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Cyclooctatetraene dianion from 1,5-cyclooctadiene. A synthesis in the presence of naphthalene radical anion

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Abstract—A novel synthesis of cyclooctatetraene dianion from 1,5-cyclooctadiene (1,5-COD) is described. The reaction of the potassium–naphthalene adduct with 1,5-COD proceeds at room temperature over 3 days in heptane/tetrahydrofuran to produce the target compound. © 2002 Elsevier Science Ltd. All rights reserved.

Cyclooctatetraene (COT) dianions are synthetically useful in organic and organometallic chemistry,[1] having generally been prepared by reaction of an alkali metal with the COT in solvents such as ammonia or tetrahydrofuran (THF). COT dianion has also been prepared by the reaction of potassium with 1,5-cyclooctadiene (1,5-COD)[2] over 4 or 5 days circa 100°C. Our interest in the organometallic chemistry of COT[3] has prompted us to seek a more facile synthesis of COT dianion from the readily available 1,5-COD by use of solubilized potassium reagent systems.

Experimentation led us to consider naphthalene radical anion systems, which have both electron-transfer and basic properties.[4] If potassium, naphthalene and an inert hydrocarbon solvent are stirred in N_2 and heated above the melting point of potassium, a powdery, black, insoluble potassium–naphthalene addition product is formed. Less than 0.5 equiv. of naphthalene is needed to fully disperse the potassium. When stirring is ceased, the K-NAP adduct settles out, leaving a colorless supernatant. If THF is added at room temperature, the dark green color of naphthalene radical anion soon spreads throughout the liquid and no free K is observed. If 1,5-COD if added at this point and the mixture stirred at room temperature, little or no K_2COT is produced. However, it was found that by using *n*-heptane as the hydrocarbon and refluxing the heptane–naphthalene–1,5-COD–potassium mixture overnight in N_2, a very fine, black powdery K-NAP adduct is produced along with a colorless supernatant. NMR analysis of the liquid shows the presence of heptane and 1,5-COD along with the C_8H_{12} isomer, *cis*-bicyclo[3.3.0]oct-2-ene. This isomerization has been reported to proceed by a ring closure reaction of cyclooctadienyl anion.[5] Naphthalene is not observed in solution. If THF is added at this point and the reaction mixture stirred at room temperature for 3 days, the initial dark green color gradually changes to dark brown or to dark reddish-brown. The reaction can be summarized as follows.

$$\text{K+Naphthalene} \xrightarrow[\text{Reflux, 17 h}]{\text{Heptane, 1,5-COD}} \text{(K-NAP)}$$

$$\text{1,5-COD} \xrightarrow[\text{Heptane, rt, 3 days}]{\text{(K-NAP), THF}} K_2COT$$

The powdery, brownish product can be isolated by multiple extractions and filtrations with diethyl ether. Preparation of K_2COT is confirmed by NMR and mass spectrometry.

Among other solvent systems tested was liquid ammonia. When 1,5-COD is added to a dark blue potassium/ammonia solution at dry ice temperature, the colorless olefin forms a separate lower layer. Refluxing for 4 h (ca. −33°C) continues the dark blue K/NH_3 color and the separate, colorless diene layer. After evaporation of NH_3, NMR analysis shows only 1,5-COD with no isomers formed. A pressure device was constructed to contain liquid ammonia at room temperature; this enabled the dark blue K/NH_3 phase to interact with the diene phase as it warmed above the reflux temperature of NH_3. After several hours at room temperature a dark red one-phase system results. Venting of NH_3 and extraction with THF gives red solutions from which yellow and red solids are obtained. These solids do not contain K_2COT when examined by mass spectrometry.

Keywords: cyclooctatetraene dianion; potassium; naphthalene; 1,5-cyclooctadiene; K_2COT; dipotassium cyclooctatetraenide; $K_2C_8H_8$; uranocene; $U(C_8H_8)_2$.

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Pressurized methylamine, at room temperature or at 47°C, and isopropylamine, at reflux, also give one-phase red solutions in reactions of potassium with 1,5-COD. After removal of the amine solvent, extraction with THF produces red solutions, which yield yellowish and reddish solids. These materials give no evidence of K_2COT when analyzed by mass spectrometry.

1,2-Dimethoxyethane (DME) is capable of dissolving sufficient potassium–sodium alloy at room temperature to produce dark blue solutions. When 1,5-COD is added to this reducing system, the color immediately changes from dark blue to light yellow. While stirring for about 1 h, the solution becomes green and, after 1 day, has become a cloudy brownish–green. Stirring in N_2 for two (2) additional days generates a greenish–brown liquid with more suspended particulates. Removal of solvent and extraction with THF gave an orange liquid from which red solids could be isolated. NMR analysis of these solids gave no evidence of COT dianion.

1. Preparation of K_2COT

CAUTION: **When dry, K_2COT can explode in air and must be handled in an inert atmosphere[6] at all times**. In an evacuated, N_2-filled, long-necked 500 mL Schlenck flask are placed a glass-encased magnetic stir bar, 3.28 g (83.9 mmol) of hexanes-washed, N_2-flushed K, and 2.64 g (20.6 mmol) of naphthalene. 60 mL of sodium-dried, nitrogen-sparged *n*-heptane is cannula-transferred into the flask. Sodium-dried, nitrogen-sparged 1,5-COD (20 mL, 163 mmol) is added to the flask with a gas-tight syringe. The flask is warmed and stirred under N_2 on a mercury bubbler. As the potassium begins to melt and breaks into smaller pieces, black particles form and disperse throughout the liquid. The black suspension is gently boiled, with a colorless reflux, for about 17 h, then cooled to room temperature. When stirring is ceased, a very fine black powder settles out, leaving a colorless supernatant. Analysis of the colorless liquid by NMR in $DCCl_3$ shows *n*-heptane, 1,5-COD, and about 3% *cis*-bicyclo[3.3.0]oct-2-ene (^{13}C NMR: 134.6, 129.5, 50.7, 41.1, 40.2, 35.8, 32.4, 25.3 ppm). Only a trace of naphthalene is observed by NMR spectroscopy. At room temperature, 120 mL of sodium-dried, nitrogen-sparged THF is added by cannula and a dark green coloration quickly spreads throughout. The dark green liquid is then stirred at room temperature. After about 3 h, the color has changed to dark brownish-green with visible particulate. Overnight stirring gives a dark brown liquid with more particles. Stirring is continued for a total of 3 days at room temperature, then volatiles are removed under vacuum. Warming the flask to 50°C under vacuum removes some naphthalene. The flask is then extracted with 4×100 mL portions of warm sodium-dried, nitrogen-sparged hexanes to remove free naphthalene. The product K_2COT is obtained by extraction and filtration with 10×100 mL portions of sodium-dried, nitrogen-sparged diethyl ether. Any potassium naphthalenide remaining in the flask is insoluble in the ether extractant. The ether filtrate is dark brown with brown–yellow highlights. The solvent is removed under vacuum and the solids are reextracted and refiltered with ether to remove fine particulates. Ether is again removed under vacuum, leaving brown powdery solids, which are dried at 50°C under vacuum for 2 h before transfer and weighing in the dry box. K_2COT is characterized by NMR[7] and mass spectrometry.[8] The yield is 3.52 g (46%).

2. COT by air oxidation of K_2COT

CAUTION: **When dry, the insoluble, non-volatile oxidation residues are shock- and heat-sensitive and should not be warmed during vacuum transfer of volatiles**. K_2COT (1.51 g, 8.3 mmol) is dissolved in 25 mL of THF under positive N_2 pressure to give a dark-brown solution, which is stirred magnetically with a glass-encased bar. The solution is chilled in an ice bath and compressed air, dried by passage through a 30×175 mm column of indicating Drierite, is then slowly admitted via cannula through a septum cap. Over a 1.5 h period, the dark brown liquid changes to an orange–brown suspension, then, the trickle of air is ceased and the reaction mixture is allowed to warm to room temperature under N_2. Volatiles are removed by vacuum transfer at room temperature and analyzed by NMR in $DCCl_3$ solution. COT (^{13}C NMR = 132.1 ppm, ^1H NMR = 5.78 ppm) is prepared very selectively and is present in a concentration equivalent to 49% of theory.

3. COT by iodine oxidation of K_2COT

K_2COT (1.91 g, 10.5 mmol) is dissolved in 100 mL ether under N_2. The dark brown ether solution is stirred magnetically with a glass-encased bar and chilled in an ice bath. Iodine (3.15 g, 12.4 mmol) is dissolved in 105 mL ether under N_2 and stirred magnetically. The I_2/ether solution is cannula-transferred to an N_2 filled 250 mL pressure-equalizing dropping funnel, which is placed atop the chilled K_2COT/ether flask. The dark red-brown I_2/ether solution is added dropwise to the magnetically stirred K_2COT/ether solution. Over 45 min about 25% of the I_2/ether has been added and the reaction mixture has become a murky brownish suspension. After one-half of the I_2/ether is added, the reaction mixture is a lighter brown suspension and soon becomes a yellow-brown suspension. After about 1.5 h, two-thirds of the I_2/ether had been added and the mixture has become reddish-yellow-brown. When about 80% of the I_2/ether is added, the mixture has become more red, the addition is ceased, and the flask is allowed to warm to room temperature under nitrogen. Most of the ether is removed by vacuum transfer, then a second LN_2 trap is used to collect the remaining volatiles. After thawing, the liquid is transferred to a tared, conical tube and most of the ether is removed by nitrogen flushing to give a solution weighing 5.34 g. This liquid is analyzed by NMR in $DCCl_3$ solution. COT (^{13}C NMR = 132.1 ppm, ^1H NMR = 5.78 ppm) is produced very selectively and is present in a concentration equivalent to 22% of theory.

4. Preparation of uranocene ($U(COT)_2$)

UCl_4 is prepared by the reaction of hexachloropropene with anhydrous UO_3.[1a,9] The green product is washed with CCL$_4$ and vacuum dried for 21 h at 165–170°C before storing in the dry box. When examined by electron-impact mass spectrometry, UCl_4 exhibits the molecular ion at *m*/*e* 380, along with successive loss of Cl at *m*/*e* 345, 308, 273. Uranium is seen in the vapor phase at *m*/*e* 238. The yield of UCl_4 is about 93%.

In the dry box, 1.95 g (10.7 mol) K_2COT and a glass-encased stir bar are placed in a 70 mm OD Schlenck storage tube equipped with a J. Young Teflon stopcock and a male 24/40 joint. UCl_4 (2.02 g, 5.3 mmol) is weighed into a 500 mL Schlenck flask. At the vacuum-nitrogen line, 100 mL of THF is cannula-transferred onto the K_2COT producing a dark brown solution. The K_2COT solution is stirred and chilled in a −35°C slush bath. THF (75 mL) is cannula-transferred onto the UCl_4, producing a murky, green liquid, which is then cannula-transferred, in one portion, into the stirring, chilled K_2COT solution. The reaction mixture quickly becomes dark green throughout and is stirred for 3 h in the range of −33 to −39°C under N_2 on a mercury bubbler. The reaction mixture is stirred overnight as the slush bath warms to room temperature. THF is removed by vacuum transfer, leaving fine, green solids. The solids are washed with ether to remove organic impurities, then, vacuum dried at 50°C and transferred into the dry box where 3.112 g fine, green solids are weighed. A 559 mg portion of the green powder is placed in a short-path sublimation device. On the vacuum line, the green powder is sublimed for 2 h at 211°C and 3×10^{-3} torr to produce 43 mg of a dark green sublimate on the water-cooled cold finger. This corresponds to a 12% isolated yield of uranocene, which is characterized by NMR[10] and mass spectrometry.[11] In the proton NMR, at 300 K, a broad peak is observed at −36.4 ppm, which corresponds well to the temperature-dependent NMR spectra reported by Edelstein et al.[12] The carbon NMR, at 300 K, shows a broad peak at 297.1 ppm, which is in excellent agreement with the value of 297 ppm indicated by Streitwieser et al.[13]

In summary, a new naphthalene radical anion mediated preparation of COT dianion from 1,5-COD is described. COT is prepared by oxidation of K_2COT with air and iodine. Reaction of K_2COT with UCl_4 in THF produces uranocene. Further reactions of COT dianion will be reported elsewhere.

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8. Mass spectral data for $K_2C_8H_8$: Electron impact: *m*/*e* 182, 104, 78. Chemical ionization (positive mode): *m*/*e* 182, 105. High resolution calcd for $C_8H_8K_2$: 181.990016. Found: 181.991086.
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11. Mass spectral data for $U(C_8H_8)_2$: Electron impact: *m*/*e* 446, 342, 104. Chemical ionization (positive mode): *m*/*e* 447, 105. High resolution calcd for $C_{16}H_{16}U$: 446.175986. Found: 446.175329.
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