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MELVIN NEWMAN, EDITOR

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OF ORGANIC CHEMICALS

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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 which are of general interest, as well as procedures which 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 some instances, it is desirable to include additional physical properties of the product, such as ultraviolet, infrared, or nuclear magnetic resonance spectra. 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 rather 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. In section 3, **Methods of Preparation**, there should be described other practical methods for preparing the compound which have appeared in the literature. It is unnecessary to mention methods which have been published but are of no practical synthetic value. There should also be included a statement of the merits of the preparation which recommend it for publication in *Organic Syntheses* (synthetic method of considerable scope, specific compound of interest, method gives better yield or is less laborious than other methods, etc.). This information is necessary because subsequent volumes of *Organic Syntheses* will include under **Methods of Preparation** a statement explaining why the preparation is published in *Organic Syntheses*. Two 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 which are of interest.

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

Ethyl Azodicarboxylate

WARNING

A report has been received that a sample of ethyl azodicarboxylate [*Org. Syntheses*, 28, 59 (1948); Coll. Vol. 3; 375 (1955)] decomposed upon attempted distillation with sufficient violence to shatter the distillation apparatus.

It is possible that the explosion may have been due to over-chlorination or to insufficient washing of the product with sodium bicarbonate solution.

It is recommended that ethyl azodicarboxylate be distilled only behind a safety shield, and protected from direct sources of light.

Please insert this sheet opposite page 59 of *Org. Syntheses*, 28 (1948) and/or opposite page 375 of *Org. Syntheses*, Coll. Vol. 3 (1955).

Diazomethane

WARNING

Diazomethane is not only toxic, but also potentially explosive. Hence one should wear heavy gloves and goggles and work behind a safety screen or a hood door with safety glass, as is recommended in the preparation of diazomethane described by DeBoer and Backer, *Org. Syntheses*, 36, 16 (1956). As is also recommended there, ground joints and sharp surfaces should be avoided. Thus all glass tubes should be carefully fire-polished, connections should be made with rubber stoppers, and separatory funnels should be avoided, as should etched or scratched flasks. Furthermore, at least one explosion of diazomethane has been observed at the moment crystals (sharp edges!) suddenly separated from a supersaturated solution. Stirring by means of a Teflon-coated magnetic stirrer is greatly to be preferred to swirling the reaction mixture by hand, for there has been at least one case of a chemist whose hand was injured by an explosion during the preparation of diazomethane in a hand-swirled reaction vessel.

It is imperative that diazomethane solutions not be exposed to direct sunlight or placed near a strong artificial light because light is thought to have been responsible for some of the explosions that have been encountered with diazomethane. Particular caution should be exercised when an organic solvent boiling higher than ether is used. Because such a solvent has a lower vapor pressure than ether, the concentration of diazomethane in the vapor above the reaction mixture is greater and an explosion is more apt to occur.

Most diazomethane explosions occur during its distillation. Hence diazomethane should not be distilled unless the need justifies it. An ether solution of diazomethane satisfactory for many uses can be prepared as described by Arndt, *Org. Syntheses*, Coll. Vol. 2, 165 (1943), Note 3, where nitrosomethylurea is added to a mixture of ether and 50% aqueous potassium hydroxide and the ether solution of diazomethane is subsequently decanted from the aqueous layer and dried over potassium hydroxide pellets (not sharp-edged sticks!). When distilled diazomethane is required, the procedure of DeBoer and Backer (*loc. cit.*) is particularly good because at no time is there much diazomethane present in the distilling flask.

The hazards associated with diazomethane are discussed by C. D. Gutsche, *Org. Reactions*, 8, 391-394 (1954).

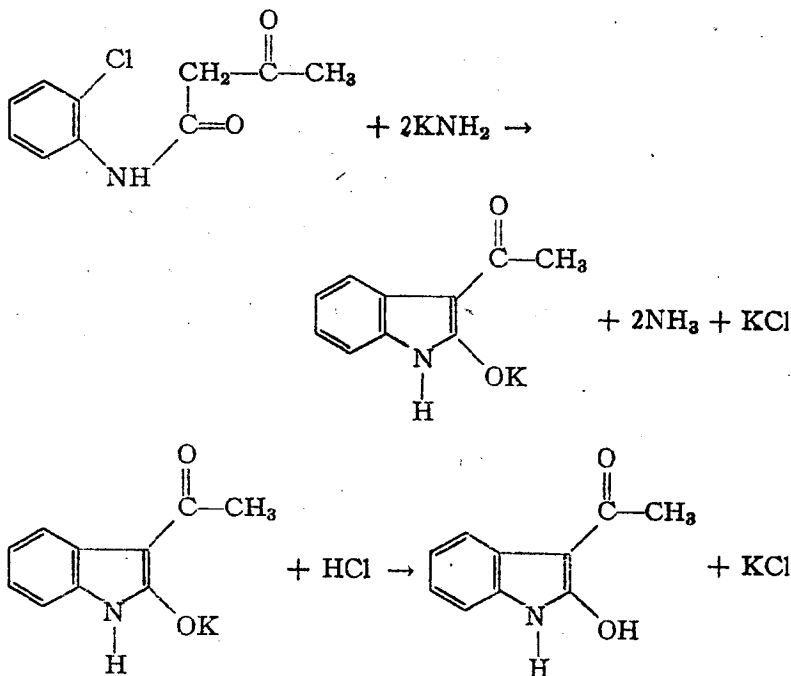
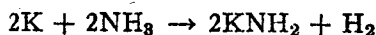
Please insert a copy of this sheet opposite page 165 of *Org. Syntheses*, Coll. Vol. 2 (1943); page 244 of *Org. Syntheses*, Coll. Vol. 3 (1955); and page 16 of *Org. Syntheses*, 36 (1956).

CONTENTS

3-ACETYLOXINDOLE	1
2-AMINOFLUORENE	5
3-BROMOACETOPHENONE	7
3-CHLORO-2,2,3-TRIFLUOROPROPIONIC ACID	11
3-CYCLOHEXENONE	14
DEOXYANISOIN	16
4,4'-DIAMINOAZOBENZENE	18
DIETHYL ACETAMIDOMALONATE	21
DIETHYL AMINOMALONATE HYDROCHLORIDE	24
DIETHYL BIS(HYDROXYMETHYL)MALONATE	27
2,5-DIMETHOXY-2,5-DIHYDROFURAN	29
N,N-DIMETHYLAMINOMETHYLFERROCENE METHIODIDE	31
2,4-DINITROIODOBENZENE	34
1,4-DIPHENYL-1,3-BUTADIENE	36
α - β -DIPHENYLPROPIONIC ACID	38
3-ETHOXY-2-CYCLOHEXENONE	41
ETHYL 6,7-DIMETHOXY-3-METHYLINDENE-2-CARBOXYLATE	43
FERROCENYLACETONITRILE	45
3-(2-FURYL)ACRYLONITRILE	46
2-HYDROXYISOPHTHALIC ACID	48
HYDROXYMETHYLFERROCENE	52
3-HYDROXYQUINOLINE	54
HYDROXYUREA	60
METHANESULFINYL CHLORIDE	62
METHYLENECYCLOHEXANE	66
1-METHYLINDOLE	68
2,6-NAPHTHALENEDICARBOXYLIC ACID	71
N- β -NAPHTHYLPYPERIDINE	74
NEOPENTYL ALCOHOL	76
m-NITROPHENYL DISULFIDE	80
N-PHTHALYL-L- β -PHENYLALANINE	82
p-QUINQUEPHENYL	85
2,2,5,5-TETRAMETHYLTETRAHYDRO-3-KETOFURAN	88
$\alpha,\alpha,\alpha',\alpha'$ -TETRAMETHYLTETRAMETHYLENE GLYCOL	90
p-TOLUENESULFONYLHYDRAZIDE	93
2,4,5-TRIAMINONITROBENZENE	96
1,2,4-TRIAZOLE	99
α,α,α -TRICHLOROACETANILIDE	103
TRIPHENYLENE	105
SUBJECT INDEX	109

3-ACETYLOXINDOLE

(Oxindole, 3-acetyl-).



Submitted by J. F. BUNNETT, B. F. HRUTFIORD and S. M. WILLIAMSON.¹

Checked by B. C. McKUSICK and D. C. BLOMSTROM.

1. Procedure

An apparatus resembling that pictured by Schlatter² is assembled in a good hood. Two 5-l. three-necked flasks are mounted side by side about 10 cm. apart and about 10 cm. above the bench top or stand base. These are referred to as the "left" and "right" flasks. Each flask is provided with a dry ice condenser in the outermost neck, and each condenser is protected from the

air by a soda-lime drying tube. Each flask is provided through the center neck with a motor-driven stirrer. The left stirrer should have a large sweep blade, and the right stirrer should have a small propeller-type blade. The bearing on each stirrer should be capable of holding a small positive pressure (the submitters used ball-joint bearings). The innermost neck of each flask is fitted with a two-holed rubber stopper. One hole in each stopper is for nitrogen supply; a short piece of glass tubing is inserted through each stopper, and these pieces of glass tubing are connected by rubber tubes to a glass "Y" tube which in turn is connected by rubber tubing to a tank of dry nitrogen. The rubber tubes between the "Y" tube and the flasks are provided with pinch clamps so that the flow of nitrogen can be directed into either flask or into both at once. The other hole in each stopper is for transfer of liquid ammonia from the right flask to the left. A glass tube reaching to the very bottom of the right flask is inserted through the right stopper. A glass tube is inserted through the left stopper so that it projects only a few centimeters into the left flask. These glass tubes are bent so that they point toward each other, and they are connected by a piece of rubber tubing provided with a pinch clamp.

With nitrogen flowing and all pinch clamps open, the apparatus is flamed to drive away traces of moisture. The condensers are then provided with dry ice covered by isopropyl alcohol, and the lower part of the right flask is embedded in crushed dry ice. Liquid ammonia (4 l.) is introduced into the right flask through the nitrogen inlet from which the rubber tubing is temporarily disconnected, and 105.8 g. (0.5 mole) of *o*-acetoacetochloroanilide (Note 1) is placed in the left flask. In order to destroy any water in the ammonia, the right stirrer is started and small pieces of potassium metal are dropped into the ammonia, by briefly lifting the right two-holed stopper, until the blue color persists for 3 minutes. The nitrogen connection to the left flask is clamped shut and, by partially blocking the escape of nitrogen from the right drying tube, about 1 l. of ammonia is forced into the left flask. The connection between the two flasks is now clamped shut. Brief operation of the left stirrer facilitates solution of the *o*-acetoacetochloroanilide in the ammonia.

Potassium metal (78 g.; 2 moles) is cut into chunks just small enough to pass through the neck of the right flask; these are stored in a beaker under xylene until needed. About 5 g. of potassium is introduced into the right flask by briefly lifting the two-holed stopper. The right stirrer is started and the potassium is allowed to dissolve. To the resulting deep blue solution is added 0.1 g. of finely crushed ferric nitrate hydrate, a catalyst for the reaction of potassium with ammonia. The solution should begin to boil with evolution of hydrogen. (*Caution: No flames or sparks should be nearby.*) The rest of the potassium is added at such a rate as to maintain active gas evolution (Note 2). Stirring is continued in the right flask until all the potassium is consumed, i.e., until the blue color disappears. The right flask now contains a solution of potassium amide in liquid ammonia; 30-60 minutes is required for its preparation.

The tube between the two flasks is opened by releasing the pinch clamp, and the left stirrer is started. With nitrogen flow to the left flask still blocked, the potassium amide solution is caused to flow into the left flask by partially blocking the right nitrogen exit. The solution in the left flask slowly assumes a chartreuse color. As soon as the right flask is as nearly empty as the apparatus will permit, nitrogen flow is opened to the left flask and closed to the right flask and the connection between the two flasks is clamped shut. The right flask is then disconnected and immediately cleaned by rinsing it carefully with ethyl or isopropyl alcohol to destroy potassium amide and then washing it with water. (*Caution: Potassium amide is inflammable and will ignite on contact with moisture.*)

The solution in the left flask is stirred for 30 minutes after all the potassium amide has been added. The nitrogen inlet is briefly removed and 120 g. (1.5 moles) of ammonium nitrate is added; this discharges the chartreuse color. (*Caution: Vigorous foaming occurs.*) Ethyl ether (500 ml.) is added and the dry ice condenser is replaced by a standard water-cooled condenser. The ammonia is evaporated by allowing the stirred reaction mixture to warm to room temperature; this takes several hours and it is convenient to have it occur overnight.

Water (1.5 l.) is added and the mixture is transferred to a

separatory funnel. The lower aqueous layer, which contains the potassium salt of 3-acetyloxindole, is separated and is then extracted with ethyl ether three times to remove a purple impurity. The aqueous layer is then made acidic to litmus by addition of hydrochloric acid; this causes precipitation of crude, tan-colored 3-acetyloxindole. The mixture is chilled, and the product is collected by suction filtration and washed well on the filter with water. The yield of crude 3-acetyloxindole, m.p. 204–206°, is 65–68 g. (74–78%). It may be purified by recrystallizing it from 1.7 l. of chloroform in the presence of 2 g. of decolorizing carbon. A heated filter funnel must be used in separating the carbon because the product starts to crystallize only slightly below the boiling point of chloroform. The recrystallized 3-acetyloxindole weighs 53–59 g. (61–67%) and is in the form of white needles, m.p. 204–205.5°.

2. Notes

1. The *o*-acetoacetochloroanilide used was the technical product of Union Carbide Chemicals Co.; m.p. 107–109°.
2. If the reaction of potassium with liquid ammonia slows down before all the potassium is consumed, an additional pinch of ferric nitrate hydrate is added.

3. Methods of Preparation

3-Acetyloxindole has been made by condensing ethyl acetate with oxindole in the presence of sodium ethoxide.³ and by heating *N*-acetyloxindole with sodium amide in xylene.⁴ The present method was developed by Hrutfiord and Bunnett.⁵ It illustrates a general principle for the synthesis of heterocyclic and homocyclic compounds. This principle involves the creation of an intermediate species that is of the benzyne type and has a nucleophilic center located so that it can add, intramolecularly, to the "triple bond" of the benzyne structure. Other applications of the principle using essentially the present procedure are the conversion of thiobenz-*o*-bromoanilide or thiobenz-*m*-bromoanilide to 2-phenylbenzothiazole (90% and 68% respectively);

of benz-*o*-chloroanilide to 2-phenylbenzoxazole (69%); and of 2-amino-2'-bromodiphenyl sulfide to phenothiazine (35%).⁵

¹ University of North Carolina, Chapel Hill, North Carolina.

² M. Schlatter, *Org. Syntheses*, Coll. Vol. 8, 223 (1955).

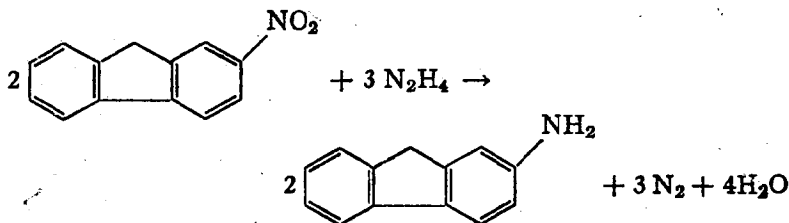
³ L. Horner, *Ann.*, 548, 131 (1941).

⁴ H. Behringer and H. Weissauer, *Ber.*, 85, 774 (1952).

⁵ B. F. Hrutford and J. F. Bunnett, *J. Am. Chem. Soc.*, 80, 2021 (1958).

2-AMINOFLUORENE

(2-Fluorenylamine)



Submitted by P. M. G. Bavin.¹

Checked by JOHN C. SHEEHAN and ROGER E. CHANDLER.

1. Procedure

In a 2-l. three-necked round-bottomed flask, equipped with a mechanical stirrer (Note 1), reflux condenser, and dropping funnel, are placed 30 g. of pure 2-nitrofluorene, m.p. 157° [*Org. Syntheses*, Coll. Vol. 2, 447 (1943)], and 250 ml. of 95% ethanol. After warming to 50° on a steam bath, 0.1 g. of palladized charcoal catalyst (previously moistened with alcohol) is added (Note 2) and the stirrer is started. About 15 ml. of hydrazine hydrate is added from the dropping funnel during 30 minutes (Note 3). At this point an additional 0.1 g. of catalyst (previously moistened with alcohol) is added and the mixture is heated until the alcohol refluxes gently. After 1 hour the nitrofluorene has dissolved completely and the supernatant liquor is almost colorless.

The catalyst is removed by filtration with gentle suction through a thin layer of Celite (Note 4). The flask is rinsed with

30 ml. of hot alcohol which is then used to wash the catalyst and Celite. The combined filtrates are concentrated under reduced pressure to about 50 ml. (Note 5) and then heated to boiling at atmospheric pressure. When 250 ml. of hot water is added slowly, 2-aminofluorene is precipitated as a colorless, crystalline powder. After cooling in an ice bath, the 2-aminofluorene is collected, washed with water, and dried in the dark in a vacuum desiccator. The product melts at 127.8–128.8° (Note 6) and amounts to 24–25 g. (93–96%).

2. Notes

1. If the stirring is omitted, the nitrofluorene takes longer to dissolve.

2. A suitable catalyst is 10% palladium-on-charcoal, such as is supplied by Baker and Company, Inc., 113 Astor Street, Newark 5, New Jersey.

3. The reaction is exothermic, and too rapid addition of the hydrazine may cause the mixture to foam out of the condenser.

4. *Caution!* The catalyst is often pyrophoric and should be kept moistened with alcohol. Celite is a diatomaceous earth filter aid.

5. A rotary evaporator is very convenient for the concentration since some of the amine invariably crystallizes toward the end.

6. The melting point is that reported in *Organic Syntheses*, Coll. Vol. 2, 448 (1943), for a recrystallized sample.

3. Methods of Preparation

The preparation of 2-aminofluorene reported previously in *Organic Syntheses* [Coll. Vol. 2, 448 (1943)] was based on the method of Diels.²

The procedure given is based on the method first developed by Pietra³ and applied by Dewar and Mole⁴ to polycyclic compounds. It gives excellent yields of toluidines, aminobiphenyls, phenylenediamines, aminophenols, *p*-aminobenzoic acid, and similar compounds,^{3,4} but it is not suitable for the reduction of some chloronitrobenzenes.⁵ When applied to azobenzene and azoxybenzene it gives hydrazobenzene in 80–90% yield.⁵

Raney nickel may be used instead of palladized charcoal as the catalyst.⁶

¹ National Research Council of Canada Post-doctorate Fellow, 1954-56, at the University of Ottawa, Ottawa, Ontario. Present address: Smith, Kline and French Ltd., Welwyn Garden City, Herts, England.

² O. Diels, *Ber.*, **34**, 1758 (1901).

³ S. Pietra, *Ann. chim. (Rome)*, **45**, 850 (1955).

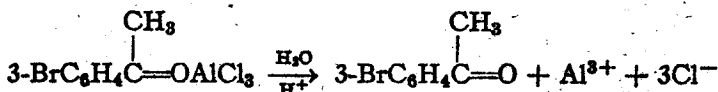
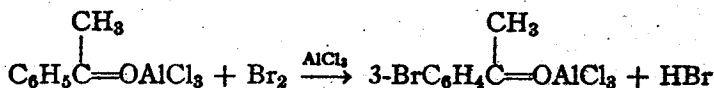
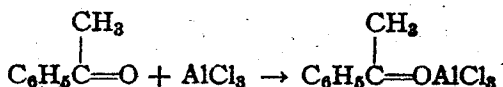
⁴ M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1956, 2556.

⁵ P. M. G. Bavin, *Can. J. Chem.*, **36**, 238 (1958).

⁶ D. Balcom and A. Furst, *J. Am. Chem. Soc.*, **75**, 4334 (1953).

3-BROMOACETOPHENONE

(Acetophenone, 3-bromo-)



Submitted by D. E. PEARSON, H. W. POPE, and W. W. HARGROVE.¹

Checked by B. C. MCKUSICK and D. W. WILEY.

1. Procedure

The apparatus consists of a 1-l. three-necked flask equipped with a condenser, a dropping funnel, and a stirrer terminating in a stiff, crescent-shaped Teflon polytetrafluoroethylene paddle. The stirrer motor must have good torque (Note 1). The assembled apparatus, which is protected from moisture by means of drying tubes in the condenser and funnel, is preferably pre-dried. About 216-224 g. (1.62-1.68 moles) of powdered anhydrous aluminum chloride is added to the apparatus with as little exposure to the moisture of the air as possible (Note 2). While

the free-flowing catalyst is stirred (Note 3), 81 g. (0.67 mole) of acetophenone is added from the dropping funnel in a slow stream over a period of 20–30 minutes. Considerable heat is evolved, and, if the drops of ketone are not dispersed, darkening or charring occurs. When about one-third of the acetophenone has been added, the mixture becomes a viscous ball-like mass that is difficult to stir. Turning of the stirrer by hand or more rapid addition of ketone is necessary at this point. The addition of ketone, however, should not be so rapid as to produce a temperature above 180°. Near the end of the addition, the mass becomes molten and can be stirred easily without being either heated or cooled. The molten mass, in which the acetophenone is complexed with aluminum chloride, ranges in color from tan to brown.

Bromine (128 g., 0.80 mole) is added dropwise to the well-stirred mixture over a period of 40 minutes (Note 4). After all the bromine has been added, the molten mixture is stirred at 80–85° on a steam bath for 1 hour, or until it solidifies if that happens first (Note 5). The complex is added in portions to a well-stirred mixture of 1.3 l. of cracked ice and 100 ml. of concentrated hydrochloric acid in a 2-l. beaker (Note 6). Part of the cold aqueous layer is added to the reaction flask to decompose whatever part of the reaction mixture remains there, and the resulting mixture is added to the beaker. The dark oil that settles out is extracted from the mixture with four 150-ml. portions of ether. The extracts are combined, washed consecutively with 100 ml. of water and 100 ml. of 5% aqueous sodium bicarbonate solution, dried with anhydrous sodium sulfate, and transferred to a short-necked distillation flask. The ether is removed by distillation at atmospheric pressure, and crude 3-bromoacetophenone is stripped from a few grams of heavy dark residue by distillation at reduced pressure. The colorless distillate is carefully fractionated in a column 20 cm. long and 1.5 cm. in diameter that is filled with Carborundum or Heli-Pak filling. The combined middle fractions of constant refractive index are taken as 3-bromoacetophenone; weight, 94–100 g. (70–75%); b.p. 75–76°/0.5 mm.; n_D^{25} 1.5738–1.5742; m.p. 7–8° (Notes 7 and 8).

2. Notes

1. Among satisfactory motors are the Sargent Cone Drive and the Waco.

2. Exposure of the aluminum chloride to air is conveniently avoided by introducing the entire contents of two 4-ounce bottles of anhydrous resublimed aluminum chloride of the Baker and Adamson Company directly into the reaction flask.

3. If the paddle width is so small as to leave isolated, unagitated portions of aluminum chloride, it should be moved near the surface to disperse the ketone rapidly. If the ketone is not dispersed, condensation to dypnone occurs. Tars found in the stripping process are believed to originate from improper addition of the ketone to the aluminum chloride.

4. The rate of addition is regulated by the rate of evolution of hydrogen bromide. The yield of product is essentially the same whether the reaction mixture is held at 80-85° or at room temperature.

5. If the reaction mixture does not solidify during the heating, it is well to work it up at once while it can still be poured from the flask. Otherwise the work-up can be postponed to the next day. If the reaction mixture is too difficult to remove from the flask, the acid-ice slurry can be added *all at once* to the reaction flask immersed in ice. The vigorous surface decomposition is thus partly quenched. However, the cake is seldom difficult to remove unless polyhalogenation has occurred.

6. The acid prevents the formation of insoluble aluminum salts that make separation of ether-water layers difficult. It is helpful in this regard to stir the mixture of water, ketone, and acid for an hour or so before extracting the ketone with ether.

7. The present procedure has been used by the submitters to prepare the following 3-bromoacetophenones and benzaldehydes in the indicated yields:³ 3-bromopropiophenone, m.p. 40-41°, 60%; 3-bromo-4-methylacetophenone, m.p. 42-43°, 56%; 3,4-dibromoacetophenone, m.p. 89-90°, 55%; 3-bromo-4-*tert*-butylacetophenone, b.p. 92°/0.1 mm., 30%; 3,5-dibromo-4-methylacetophenone, m.p. 102-103°, 57%; 3-bromobenzaldehyde, b.p. 105-106°/2 mm., 59%; 3-bromo-4-tolualdehyde, m.p. 48-49°, 44%.