*Tetrahedron* Vol. 31, pp. 885 to 890. Pergamon Press 1975. Printed in Great Britain

# ORGANOPHOSPHORUS CHEMISTRY—V

## THERMAL TRANSFORMATION OF THE CYCLOHEXYLAMMONIUM SALT OF O-ARYL N-CYCLOHEXYL PHOSPHORAMIDIC ACIDS INTO SYM-PYROPHOSPHATES

M. A. RUVEDA,* E. N. ZERBA, R. PODESTA and S. A. de LICASTRO
Lab. Química Orgánica Especial, CITEFA, Zufriategui y Varela, Villa Martelli, Buenos Aires, Republica Argentina

(*Received in the UK* 23 *October* 1974; *Accepted for publication* 12 *November* 1974)

**Abstract**—The formation of pyrophosphates from phosphorus monoamidates was studied by TGA associated with chromatographic techniques upto 320°. Above this temperature the salts decomposed completely. Other compounds were also formed: diamidophosphoric acid aryl esters, pyrophosphorus amidic acids, cyclohexylamine, phenols and a number of minor thermoproducts. The influence of substituents attached to the aromatic ring on the over-all rate of decomposition reaction showed the order: t-Bu > Me > H > Cl. Anomalous results were found for $NO_2$. Second order rate constants were measured. A mechanism in two steps is suggested for the reaction investigated. Initial formation of free phosphoramidic acid as proposed by Clark appears to be unnecessary. Pyrolysis stequiometric equation was proposed.

### INTRODUCTION

In the course of our experiments on the phosphorylation reaction from phenyl phosphorodichloridate and dimethylsulphoxide (DMSO),[1-3] it was observed that carrying out the reaction at low temp in a diluted anhydrous medium a crystalline solid was separated when cyclohexylamine was added, and was identified as the cyclohexylammonium salt of O-phenyl N-cyclohexyl phosphoramidic acid. On heating this compound, it shows a definite m.p. of 194°, becoming translucent; on further heating it resolidifies at 225–30° and melts again at 258–60°, that is characteristic for the dicyclohexylammonium $P^1P^2$-diphenyl pyrophosphate, confirmed by m.m.p., elemental analysis, TLC and IR spectra. Analogous observations were made with other salts of O-*p*-substituted phenyl N-cyclohexyl phosphoramidic acids.

Though it is well known and documented that phosphoramidic acids and their N-substituted derivatives and monoesters are useful phosphorylating agents to prepare both symmetrical and unsymmetrical esters of pyrophosphoric acids by heating them in anhydrous solutions,[3-7] no reports were found on the thermal phosphorylation of the more available salt of phosphoramidic acids **1**[4] in the absence of solvents. Therefore, behaviour during the heating of the salts of some O-*p*-substituted phenyl N-cyclohexyl phosphoramidic acids and the results and suggestions concerning the reaction mechanism reported in this work, revealed the importance of the transformation detected.

### RESULTS AND DISCUSSION

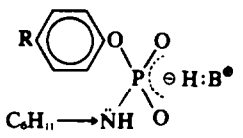
Although the phosphoramidic monoesters are usually prepared from the diesters by selective removal of one esterifying group by hydrolysis in an alkaline medium,[4,5,8] we have found that the procedure described in a previous paper[4] is simpler, with discrete yields.

We have carried out a thermogravimetric analysis (TGA), and thermograms upto about 320° are shown in Figs. 1 and 2.

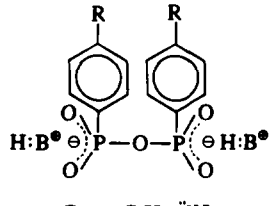
Fixed P-thermo products formed from **1** by heating in the presence of air were TLC analyzed, while volatile thermo products were GLC analyzed in parallel experiments.

The portion of the TGA curve that showed the most interesting transformation (phosphorus monoamides → phosphorus anhydrides) is the one between room temp and the first inflection point (1A) and (1B) in Fig. 1 and 2 respectively. At higher temp the formation of phenol and phosphoric acids increases rapidly.

Serial TLC analysis of the thermolysis products arising at the temperatures indicated, over the portion OA and OB of the curve (Table 1), showed that the major P-containing thermoproducts were unaffected **1**, **2**, diamidophosphoric acid aryl ester **7** (all identified by $R_f$ comparison with authentic specimens) and pyrophosphorus amidic acids **5** (TLC identified by the characteristic transient violet colour of the P–O–P bond,[4,9] when



**1a**: R = H
**1b**: = Me
**1c**: = t-Bu
**1d**: R = Cl
**1e**: = $NO_2$



B: = $C_6H_{11}\ddot{N}H_2$

**2a**: R = H
**2b**: = Me
**2c**: = t-Bu
**2d**: R = Cl
**2e**: = $NO_2$

*Cátedra de Química Orgánica, Fac. Ingeniería, UNBA, Paseo Colón 850, Buenos Aires, Argentina.

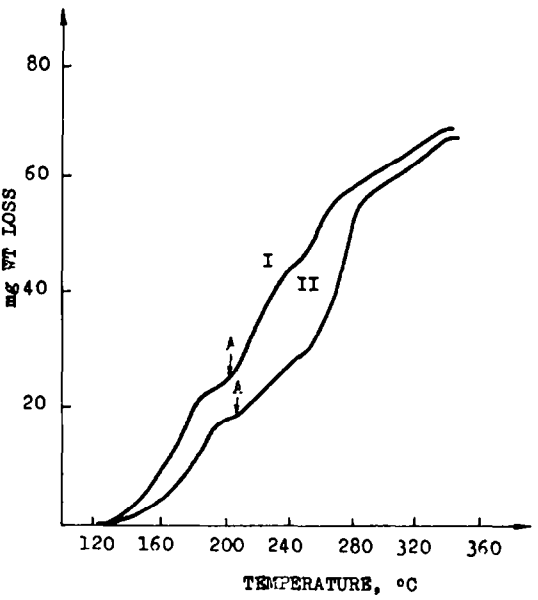



Fig. 1. Thermogram of 1 (I R = Cl; II R = $NO_2$).

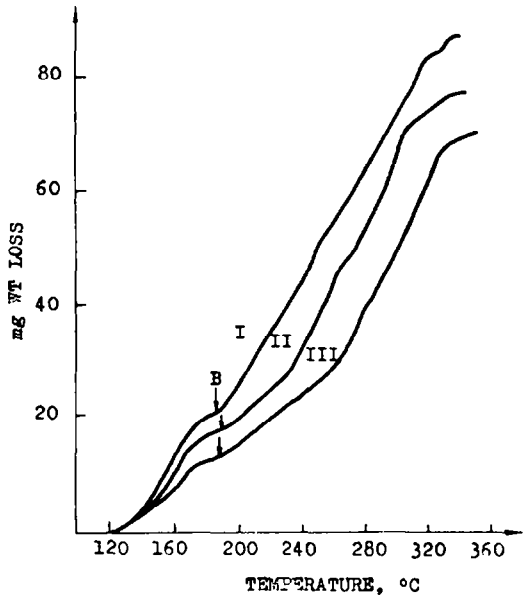



Fig. 2. Thermogram of 1 (I R = H; II R = Me; III R = t-Bu).

Table 1. Pyrolysis of cyclohexylammonium salt of O-aryl N-cyclohexyl phosphoramidic acids

| COMP. | TEMP. (5°/min. heating rate) upto °C | THERMOPRODUCTS; ANALYSIS BY GENERAL TLC. (Rf spot colour). |
|---|---|---|
| 1a | 140 | 1a(0.61 B); 2a(0.26 TV); 5a(0.78 TV). |
| | 160 | 1a; 2a; 5a; 7a(0.96 B); $U_1$(0.71*). |
| | 170 | 1a; 2a; 5a; 7a. |
| | 180 | 1a; 2a; 5a; 7a; 8a(0.00 B). |
| | 200 | 2a; 5a; 7a; 8a. |
| | 230 | 2a; 8a. |
| 1b | 140 | 1b(0.68 B); 2b(0.34 TV); 5b(0.81 TV). |
| | 160 | 1b; 2b; 5b; 7b(0.96 B); $U_2$(0.41 TV). |
| | 180 | 1b; 2b; 5b; 7b; $U_2$. |
| | 190 | 1b; 2b; 5b; 7b; $U_2$. |
| | 210 | 1b; 2b; 5b; 7b; 8b(0.04 B); $U_2$; $U_3$(0.00 B). |
| | 230 | 2b; 8b; $U_2$; $U_3$. |
| 1c | 140 | 1c(0.76 B); 2c(0.37 TV); 5c(0.88 TV). |
| | 150 | 1c; 2c; 5c; 7c(1.00 B). |
| | 160 | 1c; 2c; 5c; 7c; 8c(0.05 B); $U_4$(0.59 TV); $U_5$(0.50 TV); $U_6$(0.18*). |
| | 180 | 1c; 2c; 5c; 7c; 8c; $U_4$; $U_5$; $U_6$; $U_7$(0.00 B). |
| | 200 | 1c; 2c; 5c; 7c; 8c; $U_4$; $U_5$; $U_7$. |
| | 220 | 2c; 7c; 8c; $U_7$. |
| 1d | 140 | 1d(0.69 B); 2d(0.34 TV); 5d(0.86 TV). |
| | 150 | 1d; 2d; 5d. |
| | 160 | 1d; 2d; 5d; 7d(0.97 B). |
| | 180 | 1d; 2d; 5d; 7d; $U_8$(0.80*); $U_9$(0.74*). |
| | 200 | 1d; 2d; 5d; 7d; 8d(0.04 B); $U_8$; $U_{10}$(0.47 TV); $U_{11}$(0.18*); $U_{12}$(0.00 B). |
| | 220 | 2d; 8d; $U_{12}$. |
| 1e | 130 | 1e(0.70 B). |
| | 150 | 1e; 2e(0.50 TV) |
| | 170 | 1e; 2e; 8e(0.05 B); $U_{13}$(0.00 B). |
| | 180 | 1e; 2e; 5e(0.87 TV); 7e(0.00 B); 8e. |
| | 210 | 1e; 2e; 5e; 7e; 8e; $U_{13}$. |
| | 240 | 2e; 5e; 8e; $U_{13}$. |

References: B = Blue. TV = Transient Violet. * = traces.

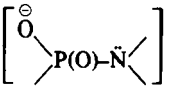
$U_{1-12}$: unidentified minor P-compounds.

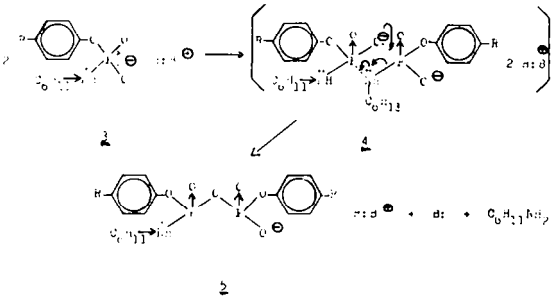
$U_{3,7,12,13}$: appear to be phosphoric acid.

developed with the Dittmer and Lester reagent[10] and by TLC of its hydrolysis products). Rupture of P–N and P–O–P bonds[11] occurs from **5** by spontaneous hydrolysis, giving **1**, **2** and phosphoric acid monoaryl esters. The major P-free fragments were cyclohexylamine and *p*-substituted phenols identified by comparison of the GLC retention times with pure samples. A number of minor P-thermolysis products were detected and one was characterized as phosphoric acid monoaryl ester **8**, while others were unidentified.

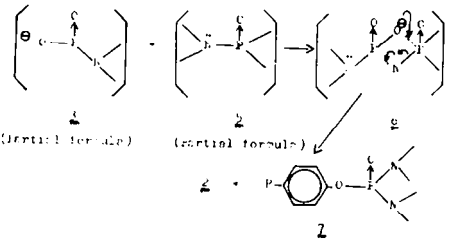
Experiments carried out with samples of **1** previously dried *in vacuo* over $P_2O_5$ at room temp. (24 hr) and then pyrolyzed in a stream of $N_2$ (99·99% pure, dried over molecular sieve 5A, 1·0–0·3 mm) gave the same results as those carried out in the presence of air.

At the lowest temp studied, formation of **2**,**5**,cyclohexylamine and traces of phenol takes place. The latter probably by R–$C_6H_4O$∓P rupture. The appearance of **7** was not simultaneous with **2** and **5** presumably because of the detection limit of the visualization reaction. The latter was detected at the next highest temp considered. Serial TLC analysis showed that spot areas corresponding to **5** decrease, while those corresponding to **2** and **7** increase as the reaction progresses. It is reasonable to suppose that **2** is formed at the expense of **5**, with formation of **7**.

In this paper, we have demonstrated that the phosphorylation reaction proceeds from **1**, in the absence of solvents and of water, by heating, to pyrophosphates **2**. Our data on thermolysis products (portion OA and OB of the curve), are best accomodated in terms of a two step mechanism represented by Schemes 1 and 2. The first appears to involve two molecules of **1**. As an ambident nucleophile fragment  with its softer



Scheme 1



Scheme 2

nucleophilic centre located at the N atom and the harder centre at the O atom, it can attack *vis-à-vis* the electrophilic P atom to give transient **4** that is intermolecularly rearranged into the detected intermediate, the pyrophosphoramidic acid **5**[8,12] and cyclohexylamine.

Clark *et al.*[12] proposed and later accepted[8,13,14] that for the reaction in an acid medium, one molecule of **1** in its acid form attacks a second one in the zwitterionic form, following a second order kinetic reaction.[8] In our case, the initial formation of free O-aryl N-cyclohexyl phosphoramidic acid by deamination of **1** appears to be unnecessary. It was demonstrated by obtaining a fixed salt such as PhO–P(O)$NHC_6H_{11}O^-Li^+$ from PhO–P(O)(OMe)$NHC_6H_{11}$ by demethylation with LiCl.[15] The subsequent transformation of the lithium salt into pyrophosphate by heating was demonstrated by TLC.

The experimental evidence for the second step (Scheme 2), despite the suggestions of all other authors[12,14] (who require the presence of water), prompted us to assume the formation of **2** as an interaction of **3** with **5** in a concerted process, as postulated for Scheme 1, to yield **6**, which subsequently undergoes fragmentation into the experimentally observed products **2** and **7**.

Electron withdrawing substituents attached to the aromatic ring in **1**, **3** and **5** should disperse the negative charge, and stabilize the anion, thus increasing the overall rate of formation of **2**. The rate of loss of weight with the temp (Scheme 1) suggested stability of **1** in the order:

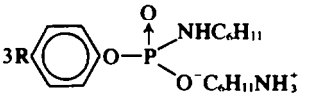
$$R = -t\text{-}Bu > -Me > -NO_2 > H > Cl.$$

This sequence corresponds to the order of mesomeric and inductive effects present in the substituents attached to the aromatic ring in **1**, except for $NO_2$, that is anomalous.

The reaction for Scheme 2 occurs without loss of weight. **7** were subjected to TGA; samples exhibited a small loss of weight, max 0·7% of the original weight from 20 to 220°.

The average reaction order n derived from TGA by the Freeman and Carroll method[16] is nearly equal to two, so the pyrolysis reaction (Scheme 1) is considered to be of the second order according to the mechanism proposed.

Schemes 1 and 2 may be summarized in Eqn (1). Stequiometric validity was determined by isothermal thermolysis of **1**. Yields of **2** are between 78 and 98%, and cyclohexylamine ranging from 85–95% was found.



$$\longrightarrow \quad 2 + 7 + 2C_6H_{11}NH_2 \qquad (1)$$

## EXPERIMENTAL

M.ps were determined with a Buchi apparatus and are uncorrected. PMR spectra were recorded on a Varian T-60 spectrometer using TMS as an internal standard.

IR spectra were measured with a Perkin-Elmer 337 spectrometer.

Authentic phosphorus monoamidates **1** were prepared as previously.[4] Pyrophosphates **2** were prepared according to the lit. 1 (m.p., elemental analysis, $R_f$ and IR are given in Table 2 for different R). O-aryl phosphates **8** were prepared from R–$C_6H_4O$–$P(O)Cl_2$ (0·1 mole) in excess of water, at reflux temp until one phase was obtained. It was extracted twice with ether, dried with $Na_2SO_4$ and the salt ppt with cyclohexylamine in ether soln (10%), one spot by TLC (m.p., elemental analysis and $R_f$ are given in Table 3). Phosphorus diamidates **7** were prepared according to the lit. 17 from R–$C_6H_4O$–$P(O)Cl_2$ (0·1 mole) and cyclohexylamine (0·44 mole) in anhyd ether (20 ml) added slowly with stirring. The cyclohexylamine hydrochloride was filtered and solv evaporated *in vacuo*; the solid recryst. from EtOH–$H_2O$ (60–40%) soln (m.p., elemental analysis, PMR and $R_f$ are given in Table 4), one spot by TLC.

*TGA curves* (Figs. 1 and 2) were made using a Netzsch thermobalance (Gerätebau GmbH, Selb/Bay.) heating rate: 5°/min in air. Samples of **1** were dried over $P_2O_5$ *in vacuo* during 24 hr at room temp.

*Thermal behavior* vs *thermoproducts.* Thermal behaviour tests were carried out in a Varian automatically programmed furnace. In independent experiments, two samples, each of 5 mg of **1** were heated: one in a sealed pyrex tube and the other in an open one, at the temp. indicated in Table 4. Automatic 5°/min programming was used in heating. When temp. was reached, rapid cooling at room temp. was permitted, then the thermolysis mixtures were dissolved in 0·7 ml $NH_4OH$ (open tubes) and TLC analyzed and extracted with 0·5 ml ether (sealed tubes) and GLC analyzed. Authentic specimens for $R_f$ and GLC retention times were used.

*TLC analysis*

*General chromatogram.* TLC was carried out on standard glass plates covered with 0·25 mm Silica Gel G (E. Merck, Germany), solvent system: t-BuOH : $Me_2CO$ : $NH_4OH$ : $H_2O$ (4:5:1:1); spots developed with Dittmer & Lester reagent[10] (D&LR). Samples were analyzed as *ca* 5% solns in EtOH–$NH_4OH$ (9:1). $R_f$ are listed in Table 4. Phosphoramides **7** run with the solvent front and were confirmed by bidimensional TLC analysis with the corresponding solvent system.

*Special TLC detection of phosphoramides* **7**. Standard glass plates with Silica Gel G (E. Merck, Germany) 0·25 mm. Solvent system: n-hexane–$Me_2CO$ (6:4). Samples were analyzed as *ca* 5% solns in EtOH or ether, $R_f$ values given in Table 3; spots developed with D&LR.

Table 2. Synthesis of pyrophosphates **2**

| R | m.p. | Elemental Analysis Calculated | | | Found | | | Rf | IR $cm^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | °C | %C | %H | %N | %C | %H | %N | | P–O–P | P–O–Ph | P=O |
| p-$NO_2$ | 246-7° | 46.6 | 5.86 | 9.08 | 46.3 | 5.82 | 8.87 | 0.50 | 985 VS<br>745 VS | 900 VS | 1250 VS |
| p-Cl | 280-1° | 48.2 | 6.03 | 4.80 | 50.1 | 6.52 | 5.15 | 0.34 | 982 VS<br>760 S | 905 VS | 1249 VS |
| p-Me | 272-4 | 56.0 | 7.55 | 5.03 | 56.1 | 7.98 | 5.50 | 0.34 | 980 S<br>730 W | 905 VS | 1245 VS |
| p-t-Bu | 196-7 | not able to purify by recryst. | | | | | | | 980 VS<br>745 M | 900 S | 1255 S |
| p-H | 258-60 | according to lit 1. | | | | | | | 980 VS<br>735 S | 900 VS | 1245 VS |

Table 3. Synthesis of O-aryl phosphates **8**

| R | m.p. | Elemental Analysis Calculated | | | Found | | | Rf. |
|---|---|---|---|---|---|---|---|---|
| | °C | %C | %H | %N | %C | %H | %N | |
| p-$NO_2$ | ------- | not able to purify by recryst. | | | | | | 0.49 |
| p-t-Bu | 215-6 | 61.6 | 9.59 | 6.54 | 61.80 | 9.95 | 6.45 | 0.75 |
| p-Me | 210-2* | 59.0 | 9.07 | 7.25 | 58.2 | 9.24 | 7.60 | 0.50 |
| p-Cl | 225-6** | 53.2 | 7.87 | 6.89 | 55.0 | 7.95 | 7.09 | 0.60 |
| p-H | 99.5*** | according to bibliographic data | | | | | | 0.36 |

* : $H_2O$–$Me_2CO$.
** : $H_2O$.
***: $Cl_3CH$–ether.

Table 4. Synthesis of phosphorus diamidates 7

| R | m.p. °C | Elemental Analysis Calculated %C | %H | %N | Found %C | %H | %N | Rf | PMR Ph(s) | NH(b) | $CH_2$ | $CH_3$(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| p-$NO_2$ | 145–6 | 56.6 | 7.35 | 11.0 | 55.98 | 7.58 | 10.7 | 0.62 | 7.4d 8.2d | 2.7–3.4 | 3.7* | --- |
| p-Me | 114–5 | 65.0 | 8.86 | 8.00 | 64.57 | 8.95 | 8.16 | 0.70 | 7.1 | 2.7–3.3 | 3.5* | 2.3 |
| p-Cl | 110–1 | 58.3 | 7.57 | 7.57 | 58.6 | 7.25 | 7.63 | 0.68 | 7.2 | 2.7–3.2 | 3.6* | --- |
| p-t-Bu | 101–2 | 67.3 | 9.44 | 7.14 | 66.7 | 10.1 | 7.27 | 0.73 | 7.2 | 2.9–3.2 | 3.4* | 1.3 |
| p-H | 127** | according to bibliographical data | | | | | | 0.72 | 7.2 | 2.7–3.2 | 3.5* | --- |

* : All PMR spectra show a multiplet over 0.8–2.2 corresponding to cyclohexylamine protons.

**: Recryst. from EtOH-$H_2O$ 6:4

*Special detection of* O-*aryl phosphates* **8**. It was carried out on precoated glass plates, cellulose (E. Merck, Germany) 0·1 mm thick. Solvent system: n-PrOH:$NH_4OH$:$H_2O$ (6:3:1). Samples were analyzed as *ca* 5% solns in EtOH or $H_2O$; $R_f$ values given in Table 2; spots developed with D&LR.

*GLC analysis.* GLC analysis of the ether extracts were carried out in an Aerograph 1522 B (pyrex column, 10 ft × ⅛" o.d., packed with 20% SF96 on 100/120 mesh Varaport. Carrier gas: $N_2$; flow rate: 25 ml/min; temp. flame detector 200°; on column injection; column temp. for R–$C_6H_4OH$ (R given): *p*-H: 100°; *p*-Me and *p*-Cl: 145°; *p*-t-Bu and *p*-$NO_2$: 185°. Column temp. for cyclohexylamine: 100°).

*Isothermal transformation of* **1** *into* **2**. Isothermal thermolysis of **1** was carried out in a thermostatized furnace (National Instruments Lab. Inc., Rockville, Md., U.S.A.). Pyrolysis was performed in a pyrex tube, 270 mm × 3 mm i.d., packed with 80–100 mg of powdered **1** between plugs of silanized glass wool and centred. Pure dry $N_2$ at 2 ml/min flowed through, heated from room temp. to 140°, and maintained during 24 hr (20 hr for R = *p*-t-Bu). This gaseous stream was allowed to bubble in 0·1N $H_2SO_4$ soln. The fixed cyclohexylamine was calculated by titration of the excess of acid with 0·1N NaOH, using bromophenol blue as an indicator and referred to Eqn (1) to determine the percentage of recovery. The recovery control reaction with pure amine was satisfactory. The residues were allowed to cool at room temp., under dry $N_2$. Crude products were washed with ether and dissolved in hot $NH_4OH$. The alkaline solutions were filtered, evaporated and dried *in vacuo* (50°). Subsequent drying was one *in vacuo* over $P_2O_5$ at room temp. (24 hr). The free flowing solids were weighed and the yields calculated on the basis of Eqn (1). TLC analysis showed that the products were nearly pure **2** with traces of **1** only.

*Separation and characterization of* **5**. Programmed thermolysis of each of **1a–d** (25 mg) upto 180° (5°/min heating rate) were carried out as described. Residues were dissolved in $NH_4OH$ and treated by preparative TLC (general chromatogram cond. 0·5 mm layers). The materials containing **5a–d** were extracted with water (0·5 ml) and centrifuged. The solns were heated in a water bath (4 hr) and TLC analyzed under conditions identical as before. **2a–d** were identified as the main product; **1** and **8a–d** as minor products.

*Preparation of* PhO–P(O)(OMe)$NHC_6H_{11}$. This product was obtained from PhO–$P(O)Cl_2$ (6·33 g, 0·03 mole/6 ml ether) to which a soln of MeOH (1·056 g, 0·03 mole + 10% excess) and pyridine (2·37 g, 0·03 mole/6 ml ether) was added with stirring during 5–10 min, whilst held in an ice bath. The ppt was filtered and the soln was added with stirring to a soln of cyclohexylamine (6·534 g, 0·06 mole + 10% excess/7·5 ml ether). The soln was cooled in an ice bath during 1/2 hr, the cyclohexylamine hydrochloride filtered and the soln washed with $H_2SO_4$ 5% (2 × 10 ml), $NaHCO_3$ 5% (3 × 10 ml), and finally $H_2O$ (3 × 10 ml), and was dried with $Na_2SO_4$ and evaporated *in vacuo*. The residue was taken up with hot $Me_2CO$ and cooled. The first portion of ppt was eliminated and the soln cooled in a refrigerator (5°) until the following day. A white cryst. ppt was obtained m.p. 79–81°; PMR ($Cl_3CD$) Ph(s) $\delta$ 7·3 and MeO(d) $\delta$ 3·8 ($J_{P-O-C}$ 11 c/s) (Found: C, 57·76; H, 7·31; N, 5·27; P, 11·48 Calc. for $C_{13}H_{20}NO_3P$: C, 57·9; H, 7·43; N, 5·2; P, 11·5%).

*Thermal transformation of* PhO(OMe)P(O)$NHC_6H_{11}$ *with* LiCl. PhO–P(O)(OMe)$NHC_6H_{11}$ (0·269 g, 0·001 mole) and LiCl (0·424 g, 0·001 mole) each dissolved in a minimum of EtOH were mixed and the soln evaporated *in vacuo*. The oily residue was taken up in a capillary tube and heated; at 145° it solidified (a sample of it was TLC analyzed, only **1a** being detected). On further heating upto 260°, TLC analysis showed **1a** and **2a** (major products) and **5a** and **8a** (general chromatogram conditions).

Programmed thermolysis of the oily residue (10 mg) upto 180° (4°/min heating rate) was carried out as described. The residue was taken up with EtOH:$NH_4OH$ (4:1) and analyzed by TLC (general chromatogram conditions). **2a** was found as main product, besides some **1a**, **5a** **8a** and some unidentified spots.

*Acknowledgements*—We wish to thank Dr. A. O. Rucci and Mr. J. A. Blanco for IR spectra, and Mrs. Casanelo for the elemental analysis (Fac. Farmacia y Bioquímica, UNBA, Buenos Aires, Argentina), and the Consejo Nacional de Investigaciones Científicas y Técnicas (Buenos Aires, Argentina) for financial support.

## REFERENCES

[1]M. A. Rúveda, E. N. Zerba and E. M. de Moutier Aldao, *Tetrahedron* **28**, 5011 (1972).
[2]M. A. Rúveda, E. N. Zerba and E. M. de Moutier Aldao, *Ibid.* **29**, 585 (1973).
[3]M. A. Rúveda, E. N. Zerba and E. M. de Moutier Aldao, *An. Asoc. Quim. Arg.* **61**, 233 (1973).

[4]M. A. Rúveda, S. A. de Licastro, E. N. Zerba and E. M. de Motier Aldao, *Phosphorus*, in press.
[5]D. M. Brown, *Phosphorylation, Advances in Organic Chemistry* Vol. 3, pp. 75. Wiley, New York (1963).
[6]V. M. Clark and D. M. Hutchinson, *Progr. Org. Chem.* **7**, 75 (1968).
[7]F. Cramer, *Preparation of esters, amides and anhydrides of phosphoric acid. Newer methods of Organic Chemistry* Vol. 3, pp. 319. Academic Press, New York, (1964).
[8]N. K. Hamer, *J. Chem. Soc.* 46 (1965).
[9]S. A. de Licastro and M. A. Rúveda, *J. Chromatog.* **92**, 207 (1974).
[10]J. C. Dittmer and R. L. Lester, *J. Lipid. Res.* **5**, 126 (1964).
[11]E. Boger and O. M. Friedman, *J. Am. Chem. Soc.* **80**, 2583 (1958).
[12]V. M. Clark, G. W. Kirby and A. Todd, *J. Chem. Soc.* 1497 (1957).
[13]V. M. Clark, D. W. Hutchinson, G. W. Kirby and A. Todd, *Ibid.* 715 (1961).
[14]A. R. Todd, *Proc. Chem. Soc.* 199 (1962).
[15]V. M. Clark and A. R. Todd, *J. Chem. Soc.* 2030 (1950).
[16]E. S. Freedman and B. Carroll, *J. Phys. Chem.* **62**, 394 (1958).
[17]G. M. Kosolapoff, *Organophosphorus Compounds* pp. 278. Wiley, New York (1950).
[18]E. C. Corbridge, *The Infrared Spectra of Phosphorus Compounds, Topics in Phosphorus Chemistry* Vol. 6, pp. 235. Wiley, New York (1969).