Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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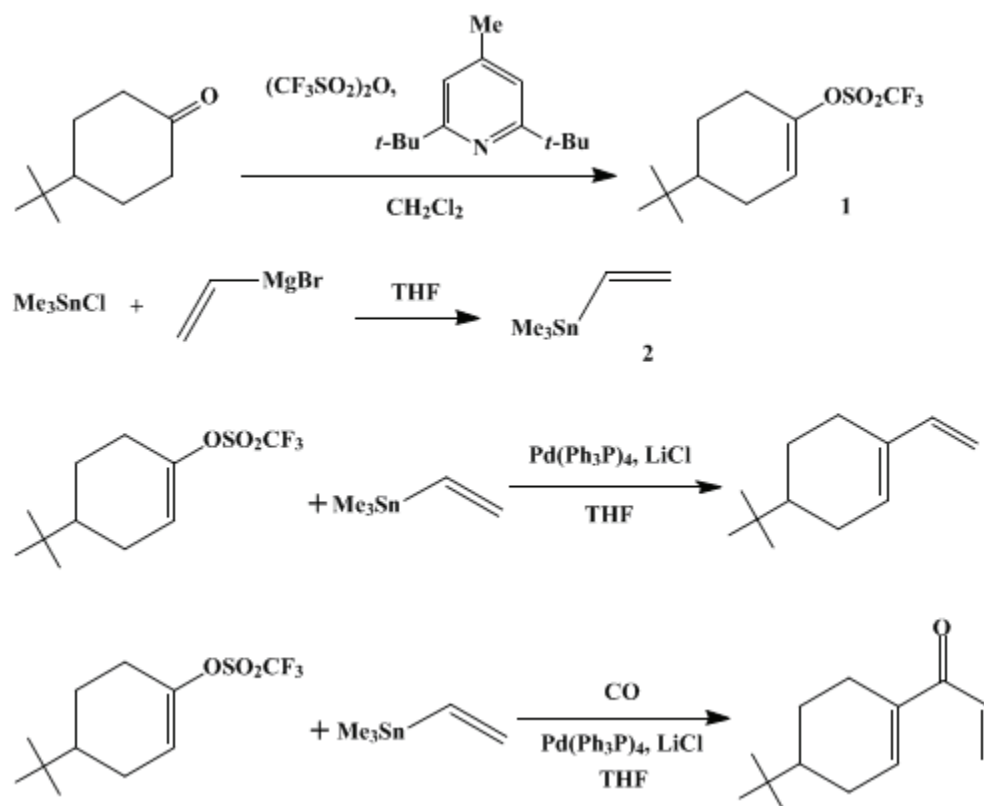
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

PALLADIUM-CATALYZED COUPLING OF VINYL TRIFLATES WITH ORGANOSTANNANES: 4-*tert*-BUTYL-1-VINYLCYCLOHEXENE AND 1-(4-*tert*-BUTYLCYCLOHEXEN-1-YL)-2-PROPEN-1-ONE

[Cyclohexene, 4-(1,1-dimethylethyl)-1-ethenyl- and 2-propen-1-one, 1-[4-(1,1-dimethylethyl)-1-cyclohexen-1-yl]]

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Checked by Dean R. Lagerwall and Leo A. Paquette.

1. Procedure

Caution! Many organotin compounds are toxic.[4] Their preparation and use should be carried out in a well-ventilated hood.

A. *4-tert-Butylcyclohexen-1-yl trifluoromethanesulfonate*. A dry, 2-L, three-necked, round-bottomed flask equipped with a magnetic stirring bar, an argon inlet, and a condenser (Note 1) is charged with 33.0 g (0.214 mol) of 4-*tert*-butylcyclohexanone (Note 2), 1.5 L of dichloromethane (Note 3), and 49.5 g (0.241 mol) of 2,6-di-*tert*-butyl-4-methylpyridine (Note 4). The solution is stirred under a static argon atmosphere and cooled to 0°C, at which time the dropwise addition of 40.0 mL (0.238 mol) of trifluoromethanesulfonic anhydride (Note 5) is begun. After the addition is complete, the brown mixture is allowed to warm slowly to room temperature and is stirred at that temperature for 10 hr. At this point, the consumption of starting ketone is verified by thin-layer chromatography (hexane; silica gel). If the reaction is incomplete, more trifluoromethanesulfonic anhydride is added and additional time is allowed. The solvent is removed by distillation and the resulting light-tan material is treated with 1 L of pentane and heated to reflux for 30 min. The tan salts thus obtained are removed by filtration and washed with five 100-mL portions of pentane (Note 6). The combined pentane solutions are washed

with two 250-mL portions each of a 10% hydrochloric acid solution, a 10% sodium hydroxide solution, and a saturated sodium chloride solution, dried with magnesium sulfate, filtered through a 6 × 4-cm pad of silica gel (Note 7), and concentrated by distillation. Bulb-to-bulb distillation (Note 8) of the resulting yellow oil at 75–80°C (0.5 mm) gives 43–45 g (70–73%) of the product as a colorless oil (Note 9).

B. *Trimethylvinyltin*. To a dry, 1-L, three-necked, round-bottomed flask, equipped with a Dewar-type condenser cooled to −78°C, a magnetic stirring bar and a gas inlet leading to a static supply of dry argon (Note 1) are added 11.4 g (0.469 mol) of clean magnesium turnings, 50 mL of dry tetrahydrofuran (Note 10), 3 mL of vinyl bromide, and 0.3 mL of methyl iodide to initiate formation of vinylmagnesium bromide. To this is added a solution of 41 mL (0.624 mol or 66.7 g total) of vinyl bromide in 125 mL of dry tetrahydrofuran via cannula at a rate that maintains a gentle reflux. After addition the mixture is heated to reflux for 1 hr with an oil bath and then cooled to 60°C.

To the resulting slurry of vinylmagnesium bromide (with the condenser still maintained at −78°C) is added via cannula a solution of 61.3 g (0.307 mol) of trimethyltin chloride (Note 11) in 50 mL of dry tetrahydrofuran at a rate suitable to maintain a gentle reflux. The temperature is maintained at 60°C for 5 hr and then the mixture is cooled to room temperature. With the condenser still maintained at −78°C, 200 mL of a saturated ammonium chloride solution is added by syringe at a rate that maintains a gentle reflux, followed by 200 mL of water. The resulting solution is transferred to a separatory funnel with the aid of 200 mL of pentane and the organic layer is washed with 250 mL of a saturated ammonium chloride solution. The combined aqueous layers are back-extracted twice with 250 mL of pentane, and the combined organic layers are washed 5 times with 250 mL of saturated ammonium chloride, 10 times with a 10% hydrochloric acid solution, and twice with a saturated sodium chloride solution, and then gravity-filtered through a 9 × 4-cm pad of silica gel (Note 7) to give approximately 500 mL of a slightly yellow solution. Pentanes are removed by distillation using a 16-cm Vigreux column and a short-path stillhead (Note 12). Continued distillation affords a fraction boiling from 60–90°C, which contains a mixture of 4.9 g of trimethylvinyltin in 16.3 g of tetrahydrofuran (Note 13). At this point the still is cooled to room temperature, the Vigreux column is removed, and the remaining oil is distilled at 95–100°C to give 38–39 g (64–66% purified yield) of trimethylvinyltin (Note 14).

C. *4-tert-Butyl-1-vinylcyclohexene*. A dry, 2-L, one-necked, round-bottomed flask equipped with a magnetic stirring bar, an argon inlet, and a condenser (Note 1) is charged with 1.18 g (1.02 mmol) of tetrakis(triphenylphosphine)palladium(0) (Note 15), 12.9 g (0.305 mol) of lithium chloride (Note 16), and 500 mL of tetrahydrofuran (Note 10). This mixture is stirred for 15 min under a static argon atmosphere; then a solution of 28.0 g (0.0979 mol) of 4-*tert*-butylcyclohexen-1-yl trifluoromethanesulfonate and 19.0 g (0.0997 mol) of trimethylvinyltin in 250 mL of tetrahydrofuran is added, followed by an additional 250 mL of tetrahydrofuran. The resulting, almost colorless solution is heated to a gentle reflux for 48 hr (Note 17). The mixture is cooled to room temperature and partitioned between 500 mL of water and 250 mL of pentane. The aqueous layer is back-extracted with two 200-mL portions of pentane. The combined organic layers are washed with two 250-mL portions each of a concentrated sodium bicarbonate solution, water, and a concentrated sodium chloride solution, dried over magnesium sulfate, filtered through a 4 × 4-cm pad of silica gel (Note 7) and concentrated by distillation using a 10-cm Vigreux column. Bulb-to-bulb distillation (Note 8) of the resulting yellow oil at 65–68°C (0.55 mm) gives 12.6–12.8 g (78–79%) of the coupled product (Note 18).

D. *1-(4-tert-Butylcyclohexen-1-yl)-2-propen-1-one*. To a dry, 2-L, round-bottomed flask, equipped with a magnetic stirring bar, a condenser, and a gas inlet connected to a static argon atmosphere (Note 1), are added 1.12 g (0.968 mmol) of tetrakis(triphenylphosphine)palladium(0) (Note 15), 13.2 g (0.312 mol) of lithium chloride (Note 16), and 500 mL of tetrahydrofuran (Note 10), followed by a solution of 28.6 g (0.100 mol) of 4-*tert*-butylcyclohexen-1-yl trifluoromethanesulfonate and 19.1 g (0.100 mol) of trimethylvinyltin in 250 mL of tetrahydrofuran, and then an additional 250 mL of tetrahydrofuran. A gas bag (Note 19) filled with carbon monoxide is attached to the gas inlet and the apparatus is flushed with carbon monoxide. The gas bag is refilled with carbon monoxide and reattached to the gas inlet. The mixture is then heated to 55°C (Note 20). After 2–4 hr, a large amount of the carbon monoxide has been absorbed into solution and the gas bag is refilled and reattached to the gas inlet. After a total of 40 hr, the reaction mixture darkens and is cooled to room temperature (Note 21). This solution is transferred to

a 2-L separatory funnel, diluted with 500 mL of pentane, and washed successively with two 300-mL portions each of water, saturated sodium bicarbonate solution, water again, and saturated sodium chloride solution. The resulting yellow solution is dried over magnesium sulfate, filtered through a 6 × 4-cm pad of silica gel (Note 7), and concentrated using a rotary evaporator. Slow bulb-to-bulb distillation (Note 8) and (Note 22) of the brown oil at 85–95°C (0.35 mm) gives 14.3–14.5 g (74–75%) of the product as a colorless oil (Note 23).

2. Notes

1. The glassware is dried in an oven at 140°C overnight and assembled warm under a static argon atmosphere.
2. 4-*tert*-Butylcyclohexanone is purchased from the Aldrich Chemical Company, Inc.
3. Dichloromethane is freshly distilled from calcium hydride.
4. 2,6-Di-*tert*-butyl-4-methylpyridine can be purchased from the Aldrich Chemical Company, Inc. or prepared from pivaloyl chloride.[5]
5. Trifluoromethanesulfonic anhydride can be purchased from the Aldrich Chemical Company, Inc. or prepared from trifluoromethanesulfonic acid.[6]
6. The solids can range in color from off-white to brown. 2,6-Di-*tert*-butyl-4-methylpyridine can be recovered by separation of the tan solids between 500 mL of pentane and 650 mL of a 1.2 N sodium hydroxide solution. The aqueous layer is extracted with two 200-mL portions of pentane. The combined organic phases are washed with two 200-mL portions of water and two 200-mL portions of a saturated sodium chloride solution dried with sodium sulfate, filtered through a 6 × 4-cm pad of silica gel (Note 7), and concentrated using a rotary evaporator. Bulb-to-bulb distillation (Note 8) of the yellow oil at 65–75°C (0.55 mm) with trapping of the distillate in two connected receiving flasks cooled to −78°C gives 42.1–48.1 g (85–97%) of colorless oil, which solidifies on standing.
7. Woelm 230–400-mesh silica gel is used.
8. An Aldrich Chemical Company, Inc. Kugelrohr apparatus is used.
9. 4-*tert*-Butylcyclohexen-1-yl trifluoromethanesulfonate has the following properties: mp 17°C; TLC R_f (hexanes): 0.65; IR (neat) cm^{-1}: 1698, 1440, 1425, 1250, 1225; ^{1}H NMR (CDCl$_3$, 270 MHz) δ: 0.89 (s, 9 H), 1.26–1.38 (m, 3 H), 1.90–2.18 (m, 2 H), 2.23–2.39 (m, 2 H), 5.73–5.75 (m, 1 H): ^{13}C NMR (CDCl$_3$, 68 MHz) δ: 23.9, 25.4, 27.2 (3C), 28.6, 32.0, 43.1, 118.3, 118.7 (q, $J = 319$, CF$_3$), 149.3.
10. Tetrahydrofuran is freshly doubly distilled from potassium.
11. Trimethyltin chloride can be purchased from Strem Chemicals, Inc. or prepared by the reaction of tetramethyltin with tin tetrachloride as follows. To a 100-mL, round-bottomed flask, equipped with a magnetic stirring bar, a septum, and a gas inlet connected to a static argon atmosphere, containing 41.2 g (0.230 mol) of tetramethyltin cooled to −20°C with a dry ice–carbon tetrachloride slurry, is added 9.0 mL (0.0768 mol) of tin tetrachloride at a slow dropwise rate. After the addition is complete, the mixture is heated to 60°C for 16 hr. The mixture is cooled to room temperature to afford 61.3 g (100% yield) of a colorless solid.
12. In order to maximize the yield of trimethylvinyltin, pentanes should be removed as carefully as possible. The authors employed only 14/20-ground glassware in the distillation and carefully controlled the oil bath temperature to maintain a collection rate of approximately 0.3 mL per min.
13. The ratio of trimethylvinyltin to tetrahydrofuran is determined by NMR. The trimethylvinyltin/THF solution may be used in palladium-catalyzed coupling reactions without further purification.
14. Trimethylvinyltin is >97% pure as shown by gas chromatography on a 1/8-in. × 6-ft column packed with 6% SP-2100 on Supelcoport, 80–100 mesh, operated at 50°C. The relative retention times are 1.9 min for tetrahydrofuran, 4.0 min for trimethylvinyltin, and 7.0 min for trimethyltin chloride (not seen). The distilled product has the following properties: ^{1}H NMR (CDCl$_3$, 270 MHz) δ: 0.12 (s, 9 H), 5.66 (dd, 1 H, $J = 3.4, 20.5$), 6.11 (dd, 1 H, $J = 3.6, 13.9$), 6.52 (dd, 1 H, $J = 13.9, 20.5$); ^{13}C NMR (CDCl$_3$, 68 MHz) δ: −9.9 (3C) 133.2, 140.0
15. Tetrakis(triphenylphosphine)palladium(0) can be purchased from Strem Chemicals, Inc. or prepared from palladium chloride.[7] On standing for a period of time (at least a few weeks) the catalyst gradually darkens, turning tan in the absence of oxygen or turning green in the presence of oxygen. However, the coupling reactions run equally well with catalyst that has aged for a year.
16. Lithium chloride is dried at 140°C for 24 hr prior to use.
17. The progress of the reaction is conveniently monitored by gas chromatography using a 1/8-in. × 6-ft column packed with 6% SP-2100 on Supelcoport, 80–100 mesh. operated at 50°C for 4 min, then

heated at 15°C/min to 250°C. The relative retention times are 4.0 min for trimethylvinyltin, 6.5 min for trimethyltin chloride, 12.0 min for 4-*tert*-butyl-1-vinylcyclohexene, and 13.1 min for 4-*tert*-butylcyclohexen-1-yl trifluoromethanesulfonate. Because of the extreme volatility of trimethylvinyltin, it may be necessary to add additional small amounts in order to drive the reaction to completion.

18. 4-*tert*-Butyl-1-vinylcyclohexene has the following properties: bp 45°C (0.1 mm); TLC R_f (hexanes): 0.74; IR (neat) cm^{-1}: 3100, 3020, 1650, 1610, 1395, 1365, 985, 890; ^{1}H NMR (CDCl$_3$, 270 MHz) δ: 0.87 (s, 9 H), 1.08–1.34 (m, 3 H), 1.84–2.36 (m, 4 H), 4.88 (d, 1 H, *J* = 10.7), 5.04 (d, 1 H, *J* = 17.5), 5.73–5.75 (m, 1 H), 6.35 (dd, 1 H, *J* = 10.7, 17.5); ^{13}C NMR (CDCl$_3$, 68 MHz) δ: 23.8, 25.3, 27.2 (3C), 27.4, 32.2, 44.4, 109.7, 129.8, 136.0, 139.7.

19. The gas bag can be purchased from the Fisher Scientific Company and is filled to approximately 5 psig (pounds per square inch gauge) with carbon monoxide.

20. Refluxing conditions must be avoided in order to maximize the amount of carbon monoxide in solution.

21. The progress of the reaction is conveniently monitored by gas chromatography on a 1/8-in. × 6-ft column packed with 6% SP-2100 on Supelcoport, 80–100 mesh, operated at 50°C for 4 min, then heated at 15°C/min to 250°C. The relative retention times are 4.0 min for trimethylvinyltin, 6.5 min for trimethyltin chloride, 13.1 min for 4-*tert*-butylcyclohexen-1-yl trifluoromethanesulfonate, and 14.7 min for 1-(4-*tert*-butylcyclohexen-1-yl)-2-propen-1-one. Because of the extreme volatility of trimethylvinyltin, it may be necessary to add additional small amounts of this reagent in order to drive the reaction to completion.

22. The purification procedure occasionally leads to product contaminated with organotins. The submitters have found that careful washing with water minimizes this problem. The checkers found that distillation of product at a slow rate allows the unwanted tin to escape to the cold trap.

23. 1-(4-*tert*-Butylcyclohexen-1-yl)-2-propen-1-one has the following properties: bp 75°C (0.1 mm); IR (neat) cm^{-1}: 1665, 1645, 1612; ^{1}H NMR (CDCl$_3$, 270 MHz) δ: 0.81 (s, 9 H), 1.21–2.65 (m, 7 H), 5.58 (d, 1 H, *J* = 9.0), 6.14 (d, 1 H, *J* = 17.2), 6.75–7.00 (m, 2 H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ: 23.3, 24.6, 26.9 (3C), 27.8, 32.0, 43.4, 127.1, 131.5, 139.4, 141.1, 190.8.

3. Discussion

The conversion of a ketone into a substituted olefin is classically achieved by the addition of a Grignard reagent to a ketone, followed by the dehydration of the resulting alcohol. Such a scheme can often lead to a mixture of regioisomers. By converting the ketone into a vinyl iodide,[8] followed by a cuprate coupling reaction,[9] it is possible to form selectively the less-hindered, substituted olefin. Group 10[10]-catalyzed coupling reactions of vinyl iodides also lead to the formation of olefins in good yields.[11,12,13] However, the synthesis of the more hindered vinyl iodides can be quite difficult.

A number of enolate derivatives have recently been offered as alternatives to vinyl iodides. The advantage to such a scheme lies in the ability to form regioselectively either the kinetic or the thermodynamic enolate using known methodology,[14] and then to trap that enolate to give the required derivative. In general, enolate derivatives, such as methyl vinyl ethers,[15] silyl enol ethers,[16] and enol phosphates,[17] have undergone coupling only in the presence of nickel catalysts, thus requiring the use of very strong nucleophiles. However, such nucleophiles severely restrict the functionality that may be present in either the enolate derivative or the nucleophile.

Vinyl trifluoromethanesulfonates[18] have provided a solution to this problem. Vinyl trifluoromethanesulfonates can be formed by the action of trifluoromethanesulfonic anhydride with a ketone.[6,18] Enolates may be trapped using *N*-phenyltrifluoromethanesulfonimide to form selectively either the kinetic or thermodynamic derivative.[9,10,11,12,13,14,15,16,17,18,19,20,21] The resulting enolate derivatives couple readily with organocuprates.[22] Palladium-catalyzed coupling reactions may also be run to give directly coupled products,[21] Heck-type coupled products,[23,24,25] or reduced products.[21,22,23,24,25,26] Direct coupling reactions of vinyl trifluoromethanesulfonates have been used in the synthesis of pleraplysillin-1,[21] the synthesis of cardenolides,[24] the synthesis of vinylstannanes,[27,28,29] and in intramolecular cyclization reactions.[30,31,32]

The synthesis of ketones is very important to the organic chemist. Two common methods involve the addition of Grignard reagents to aldehydes, followed by oxidation of the secondary alcohol, and the

addition of organolithium reagents to carboxylic acids.[33] In addition, acid chlorides have been coupled with Grignard reagents,[34,35] organoaluminum reagents,[36] organocadmium reagents,[35] organocuprates,[9] or organozinc reagents[35] to give the corresponding ketone. More recently, the palladium-catalyzed coupling of acid chlorides with organozinc reagents,[37] organostannanes,[38] or organomercury reagents[39] has provided a very mild method for ketone synthesis.

In order to avoid the necessity of using acid chlorides in the coupling reactions, the palladium-catalyzed coupling of electrophiles in the presence of carbon monoxide was developed.[40,41] Again, the necessity of using vinyl iodides limits this methodology. On palladium-catalyzed coupling of vinyl trifluoromethanesulfonates in the presence of lithium chloride, the desired enones are formed in good yield.[42,43] The carbonylative coupling reaction has been used in the synthesis of (±)-$\Delta^{9,12}$-capnellene.[42]

References and Notes

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2. Department of Organic Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia;
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Pentanes

vinyl iodides

methyl vinyl ethers

silyl enol ethers

Vinyl trifluoromethanesulfonates

N-phenyltrifluoromethanesulfonimide

pleraplysillin-1

vinylstannanes

hydrochloric acid (7647-01-0)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

carbon monoxide (630-08-0)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

tin (7440-31-5)

nickel (7440-02-0)

potassium (7440-09-7)

Methyl iodide (74-88-4)

vinyl bromide (593-60-2)

vinylmagnesium bromide (1826-67-1)

Pentane (109-66-0)

dichloromethane (75-09-2)

palladium chloride (7647-10-1)

tin tetrachloride (7646-78-8)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

hexane (110-54-3)

Lithium chloride (7447-41-8)

argon (7440-37-1)

calcium hydride (7789-78-8)

trifluoromethanesulfonic acid (1493-13-6)

4-tert-Butylcyclohexanone (98-53-3)

pivaloyl chloride (3282-30-2)

Trifluoromethanesulfonic anhydride (358-23-6)

tetrakis(triphenylphosphine)palladium(0) (14221-01-3)

4-tert-Butyl-1-vinylcyclohexene,
Cyclohexene, 4-(1,1-dimethylethyl)-1-ethenyl- (33800-81-6)

2-propen-1-one, 1-[4-(1,1-dimethylethyl)-1-cyclohexen-1-yl],
1-(4-tert-Butylcyclohexen-1-yl)-2-propen-1-one (92622-56-5)

trimethyltin chloride (1066-45-1)

Trimethylvinyltin (754-06-3)

tetramethyltin (594-27-4)

vinyl iodide (593-66-8)

2,6-Di-tert-butyl-4-methylpyridine (38222-83-2)

4-tert-Butylcyclohexen-1-yl trifluoromethanesulfonate (77412-96-5)