chilled, m.p. 42–45° (recorded[19] m.p. 45–46°), yield 69.5%. The 1,3,5-trinitrobenzene derivative melted at 100.5–101.5° (recorded m.p. 101.2–102.5°[19]). The carbon monoxide test was again positive.

Pyrolysis of the *p*-Tolyl Addition Compound.—From this ketone (0.5 g., 0.001 mole), heated at 235–245° for 4.5 hr., was obtained an oil. When chromatographed on 50 g. of alumina, it gave triphenylmethane (90% yield) and 2-*p*-tolylnaphthalene, m.p. 96–97° (85% yield). The infrared spectrum of this compound has peaks which can be assigned to aliphatic hydrogen (2910 cm.$^{-1}$) and *p*-substituted phenyl (810 cm.$^{-1}$); three bands (850, 890, 945 cm.$^{-1}$) of medium to strong intensity are also present. Likewise these three bands are found in the spectra of 2-phenyl- and 2-*o*-tolylnaphthalene. The test for carbon monoxide was found to be positive for this reaction also. The tolylnaphthalene was analyzed.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.83; H, 6.27.

Synthesis of 2-*p*-Tolylnaphthalene.—The procedure employed here is similar to that used by Friedel, Orchin and Reggel in the preparation of 2-*o*-tolylnaphthalene.[19] The lithium reagent from 2-bromonaphthalene was prepared by heating a mixture of 1.90 g. (0.27 g. atom) of freshly-cut lithium pieces and 20.0 g. (0.096 mole) of 2-bromonaphthalene in a solvent system consisting of 95 ml. of anhydrous ether and 25 ml. of sodium-dried benzene. After the mixture had been boiled for 2 hr., much of the lithium had disappeared. To this red-colored mixture was added a solution of 11.9 g. (0.106 mole) of freshly distilled *p*-methylcyclohexanone in 45 ml. of anhydrous ether. The mixture became orange in color within a few minutes. After being heated under reflux for 6.5 hr., it was decomposed by cautious addition of 100 ml. of ice-water. The organic layer was concentrated to an oil, the spectrum of which possessed an intense, broad band at 3500 cm.$^{-1}$. Twenty grams of freshly fused, powdered potassium bisulfate was added to the crude oil, and the mixture was heated at 160–170° for 2.5 hr. The flask was cooled, and its contents were extracted with benzene. Removal of the organic solvent left an oil which was partially fractionated. All fractions boiling at or below 110° at 5 mm. pressure were discarded. To the crude, residual, fluorescent material was added 1.2 g. of 10% palladium-on-charcoal, and this mixture was heated for 2.5 hr. at 310–325°. After the flask had cooled, its contents were leached with benzene. Removal of the organic solvent left an oil which deposited impure crystals of 2,2-binaphthyl. This hydrocarbon was purified and identified by a mixture melting point determination with an authentic sample. The remaining oil was chromatographed on 320 g. of alumina. A white, crystalline compound melting at 95–96.5° was isolated, yield 4.52 g. (20% yield, based on the 2-bromonaphthalene converted). A mixture melting point determination and an infrared analysis showed the synthetic compound to be identical to the 2-*p*-tolylnaphthalene obtained from the pyrolysis.

Hydrogenation of the Phenylated Compound.—The hydrogenation was accomplished in a microhydrogenation apparatus by use of sodium-dried, thiophene-free benzene. The benzene was necessary since the ketone was very sparingly soluble in the solvents normally employed for such reductions. When 0.026 g. of platinum oxide had been reduced, a solution of 0.30 g. (0.0006 mole) of the ketone in 18 ml. of dry, thiophene-free benzene was added. The hydrogenation was completed within 1 hr. Removal of the catalyst and evaporation of the benzene left an oil which, when triturated with alcohol, became a solid. Recrystallization from acetic acid gave white crystals melting at 163–164.5°, identified tentatively as 1-(1,2,3,4-tetrahydro-2-phenyl)-naphthyl trityl ketone. The yield was practically quantitative. The infrared spectrum of this compound has peaks for aromatic hydrogen (3050, 3080 cm.$^{-1}$), aliphatic hydrogen (2925 cm.$^{-1}$), a non-conjugated ketone group (1704 cm.$^{-1}$), monosubstituted phenyl (700 cm.$^{-1}$) and *o*-substituted phenyl (745 cm.$^{-1}$). The only bands in the range 700–900 cm.$^{-1}$ are those assigned to mono- and *o*-substituted phenyl. In mixture melting point determinations the compound depressed the melting points of both the starting material and 1-naphthyl trityl ketone.

Anal. Calcd. for $C_{36}H_{30}O$: C, 90.34; H, 6.32. Found: C, 90.16; H, 6.18.

When a mixture of 0.030 g. of platinum oxide, 0.20 g. (0.0005 mole) of 1-naphthyl trityl ketone and 30 ml. of sodium-dried thiophene-free benzene was subjected to hydrogenation under the conditions employed with the phenylated compound, the ketone was recovered nearly quantitatively. An attempted high-pressure hydrogenation (1000 lb. per sq. in.) of 1-naphthyl trityl ketone also failed, starting material again being recovered unchanged.

URBANA, ILL.

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(19) R. A. Friedel, M. Orchin and L. Reggel, THIS JOURNAL, **70**, 199 (1948).

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Reactions of Amines. IV. Pyrolysis of Dialkyl N-Alkylphosphoramidates[1,2]

BY HENRY E. BAUMGARTEN AND ROBERT A. SETTERQUIST[3]

RECEIVED OCTOBER 11, 1958

The preparation of six dialkyl N-alkylphosphoramidates is described. The pyrolysis at 350–400° of these phosphoramidates gave mixtures of olefin and tertiary amine.

The pyrolysis of N-alkylacetamides to olefins[1,4] appears to require temperatures 100° or more above those required for the pyrolysis of the corresponding alkyl acetates, whereas the pyrolysis of alkyl phosphates[5] requires temperatures of 50–100° less than those for the acetates. Since the foregoing reactions are not necessarily related mechanistically, it may not be valid to predict that the pyrolysis of dimethyl N-alkylphosphoramidates to olefins should require lower pyrolysis temperatures than the N-alkylacetamides. Nevertheless, the work described in this communication was undertaken to test such a prediction.

While this work was in progress two other studies of the pyrolysis of phosphoramidates were described. Thus, Gerrard and Jeacocke[6] reported that heating dialkyl N-arylphosphoramidates to 240–250° gave about 95% yields of N-alkylanilines. According to their results the phosphoramidates of primary aromatic amines gave almost exclusively the secondary alkylarylamine. The latter results have been challenged recently by Cadogan,[7] who obtained largely the tertiary dialkylarylamine in similar pyrolyses. Codogan reported also that

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(1) Paper III, THIS JOURNAL, **80**, 4588 (1958).

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

(3) Minnesota Mining and Manufacturing Co. Fellow, 1955–1956.

(4) W. J. Bailey and C. N. Bird, *J. Org. Chem.*, **23**, 996 (1958).

(5) H. E. Baumgarten and R. A. Setterquist, *ibid.*, **78**, 2605 (1957).

(6) W. Gerrard and G. J. Jeacocke, *Chemistry & Industry*, 1538 (1954).

(7) J. I. G. Cadogan, *J. Chem. Soc.*, 1079 (1957).

TABLE I

DIALKYL N-ALKYLPHOSPHORAMIDATES

Phosphoramidate	Method[a]	Yield, %	B.p., °C.	B.p., Mm.	$n^{25}D$	Composition	Nitrogen, % Calcd.	Nitrogen, % Found
Dimethyl N-(*n*-hexyl)	A	63	119	0.5	1.4337	$C_8H_{20}NO_3P$	6.69	6.45
Dimethyl N-cyclohexyl	A	93	65.5–66.2[b]			$C_8H_{16}NO_3P$	6.76	6.60
	B	69						
Dimethyl N-(*n*-octyl)	A	51	127	1.0	1.4283	$C_{10}H_{24}NO_3P$	5.89	5.93
Dimethyl N-(2-ethylhexyl)	A	69	142.5	1.5	1.4403	$C_{10}H_{24}NO_3P$	5.89	6.13
Dimethyl N-pentamethylene[c]	A	61	88	1.0	1.4517	$C_7H_{16}NO_3P$	7.25	7.19
Diethyl N-cyclohexyl-N-methyl	C	49	110	1.0	1.4511	$C_{11}H_{24}NO_3P$	5.62	5.74

[a] See Experimental part. [b] Melting point. [c] N-(Dimethoxyphosphinyl)-piperidine.

TABLE II

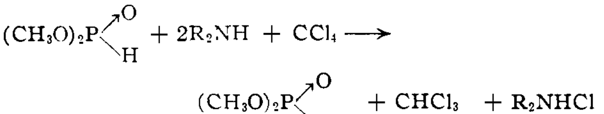
INFRARED SPECTRA[a]

Phosphoramidate	Frequency,[b] cm.$^{-1}$ P → O stretch	P–O–Me stretch	P–O–C stretch	N–H stretch
Dimethyl N-(*n*-hexyl)	1240(s)	1187(w)	1040(s)	3180(m)
Dimethyl N-cyclohexyl[d]	1230(s) 1247(s)	1187(w)	1038(s)	3420(w) 3220(m)
Dimethyl N-(*n*-octyl)	1240(s)	1188(w)	1060(s)	
Dimethyl N-(2-ethylhexyl)	1245(s)	1188(w)	1038(s)	3240(m)
Dimethyl N-pentamethylene	1256(s)	1188(w)	1030(s)	
Diethyl N-cyclohexyl-N-methyl	1256(s)	1170(m)[c]	1051(s)	

[a] Determined for the neat liquid using a model 21, Perkin-Elmer spectrophotometer having sodium chloride optics. [b] L. J. Bellamy ("The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954, Chap. 18) quotes for the P → O stretching vibration, 1250–1300 cm.$^{-1}$, for the P–O–CH$_3$ stretching vibration, 1190 + 3 cm.$^{-1}$ and for the P–O–C (aliphatic) stretching vibration, 1000 to 1050 cm.$^{-1}$ and for the P–O–Et stretching vibration, 1156–1163 cm.$^{-1}$ [c] P–O–Et stretching vibration. [d] Determined using carbon tetrachloride solution (5 mg./ml.).

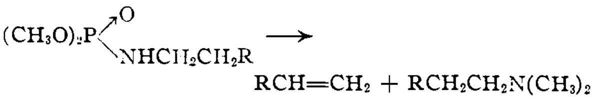
diethyl N,N-diethylphosphoramidate was much more stable than the aryl derivatives, the only isolable pyrolysis products obtained after eighteen hours at the boiling point being triethylamine (and its salts). Ethyl N-cyclohexyl-P-ethylphosphonamidate gave both mono- and diethylcyclohexylamine, but in low yield. Neither of these reports mention olefin formation during the relatively low-temperature, liquid-phase pyrolyses.

The dimethyl N-alkylphosphoramidates used in the present work were prepared by a variation of a procedure described by Todd and Atherton[8] in which an amine was treated with dimethyl phosphite in carbon tetrachloride solution. This procedure had the disadvantage that two moles of the amine were required per mole of amide prepared. In order to decrease the consumption of primary or secondary amine in the reaction, several experiments were made in which one equivalent each of primary or secondary amine, dimethyl phosphite and a tertiary amine were used. Triethylamine was the most effective base followed by dimethylaniline and pyridine. Thus, using these amines in the preparation of dimethyl N-cyclohexylphosphoramidate, yields of 69, 40 and 39% were obtained. Diethyl N-cyclohexyl-N-methylphosphoramidate was prepared by the reaction of the commercially available diethyl phosphorochloridate with N-methylcyclohexylamine in the presence of dimethylaniline. The phosphoramidates prepared are described in Table I, and characteristic infrared peaks are given in Table II.


$$(CH_3O)_2P\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix} + 2R_2NH + CCl_4 \longrightarrow (CH_3O)_2P\begin{smallmatrix}\nearrow O\\ \searrow NR_2\end{smallmatrix} + CHCl_3 + R_2NHCl$$

The phosphoramidates were pyrolyzed by dropping them through a 1-in. Pyrex or Vycor glass tube packed with $^1/_{16}$-in. glass helices and heated to various temperatures by a tube furnace. The results of several typical pyrolyses are given in Table III. Although the pyrolyses were relatively clean with respect to carbonization, considerable fouling of the tube was caused by the phosphorus-containing by-products.

The results of Table III indicate that dimethyl N-alkylphosphoramidates pyrolyze readily at temperatures of 350–400° to give mixtures of olefin and tertiary amine. No evidence for the presence of secondary amine in any quantity could be obtained, either by gas chromatography or infrared spectroscopy.[9] In general, the combined yields of amine and olefin were fairly good. Some of the phosphoramidate was recovered also, but in the present work no effort was made to correct the yields for the recovered starting materials.


$$(CH_3O)_2P\begin{smallmatrix}\nearrow O\\ \searrow NHCH_2CH_2R\end{smallmatrix} \longrightarrow RCH{=}CH_2 + RCH_2CH_2N(CH_3)_2$$

The pyrolyses of dimethyl N-cyclohexylphosphoramidate and diethyl N-cyclohexyl-N-methylphosphoramidate were exceptional in that no tertiary amine could be isolated and yields of olefin were about 15% higher than those from the other phosphoramidates.[10] Also interesting were the results of the pyrolysis of N-(dimethoxyphosphinyl)-piperidine which gave in addition to the tertiary amine, N-methylpiperidine, a mixture of the diolefins, 1,4-pentadiene and 1,3-pentadiene.

The identity of the olefins was determined by their infrared spectra and, in some experiments, by gas chromatography. In every example in which rearrangement might be reasonably expected, the product was contaminated with rearranged olefin. The extent of rearrangement varied considerably as compared with that observed in the

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(8) A. R. Todd and F. R. Atherton, *Chemistry & Industry*, 660 (1945).

(9) None of the amine fractions showed absorption in the N–H stretching region (lithium fluoride prism); however, the gas chromatography curves showed very weak peaks at approximately the correct retention volumes for the secondary amines. It was estimated that the amount of secondary amine present, if any, was less that 5%.

(10) The gas chromatography curves indicated the presence of traces of higher-boiling components in the olefin fraction; however, the amount of such material was very small.

TABLE III

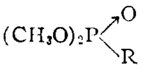
PYROLYSIS OF DIALKYL N-ALKYLPHOSPHORAMIDATES

Phosphoramidate	Rate of addn., g./min.[a]	Temp., °C.	Olefin Yield, %	 B.p. range, °C.	t-Amine Yield, %	 B.p. range, °C.
Dimethyl N-(*n*-hexyl)	0.26	360	46	52–64	40	120–146[b,c]
	.25	400	49	55–65	28	120–145
	.28	400	31	63–67	22	140–151
Dimethyl N-cyclohexyl	.17	340	49	80–84	0	
	.13	350	69	80–85	0	
	.09	360	55	80–85	0	
	.10	400	53	79–83	0	
	.24	450	65	79–82	0	
Dimethyl N-(*n*-octyl)	.10	400	31	120–130	33	180–190[d]
Dimethyl N-(2-ethylhexyl)	.22	305	20	120–125	27	166–170[e,f]
	.18	350	35	100–140	37	160–170
	.13	360	40	100–130	19	150–164
	.23	410	52	110–130	27	155–170
Dimethyl N-pentamethylene	.15	350	21	25–30		
			32	30–45		
	.20	400	20	25	7	102–106[g,h]
			18	40–45		
	.31	400	32	25	18	105
			8	40–44		
Diethyl N-cyclohexyl-N-methyl	.16	400	67	75–82	0	

[a] Average size of run = 10–20 g. [b] On redistillation, b.p. 145–147° (lit.[12] b.p. 146°). [c] *Anal.* Calcd. for $C_8H_{19}N$: N, 10.85. Found: N, 10.90. [d] Lit.[13] b.p. 191°. [e] On redistillation, b.p. 76° (12 mm.), $n^{25}D$ 1.4219. [f] *Anal.* Calcd. for $C_{10}H_{23}N$: N, 8.90. Found: N, 9.17. [g] On redistillation, b.p. 105–107° (lit.[13] b.p. 107°). [h] Hydrochloride, m.p. 184° (lit.[13] m.p. 185°).

pyrolysis of the corresponding alkyl phosphates.[5] In Table IV are given some estimates of the extent of isomerization of olefinic product during the pyrolysis of both phosphates and phosphoramidates.

TABLE IV


ISOMERIZATION DURING PYROLYSIS OF $(CH_3O)_2P(\rightarrow O)R$

R	Pyrolysis temp.,[a] °C.	Fraction isomerized[b]
$O(CH_2)_5CH_3$	370	0.61[c]
$NH(CH_2)_5CH_3$	370	.43[c]
$NH(CH_2)_5CH_3$	420	.55[c]
$O(CH_2)_7CH_3$	370	.67
$NH(CH_2)_7CH_3$	400	.25
$OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$	360	.91
$NHCH_2CH(CH_2CH_3)(CH_2)_3CH_3$	410	.91

[a] Rate = *ca.* 0.25 g./min. [b] Calculated from gas chromatograms run on $AgNO_3$–glycol columns using the formula, fraction = (total area − area due to terminal olefin)/total area. [c] Principal isomerization product was 2-hexene. Some 3-hexene was also formed as well as at least two hexenes with rearranged carbon skeletons.

Because of the assumptions made in the analysis of the crude olefins, these estimates can be regarded only as lower limits.[11] Nevertheless, it appears that the N-(*n*-hexyl)- and N-(*n*-octyl)-phosphoramidates gave less of the rearranged olefin than the corresponding phosphates, but N-(2-ethylhexyl)-phosphoramidate gave essentially the same mixture of olefins as that obtained from the phosphate.

Although Cadogan[3] has made some general suggestions as to the mechanism of the alkylation reaction, no detailed mechanism has been proposed. One attractive scheme involves a concerted, bimolecular reaction proceeding through the quasi six-membered, cyclic transition state II and leading to the formation of the pyrophosphoric acid derivative III and the secondary amine IV. This mechanism would account for the alkylation of the relatively non-basic amide nitrogen atom. The further alkylation of IV to form the tertiary amine can be accounted for by any of several mechanistic routes. Thus, III and IV may react to form the intermediates V and VI or VII and VIII. Through cyclic transition states similar to II either V or VIII could yield the tertiary amine, whereas either VI or VIII could form more of the secondary amine IV. Alternatively, by a reaction analogous to the alkylation of amines by alkyl phosphates,[14] IV could be alkylated by any of the various species present having the structural unit $>P(O)OCH_3$.

A cyclic transition state IX can be written for the olefin-forming reaction, which resembles that commonly proposed for pyrolysis of acetates and acetamides. Because of the presence of a strong acid in the pyrolysate (VI, VII, etc.), however, a reaction proceeding *via* ionic intermediates cannot be discounted. Furthermore, if the first mechanism cited above is essentially correct, free secondary amine (or its salts) will be present during the pyrolysis, so that the olefin-forming reaction may not involve the phosphoramidate but rather the amine phosphate (or a related salt) and thereby

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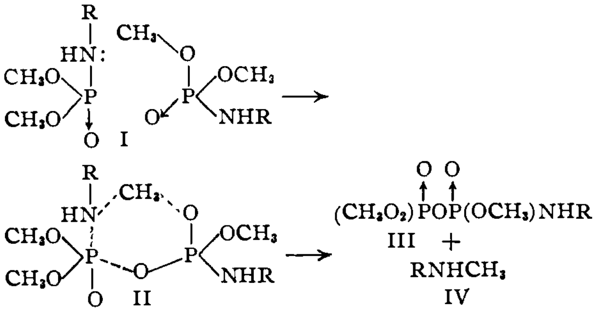
(11) Poor resolution of some of the olefinic components on the gas chromatography columns at hand prevented a complete quantitative analysis of the mixtures. However, the use of a silver nitrate-glycol column permitted a clean resolution of the terminal (unrearranged) olefin from the other components. The possibility remains that the resolution was only apparent, not real, and that the extent of isomerization may be somewhat greater than indicated in the table. However, analysis by infrared techniques for the principal components of the hexene and octene mixtures gave results not greatly different from those in Table IV.

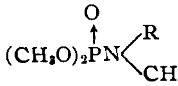
(12) J. v. Braun and E. Anton, *Ber.*, **64B**, 2865 (1931).

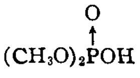
(13) H. T. Clarke, *J. Chem. Soc.*, **103**, 1689 (1913).

(14) J. H. Billman, B. W. Mundy and A. Radike, THIS JOURNAL, **64**, 2977 (1912).

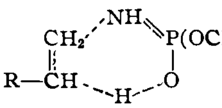
resemble the amine phosphate degradation of Harries,[15,16] the mechanism of which has not been determined. The presence of strong acid in the pyrolysate may be responsible also for the rearrangement of the double bond in the olefin fraction of the pyrolysate.

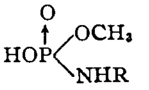


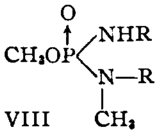

V


$(CH_3O)_2\overset{O}{\overset{\uparrow}{P}}OH$

VII


IX


VI


VIII

From the mechanisms proposed one might infer that the alkylation reaction (and, hence, the isomerization reaction) could be eliminated or minimized by carrying out the pyrolysis using high dilution techniques. However, the minimum requirements for steps I→II are one molecule of amide and one molecule containing the >P(O)-OCH$_3$ unit. The phosphorus-containing by-products of the pyrolyses were thick, viscous oils (even at 450°) that were held rather strongly on the glass packing, so that, even using dilution techniques, the incoming amide passed over a growing bed of alkylating and isomerizing agent. In several experiments with *n*-pentane as a diluent little change in the amine–olefin ratio or in the extent of isomerization was observed.

The temperatures required for pyrolysis of the dimethyl N-alkylphosphoramidates are below those required for the pyrolysis of the corresponding acetates. If it were not for the concurrent formation of tertiary amine and the rearrangement of the olefinic bond, the present pyrolysis would be a useful degradative or synthetic process. The elimination of these unfavorable characteristics is under study.

Experimental[17]

Dimethyl N-Alkylphosphoramidates. (a) **Method A.**—This method can be illustrated by two examples. The principal differences among individual examples were the variations necessary to remove the amine hydrochloride from the reaction mixtures.

It should be noted that the specific experimental procedures described here are not necessarily satisfactory for use with the higher amines for which different reaction times and procedures for work-up seem to be indicated. Even with *n*-octylamine occasional failures were encountered and limited attempts to prepare the *n*-decyl and *n*-dodecyl derivative were unsuccessful.

To a solution of 11 g. (0.20 mole) of dimethyl phosphite in 150 ml. of dry carbon tetrachloride cooled to 10°, 50 g. (0.50 mole) of cyclohexylamine was added dropwise with stirring under reflux. A reaction took place immediately and a precipitate of cyclohexylamine hydrochloride formed. After the addition was complete, the reaction mixture was heated to reflux and then allowed to stand for four hours. The cyclohexylamine hydrochloride was removed by filtration and the filtrate was washed twice with 50-ml. portions of 10% sulfuric acid and twice with 50-ml. portions of 10% sodium bicarbonate solution. The filtrate was treated with decolorizing charcoal, dried over magnesium sulfate and filtered. Evaporation of the carbon tetrachloride under reduced pressure on the steam-bath gave a pale tan liquid which solidified on standing to a tan, crystalline solid, 38 g. (93%), m.p. 63.5–66°. After recrystallization from ether–petroleum ether or from cyclohexane, the resulting white needles of dimethyl N-cyclohexylphosphoramidate melted at 65.5–66.2°.

To a cooled solution of 33 g. (0.30 mole) of dimethyl phosphite in 200 ml. of dry carbon tetrachloride was added dropwise 80 g. (0.62 mole) of 2-ethylhexylamine. Although the reaction took place immediately no precipitate of 2-ethylhexylamine hydrochloride formed. The reaction mixture was heated under gentle reflux for 0.5 hr. and allowed to stand overnight. The reaction mixture was washed with two 100-ml. portions of 10% hydrochloric acid (or sulfuric acid) and then with 200 ml. of hot water. The organic layer was dried as above and the carbon tetrachloride was evaporated under reduced pressure on the steam-bath. The yield of crude amide was 65 g. (91%). Distillation of the crude product through a 24-in. Podbielniak column[18] gave 49 g. (69%) of dimethyl N-(2-ethylhexyl)-phosphoramidate, b.p. 143° (1.5 mm.), n^{25}_D 1.4403.

In some experiments the amine hydrochloride was induced to precipitate by the addition of two volumes (relative to carbon tetrachloride) of dimethyl ether. In others (*e.g.*, the preparation of dimethyl N-(*n*-octyl)-phosphoramidate) the amine hydrochloride was most efficiently removed by washing with large quantities of hot water.

(b) **Method B.**—Dimethyl N-cyclohexylphosphoramidate was prepared as described in (a) except that only 9.9 g. (0.10 mole) of cyclohexylamine was used and 10 g. (0.10 mole) of triethylamine was added to the carbon tetrachloride solution before addition of the dimethyl phosphite. The triethylamine hydrochloride precipitated cleanly and was removed by filtration. The resulting reaction mixture was worked up as described in (a).

(c) **Method C.**—To a solution of 24 g. (0.20 mole) of dimethylaniline and 23 g. (0.20 mole) of N-methylcyclohexylamine in 200 ml. of dry ether was added dropwise with stirring 35 g. (0.20 mole) of diethyl phosphorochloridate at such a rate as to maintain gentle reflux. The white solid that formed was removed by filtration and the filtrate was washed with 200 ml. of 5% hydrochloric acid and 200 ml. of water, dried and distilled under reduced pressure, giving 24 g. (49%) of diethyl N-cyclohexyl-N-methylphosphoramidate, b.p. 110° (1.0 mm.), n^{25}_D 1.4511.

Pyrolysis.—The pyrolysis procedure and apparatus were essentially the same as those described previously.[4,6] In view of the viscous nature of the by-products (*vide supra*) sample size was limited to 20 g. to avoid complete plugging of the pyrolysis tube. Normally the pyrolysate was distilled through a short Vigreux column to separate the volatile products from recovered amide and other materials. The volatile fraction was then separated into olefin and amine fractions by fractional distillation through a 24-in. Podbielniak column.[18] The wide separation in boiling point between the amine and olefin fractions permitted an apparent easy separation of the two. In a few experiments the amine was separated by extraction with dilute hydrochloric acid or by precipitation as the hydrochloride with anhydrous hydrogen chloride. The amine and olefin fractions were

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[15] C. Harries, *Ber.*, **34**, 300 (1901); **36**, 2997 (1903); **38**, 1832 (1905).

[16] H. L. Lochte and E. R. Littmann, "The Petroleum Acids and Bases," Chemical Publishing Co., Inc., New York, N. Y., 1955, p. 177.

[17] Melting points are corrected; boiling points are uncorrected. Analyses by the authors or Clarke Microanalytical Laboratory, Urbana, Ill. We are indebted to Dr. H. A. Pagel for advice and assistance in connection with these analyses.

[18] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

analyzed by infrared spectrometry. Later[11] most of the samples were reanalyzed by gas chromatography essentially as described previously.[5] The retention volumes of the amine components were always much greater than those of the olefin components (on Perkin-Elmer packing B) so that the two fractions could be very cleanly separated by gas chromatography. The results of these analyses indicated that the separation by distillation alone was not as complete as might be desired but for most practical purposes was adequate.

For the isomerization studies described in Table IV, the crude pyrolysate was washed with cold, dilute hydrochloric acid, cold 5% sodium bicarbonate, and water, dried over magnesium sulfate and analysed without further treatment. In some experiments the olefin was picked up in *n*-pentane prior to the washing. The presence of the *n*-pentane did not interfere in any way with the analysis by gas chromatography.

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Reduction of Vinylaromatic Nitro Derivatives[1]

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Using either zinc and ammonium chloride, or aluminum amalgam in moist ether, *o*, *m* and *p*-nitrostyrenes, stilbenes and -cinnamic acids are reduced to corresponding amines. Intermediate hydroxylamines cannot be isolated.

Derivatives of nitrosobenzene with vinyl or substituted vinyl side-chains are desired monomers in investigations on polymers containing nitroso groups. There are apparently no known examples of such polymerizable monomers; however, the literature describes nitrosocinnamic acids and esters[2] and contains disputed reports for 4,4′-dinitrosostilbene and derivatives.[3]

A transformation of a nitro group into a nitroso group requires initial reduction into an hydroxylamine followed by oxidation. In the present work reduction of nitrostyrenes, -stilbenes and -cinnamic acids using either zinc and ammonium chloride or aluminum amalgam in moist ether has been investigated. These reagents are known to reduce nitrobenzene,[4] and derivatives with deactivating[5] or weakly activating[6] substituents attached to the aromatic ring, into corresponding β-arylhydroxylamines. In contrast, strongly activating ring substituents on nitrobenzene promote reduction by these mild reagents into anilines.[7] The reduction of *m*-nitroaniline into *m*-phenylenediamine using aluminum amalgam has now confirmed that even in a *m*-position the amino group may not allow chemical reduction of an aromatic nitro group to stop at the hydroxylamino stage.

A vinyl substituent attached at any available ring position in nitrobenzene has now been observed to promote chemical reduction to a primary amine. In no case was it possible to detect hydroxylamines in reductions, using zinc and ammonium chloride, of nitrostyrenes, -stilbenes[8] or -cinnamic acids. Instead, corresponding amines were obtained in good to excellent yields. Similar results were obtained in good to excellent yields. Similar results were obtained from experiments on nitrostyrenes and aluminum amalgam in moist ether. These results were unexpected insofar as negatively substituted vinyl groups, such as is present in cinnamic acid and presumably stilbene, deactivate an attached aromatic ring.[9] In contrast *p*-nitrobiphenyl has been reduced to *p*-hydroxylaminobiphenyl with zinc and ammonium chloride[10] and with aluminum amalgam.[11]

Experimental

o- and *p*-nitrostyrenes were prepared by dehydrobromination of the corresponding bromides[12] and *m*-nitrostyrene by decarboxylation of *m*-nitrocinnamic acid with copper powder and quinoline.[13] *cis*-*o*-Nitrostilbene was prepared by decarboxylation of *trans*-β-phenyl-*o*-nitrocinnamic acid with Ad-

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[2] F. J. Alway and W. D. Bonner, *Amer. Chem. J.*, **32**, 392 (1904), claimed the preparation of *m*- and *p*-nitrosocinnamic acids and esters by the oxidation, using ferric chloride, of corresponding unisolated hydroxylamines, in turn prepared in unspecified poor yield by the reduction of nitro compounds using zinc and acetic acid. In contrast, G. Heller, *Ber.*, **43**, 1918 (1910), found that *o*-nitrocinnamic acid was reduced by zinc and acetic acid buffered with sodium acetate into *o*-aminocinnamic acid.

[3] O. Fischer and E. Hepp, *ibid.*, **26**, 2231 (1893); **28**, 2281 (1895), reported that *p*,*p*,-dinitrostilbene resulted from *p*-nitrotoluene and strong alkali in methanol; F. Bender, *ibid.*, **28**, 422 (1895), claimed that alkaline treatment of 4-nitrotoluene-2-sulfonic acid resulted in the formation of a mixture of dinitrodibenzyldisulfonic acid and azoxystilbenedisulfonic acid; A. G. Green, A. H. Davies and R. S. Horsfall, *J. Chem. Soc.*, **91**, 2076 (1907), suggested that "*p*,*p*′-dinitrosostilbene" and derivatives were, instead, dinitroazodistilbenes.

[4] C. H. Coleman, C. M. McCloskey and F. A. Stuart, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 668, used zinc and ammonium chloride; H. Wislicenus and L. Kaufmann, *Ber.*, **28**, 1323 (1895), used aluminum amalgam.

[5] F. J. Alway and A. B. Walker, *ibid.*, **36**, 2312 (1902), reduced *o*- and *m*-nitrobenzoic esters using zinc and acetic acid; E. Bamberger and F. L. Pyman, *ibid.*, **36**, 2700 (1903), **42**, 2306 (1909), used zinc and ammonium chloride; for a similar reduction of nitrobenzaldehydes see A. Kirpal, *ibid.*, **30**, 1597 (1897), and F. J. Alway, **36**, 2312 (1902), and for reductions of halonitrobenzenes see R. D. Haworth and A. Lapworth, *J. Chem. Soc.*, **119**, 768 (1921).

[6] E. Bamberger and A. Rising, *Ann.*, **316**, 278 (1901), reduced nitrotoluenes.

[7] With zinc dust and water, or zinc dust, water and calcium chloride, *o*- and *p*-nitrophenols and *o*- and *p*-nitroanilines were reduced to corresponding aminophenols and diamines; E. Bamberger, *Ber.*, **28**, 245 (1895), and M. Lumière and A. Seyewetz, *Bull. soc. chim.*, [3] **11**, 1038 (1894); see also R. D. Haworth and A. Lapworth, ref. 5.

[8] G. Drefahl, O. Henning and G. Rudakoff, *Chem. Ber.*, **91**, 286 (1958), reduced 4-nitrostilbene into azoxystilbene using magnesium and ammonium chloride.

[9] F. G. Bordwell and K. Rohde, THIS JOURNAL, **70**, 1191 (1948).

[10] H. Gilman and H. E. Kirby, *ibid.*, **48**, 2192 (1926).

[11] F. Bell, J. Kenyon and P. H. Robinson, *J. Chem. Soc.*, 1239 (1926).

[12] R. W. Strassburg, R. A. Gregg and C. Walling, THIS JOURNAL, **69**, 2112 (1947); E. L. Foreman and S. M. McElvain, *ibid.*, **62**, 1435 (1940).

[13] R. H. Wiley and N. R. Smith, *Org. Syntheses*, **33**, 62 (1953); W. J. Dale and C. W. Strobel, THIS JOURNAL, **76**, 6173 (1954).