*Anal.* Calcd. for $C_{22}H_{19}N$: C, 88.90; H, 6.40; N, 4.70. Found: C, 89.21; H, 6.30; N, 4.79.

**Dehydrocyanation of II**, conducted as described for I, gave an 80% yield of 1,1,2-triphenylpropene-1 (V), m.p. 86–87°;[10] reported m.p. 86–87° and 89–90°.[11]

**2,2,3,3-Tetraphenylpropionitrile (III).**—This compound was prepared by the alkylation of diphenylacetonitrile with either benzhydryl chloride or bromide essentially as described for the benzylation. The crude product was crystallized from ethylene glycol diether to give a 96% yield of III melting at 242° dec.

*Anal.* Calcd. for $C_{27}H_{21}N$: C, 90.21; H, 5.89; N, 3.90. Found: C, 90.36; H, 6.06; N, 4.09.

**Dehydrocyanation of III** was carried out as described for I except that the liquid ammonia–ether reaction solution was stirred for two hours. The ammonia was then removed and water added. After removal of the ether the aqueous mixture was filtered, and the solid recrystallized three times from a mixture of benzene and methanol to yield 44% of tetraphenylethylene, m.p. and mixed m.p. 220–221°. Titration of the aqueous filtrate with silver nitrate[12] accounted for 37% of the cyanide ion. Since a blank experiment employing potassium cyanide showed that only 47% of the original cyanide ion would have remained in the aqueous filtrate, it may be concluded that about 75% of nitrile III was dehydrocyanated.

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(10) K. Ziegler, H. Grabbe and F. Ulrich, *Ber.*, **57B**, 1983 (1924).

(11) J. Levy, *Bull. soc. chim. France*, [4] **29**, 878 (1921).

(12) W. C. Pierce and E. L. Haenisch, "Qualitative Analysis," John Wiley and Sons, Inc., New York, N. Y., p. 305.

DURHAM, NORTH CAROLINA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON COLLEGE]

# The Synthesis of α-Amino-*o*-tolualdehyde Diethylacetal and its Attempted Conversion to Pseudoisoindole

BY JOSEPH BORNSTEIN, STANLEY F. BEDELL,[1] PAUL E. DRUMMOND[1] AND CLEMENT L. KOSLOSKI[1]

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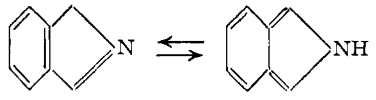
A number of attempts to prepare pseudoisoindole (I) by the acid-catalyzed pyrolysis of α-amino-*o*-tolualdehyde diethylacetal (III) has given only resinous substances. The starting compound for the synthesis of III, α-phthalimido-*o*-toluic acid (IV), was obtained by the condensation of phthalide with potassium phthalimide in dimethylformamide followed by acidification. The structure of the acid IV was established by an independent, but less direct, Gabriel phthalimide synthesis, and also by degradation. Treatment of IV with thionyl chloride followed by a Rosenmund–Zetzsche reduction of the resulting α-phthalimido-*o*-toluyl chloride (V) produced α-phthalimido-*o*-tolualdehyde (VI). The aldehyde VI afforded α-phthalimido-*o*-tolualdehyde diethylacetal (VII) on treatment with ethyl orthoformate. Cleavage of VII by hydrazine yielded the amino acetal III. The average over-all yield of III in four preparations was *ca.* 25%.

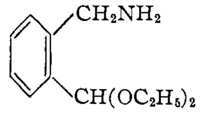
In connection with studies on the aromatic character of heterocyclic compounds, we undertook the preparation of pseudoisoindole (I), the tautomer of the hypothetical compound, isoindole (II).[2]

Since Barber and co-workers[3] were able to prepare Schiff bases by the pyrolysis of mixtures of ketals and primary amines in the presence of catalytic amounts of ammonium chloride, this method was chosen as the most promising route to pseudoisoindole, a cyclic Schiff base.



I II

Accordingly the amino acetal necessary for the attempted synthesis of I, α-amino-*o*-tolualdehyde diethylacetal (III), was prepared in consistently good yield by a convenient five-step process employing phthalide and potassium phthalimide as the starting materials.



III

Condensation of phthalide with potassium phthalimide in dimethylformamide at reflux temperature followed by acidification of the reaction mixture afforded, after purification, 60% yields of α-phthalimido-*o*-toluic acid (IV). The structure of the acid was proved by comparison with a sample of IV obtained from ethyl α-phthalimido-*o*-toluate (IVa) by acidolysis with formic acid containing catalytic amounts of concentrated sulfuric acid, since treatment of IVa with even mildly alkaline reagents invariably opened the ring of the phthalimido substituent. The ethyl ester IVa was obtained by treating ethyl α-bromo-*o*-toluate[4] with potassium phthalimide in dimethylformamide. In addition to having identical melting points (not depressed on admixture), both specimens of IV yielded the same dibasic acid, α-(*o*-carboxybenzamido)-*o*-toluic acid (IVb), on solution in aqueous sodium hydroxide followed by precipitation with dilute hydrochloric acid. Heating of the dicarboxylic acid IVb in glacial acetic acid for eight hours re-formed the monobasic acid IV. It was of interest to note that the direct heating of IVb in the absence of a solvent at temperatures slightly above its melting point not only yielded the expected acid IV, but also a sublimate of phthalic anhydride, indicating that some cleavage of IVb had occurred. Cleavage of a sample of IVb (from IV prepared by the phthalide–potassium phthalimide procedure) by hydrochloric acid yielded the expected products, phthalic acid and phthalimidine, both characterized by com-

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(1) Abstracted in part from the M.S. theses of Stanley F. Bedell, Paul E. Drummond and Clement L. Kosloski.

(2) *Cf.* R. C. Elderfield and T. N. Dodd, Jr., in R. C. Elderfield, "Heterocyclic Compounds," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 275, for a summary of the historical background of isoindole.

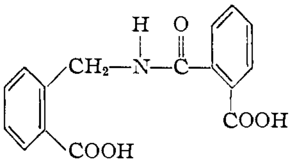
(3) H. J. Barber and W. R. Wragg, *J. Chem. Soc.*, 610 (1946); H. J. Barber, D. H. O. John and W. R. Wragg, THIS JOURNAL, **70**, 2282 (1948).

(4) W. Davies and W. H. Perkin, *J. Chem. Soc.*, **121**, 2022 (1922); J. C. Sheehan and W. A. Bolhofer, THIS JOURNAL, **72**, 2786 (1950).

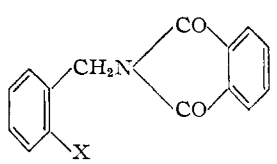
parison with authentic samples, and by comparison of their derivatives with authentic specimens as well. Finally, treatment of the acid obtained from the phthalide–potassium phthalimide condensation with ethereal diazoethane yielded a compound identical with the ethyl ester IVa obtained from the reaction of ethyl α-bromo-*o*-toluate with potassium phthalimide.

Treatment of IV with thionyl chloride gave 80–90% yields of the corresponding acid chloride, α-phthalimido-*o*-toluyl chloride (V). Hydrogenation of V in xylene by the Rosenmund–Zetzsche method[5] yielded α-phthalimido-*o*-tolualdehyde (VI) (80%). The aldehyde VI was characterized as the crystalline 2,4-dinitrophenylhydrazone. The conversion of VI to α-phthalimido-*o*-tolualdehyde diethylacetal (VII) was best effected with ethanolic ethyl orthoformate in the presence of catalytic amounts of ferric chloride. The infrared absorption spectrum of VII in carbon tetrachloride showed the two characteristic carbonyl bands of the phthalimido moiety, one at 5.62 $\mu$ and the other (more intense) at 5.82 $\mu$. Hydrazinolysis[5a,b] of the phthalimido acetal VII followed by aqueous potassium hydroxide yielded α-amino-*o*-tolualdehyde diethylacetal (III) as a colorless oil (68–72%), which rapidly absorbed carbon dioxide from the air to give a white solid (presumably the carbamate).[6] The infrared spectrum of III (carbon tetrachloride solution) exhibited two bands, one at 2.92 $\mu$ and the other at 3.01 $\mu$ indicative of a primary aliphatic amine, and very strong absorption throughout the acetal region.[7] III was further characterized by conversion to the solid phenylthiourea derivative.

Originally, we had hoped to prepare III by treating α-bromo-*o*-tolualdehyde diethylacetal with ammonia.[8] However, this approach was abandoned when preliminary attempts to synthesize the intermediate bromoacetal by the halogenation of *o*-tolualdehyde diethylacetal with elemental bromine[9] indicated the method to be unpromising. Our efforts to effect this bromination with N-bromosuccinimide or N-bromoacetamide under a variety of conditions were also disappointing.



IVb



IV, X = COOH
IVa, X = $COOC_2H_5$
V, X = COCl
VI, X = CHO
VII, X = $CH(OC_2H_5)_2$

No pseudoisoindole could be isolated from the pyrolysis of α-amino-*o*-tolualdehyde diethylacetal in a nitrogen atmosphere in the presence of small amounts of ammonium chloride. In addition to the reddish-violet resins which were consistently obtained in the course of several attempts to effect ring closure by this method, nearly the theoretical yields of ethanol were always isolated from the distillates, indicating possibly that the desired intramolecular aminolysis was occurring, although an intermolecular aminolysis could likewise account for the formation of ethanol. It was thought that the polymerization might be avoided by carrying out the reaction in a solvent, but heating benzene or xylene solutions of III under reflux in the presence of ammonium chloride or *p*-toluenesulfonic acid gave mixtures of polymer and unreacted starting material. Further efforts to convert III to I (*via* the intermediate amino aldehyde derived from III) over a wide temperature range in aqueous ethanol containing acids of various strengths were likewise unrewarding; only mixtures of unreacted III and polymers were isolated. All attempts to depolymerize the resinous products by heating them under vacuum failed.

Although the formation of resins from the acid-catalyzed pyrolysis of III may be due to a number of causes, two possibilities merit particular consideration. Either an intermolecular reaction occurs to yield directly a chain-like polymer held together by azomethine linkages or, more probably, the desired intramolecular aminolysis takes place to yield pseudoisoindole which subsequently polymerizes under the conditions of the experiment. Since pseudoisoindole is a nitrogen analog of indene, a molecule well known for its marked tendency to polymerize in the presence of acids,[10] it is not unreasonable to assume that pseudoisoindole by virtue of the basic properties of the nitrogen atom, might undergo an indene-type polymerization even more readily than indene. Some evidence for such a basic polymer is found in the ready solubility of the polymer in dilute hydrochloric acid. Basification of the resulting solution afforded a precipitate which was polymeric, but which was not examined further.

It appears, therefore, that pseudoisoindole is unstable under the acidic conditions needed for the ring closure of III.

## Experimental[11]

**Ethyl α-Phthalimido-*o*-toluate (IVa).**—A mixture of 28.0 g. (0.115 mole) of ethyl α-bromo-*o*-toluate[4] and 41.5 g. (0.222 mole) of potassium phthalimide (purified by digestion with acetone) in 200 ml. of dimethylformamide was stirred for 30 minutes without external heating and was then warmed for one hour at 60° with continued stirring. Upon cooling to room temperature the reaction mixture was treated with 100 ml. of chloroform and the resulting mixture was poured into 250 ml. of water. The aqueous layer was separated and extracted with two 50-ml. portions of chloroform. The combined chloroform extract was dried over anhydrous sodium sulfate after being washed successively

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(5) (a) K. Balenović, I. Jambrešić and I. Furić, *J. Org. Chem.*, **17**, 1459 (1952); (b) K. Balenović, N. Bregant, D. Cerar, D. Fleš and I. Jambrešić, *ibid.*, **18**, 297 (1953); (c) E. Mosettig and R. Mozingo in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 362; (d) E. Radde, *Ber.*, **55**, 3176 (1922).

(6) H. B. Wright and M. B. Moore, This Journal, **70**, 3865 (1948).

(7) E. D. Bergmann and S. Pinchas, *Rec. trav. chim.*, **71**, 161 (1952).

(8) *Cf.* O. Bayer, "Methoden der Organischen Chemie," Vierte Auflage, Vol. VII/1, Georg Thieme Verlag, Stuttgart, 1954, pp. 289, 380–382, 403–404, 425–426, for a detailed discussion of the general method for preparing amino acetals by the ammonolysis or aminolysis of halo acetals.

(9) W. H. Hartung and H. Adkins, This Journal, **49**, 2520 (1927); W. T. Simpson, *ibid.*, **71**, 754 (1949).

(10) G. S. Whitby and M. Katz, *ibid.*, **50**, 1160 (1928); *Can. J. Research*, **4**, 344 (1931); J. Risi, *ibid.*, **13B**, 228 (1935).

(11) Melting points are corrected and boiling points are uncorrected. Infrared measurements were made using a Baird double beam recording spectrophotometer equipped with a sodium chloride prism. Elemental analyses were performed by Dr. Carol K. Fitz, Needham Heights, Massachusetts.

with 60 ml. of cold 10% sodium carbonate and 60 ml. of water. Evaporation of the chloroform under a stream of nitrogen while warming on the steam-bath yielded a white solid which was washed with ether and recrystallized twice from 60% ethanol, Norit being used in the first recrystallization. The yield of IVa, obtained as white, felted needles, was 25 g. (70%), m.p. 135.2–136°.

*Anal.* Calcd. for $C_{18}H_{15}O_4N$: C, 69.87; H, 4.89; N, 4.53. Found: C, 69.9; H, 5.0; N, 4.7.

**α-Phthalimido-*o*-toluic Acid (IV). A. By Acidolysis of Ethyl α-Phthalimido-*o*-toluate (IVa).**—A suspension of 30.0 g. (0.097 mole) of IVa, 100 ml. of formic acid (98–100%) and 1 ml. of concentrated sulfuric acid was heated under reflux for two hours. Concentration of the resulting solution to a small volume by distillation at atmospheric pressure, followed by addition of 150 ml. of water to the residue, gave a grey solid which was filtered and recrystallized from glacial acetic acid (Norit). The acid IV was obtained in nearly quantitative yield as coarse, white needles, m.p. 266–267°. The compound was identical (no depression of the m.p. on admixture) with the material described below, prepared by the condensation of phthalide with potassium phthalimide.

**B. By Condensation of Phthalide with Potassium Phthalimide.**—A mixture of 100.0 g. (0.745 mole) of phthalide, 150.0 g. (0.811 mole) of potassium phthalimide (purified by digestion with acetone) and 500 ml. of dimethylformamide was heated under reflux for six hours and then allowed to cool to room temperature. The resulting deep blue solution was poured slowly into a stirred solution of 300 ml. of glacial acetic acid in 500 ml. of water. Stirring of the light yellow suspension was continued for 30 minutes. The solid was separated, washed with 100 ml. of water and 100 ml. of 95% ethanol, and then digested with 500 ml. of 60% ethanol at reflux temperature for ten minutes. The crude IV was collected by filtration and dried in the oven at 85° overnight. Recrystallization from propionic acid (Norit, solution allowed to cool gradually to room temperature and then refrigerated overnight) gave 123 g. (59%) of IV as thick white needles, m.p. 266–267°, sufficiently pure for use in preparing V. The average yield of IV in six preparations was 60%. The analytical sample was recrystallized twice from glacial acetic acid, m.p. unchanged.

*Anal.* Calcd. for $C_{16}H_{11}O_4N$: C, 68.32; H, 3.94; N, 4.98. Found: C, 68.4: H, 4.0; N, 5.1.

The mixed m.p. with a sample of IV prepared by the procedure described above was 266–267°.

The ethyl ester of IV (from phthalide and potassium phthalimide) was prepared by treating a suspension of IV in ether with ethereal diazoethane. Removal of solvent *in vacuo* from the solution left white crystals which melted at 135–136° after recrystallization from 60% ethanol.

**α-(*o*-Carboxybenzamido)-*o*-toluic Acid (IVb).**—α-Phthalimido-*o*-toluic acid (5.0 g., 17.8 mmoles) was dissolved in a solution of 2.0 g. of sodium hydroxide in 30 ml. of water at room temperature. The solution was treated with Norit, filtered, and the stirred filtrate made acidic by the gradual addition of dilute hydrochloric acid. After standing at room temperature for four hours, the white product was collected by filtration, washed three times with 10-ml. portions of cold water, and dried at 100° for two hours. The yield of IVb was 5.0 g. (94%), m.p. 186–212°, with vigorous effervescence. The analytical sample was recrystallized twice from 60% ethanol to give long, white, felted needles, m.p. unaltered.

*Anal.* Calcd. for $C_{16}H_{13}O_5N$: C, 64.21; H, 4.38; N, 4.68; neut. equiv., 149.6. Found: C, 64.5; H, 4.3; N, 4.8; neut. equiv., 147.1, 149.3.

When the dicarboxylic acid IVb (200 mg.) was heated under reflux with 5 ml. of glacial acetic acid for eight hours the phthalimido ring was re-formed, since 60 mg. of IV (m.p. 265.6–267°, mixed melting point with authentic sample of IV not depressed) deposited from the solution on standing at room temperature overnight. Evaporation of the mother liquor gave a crystalline residue, m.p. 71–150°, apparently a mixture, which was not further examined.

Heating of IVb in the absence of a solvent in a bath of silicone oil at 210–215° for 15 minutes yielded a sublimate of phthalic anhydride, m.p. 131.5–132.0°, not depressed on admixture with an authentic sample,[12] and a residue which after recrystallization from glacial acetic acid had m.p. 266–267°, not depressed on admixture with an authentic sample of IV, prepared from phthalide and potassium phthalimide, by the procedure described above.

A mixture of 2.0 g. of α-(*o*-carboxybenzamido)-*o*-toluic acid (IVb), 20 ml. of concentrated hydrochloric acid and 10 ml. of glacial acetic acid was heated under reflux for 27 hours. The solution was diluted with 3 ml. of water and allowed to stand at room temperature overnight. The precipitate of phthalic acid was filtered and purified by reprecipitation from dilute ammonium hydroxide with dilute hydrochloric acid (Norit). The identity of the phthalic acid was confirmed by its m.p. 201–202°, mixed m.p. 201–202° with an authentic sample, and by conversion to phthalanil, m.p. 207–208°, not changed on admixture with an authentic specimen.[12] On concentration of the mother liquor from the hydrolytic cleavage to a volume of *ca.* 4 ml., an additional small amount of phthalic acid separated which was removed by filtration. The mother liquor was then divided into two equal portions. One portion was made strongly acid with dilute hydrochloric acid and on treatment with aqueous sodium nitrite gave immediately a precipitate of N-nitrosophthalimidine, identified after recrystallization from water by its m.p. 158.5–159.2°, not depressed on admixture with an authentic sample.[13] The second portion of the mother liquor was made slightly basic to litmus by adding dilute sodium hydroxide. Refrigeration of the solution for several hours yielded phthalimidine, which on recrystallization from water (Norit) was obtained as fine, white, felted needles, m.p. 152.5–152.8°, not depressed on admixture with an authentic specimen.[13]

**α-Phthalimido-*o*-toluyl Chloride (V).**—A suspension of 100.0 g. (0.355 mole) of α-phthalimido-*o*-toluic acid in 110 ml. (180.2 g., 1.51 moles) of freshly redistilled thionyl chloride was heated under reflux for four hours. Dry benzene (100 ml.) was then added to the reaction mixture and refluxing continued for an hour. The reaction mixture was concentrated almost to dryness by cautious distillation at atmospheric pressure of the benzene and excess thionyl chloride (oil-bath at 108–110°). To the crystalline residue was added 100 ml. of benzene and the suspension was concentrated to dryness by distillation as described above in order to remove further traces of thionyl chloride; the process was repeated twice with 100-ml. portions of benzene. The solid residue was dissolved in the minimum amount of boiling toluene (dried over sodium), the solution treated with Norit and filtered. After refrigeration of the filtrate, the product was collected by filtration, washed with a small volume of dry ether, and dried over phosphorus pentoxide and paraffin chips under vacuum. The yield of V, obtained as thick, white prisms, sufficiently pure for use in preparing the aldehyde VI, was 98.0 g. (92%), m.p. 182.5–184.0°. The average yield in five preparations was 85%. The analytical sample was recrystallized twice from benzene to give m.p. 183.5–184.8°.

*Anal.* Calcd. for $C_{16}H_{10}NO_3Cl$: Cl, 11.83. Found: Cl, 11.7.

The acid chloride V was characterized by conversion to ethyl α-phthalimido-*o*-toluate (IVa), effected by heating under reflux a mixture of 1.0 g. of V and 10 ml. of anhydrous ethanol for three hours. Evaporation of the solution to dryness, followed by recrystallization of the resulting solid residue from 60% ethanol, yielded IVa as white needles, m.p. 135–136°, not depressed on admixture with an authentic sample of IVa, prepared from the reaction of ethyl α-bromo-*o*-toluate with potassium phthalimide as described above.

**α-Phthalimido-*o*-tolualdehyde (VI).**—A rapid stream of purified hydrogen was passed into a boiling suspension of 15 g. of 5% palladium–barium sulfate catalyst in 700 ml. of xylene (redistilled, dried over sodium) containing 1.5 ml. of quinoline-sulfur regulator (ref. 5c, p. 368) in a 1-l. three-necked flask equipped with a small distilling head and a sealed stirrer. The gas inlet tube was provided with a sliding glass rod plunger, which was sealed by means of a piece of heavy rubber tubing. After *ca.* 20 ml. of distillate had been collected, 97.0 g. (0.323 mole) of V was added and the distilling head was replaced with a condenser connected to a trap to absorb the evolved hydrogen chloride. Gentle refluxing and vigorous stirring were maintained while a brisk

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[12] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Order I, John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 148–149, 163–164.

[13] C. Graebe, *Ann.*, **247**, 291 (1888); A. Oppe, *Ber.*, **46**, 1099 (1913).

stream of hydrogen was passed through the mixture for 6.5 hours. Usually, over 85% of the theoretical amount of hydrogen chloride was evolved during this length of time. Plugging of the gas inlet tube was avoided by occasional use of the glass plunger. The hot reaction mixture was treated with Norit and filtered immediately through a heated funnel. Refrigeration of the filtrate overnight yielded 70.0 g. (82%) of VI as white plates, after being washed on the funnel with cold xylene and being dried *in vacuo*. We could not obtain a sharp melting point in open capillary tubes for VI, which apparently decomposes on heating. The most reproducible value for the melting point of VI, sealed capillary tube inserted in bath at 170°, was 183–185°. The product is of adequate purity for use in preparing the corresponding diethylacetal (VII), however. Attempts to recrystallize VI from high boiling solvents in air often led to extensive decomposition. The analytical sample was recrystallized once from absolute ethanol, m.p. unchanged.

*Anal.* Calcd. for $C_{16}H_{11}O_3N$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.3; H, 4.3; N, 5.3.

The average yield of VI in three preparations was 80%.

The **2,4-dinitrophenylhydrazone of VI**, prepared in the usual manner, was obtained as orange-yellow needles from glacial acetic acid, m.p. 259.5–260°.

*Anal.* Calcd. for $C_{22}H_{15}O_6N_5$: N, 15.71. Found: N, 15.8.

**α-Phthalimido-*o*-tolualdehyde Diethylacetal (VII).**—A mixture of 69.0 g. (0.260 mole) of α-phthalimido-*o*-tolualdehyde, 44.0 g. (0.297 mole) of freshly redistilled ethyl orthoformate, 150.0 g. of freshly dried ethanol and *ca.* 100 mg. of ferric chloride was heated under reflux, under anhydrous conditions, for 2.5 hours. Usually complete solution was attained within 20 minutes from the start of refluxing. The yellow solution was allowed to cool slowly to room temperature and the resulting suspension was chilled overnight in the freezing compartment of the refrigerator. The solid was pulverized while still in the flask, filtered and washed with a small volume of chilled commercial absolute ethanol in order to remove traces of ferric chloride. All of these operations were carried out as rapidly as possible so as to avoid excessive exposure to VII to the moisture of the atmosphere. Final drying of the acetal VII, obtained as white needles, m.p. 72–73°, was carried out *in vacuo* over phosphorus pentoxide. The yield of VII, of sufficient purity for use in the following reaction, was 71.0 g. (80%). Dilution of the mother liquor with 250 ml. of water containing 1 ml. of concentrated hydrochloric acid caused 12.5 g. of α-phthalimido-*o*-tolualdehyde to precipitate. The analytical sample was recrystallized from petroleum ether (b.p. 30–65°) to a constant melting point of 73.0–73.5°.

*Anal.* Calcd. for $C_{20}H_{21}O_4N$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.6; H, 6.3; N, 4.2.

The average yield of VII in four preparations was 80%. The infrared spectrum of VII in carbon tetrachloride showed absorptions at 5.62 and 5.82 $\mu$ consistent with the presence of a phthalimido substituent, and very strong absorption in in the region from 8.55 to 9.55 $\mu$, compatible with the presence of an acetal function.

**α-Amino-*o*-tolualdehyde Diethylacetal (III).**—To a solution of 6.5 ml. of 85% hydrazine hydrate in 275 ml. of 95% ethanol was added 35.0 g. (0.103 mole) of α-phthalimido-*o*-tolualdehyde diethylacetal. The stirred mixture was heated under reflux for 1.5 hours. Within 15 minutes from the start of refluxing, the solution turned light green and a white solid (probably the salt of the base, α-amino-*o*-tolualdehyde diethylacetal, with phthalyl hydrazide[14]) began to separate. Ether (250 ml.) was added to the cooled suspension, which was then treated with a solution of 30.0 g. of potassium hydroxide in 175 ml. of water with stirring. The two layers were separated and the aqueous layer was extracted with three 150-ml. portions of ether which were added to the organic layer. The ether extract was dried over potassium carbonate, after being washed with four 100-ml. portions of water containing a trace of potassium carbonate. The solvent was removed at diminished pressure under nitrogen and the residue distilled to yield 15.0 g. (70%) of III as a colorless oil, b.p. 105–106° (1.2 mm.), $n^{25}$D 1.5059.

*Anal.* Calcd. for $C_{12}H_{19}O_2N$: C, 68.87; H, 9.15; N, 6.66. Found: C, 68.6; H, 9.1; N, 6.7.

The product rapidly absorbed carbon dioxide from the air to give a white solid (probably the carbamate).[6] The infrared spectrum of III in carbon tetrachloride exhibited bands at 2.92 and 3.01 $\mu$ consistent with the presence of an aliphatic primary amine function, and strong absorptions in the acetal region.

**The phenylthiourea derivative of III**, prepared in the usual manner from phenyl isothiocyanate, was obtained as white, felted needles, m.p. 95.6–96.3°, after successive recrystallizations (four times) from ethanol containing a trace of potassium hydroxide and anhydrous ligroin (twice).

*Anal.* Calcd. for $C_{19}H_{24}O_2N_2S$: C, 66.25; H, 7.02. Found: C, 66.4; H, 7.0.

**Pyrolysis of α-Amino-*o*-tolualdehyde Diethylacetal in the Presence of Ammonium Chloride.**—A stirred mixture of α-amino-*o*-tolualdehyde diethylacetal (3.8 g., 18.2 mmoles) and ammonium chloride (100 mg., 1.87 mmoles), under an atmosphere of nitrogen, in a flask fitted with a small distilling head, was inserted in an oil-bath preheated to 100°. The temperature of the bath was raised to 155° over a period of 25 minutes at the end of which time the heating was stopped. Redistillation of the straw-colored, ammoniacal distillate afforded 1.60 g. (96%) of ethanol and traces of a yellow, oily residue, which could not be identified because of the lack of material. The identity of the ethanol was established by means of its b.p. (78°), positive iodoform test and the 3,5-dinitrobenzoate, m.p. 92–93°, not depressed on admixture with an authentic sample.[15]

The pyrolysate was a reddish-violet, granular polymer which was readily soluble in ethanol, in acetone and in dilute hydrochloric acid. Treatment of the light-green hydrochloric acid solution of the polymer with excess 1 *N* sodium hydroxide gave a polymeric precipitate, which was not examined further. The polymer could not be depolymerized by heating it at 160° and 0.5 mm.

No evidence of pseudoisoindole was obtained from this procedure or from modified procedures.

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(14) H. J. Barber and W. R. Wragg, *Nature*, **158**, 514 (1946).

(15) Reference 12, p. 428.