A solution of this oxime (451 g.) in a mixture of 1080 cc. of glacial acetic acid and 455 cc. of acetic anhydride was cooled in ice and saturated with gaseous hydrogen chloride. The solution was then allowed to stand at 40° for sixty to seventy hours, cooled in ice and filtered (sintered glass!) with suction, using a rubber dam to squeeze out as much of the liquid as possible. The filter cake was immediately mixed with 820 cc. of concentrated hydrochloric acid and refluxed until a homogeneous solution was obtained (two hours). The 3,4-dimethylaniline hydrochloride could be obtained merely by crystallization from the cooled reaction mixture. However, to obtain the free base, the reaction mixture was made alkaline with aqueous sodium hydroxide, extracted with ether, dried and distilled. In this manner there was obtained 238 g. (25% yield from fenchone) of pure 3,4-dimethylaniline, b. p. 132–134° (45 mm.); m. p. 50–51°

Acknowledgment.—The author wishes to thank Dr. E. H. Volwiler and Dr. D. L. Tabern for advice and encouragement during the course of this work.

ABBOTT LABORATORIES
NORTH CHICAGO, ILLINOIS RECEIVED AUGUST 10, 1945

NEW COMPOUNDS

p-Di-(β-chloro-*t*-butyl)-benzene

Although the preparation of (β-chloro-*t*-butyl)-benzene by the reaction of benzene with methallyl chloride in the presence of sulfuric acid[1] or hydrogen fluoride[2] has been described, the formation of a crystalline di-substituted compound analogous to *p*-di-*t*-butylbenzene has not hitherto been reported.

A solution of 300 g. (3.3 moles) of methallyl chloride in 300 g. (3.8 moles) of benzene was added during two hours to a well-stirred mixture of 500 g. (6.4 moles) of benzene and 400 g. of 96% sulfuric acid at 0–5°. After an additional one-half hour of stirring, the upper layer was separated from the 433 g. of lower layer, washed with water, dried, and distilled under reduced pressure. Neophyl chloride (*i. e.*, (β-chloro-*t*-butyl)-benzene) boiling at 90–91° at 9 mm. mercury pressure, $n^{20}D$ 1.5250, was obtained in 67% of the theoretical yield. The higher-boiling residue (55 g.) was a dark brown oil which became partly crystalline (long white needles) on standing. The mixture of oil and crystals was cooled in an ice–salt-bath and then filtered through a sintered glass plate. Recrystallization of the solid from alcohol yielded 11 g. (2.6% of the theoretical) of *p*-di-(β-chloro-*t*-butyl)-benzene, thick needles, m. p. 54.5–55°.

Anal. Calcd. for $C_{14}H_{20}Cl_2$: Cl, 27.36. Found: Cl, 27.36. No attempt was made to recover more of the compound from the filtrates.

The orientation of the chloroalkyl groups was proved by oxidizing 1 g. of the compound by refluxing it for twenty hours with a solution of 5 g. of sodium dichromate and 5 cc. of concentrated sulfuric acid in 100 cc. of water. Terephthalic acid was obtained; its identity was confirmed by means of its dimethyl ester, m. p. 140°.

Calcott, Tinker and Weinmayr,[2] using hydrogen fluoride as catalyst, obtained a 66% yield of neophyl chloride and a 20% yield of a liquid product, boiling at 140° at 4 mm., which they considered to be "di-(1'-chloro)-*t*-butylbenzene." Their product may have been a different isomer. More probably it was impure owing to loss of hydrogen chloride during distillation; the product contained only 25.6% chlorine.

(1) F. C. Whitmore, C. A. Weisberger and A. C. Shabica, Jr., THIS JOURNAL, **65**, 1469 (1943).

(2) W. S. Calcott, J. M. Tinker and V. Weinmayr, *ibid.*, **61**, 1010 (1939).

RESEARCH LABORATORIES
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RECEIVED JULY 20, 1945

t-Butylphthalimide[1]

t-Butylurea, m. p., 175–180°, was prepared in 86% yield by the method of Harvey and Caplan.[2] An intimate mixture of *t*-butylurea (35 g., 0.3 mole) and phthalic anhydride (100 g., 0.67 mole) is placed in a large (1000 cc.) container which is then plunged into a bath at 200°. After the initial vigorous effervescence subsides (ten minutes) the temperature of the bath is raised to 240° and maintained there for five minutes. Rapid heating is essential; the reaction is usually over in fifteen minutes. The cooled product is partially dissolved in alcohol (100 cc.) and the mixture is made alkaline (litmus) by addition of aqueous sodium carbonate. The mixture is diluted with water to a volume of 1 liter, the solid is transferred to a Büchner funnel, pressed as dry as possible, and then warmed with petroleum ether (500 cc., b. p. 60–68°). The hot mixture is filtered and, after the filtrate is separated from the water layer (if any appears), it is cooled to room temperature. Any insoluble material is removed, and the clear filtrate is concentrated by distillation to about one-third of its original volume and set aside in a refrigerator. The crystalline material is filtered with suction and pressed as dry as possible. It weighs 43.5 g. and melts at 59–60° By concentration of the filtrate, a further 3 g. may be obtained; this also melts at 59–60°. The total yield, 46.5 g., is 76%.

Anal. Calcd. for $C_{12}H_{13}O_2N$: C, 70.93; H, 6.40 Found: C, 70.95; H, 6.26.

This procedure is based upon the general procedure of Manske for conversion of alkyl ureas to phthalimides.[3] When an alcoholic solution of the phthalimide is hydrolyzed by action of hydrazine hydrate[4] and then acidified, *t*-butylamine hydrochloride can be obtained in 89% yield. The combination of the three steps from *t*-butyl alcohol to *t*-butylamine *via* the urea and phthalimide constitutes the best method for preparation of *t*-butylamine.

(1) The work described herein was done under contract with the Office of Scientific Research and Development, which assumes no responsibility for the accuracy of the statements herein.

(2) Harvey and Caplan, U. S. Patent 2,247,495, July 1, 1941; *Chem. Abs.*, **35**, 6267 (1941).

(3) Manske, THIS JOURNAL, **51**, 1202 (1929); see also Tingle and Brenton, *ibid.*, **32**, 116 (1910).

(4) Ing and Manske, *J. Chem. Soc.*, 2348 (1926).

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RECEIVED AUGUST 29, 1945

p-Aminobenzanilide and Derivatives

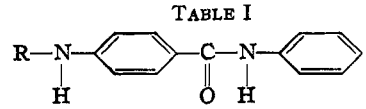
In the course of other investigations a considerable amount of *p*-aminobenzanilide was needed. Its preparation was previously described by several authors.[1,2,3] Rivier and Kunz[3] reported a yield of 70% of *p*-aminobenzanilide by reduction of *p*-nitrobenzanilide with stannous chloride and hydrochloric acid. Their method has been repeated, resulting in a yield of 90%. Other reducing agents, such as tin and hydrochloric acid, zinc and acetic acid, zinc and hydrochloric acid, or Raney nickel in alcohol,

(1) *Friedlander*, **4**, 752 (1895).

(2) H. Kupferberg, *J. prakt. Chem.*, [2] **16**, 444 (1877).

(3) H. Rivier and S. Kunz, *Helv. Chim. Acta*, **15**, 376 (1932).

TABLE I



R	Solvent for recrystn.	Cryst. form	Yield, %	M. p., °C.	Empirical formula	N Analyses, % Calcd.	Found
Acetyl	Acet. + alc.	Prisms	65	211.5	$C_{15}H_{14}N_2O_2$	11.02	11.05
n-Propionyl	Alcohol	Prisms	100	230 (dec.)	$C_{16}H_{16}N_2O_2$	10.45	10.57
n-Butyryl	Acet. + alc.	Prisms	86	231	$C_{17}H_{18}N_2O_2$	9.93	9.90
iso-Butyryl	Alcohol	Prisms	97	285 (dec.) m. > 360	$C_{17}H_{18}N_2O_2$	9.93	9.81
n-Valeryl	Alcohol	Cluster of needles	78	227	$C_{18}H_{20}N_2O_2$	9.46	9.89
Benzoyl	Acetic acid	Plates	98	323–324 (dec.)	$C_{20}H_{16}N_2O_2$	8.86	8.51
p-Nitrobenzoyl	Pyridine	Needles	100	298 (dec.)	$C_{20}H_{15}N_3O_4$	11.64	11.52
N-Acetyl-4-aminobenzoyl	Acetone	Granules	...	245–246 (dec.)	$C_{22}H_{19}N_3O_3$	11.26	11.13
Benzenesulfonyl	Alcohol	Fine needles	100	210.5 (dec.)	$C_{19}H_{16}N_2O_3S$	7.95	7.75
p-Bromobenzenesulfonyl	Acetone	Needles	74	240–241	$C_{19}H_{15}BrN_2O_3S$	6.50	6.66
2-Naphthalenesulfonyl	Acetone	Cluster of fine needles	95	230	$C_{23}H_{18}N_2O_3S$	6.96	6.94

have been tried. Only the reduction by tin and hydrochloric acid is satisfactory. The picrate of *p*-aminobenzanilide was prepared in a yield of 96%, yellow prisms, m. p. 163–164° (dec.).

Anal. Calcd. for $C_{19}H_{15}N_5O_8$: N, 15.87. Found: N, 15.88%.

A number of acyl and aroyl derivatives were prepared by refluxing equivalent weights of *p*-aminobenzanilide and acyl or aroyl chloride (in the case of acetyl derivative acetic anhydride was used instead) in dry benzene or toluene on a steam-bath for thirty minutes to one hour. The solvent was removed by vacuum distillation. The residue was stirred with cold water, filtered, and then recrystallized from a suitable solvent.

N-(N-Acetyl-*p*-aminobenzoyl)-*p*-aminobenzanilide was prepared by reduction of N-(*p*-nitrobenzoyl)-*p*-aminobenzanilide with stannous chloride and hydrochloric acid and subsequent acetylation.

Several aromatic sulfonyl derivatives were similarly prepared. The properties of these compounds are listed in the table.

Since Hirsch[4] demonstrated that *p*-aminobenzamide possessed bacteriostatic properties, it would be interesting to see whether these derivatives are bacteriostatic or not. Only a few more soluble ones have been tested on *Lactobacillus arabinosus* 17–5. N-Acetyl-*p*-aminobenzanilide, N-propionyl-*p*-aminobenzanilide, N-*n*-butyryl-*p*-aminobenzanilide, N-isobutyryl-*p*-aminobenzanilide and N-*n*-valeryl-*p*-aminobenzanilide are toxic at a concentration of 500 γ per 10 ml. of medium, but the toxic action is not reversed by addition of *p*-aminobenzoic acid. However, *p*-aminobenzanilide possesses slight growth-promoting action similar to that of *p*-aminobenzoic acid.

THE BIOCHEMICAL INSTITUTE AND
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RECEIVED JULY 9, 1945

(4) J. Hirsch, *Science*, **96**, 140 (1942).

(5) On leave from the University of Peking, Kunming, Yunnan, China. Present address: Department of Medicine, University of Minnesota, Minneapolis, Minnesota.

COMMUNICATIONS TO THE EDITOR

A NEW SYNTHESIS OF MONO SUBSTITUTED CYCLOBUTANES

Sir:

The authors have prepared a tribromide, 1,1,1-tris-(bromomethyl)-propane (I) from a new triol, 1,1,1-tris-(hydroxymethyl)-propane (II), obtained from the Heyden Chemical Corp., Garfield, N. J., Debromination of I by zinc in acetamide, the method of Hass and McBee,[1] gave a mixture of olefins which was separated by distillation at 50-plate efficiency into three distinct fractions. The highest boiling and preponderant fraction has been conclusively identified as ethylidenecyclobutane.

This recalls the fact that methylenecyclobutane[2] is one of the products from the zinc–acetamide debromination of pentaerythrityl tetrabromide, and is the chief product from the zinc–alcohol debromination. On the other hand, the zinc–alcohol debromination of (I) gave no hydrocarbons but chiefly an ether (b. p. 135°, uncor.) which probably was ethyl 1-ethylcyclopropylcarbinyl ether. We believe that in the zinc–acetamide debromination of I a ring closure occurs to give 1-(bromomethyl)-1-ethylcyclopropane which subsequently undergoes dehydrobromination with ring expansion and some ring opening.

The crude brownish triol (II) softened and melted over a wide temperature range; purified by vacuum distillation, and recrystallization from

(1) Hass, McBee, Hinds and Gluesenkamp, *J. Ind. Eng. Chem.*, **28**, 1178 (1936).

(2) Murray and Stevenson, THIS JOURNAL, **66**, 812 (1944).