tion of the remaining isomer, 3-nitro-*p*-terphenyl is reported in this study.

p-Terphenyl was nitrated using a modification of the method of Allen and Burness.[3] Slow addition of a dilute nitrating mixture apparently decreased dinitration and oxidation and gave an improved yield of the desired 4-nitro-*p*-terphenyl (I). Reduction of I was carried out in a high pressure bomb with a Raney nickel catalyst. The resulting 4 amino-*p*-terphenyl (II) was acetylated by treatment with acetic anhydride. The amide thus produced was nitrated directly without isolation, affording 3-nitro-4-acetylamino-*p*-terphenyl (III) in good yield. Hydrolysis of III in a warm dioxane solution was effected by aqueous potassium hydroxide. The brightly colored hydrolysis product proved to be the desired 3-nitro-4-amino-*p*-terphenyl (IV).[4]

A diazotized solution of IV was deaminated by refluxing with ethyl alcohol. The resulting 3-nitro-*p*-terphenyl (V), on oxidation, yielded the known 3-nitrodiphenyl-4′-carboxylic acid.[5] This is in accordance with the observation of France, Heilbron, and Hey[2] who reported that oxidation of I and 2-nitro-*p*-terphenyl yielded 4-nitrodiphenyl-4′-carboxylic acid and 2-nitrodiphenyl-4′-carboxylic acid respectively.

Catalytic hydrogenation of V gave 3-amino-*p*-terphenyl (VI). Acetylation of VI with acetic anhydride gave 3-acetylamino-*p*-terphenyl (VII).

EXPERIMENTAL[6]

4-Nitro-p-terphenyl (I). A suspension of 23.0 g. of *p*-terphenyl in 110 ml. refluxing glacial acetic acid was stirred vigorously while a mixture of 15 ml. of red fuming nitric acid and 25 ml. of acetic acid was added during 3.5 hr. After cooling in an ice bath the yellow solid was removed by filtration on a sintered glass funnel. The crude yield of I was 23.3 g. (85%). Recrystallization from nitromethane yielded I as a pale yellow solid, m.p. 210-211°.

4-Amino-p-terphenyl (II). A suspension of 11.0 g. of I in 130 ml. of dioxane was reduced by hydrogen under a cold pressure of 2200 p.s.i. The reduction was carried out with 1 teaspoon of Raney nickel catalyst in a 270-ml. void bomb. The reduction required 2 hr. at 90° after which the bomb was cooled and rinsed with a small amount of dioxane. The catalyst was removed by filtration and evaporation of the solvent under reduced pressure yielded 9.15 g. (94%) of II, m.p. 186-193°. Recrystallization from ethyl alcohol produced light tan crystals melting at 199.5-200.5°.

3-Nitro-4-acetylamino-p-terphenyl (III). A solution of 12.25 g. of II in 300 ml. of acetic acid was warmed and stirred while 10 ml. of acetic anhydride was added dropwise. Heating and stirring were continued for an hour. The reaction mixture was cooled to 70° and a mixture of 10 ml. of fuming nitric acid (*d.* 1.5) and 20 ml. of acetic acid was added during 20 min. Nitration was completed by warming to 90° for 0.5 hr. After chilling, the suspension was filtered and 13.24 g. (88%) of an orange solid was obtained, m.p. 202.5-205°. An analytical sample, m.p. 204.7-206°, was prepared by recrystallization from acetic acid.

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.27; H, 4.85; N, 8.42. Found: C, 72.38; H, 4.89; N, 8.42.

3-Nitro-p-terphenyl (V). A suspension of 3.24 g. of IV in 110 ml. of acetic acid was added to 30 ml. of cold, concentrated sulfuric acid containing 0.84 g. of sodium nitrite. The resulting deep red diazonium solution was added dropwise to a refluxing solution of 0.25 g. of copper sulfate and 20 ml. of water in 400 ml. of ethyl alcohol. The mixture, contained in a 1000-ml. flask, was stirred vigorously during the addition which required 2.5 hr. Refluxing and stirring were continued for 1 hr. after which the mixture was diluted with water. The solid was removed by filtration and dried by suction. After crystallization from petroleum ether (b.p. 110-120°) 2.69 g. (88%) of a light orange solid was obtained, m.p. 178-180°. Three recrystallizations from petroleum ether gave an analytical sample, m.p. 180-181.2°.

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76. Found: C, 78.21; H, 4.83.

Oxidation of 3-nitro-p-terphenyl. The method of France, Heilbron, and Hey[2] was employed in the oxidation of 0.25 g. of V. The yield of 2-nitrodiphenyl-4′-carboxylic acid was 0.12 g., m.p. 308-312°. Two recrystallizations from absolute ethanol raised the m.p. to 312-312.3° (lit.,[5] m.p. 313-315.1°).

3-Amino-p-terphenyl (VI). A solution of 5.5 g. of V in 130 ml. of dioxane was reduced catalytically using the method reported above for the preparation of II. A cream-colored solid, 4.43 g. (91%), was obtained, m.p. 163-173°. Recrystallization from petroleum ether gave a solid, m.p. 181-181.9°.

Anal. Calcd. for $C_{18}H_{15}N$: C, 88.13; H, 6.16. Found: C, 87.68; H, 6.12.

3-Acetylamino-p-terphenyl (VII). A solution of 2.27 g. of VI in 150 ml. of refluxing benzene was stirred while 4 ml. of acetic anhydride and 5 drops of pyridine were added. After stirring at room temperature for 1 hr. the solvent was removed by warming on a steam bath in a current of air. The amide was crystallized from an alcohol-petroleum ether mixture. The fine, white needles weighed 2.08 g. (76%), m.p. 218-219°.

Anal. Calcd. for $C_{20}H_{17}ON$: C, 83.59; H, 5.97. Found. C, 83.36; H, 5.96.

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(6) Melting points are uncorrected.

α-Oximino Ketones. IX. The Synthesis of α,ω-Diamino Acids from Cyclic Ketones

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In a series of publications from this laboratory several related routes for the conversion of cyclohexanone to DL-lysine have been described.[2-5]

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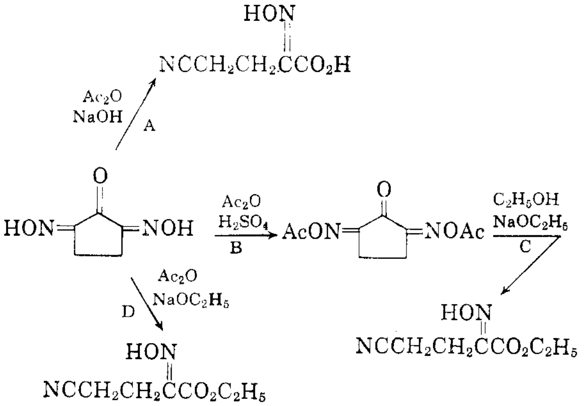
(1) Present address: General Aniline and Film Corp., Linden, N. J.

(2) A. F. Ferris, F. E. Gould, G. S. Johnson, H. K. Latourette, and H. Stange, *Chem. & Ind.* (*London*), **1959**, 996.

In all of these syntheses the first step was the nitrosation of cyclohexanone to 2,6-dioximinocyclohexanone, the second and key step was the partial cleavage of this molecule or an acylated derivative under the conditions of the second order Beckmann rearrangement[6] to 5-cyano-2-oximinovaleric acid or one of its esters, and the final step was the reduction of the acid or ester to DL-lysine. In the most successful variant of this reaction scheme an ethanolic solution of the sodium salt of 2,6-dioximinocyclohexanone was treated with acetic anhydride to give ethyl 5-cyano-2-oximinovalerate, and the ester was hydrogenated in acetic anhydride over Raney nickel and a basic co-catalyst. The overall yield of DL-lysine monohydrochloride from cyclohexanone was 63%.

In more recent work a study has been made to determine whether the techniques developed in the lysine work can be extended to the synthesis of other α,ω-diamino acids from cyclic ketones. Cyclopentanone and 4-methylcyclohexanone were chosen as model compounds. The nitrosation of these ketones to the α,α'-dioximino derivatives was described first by Borsche.[7] Nitrosation of the latter has been studied more recently by Batesky and Moon.[8] In our work 2,5-dioximinocyclopentanone was prepared in 47% yield and 2,6-dioximino-4-methylcyclohexanone was prepared in 72% yield by the technique described previously,[3] namely the treatment of the cyclic ketone in ether with methyl nitrite in the presence of hydrochloric acid. All three methods developed in the lysine studies for bringing about the partial cleavage of 2,6-dioximinocyclohexanone were tried with the new α,α'-dioximino compounds. The reactions involved were treatment of a solution of the dioxime in aqueous base with a deficiency of acetic anhydride (A), conversion of the α,α'-dioximino compound to the diacetyl derivative and treating the latter with sodium ethoxide in ethanol (B + C), and treatment of a suspension of the monosodium salt of the dioxime in ethanol with the stoichiometric amount of acetic anhydride (D). The three reaction schemes are shown in equation form below, using 2,5-dioximinocyclopentanone as the example.



As expected, relatively poor yields were obtained with reaction sequence A, almost certainly because of the fact, noted previously,[3] that the α-oximino acids themselves are cleaved under second order Beckmann conditions. Better yields were obtained in sequences BC and D, wherein advantage was taken of the discovery made in the course of the lysine work[4] that esters of α-oximino acids are not cleaved by Beckmann reagents. Since the ester partial cleavage products were obtained in much better yields than the free acids, reduction studies were carried out only with the esters. As in the lysine work[5] much better yields of α,ω-diamino acids were obtained when Raney nickel catalyst was used with acetic anhydride solvent in the hydrogenation step than when platinum was used. A summary of all yields obtained is presented in Table I.

TABLE I

YIELDS IN CONVERSION OF CYCLIC KETONES TO α,ω-DIAMINO ACIDS

	% Yields	
Step	Cyclopentanone	4-Methyl-cyclohexanone
Nitrosation	47	72
A[a]	18	24
B	30	53
C	82	86
D	59	62
Hydrogenation, Ni	77	63
Hydrogenation, Pt	16	18
Overall[b]	21	28

[a] Capital letters refer to letter steps in equations above. [b] Cyclic ketone to α,ω-diamino acid by best route.

The overall yields of ornithine and 4-methyllysine are considerably poorer than the 63% yield of lysine obtained from cyclohexanone, but this probably reflects only the more extensive study given to the lysine synthesis. It thus appears reasonable to predict that many α,ω-diamino acids can be obtained from the corresponding cyclic ketones in overall yields of 20–30%, with considerably better yields being possible if the significance of the synthesis justifies a study of refinements.

EXPERIMENTAL

All the techniques used in this study have been described in previous papers.[3-5] The physical properties and analyses of the compounds prepared are reported in Table II. The final column of the table gives the footnote number of the paper wherein the procedure used to prepare each compound was described in detail.

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TABLE II

INTERMEDIATES IN THE CONVERSION OF CYCLIC KETONES TO α,ω-DIAMINO ACIDS

Compound	M.P.[a]	Calcd.			Found			Ref.
		C	H	N	C	H	N	
2,5-Dioximinocyclopentanone	214 d.[b]	42.25	4.26	19.72	42.41	4.23	19.97	(3)
2,6-Dioximino-4-methylcyclohexanone	[c]	49.40	5.92	16.47	49.72	5.64	16.22	(3)
4-Cyano-2-oximinobutyric acid	123–125	42.25	4.26	19.72	42.24	4.11	19.84	(3)
5-Cyano-4-methyl-2-oximinovaleric acid	109–111	49.40	5.92	16.47	49.30	5.72	16.56	(3)
2,5-Diacetoximinocyclopentanone	177 dec.	47.79	4.46	12.39	48.02	4.42	12.38	(4)
2,6-Diacetoximino-4-methylcyclohexanone	171–172	51.96	5.55	11.02	51.80	5.64	11.32	(4)
Ethyl 4-cyano-2-oximinobutyrate	Liq.[d]	49.40	5.92	16.47	49.31	6.14	16.29	(5)
Ethyl 5-cyano-4-methyl-2-oximinovalerate	61	54.53	7.12	14.14	54.71	6.87	14.25	(5)
DL-Ornithine monohydrochloride	205–211 dec.	[e]						(5)
DL-4-Methyllysine monohydrochloride	229–230	42.74	8.71	14.25[f]	42.71	8.71	14.46[f]	(5)

[a] All melting points are uncorrected. [b] Lit.[7] m.p. 215° dec. [c] Decomposed at about 200°. [d] Not distilled, n_D^{25} 1.4750. [e] Infrared spectrum identical to that of authentic DL-ornithine monohydrochloride. [f] Calcd.: Cl, 18.03. Found: Cl, 18.10.

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Neopentyl Group Analogs. IV. Trimethylsilylmethyldichlorophosphine[1]

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Our recent work on the tris(trimethylsilylmethyl) derivatives of the Group VB elements[2] has prompted further work in the area of silicon-substituted phosphorus compounds. Of particular interest as a possible intermediate in the synthesis of silicon-substituted phosphonitrilic compounds was trimethylsilylmethyldichlorophosphine.

Conventional methods used to synthesize alkyldichlorophosphines utilize the reaction of phosphorus trichloride with mild alkylating agents, such as dialkylmercury[3] or tetraalkyllead[4] compounds. Accordingly, bis(trimethylsilylmethyl)mercury and tetrakis(trimethylsilylmethyl)lead, both new compounds, were prepared by the usual Grignard procedure, and their action on phosphorus trichloride was investigated. The mercurial did not react with phosphorus trichloride either when a mixture of the reactants was refluxed in hexane solution, or in the absence of solvent at *ca.* 76°. In contrast, the lead compound was cleaved by phosphorus trichloride, giving crystalline, sublimable tris(trimethylsilylmethyl)lead chloride and trimethylsilylmethyldichlorophosphine. However, the isolated yield of the phosphine was not very high, and a better synthesis was desired.

$$[(CH_3)_3SiCH_2]_4Pb + PCl_3 \longrightarrow [(CH_3)_3SiCH_2]_3PbCl + (CH_3)_3SiCH_2PCl_2$$

Although the Grignard procedure is not generally applicable to the synthesis of pure $RPCl_2$ compounds because mixtures of mono-, di-, and trisubstituted products result, it seemed possible that with the relatively bulky trimethylsilylmethyl group, monosubstitution could be realized in acceptable yield. Indeed, our previous work[2] showed that complete substitution of all three chlorine atoms of phosphorus trichloride with trimethylsilylmethyl groups by the Grignard procedure requires drastic conditions. It was found in the present work that addition of one equivalent of trimethylsilylmethylmagnesium chloride to one mole of phosphorus trichloride in ether at low temperature resulted in the desired trimethylsilylmethyldichlorophosphine in *ca.* 40% yield.

Attempted conversion of trimethylsilylmethyldichlorophosphine to trimethylsilylmethyltetrachlorophosphorane was not successful. Even at −20° in the dark addition of a solution of chlorine in *sym*-tetrachloroethane to trimethylsilylmethyldichlorophosphine caused cleavage of the carbon-silicon bond to form trimethylchlorosilane. This facile cleavage of the carbon-silicon bond may be due to the inductive effect of the PCl_4 group; electron withdrawal by this group would make the Si-C bond more polar, hence more susceptible toward ionic fission.

Investigation of the solid formed in the chlorination reaction showed it to be impure phosphorus pentachloride rather than the expected chloromethyltetrachlorophosphorane. The hydrolysis product of this solid formed a barium salt of very low carbon content, and an anilinium salt could be prepared which was shown to be $[C_6H_5NH_3][H_2PO_4]$. It is not known at what point fission of the

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