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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.

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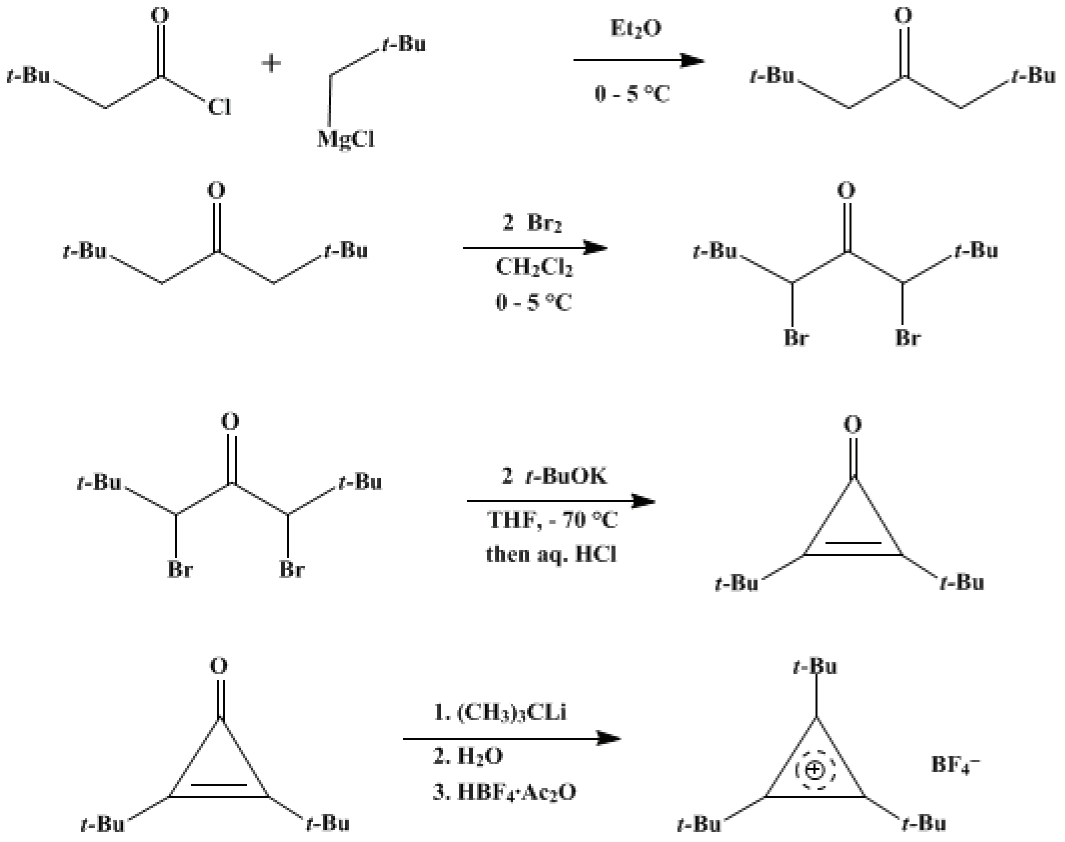
TRI-*tert*-BUTYLCYCLOPROPENYL TETRAFLUOROBORATE

[Cyclopropenylium, 1,2,3-tris(1,1-dimethylethyl)-, tetrafluoroborate(1-)]



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1. Procedure

Caution! tert-Butylithium is extremely pyrophoric and must not be allowed to come into contact with the atmosphere. This reagent should only be handled by individuals trained in its proper and safe use. It is recommended that transfers be carried out by using a 20-mL or smaller glass syringe filled to no more than 2/3 capacity, or by cannula. For a discussion of procedures for handling air-sensitive reagents, see Aldrich Technical Bulletin AL-134. [Note added August 2009].

A. *Dineopentyl ketone*. A dry, 2-l., three-necked flask is fitted with a reflux condenser, a precision, pressure-equalizing addition funnel, and a mechanical stirrer. A gas-inlet tube at the top of the condenser is used to maintain a static nitrogen atmosphere in the reaction vessel throughout the reaction. The flask is charged with 900 ml. of anhydrous diethyl ether, 45 g. (1.85 g.-atoms) of magnesium turnings, and 74.6 g. (0.700 mole) of 1-chloro-2,2-dimethylpropane (Note 1). The vigorously stirred mixture is heated to gentle reflux before 156 g. (0.839 mole) of 1,2 dibromoethane in 150 ml. of dry ether is added over a 12-hour period (Note 2). After addition is complete, the reaction mixture is refluxed for an additional 2 hours. The mixture is then cooled to 0–5° in an ice bath, and 71.7 g. (0.533 mole) of *tert*-butylacetyl chloride (Note 3) in 150 ml. of dry ether is added dropwise to the rapidly stirred Grignard reagent over a period of 1.5 hours (Note 4). The mixture is then stirred at 0–5° for an additional 1.5 hours and poured with stirring onto a mixture of 800 g. of cracked ice and 150 ml. of concentrated hydrochloric acid. The ether layer is separated and washed consecutively with 100 ml. each of water, 5% aqueous sodium carbonate solution, and finally saturated aqueous sodium chloride. After drying over anhydrous magnesium sulfate, filtration, and removal of solvent with a rotary evaporator, the yellow residual oil is distilled under reduced pressure, yielding 81.2 g. (90%) of dineopentyl ketone as a colorless oil, b.p. 86–90° (22 mm.) (Note 5) and (Note 6).

B. α,α'-*Dibromodineopentyl ketone*. *Caution! The dibromoketone, a highly volatile compound with lachrymatory properties, is a skin irritant which may induce allergic effects. Therefore, steps B and C should be performed in a well-ventilated hood. Rubber gloves should be worn.* A 1-l., three-necked flask fitted with a thermometer, an addition funnel, a magnetic stirring bar, and a gas-exit tube, which is connected with Tygon tubing to a funnel inverted over a beaker of water for trapping hydrogen bromide, is charged with 82 g. (0.48 mole) of dineopentyl ketone in 500 ml. of dichloromethane, and the solution is cooled to 0–5° in an ice bath. Over a period of 5 hours, 160 g. (1.00 mole) of bromine is added dropwise (Note 7), and the mixture is stirred an additional hour at 0–5°. The reaction mixture is carefully transferred to a 1-l. separatory funnel, and the excess bromine is destroyed by extraction with 100 ml. of saturated aqueous sodium sulfite (Note 8). After washing with 100 ml. of 5% aqueous sodium hydrogen carbonate solution and 100 ml. of aqueous saturated sodium chloride, the organic layer is dried over magnesium sulfate, filtered, and evaporated with a rotary evaporator. The yellow, crystalline residue is dissolved in 350 ml. of hot hexane and cooled in ice, giving the dibromoketone as white needles, which are collected by suction filtration, washed with 100 ml. of cold hexane (Note 9), and air dried in a well-ventilated hood, yielding 83 g. of product. Concentration of the mother liquors provides two additional crops of crystals (40 g. and 12 g.) for a total yield of 135 g. (85%) of dibromoketone, m.p. 69–72° (Note 10).

C. *Di*-tert-*butylcyclopropenone*. *Caution! The same precautions described in Part B should be exercised in this step.* A dry, 1-l., three-necked flask fitted with an efficient mechanical stirrer, a low temperature thermometer, and a solid addition assembly (Note 11) is charged with 97 g. (0.30 mole) of the dibromoketone and 700 ml. of anhydrous tetrahydrofuran (Note 12). After the reaction vessel has been flushed with nitrogen, a static nitrogen atmosphere is maintained in the reaction vessel throughout the remainder of the reaction. The vigorously stirred solution is cooled to −70° in an acetone–dry ice bath before 80 g. (0.71 mole) of powdered potassium *tert*-butoxide (Note 13) is added over a 2-hour period. The addition is completed, the mixture is stirred an additional hour at −70°, and 50 ml. of 10% hydrochloric acid is added dropwise. The cooling bath is then removed, and the mixture is allowed to warm to room temperature. The precipitated salts are filtered and washed with 100 ml. of tetrahydrofuran, and the filtrate and washing are combined. Most of the tetrahydrofuran is removed under reduced pressure, the nearly colorless residue is dissolved in 450 ml. of hexane (Note 14), and this solution is extracted twice with 100 ml. of water and once with 100 ml. of saturated aqueous sodium chloride. The organic layer is dried over magnesium sulfate, filtered, and concentrated with a rotary evaporator, leaving a pale-yellow oil which crystallizes upon standing. Sublimation of the crude product at 55° (1 mm.) provides 39–41 g. (79–83%) of the cyclopropenone, m.p. 61–63° (Note 15) and (Note 16).

D. *Tri*-tert-*butylcyclopropenyl tetrafluoroborate*. A dry, 500-ml., three-necked flask equipped with a magnetic stirring bar, a pressure-equalizing addition funnel, and a nitrogen inlet system is charged with 56 ml. of a 2.34 *M* commercial solution of *tert*-butyllithium (0.126 mole) in pentane (Note 17) and cooled in an ice bath to 0°. A solution of 20.0 g. (0.120 mole) of di-*tert*-butylcyclopropenone in 200 ml. of pentane is added over 30 minutes, and then the ice bath is removed. The reaction mixture is stirred an additional 30 minutes, and the nearly colorless mixture is poured, with vigorous stirring, into 150 ml. of water. The pentane layer is separated, washed with two 75-ml. portions of water, dried over magnesium sulfate, filtered, and concentrated using a rotary evaporator, leaving a pale-yellow oil which is transferred to a 1-l. Erlenmeyer flask and diluted with 600 ml. of ether. After cooling the ether solution to 0° with an ice bath, a freshly prepared 10% solution of fluoroboric acid in acetic anhydride (Note 18) is added with rapid magnetic stirring. After the resulting suspension is stirred for 20 minutes the white precipitate is collected on a sintered glass funnel (medium porosity) under vacuum and washed thoroughly with 75-ml. portions of ether. The product is dissolved in a minimal amount of boiling acetone (*ca.* 300 ml.), cooled in a freezer (*ca.* −25°), filtered, and washed with ether, yielding 15.3 g. of tri-*tert*-butylcyclopropenyl tetrafluoroborate as white needles. Concentration of the mother liquors gives two additional crops (6.6 and 2.1 g.) of pure product, for a total yield of 24–28 g. (68–79%). When heated on a hot stage, the material darkens with decomposition above 300° (Note 19).

2. Notes

1. Reagent grade anhydrous ether is employed in all operations without prior purification. The magnesium turnings were available from the J. T. Baker Chemical Company, and the 1-chloro-2,2-dimethylpropane (b.p. 84–85°), obtained from Matheson, Coleman and Bell, should be distilled before use.

2. The 1,2-dibromoethane (Eastman Organic Chemicals) was used without prior purification.

3. The *tert*-butylacetyl chloride (b.p. 126–129°) was purchased from Aldrich Chemical Company, Inc., and used without prior purification.

4. Inverse addition of the Grignard reagent to an ethereal solution of the *tert*-butylacetyl chloride does not improve the yield.

5. Fractional distillation is not necessary since the only volatile components are ether and dineopentyl ketone. A dark, high-boiling residue remains in the pot.

6. The ^{1}H NMR spectrum ($CDCl_3$) shows two singlets at δ 1.03 (18H) and 2.29 (4H). The IR spectrum (CCl_4) exhibits bands at 2950 (s), 2900 (s), 2865 (s), 1715 (s), 1480 (s), 1470 (s), 1370 (s), and 1355 cm^{-1} (s).

7. Irradiation with a sun lamp or addition of one drop of concentrated hydrochloric acid may be necessary to initiate the bromination.

8. *Caution! The extraction with sodium sulfite should be performed with caution since a considerable amount of heat is evolved.*

9. The dibromoketone is quite soluble in hexane; therefore, filtration should be conducted as rapidly as possible. The hexane should be precooled to at least 0°.

10. Very pure dibromoketone (m.p. 70–71°) may be obtained by sublimation at 25° (1 mm.); however, the product obtained by recrystallization is sufficiently pure for the next step. The ^{1}H NMR spectrum ($CDCl_3$) shows singlets at δ 1.18 (18H) and 4.42 (2H). The IR spectrum (CCl_4) shows peaks at 2960 (s), 2935 (m), 2910 (m), 2870 (m), 1740 (s), 1720 (m), 1715 (m), 1485 (s), 1475 (s), 1400 (m), 1375 (s), and 1340 cm.$^{-1}$ (s).

11. A convenient apparatus for the addition of pottassium *tert*-butoxide consists of a 250-ml. filter flask connected to the reaction vessel with Gooch tubing. The sidearm of the filter flask serves as a nitrogen inlet.

12. The tetrahydrofuran should be freshly distilled from lithium aluminium hydride. See *Org. Synth.*, **Coll. Vol. 5**, 926 (1973) for a warning concerning the purification of tetrahydrofuran.

13. Alcohol-free potassium *tert*-butoxide, obtained from the MSA Research Corporation, Callery, Pennsylvania, should be weighed and transferred under anhydrous conditions.

14. Hexane is most effective in permitting extraction of residual tetrahydrofuran into water. Failure to remove the tetrahydrofuran can delay the crystallization of the cyclopropenone.

15. The checkers noted the presence of an oil which also distilled onto the cold-finger during the sublimation. The easiest way to remove this oil is to press the sublimed cyclopropenone between two sheets of filter paper. The melting point is recorded after having removed the oil in this manner. This oil poses no hindrance in the next step. Alternatively, the submitters report that the pure cyclopropenone can be obtained more rapidly, but in slightly reduced yield, by recrystallization of the crude product from pentane at low temperature (*ca.* −70°).

16. The ^{1}H NMR spectrum ($CDCl_3$) shows a singlet at δ 1.34. The IR spectrum (CCl_4) shows bands at 2980 (s), 2945 (m), 2920 (m), 2880 (m), 1875 (m), 1855 (s), 1820 (s), 1640 (s), 1485 (m), 1465 (m), and 1375 cm.$^{-1}$ (m). The UV spectrum exhibits a maximum at 260 nm (log ε 1.66) in 95% C_2H_5OH and at 285 nm (log ε 1.79) in cyclohexane. The mass spectrum shows peaks at *m/e* 166, 138, 123, 95, 81, and 67.

17. The *tert*-butyllithium was obtained from Alfa Inorganics, Inc.

18. *Caution! The reaction of fluoroboric acid with acetic anhydride is exothermic and should be conducted with caution.* Under an atmosphere of nitrogen, 102 g. (1.00 mole) of acetic anhydride (J. T. Baker Chemical Company) is cooled to −40° in an acetone–dry ice bath. With magnetic stirring, 20.4 g. (0.116 mole) of 50% fluoroboric acid (J. T. Baker Chemical Company) is added over 10 minutes. After carefully warming to 0°, the freshly prepared solution is used immediately.

19. The ^{1}H NMR spectrum ($CDCl_3$) shows a singlet at δ 1.58. The IR spectrum (KBr) exhibits bands at 2980 (s), 1485 (s), 1465 (m), 1425 (m), 1370 (s), 1225 (s), 1197 (m), 1070 (s), 940 (m), 860 (m), and 525 cm.$^{-1}$ (m).

3. Discussion

The preparation of tri-*tert*-butylcyclopropenyl tetrafluoroborate involves a modification of the method originally employed in the synthesis of triphenylcyclopropenyl perchlorate[2] from diphenylcyclopropenone.[2,3] The overall yields of tri-*tert*-butylcyclopropenyl tetrafluoroborate and di-*tert*-butylcyclopropenone are 40% and 52%, respectively. Other substituted di-*tert*-butylcyclopropenyl cations have also been prepared by the above procedure.[4] It should be pointed out, however, that the synthesis of cyclopropenyl cations using the reaction of cyclopropenones with organometallic reagents is not general.[2,4] Possible competing side reactions include conjugate addition[5] and proton abstraction (if the cyclopropenone contains an acidic hydrogen).

References and Notes

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

α,α'-Dibromodineopentyl ketone

pottassium tert-butoxide

hydrochloric acid (7647-01-0)

ether,
diethyl ether (60-29-7)

acetic anhydride (108-24-7)

hydrogen (1333-74-0)

sodium sulfite (7757-83-7)

sodium hydrogen carbonate (144-55-8)

magnesium turnings (7439-95-4)

sodium chloride (7647-14-5)

hydrogen bromide (10035-10-6)

sodium carbonate (497-19-8)

bromine (7726-95-6)

nitrogen (7727-37-9)

acetone (67-64-1)

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

Pentane (109-66-0)

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

lithium aluminium hydride (16853-85-3)

hexane (110-54-3)

Diphenylcyclopropenone (886-38-4)

fluoroboric acid (16872-11-0)

Cyclopropenylium, 1,2,3-tris(1,1-dimethylethyl)-, tetrafluoroborate(1-),
Tri-tert-butylcyclopropenyl tetrafluoroborate (60391-90-4)

1-chloro-2,2-dimethylpropane (753-89-9)

Dineopentyl ketone (4436-99-1)

triphenylcyclopropenyl perchlorate

tert-Butyllithium (594-19-4)

potassium tert-butoxide (865-47-4)

tert-butylacetyl chloride (7065-46-5)

Di-tert-butylcyclopropenone (19985-79-6)