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# NMR SPECTROSCOPIC STUDIES OF FORMYLMETHYLENETRIPHENYLPHOSPHORANES AND THEIR ALKYLATION PRODUCTS

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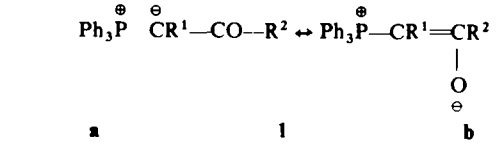
**Abstract**—Formyl-stabilized phosphonium ylids, unlike their β-keto analogues, show both *cis* and *trans* isomers in their NMR spectra, presumably due to decreased steric interaction. The α-formylbenzylidene ylid (**3b**) differs from the parent[1] formylmethylene phosphorane (**3a**) in showing a solvent dependent isomer ratio; the proportion of *trans* isomer increasing with increasing solvating power. Values for barriers to rotation, measured by NMR are probably due to an acid catalysed process, although inhibition of this process by basic alumina is far from satisfactory. Alkylation of formyl ylids took place exclusively at oxygen to give isomeric mixtures of phosphonium salts, which in some cases showed a marked dependence on the alkylating agent. Apparent decomposition in certain NMR solvents was also due to alkylation at oxygen.

THE NMR SPECTRA of carbonyl stabilized phosphonium ylids (**1**) have been extensively studied in recent years.[1] Much of this interest involves the observation of geometrical isomers in these compounds, caused by substantial contributions to the ylid structure from the canonical form (**1b**).

NMR spectra of ester-stabilized ylids (**2**; $R^2$ = OR) show a mixture of *cis* (**2a**) and *trans* (**2b**) isomers,[2] the amount of *trans* increasing with the bulk of $R^1$ and solvent



**a** **1** **b**

**a** **2** **b**

*cis* *trans*

polarity.[1] Keto-stabilized ylids (**2**; $R^2$ = alkyl or aryl) on the other hand, show only the *cis* isomer (**2a**) unless $R^2$ is large and $R^1$ is strongly electron withdrawing,[3,1] a preference which precludes any study of isomer interconversion.

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The one example of a formyl-stabilized ylid (**3a**) so far studied exists as a mixture of *cis* and *trans* isomers,[3–6] which encouraged us to investigate isomer ratios and isomer interconversion in a range of formyl-stabilized ylids in an attempt at correlation with the results obtained from ester-stabilized ylids.[7] The isomer ratios for a number of substituted formyl ylids (**3**) are given in Table 1 together with $^1H$ and $^{31}P$ NMR data. The $^1H$ spectral assignments were made on the basis of $J_{PCCH}$ in the *cis* isomer (**3**) being greater than in the *trans*, while those for the $^{31}P$ spectra were


**3a** R = H
**b** R = Ph
**c** R = 3-$NO_2C_6H_4$
**d** R = 4-$NO_2C_6H_4$
**e** R = 3-$ClC_6H_4$
**f** R = Me

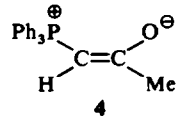
TABLE 1. ISOMER RATIOS AND NMR DATA FOR FORMYL-STABILIZED YLIDS IN $CDCl_3$


| Ylid | R | *cis/trans* (+27°C) | $^1H$ NMR | | | | $^{31}P$ NMR[a] | |
|---|---|---|---|---|---|---|---|---|
| | | | $H_A$ (τ) | $H_B$ (τ) | $J_{PH_A}$ (Hz) | $J_{PH_B}$ (Hz) | cisoid | transoid |
| **3a** | H | 55/45[b] | 1·02 | 1·76 | 38 | 4 | −15·0 | −19·1 |
| **3b** | Ph | 50/50 | 0·86 | 1·68 | 30 | 6 | -- | -- |
| **3c** | 3-$NO_2C_6H_4$ | 50/50 | 0·76 | 1·50 | 30 | 5 | -- | -- |
| **3d** | 4-$NO_2C_6H_4$ | 33/67 | 0·82 | 1·70 | 27 | 5 | −16·4 | −22·4 |
| **3e** | 3-$ClC_6H_4$ | 54/46 | 0·88 | 1·60 | 27 | 5 | -- | -- |
| **3f** | Me | 0/100 | -- | 2·00 | -- | 4 | -- | −25·4 |

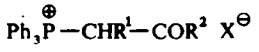
[a] ppm from external $H_3PO_4$
[b] measured at −20°C

based on the presumed shielding in the *cis* case.[8] Unlike the keto ylids (**2**: R = alkyl or aryl)[9] *trans* isomer is present in all cases of formyl ylids (**3**), to the extent of being the only observable isomer in **3f**, presumably because of the reduced steric interaction between phosphorus and hydrogen. This is exemplified by a comparison of isomer ratios in ylids **4** (100% *cis* in $CDCl_3$)[9] and **3f** (100% *trans* in $CDCl_3$).

Any comparison with ester ylids (**2**; $R^2$ = OR) is complicated by the amount of *trans* isomer increasing (*sic*) with the bulk of $R^2$, ingeniously explained by Snyder in




**4**




**5**

terms of the energy gain from solvation forcing the $Ph_3P^+$ group *trans* in the face of increasing steric inhibition by $R^2$ of solvation. Further, the lack of data for suitably substituted ester-stabilized ylids makes a comparison with formyl ylids of substituent effects on isomer ratios less than satisfactory. However comparison with data which is available[2] suggests that substituent effects are very similar, although formyl ylids show a greater proportion of *trans* isomer in all cases, presumably again due to steric effects.

The NMR spectrum of formylmethylenetriphenylphosphorane (**3a**) has been studied in a variety of solvents and although expected, small changes in chemical shift occur, the *cis/trans* isomer ratio remains constant.[5] However, the data given in Table 2 shows that the isomer ratio of formyl ylid **3b** is highly solvent dependent. Although solvent polarity and solvating ability are not necessarily directly related,[10]

TABLE 2. SOLVENT EFFECTS ON THE ISOMER RATIO IN **3b**

| Solvent | D[a] | $E_T$[e] (Kcal/Mole) | *cis/trans* |
|---|---|---|---|
| $C_2Cl_4$ | 2·3[c] | -- | >30[f] |
| $CHCl_2CHCl_2$ | 8·2[d] | -- | >30[f] |
| $CDCl_3$ | 4·80 | 39·1 | 1·17 |
| MeSOMe | 48·9 | 45 | 1·0 |
| $CH_2Br_2$ | 7·2[b] | -- | 0·85 |
| MeOH | 32·6 | 55·5 | 0·61 |
| $CD_3OD$ | 32·6 | 55·5 | 1·86 |

[a] *Handbook of Chemistry and Physics* R. C. Weast (Ed.), The Chemical Rubber Co. p. E58 (1968)
[b] A. D. Buckingham and R. J. W. Le Fevre, *J. Chem. Soc.* 3432 (1953)
[c] R. Bramley, C. G. Le Fevre, R. J. W. Le Fevre and B. Purnachandra Rao, *J. Chem. Soc.* 1183 (1959)
[d] Van Braam Houckgeest, *Rec. Trav. Chim.* **60**, 435 (1941)
[e] C. Reichardt, *Angew. Chem. Internat. Edit.* **4**, 36 (1965)
[f] These ratios assume that observation by NMR of an isomer present to the extent of 3% or more is possible.

the proportion of *trans* isomer does increase consistently with $E_T$ which presumably reflects increasing steric hindrance through oxygen solvation. Similar behaviour is found in ester-stabilized ylids.[1]

The considerable divergence in isomer ratios measured in MeOH and in $CD_3OD$ was confirmed by several determinations. The ratio obtained in MeOH seems closest to the value inferred from ratios in other solvents and it may be that traces of impurities present in $CD_3OD$ grossly affect the ylid isomer ratios; for example acid may inhibit solvation at oxygen and so increase the proportion of *cis* isomer. Although the addition of LiBr to $CDCl_3$ solutions of ester ylids increases the amount of *trans* isomer in each case,[1] isomer ratios in formyl ylids are virtually unaffected by added LiBr.

*Rotational barriers in formyl-stabilized ylids.* The barrier to interconversion of *cis* and *trans* forms of stabilized ylids (**2**) has been measured by NMR methods[1] and two mechanisms have been suggested. The lower energy process is thought to involve protonation of the ylid at carbon to give a phosphonium salt (**5**),[11] while the higher

energy process is visualized as pure rotation about the ylid C—C double bond. Distinction between these processes is often difficult; however it has been achieved by the addition of traces of base which inhibit the acid-catalysed process.[11] Application of base inhibition to ester-stabilized ylids indicates a NMR coalescence temperature for *cis–trans* interconversion for the pure rotation process about 30° higher than for the acid-catalyzed mechanism.[2]

The variation with temperature of the NMR spectrum of formylmethylene triphenylphosphorane (**3a**) has been studied by a number of workers.[3,5,6] Originally Bestmann and Snyder claimed a coalescence temperature ($T_c$) of 80° for **3a** in $CDCl_3$, while Wilson and Tebby state[3] that no coalescence was observed even at 150°* and suggest that the observed lower $T_c$ is due to an acid-catalyzed process. Other workers[5] have also failed to observe coalescence, but only up to 70°C. In view of these conflicting reports we have investigated the variation with temperature of the NMR spectrum of the formyl ylids (**3b–f**) together with a reinvestigation of ylid **3a**.†

Spectra of ylid **3a** were determined in the presence of basic alumina (10 mg) which, it is claimed, removes the possibility of acid catalysis.[11] However, we were unable to obtain interpretable spectra even at high concentrations, due to poor resolution and low intensities at the temperatures required (>70°C). Spectra of samples not containing alumina were readily obtained and substantially confirmed the results of Bestmann and Snyder. This is indirect evidence for an acid catalysed process, which should show a lower coalescence temperature and is expected in the absence of basic alumina.

The results shown in Table 3 were obtained from NMR spectra of formyl ylids (**3**)

TABLE 3. VARIABLE TEMPERATURE NMR SPECTRA OF YLIDS 3

| Ylid | R | Coalescence temperature | $\Delta G^{\ddagger}$ kcal per mole | $\Delta\nu^a$ (Hz) at 100 MHz |
|---|---|---|---|---|
| **a** | H | 80 | — | 76 |
| **b** | Ph | 66 | 16·5 ± 0·5 | 84 |
| **c** | 3-$NO_2C_6H_4$ | >70 | >16·7 | 78 |
| **d** | 4-$NO_2C_6H_4$ | 55 | [b] | 89 |
| **e** | 3-$ClC_6H_4$ | 96[c] | 18·4 ± 0·5 | 42[c] |

[a] $\Delta\nu$ refers to the limit of the line separation of the coalescing absorptions ($H_A$ and $H_B$ Table 1) under conditions of no exchange.

[b] The method used to determine $\Delta G^{\ddagger}$ from the rate constant for interconversion at the coalescence temperature (H. Kessler, *Angew. Chem. Internat. Edit.* **9**, 219 (1970)) depends on the interconverting isomers being equal, or very nearly equal, in free energy.

[c] Determined at 60 MHz, all other measurements were taken at 100 MHz.

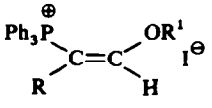
* NMR spectra obtained at temperatures well above the boiling point of the solvent used (in this case $CDCl_3$) are often distorted (poor resolution and 'false coalescence) due to isolated boiling of the solvent. In addition to this our samples of formyl ylid (**3a**) decomposed at temperatures > 120°C, although this may be due to traces of acid.

† In a footnote to a paper[2] published after completion of our present work, Snyder withdraws his previous claims[7] and agrees with the results of Wilson and Tebby.[4]

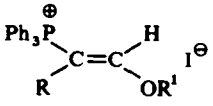
recorded in the absence of basic alumina, the presence of alumina at temperatures >50°C again caused massive loss of resoltuion and intensity. However, spectra obtained from the *p*-nitrophenyl substituted ylid (**3d**) in the *presence* of basic alumina (up to 15 mg per sample) were readily interpreted and gave an identical coalescence temperature to that obtained from spectra of **3d** in the absence of alumina. This suggests that the barrier measured for ylid **3d** is not due to acid catalysis, but the result cannot be extended to the other ylids studied.† In an attempt to overcome the problems associated with the use of alumina, NMR samples containing basic alumina were shaken, filtered and their spectra immediately determined. The results obtained were identical to those in Table 3.

In an attempt to induce an acid-catalyzed process sulphuric acid was added to each NMR sample; however this caused no detectable difference in their NMR spectra over the temperature range studied. This suggests that the coalescence observed is due to an acid-catalyzed process and some doubt must be thrown on the efficacy of basic alumina to stop such a process in $CDCl_3$.

*Alkylation of formyl-stabilized ylids.* Alkylation of ylids (**3**) with methyl or ethyl iodide took place exclusively at oxygen to give salts **6a** and **6b**. The stereochemistry of these salts was assigned on the basis of $J_{PCCH}$ values (28–34 Hz for **6a** and 11–13 Hz



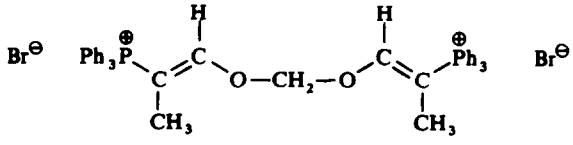
**6a**



**6b**

for **6b**) and on the assumption that the protons of the $OR^1$ group *cis* to the phosphorus are shielded by the phenyl rings and appear at higher $\tau$ values than the protons of the $OR^1$ group *trans* to the phosphorus. NMR data for **6a** and **6b** is given in Table 4. The ratios of **6a** and **6b** obtained from each ylid, given in Table 5, differed from the isomer ratios observed in the corresponding ylids (Table 1) and in some cases (**3c** and **d**) showed a marked dependence on the alkylating agent.

The use of methylene dibromide as a NMR solvent for formyl ylids (**3**) above room temperature led to decomposition. Heating ylid **3f** in methylene dibromide gave an oil with a highest *m/e* value at 318 which had an NMR spectrum identical with that obtained after heating NMR samples of **3f** in methylene bromide. The decomposition product was assigned structure **7**, with *trans–trans* stereochemistry, on the basis of

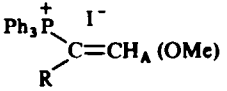


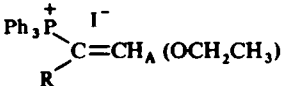
**7**

† In the case of ester-stabilized ylids the barrier to rotation was markedly lowered by electron-withdrawing substituents on the α-carbon atom.[3]

‡ We thank Professor Snyder for his assistance in specifying the conditions required for inhibition of acid-catalysis.

TABLE 4. NMR SPECTRA OF ALKYLATED FORMYL YLIDS 6





| Ylid | R | *trans* | | | *cis* | | | *trans* | | | | *cis* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | OMe (τ) | $H_A$ (τ) | $J_{PCCH_A}$ (Hz) | Ome (τ) | $H_A$ (τ) | $J_{PCCH_A}$ (Hz) | $OCH_2$ (τ) | Me (τ) | $H_A$ (τ) | $J_{PCCH_A}$ (Hz) | $OCH_2$ (τ) | Me (τ) | $H_A$ (τ) | $J_{PCCH_A}$ (Hz) |
| a | H | 6·8 | — | — | 7·10 | 1·88 | 32 | 5·52 | 8·61 | 3·22 | 13 | 5·84 | 9·06 | 1·88 | 34 |
| b | Ph | 5·19 | — | — | 6·14 | — | — | 5·76 | 8·74 | | — | 5·76 | 9·16 | — | — |
| c | 3-$NO_2C_6H_4$ | 5·84 | — | — | 6·02 | 1·80 | 28 | — | — | — | — | 5·64 | 9·16 | 1·74 | 28 |
| d | 4-$NO_2C_6H_4$ | 5·88 | — | — | 6·04 | — | — | — | — | — | — | 5·64 | 9·18 | 1·76 | 28 |
| e | 3-$ClC_6H_4$ | 5·43 | — | — | 5·63 | — | — | — | — | — | — | — | — | — | — |
| f | Me | 6·0 | 3·34 | 11 | 6·32 | — | — | 5·74 | 8·66 | 3·28 | 11 | — | — | — | — |

TABLE 5. ISOMER RATIOS IN ALKYLATION PRODUCTS OF YLIDS 3

| Ylid | R | Methylation | | Ethylation | |
|---|---|---|---|---|---|
| | | *cis* | *trans* | *cis* | *trans* |
| **a** | H | 55 | 45 | 80[a] | 20[a] |
| **b** | Ph | 79 | 21 | 76 | 24 |
| **c** | 3-$NO_2C_6H_4$ | 28 | 72 | 100 | 0 |
| **d** | 4-$NO_2C_6H_4$ | 40 | 60 | 100 | 0 |
| **e** | 3-$ClC_6H_4$ | 60 | 40 | — | — |
| **f** | Me | 10 | 90 | 0 | 100 |

[a] J. P. Snyder and H. J. Bestmann, *Tetrahedron Letters* 3317 (1970)

these spectra. A similar product was obtained by heating ylid **3f** in methylene diiodide. Pure methylene chloride did not react, although commercial samples of the solvent gave a salt (**8**), presumably due to traces of hydrogen chloride.

$$Ph_3\overset{\oplus}{P}-CHMe-CHO \qquad Cl^{\ominus}$$

**8**

## EXPERIMENTAL

$^1H$ nuclear magnetic resonance spectra were obtained at 100 MHz on a Varian HA-100 spectrophotometer or at 60 MHz on a Varian A-60D with TMS as standard. $^{31}P$ Spectra were obtained on ~2·5 M solutions in $CHCl_3$ on a Varian HA-100 spectrophotometer fitted with a $^{31}P$ probe using a capillary sample of 85% $H_3PO_4$ as external standard. Isomer ratios were obtained by three integrations and are within ±5%. Temperatures at which spectra were recorded are within ±2°. All $^1H$ NMR spectra were determined on 0·5 M solutions. Samples containing basic alumina were prepared in the following ways (a) basic alumina (10 mg) or (b) a mixture of neutral alumina (10 mg) and finely ground KOH (10 mg), was added to the sample. Spectra obtained at temperatures above the b.p. of the solvent employed were determined in tubes sealed at liquid nitrogen temperatures at a pressure of $< 10^{-3}$ mm. Spectra were obtained under acidic conditions by adding $CCl_4$ (0·05 ml) which had been saturated with conc $H_2SO_4$, to each sample. All solvents used in NMR spectroscopy were purified by standard methods, except $CDCl_3$ and $CD_3OD$ which were commercial samples used without further purification.

IR spectra were recorded on a Perkin-Elmer Grating Infracord Spectrophotometer 457. Mass spectra were recorded on an A.E.I. MS 902 mass spectrometer. M.p. s are uncorrected.

*Preparation of ylids* (**3**). 1-Phenyl-1-formylmethyltriphenylphosphonium bromide: Triphenylphosphine (6·55 g, 0·025 mole) in benzene (200 ml) was added to α-bromophenylacetaldehyde[14] (4·98 g, 0·025 mole) in benzene (50 ml) in one portion at 5–10°C. The solution was allowed to reach room temp and stand for 2 hr. The solvent was decanted from the colourless oil, which on washing with EtOAc (200 ml) and ether (200 ml) gave crystals of *1-phenyl-1-formyl-methyltriphenylphosphonium bromide* (6·2 g, 54%), m.p. ($CHCl_3$–EtOAc) 233–237°: $\nu_{max}$ (KBr) 2760, 2550, 1610, 1440 $cm^{-1}$: *m/e* 380 (100), 379 (100), 183 (44): τ ($CDCl_3$) 1·76 (1H, d, $J_{PH}$ = 32 Hz), 2·40 (15 H, m) and 2·90 (5 H, m). (Found: C, 67·4; H, 4·7; Br, 17·1; P, 6·9. $C_{26}H_{22}BrOP$ requires: C, 67·7; H, 4·8; Br, 17·4; P, 6·7%).

*1-Phenyl-1-formylmethylenetriphenylphosphorane* (**3b**). 1-Phenyl-1-formylmethylenetriphenylphosphonium bromide (3·2 g, 0·007 mole) in $CHCl_3$ (50 ml) was shaken with 5N NaOH aq. (50 ml) for 5 min. The $CHCl_3$ layer was washed with water (2 × 50 ml), dried and evaporated to give a white oil. Crystallization from EtOAc gave *1-phenyl-1-formylmethylenetriphenylphosphorane* (**3b**) (0·74, 30%), m.p. 157–158°: $\nu_{max}$ (KBr) 3060, 2740, 1600, 1560, 1490 $cm^{-1}$: *m/e* 380 (100), 379 (90), 183 (35). (Found: C, 82·1; H, 5·5; P, 8.2. $C_{26}H_{21}OP$ requires: C, 82·0; H, 5·5; P, 8·2%).

TABLE 6. PRODUCTS FROM METHYLATION OF YLIDS 3

| Ylid 3 | R | Conditions | Isomer mixture of salt 6 | | | m.p. of a pure isomer | Found % | | | Salt requires % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *cis/trans* | m.p. | $\nu_{max}$ ($cm^{-1}$) | | C | H | I | C | H | I |
| a | H | R.T. 14 h reflux 20 min | 55/45 | 140–144° | 1600 | 141–142° *cis* | 56·4 | 4·6 | 28·5 | 56·5 | 4·5 | 28·5 |
| b | Ph | R.T. 12 h reflux 15 min | 79/21 | 172° | 1600 | 173° *cis* | 61·8 | 5·0 | 24·1 | 62·1 | 4·6 | 24·3 |
| c | 3-$NO_2C_6H_4$ | R.T. 18 h reflux 1 h | 28/72 | 145–146° | 1600 1515 1340 | — | 55·4 | 4·2 | 22·6 | 55·0 | 3·9 | 22·1 |
| d | 4-$NO_2C_6H_4$ | reflux 12 h | 40/60 | 149–152° | 1600 1510 1340 | — | 55·4 | 4·3 | 22·4 | 55·0 | 3·9 | 22·1 |
| e | 3-$ClC_6H_4$ | R.T. 24 h | 60/40 | semicrystalline | 1600 | — | — | — | — | — | — | — |
| f | Me | R.T. 12 h reflux 15 min | 10/90 | 187–190° | 1625 | 186–187° *trans* | 57·6 | 4·9 | 27·4 | 57·4 | 4·8 | 27·4 |

TABLE 7. PRODUCTS FROM ETHYLATION[a] OF YLIDS 3

| Ylid 3 | R | Isomer Mixutre of Salt (6) | | | m.p. of pure isomer | Found % | | | Salt requires % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *cis/trans* | m.p. | $\nu_{max}$ ($cm^{-1}$) | | C | H | I | C | H | I |
| a | H | 55/45 | oil | 1600 | 147–148° *cis* | 57·0 | 5·0 | 28·0 | 57·4 | 4·8 | 27·6 |
| b | Ph | 76/24 | 179–181° | 1600 | 188–189° *cis* | 63·1 | 5·3 | 23·9 | 62·7 | 4·9 | 23·7 |
| c | 3-$NO_2C_6H_4$ | 100/0 | 174–175° | 1600<br>1510<br>1340 | 174–175° *cis* | 57·9 | 4·3 | 21·6 | 57·8 | 4·3 | 21·9 |
| d | 4-$NO_2C_6H_4$ | 100/0 | 183–184° | 1595<br>1510<br>1340 | 183–184° *cis* | 57·5 | 4·5 | 22·3 | 57·8 | 4·3 | 21·9 |
| f | Me | 100/0 | 213–215° | 1625 | 213–215° *cis* | 58·6 | 5·3 | 26·4 | 58·2 | 5·1 | 26·8 |

[a] The mixture in each case was allowed to stand at room temp for 24 hr and then refluxed for 20 min.

Ylids **3b**, **c**, **d**, **e** were prepared by the reaction of triphenylphosphine with the corresponding β-nitrostyrene in MeOH.[15] Formylmethylenetriphenylphosphorane (**3a**) was prepared by the method of Saikachi *et al.*[12] Mass spectral data indicates that the intermediate formylmethyltriphenylphosphonium salt obtained in this experiment is a mixture of iodide and bromide rather than the pure bromide originally claimed, but treatment with NaOH aq as reported[12] gave ylid **3a** m.p. 186–188° (lit. m.p. 186–187°): $\nu_{max}$ (KBr) 2760, 1570 $cm^{-1}$; *m/e* 304 (55), 303 (100), 275 (39), 183 (55). (Found: C, 73·8; H, 5·8. $C_{20}H_{17}OP$ requires: C, 78·9; H, 5·6%).

Pure *formylmethyltriphenylphonium bromide* was prepared by treating formyl methylenetriphenylphosphorane (**3a**) (1·52 g; 0·005 mole) in $CHCl_3$ (30 ml) with excess anhydrous HBr. The resulting solution was evaporated under reduced pressure to give an oil. Trituration with EtOAc and ether gave the phosphonium bromide (1·0 g; 52%), m.p. 191–192° ($CHCl_3$–EtOAc) (lit.[12] m.p. 146°): $\nu_{max}$ (KBr) 2780, 2600, 2520, 1625 $cm^{-1}$; *m/e* 304 (8), 278 (55), 277 (100). (Found: C, 62·2; H, 4·8; Br, 20·9. $C_{20}H_{18}BrOP$ requires: C, 62·3; H, 4·7; Br, 20·8%).

α-*Formylethylidenetriphenylphosphorane* (**3f**) was prepared by the method of Trippett and Walker[13] except that the intermediate α-*formylethyltriphenylphosphonium bromide* was isolated, m.p. 218–224°. Treatment of this salt with 1N NaOH in iced water and stirring for 30 min gave the ylid (**3f**), m.p. 217–218° (lit.[13] 220–222°).

*The reaction of formyl ylids* (**3**) *with methyl and ethyl iodide.* The ylid (0·001 mole) in EtOAc (15–30 ml) was treated with methyl or ethyl iodide (2 ml). The conditions for reaction of each ylid are given in Table 6. The solvent was removed and the residue washed with hot EtOAc (5 ml) and ether (20 ml) to give crystalline salts. The yields in all cases were virtually quantitative. Isomer ratios were determined by NMR directly from the crude salt after removal of solvent to avoid changes in isomer ratio on crystallization. In some cases a pure isomer could be obtained by recrystallization from $CHCl_3$–EtOAc. The characteristics of all these salts are given in Table 6.

*Reactions of ylid* (**3f**) *with solvents.* (a) *Commercial methylene chloride.* Ylid **3f** (1·59 g, 0·005 mole) was refluxed in commercial $CH_2Cl_2$ (30 ml, once distilled) for 3 hr. Solvent was removed and the resulting white oil triturated with EtOAc until it solidified. Recrystallization from $CHCl_3$–EtOAc gave crystalline α-formylethyltriphenylphosphonium chloride (**8**) (1·15 g, 65%), m.p. and m.m.p. 227–230° (lit.,[13] m.p. 231–233°).

(b) *Methylene bromide.* Ylid **3f** (0·795 g, 0·0025 mole) was heated in dry, $Na_2CO_3$ washed $CH_2Br_2$ (30 ml) for 2 hr at reflux. The solvent was removed at the pump to leave an oil which gave a sticky oily solid on washing with EtOAc or on attempted recrystallization. This oil showed $\nu_{max}$ in the IR spectrum (KBr disc) at 3000–2800, 1630, 1430 $cm^{-1}$ and its mass spectrum showed a similar fragmentation pattern to ylid **3f** with the highest *m/e* value at 318. NMR τ ($CH_2Br_2$) 2·04–2·50 (30 H, m), 2·80 (2H, broad d, $J_{PH}$ = 11 Hz), 3·9 (2H, s), 8·06 (6H, dd, $J_{PH}$ = 13 Hz, $J_{HH}$ = 1 Hz).

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