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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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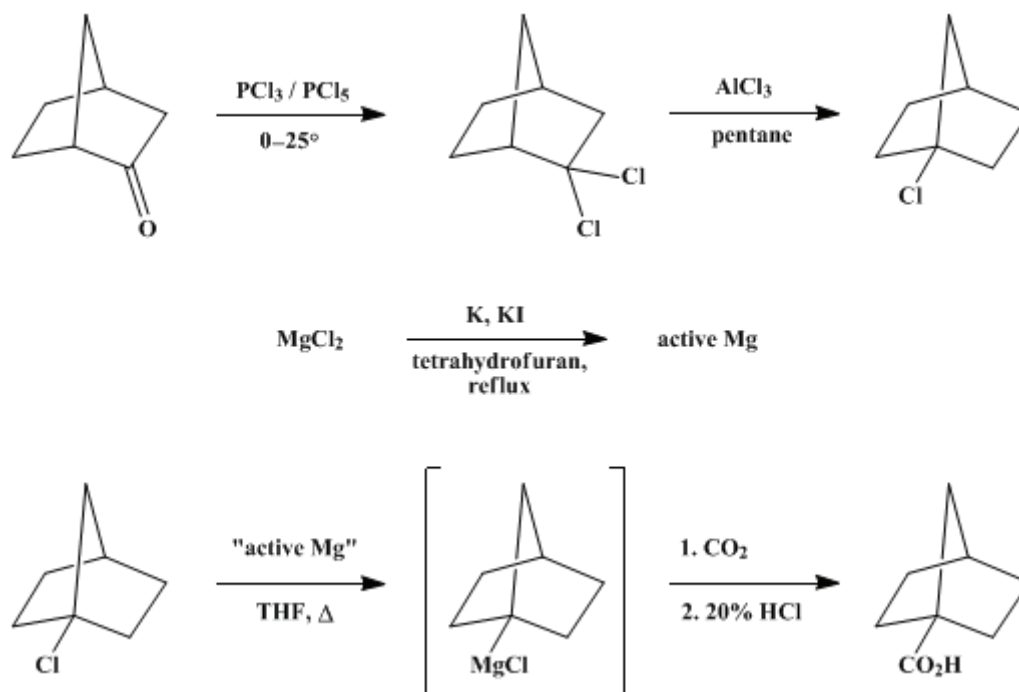
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.845 (1988); Vol. 59, p.85 (1979).

HIGHLY REACTIVE MAGNESIUM FOR THE PREPARATION OF GRIGNARD REAGENTS: 1-NORBORNANECARBOXYLIC ACID

[Bicyclo[2.2.1]heptane-1-carboxylic acid]



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Checked by Dennis P. Stack and Robert M. Coates.

1. Procedure

Caution! Potassium is highly reactive. Although it may be handled safely in air if it is covered with a hydrocarbon solvent such as heptane or mineral oil, it will spark and ignite flammable organic vapors on contact with water. The magnesium formed in this reaction is highly reactive and pyrophoric (Note 1). Accordingly, Parts C and D of this procedure should be carried out behind a safety shield.

A. **2,2-Dichloronorbornane.** A 1-l., round-bottomed flask equipped with a mechanical stirrer and a calcium sulfate drying tube is charged with 91.3 g. (0.665 mole) of phosphorus trichloride and 90.0 g. (0.817 mole) of norcamphor (Note 2). The solution is stirred and cooled to 0° in an ice-salt bath, then 193 g. (0.927 mole) of phosphorus pentachloride is added in portions over a 1-hour period. The mixture is allowed to warm to room temperature and stand overnight. The contents of the flask are poured carefully onto 1000 g. of crushed ice. The mixture is thoroughly dispersed and extracted with four 500-ml. portions of pentane. The combined pentane layers are washed with two 600-ml. portions of water, and the aqueous layers are extracted with one 500-ml. portion of pentane. The pentane extracts are combined, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. Distillation of the residual brown liquid affords 111–114 g. (82–85%) of 2,2-dichloronorbornane as a clear liquid, b.p. $70-74^\circ$ (14 mm.), which solidifies on standing (Note 3).

B. **1-Chloronorbornane.** A 5-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, a condenser fitted with a drying tube, and a stopper is charged with 230 g. (1.39 moles) of 2,2-

dichloronorbornane and 3 l. of pentane (Note 4). The solution is stirred as 87.0 g. (0.652 mole) of aluminum chloride is added over 4.5 hours. The mixture is stirred for 40 hours, during which time hydrogen chloride gas evolves and a brown sludge accumulates on the walls of the flask. The supernatant pentane solution is decanted, and the brown sludge remaining in the flask is thoroughly extracted with four 200-ml. portions of pentane. The combined pentane extracts are washed with three 600-ml. portions of water and one 600-ml. portion of saturated sodium chloride. The combined aqueous washes are extracted with two additional 500-ml. portions of pentane, which are combined with the preceding pentane solution and dried over anhydrous sodium sulfate. The pentane solution is concentrated by distillation through a 3×30 cm. Vigreux column, and the residual liquid is distilled, affording 110–114 g. (60–63%) of 1-chloronorbornane as a colorless liquid, b.p. 70–74° (55 mm.), which solidifies on standing at room temperature (Note 5).

C. *Active magnesium*. A 200-ml., three-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, stopper, rubber septum, and condenser connected to an argon inlet (Note 6) is charged with 1.5 g. (0.038 g.-atom) of freshly cut potassium (Note 7), (Note 8), and (Note 19), 2.01 g. (0.0211 mole) of anhydrous magnesium chloride (Note 9), 3.55 g. (0.0214 mole) of anhydrous potassium iodide (Note 10), and 50 ml. of tetrahydrofuran (Note 11). The mixture is stirred vigorously (Note 12) and heated to reflux with an electric heating mantle (Note 13). A black precipitate starts to form within a few minutes. After 3 hours at reflux temperature, the reduction should be complete (Note 14), producing active magnesium as a black powder that settles very slowly when the stirring is stopped (Note 15).

D. *1-Norbornanecarboxylic acid*. The mixture of active magnesium metal and potassium salts is allowed to cool to room temperature, after which 1.25 g. (0.00958 mole) of 1-chloronorbornane is injected with a syringe through the septum into the flask (Note 16). The reaction mixture is heated under reflux for 6 hours and cooled to room temperature. A large excess of freshly sublimed dry ice chunks is added quickly to the Grignard reagent through the extra neck of the flask. The mixture is stirred vigorously, warmed to room temperature, acidified with 50-ml. of 20% hydrochloric acid, and extracted with three 100-ml. portions of diethyl ether. The combined ether layers are extracted with 100 ml. of 10% aqueous sodium hydroxide. The alkaline solution is acidified with concentrated hydrochloric acid, and the acidic solution is extracted with two 100-ml. portions of ether. The ether extracts are combined, washed with two 50-ml. portions of water, dried over anhydrous sodium sulfate, and evaporated, giving 0.80–0.94 g. (60–70%) of 1-norbornanecarboxylic acid as a slightly yellow crystalline solid, m.p. 106–109° (Note 17) and (Note 18).

2. Notes

1. Although the submitters have never had a fire or explosion caused by active magnesium or other activated metals, they suggest extreme caution in working with these reactive materials, especially while the worker familiarizes him- or herself with the characteristics of each step in the procedure. If the active magnesium is wet with solvent when removed from the reaction vessel, it does not ignite spontaneously. If, however, the magnesium is allowed to dry first, it begins to glow when exposed to air. The submitters advise that the magnesium powder be kept under an argon atmosphere at all times.
2. The submitters purchased norcamphor from Aldrich Chemical Company, Inc. The checkers prepared this compound according to *Org. Synth., Coll. Vol. 5*, 852 (1973).
3. The spectral characteristics of 2,2-dichloronorbornane are as follows: IR (CCl_4) cm^{-1} : 1449, 1307, 1072, 966, 933, 713; ^1H NMR (CCl_4), δ (number of protons): 1.1–2.8 (10H).
4. Pentane was dried by distillation from aluminum chloride.
5. 1-Chloronorbornane has the following spectral properties: IR (CCl_4) cm^{-1} : 1451, 1310, 1298, 1037, 992, 947, 905, 838; ^1H NMR (CCl_4), δ (multiplicity, number of protons, assignment): 1.2–1.9 (broad m, 10H, 5CH_2) and 2.2 (broad s, 1H, CH); ^{13}C NMR (CDCl_3): δ (off-resonance multiplicity, assignment): 31.0 (m, C-2 and C-6 or C-3 and C-5), 34.8 (d, C-4), 38.4 (m, C-2 and C-6 or C-3 and C-5), 46.8 (t, C-7), 70.0 (s, C-1).
6. The apparatus is dried in an oven and maintained under an argon atmosphere during the reaction. The submitters recommend against the use of nitrogen, since there are indications that nitrogen reacts with active magnesium. Argon, used as supplied by Matheson Gas Products or the Linde Division of Union Carbide Corporation, was delivered to the gas-inlet through a combination of glass and Tygon tubing. A

minimum of Tygon tubing is advised to avoid the diffusion of air into the [argon](#) stream.

7. Purified grade [potassium](#) from J. T. Baker Chemical Company has been found by the submitters to give the most consistent results. The checkers used [potassium](#) metal from Allied Chemical Corporation. Very impure [potassium](#) or [sodium](#) generally gives [magnesium powder](#) with much reduced reactivity. [Sodium](#) may be used in place of [potassium](#) provided that the boiling point of the solvent chosen ([Note 11](#)) is higher than the melting point of the metal.

8. The [potassium](#) is usually cut into two or three pieces under [hexane](#) or [heptane](#) and placed wet in a tared flask that has been purged with [argon](#). The flask is evacuated, removing the hydrocarbon, filled again with [argon](#), and weighed to determine the exact amount of [potassium](#). The amount of [potassium](#) used by the checkers varied from 1.4 to 1.6 g., the weights of the other reagents being adjusted proportionately. With this procedure the pieces of [potassium](#) are shiny and relatively free from oxide coating. Alternatively, the [potassium](#) cuttings may be wiped free of solvent, quickly weighed in air, and placed in the flask. The submitters recommend that the first procedure be used.

9. Anhydrous [magnesium chloride](#) from Alfa Division, Ventron Corporation, was used as supplied by both the submitters and checkers. The submitters have subsequently had success with anhydrous [magnesium chloride](#) and bromide purchased from Cerac, Inc., P.O. Box 1178, Milwaukee, Wisconsin 53201. The checkers were unsuccessful in several attempts to prepare suitably active [magnesium](#) from analytical grade anhydrous [magnesium chloride](#), purchased from Research Organic/Inorganic Chemical Corporation. The submitters stress that the reagent must be anhydrous. It may be stored in a desiccator containing anhydrous [calcium sulfate](#) and, if required, dried overnight in an oven at 120°. Anhydrous [magnesium chloride](#) cannot, however, be prepared by heating the hexahydrate under vacuum, since [hydrogen chloride](#) is released before dehydration is complete. The submitters have prepared active [magnesium](#) from anhydrous magnesium bromide and iodide; however, highly insoluble magnesium salts such as the fluoride or sulfate are not reduced. A small excess of [magnesium chloride](#) is used in this procedure to ensure that the [potassium](#) is completely consumed. The submitters have also provided the following unchecked procedure, which is suitable for preparing both anhydrous [magnesium chloride](#) and bromide. The [magnesium turnings](#) and [1,2-dibromoethane](#) used were purchased from J. T. Baker Chemical Company and Aldrich Chemical Company, Inc., respectively. A 200-ml., three-necked, round-bottomed flask equipped with a magnetic stirring bar, two stoppers, and a condenser connected to an argon inlet ([Note 6](#)) is charged with 0.35 g. (0.014 g.-atom) of [magnesium turnings](#), 50 ml. of [tetrahydrofuran](#) ([Note 11](#)), and 3.0 g. (0.016 mole) of [1,2-dibromoethane](#). The suspension is warmed gently, initiating the reaction. After the initially exothermic reaction subsides, the mixture is heated at reflux for 50 minutes. The solvent is evaporated under a reduced pressure of [argon](#) or [nitrogen](#), leaving a white solid. The flask is then evacuated and heated in an oil bath at 150° for 1 hour. The dry [magnesium bromide](#) is ready for preparing active [magnesium](#) in the same flask.

10. [Potassium iodide](#) (>99% purity) from Allied Chemical Corporation or Mallinckrodt Chemical Works is finely ground with a mortar and pestle, dried overnight in an oven at 120°, and stored in a desiccator. The molar ratio of [potassium iodide](#) to [magnesium chloride](#) is not highly critical and may vary from 0.05 to 2.0. However, the optimum ratio is 1:1, as specified in the procedure. If the [potassium iodide](#) is omitted, the black [magnesium powder](#) produced reacts with [bromobenzene](#) at -78°. However, since the [magnesium](#) prepared in this way does not react with [fluorobenzene](#) in refluxing [tetrahydrofuran](#), it is evidently less reactive than that produced in the presence of [potassium iodide](#).

11. The submitters purified the [tetrahydrofuran](#) prior to use by distillation from [lithium aluminum hydride](#). For a warning concerning potential hazards of this procedure, see *Org. Synth., Coll. Vol. 5*, 976 (1973). The checkers distilled the solvent from the sodium ketyl of benzophenone. The submitters have found that [diglyme](#) and [1,2-dimethoxyethane](#) are also effective solvents. The reactivity of the [magnesium](#) obtained with [1,2-dimethoxyethane](#) as solvent is slightly reduced. Hydrocarbons, amines, and [dioxane](#) proved to be ineffective solvents, owing to the insolubility of the magnesium salts and consequent incomplete reduction.

12. Efficient stirring is essential for the generation of highly reactive [magnesium](#). If the stirring is not effective, the reduction may not be complete after the 3-hour reaction time. The remaining unreacted [potassium](#) is a fire hazard during the isolation of the product. If the scale of the reaction is increased, measures should be taken to ensure that effective stirring can be maintained throughout the reaction period. The submitters recommend that, as a precaution, the scale be increased gradually.

13. The mildly exothermic reduction may result in excessive foaming which carries [potassium](#) particles up into the condenser. This problem is avoided by using a relatively large flask (in this case, 200 ml.

instead of 100 ml.) and by carefully controlling the temperature at the beginning of the reduction.

14. The reduction appears to be essentially complete in 30–45 minutes. However, a reaction time of 3 hours is recommended to ensure complete consumption of the [potassium](#) ([Note 12](#)).

15. Although the submitters have found that the active [magnesium](#) may be stored under [argon](#) for several days, they advise that the preparation be used within a few hours to obtain the maximum reactivity. Most of the reactions carried out by the submitters with the active [magnesium](#) were performed in the same flask and solvent used for the reduction. Attempts to evaporate the [tetrahydrofuran](#) and replace it with different solvents resulted in [magnesium](#) suspensions of reduced reactivity. The active [magnesium](#) may be conveniently transferred to another reaction vessel, if desired, as a slurry under an atmosphere of [argon](#).

16. The solid chloride was melted by warming on a steam bath and drawn into a syringe that had been warmed briefly in an oven.

17. The submitters reported a melting point of 114–116°. The checkers obtained analytically pure material with a recovery of 80% after decolorization with activated [carbon](#) and recrystallization from 2–3 ml. of [hexane](#) at 0°. The product was also purified with comparable efficiency by sublimation at 85–90° (10 mm.). A small amount of a yellow, volatile impurity was removed from the cold finger before the product began to sublime. The melting point of the product after purification by the checkers was 110–112° (lit.,² m.p. 114–116°).

18. The spectral properties of the product are as follows: IR (KBr) cm^{-1} : 2960 (OH), 1693 (C=O), 1422, 1312, 1262, 952, 734; ^1H NMR (CCl_4), δ (multiplicity, number of protons, assignment): 1.1–1.9 (m, 10H, 5 CH_2), 2.2 (broad s, 1H, CH), 12.5 (s, CO_2H); ^{13}C NMR (CDCl_3), δ (off-resonance multiplicity, assignment): 30.0 and 33.0 (m, C-2, C-3, C-5, C-6), 37.8 (d, C-4), 42.4 (t, C-7), 52.2 (s, C-1), 183.8 (s, carboxyl C).

19. The submitters have recently developed the following unchecked procedure, which is suitable for preparing highly reactive [magnesium powder](#), using [lithium](#) as a reducing agent.³ This procedure avoids [potassium](#) and produces a [magnesium powder](#) equal in reactivity to that obtained using [potassium](#) as the reducing agent. A 50-ml., two-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, rubber septum, and condenser connected to an argon inlet ([Note 6](#)) is charged with 0.224 g. (0.0325 g.-atom) of freshly cut [lithium](#) ([Note 20](#)), 1.57 g. (0.0165 mole) of anhydrous [magnesium chloride](#) ([Note 9](#)), 0.436 g. (0.00341 mole) of [naphthalene](#) and 10 ml. of [tetrahydrofuran](#) ([Note 11](#)). The mixture is stirred vigorously at room temperature for 24 hours ([Note 21](#)). After complete reduction, the highly reactive [magnesium](#) appears as a dark gray to black powder which slowly settles after stirring is stopped. In some cases, the [tetrahydrofuran](#) has a slight olive green color due to a small amount of [lithium naphthalide](#). This can be ignored when the highly reactive [magnesium](#) is reacted. If desired this can be removed by withdrawing the [tetrahydrofuran](#) with a syringe and adding fresh, dry [tetrahydrofuran](#) or other solvent.

20. [Lithium](#) (99.9%, rod, 1.27 cm. dia.) from Alfa has been used extensively in our studies. The [lithium](#) is cut under oil, rinsed in [hexane](#), and transferred to a tared 24/40 adapter with a stopcock and rubber septum which has been filled with [argon](#). The adapter is evacuated, removing the [hexane](#), filled with [argon](#) and weighed. The [lithium](#) is then transferred to the reaction vessel under an [argon](#) stream.

21. It is important that the reaction be stirred vigorously and that the [lithium](#) make frequent contact with the stirring bar, as the [lithium](#) has a tendency to become coated with [magnesium](#) and stop the reduction from continuing. If reduction does stop, it can be initiated again by gently rubbing the piece of [lithium](#) against the wall of the flask with a metal spatula, the rubber septum can be temporarily removed under a stream of [argon](#) to carry out this procedure.

3. Discussion

The procedures for the preparation of [2,2-dichloronorbornane](#) and [1-chloronorbornane](#) are based on those of Bixler and Nieman.² The active [magnesium](#) generated in Part C of this procedure^{4,5,6} is useful for the formation of Grignard reagents from alkyl and aryl halides that do not react, or react only slowly, with [magnesium turnings](#) or [magnesium](#) activated by previously known methods. Prior to the development of this procedure, four basic modifications of the usual methods for preparing Grignard reagents were utilized for relatively unreactive halides: the use of (1) higher reaction temperatures by variation of the solvent, (2) more strongly coordinating solvents such as [tetrahydrofuran](#),^{7,8,9} (3) various procedures to activate the surface of the [magnesium](#),^{10,11,12,13,14} and (4) [magnesium](#) slurries prepared by co-condensation of [magnesium](#) vapor and solvent.¹⁵

Activation of [magnesium](#) in the third method has been effected by reduction of the size of the metal particles¹³ and chemical reactions. The Gilman procedure,¹⁰ which consists of adding [iodine](#) to activate the [magnesium](#) surface, is representative of the latter technique. [Ethyl bromide](#) and [1,2-dibromoethane](#) have been employed in catalytic amounts to activate the metal surface, and in stoichiometric proportions for entrainment.¹¹ Certain transition metal halides have also proved to be effective catalysts.¹² The [magnesium](#) preparations obtained by the co-condensation method are quite active, though considerably less active than those generated by the reduction process.¹⁶ An alternative procedure has recently been published for the reduction of magnesium halides to activated [magnesium](#) with sodium naphthalene radical anion.¹⁷

Some results from an investigation into the reactions of activated [magnesium](#) with various halides and dihalides, some of which react with difficulty under the conditions of normal Grignard preparations, are given in Table I.⁶ A number of important features can be noted from the table, including the facile formation of di-Grignard reagents and allyl- and vinylmagnesium halides. Alkyl and aryl fluorides are easily converted to the corresponding magnesium fluorides. The formation of Grignard reagents may be effected at temperatures of -78° or below with active [magnesium](#), thus allowing Grignard reactions to be carried out with unstable compounds.

TABLE I
REACTION OF VARIOUS HALIDES WITH ACTIVATED MAGNESIUM

Halide	Magnesium/Halide ^a Ratio	Temperature ($^{\circ}$)	Time (minutes)	Yield of Product (%)		
				Mono- Grignard ^b	Di- Grignard ^b	Carboxylic Acid ^c
1,4-Dibromobenzene	4	25	15		100	
1,4-Bromochlorobenzene	4	25	15	100	10	
	4	25	120	100	100	
1,4-Dichlorobenzene	2	25	180	90	0	80
	4	25	120	100	30	
Fluorobenzene	4	66	60			69
tert-Butyl chloride	2	25	10	100		52
1-Chloronorbornane	1.7	66	360	74		63
Methallyl chloride	2	25	60			82
2-Bromopropene	2	25	5	100		71

^aWith the aryl halides and [1-chloronorbornane](#) the activated [magnesium](#) was formed in the presence of [potassium iodide](#).

^bYield of hydrocarbon determined by GC after hydrolysis.

^cIsolated yield based on halide after carbonation.

The Grignard reagents prepared from activated [magnesium](#) appear to react normally with electrophiles. Thus, reactions with proton donors, ketones, and [carbon dioxide](#) afford hydrocarbons, alcohols, and carboxylic acids, respectively. The reductive coupling of ketones to pinacols had also been accomplished with activated [magnesium](#).¹⁶

[1-Norbornanecarboxylic acid](#) has been prepared by concurrent rearrangement and hydrogenolysis of [endo-2-bromo-2-norbornanecarboxylic acid](#),¹⁸ by sequential reduction and hydrolysis of [exo-2-bromo-1-norbornanecarboxamide](#),¹⁹ by ozonolysis of [1-\(4-methoxyphenyl\)norbornane](#),²⁰ and by carbonation of [1-norbornyllithium](#).²

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 9, 580](#)

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

sodium ketyl of benzophenone

magnesium bromide and iodide

hydrogen chloride,
hydrochloric acid (7647-01-0)

ether,
diethyl ether (60-29-7)

sodium hydroxide (1310-73-2)

phosphorus pentachloride (10026-13-8)

magnesium,
magnesium turnings,
magnesium powder (7439-95-4)

sodium chloride (7647-14-5)

bromide (24959-67-9)

Ethyl bromide (74-96-4)

sodium sulfate (7757-82-6)

potassium iodide (7681-11-0)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

calcium sulfate (7778-18-9)

iodine (7553-56-2)

carbon (7782-42-5)

aluminum chloride (3495-54-3)

sodium (13966-32-0)

bromobenzene (108-86-1)

phosphorus trichloride (7719-12-2)

1,2-dibromoethane (106-93-4)

Naphthalene (91-20-3)

tert-Butyl chloride (507-20-0)

potassium (7440-09-7)

magnesium bromide (7789-48-2)

Pentane (109-66-0)

lithium (7439-93-2)

dioxane (123-91-1)

Fluorobenzene (462-06-6)

magnesium chloride (7786-30-3)

Tetrahydrofuran (109-99-9)

heptane (142-82-5)

[lithium aluminum hydride \(16853-85-3\)](#)

[hexane \(110-54-3\)](#)

[argon \(7440-37-1\)](#)

[1,2-dimethoxyethane \(110-71-4\)](#)

[diglyme \(111-96-6\)](#)

[methallyl chloride \(563-47-3\)](#)

[1-Chloronorbornane \(765-67-3\)](#)

[Norcamphor \(497-38-1\)](#)

[1,4-Bromochlorobenzene \(106-39-8\)](#)

[1-Norbornanecarboxylic acid,
Bicyclo\[2.2.1\]heptane-1-carboxylic acid \(18720-30-4\)](#)

[2,2-Dichloronorbornane \(19916-65-5\)](#)

[lithium naphthalide](#)

[1,4-Dibromobenzene \(106-37-6\)](#)

[1,4-Dichlorobenzene \(106-46-7\)](#)

[2-Bromopropene \(557-93-7\)](#)

[1-\(4-methoxyphenyl\)norbornane](#)

[1-norbornyllithium](#)

[endo-2-bromo-2-norbornanecarboxylic acid](#)

[exo-2-bromo-1-norbornanecarboxamide](#)