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NOMENCLATURE

Preparations appear in the alphabetical order of common names of the compounds. For convenience in surveying the literature concerning any preparation through *Chemical Abstracts* subject indexes, the *Chemical Abstracts* indexing name for each compound is given as a subtitle if it differs from the common name used as the title.

SUBMISSION OF PREPARATIONS

Chemists are invited to submit for publication in *Organic Syntheses* procedures for the preparation of compounds that are of general interest, as well as procedures that illustrate synthetic methods of general utility. It is fundamental to the usefulness of *Organic Syntheses* that submitted procedures represent optimum conditions, and the procedures should have been checked carefully by the submitters, not only for yield and physical properties of the products, but also for any hazards that may be involved. Full details of all manipulations should be described, and the **range** of yields should be reported rather than the maximum yield obtainable by an operator who has had considerable experience with the preparation. For each solid product the melting-point **range** should be reported, and for each liquid product the **range** of boiling point and refractive index should be included. In most instances, it is desirable to include additional physical properties of the product, such as ultraviolet, infrared, mass, or nuclear magnetic resonance spectra, and criteria of purity such as gas chromatographic data. The methods of preparation or sources of the reactants should be described in notes, and the physical properties (such as boiling point, index of refraction, melting point) of the reactants should be included except where standard commercial grades are specified.

Procedures should be written in the style and format employed in the latest published volume of *Organic Syntheses*. Copies of

the current style sheet may be obtained from the Secretary of the Editorial Board.

Beginning with Vol. 49, **Sec. 3., Methods of Preparation,** and **Sec. 4., Merits of the Preparation,** will be combined into a single new **Sec. 3., Discussion.** In this section should be described other practical methods for accomplishing the purpose of the procedure that have appeared in the literature. It is unnecessary to mention methods that have been published but are of no practical synthetic value. Those features of the procedure that recommend it for publication in *Organic Syntheses* should be cited (synthetic method of considerable scope, specific compound of interest not likely to be made available commercially, method that gives better yield or is less laborious than other methods, etc.). If possible, a brief discussion of the scope and limitations of the procedure as applied to other examples as well as a comparison of the method with the other methods cited should be included. If necessary to the understanding or use of the method for related syntheses, a brief discussion of the mechanism may be placed in this section. The present emphasis of *Organic Syntheses* is on model procedures rather than on specific compounds (although the latter are still welcomed), and the **Discussion** section should be written to help the reader decide whether and how to use the procedure in his own research. Three copies of each procedure should be submitted to the Secretary of the Editorial Board. It is sometimes helpful to the Board if there is an accompanying letter setting forth the features of the preparation that are of interest.

Additions, corrections, and improvements to the preparations previously published are welcomed and should be directed to the Secretary.

EDITOR'S PREFACE

The preparations in this volume, like those in earlier volumes of *Organic Syntheses*, fall into two major categories. In one category are procedures that illustrate general synthetic methods of importance and novelty; while in the other are procedures for the preparation of compounds of specific interest in many fields of organic chemistry. The trend in recent volumes toward an emphasis on the first category, maintained in the present volume, reflects the continuing development of new general synthetic methods in the current remarkable upsurge of synthetic organic chemistry.

In this first category are procedures that illustrate the conversion of alcohols to halides by triphenylphosphine-halogen adducts (cinnamyl bromide), preparation of phenols from alkyl halides without cinesubstitution (3-hydroxypyrene), allylic oxidation with *t*-butyl perbenzoate (3-benzoyloxycyclohexene), conversion of tertiary hydrocarbons by nitrogen trichloride to *t*-alkylamines (1-amino-1-methylcyclohexane), preparation of amines by reductive cleavage of sulfonamides by hydrobromic acid in the presence of phenol (1,3-dihydroisoindole), reductive dechlorination of polychloro compounds with sodium and *t*-butyl alcohol in tetrahydrofuran (7,7-dimethoxybicyclo[2.2.1]-heptene), preparation of α-keto aldehydes via treatment of esters with the potassium salt of dimethyl sulfoxide (phenylglyoxal), synthesis of diazo compounds from compounds with active methylene groups by reaction with *p*-toluenesulfonyl azide (*t*-butyl diazoacetate), preparation of carbamates from alcohols with sodium cyanate and trifluoroacetic acid (*t*-butyl carbamate), preparation of carbodiimides by dehydration of ureas with *p*-toluenesulfonyl chloride and triethylamine [1-ethyl-3-(3-dimethylamino)propylcarbodiimide], selective alkylation of ketones via the dianion of their formyl derivatives (2-*n*-butyl-2-methylcyclohexanone), preparation of 1,1-diphenyl-substituted hydrocarbons by alkylation of diphenylmethane (1,1-diphenylpentane),

preparation of diarylmethanes via reaction of aromatic aldehydes with chloral (*p*-bromodiphenylmethane), synthesis of cyclic ketones by ring expansion of their lower homologs via enamine formation and cycloaddition of ethyl propiolate (cyclodecanone), conversion of cinnamic acid and its derivatives to phenylcyclopropanes with lithium aluminum hydride (1,1-diphenylcyclopropane), preparation of arenediazonium-2-carboxylates and their conversion to biphenylenes (benzenediazonium-2-carboxylate and biphenylene), preparation of 1-substituted benzocyclobutenes by addition of a side-chain carbanion to an aryne bond (1-cyanobenzocyclobutene), oxidation of polyalkylbenzenes to 2,4-cyclohexadienones by peroxytrifluoroacetic acid (2,3,4,5,6,6-hexamethyl-2,4-cyclohexadien-1-one), reductive cyclization of oximes to aziridines (*cis*-2-benzyl-3-phenylaziridine), synthesis of 2-hydroxyisocarbostyrils via nitrosation of 1-indanones (2-hydroxy-3-methylisocarbostyril), reductive cyclization of nitro compounds to nitrogen heterocycles by triethyl phosphite (2-phenylindazole), preparation of ketene S,N-acetals from thioamides (2-methylmercapto-N-methyl-Δ^2-pyrroline), and the preparation of 1-alkyl-3-aryltriazenes and their use in the esterification of acids (1-methyl-3-*p*-tolyltriazene).

Procedures for the preparation of several compounds of considerable utility are described. These include 1,1′-carbonyldiimidazole, which has been used in the preparation of esters, amides, and anhydrides, the hydrochloride and methiodide of 1-ethyl-3-(3-dimethylamino)-propylcarbodiimide, which can be used for similar purposes and are especially useful in the preparation of peptides, and (+)- and (−)-α-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy) propionic acid (TAPA), which is used for the resolution of polycyclic aromatic compounds.

The members of the Editorial Board take this opportunity to thank the contributors of preparations. They welcome suggestions of changes that would improve the usefulness of *Organic Syntheses*. The attention of submitters of preparations is particularly drawn this year to the instructions on pages v and vi, which reflect changes that will be introduced in the next volume.

PETER YATES

CONTENTS

AMINOMALONONITRILE *p*-TOLUENESULFONATE

(Malononitrile, amino-, *p*-toluenesulfonate)

$$CH_2(CN)_2 + NaNO_2 + CH_3COOH \rightarrow HON{=}C(CN)_2 + CH_3CO_2Na + H_2O$$

$$3HON{=}C(CN)_2 + 4Al + 9H_2O \rightarrow 3NH_2CH(CN)_2 + 4Al(OH)_3$$

$$NH_2CH(CN)_2 + p\text{-}CH_3C_6H_4SO_3H \rightarrow p\text{-}CH_3\dot{C}_6H_4SO_3^- \overset{+}{N}H_3CH(CN)_2$$

Submitted by J. P. Ferris, R. A. Sanchez, and R. W. Mancuso[1]
Checked by O. W. Webster and R. E. Benson

1. Procedure

A. *Oximinomalononitrile.* Malononitrile (Note 1) (25 g., 0.38 mole) is dissolved in a mixture of 20 ml. of water and 100 ml. of acetic acid in a 1-l. round-bottomed flask equipped with a stirrer, a thermometer, and a powder funnel. The solution is cooled to $-10°$ with a dry ice-acetone bath, and 50 g. (0.72 mole) of granulated sodium nitrite is added in approximately 2-g. portions over a 30-minute period while the temperature is maintained at 0° to $-10°$. After the addition is complete a wet ice bath is used to maintain the temperature below 5° while the mixture is stirred for 4 hours. Four hundred milliliters of tetrahydrofuran (Note 2) and 400 ml. of ether are added in separate portions, and the mixture is stored at $-40°$ overnight. The mixture is filtered rapidly, and the solid is washed with a mixture of 200 ml. of tetrahydrofuran (Note 2) and 200 ml. of ether. The filtrate and washings are combined and concentrated by distillation to a volume of 250 ml. by the use of a water aspirator and a bath at 40° (Note 3). This solution of oximinomalononitrile is used directly in the next step.

B. *Aminomalononitrile p-toluenesulfonate.* Aluminum foil (13.7 g., 0.51 g. atom) is cut into half-inch squares and is covered with a 5% aqueous solution of mercuric chloride until a mercury coating is visible on the aluminum (*ca.* 30 seconds). The mercuric chloride solution is decanted, and the amalgamated aluminum is washed twice with water, once with ethanol, and twice with tetrahydrofuran (Note 2). The amalgamated aluminum is transferred to a 2-l. round-bottomed flask fitted with a condenser, a stirrer, and a 250-ml. addition funnel and is covered immediately with 300 ml. of tetrahydrofuran (Note 2). The mixture is cooled in a dry ice-acetone bath, and the solution of oximinomalononitrile from procedure A is added with stirring over a 15-minute period while the temperature is maintained at $-15°$ to $-30°$. Stirring is continued for an additional 5 minutes. The dry-ice acetone bath is then removed, and the mixture is allowed to warm to room temperature. (*Caution! Cooling with a dry ice-acetone bath is usually needed to control the reaction.*) After the spontaneous reaction subsides, the mixture is warmed to reflux until most of the aluminum is consumed (45 minutes). The reaction mixture is cooled to room temperature, 200 ml. of ether is added with stirring, and the aluminum salts are removed by vacuum filtration through Celite filter aid. The solid is washed with 250 ml. of tetrahydrofuran (Note 2) followed by 500 ml. of ether (Notes 3 and 4). The original filtrate and washings are combined and concentrated to about 250 ml. by the use of a water aspirator and a bath at 40°. To the resulting brown solution is slowly added with stirring a mixture of 60 g. (0.32 mole) of *p*-toluenesulfonic acid monohydrate as a slurry in 250 ml. of ether (Note 5). The total volume is brought to 1 l. with ether, the mixture is cooled to 0°, and the crystalline solid is collected by vacuum filtration. The product is washed successively with 200 ml. of ether, 200 ml. of cold (0°) acetonitrile, and 200 ml. of ether and dried at 25° (1 mm.) to give light tan crystals, m.p. 169–171° (dec.); yield, 75–79 g. (78–82%).

This product is suitable for most synthetic purposes. An almost colorless product may be obtained by recrystallization from boiling acetonitrile (100 ml. dissolves 1.8 g. of product) with

treatment with activated carbon. The recovery of aminomalononitrile *p*-toluenesulfonate, m.p. 172° (dec.), is *ca.* 80%.

2. Notes

1. Commercial malononitrile is purified by dissolving 260 g. in 1 l. of ether, refluxing the solution with 5 g. of activated carbon for 10 minutes, and filtering through Celite under vacuum. The malononitrile crystallizes from the filtrate as a result of the cooling and concentration during the filtration. It is collected by filtration and washed with 350 ml. of cold (−20°) ether to give 214 g. of white crystals.

2. Tetrahydrofuran from Fisher Scientific Co. was used by the checkers. [*Caution! See Org. Syntheses*, **46**, *105* (*1966*), *for a warning regarding the purification of tetrahydrofuran.*]

3. Occasionally a precipitate may form in the filtrate. It is removed by filtration before proceeding to the next step.

4. Additional washing is necessary if the washings are not colorless at this point.

5. One can check for complete precipitation of the aminomalononitrile by adding *p*-toluenesulfonic acid to the clear supernatant liquid.

3. Methods of Preparation

The present procedure is a modification of the original synthesis.[2] Previous reports of the synthesis of aminomalononitrile are in error.[2] Oximinomalononitrile was prepared by a modification of the procedure of Ponzio.[3]

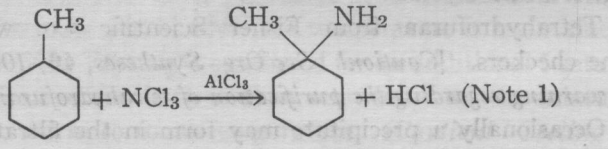
4. Merits of the Preparation

This procedure provides a convenient synthesis of aminomalononitrile, which has been demonstrated to be a useful intermediate for the preparation of substituted imidazoles, thiazoles, oxazoles, purines, and purine-related heterocycles.[2] It is also a convenient starting material for the preparation of diaminomaleonitrile.[2, 4]

1. The Salk Institute for Biological Studies, San Diego, California [Present address (J.P.F.): Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181].
2. J. P. Ferris and L. E. Orgel, *J. Am. Chem. Soc.*, **88**, 3829 (1966); **87**, 4976 (1965).
3. G. Ponzio, *Gazz. Chim. Ital.*, **61**, 561 (1931).
4. J. P. Ferris and R. A. Sanchez, *Org. Syntheses*, this volume, p. 60.

1-AMINO-1-METHYLCYCLOHEXANE

(Cyclohexylamine, 1-methyl-)



Submitted by PETER KOVACIC and SOHAN S. CHAUDHARY [1]
Checked by R. A. HAGGARD and WILLIAM D. EMMONS

1. Procedure

Caution! The reactions should be carried out in a hood behind a protective screen since trichloramine is noxious and potentially explosive; however, no difficulties from decomposition have been encountered under the conditions described.

A. *Trichloramine.* A mixture of 600 ml. of water (Note 2), 900 ml. of methylene chloride (Note 3), and 270 g. (1.32 moles) of calcium hypochlorite (Note 4) is cooled to 0–10° in a 3-l., three-necked, vented flask equipped with a stirrer, a thermometer, and a dropping funnel. A solution of 66.0 g. (1.23 moles) of ammonium chloride in 150 ml. of concentrated hydrochloric acid and 450 ml. of water is added dropwise with stirring over a 1-hour period at 0–10°. After an additional 20 minutes of stirring, the organic layer is separated, washed with three 200-ml. portions of cold water, and dried over anhydrous sodium sulfate. The yellow solution is filtered, and the trichloramine concentration is determined by iodometric titration (Note 5).

B. *1-Amino-1-methylcyclohexane.* A 3-l. three-necked flask is fitted with a paddle stirrer, a condenser, a thermometer, and a

dropping funnel with an extension for below-surface addition. Provision is made for introduction of nitrogen by use of a side-arm adapter. The vessel is charged with 196 g. (2.0 moles) of methylcyclohexane (Note 6) and 106 g. (0.80 mole) of anhydrous aluminum chloride. A solution (*ca.* 600 ml.) of trichloramine (0.40 mole) in methylene chloride is added with efficient stirring over a period of 2 hours at $-5°$ to 5° (Note 7). Throughout the reaction a stream of nitrogen is passed through the flask (Note 8). The brown mixture is stirred for an additional 20–30 minutes at the same temperature.

The reaction mixture is then added with good stirring to a slurry of 800–900 g. of ice and 50 ml. of concentrated hydrochloric acid (Note 9). The layers are separated, and the dark organic layer is washed with three 100-ml. portions of 5% hydrochloric acid and discarded. Traces of non-basic organic material are removed from the combined aqueous layer and washings by extraction with pure ether (Note 10) until the extract is colorless. The aqueous solution is treated with 600 ml. of 50% aqueous sodium hydroxide (Note 11) with cooling, and the basic organic product is extracted with three 125-ml. portions of pure ether (Note 10). The ethereal solution is dried over sodium sulfate, and the solvent is distilled on the steam bath to give 42–46 g. of a clear, amber product (Note 12). To this crude product is added 10 g. of triethylenetetramine (Note 13). Distillation through a small Vigreux column yields 21.5–30 g. (48–67%, based on trichloramine) of 1-amino-1-methylcyclohexane, b.p. 44–49° (20–25 mm.), $n^{22}D$ 1.4516 (Note 14).

2. Notes

1. The stoichiometry of the reaction is not known.
2. Deionized water is used throughout.
3. Commercial methylene chloride was distilled before use by the submitters. The checkers used reagent grade methylene chloride without distillation.
4. Calcium hypochlorite is obtained as "HTH" (Olin Mathieson Chemical Co., 70% purity).
5. Iodometric determination of positive chlorine is carried out

as follows: 2.0 g. of potassium iodide or sodium iodide is dissolved in 10 ml. of water, and 40 ml. of glacial acetic acid is added. Into this solution is pipetted 1.0 ml. of the methylene chloride solution of trichloramine. The liberated iodine is titrated with 0.100*N* sodium thiosulfate. The solution is found to be 0.6–0.7*M* in trichloramine. Storage for several days at 0–5° results in negligible decomposition, although it is not recommended unless adequate safety precautions are observed. Excess methylene chloride-trichloramine solution can be conveniently disposed of by its slow addition to a cold, stirred, dilute aqueous solution of sodium metabisulfite.

6. A pure grade of methylcyclohexane (Eastman Organic Chemicals) is used. Subsequent to the checking of this preparation, the submitters reported 69–72% yields with 78.4 g. (0.80 mole) of methylcyclohexane.[2] In this case a 1-l. three-necked flask is employed for the reaction; the remainder of the procedure is unchanged.

7. Cooling is accomplished with either an ice-salt bath or preferably a dry ice-acetone bath. The time of addition can be reduced to 1 hour by use of the latter. However, if the temperature is much below that designated, unchanged trichloramine accumulates, resulting eventually in an uncontrollable reaction.

8. Purging with nitrogen results in some increase in yield. If the flow is too vigorous, trichloramine is lost by volatilization.

9. The mixture can be stored overnight at this stage.

10. High-purity ether (*e.g.*, Baker Analyzed Reagent) is used since a grade of lower quality gives a product that is more difficult to purify because of contamination with alcohol.

11. Excess sodium hydroxide is needed to dissolve the aluminum-containing precipitate.

12. The last portion of solvent is carefully removed at the water aspirator.

13. Triethylenetetramine (redistilled, Eastman Organic Chemicals) prevents bumping and foaming and acts as a chaser for the distillation.

14. The product contains less than 10% of lower-boiling impurities determined (by the checkers) by vapor-phase chromatography with a column packed with 15% XF-1150 on Chromo-

sorb W. Further purification can be effected readily with good recovery by drying over sodium hydroxide pellets and fractionating at atmospheric pressure through an efficient spinning band column, with collection of the fraction, b.p. 142–146°, n^{22}D 1.4522.

3. Methods of Preparation

In addition to the present method,[2] 1-amino-1-methylcyclohexane has been synthesized by the following procedures: Ritter reaction, *e.g.*, with 1-methylcyclohexanol (76%, 67%)[3, 4] or 1-methylcyclohexene (35%);[4] Hofmann reaction with 1-methylcyclohexanecarboxamide (80% as hydrochloride);[5] reduction of 1-methyl-1-nitrocyclohexane (63%);[5] Schmidt reaction with 1-methylcyclohexanecarboxylic acid (42%).[6]

4. Merits of the Preparation

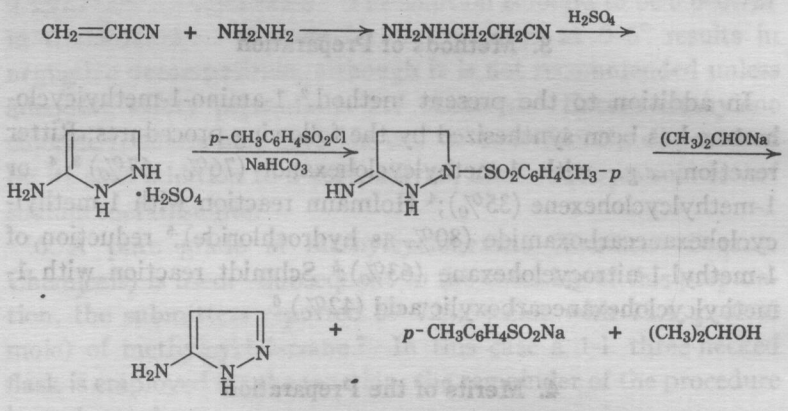
This procedure constitutes the first example of one-step conversion of a *t*-alkane to the corresponding *t*-alkylamine. Other hydrocarbons in this class, such as isobutane, have also been aminated with good results.[7] Only a very limited number of convenient routes, *e.g.*, the Ritter reaction, are available for the preparation of *t*-carbinamines. The present preparation illustrates a simple method that utilizes a novel substrate.

1. Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

2. P. Kovacic and S. S. Chaudhary, *Tetrahedron*, **23**, 3563 (1967).
3. H. J. Barber and E. Lunt, *J. Chem. Soc.*, 1187 (1960).
4. W. Haaf, *Ber.*, **96**, 3359 (1963).
5. K. E. Hamlin and M. Freifelder, *J. Am. Chem. Soc.*, **75**, 369 (1953).
6. C. Schuerch, Jr., and E. F. Huntress, *J. Am. Chem. Soc.*, **71**, 2233 (1949).
7. P. Kovacic and S. S. Chaudhary, unpublished work.

3(5)-AMINOPYRAZOLE

[Pyrazole, 3(or 5)-amino-]



Submitted by H. DORN and A. ZUBEK [1]
Checked by L. G. VAUGHAN and R. E. BENSON

1. Procedure

A. *β-Cyanoethylhydrazine.* To a 2-l. two-necked flask fitted with a thermometer and a pressure-equalizing funnel are added a large magnetic stirring bar and 417 g. (6.00 moles of $N_2H_4 \cdot H_2O$) of 72% aqueous hydrazine hydrate. Acrylonitrile (318 g., 6.00 moles) is gradually added with stirring during 2 hours. The internal temperature is kept at 30–35° by occasional cooling of the flask. The funnel is replaced by a distillation condenser. Removal of water by distillation at 40 mm. at a bath temperature of 45–50° gives 490–511 g. (96–100%) of β-cyanoethylhydrazine as a yellow oil that is suitable for use in the next step. This product can be purified by distillation; b.p. 76–79° (0.5 mm.).

B. *3-Amino-3-pyrazoline sulfate.* In a 2-l. four-necked flask equipped with a reflux condenser, a dropping funnel, a thermometer, and a mechanical stirrer with four blades (Note 1) is placed 308 g. (169 ml., 3.0 moles) of 95% sulfuric acid (sp. gr. 1.834). Absolute ethanol (450 ml.) is added dropwise over 20–30 minutes. The internal temperature is maintained at 35° by cooling. A solution of 85.1 g. (1.00 mole) of β-cyanoethylhydra-

zine in 50 ml. of absolute ethanol is added with vigorous stirring over 1–2 minutes without further cooling (Note 1). The mixture warms spontaneously to 88–90° and is kept at this temperature for 3 minutes until the product begins to crystallize. The temperature of the stirred mixture is gradually lowered during the next hour to 25° by cooling with water, and the mixture is then allowed to stand at room temperature for 15–20 hours. The crystals are collected by filtration and washed three times with 80 ml. of absolute ethanol and finally with 80 ml. of ether. After being dried at 80° the product weighs 177–183 g. (97–100%), m.p. 143–144° (Note 2). The product is sufficiently pure for use in the following step; it may be recrystallized from methanol to give white needles, m.p. 144–145° (Note 2).

C. *3-Imino-1-(p-tolylsulfonyl)pyrazolidine.* To a 3-l. four-necked flask fitted with a condenser, a thermometer, a wide-mouthed funnel, and a high-speed mechanical stirrer having five pairs of blades are added 183 g. (1.00 mole) of 3-amino-3-pyrazoline sulfate and 1 l. of water. Sodium bicarbonate (210 g., 2.5 moles) is gradually added during 10 minutes with stirring. The rate of stirring is increased to 5000–6000 r.p.m., and a solution of 229 g. (1.20 moles) of *p*-toluenesulfonyl chloride in 400 ml. of benzene containing 0.5 g. of sodium dodecylbenzenesulfonate (Note 3) is added at one time. Three further portions of sodium bicarbonate are added sequentially: 25.2 g. (0.30 mole) after 15 minutes; 16.8 g. (0.20 mole) after 30 minutes; 16.8 g. (0.20 mole) after 55 minutes. The mixture is stirred for 5 hours at 18–25°, occasional cooling being required. Sodium bicarbonate (8.4 g., 0.10 mole) is added, then 200 ml. of ether, and stirring is continued for another hour. The colorless product is collected by filtration on a sintered-glass funnel, washed with three 50-ml. portions of ether followed by 50 ml. of water, and dried at 90°. The yield is 139–180 g. (58–75%); m.p. 183–185° (Note 4). The product is used directly in the next step.

D. *3(5)-Aminopyrazole* (Note 5). (*Caution! Because hydrogen gas is evolved, this reaction should be conducted in an efficient hood in the absence of an ignition source.*) A solution of sodium isopropoxide is prepared from 18.4 g. (0.80 g. atom) of sodium and 500 ml. of isopropyl alcohol in a 2-l. four-necked flask fitted with a mechanical stirrer, a thermometer, a reflux condenser, and a

stopper. The reflux condenser is fitted with a nitrogen-inlet line attached to a bubbler device to maintain an anhydrous atmosphere. After all the sodium has dissolved, the temperature is adjusted to 60–70°, the stopper is replaced by a wide-mouthed funnel, and 191 g. (0.80 mole) of 3-imino-1-(*p*-tolylsulfonyl)-pyrazolidine is added gradually over 10 minutes to the hot solution under a blanket of nitrogen. The funnel is replaced by the stopper, and the mixture is stirred vigorously and then refluxed briefly. Stirring is continued, and the mixture is allowed to cool to room temperature during 2 hours. The precipitated sodium *p*-toluenesulfinate (140–142 g.) is removed by filtration and washed with a total of 100 ml. of isopropyl alcohol in several portions. The filtrate is treated twice with 4-g. portions of Norit activated carbon. The solvent is removed by distillation, the final trace being removed at a bath temperature of 50° (20 mm.) to give 62–66 g. (93–99%) of 3(5)-aminopyrazole as a light yellow oil. This is purified by distillation to give the product as a yellow oil, b.p. 100–102° (0.01 mm.), in 74–84% recovery (Note 6). The product crystallizes on cooling; m.p. 37–39° (Note 7). Its n.m.r. spectrum (60 MHz, dimethyl sulfoxide-d_6) shows two one-proton doublets at δ 7.33 and 5.52 p.p.m. (J = 2 Hz) and a broad three-proton singlet at δ 7.05 p.p.m. that is absent after addition of D_2O.

2. Notes

1. A stirrer with large blades operating at high speed is essential. Inadequate stirring results in solidification of the reaction mixture and makes proper washing of the product very difficult.

2. The checkers found melting points of 138–141° and 140–142°. After three recrystallizations from methanol the product has a melting point of 139.7–140°. The product appeared to be unstable to prolonged heating in methanol.

3. This salt serves as an emulsifying agent.

4. A sample, m.p. 184–185°, prepared by recrystallization of the product from nitromethane, gives satisfactory elemental analytical data. Its n.m.r. spectrum (60 MHz, dimethyl sulfoxide-d_6) reveals that the compound exists in the iminopyra-