and Discussion

The results from the reactions of a number of dialkyl acylphosphonates with toluene-*p*-sulphonic acid (TsOH) in different molar ratios in refluxing benzene are summarized in the Table.

Examination of the Table reveals that all experiments using equimolar amounts of the reactants (entries 1 and 7) yielded alkyl carboxylates and alkyl tosylates in high yields. Doubling the sulphonic acid : acylphosphonic ester ratio did not produce any increase in the yield of the sulphonate nor a decrease in the yield of the carboxylate ester (compare entries 1 and 2). Heating dialkyl acylphosphonates with 10 mol% of toluene-*p*-sulphonic acid monohydrate afforded only the corresponding methyl carboxylates in good yield (experiments 8 and 9), as reported in our preliminary communication. In the absence of water however, the formation of both products in *ca.* 10% yield is observed (experiment 3). This experiment emphasizes the importance of small amounts of water. Its presence is necessary for the catalytic effect of acid for the carboxylate ester formation on the one hand, and on the other hand its absence is crucial for the side-by-side formation of carboxylate and tosylate esters.

Monitoring the reaction between equimolar amounts of (**1**) and TsOH in reluxing benzene by gas chromatography, revealed significant differences between the rates of formation of the two products. While the yields of methyl toluenesulphonate reached values of 78, 87, and 98% after 3, 15, and 24 h, at the same times methyl benzoate was formed only in yields of 23, 56, and 73%. These data suggested to us that the two products were formed by two different processes.

Concurrently with the experimental work we also carried out quantum mechanical calculations which indicated that the preferred site of protonation in acylphosphonates is the P=O oxygen, and that the protonated species [such as (**7**)] suffer C–P bond cleavage with zero activation energy yielding dimethyl phosphite and benzoylium ion (Scheme 3).

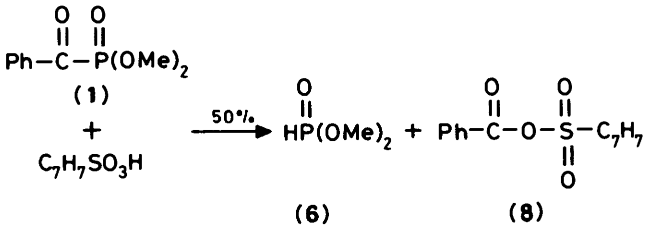


$$(\mathbf{1}) + H^+ \longrightarrow Ph-\overset{O}{\overset{\|}{C}}-\overset{\overset{+}{OH}}{\overset{\|}{P}}(OMe)_2 \longrightarrow Ph\overset{+}{C}=O + \overset{OH}{\overset{|}{P}}(OMe)_2$$

Scheme 3.

These calculations were borne out by experiment, when the interaction between dimethyl benzoylphosphonate (**1**) and toluene-*p*-sulphonic acid was studied by ^{31}P n.m.r. spectroscopy. This examination revealed that when equimolar amounts of the two compounds are dissolved in benzene at room temperature, there is a rapid decrease in the intensity of the signal of dimethyl benzoylphosphonate (**1**), $\delta_{^{31}P}$ −0.59 p.p.m. (septet), accompanied by the appearance of a doublet of septets attributable to dimethyl phosphonate (**6**), δ 10.9 p.p.m. (J_{HP} 728 Hz). A steady state, which is composed of *ca.* 50% of (**1**) and 50% of (**6**) is attained in *ca.* 4 h at ambient temperature, which does not show any change even after several days. Similarly, i.r. spectroscopic examination revealed a decrease in the intensity of the band of 1 250 cm^{-1}, characteristic for the P=O bond in compound (**1**) and the gradual appearance of a band, at 1 220 cm^{-1}, characteristic for the P=O bond in (**6**), and one at 2 400 cm^{-1} characteristic of P–H bonds. In addition, new bands appeared at 900 and 1 360 cm^{-1}, that could subsequently be assigned to toluene-*p*-sulphonic anhydride (**9**). Refluxing this solution caused changes in the ^{31}P n.m.r. spectrum. After 4 h this spectrum showed the presence of a broad peak centred at δ 15.5 p.p.m. (6% of total integration), dimethyl phosphonate (35%), methyl hydrogen phosphonate, δ 8.7 p.p.m. (dq), J_{PH} 718 Hz), 46%, and phosphorous acid, δ 7.9 p.p.m. (d, J_{PH} 718 Hz), 13%. After completion of the methyl benzoate and methyl toluene-*p*-sulphonate formation the spectrum showed a multitude of broad and ill-defined peaks in the range 28 to −12 p.p.m. Heating this solution produced methyl benzoate and methyl toluene-*p*-sulphonate as in the previously described experiments.

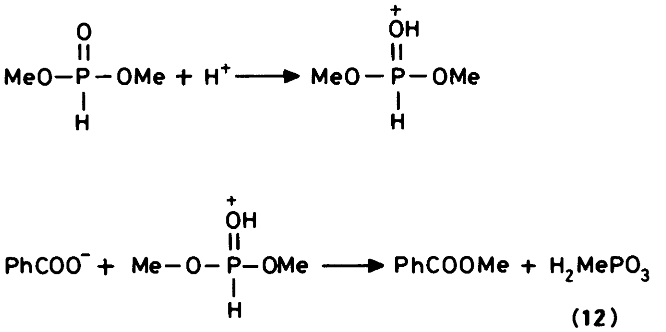
The formation of dimethyl phosphonate (**6**) as a result of protonation of (**1**) raises the question of the identity of the other product of this reaction. Balancing the equation leads to the mixed sulphonic carboxylic anhydride (**8**) (Scheme 4) as the predicted by-product in this reaction. The preparation and the properties of mixed sulphonic carboxylic anhydrides have been reported previously.[8] Such anhydrides show carbonyl bands in the i.r. spectrum at *ca.* 1 780 cm^{-1}. Examination of the reaction mixture of (**1**) with TsOH, containing 50% of (**6**), by i.r. spectroscopy did not indicate the presence of (**8**) in appreciable amounts. A strong band at 1 780 cm^{-1} could be seen, however, when synthetic (**8**) was added to this mixture. The rather rapid attainment of steady state in the reaction of (**1**) with TsOH leading to 50% of (**6**), led to the key for the solution of this problem. We assumed that the reason the formation of dimethyl phosphonate stops at a yield of 50% is that there is no more toluene-*p*-sulphonic acid in the reaction mixture even though only half of it took part in C–P bond fission (Scheme 4). The rest of the toluene-*p*-sulphonic acid could be consumed by reacting with the mixed sulphonic carboxylic anhydride (**8**) (Scheme 5) leading to the formation of the disulphonic anhydride (**9**)[8] and benzoic acid. This assumption was confirmed by i.r.



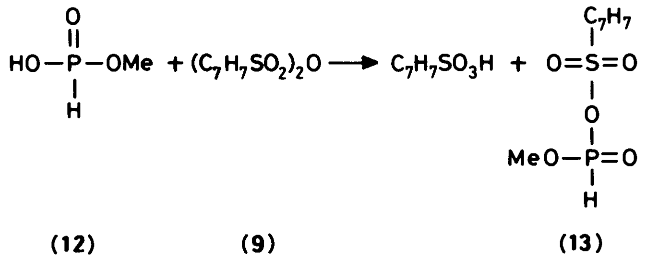
Scheme 4.

$$\underset{(8)}{C_7H_7SO_3H + C_7H_7SO_2{-}O{-}COPh} \longrightarrow \underset{(9)}{(C_7H_7SO_2)_2O} + PhCO_2H$$

Scheme 5.



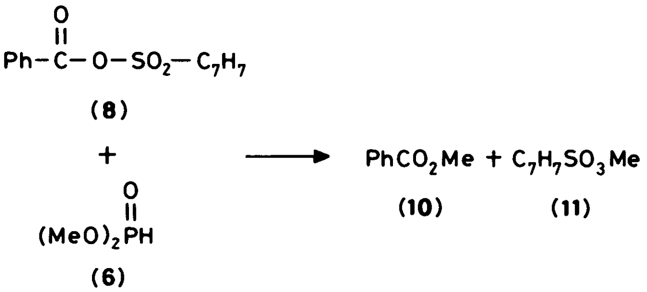
Scheme 6.



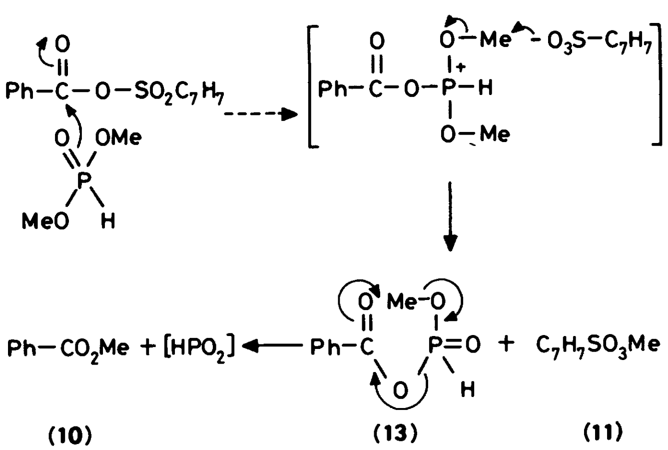
Scheme 7.

$$\underset{(9)}{(C_7H_7SO_2)_2O} + (MeO)_2P(O)H \longrightarrow \underset{(11)}{C_7H_7SO_3Me}$$

Scheme 8.



Scheme 9.



Scheme 10.

examination of a solution of equimolar amounts of (**8**) and TsOH in benzene. This study revealed that upon addition of acid the band at 1 780 cm^{-1} started diminishing in intensity, and strong bands at 1 700, 1 360, and 900 cm^{-1} started appearing. The band at 1 780 cm^{-1} disappeared completely if a slight excess of toluene-*p*-sulphonic acid was present. The band at 1 700 cm^{-1} was attributed to benzoic acid while those at 1 360 and 900 cm^{-1} are characteristic of anhydride (**9**), which was prepared by an independent method.[8]

The results presented so far may be summarized by saying that mixing equimolar amounts of dimethyl benzoylphosphonate and toluene-*p*-sulphonic acid leads, apparently, to a mixture composed of approximately equimolar amounts of unchanged (**1**), benzoic acid, dimethyl phosphonate (**6**), and toluene-*p*-sulphonic anhydride (**9**). We now describe some experiments that indicate possible reaction paths for the conversion of this mixture to the two end-products: methyl benzoate (**10**) and methyl toluene-*p*-sulphonate (**11**).

The alkylation of carboxylic acids by phosphites has been a well recognized procedure for the preparation of carboxylic esters.[9] Although most procedures employ trialkyl phosphites, dialkyl phosphites may also be used. Hoffmann and Weiss reported that heating benzoic acid with dimethyl phosphite without solvent at 200 °C affords methyl benzoate in 75—85% yield.[9e] We observed formation of methyl benzoate in 50% yield by heating benzoic acid and dimethyl phosphonate in benzene solution for 20 h. In the presence of 10 mol% TsOH the yield could be raised to 76%. This reaction can reasonably be described by a mechanism consisting of protonation of the phosphoryl oxygen followed by nucleophilic attack by the carboxylate (Scheme 6) leading to the carboxylate ester and monomethyl phosphite (**12**) which may react further, for example with toluene-*p*-sulphonic anhydride to regenerate toluene-*p*-sulphonic acid, necessary for the cleavage of the hitherto unchanged dimethyl benzoylphosphonate (**1**), and to give sulphonic phosphonic anhydride (**13**) (Scheme 7).

As for the formation of methyl tosylate, we have found that both anhydrides (**8**) and (**9**) may be potential sources for this product. Heating toluene-*p*-sulphonic anhydride (**9**) with dimethyl phosphonate in benzene for 20 h afforded (**11**) in 74% yield (Scheme 8).

Similarly, heating equimolar amounts of (**8**) and (**6**) gave the two esters (**10**) and (**11**) in 56 and 62% yields (Scheme 9).

The reactions of dimethyl phosphite with the two anhydrides (**8**) or (**9**) may be visualized by mechanisms that are shown in Schemes 10 and 11.*

The initial putative products of these reactions (Schemes 10 and 11) are mixed anhydrides (**13**) and (**14**) (see Scheme 7) which may presumably undergo further fragmentation to yield

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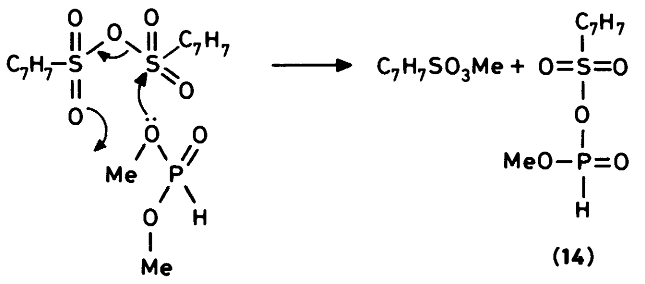
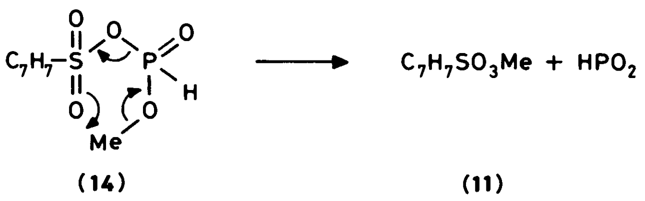
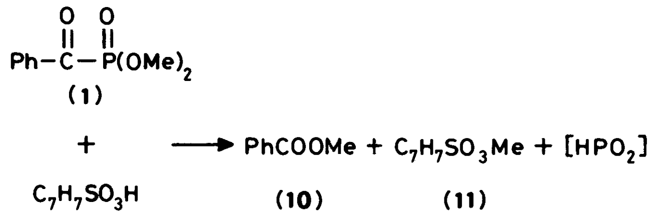
* We thank one of the referees for suggesting the mechanism in Scheme 10.



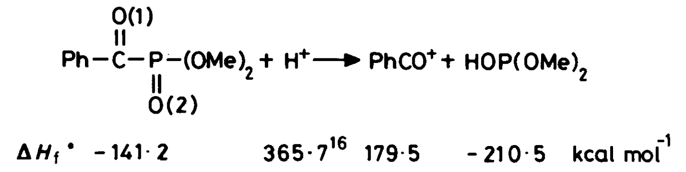
Scheme 11.



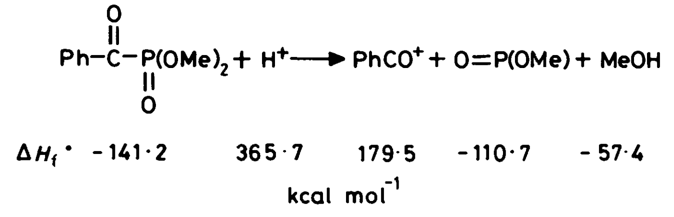
Scheme 12.



Scheme 13.



Scheme 14.



Scheme 15.

the final product (**11**) possibly by cyclic mechanisms shown in Schemes 10 and 12.[10]

These proposed Schemes are also consistent with the previously described effect of water upon the course of the reaction. Clearly the absence of water is critical for the existence of the mixed carboxylic sulphonic and the sulphonic anhydrides described. On the other hand, in the presence of water the initially formed carboxylic sulphonic anhydride (**8**) (Scheme 4) would suffer hydrolysis to benzoic acid, which may react further with dimethyl phosphonate (**6**) to give methyl benzoate and toluene-*p*-sulphonic acid. The latter would be recycled to catalyse the cleavage of a new acylphosphonate molecule.

The elements of HPO_2 are left unaccounted for by our studies as they are in our previously described thermal fragmentation-transformation of alkyl hydrogen acylphosphonates to alkyl carboxylates (Scheme 1). It seems likely that such species would yield polymeric end-products. Indeed the complex spectrum obtained upon examination of the reaction mixture by ^{31}P n.m.r. spectroscopy after completion of the reaction is compatible with the possible presence of cyclic and linear polymeric products.

Quantum Mechanical Calculations.—Dimethyl benzoylphosphonate (**1**) was used as a model compound for the series. Semiempirical calculations were run with a modified version of MNDO,[11,12] which was recently corrected for its failures to describe hydrogen bonding appropriately.[12,13] Total geometry optimization was done with estimations of second derivatives (Hessian matrix) for each of the $3n - 6$ parameters in each species. The optimizations started from a few conformations in order to verify global minima. Rotational barriers were checked by the 'reaction co-ordinate' method,[14] where a torsional angle was kept 'frozen' at each of a few angular variation steps (10—30°) leading to full rotations. In addition to the enthalpies obtained by MNDO (at 298.15 K), entropies were calculated by adding their translational, rotational, and vibrational components.[15] The '*in vacuo*' calculations of the type performed in this study are partly justified by the apolar nature of the reaction solvents.

Compound (**1**) was found to be most stable in its *s-trans* carbonyl-phosphoryl arrangement (ΔH_f 141.18 kcal mol^{-1}). From the molecular orbitals we find that the lone pairs on the phosphoryl oxygen [O(2)] are the main contributors to three of the four highest occupied orbitals, while those of the carbonyl oxygen [O(1)] are lower in energy.

As the oxygen of P=O [O(2)] was found to carry the largest negative charge in the molecule of (**1**) by our calculations, we expect both hard and soft acids to attack this oxygen preferentially. However, protonations were studied for all three oxygen types and the possibility of stabilizing the protonated species by internal hydrogen bonding was thoroughly investigated.

Protonation of O(2) took place from both in-plane directions which led both to C–P bond cleavage with the formation of a benzoylium cation, $PhCO^+$ (ΔH_f 179.5 kcal mol^{-1}) and dimethyl phosphite, HO–P(OMe)$_2$ (ΔH_f -210 kcal mol^{-1}). The overall reaction is strongly exothermic (ΔH_r -255.5 kcal mol^{-1}) (Scheme 14).

Protonation of the other phosphoryl oxygens [those of the two OMe groups, O(3) and O(4)] leads to C–P bond cleavage and P–O cleavage (Scheme 15) which is much less exothermic (ΔH_r -213 kcal mol^{-1}) than the previous reaction. The free energy in Scheme 15 is closer to that of Scheme 14 than their respective enthalpies due to a gain of additional 30 cal mol^{-1} K^{-1}, which amount to *ca.* 10 kcal mol^{-1} at room temperature.

The protonation of the carbonyl oxygen O(1) is the least favourable energetically (ΔH_r -191.3 kcal mol^{-1}), and is better from the direction of the phosphoryl group. No bond breaking is found in this case. Rotation around the C–P bond in this protonated stable species needed much higher energies than in the neutral molecule. Rotations of 20, 40, 60, and 80° from the equilibrium position {with φ [O(2)=P–C=O(1)] 235.5°} required energies of 1.1, 4.3, 6.8, and 7.4 kcal mol^{-1}, respectively. Hydrogen bonding between O(1) and both O(2) and O(3) (O–O distances varying between 2.5 and 3.25 Å) were detected along these rotations, but at φ 335.5° C–P bond breaking took place with proton transfer from carbonyl O(1) to O(2).

Under the acidic conditions of this reaction it seems most probable that C–P bond cleavage is the leading reaction, with formation of the benzoylium cation $PhCO^+$. This species has a highly electrophilic carbon (q_C $+0.55$) and will easily react with any electron donor, such as $C_7H_7SO_3^-$ present in the mixture, to yield (**8**).

In our gas-phase calculations, $\mathrm{HO{-}P(OMe)_2}$ is more stable than $\mathrm{H{-}P(O)(OMe)_2}$, and its proton affinity (PA −192.1 kcal mol^{-1}) is much less than the affinity of the phosphoryl group. We may thus assume that as long as the benzoyl phosphonate is present, even in low concentrations, it will be protonated preferentially.

Experimental

General.—I.r. spectra were recorded on Perkin-Elmer 457 spectrophotometer, ^{31}P n.m.r. spectra were obtained either on a Varian XL100 or Bruker WM250 MHz instrument, and ^{1}H n.m.r. spectra were measured on a Bruker WH-300 instrument. Mass spectra were run on an LKB 8091 mass spectrometer. Gas chromatographic work was carried out with a Varian model 1400 gas chromatograph equipped with a copper tube (1.5 m × $\frac{1}{4}$ in O.D.) packed with 10% Carbowax on Chromosorb W 60—80. Peak areas were determined by the internal standard method.

Materials.—Trimethyl phosphite, triethyl phosphite, tributyl phosphite, heptanoyl chloride, acetyl chloride, and benzoyl chloride were obtained from Aldrich Chemical Company and were distilled before use. Anhydrous toluene-*p*-sulphonic acid was obtained by azeotropic distillation of the monohydrate using benzene. Dimethyl benzoylphosphonate,[17] diethyl benzoylphosphonate,[7] benzoic toluene-*p*-sulphonic,[8] and toluene-*p*-sulphonic anhydride[8] were reported previously. Other common reagents were obtained commercially in high purity.

General Procedure for the Synthesis of Dialkyl Acylphosphonates (**1**)—(**5**) *from Trialkyl Phosphites and Acyl Chlorides.*—A modification of Kabachnik's[17] method was used. To the acyl chloride (0.2 mol), stirred at 5 °C, was added dropwise trialkyl phosphite (0.2 mol). After addition was complete the cooling bath was removed and the mixture was stirred for 2 h at ambient temperature. The products were purified by vacuum distillation and identified by i.r. and n.m.r. spectra.

Dimethyl benzoylphosphonate (**1**). Benzoyl chloride (28.3 g, 0.8 mol) and trimethyl phosphite (24.88, 0.2 mol) gave product (37.7 g, 85%), b.p. 120—121 °C at 1 mmHg (lit.,[18] 146 °C at 2.5 mmHg), $\delta_{\mathrm{H}}(\mathrm{CDCl_3; Me_4Si})$ 8.16 (m, 2 H, aromatic), 7.51 (m, 3 H, aromatic), and 3.89 (d, 6H, *J* 10.63 Hz, $\mathrm{OCH_3}$), $\delta_{\mathrm{P}}(\mathrm{CDCl_3}$; external 10% $\mathrm{H_3PO_4}$) −0.87 p.p.m. (septet); $\nu_{\mathrm{max.}}$(neat) 1 660 (C=O), 1 580—1 600 (C=C aromatic), 1 255 (P=O), and 1 030 cm^{-1} (P–O–C).

Diethyl benzoylphosphonate (**2**). Benzoyl chloride (28.3 g, 0.2 mol) and triethyl phosphite (33.2 g, 0.2 mol) gave product (42.1 g, 88%), b.p. 158—160 °C at 1.2 mmHg (lit.,[8] 116—118 °C 0.15—0.20 mmHg), $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ δ 8.23 (m, 2 H, aromatic), 7.51 (m, 3 H, aromatic), 4.28 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$), and 1.36 (t, 6 H, *J* 7.0 Hz, $\mathrm{OCH_2C}H_3$), $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ − 3.27 p.p.m. (quintet); $\nu_{\mathrm{max.}}$(neat) 1 660 (C=O), 1 580—1 600 (C=C aromatic), 1 255 (P=O), and 1 020 cm^{-1} (P–O–C).

Dimethyl heptanoylphosphonate (**3**). Heptanoyl chloride (24.1 g, 0.2 mol) and trimethyl phosphite (24.8 g, 0.2 mol) gave (**3**) (37.7 g, 85%), b.p. 109—111 °C at 0.8 mmHg, $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 3.85 (d, 6 H, *J* 11.0 Hz, $\mathrm{OCH_3}$), 2.83 (t, 2 H, *J* 7.0 Hz, $\mathrm{C}H_2\mathrm{{-}C{=}O}$), 1.52 [m, 8 H, $(\mathrm{C}H_2)_4\mathrm{{-}CH_2{-}C}$], and 1.00 (t, 3 H, *J* 7.0 Hz, $\mathrm{C}H_3\mathrm{CH_2}$), $\delta_{\mathrm{P}}(\mathrm{CDCl_3})$ − 2.56 p.p.m. (septet); $\nu_{\mathrm{max.}}$(neat) 1 695 (P=O) and 1 025 cm^{-1} (P–O–C) (Found: C, 46.8; H, 8.7. Calc. for $\mathrm{C_9H_{19}O_4P}$: C, 48.6; H, 8.55%).

Diethyl heptanoylphosphonate (**4**). Heptanoyl chloride (24.1 g, 0.2 mol) and triethyl phosphite (33.2 g, 0.2 mol) gave (**4**) (41 g, 82%), b.p. 114—117 °C at 0.7 mmHg; $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 4.18 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.79 (t, 2 H, *J* 7.25 Hz, $\mathrm{C}H_2\mathrm{{-}C{=}O}$), 1.59 (m, 2 H, $\mathrm{C}H_2\mathrm{CH_2{-}C{=}O}$), 1.34 (t, 6 H, *J* 7.10 Hz, $\mathrm{OCH_2C}H_3$), 1.25 [m, 6 H, $\mathrm{CH_3(C}H_2)_3$], and 0.86 (t, 3 H, $\mathrm{C}H_3\mathrm{CH_2}$); $\nu_{\mathrm{max.}}$(neat) 1 695 (C=O), 1 250 (P=O), and 1 015 cm^{-1} (P–O–C) (Found: C, 52.6; H, 9.1. Calc. for $\mathrm{C_{11}H_{23}O_4P}$: C, 52.8; H, 9.2%).

Dibutyl acetylphosphonate (**5**). Acetyl chloride (15.9 g, 0.2 mol) and tributyl phosphite (50 g, 0.2 mol) gave (**5**) (43.4 g, 92%), b.p. 123—125 °C at 3 mmHg; $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 4.14 (m, 4 H, $\mathrm{OC}H_2$), 2.47 (d, 3 H, *J* 5.0 Hz), 1.68 (m, 4 H, $\mathrm{OCH_2C}H_2$), 1.39 (m, 4 H, $\mathrm{CH_3C}H_2\mathrm{CH_2CH_2O}$), and 0.94 (t, 6 H, *J* 7.3 Hz, $\mathrm{C}H_3\mathrm{CH_2}$); $\nu_{\mathrm{max.}}$(neat) 1 700 (C=O), 1 250 (P=O), and 1 025 cm^{-1} (P–O–C) (Found: C, 50.7; H, 9.0. Calc. for $\mathrm{C_{10}H_{21}O_4P}$: C, 50.85; H, 8.9%).

Reactions of Dialkyl Acylphosphonates with Anhydrous Toluene-p-*sulphonic Acid.*—Dialkyl acylphosphonate (0.1 mol) and anhydrous toluene-*p*-sulphonic acid (0.1 mol) were refluxed in dry benzene (100 ml) for 12 h. The cooled mixture was washed with 10% sodium carbonate solution (150 ml) and water (150 ml), dried ($\mathrm{Na_2SO_4}$), concentrated, and distilled under vacuum. The yields of distilled products are given in the Table. The esters were identified by comparison of their i.r. and n.m.r. spectra with those of independently synthesized esters.

Reaction of Dimethyl Benzoylphosphonate (**1**) *with Anhydrous Toluene*-p-*sulphonic Acid in Benzene at Room Temperature.*—A solution of dimethyl benzoylphosphonate (4.28 g, 0.02 mol) and anhydrous toluene-*p*-sulphonic acid (3.44 g, 0.02 mol) in dry benzene (100 ml) was stirred at room temperature for 12 h. The progress of the reaction was monitored by i.r. and ^{31}P n.m.r. spectroscopy.

Reaction of Benzoic Toluene-p-*sulphonic Anhydride* (**8**) *with Dimethyl Phosphonate* (**6**).—A solution of (**8**) (27.6 g, 0.1 mol) and of (**6**) (11 g, 0.1 mol) in dry benzene was refluxed for 20 h and then cooled. Estimation of the yields was based on the areas of the peaks in g.c. analysis which showed the presence of methyl benzoate (7 g, 56%), methyl toluene-*p*-sulphonate (10.5 g, 62%), and unchanged dimethyl phosphonate (2.4 g, 27%).

Reaction of Toluene-p-*sulphonic Anhydride* (**9**) *with Dimethyl Phosphonate* (**6**).—A solution of toluene-*p*-sulphonic anhydride (3.26 g, 0.01 mol) and dimethyl phosphonate (1.1 g, 0.01 mol) in dry benzene (50 ml) was refluxed for 20 h. The cooled mixture was washed with 10% sodium carbonate solution (50 ml) and water (50 ml), dried ($\mathrm{Na_2SO_4}$), concentrated, and distilled under vacuum, yielding methyl toluene-*p*-sulphonate (1.37 g, 74%), which was identified by i.r. and n.m.r. spectroscopy.

Reaction of Benzoic Acid with Dimethyl Phosphonate.—A solution of benzoic acid (12.2 g, 0.1 mol) and dimethyl phosphonate (**6**) (11 g, 0.1 mol) in dry benzene (200 ml) was refluxed for 20 h. The cooled mixture was washed successively with 10% sodium carbonate solution (100 ml) and water (100 ml), dried ($\mathrm{Na_2SO_4}$), concentrated, and distilled to yield methyl benzoate (6.8 g, 50%) which was characterized by i.r. and ^{1}H n.m.r. spectroscopy.

The same procedure was repeated with toluene-*p*-sulphonic acid monohydrate (1.9 g, 0.01 mol) and then again with the addition of toluene-*p*-sulphonic acid monohydrate (19 g, 0.1 mol) yielding methyl benzoate (10.33 and 13.33 g, respectively corresponding to yields of 76 and 98%).

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