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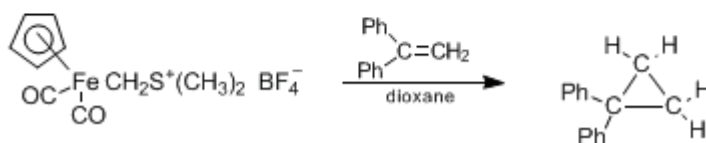
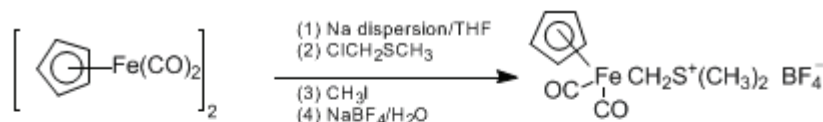
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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CYCLOPROPANATION USING AN IRON-CONTAINING METHYLENE TRANSFER REAGENT: **1,1-** **DIPHENYLCYCLOPROPANE**

[Iron (1+), dicarbonyl(η^5 -2,4-cyclopentadien-1-yl)(dimethylsulfonium η -methylide)-, tetrafluoroborate (1-)] and **Benzene, 1,1'-cyclopropylidenebis-]**



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Checked by Jörn-Bernd Pannek and Ekkehard Winterfeldt.

1. Procedure

CAUTION! This experiment should be performed in an efficient fume hood because of the unpleasant odors of sulfide-containing materials. In addition, the first part of this procedure should be conducted behind a safety shield because of the use of highly reactive sodium metal.

Into a dry, one-necked, 2000-mL, round-bottomed flask is placed a medium-sized magnetic stirring bar (Note 1) and cyclopentadienyliron dicarbonyl dimer $[\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}]_2$, (0.50 mol equiv, 0.21 mol, 74.4 g; (Note 2) and (Note 3)). Sodium dispersion (40% by weight) in light mineral oil (1.25 mol equiv, 0.52 mol, 30.1 g; (Note 4) and (Note 5)) is weighed into the flask (Note 6). The flask is then equipped with a reflux condenser topped with a three-way stopcock (Note 7) having a vertical tubulation capped with a septum through which solvents and reagents can be introduced with long needles or cannulas. By evacuation through the other tubulation of the stopcock, the apparatus is evacuated and filled with nitrogen twice, then placed under vacuum (≤ 0.1 mm) for 1 to 2 hr to remove the bulk of the mineral oil. The flask is filled with nitrogen, and tetrahydrofuran (THF; 850 mL; (Note 8)) is transferred into the flask. Rapid stirring is begun and maintained while an oil bath or a heating mantle is employed to heat the mixture at reflux for ≥ 18 hr.

The flask is cooled to 0°C in an ice bath, and chloromethyl methyl sulfide (1.00 mol equiv, 0.42 mol, 35.2 ml) is added dropwise with a syringe over 25 min (Note 9) and (Note 10). After residues of the sulfide are rinsed into the flask with additional THF (ca. 5–10 mL), the mixture is stirred at 0°C for 1 hr and then at 25°C for 1 hr (Note 11). Iodomethane (1.30 mol equiv, 0.55 mol, 34.0 mL; (Note 12)) is added over 5 min using a syringe. After residues of iodomethane are rinsed into the flask with THF (5–10 mL), the mixture is stirred at 25°C for ≥ 15 hr. Stirring is stopped (Note 13), and the volatile materials are removed under vacuum (≤ 0.1 mm) using a large, liquid nitrogen-cooled trap (Note 14). The vacuum in the apparatus is relieved with nitrogen, and the three-way stopcock is removed from the top of the condenser, exposing the reaction mixture to air.

In a 2000-mL Erlenmeyer flask containing a magnetic stirring bar, a solution of sodium tetrafluoroborate (6.00 mol equiv, 2.52 mol, 277 g) in water (1200 mL total volume of solution) is

prepared and heated to 95°C while being stirred. A 1000-mL portion of the hot [sodium tetrafluoroborate](#) solution is slowly poured down the condenser into the reaction mixture which is kept at ca. 95°C while being stirred. At the same time, a 350-mL, medium-frit, sintered-glass Büchner funnel is prepared with a 2.5-cm layer of diatomaceous earth and a 1-cm layer of sand covered with a piece of filter paper with holes punched in it, and the funnel is preheated by passage, with suction, of 700–1000 mL of hot, distilled water which is then discarded. The condenser is removed from the reaction flask, and the contents are suction-filtered through the hot funnel into a heated, 2000-mL filter flask ([Note 15](#)). The remaining hot [sodium tetrafluoroborate](#) solution is used to rinse the reaction flask and the hot funnel. The combined filtrates are swirled while being cooled. If necessary, a seed crystal can be added. The filtration flask is placed in an ice bath while swirling is continued. After the temperature reaches 0°C, the flask is placed in a freezer at ca. –10°C for 1–3 hr. The product is collected by suction filtration using a large, chilled Büchner funnel (Whatman no. 1 filter paper) and is rinsed with ice-cold distilled water (150 mL) and cold [diethyl ether](#) (1500 mL). The filter cake is broken up, and the crystals are dried in a stream of air overnight. There is obtained 100.6 g (70.4%) of (η^5 -C₅H₅)(CO)₂FeCH₂S⁺(CH₃)₂ BF₄⁻ as free-flowing, flake-like, amber crystals ([Note 16](#)), ([Note 17](#)), ([Note 18](#)). The yields were found to be considerably lower on runs of smaller scale ([Note 19](#)).

Into a 200-mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar are placed the crystalline reagent (35 g, 0.10 mol; [Note 20](#)), [1,1-diphenylethene](#) (9.1 mL, 9.3 g, 0.05 mol; [Note 21](#)), and [dioxane](#) (25 mL; [Note 22](#) and [Note 23](#)). The flask is equipped with a reflux condenser topped with a stopcock, and a [nitrogen](#) atmosphere ([Note 24](#)) is established within the apparatus. While being stirred vigorously, the heterogeneous mixture is heated to reflux in an oil bath (120°C) for 14 hr ([Note 25](#)). The brown mixture is removed from the oil bath and allowed to cool sufficiently to permit the addition of [hexane](#) (75 mL, [Note 26](#)) to the flask. The mixture is stirred in the air until the flask reaches 25°C. The supernatant liquid containing the product is poured from the flask and filtered through Whatman no. 1 filter paper. The remaining solid is repeatedly suspended and washed with several portions of [hexane](#) (ca. 1000 mL total; [Note 27](#)). The combined filtrates are filtered through a pad of silica gel in a sintered glass Büchner funnel and are then concentrated by rotary evaporation. The residual dark brown oil is dissolved in [methanol](#) (200 mL) to give an orange-brown solution which immediately becomes dark green when solid [ferric chloride](#) (7 g; [Note 28](#)) is added at 25°C. The mixture is stirred for 15 min and then concentrated by rotary evaporation. The residual dark green oil is extracted with two 200-mL portions of [hexane](#), and the combined extracts are filtered through a pad of silica gel and concentrated by rotary evaporation. The colorless oil that remains is distilled through a short-path apparatus to give 8.76 g (88%) of [1,1-diphenylcyclopropane](#) as a clear, colorless liquid, bp 89°C (0.8 mm; lit³ 110–111°C, 1.3 mm; [Note 29](#)). The checkers obtained 65–77% yield of product on roughly half the scale.

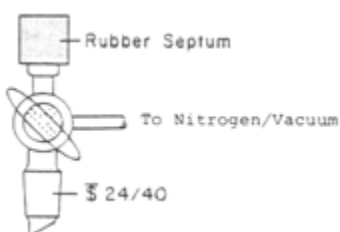
2. Notes

1. The stirring bar must be able to stir the heterogeneous reaction mixture rapidly. Very good stirring is required for the [metallic sodium](#) dispersion to react efficiently. A medium-sized, egg-shaped stirring bar (32 × 16 mm, available from Fisher Scientific Company) was found to be particularly effective.
2. Cyclopentadienyliron dicarbonyl dimer [C₅H₅(CO)₂Fe]₂ can be purchased from Alfa Products, Morton/Thiokol Inc. or Aldrich Chemical Company, Inc. Alternatively, it is easily and inexpensively prepared by heating [dicyclopentadiene](#) with [iron pentacarbonyl](#). Our yield (80–90%) of this reagent is considerably higher than that reported in the literature procedure.⁴
3. In order to allow for proper placement of the [sodium](#) dispersion in the flask later ([Note 5](#)), the [C₅H₅(CO)₂Fe]₂ was neatly piled in a mound on top of the stirring bar in the middle of the bottom of the flask.
4. The 40% (by weight) [sodium](#) dispersion in light mineral oil was used as obtained from Aldrich Chemical Company, Inc., except for thorough shaking immediately prior to transfer of the dispersion.
5. A 1-cm diameter glass tube narrowed to a tip at one end and equipped with a pipet bulb was used to transfer the dispersion which was carefully placed around the perimeter of the mound of [C₅H₅(CO)₂Fe]₂. After evaporation of the oil, the stirring bar should rest in the center of the ring of [sodium](#) without contacting it. In this way, the reaction mixture can subsequently be stirred more efficiently. Also, all of the [sodium](#) should lie below the surface of the [tetrahydrofuran](#) solution formed, so that the mixture reacts efficiently upon being heated at reflux.
6. The procedure described here for reductive cleavage of this compound with [sodium](#) dispersion⁵ to

give sodium cyclopentadienyldicarbonylferrate is considerably more convenient and less hazardous than the more traditional use of sodium amalgam that was reported previously.^{6 7 8}

7. The stopcock used in this procedure is of the design shown in Figure 1. A source of inert gas and vacuum can be attached to the horizontal tubulation. The vertical tubulation is capped with a septum to allow introduction of liquid reagents and solvents through use of a long syringe needle or cannula inserted through the septum and down through the body of the stopcock. In order to avoid air leaks through the septum into the reaction apparatus when reagents are not being added, the stopcock is normally turned to close off the vertical tubulation, but to leave the flask open to the nitrogen/vacuum source.

Figure 1



8. Commercial, anhydrous-grade tetrahydrofuran (THF) is further purified by distillation from a dark blue or purple solution of sodium benzophenone ketyl or dianion under nitrogen. One method for transferring the THF into the reaction flask is through the use of cannulas. The cannulas (available from Aldrich Chemical Company, Inc.) are constructed from 60-cm sections of 18-gauge stainless steel tubing with a needle tip at each end. It is perhaps more convenient to use two short sections of needle tubing (each having a needle point at only one end) joined with 25–50 cm of small-diameter Teflon tubing. Transfer through the cannula is facilitated by applying a slight vacuum to the reaction apparatus while maintaining a positive pressure of nitrogen in the flask originally containing the distilled THF. Alternatively, the THF can be distilled directly into the reaction flask.

9. Chloromethyl methyl sulfide was obtained from Aldrich Chemical Company, Inc. and distilled under nitrogen prior to use, although direct use of the commercial material without distillation had little effect on the overall efficiency of this procedure.

10. **WARNING:** Chloromethyl methyl sulfide has a very unpleasant, penetrating odor and should be handled in a properly ventilated fume hood. Also, because of its structural similarity to chloromethyl methyl ether which is highly toxic and an OSHA-regulated carcinogen, this sulfide should be handled as a substance having potentially similar toxic properties.

11. The product of this alkylation step is $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeCH}_2\text{SCH}_3$ which is used directly in the next step but which, if desired, can be isolated as a dark yellow-brown, somewhat air-sensitive oil in greater than 90% yield.^{9,10 11}

12. Iodomethane (99%) was used as obtained from Aldrich Chemical Company, Inc. Excess iodomethane is used to quench any unreacted sodium metal.

13. At this point, the flask can be swirled so that any small amounts of sodium adhering to the wall of the flask above the solution level can be coated with the reaction mixture.

14. Trapping of the unreacted chloromethyl methyl sulfide in the cold trap is recommended because of the problems summarized in (Note 10).

15. In order for this filtration to proceed smoothly, the funnel and its contents must remain hot to avoid premature crystallization of the product and clogging of the funnel. Minor clogging can be remedied by addition of a 100-mL portion of boiling distilled water to the funnel. Major clogging may require addition of boiling water and agitation of the filtration media with a spatula. This addition, however, may reduce the yield of the crystallized product.

16. Physical data for this compound are the following: mp 129–130°C (corrected); IR (KBr pellet) cm^{-1} : 3120, 3035, 2040, 1955, 1417, 1328, 1280, 1055, 852; ^1H NMR (80 MHz, CD_3NO_2) δ : 2.72 (s, 2 H, CH_2), 3.00 (s, 6 H, 2 CH_3), 5.34 (s, 5 H, C_5H_5); ^{13}C NMR (20 MHz, CD_3NO_2) 13.35 (CH_2), 31.20 (CH_3), 87.88 (C_5H_5), 215.56 (CO).

17. This material is satisfactory for alkene cyclopropanation reactions, although recrystallization can be effected very easily by dissolving the crude product in nitromethane at 25°C in the air and by slowly cooling the filtered solution to –70°C. The recrystallization recovery is greater than 80% and provides large, "gem-like," amber-colored crystals. Acetone can also be used as the recrystallization solvent.

18. This reagent can be stored in ordinary flasks or bottles in the air, but it should be protected from bright light, which leads to slow decomposition. Storage in a dark brown bottle is recommended.
19. The checkers' yields ranged from 25–46% in preparations that were run on one-fourth to one-half of the scale used by the submitters.
20. A two-fold excess of the **iron** reagent is employed to assure high conversion of the alkene to the **cyclopropane**. Equimolar amounts of the starting materials can be used, but the **cyclopropane** yield is ca. 20% lower.
21. **1,1-Diphenylethene** is obtained from Aldrich Chemical Company, Inc. and is used without further purification.
22. **1,4-Dioxane** is distilled from sodium benzophenone ketyl under **nitrogen**.
23. **Nitromethane** is also a good solvent for this reaction, and in some cases gives somewhat higher yields of cyclopropanes. Also, the reaction times are reduced to 2–4 hr when **nitromethane** is used. Before use, this solvent is purified according to a published procedure.¹² Commercially obtained solvent is first dried over anhydrous **magnesium sulfate** and then over anhydrous **calcium sulfate**. The solvent is filtered into a flask containing activated 3 Å molecular sieves and is heated at 60°C for 8 hr while being stirred. **Nitromethane** is distilled from the powdered molecular sieves under reduced pressure (bp 58°C, 150 mm; lit.¹² 58°C, 160 mm) directly into a flask containing additional 3 Å molecular sieves. The purified solvent is stored in the dark. When "wet" **nitromethane** from commercial sources is used directly as the reaction solvent, the percent conversions of alkenes to cyclopropanes are reduced substantially. **CAUTION:** Distillations of **nitromethane** and reactions using this solvent at elevated temperature should be conducted behind a safety shield.
24. When the cyclopropanation reactions are run in the presence of air, the yields are slightly reduced.
25. Vigorous stirring is necessary for a reasonable rate of reaction. The mixture remains heterogeneous both before and after the **iron** reagent melts. Monitoring of the reaction by GLPC (2-m 5% OV-1 or SE-30) is recommended to assure maximum conversion before the reaction is stopped.
26. The function of the **hexane** (or **pentane**) is to promote precipitation of organometallic byproducts.
27. The solid is bright yellow after these washings and consists primarily of $[\text{C}_5\text{H}_5(\text{CO})_2\text{FeS}(\text{CH}_3)_2]^+ \text{BF}_4^-$ and some unreacted cyclopropanation reagent. The latter can be recovered if desired by recrystallization of this mixture from **acetone**.
28. **Ferric chloride** destroys ferrocene, a contaminating side product that is difficult to remove by physical means because of its hydrocarbon-like characteristics.
29. The purity of this product is greater than 98% as determined by GLPC (2-m 5% OV-1 or SE-30). The spectral properties are as follows: ¹H NMR (300 MHz, CDCl₃, cf. lit.³) δ: 1.30 (s, 4 H, 2 cyclopropyl CH₂), 7.12–7.40 (m, 10 H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ: 16.33 (cyclopropyl CH₂), 29.97 (quaternary cyclopropyl C), 125.9 (para C), 128.2, 128.4 (ortho and meta C), 145.8 (ipso C); MS (EI, 70 eV) m/e (rel intensity) 194 (M⁺, 86), 193 (100), 178 (64), 115 (9).

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

Despite their high ring strain, cyclopropanes are commonly encountered among naturally occurring as well as synthetic compounds. Cyclopropanes are most commonly synthesized by addition of alkylidene units to alkenes.^{13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32} These reactions employ various types of carbenes, carbenoids, or diazo compounds. One particularly important method is the Simmons-Smith reaction¹⁴ which, according to the original procedure, involves the treatment of **diiodomethane** with **zinc-copper** couple to generate a reactive intermediate that serves as a cyclopropanation reagent. Several modifications of this procedure have been reported more recently. Another common approach is to employ a dihalocarbene to give a 1,1-dihalocyclopropane which is treated subsequently with a reducing agent to effect replacement of the halide substituents by **hydrogen**.

In the mid-1960's, transition metal carbene complexes were first reported by E. O. Fischer.^{33 34 35 36 37 38 39 40 41 42 43 44} Although their structures may be suggestive of classical carbene-like behavior, relatively few of these complexes serve as useful cyclopropanation reagents.^{45 46 47 48 49 50 51 52 53 54 55 56 57}

58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 Rather, these compounds exhibit their own characteristic types of reactions, many of which are useful in synthetic transformations other than cyclopropanations. Contrary to this more general case, Pettit⁷⁹ ⁸⁰ and then Green⁸¹ reported some early findings that indicated the possible utility of certain iron carbene complexes for three-membered ring construction. Their studies were followed by investigations of iron complexes by many others,^{25,82 83 84 85} ^{86 87 88 89 90 91 92 93 94 95 96 97 98 99 100} among which has been the recent work of Brookhart^{101 102 103 104} and Casey.^{105 106 107}


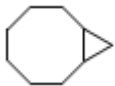


Helquist has focused efforts on developing synthetically useful cyclopropanation reagents based upon the use of stable organoiron compounds which may be regarded, at least formally, as direct precursors of reactive carbene complexes. Sulfonium derivatives^{11,108 109 110 111 112 113} and alkenyl complexes^{114 115} have proven to be useful in this regard. The presently described **methylene** transfer reagent^{11,108,109} and a related **ethylidene** transfer reagent^{110,111} are included among the former sulfonium salt complexes. Among the many compounds reported by Brookhart is a useful silyl ether-based reagent for **ethylidene** transfer¹⁰¹ as well as a reagent for asymmetric cyclopropanations.¹⁰² Helquist^{114,115} and Casey^{105,106,107} have also reported complexes for transfer of several more complex types of alkylidene units.

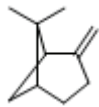
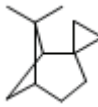


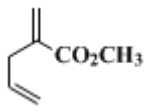
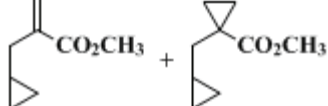
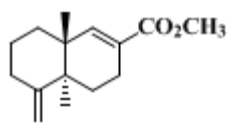
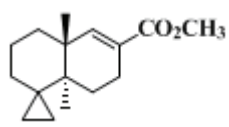
An important advantage of the presently described procedure is that the cyclopropanation reagent is unusually stable for an organometallic compound. Not only is the solid reagent stable to air indefinitely, but its crystallization is accomplished from hot aqueous solutions. Samples of this reagent have been stored in ordinary laboratory reagent bottles for more than five years with no noticeable decomposition. This stability is in contrast to typical Simmons-Smith intermediates and diazoalkanes. Another advantage of the present reagent is that once it has been prepared, its subsequent use in cyclopropanation reactions is trivially straightforward. The reagent can be handled as an ordinary laboratory reagent and combined with an alkene substrate and a suitable solvent in an ordinary flask. Although an inert atmosphere is specified for the present cyclopropanation, these reactions have also been performed routinely in the air with only small reductions in yields.

1,1-Diphenylcyclopropane has been prepared previously by (1) the Simmons-Smith procedure (24% yield)^{14,116} and modified versions of this method (up to 72%),^{117 118} (2) **sulfonium ylide** addition to **1,1-diphenylethene** (61% yield),^{119 120} (3) reduction of 1,1-diphenyl-2,2-dihalocyclopropanes with **sodium** in **ammonia** (47% yield),^{121 122} with **sodium** and **tert-butyl alcohol** (80%),³ or with **diethyl lithiomethanephosphonate** (62%),¹²³ (4) base-promoted cyclization of **trimethyl(3,3-diphenylpropyl) ammonium iodide** (78%),^{124 125} (5) **boron trifluoride**-promoted cyclization of a corresponding **3-hydroxypropylstannane** (97%),¹²⁶ (6) reaction of **3,3-diphenylpropenoic acid** with **lithium aluminum hydride** (62%),¹²⁷ (7) reaction of **diphenylmethane** with $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ (20%),¹²⁸ (8) decomposition of the **pyrazoline** (unspecified yield) obtained by addition of **diazomethane** to **1,1-diphenylethene**,^{129 130} (9) thermolysis of a corresponding acyldiazene (43%),¹³¹ (10) photolysis of **2,2-diphenylcyclobutanone** (19%),¹³¹ and (11) decarboxylation of **1,1-diphenyl-2-carboxycyclopropane** (unspecified yield).¹³²

The Table summarizes some of the other examples of cyclopropanations that have been performed by the presently described procedure.^{11,108,110,133}

TABLE I
OTHER CYCLOPROPANATIONS USING $\text{C}_5\text{H}_5(\text{CO})_2\text{FeCH}_2\text{S}^+(\text{CH}_3)_2\text{BF}_4^-$

Alkene	Cyclopropane Product(s)	Consumption of Alkene (%) ^a	Yield (%) ^b
		96	92
		81	70

		100	58
		86	96
		99	62 + 5
		100	86 ^c

^aThe % consumption values were determined by quantitative GLPC measurement of unreacted alkenes using an internal standard. ^bThe yields were determined by quantitative GLPC using an internal standard and are corrected for unreacted alkenes. The reactions were typically run on 1-mmol scales. ^cTaken from ref. ¹³³.

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

BF₄

sodium benzophenone ketyl

Ferrocene

Iron (1+), dicarbonyl(η^5 -2,4-cyclopentadien-1-yl)(dimethylsulfonium η -methylide)-, tetrafluoroborate
 (1-)

cyclopentadienyliron dicarbonyl dimer

sodium cyclopentadienyldicarbonylferrate

1,1-diphenyl-2,2-dihalocyclopropanes

acyldiazene

[ammonia](#) (7664-41-7)

methanol (67-56-1)

diethyl ether (60-29-7)

hydrogen (1333-74-0)

iron (7439-89-6)

sulfonium ylide (7783-06-4)

nitrogen (7727-37-9)

calcium sulfate (7778-18-9)

acetone (67-64-1)

sodium,
metallic sodium (13966-32-0)

Diphenylmethane (101-81-5)

ferric chloride (7705-08-0)

iodomethane (74-88-4)

1,1-diphenylethene (530-48-3)

methylene,
carbene (2465-56-7)

Pentane (109-66-0)

Nitromethane (75-52-5)

diiodomethane (75-11-6)

chloromethyl methyl ether (107-30-2)

cyclopropane (75-19-4)

magnesium sulfate (7487-88-9)

dioxane (5703-46-8)

Diazomethane (334-88-3)

zinc-copper

boron trifluoride (7637-07-2)

Tetrahydrofuran (109-99-9)

lithium aluminum hydride (16853-85-3)
hexane (110-54-3)
sodium tetrafluoroborate (13755-29-8)
ethylidene
dicyclopentadiene (77-73-6)
tert-butyl alcohol (75-65-0)
iron pentacarbonyl
1,1-Diphenylcyclopropane,
Benzene, 1,1'-cyclopropylidenebis- (3282-18-6)
3,3-diphenylpropenoic acid (606-84-8)
trimethyl(3,3-diphenylpropyl)ammonium iodide
pyrazoline
cyclopropyl (2417-82-5)
1,4-dioxane (123-91-1)
chloromethyl methyl sulfide (2373-51-5)
diethyl lithiomethanephosphonate
3-hydroxypropylstannane
2,2-diphenylcyclobutanone
1,1-diphenyl-2-carboxycyclopropane