and **2** are calculated to be 82 and 64 kcal/mol, respectively, with a propagated error of probably less than 1 kcal/mol.

The method can also be used for solution-phase anion oxidations that are not fully reversible, although only an inequality for the BDE can be calculated. For example, phenol has a pK_a of 10.0 and a literature $E_{p/2}$ of 0.48 V (vs. NHE) in water at pH 13.[8] The calculated BDE is ≥87 kcal/mol, whereas the accepted value seems to be ~85 kcal/mol[2c] but ranges from 80 to 88 kcal/mol.[9] The fact that the calculated BDE for phenol is near the upper range of the literature values may be due to the inequality, but Breslow has shown that even poorly behaved cyclic voltammetric measurements are likely to be reasonable approximations of reversible potentials.[4] Also, the calculated BDE by this method may be affected by hydrogen bonding effects with the solvent (water).

Acknowledgment. Thanks to Dr. Eric Brown for many helpful discussions.

Registry No. Hydroquinone, 123-31-9.

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Organic Metals. Preparation and Properties of 7,7,8,8-Tetracyano-*p*-quinodimethaneacetic and -propanoic Acids

Jamil Baghdadchi and Charles A. Panetta*

Department of Chemistry, University of Mississippi, Univeristy, Mississippi 38677

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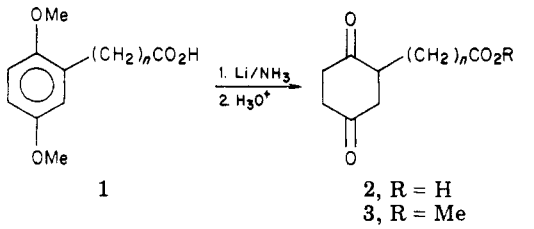
In recent years, some attention has been focused on organic metals: solid carbon compounds with interesting electrical properties.[1] The charge-transfer (CT) complex between the electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)[2] and the electron donor tetrathiafulvalene (TTF)[3] is probably the best known and most widely investigated example of an organic metal.[4]

Many derivatives[5] of TCNQ hve been prepared in efforts to improve the metallic character of the CT salts and to better understand the electron transport properties of these systems. As far as we could determine, none of the above derivatives included the carboxyl-type moiety which we required for a related research project.

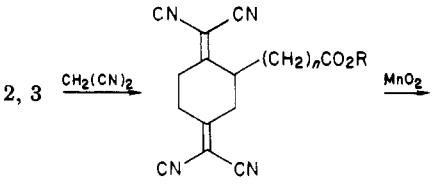
7,7,8,8-Tetracyano-*p*-quinodimethaneacetic (**6a**) and -propanoic acids (**6b**) wer prepared from commercially available (2,5-dimethoxyphenyl)acetic and -cinnamic acids., respectively. An outline of most of the synthetic steps is presented in Scheme I.

Scheme I[a]

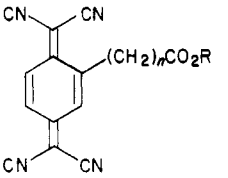


1 — 2, R = H; 3, R = Me

[a] a, n = 1; b, n = 2.



4, R = H; 5, R = Me



6, R = H; 7, R = Me

Tabie I. Half-Wave Reduction Potentials[a]

	TCNQ[b]	Me-TCNQ[b]	6a	6b
$E_{1/2}^1$	0.190	0.170	0.236	0.222
$E_{1/2}^2$	−0.350	−0.340	−0.267	−0.275

[a] In volts vs. SCE as determined by cyclic voltammetry at a Pt-button electrode in acetonitrile, n-$Bu_4N{\cdot}ClO_4$, or n-$Bu_4N{\cdot}BF_4$, (0.1 M). [b] Data from ref 5b.

Table II. Room-Temperature Conductivities (Ω^{-1} cm^{-1}) of TTF Complexes

TTF complexes	conductivity
TCNQ	1-3[a,b]
Me-TCNQ	500[b,c]
6a	1[a]
6b	1[a]

[a] Compacted pellet. [b] From ref 5b. [c] Single crystal.

The overall yield of **6a** from **1a** was approximately 4% and that of **6b** from 2,5-dimethoxycinnamic acid was about 18%. The last step, which involved the dehydrogenation of **4**, was chiefly responsible for the low overall yields. In the acetic acid series, these were improved to about 13% by the utilization of methyl esters (**1a** → **2a** → **3a** → **5a** → **7a** or **1a** → **2a** → **4a** → **5a** → **7a**).

The relative electron accepting abilities of TCNQ, Me-TCNQ, **6a**, and **6b** were determined by measuring the reduction potentials of the last two products and comparing these to the reported[5b] values of the first two (Table I). Both **6a** and **6b** are better electron acceptors than either Me-TCNQ or TCNQ itself. The cyclic voltammograms of **6a** and **6b** showed two reversible one-electron reduction waves (Figure 1 in the supplementary material; see the paragraph at the end of the paper).

Since the new products exhibit reversible electrochemical reduction at potentials more positive than the parent compound, charge-transfer complexes between each of

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them and TTF were prepared in acetonitrile by the H-tube method.[5b] Room-temperature electrical conductivities were roughly equivalent to that of TTF–TCNQ (Table II). Although X-ray diffraction analyses were not performed on the new CT complexes, we assume that the crystals are composed of segregated stacks of donor and acceptor molecules, such as those of TTF–TCNQ. The ion–radical salts of **6a** and **6b** with TTF showed the characteristic broad absorption in the near infrared (1.5–3.0 μm) that has been reported[6] for similar complexes.

Experimental Section

IR spectra were recorded on a Beckman Acculab 3, ^{1}H NMR spectra on a Perkin Elmer R-32 (90 MHz), both proton and ^{13}C NMR spectra on a JOEL FX60Q spectrometer, UV–visible spectra on a Perkin-Elmer Hitachi 200, and near IR on a Cary 17. Cyclic voltammograms were obtained by using a Amel Model 551 potentiostat programmed by a Parc 175 universal programmer. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Solvents used with the TCNQ products **6** and **7** were usually purified and degassed. CH_3CN and CH_2Cl_2 were distilled from P_2O_5, THF, toluene, and hexane were distilled from sodium benzophenone ketyl, and *t*-BuOH was distilled from CaH_2.

2,5-(Dioxocyclohexyl)acetic Acid (2a). A solution of 3.6 g (20 mmol) of (2,5-dimethoxyphenyl)acetic acid, 30 g (0.4 mol) of anhydrous *t*-BuOH, and 40 mL of freshly distilled and anhydrous THF was added to 200 mL of liquid NH_3, and the resultant mixture was cooled to −65 °C. Lithium wire (1.5 g, 0.21 mol) was cut into small pieces and then added to the above in three portions. After 3–4 h, the blue color of the reaction mixture disappeared, excess NH_4Cl was added, and the NH_3 was allowed to evaporate under a stream of Ar. The residue was then treated with 80 mL of 6 N HCl, and the resultant mixture was heated to the reflux temperature for 1.5 h. It was then cooled and extracted with EtOAc (5 × 150 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent evaporated to yield the product as a viscous yellow oil which solidified during storage. It was purified by chromatography on normal silica (silica gel 60, E. Merck 7734 or equivalent) by using 60% $CHCl_3$, 39.5% EtOAc, and 0.5% HOAc. Recrystallization from EtOAc–hexane afforded 2.0 g (58%) of the product as colorless prisms: mp 94.0–95.0 °C; IR (KBr) 3200–2600, 1730, 1710 cm^{-1}, ^{1}H NMR (acetone-d_6) δ 3.3 (m, 1 H), 2.9–2.5 (m, 6 H), 2.1 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 208.7, 207.8 (two ketone carbonyls), 173.2 (carboxyl), 42.8 (α-methylene), 42.6, 37.5, 36.6, and 35.9 (ring carbons). Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.25; H, 5.89.

Methyl (2,5-Dioxocyclohexyl)acetate (3a). This was prepared by esterification of **2a** with CH_2N_2 by a standard procedure. The product was purified by column chromatography on silca gel 60 (E. Merck 7734) with 40% EtOAc and 60% $CHCl_3$. Recrystallization from ether–hexane afforded a 90% yield of the product as white needles: mp 40.0–41.0 °C; IR (Nujol) 1740, 1715, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.7 (s, 3 H), 3.2–2.9 (m, 1 H), 2.9–2.5 (m, 8 H). Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.67; H, 6.67.

3-(2,5-Dioxocyclohexyl)propanoic Acid (2b). The procedure for the preparation of **2a** was used on 3-(2,5-dimethoxyphenyl)propanoic acid (which, in turn, was prepared in 95% yield by the catalytic hydrogenation of 2,5-dimethoxycinnamic acid). Column chromatography of the crude product was performed with 40% EtOAc, 59.5% hexane, and 0.5% HOAc as the eluting solvent. The recrystallized product was obtained in 55% yield as colorless prisms: mp 86.0–86.5 °C; IR (KBr) 3100–2600, 1720–1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.3–3.15 (m, 1 H), 2.9–2.4 (m, 6 H), 2.3–2.1 (m, 4 H). Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.48; H, 6.38.

[2,5-Bis(dicyanomethylene)cyclohexyl]acetic Acid (4a). (2,5-dioxocyclohexy)acetic acid (**2a**; 6.0 g, 35.3 mmol) was melted by heating it on a steam bath in the presence of 4.65 g (70.4 mmol) of malononitrile and 10 mL of water. A solution of 60 mg of β-alanine in 5 mL of water was added, and the resultant mixture was stirred and heated for 6 h (a pink suspension was formed after the first 5 min). The thick slurry was cooled and filtered, and the residue was washed thorougly with water, ether, and EtOAc. The solid was recrystallized from a large volume of EtOAc to afford colorless prisms: 8.0 g (85%); mp 209.0–211.0 °C; IR (KBr) 3200–2600, 2225, 1705, 1610 cm^{-1}; UV (CH_3CN) λ_{max} 245 mm (ϵ 18300). Anal. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 62.86; H, 3.84; N, 23.12.

Methyl [2,5-Bis(dicyanomethylene)cyclohexyl]acetate (5a). Method A. By Esterification of 4a. Methylation of **4a** with CH_2N_2 was performed in the standard manner. The crude product was recrystallized from CH_2Cl_2 to afford the methyl ester **5a**: 90% yield; mp 150.0–151.0 °C; IR (Nujol) 2230, 1735, 1600, 1240 cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_4O_2$: C, 64.28; H, 4.32; N, 19.99. Found: C, 63.17; H, 4.36; N, 20.10.

Method B. By Treatment of 3a with Malononitrile. The methyl ester **3a** was treated with 2 equiv of malononitrile in a procedure similar to that used on **2a** (above). The yield of **5a** by this method was 84%.

3-[2,5-Bis(dicyanomethylene)cyclohexyl]propanoic Acid (4b). Compound **2b** was treated with 2 equiv of malononitrile in a procedure similar to that used on **2a** (above) except that the heating period was reduced to 3 h, when the reaction was complete. The product was recrystallized from EtOAc: white prisms (85%); mp 178.5–180.0 °C; IR (KBr) 3200–2500, 2220, 1705, 1600 cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_4O_2$: C, 64.28; H, 4.31; N, 19.99. Found: C, 63.98; H, 4.11; N, 19.55.

Methyl 3-[2,5-Bis(dicyanomethylene)cyclohexyl]-propanoate (5b). Methylation of **4b** with CH_2N_2 was performed in the standard manner to afford a product that was recrystallized from EtOAc: pink prisms (90%); mp 118.0–118.5 °C; IR (KBr) 2225, 1725, 1600, 1210 cm^{-1}. Anal. Calcd for $C_{16}H_{14}N_4O_2$: C, 65.30; H, 4.79; N, 19.04. Found: C, 64.96; H, 4.74; N, 19.14.

7,7,8,8-Tetracyano-*p*-quinodimethaneacetic Acid (6a). Activated[7] MnO_2 (0.49 g, 5.6 mmol) was added during a 7-min period to a slurry of 0.15 g (0.56 mmol) of **4a** in 30 mL of toluene at 95 °C. After 1 h of refluxing, the reaction mixture was filtered, and the residue was washed with hot toluene several times. The filtrate and washings were combined and distilled under reduced pressure to yield a solid yellow residue. This was recrystallized from CH_3CN to afford 7.4 mg (5%) of product: mp 218.0–221.0 °C; UV (toluene) λ_{max} 348 nm. Anal. Calcd for $(C_{14}H_6N_4O_2)_4 \cdot 3H_2O$: C, 60.98; H, 2.78. Found: C, 60.87; H, 2.89.

All TCNQ-type products are generally air- and light-sensitive compounds. They are reactive materials which form charge-transfer complexes or covalent compounds with a wide variety of reagents.[8]

Methyl 7,7,8,8-Tetracyano-*p*-quinodimethaneacetate (7a). The methyl ester **5a** was dehydrogenated with active MnO_2 in the same manner as was **4a** (above) except the reflux period was reduced to 15 min. The product was recrystallized from CH_3CN to afford yellow crystals: 30%; mp 167.0–168.0 °C; IR (KBr) 3025, 2200, 1730, 1600, 1535 cm^{-1}; UV (CH_3CN) λ_{max} 404 nm (ϵ 59700). Anal. Calcd for $C_{15}H_8N_4O_2$: C, 65.22; H, 2.92; N, 20.28. Found: C, 64.74; H, 2.98; N, 20.83.

7′,7′,8′,8′-Tetracyano-*p*-quinodimethanepropanoic Acid (6b). The tetrahydro intermediate **4b** was dehydrogenated with MnO_2 by using the same procedure that was used on **4a** (above). The yield was improved somewhat when a few drops of concentrated HCl were combined with hot toluene before using the mixture to wash the residue in a filter funnel. This treatment was repeated several times until the washings removed no more yellow color. These were evaporated in vacuo to afford the product which was recrystallized from CH_3CN: 42%; mp 210.0–211.0 °C; IR (KBr) 3040, 2220, 1600, 1535 cm^{-1}; UV (CH_3CN) λ_{max} 397 nm (52300); ^{1}H NMR (CD_3CN) δ 7.8–7.1 (m, 3 H)m, 3.4–2.2 (m, 4 H). Anal. Calcd for $C_{15}H_8N_4O_2$: C, 65.22; H, 2.92; N, 20.28. Found: C, 65.22; H, 3.08; N, 20.60.

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Registry No. **1a**, 1758-25-4; **1b**, 10538-49-5; **2a**, 87145-73-1; **2b**, 87145-74-2; **3a**, 87145-75-3; **4a**, 87145-76-4; **4b**, 87145-77-5; **5a**, 87145-78-6; **5b**, 87145-79-7; **6a**, 87145-80-0; **6a**·TTF, 87145-81-1; **6b**, 87145-82-2; **6b**·TTF, 87145-83-3; **7a**, 87145-84-4.

Supplementary Material Available: Cyclic voltammograms of products **6a,b** (1 page). Ordering information is given on any current masthead page.

Stereocontrolled Synthesis of (*E*)- and (*Z*)-3-Deuteriophosphoenolpyruvate

Paul A. Bartlett* and Paul M. Chouinard

Department of Chemistry, University of California, Berkeley, California 94720

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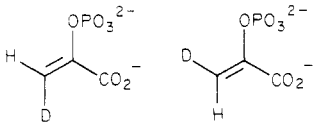
Phosphoenolpyruvate (PEP) derivatives which are stereospecifically labeled at the methylene position with hydrogen isotopes are important substrates for probing the stereochemistry of a number of enzymatic transformations.[1,2] These materials are currently available by an enzymatic synthesis developed by Rose.[3] In connection with model studies of the chorismate-to-prephenate rearrangement,[1,4] we required substantial quantities of stereoselectively deuterated PEP (1) and were therefore led to develop an alternative nonenzymatic synthesis.

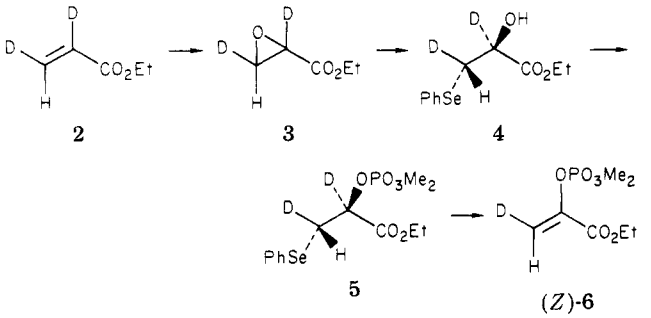


(*E*)-1 (*Z*)-1

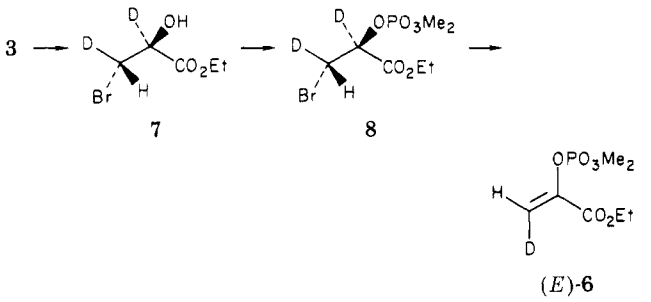
Ethyl (*E*)-2,3-dideuterioacrylate (**2**) is prepared by the method of Hill and Newkome,[5] involving catalytic deuterogenation of the anthracene–propiolate Diels–Alder adduct followed by pyrolysis. Of the material produced by this route, 96% is the desired isomer. Epoxidation of **2** with 3,5-dinitroperoxybenzoic acid[6] affords the labeled glycidate **3** with no apparent stereoisomerization.

Conversion of **3** to the *Z* isomer of **1** (Scheme I) involves opening of the epoxide ring with diisobutylaluminum phenylselenide in hexane, leading to a 3:1 mixture of phenylselenide **4** and its regioisomer. A number of reagents were investigated for accomplishing this conversion, including the alkali metal salts of phenylselenide in both protic and aprotic solvents, and the diisobutylaluminum derivative proved to be the most regioselective. After chromatographic purification, **4** is converted to the lithium

Scheme I



Scheme II



salt and phosphorylated with dimethyl phosphorochloridate at low temperature. Hydrogen peroxide oxidation of **5** and concomitant selenoxide elimination afford the triester of (*Z*)-3-deuteriophosphoenolpyruvate, (*Z*)-**6**. This material is hydrolyzed by a two-step procedure using bromotrimethylsilane[7] followed by aqueous potassium hydroxide, and the desired product is isolated as the crystalline cyclohexylammonium salt after ion-exchange chromatography. The overall yield from acrylate **2** to (*Z*)-**1** is 27%, and the stereochemical purity is comparable to that of the starting acrylate.

A complementary route, leading to the *E* isomer of **1** via an anti elimination process, is depicted in Scheme II. In this instance the epoxide moiety of **3** is opened with bromotrimethylsilane catalyzed by zinc bromide to give the bromohydrin **7** in 92% yield along with <5% of its regioisomer. A number of other catalysts, including triphenylphosphine and zinc iodide, were investigated in order to optimize the regioselectivity of this ring-opening process as well. Zinc bromide was the most selective and the easiest to remove from the reaction mixture.

Conversion of bromohydrin **7** to the *E* isomer of **6** is carried out in a single pot. Dimethyl phosphate **8** is formed at −78 °C by deprotonation with lithium diisopropylamide and addition of dimethyl phosphorochloridate; subsequent warming of the basic reaction mixture to room temperature effects the desired anti elimination and provides (*E*)-**6** in quantitative yield. Hydrolysis and purification according to the procedure described above gives the monocyclohexylammonium salt of (*E*)-**1** in 66% overall yield from **2** and with undiminished stereochemical purity.

Experimental Section

Unless otherwise noted, IR spectra were recorded in $CHCl_3$ solution on a Perkin-Elmer Model 1420 spectrophotometer. ^1H NMR spectra were recorded on the UCB-250 FT instrument, operating at a field strength of 250 MHz. Chemical shifts are reported in parts per million on the δ scale relative to internal tetramethylsilane; data are presented as follows: chemical shift (multiplicity, number of protons, coupling constants in hertz).

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