furan was added dropwise over 45 min. to a slurry of 7.6 g. (0.2 mole) of lithium aluminum hydride in 70 ml. of tetrahydrofuran. After being stirred and refluxed for 3.5 hr., the reaction mixture was cooled in an ice bath and treated with 10.8 ml. of water. The resulting slurry was filtered and the filter cake extracted with two 150-ml. portions of ethanol. The combined filtrate and extracts were concentrated and the residue distilled under reduced pressure to yield 8.8 g. (70%) of colorless product, b.p. 101–103.5° (19 mm.), n_D^{25} 1.4691.

2-(1-Methyl-2-pyrrolidinyl)ethyl benzilate. A mixture of methyl benzilate (12.1 g., 0.05 mole), 1-methyl-2-pyrrolidineethanol (I) (6.5 g., 0.05 mole), a small piece of freshly-cut sodium about the size of a pea, and 100 ml. of *n*-heptane was refluxed for 3 hr. in a flask attached to a Dean and Stark apparatus. During the refluxing, 2.55 ml. of methanol separated. The reaction mixture was filtered to remove gelatinous impurities. The filtrate was washed with 50 ml. of water, dried over anhydrous magnesium sulfate, decolorized with activated carbon, and concentrated to give 8.5 g. (72%) of the product, m.p. 78.5–80°.

Anal. Calcd. for $C_{21}H_{25}NO_3$: C, 74.30; H, 7.42; N, 4.13. Found: C, 74.19; H, 7.20; N, 3.97.

2-(2-Chloroethyl)-1-methylpyrrolidine. A solution of 20 g. (0.168 mole) of thionyl chloride in 25 ml. of chloroform was added over 15–20 min. to a stirred solution of 8.0 g. (0.062 mole) of 1-methyl-2-pyrrolidineethanol in 50 ml. of chloroform. The reaction mixture was refluxed for 2 hr. and then concentrated. Ethanol was added and removed by distillation and the residue dissolved in 40 ml. of water. The aqueous solution was made strongly alkaline with 56% potassium hydroxide and the liberated oil extracted into isopropyl ether. Fractional distillation of the ethereal extract yielded 5.3 g. (57.5%) of a colorless, but cloudy, oil, b.p. 72° (18 mm.), n_D^{25} 1.4631. The same chloride has recently been prepared by Bourquin, *et al.*[15]

10-[2-(1-Methyl-2-pyrrolidinyl)ethyl]phenothiazine. A mixture of phenothiazine (6.8 g., 0.034 mole), sodium amide (1.7 g., 0.042 mole), 2-(2-chloroethyl)-1-methyl-pyrrolidine (5.0 g., 0.034 mole), and 75 ml. of dry toluene was refluxed for 8 hr. The mixture was carefully treated with 50 ml. of water and the toluene layer separated after thorough mixing. The organic phase was washed with water and then extracted with 50 ml. of 3*N* hydrochloric acid in three portions. The combined acid extracts were made strongly basic with 56% potassium hydroxide to liberate the base. The oily product was extracted with ether and the ether solution dried over anhydrous magnesium sulfate. Fractional distillation gave 5.9 g. (56%) of a pale yellow viscous oil as the product, b.p. 168–175° (0.15 mm.).

Anal. Calcd. for $C_{19}H_{22}N_2S$: C, 73.50; H, 7.14; S, 10.33. Found: C, 73.66; H, 6.83; S, 10.36.

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[15] J. P. Bourquin, G. Schwarb, G. Gamboni, R. Fischer, L. Ruesch, S. Guldiman, V. Theus, E. Schenker, and J. Renz, *Helv. Chim. Acta*, 41, 1079 (1958).

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Reactions of Amines. VIII. Pyrolysis of Diphenyl *N*-Alkylphosphoramidates[1,2]

HENRY E. BAUMGARTEN AND ROBERT E. ALLEN

Received July 5, 1960

The preparation of four diphenyl *N*-alkylphosphoramidates is described. The pyrolysis of these materials at 350–450° gave high yields of olefin, but the olefins showed evidence of considerable isomerization.

In an earlier paper[3] in this series it was shown that the pyrolysis at 350–400° of dimethyl *N*-alkylphosphoramidates gave in most instances mixtures of olefin and the tertiary amine formed by dimethylation of the alkylamine. Furthermore, the olefin was found to be extensively isomerized during the process. It was suggested that reactions involving the methoxy groups of the phosphoramidate were responsible in large part for both the formation of isomerized olefin and tertiary amine. This communication reports experiments designed to eliminate one or more of these side reactions by replacement of the methoxy by phenoxy groups.

In this work the diphenyl *N*-alkylphosphoramidates were prepared by the reaction of diphenyl phosphite with the appropriate amine in carbon tetrachloride. Other polyhalogen compounds (*e.g.*, bromotrichloromethane) could be used but appeared to have no advantage over carbon tetrachloride. The compounds prepared by this procedure and their infrared spectra are listed in Tables I and II.

$$(C_6H_5O)_2P(O)H + 2\ RNH_2 + CCl_4 \longrightarrow (C_6H_5O)_2P(O)NHR + CHCl_3 + RNH_3Cl$$

The disadvantage of having to use two moles of the amine to one of the secondary phosphite was not compensated for in the present examples by the use of a tertiary amine (*e.g.*, triethylamine) to form the amine hydrochloride, as the separation procedure became more complicated.

A second method employed for the preparation of diphenyl *N*-cyclohexylphosphoramidate involved the reaction of diphenyl phosphorochloridate with cyclohexylamine in carbon tetrachloride solution.

$$(C_6H_5O)_2P(O)Cl + 2\ C_6H_{11}NH_2 \longrightarrow (C_6H_5O)_2P(O)NHC_6H_{11} + C_6H_{11}NH_3Cl$$

The reaction proceeded smoothly, but since comparable yields were obtained with the less

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[1] Paper VII. *J. Am. Chem. Soc.*, 83, 399 (1961).

[2] This work was supported in part by grant G-3689 of the National Science Foundation.

[3] H. E. Baumgarten and R. A. Setterquist, *J. Am. Chem. Soc.*, 81, 2132 (1959).

TABLE I

DIPHENYL *N*-ALKYLPHOSPHORAMIDATES

$(C_6H_5O)_2P(O)NHR$

R	Method[a]	Yield, %	M.P.[b]	Composition	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Cyclohexyl	A	79	102.5 (S)	$C_{18}H_{22}NO_3P$	65.30	65.44	6.64	7.02	4.23	4.46
Cyclohexyl	B	73	102.5 (S)							
n-Hexyl	A	78	48 (P)[c]	$C_{18}H_{24}NO_3P$	64.82	64.74	7.23	7.13	4.21	4.22
2-Ethylhexyl	A	82	68.5 (P)	$C_{20}H_{28}NO_3P$	66.51	66.50	7.77	7.83	3.89	4.08
n-Decyl	A	71	52 (P)[c]	$C_{22}H_{32}NO_3P$	67.90	67.97	8.23	8.32	3.61	3.64

[a] See Experimental. [b] Letter in parentheses indicates crystallization solvent: S = Skellysolve B, P = *n*-pentane. [c] Crystallization required two to three days at 5°.

TABLE II

INFRARED SPECTRA[a]

Phosphoramidate	Frequency,[b] Cm.$^{-1}$ P→O Stretch	(P)—O—C Stretch	P—O—(C) Stretch	N—H Stretch[c]	950 Cm.$^{-1}$ Region[d]	Aromatic Stretching
Diphenyl *N*-cyclohexyl	1256 (m)	1168 (s)	1197 (s)	3420 (m) (3220) (w)	933 (s)	1593 (s), 1494 (s)
Diphenyl N-(2-ethylhexyl)	1253 (m)	1170 (s)	1192 (s)	3420 (m) (3270) (w)	938 (s)	1589 (s), 1490 (s)
Diphenyl *N*-hexyl	1250 (m)	1168 (s)	1192 (s)	3435 (m) (3275) (w)	940 (s)	1593 (s), 1492 (s)
Diphenyl *N*-decyl	1250 (m)	1175 (s)	1192 (s)	3440 (m) (3278) (w)	943 (s)	1593 (s), 1493 (s)

[a] Determined with a Model 21, Perkin-Elmer Spectrophotometer having sodium chloride optics. Data are reported for spectra run in potassium bromide pellets. [b] L. J. Bellamy (*The Infrared Spectra of Complex Molecules*, Methuen and Co., London, 1958, 2nd Ed.) quotes for the P → O stretching vibration, 1350–1250 cm.$^{-1}$, for one P—O—Ar stretching vibration, 1150–1170 cm.$^{-1}$, and for the P—O—C (aromatic) stretching vibration, 1190–1240 cm.$^{-1}$ [c] The N—H stretch (hydrogen bonded) in chloroform solution (6 mg./ml.) is given in parentheses. [d] Each of these compounds showed a strong band in the range 930–940 cm.$^{-1}$ rather than at 980 cm.$^{-1}$ as suggested by Bellamy.

TABLE III

PYROLYSIS OF DIPHENYL *N*-ALKYLPHOSPHORAMIDATES

$(C_6H_5O)_2P(O)NHR$

R	Rate of Addn., G./Min.[a]	Temp.	Olefin Yield,[b] %	Fraction Isomerized[c]	No. of Components[d]
Cyclohexyl	0.23	350	95		
	0.23	400	95		
n-Hexyl	0.18	353	71	0.43[f]	3
	0.20	400	88	0.42[f]	3
2-Ethylhexyl	0.21	350	93	0.95	7
	0.16	400	56	0.95	7
n-Decyl	0.24	350	0		
	0.20	400	73	0.59	5
	0.17	450	78	0.63	5
n-Hexyl alcohol[g]				0.71	6

[a] Average size of run = 10–20 g. [b] Crude, undistilled olefin (see Experimental). [c] Unless otherwise noted, calculated from gas chromatograms run on silver nitrate–glycol column using the formula, fraction = (total area − area due to terminal olefin)/total area. [d] No. of peaks on chromatogram; therefore, may be only a lower limit. [e] Contained traces of the same isomers in about the same amounts as commercial cyclohexene [A. C. Cope, H. E. Johnson, and J. S. Stephenson, *J. Am. Chem. Soc.*, **78,** 5599 (1956)]. [f] Analyzed on column prepared according to directions of H. S. Knight, *Anal. Chem.*, **30,** 9 (1958), and using β,β′-oxydipropionitrile. This column does not distinguish between 1-hexene and trans-3-hexene and between 2-methyl-1-pentene and *cis*-2-hexene, which were indicated to be present along with *trans*-2-hexene in the ratio, 0.57:0.27:0.16 at 350°, 0.59:0.24:0.16 at 400°. [g] Dehydrated by heating with concentrated sulfuric acid, followed by simple distillation.

expensive phosphite, the first procedure described was preferred.

The pyrolyses of the phosphoramidates were carried out much as described previously by dropping the pure, melted phosphoramidates through a Pyrex glass tube packed with glass helices and heated to 350–450° in a tube furnace. The results of these pyrolyses are given in Table III.

From these results it is obvious that considerably higher yields of olefin were obtained from the diphenyl than from the corresponding dimethyl *N*-alkylphosphoramidates. No conclusive evidence of the formation of tertiary amines was obtained, although the infrared spectra of several pyrolysates indicated that compounds containing the N—H or NH_2 group may have been present in trace amounts. Traces of phenol were also apparent in the pyrolysates. Attempts to isolate the expected by-product, diphenyl phosphoramidate, were not successful, but this may have been due to the complexity of the phosphorus-containing product.

Although the formation of tertiary amines as a side reaction appeared to have been fairly effectively eliminated, unfortunately the isomerization of the olefinic product was not. Analysis by gas chromatography of the crude olefinic products indicated that rather extensive isomerization occurred in all examples except that of the cyclohexyl derivative (and even here traces of the isomeric olefins were noted)(Table III). Actually the extent of isomerization was well below that observed in the sulfuric acid dehydration of a typical alcohol, and somewhat below that observed previously in the pyrolysis of the dimethyl *N*-alkylphosphoramidates. However, the extent of such isomerization was still too high to recommend this procedure as one for the degradation of amines to olefins.

Presumably the isomerization may be attributed to acidic by-products of the reaction, possibly resulting from hydrolysis of the phosphoramidate by traces of water present, giving rise to the traces of phenol in the product, although the latter could have been formed equally well from the reaction of two moles of phosphoramidate (or some similar species) to give phosphorimidate-like species plus phenol.

In view of the present results it is apparent that further changes in structure will be required before the pyrolysis of phosphorus amides can be made a useful degradative or synthetic process. Experiments toward this objective are in progress.

EXPERIMENTAL[4]

Diphenyl N-alkylphosphoramidates. Procedure A. In a typical experiment a solution of 49.5 g. (0.50 mole) of cyclohexylamine in 250 ml. of carbon tetrachloride was cooled to 10° in the ice bath and 58.5 g. (0.25 mole) of diphenyl phosphite (Eastman Kodak Co.) was added dropwise with stirring. The amine hydrochloride began to precipitate at once. After addition was complete the mixture was heated and stirred to the reflux temperature, then allowed to stand at room temperature for 72 hr. The amine hydrochloride was removed by filtration and the carbon tetrachloride by evaporation in a rotating evaporator, giving, after recrystallization from Skellysolve B,[5] 65.3 g. (78.8%) of diphenyl *N*-cyclohexylphosphoramidate, m.p. 102.5°.

In the other preparations listed in Table I the filtration step was omitted, for the amine hydrochlorides were soluble in the reaction mixture. The hydrochlorides were most effectively removed by washing with hot, distilled water, as with some of the hydrochlorides washing with base caused emulsions to form.

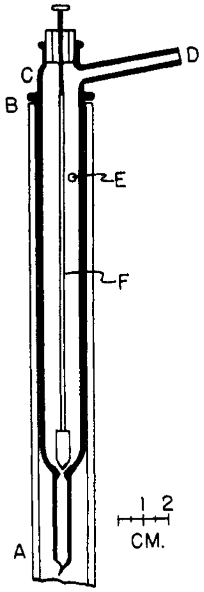

Fig. 1. Dropping Funnel. A. Pyrolysis tube. B. Ground surfaces (sealed with high vacuum grease (Dow Corning)). C. Dropping funnel. D. Nitrogen inlet. E. Hole in C for nitrogen outlet to pyrolysis tube. F. Modified Nester valve[6]

Procedure B. To a solution of 49.5 g. (0.5 mole) of cyclohexylamine in 300 ml. of dry carbon tetrachloride cooled to 10° in the ice bath 67.0 g. (0.25 mole) of diphenylphosphoryl chloride (Aldrich Chemical Co.) was added dropwise with stirring. After addition was complete the mixture was heated to the reflux temperature, then allowed to stand 72 hr. at room temperature. The amine hydrochloride was removed by filtration and the carbon tetrachloride by evaporation in the rotating evaporator. The solid remaining was washed three times with hot water, dried, and recrystallized from Skellysolve B,[5] giving 60.5 g. (73%) of diphenyl *N*-cyclohexylphosphoramidate, m.p. 102.5°. The yield of amine hydrochloride was quantitative.

Pyrolysis. The pyrolysis tube was a thick-walled Pyrex glass tube, 1.0 in. o.d. and 26 in. long, inserted in a 12-in. FD303 Hoskins electric furnace. The tube was packed the length of the furnace with a mixture of 0.125- and 0.063-in. Pyrex glass helices. The latter were cleaned by sequential application of the following operations: soaking in hot concentrated nitric-sulfuric acid mixture, washing with distilled water, burning off of any carbon deposit in the annealing oven, washing with dilute base, washing with water, washing with acetone, and drying in the oven at 80°. Inasmuch as all of the compounds pyrolysed were solids, the compounds were melted in the dropping funnel fitted with a modified Nester[6] needle valve shown in Fig. 1. The funnel was inserted into the pyrolysis column with its tip just above the glass helices packing. A short heating jacket (18.5 cm. in length) constructed as described by Cason and Rapoport[7] was fitted around that portion of the pyrolysis tube containing the dropping funnel and was used to melt the phosphoramidates. The pyrolysate was collected in a receiver immersed in a Dry Ice–alcohol bath (a second such receiver was placed in series with the first, but in only one

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[4] Melting points are corrected. Analyses by Micro-Tech Laboratories, Skokie, Ill.

[5] A hydrocarbon solvent, b.p. 60–69°

[6] R. G. Nester, *Anal. Chem.*, **28**, 278 (1956). The modification involved elimination of the spring-loading device and the Teflon stopper and replacement of these with a rubber stopper fitted with cylindrical Teflon insert, the latter being threaded to take the needle. This version is simpler to build and almost as durable as the original.

[7] J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, New York, 1950, p. 234.

experiment was any product found in this receiver). A slow flow of nitrogen (*ca.* 1–2 l. per hr.) was passed through the pyrolysis tube before and during the pyrolysis.

The temperature of the pyrolysis tube was controlled and measured as described previously.[8] Control was accurate to within ±5°.

The phosphoramidates were pyrolysed by dropping the melted compounds through the heated tube at the rates and temperatures listed in Table III. After pyrolysis was complete, the frozen solids in the receiver were quickly weighed and then warmed by the warmth of the hand to melt the olefinic product, which was decanted from the still frozen phosphorus-containing by-products. The crude olefin was weighed and then analysed without purification by gas chromatography, essentially as described previously.[7]

The olefinic product from the pyrolysis at 350° of diphenyl *N*-(2-ethylhexyl)phosphoramidate was separated by simple distillation because the whole product melted at the same time, preventing mechanical separation of the olefin.

The amount of carbonization accompanying the pyrolyses varied considerably from very slight to fairly heavy; being the worst with diphenyl *N*-(2-ethylhexyl)-phosphoramidate.

Most of the pyrolysates had the faint odor of phenol and the infrared spectra of the phosphorus-containing residues contained, in addition to peaks to be expected of the organo phosphorus materials, the peaks characteristic of phenol.

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(8) H. E. Baumgarten, F. A. Bower, R. A. Setterquist, and R. E. Allen, *J. Am. Chem. Soc.*, **80**, 4588 (1958); H. E. Baumgarten and R. A. Setterquist, *J. Am. Chem. Soc.*, **78**, 2605 (1957).

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Cinnolines. IX. The Stollé-Becker Synthesis[1,2]

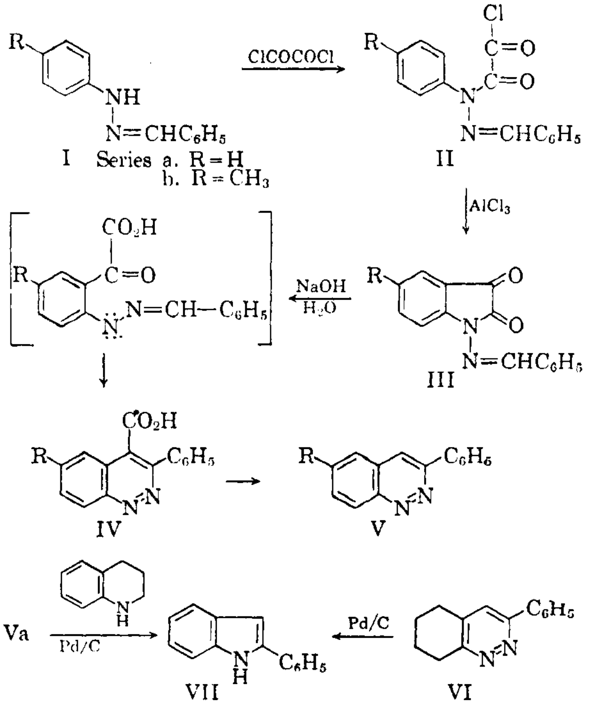
HENRY E. BAUMGARTEN AND JAMES L. FURNAS

Treatment of *N*-benzylideneaminoisatin (IIIa) with aqueous base gave 3-phenyl-4-cinnolinecarboxylic acid (IVa) as suggested previously by Stollé and Becker. The structure of IVa was proved by conversion of IVa into 3-phenylcinnoline and into 2-phenylindole. By a similar sequence 6-methyl-3-phenyl-4-cinnolinecarboxylic acid (IVb) and 6-methyl-3-phenylcinnoline (Vb) were prepared.

In 1924 Stollé and Becker[3] reported that the treatment of *N*-benzylideneaminoisatin (IIIa) with aqueous base yielded 3-phenyl-4-cinnolinecarboxylic acid (IVa). This transformation, which may be labelled the Stollé-Becker synthesis, has occupied a somewhat questionable position in cinnoline chemistry,[4] for Stollé and Becker gave at best meager experimental details and offered no proof of structure other than an elementary analysis for nitrogen. The present communication offers experimental evidence supporting the validity of the Stollé-Becker synthesis.

The complete sequence used by Stollé and Becker is shown by the changes Ia→IVa. Preliminary experiments based on such experimental detail as was given in their report quickly demonstrated the inadvisability of attempting to repeat their experiments exactly. Thus, although their sequence was followed, the experimental procedures were based on what appeared to be the best current practice.

The reaction of benzaldehyde phenylhydrazone (Ia) with a 100% excess of oxalyl chloride gave a 90–98% yield of crude *N*-benzylideneamino-*N*-phenyloxamyl chloride (IIa). Treatment of the latter with six moles of aluminum chloride in chloroform solution gave a 65–80% yield of IIIa, and the reaction of IIIa with hot 20% aqueous sodium hydroxide gave a 75–85% (48–61% overall) yield of 3-phenyl-4-cinnolinecarboxylic acid (IVa).



Although the unstable character of IIa prevented its complete characterization compounds IIIa and IVa gave analyses and infrared spectra (Table I) compatible with the structures assigned by Stollé and Becker. However, to establish the validity of

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(1) Paper VIII. *J. Org. Chem.*, **26**, 803 (1961).

(2) This work was supported in part by grant CY-3090 of the U. S. Public Health Service.

(3) R. Stollé and W. Becker, *Ber.*, **57**, 1123 (1924).

(4) *Cf.* T. L. Jacobs in R. C. Elderfield's *Heterocyclic Compounds*, Vol. 6, Wiley, New York, 1957, p. 152.