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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.

Organic Syntheses, Coll. Vol. 10, p.1 (2004); Vol. 77, p.121 (2000).

7α-ACETOXY-(1Hβ, 6Hβ)-BICYCLO[4.4.1]UNDECA-2,4,8-TRIENE VIA CHROMIUM-MEDIATED HIGHER ORDER CYCLOADDITION

## [Bicyclo[4.4.1]undeca-3,7,9-triene-2-ol, acetate, endo- (±)-]
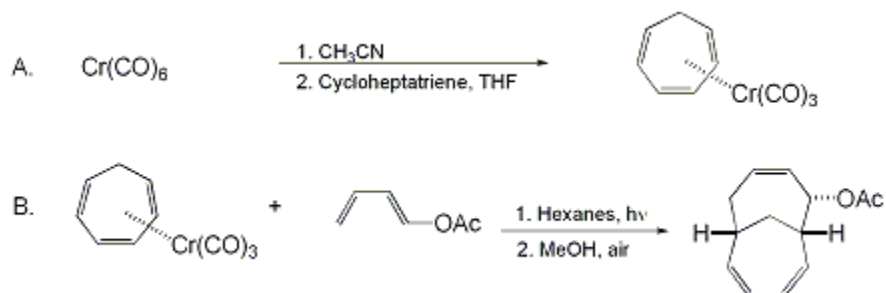
Submitted by James H. Rigby[1] and Kevin R. Fales.
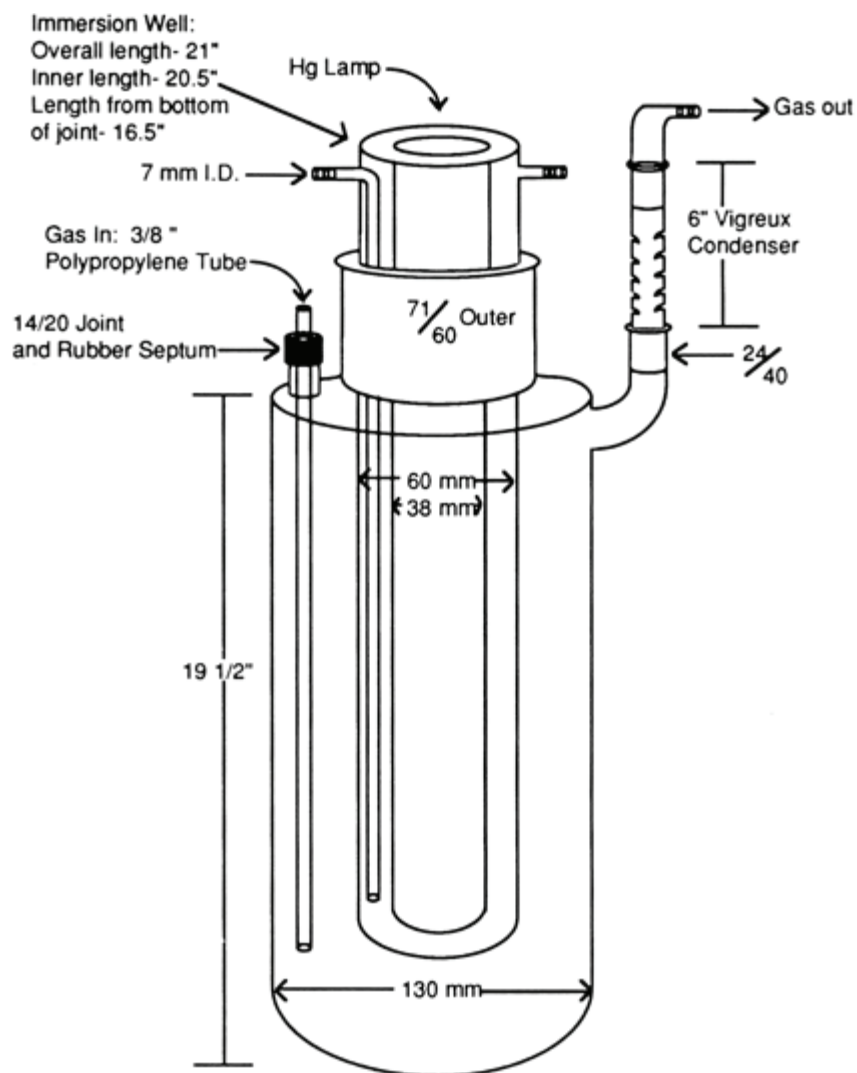Checked by Robert E. Lee Trout and Amos B. Smith, III.

1. Procedure

A. Tricarbonyl(η⁶-cycloheptatriene)chromium(0) . An oven-dried complexation flask (Figure 1), fitted with an additional condenser (Note 1) and gas adapter, is charged with acetonitrile (300 mL). The solvent is heated to ~40°C under argon (Ar) (Note 2), chromium hexacarbonyl is added (45 g, 0.2 mol) (Note 3), and the mixture is immediately heated to reflux for 24 hr (Note 4). Toward the end of this time period (i.e., after ~20 hr), the cooling jacket attached to the flask is alternately filled with water and emptied to allow for complete digestion of the starting material. After complete conversion of the chromium hexacarbonyl is evident, the free condenser is quickly changed to a 9"-Vigreux column connected through an acetone/solid carbon dioxide (CO$_2$) condenser to a vacuum/argon line using a Firestone valve (Note 5). Vacuum (~0.1 mm) is quickly and cautiously applied to the system while simultaneously removing the heating source (Note 6). The reaction mixture is evaporated to complete dryness by warming the reaction flask with a warm water bath as necessary (Note 7). The system is filled with argon and a previously prepared solution of cycloheptatriene (1.5 eq., 0.31 mol, 28.3 g, 32 mL) in tetrahydrofuran (THF) (50 mL) is added via syringe to the dry, bright yellow, solid tris (acetonitrile)chromium tricarbonyl intermediate. This addition is best performed under a very strong flow of argon through the top joint of the reaction apparatus. An additional 100 mL of THF is added to the mixture and the resulting solution is heated to reflux. After 48 hr, additional cycloheptatriene (1.0 eq., 0.2 mol, 20.5 g, 23 mL) is added and the reaction is continued until complete digestion of the (CH$_3$CN)$_3$Cr(CO)$_3$ intermediate is evident (Note 8). Solvent is removed under reduced pressure (Note 9), and the residue is dissolved in a mixture of hexanes (225 mL) and methylene chloride (225 mL). Celite (5.0 g) is added to the solution and the mixture is filtered through a Celite pad (5.5 cm × 1.0 cm). The filter cake is washed with methylene chloride (2 × 50 mL) and the filtrate is concentrated under reduced pressure to provide an oily red solid. After the solids are dried briefly under vacuum (~2 hr, 0.1 mm), they are triturated with chilled hexanes (100 mL), and the chilled solids are collected via vacuum filtration and washed with chilled hexanes (50 mL). The solids are dried under vacuum (0.1 mm) to yield the dark red tricarbonyl(η⁶-cycloheptatriene)chromium(0) (34.4-39.9 g, 75-85%, (Note 10)).

Figure 1
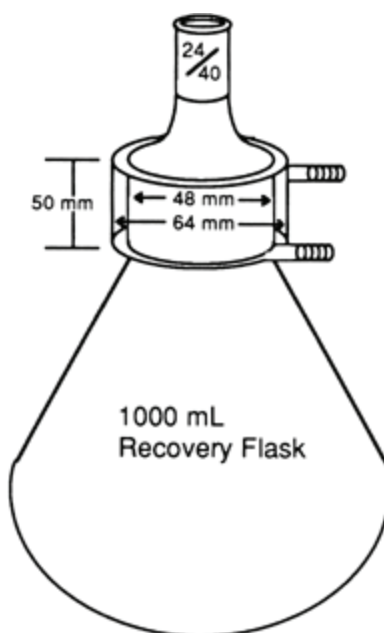
B. 7α-Acetoxy-(1Hβ, 6Hβ)-bicyclo[4.4.1]undeca-2,4,8-triene . To a large, fully assembled photochemical reaction vessel (Figure 2) are added tricarbonyl(η⁶-cycloheptatriene)chromium(0) (10.0 g, 0.044 mol) and hexanes (4 L, (Note 11)). While the mixture is stirred it is purged with argon for 20-30 min and then 1-acetoxy-1,3-butadiene (1.5 eq., 7.4 g, 7.8 mL, 0.66 mol) is added via syringe (Note 12). The solution is irradiated (Note 13) using a Hanovia medium pressure 450W mercury vapor lamp (Note 14) for 6 hr or longer (Note 15) until complete digestion of the starting chromium complex is noted by TLC (Note 16). The reaction mixture is transferred, portionwise, to a 2-L, round-bottomed flask using diethyl ether, and the solvents are removed under reduced pressure (Note 9). The residue is taken up in methanol (300 mL), with scraping as necessary, and the resultant slurry is stirred open to the atmosphere overnight. At this time, flash grade silica gel (10.0 g, Merck 230-400 mesh) is added to the green slurry and stirring is continued as necessary for complete decomplexation of the intermediate cycloadduct complex, as noted by TLC (Note 16). The reaction mixture is filtered through a Celite pad (9 cm diameter by ᷉1 cm deep), using additional methanol (3 × 50 mL) to rinse the flask and filter cake until the filtrate runs clear (Note 17). Solvent is removed under reduced pressure and the residue is dried overnight under ᷉0.1 mm vacuum to remove additional traces of solvent and unreacted diene (Note 18). The product is purified via flash column chromatography (Note 19) to yield ᷉98% pure (Note 20), 7α-acetoxy-(1Hβ, 6Hβ)-bicyclo[4.4.1]undeca-2,4,8-triene (7.7 g, 86%) (Note 21) as a white solid (mp 54-57°C).

Figure 2: Immersion well photochemical reactor

Immersion Well:
Overall length- 21"
Inner length- 20.5"
Length from bottom
of joint- 16.5"

Hg Lamp

Gas out

7 mm I.D.

6" Vigreux
Condenser

Gas In: 3/8"
Polypropylene Tube

14/20 Joint
and Rubber Septum

71/60 Outer

24/40

60 mm
38 mm

19 1/2"

130 mm

2. Notes

1. It is most convenient to attach cooling water in series to the free condenser first and then to the cooling jacket on the complexation flask.

2. The submitters used nitrogen at this point, but the checkers found that argon worked as well. The checkers also recommend the use of an Oxiclear gas purifier.

3. Fresh reagent grade acetonitrile was purchased from Fisher Scientific Co. and used without additional purification. Chromium hexacarbonyl was purchased from Strem Chemical Co. Celite and cycloheptatriene (90% technical grade) were purchased from Aldrich Chemical Company, Inc. , and used without purification. THF was distilled from sodium/benzophenone ketyl .

4. Once heating of the reaction is begun, any significant cooling or exposure to the atmosphere generally causes degradation of the tris(acetonitrile)chromium tricarbonyl intermediate. The reaction initially turns greenish yellow, but then quickly forms a bright yellow to golden color that becomes dark green upon degradation. Greenish, partially degraded intermediates can be carried through the sequence with a corresponding reduction in yield. The total time of reflux ranged from 24-26 hr.

5. This item may be purchased from Ace Glass Inc., Vineland, N.J., catalog #8766-12.

6. Vacuum must be applied carefully to avoid bumping, but must also be applied quickly and steadily to avoid degradation of the reaction intermediate.

7. *Warning!* Tris(acetonitrile)chromium tricarbonyl is highly pyrophoric and degrades rapidly when exposed to oxygen, but is reasonably stable in THF solution. Best yields are obtained when this intermediate is as free of acetonitrile as possible while avoiding formation of the green colored [Cr(III)]

decomposition product, which develops on contact with air.

8. The reaction is monitored by TLC (silica gel, 6:1 hexanes: ethyl acetate). Typical characteristics are $R_f = 0.15$, a yellow spot [tris(acetonitrile)chromium tricarbonyl intermediate], and $R_f = 0.51$, a red spot (product complex). Total reaction time averaged ~180 hr.

9. Solvent is removed via rotary evaporator.

10. This product was typically found to be $\geq 98\%$ pure based on ^{1}H NMR analysis, and it may be used without further purification. However, the compound may be recrystallized from hexanes if necessary. The complex exhibits the following characteristics: TLC: $R_f = 0.51$ (silica gel, 6:1 hexanes:ethyl acetate); ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 1.74 (d, 1 H), 2.95 (dt, 1 H, J = 9.0, 14.0), 3.40 (t, 2 H, J = 7.5), 4.87 (bs, 2 H), 6.09 (bs, 2 H) ; ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 23.9 (CH_2), 57.1 (CH), 98.4 (CH), 101.1 (CH) ; IR ($CDCl_3$) cm^{-1}: 3052, 2895, 2848, 1982, 1974, 1917, 1897, 1886, 1877 ; HRMS calcd for $C_{10}H_8CrO_3$: m/e 227.9879, found 227.9881 ; LRMS [EI] (rel. %): 227.9 (19), 199.9 (13), 172.0 (15), 144.0 (74) .

11. Performing this reaction at higher concentrations (i.e., in 1-2 L solvent) results in significantly increased reaction times, incomplete reaction, and increased side product formation.

12. The reaction conditions given were developed using (E)-1-acetoxy-1,3-butadiene prepared according to the procedure of McDonald, et al.[2] with the following modifications (unchecked). Crotonaldehyde (105 g, 125 mL) is added by addition funnel over 1 hr to a refluxing solution of isopropenyl acetate (2.5 mol, 250 g, 275 mL), p-toluenesulfonic acid (anhydrous, 2.0 g) and copper(II) acetate (0.5 g). The mixture is heated at reflux for ~30 min and then the reaction apparatus is set up for distillation. Distillation (bath temp. 110-130°C) is continued for ~2.5 hr until acetone and nearly all unreacted isopropenyl acetate is collected. The distillation residue is cooled to ~25°C and crude product is isolated via vacuum distillation (bp ~32°C, ~7 mm). This crude product typically contains traces of isopropenyl acetate and significant amounts of acetic acid . The crude distillate is dissolved in diethyl ether (500 mL), and carefully mixed with saturated aqueous sodium bicarbonate solution, adding additional anhydrous sodium bicarbonate slowly to the stirring mixture until gas evolution ceases and the pH increases to ~7.0. The layers are separated and the organic phase is washed with brine (300 mL) and dried with magnesium sulfate . The solution is carefully concentrated, and the product is purified by distillation to yield nearly pure (E)-1-acetoxy-1,3-butadiene (~35-50% yield). Frequently, sequential distillations of the product are necessary to ensure the purity of the product obtained. Pure product exhibits the following characteristics: bp 32°/10 mm; TLC: $R_f = 0.61$ (silica gel, 6:1 hexanes:ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.14 (s, 3 H), 5.08 (dd, 1 H, J = 10.5, 0.5), 5.21 (d, 1 H, J = 17.0), 6.03 (dd, 1 H, J = 12.0, 12.0), 6.26 (ddd, 1 H, J = 21.5, 10.5, 10.5), 7.39 (d, 1 H, J = 12.5) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.7 (CH_3), 116.0 (CH), 117.3 (CH_2), 131.7 (CH), 138.6 (CH), 167.8 (C) ; IR ($CDCl_3$) cm^{-1}: 3091, 3074, 3041, 1660, 1097 ; HRMS m/e calcd for $C_6H_8O_2$: 112.0524, found 112.0523 ; LRMS [EI] (rel %): 112.0 (57), 70.0 (100) .

Alternatively, 1-acetoxy-1,3-butadiene is available as a mixture of E,Z-isomers from Aldrich Chemical Company, Inc. When using the commercial reagent, 3.0 eq. (14.8 g, 15.6 mL) is necessary to ensure complete reaction, as the Z isomer does not react.

13. *Caution*: UV radiation is harmful to eyes and skin; the reaction vessel may be wrapped with aluminum foil or the reaction conducted in a closed photochemical reaction cabinet to prevent exposure to the harmful UV rays.

14. The photochemical lamp and power supply may be purchased from Ace Glass Inc., Vineland, N.J., catalog #'s 7825-32 or 7825-40 (lamp) and 7830-60 (power supply).

15. A solid buildup occurs on the immersion well that may slow the reaction considerably. To help minimize this, the submitters suggest a constant purging of the reaction mixture with argon throughout the entire reaction time.

16. Typical TLC data (silica gel, 6:1 hexanes:ethyl acetate) include $R_f = 0.61$ (1-acetoxy-1,3-butadiene); 0.51, a red spot [tricarbonyl(cycloheptatriene)chromium]; 0.45 a yellow spot (side product that often overlaps with the starting complex); and 0.31 a yellow spot (main intermediate chromium complex).

17. Prior to and between washes, the green filter cake cracks and should be "pushed down" with a spatula to form a uniform surface prior to any subsequent washes.

18. TLC at this point (silica gel, 6:1 hexanes: ethyl acetate) shows three spots (UV): $R_f = 0.76$ (trace orange); 0.55 (side product); 0.47 (main product).

19. Chromatography is performed as follows: a 3.5-cm ID glass column is packed with ~140 g of flash grade silica gel (Merck 230-400 mesh) in petroleum ether and the sample is loaded in minimal

petroleum ether. The checkers found that a 5.0-cm ID glass column packed with ∼170 g of Merck 70-270 mesh silica gel gave slightly better separation. Care must be taken during product application to minimize silica gel column separation. The column is eluted, recycling solvent as necessary, until the front running orange band is collected. This band is comprised of trace amounts of unreacted tricarbonyl (cycloheptatriene)chromium. Elution then proceeds using 500 mL of 49:1 petroleum ether:diethyl ether followed by 19:1 petroleum ether:diethyl ether to obtain the product. Prior to elution of the desired [6π+4π] cycloadduct, the side product, [6π+2π] cycloadduct **(A)** elutes, usually streaking into the desired product, but it is of little consequence. All fractions containing the desired product are combined and the solvent is removed under reduced pressure. The product sometimes solidifies during solvent removal, but may require seeding with authentic material to promote crystallization.

20. The [6π+4π] cycloadduct exhibits the following characteristics: bp: 104-107°/1.3 mm; TLC: R_f = 0.47 (silica gel, 6:1 hexanes:ethyl acetate); ^{1}H NMR (500 MHz, CDCl$_3$) δ: 2.11 (s, 3 H), 2.12-2.15 (m, 1 H), 2.31 (bd, 1 H, J = 14.0), 2.35-2.47 (m, 2 H), 2.74 (bs, 1 H), 2.92 (bs, 1 H), 5.49 (bd, 1 H, J = 11.0), 5.60-5.65 (m, 1 H), 5.66-5.68 (m, 1 H), 5.73-5.81 (m, 2 H), 5.83-5.88 (m, 2 H) ; ^{13}C NMR (125 MHz, CDCl$_3$) δ: 21.4 (CH$_3$), 31.7 (CH$_2$), 32.9 (CH$_2$), 37.3 (CH), 42.7 (CH), 76.7 (CH), 124.9 (CH), 127.1 (CH), 128.7 (CH), 133.1 (CH), 135.3 (CH), 137.8 (CH), 170.5 (C) ; IR (neat) cm^{-1}: 3011, 2924, 2905, 2884, 2872, 1737, 1447, 1430, 1368, 1241, 1199, 1055, 1020 ; HRMS calcd for C$_{13}$H$_{16}$O$_2$: m/e 204.11503, found 204.1149 ; LRMS [EI] (rel %): 204.1 (2), 162.1 (2), 144.1 (20), 129.0 (11), 112.0 (6), 92.0 (100) . Purity was determined by 500 MHz ^{1}H NMR, with the main impurity being the [6π+2π] cycloadduct **A**.

A
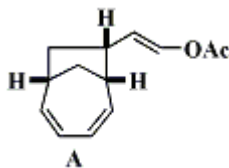
This compound exhibits the following characteristics: TLC: R_f = 0.35 (silica gel, 19:1 hexanes:ethyl acetate); ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.58 (ddd, 1 H, J = 13.5, 9.5, 3.5), 1.89 (d, 1 H, J = 12.0), 2.01 (ddd, 1 H, J = 13.5, 9.5, 9.5), 2.10 (s, 3 H), 2.14-2.19 (m, 1 H), 2.61 (dd, 1 H, J = 12.0, 5.5), 2.69 (ddd, 1 H, J = 16.5, 8.5, 4.0), 2.84 (ddd, 1 H, J = 19.5, 9.5, 6.0), 5.58 (d, 1 H, J = 10.0, 6.0), 5.62 (dd, 1 H, J = 12.0, 9.5), 5.72 (dd, 1 H, J = 12.0, 7.0), 5.83 (dd, 1 H, J = 12.0, 6.5), 6.10 (dd, 1 H, J = 10.5, 8.5), 7.09 (d, 1 H, J = 12.0) ; ^{13}C NMR (125 MHz, CDCl$_3$) δ: 20.7 (CH$_3$), 33.3 (CH$_2$), 36.7 (CH), 42.3 (CH$_2$), 46.3 (CH), 54.7 (CH), 115.5 (CH), 123.3 (CH), 126.6 (CH), 135.0 (CH), 135.2 (CH), 141.0 (CH), 168.2 (C) ; IR (neat) cm^{-1}: 3019, 2950, 2931, 2863, 1755, 1370, 1219, 1094 ; HRMS calcd for C$_{13}$H$_{16}$O$_2$: m/e 204.11503, found 204.1147 ; LRMS [EI] (rel %): 204.1 (2), 144.1 (20), 129.1 (7), 112.0 (6), 92.0 (100) .

21. The yield reported is that of the submitters and is based on the use of the pure (E)-1-acetoxy-1,3-butadiene. It was found by the checkers that use of a mixture of the E, Z-isomers (as purchased from Aldrich Chemical Company, Inc.) led to an average yield of 73%.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995. Wastes containing chromium, aqueous solutions as well as solids, were collected and disposed of separately. Prior to washing, all glassware laden with chromium by-products, were soaked overnight in a solution composed of 15-20 g of copper beads dissolved in ∼2 L of 50% aqueous nitric acid . This solution may be kept loosely capped in a fume hood and reused several times prior to disposal.

3. Discussion

Synthetic sequences that employ a cycloaddition step benefit from the convergency and stereoselectivity that characterizes these pericyclic transformations. In recent years, several new methodologies for performing so-called higher-order cycloadditions [e.g., [6π+4π], [6π+2π], [4π+4π], [4π+3π], etc.] have appeared and are now being used as key transformations in the synthesis of a

number of target molecules.[3] [4] [5] For example, a number of reports have appeared in which the generation of specific examples of bicyclo[4.4.1]undecatriene ring systems are noted as useful intermediates in the synthesis of cerorubenate sesterterpenes[6] as well as the ingenane diterpenes.[7] In particular, the general utility of chromium-mediated [6π+4π] cycloaddition in the synthesis of several bicyclo[4.4.1]undecatriene systems as potential intermediates in natural product synthesis has been demonstrated,[8] including the synthesis of members of the taxane and tigliane families.[9] Furthermore, studies involving cleavage of certain functionalized members of these ring systems, allows for the generation of medium-sized carbocycles.[10]

With these synthetic opportunities in mind, presentation of the methodology used in large scale generation of tricarbonyl(η⁶-cycloheptatriene)chromium(0) as well as an example of [6π+4π] cycloaddition is timely. Although a specific example of the submitter's higher-order cycloaddition methodology utilizing an electron-rich diene partner is presented, comparable results have also been obtained employing an electron-poor diene, methyl sorbate, with typical yields of 80-85% on a 10-g scale.[11]

Key to this large scale cycloaddition chemistry is the ability to generate large quantities of tricarbonyl(η⁶-cycloheptatriene)chromium(0). The submitters have found that the best results are obtained when the desired complex is generated with the highly reactive and pyrophoric complexation reagent $(CH_3CN)_3Cr(CO)_3$.[12] One drawback to this method, however, was the need to scrape solidified $Cr(CO)_6$ from the reflux condenser during the early stages of the reaction, causing atmospheric exposure to the reactants. For this reason, an engineering control was instituted through development of a reaction vessel (Figure 1) containing a built-in large bore condenser, thereby obviating the need to open the system for scraping and allowing, after subsequent complexation with cycloheptatriene, the isolation of highly pure product complex with little or no additional purification necessary.

References and Notes

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

7α-Acetoxy-(1Hβ, 6Hβ)-bicyclo[4.4.1]undeca-2,4,8-triene:
Bicyclo[4.4.1]undeca-3,7,9-triene-2-ol, acetate, endo- (±)- (12); (129000-83-5)

Tricarbonyl(η^6-cycloheptatriene)chromium(0):
Chromium, tricarbonyl (1,3,5-cycloheptatriene)- (8);
Chromium, tricarbonyl[(1,2,3,4,5,6-η)-1,3,5-cycloheptatriene]- (9); (12125-72-3)

Acetonitrile (8,9), (75-05-8)

Chromium hexacarbonyl: HIGHLY TOXIC:
Chromium carbonyl (8);
Chromium carbonyl (OC-6-11)- (9); (13007-92-6)

Cycloheptatriene:
1,3,5-Cycloheptatriene (8,9); (544-25-2)

Tris(acetonitrile)chromium tricarbonyl:
Chromium, tris(acetonitrile)tricarbonyl- (8,9); (16800-46-7)

(E)-1-Acetoxy-1,3-butadiene:
1,3-Butadiene-1-ol acetate, (E)- (9); (35694-20-3)

Crotonaldehyde:
Crotonaldehyde, (E)- (8);
2-Butenal, (E)- (9); (123-73-9)

Isopropenyl acetate:
1-Propen-2-ol, acetate (8,9); (108-22-5)

p-Toluenesulfonic acid (8);
Benzenesulfonic acid, 4-methyl- (9); (104-15-4)

Cupric acetate monohydrate:
Acetic acid, copper(2+) salt, monohydrate (8,9); (6046-93-1)