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NOVEL CONJUGATED MOLECULES FROM OXIDATION OF A CYCLOPENTADIENONE IRON TRICARBONYL COMPLEX[**]

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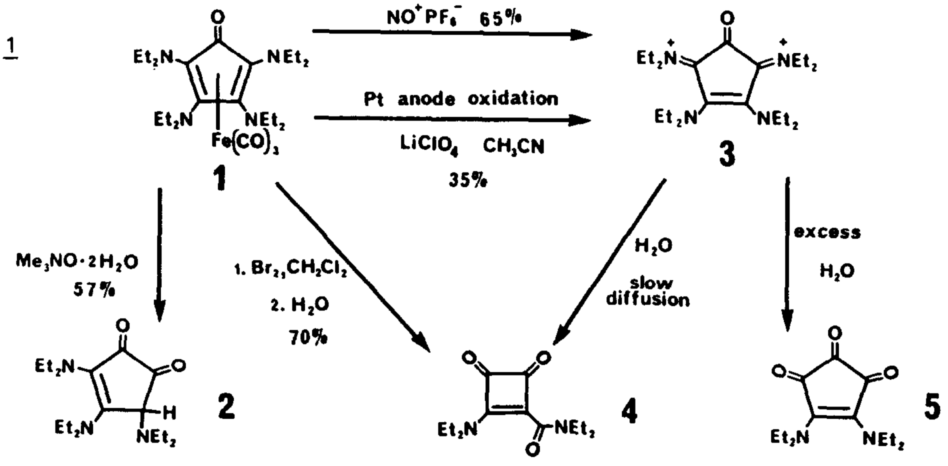
ABSTRACT: Oxidation of tetrakis-diethylaminocyclopentadienone iron tricarbonyl (1) electrochemically or with nitrosonium hexafluorophosphate afforded the dication of tetrakis-diethylaminocyclopentadienone (3). Oxidation of 1 with bromine and aqueous workup gave diethylaminocyclobutenedione-N,N-diethylcarboxamide (4), which was also formed by the hydrolysis of 3. The structures of the products were confirmed by X-ray crystallography.

Some years ago King reported[1] the facile preparation of tetrakis-diethylaminocyclopentadienone tricarbonyliron (1) from $Fe(CO)_5$ and bis-diethylaminoacetylene. We have been interested in tetraaminocyclopentadienone derivatives for the preparation of stable triplet-state cyclopentadienyl cations[2], so we examined methods to release the organic ligand from 1 (Fig. 1). Treatment with amine oxides under a variety of conditions produced 2, the hydrolysis product of the tetraaminocyclopentadienone, as the only isolable product[3]. A report[4] of the successful electrochemical liberation of the sensitive tetra-tert-butoxycyclopentadienone from its cyclopentadienyl cobalt complex encouraged us to examine the electrochemical oxidation of 1.

FIGURE 1



[**] Dedicated to Professor Harry Wasserman on the occasion of his sixty-fifth birthday.

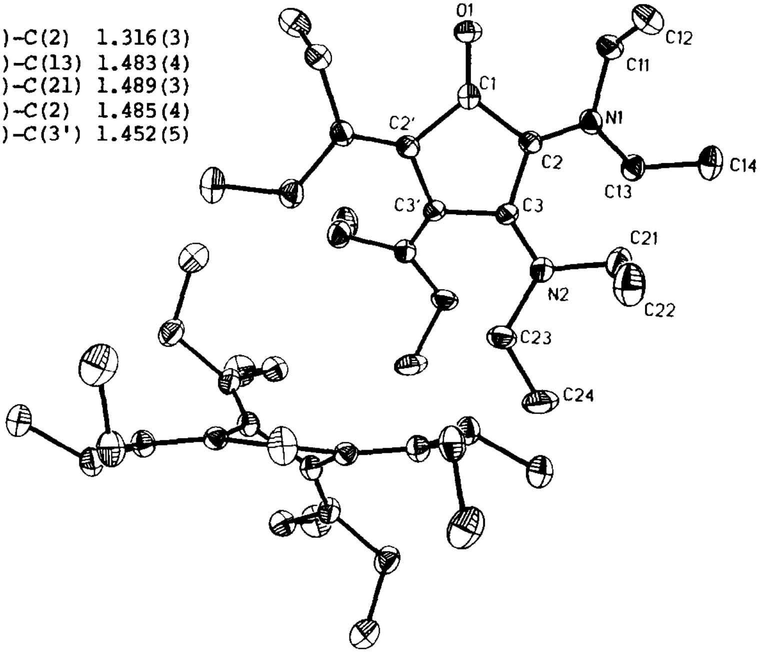
Under strictly anhydrous conditions, constant-current electrolysis of 1 at a Pt mesh anode in 0.1 M $LiClO_4/CH_3CN$ yielded a very polar, water sensitive red compound[5] that was purified from electrolyte and Fe(III) by trituration with ethyl acetate and recrystallized from CH_3CN/THF. X-ray analysis[6] (Fig. 2) showed that it was the two-electron oxidation product of the cyclopentadienone, 4,5-bis(diethylamino)-4-cyclopentene-2-one-1,3-bis(diethyliminium) dication (3) bis-perchlorate. Dication 3 was also prepared by addition of nitrosonium hexafluorophosphate (5 equiv.) to the complex 1 in CH_3CN/CH_2Cl_2. Addition of benzene drove out first Fe(III) salts, then the dication 3 as the bis-hexafluorophosphate[7]. Cyclic voltammetry of the dication 3 at 200 mV/s scan rate[8] gave a reversible first reduction potential of -0.034 V. vs. SCE, while the complex 1 was oxidized reversibly at +0.563 V. Thus at the potential needed to release the cyclopentadienone, it was easily oxidized to the dication.

The X-ray data show that the four nitrogen atoms in 3 are all nearly coplanar with their attached carbons, the C_3-$C_{3'}$ and C_2-C_3 (= $C_{2'}$-$C_{3'}$) bond lengths alternate little, and the N-C(ring) bond distances are all similar, indicating that the total positive charge is delocalized onto all four nitrogens. The somewhat longer C_1-C_2 (= C_1-$C_{2'}$) bond lengths and the normal short C=O distance of 1.208 Å suggest little electron delocalization onto the carbonyl. The steric bulk of the diethylamino groups is probably responsible for the pronounced puckering of the ring.

FIGURE 2 ORTEP diagrams of compound 3 showing 30% probability thermal ellipsoids, and selected structure data. The molecule has a crystallographic C_2 axis of symmetry corresponding to the C_1-O_1 bond. The observed perchlorate anions are not shown.

Selected Bond Lengths (Å)

O(1)-C(1)	1.208(5)	N(1)-C(2)	1.316(3)
N(1)-C(11)	1.488(4)	N(1)-C(13)	1.483(4)
N(2)-C(3)	1.325(4)	N(2)-C(21)	1.489(3)
N(2)-C(23)	1.476(4)	C(1)-C(2)	1.485(4)
C(2)-C(3)	1.448(4)	C(3)-C(3')	1.452(5)



Selected Bond Angles (deg.)

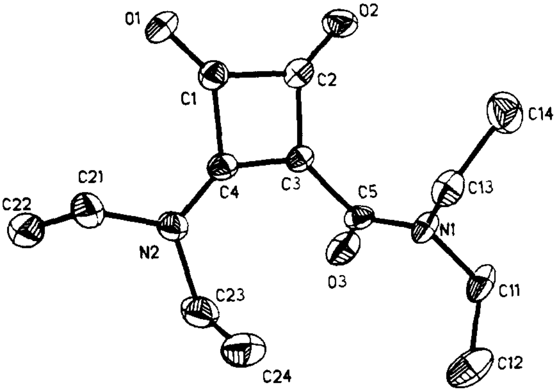
C(2)-N(1)-C(11)	120.9(2)
C(2)-N(1)-C(13)	121.5(2)
C(11)-N(1)-C(13)	116.2(2)
C(3)-N(2)-C(21)	121.4(2)
C(3)-N(2)-C(23)	120.5(2)
C(21)-N(2)-C(23)	116.0(2)
O(1)-C(1)-C(2)	128.0(2)
C(2)-C(1)-C(2')	104.1(3)
N(1)-C(2)-C(1)	126.5(3)
N(1)-C(2)-C(3)	128.2(2)
C(1)-C(2)-C(3)	105.3(2)
N(2)-C(3)-C(2)	130.1(2)
N(2)-C(3)-C(3')	127.5(2)
C(2)-C(3)-C(3')	102.2(2)

On gradual diffusion of atmospheric moisture into solutions of 3 in acetonitrile, or by reaction of 1 with Br_2 in CH_2Cl_2 followed by aqueous workup, a colorless, water-stable product was formed. Spectral evidence suggested that it was 4-diethylaminocyclobutenedione-3-N,N-diethylcarboxamide (4)[9]. The structure was confirmed by X-ray crystallography[10](Fig. 3). This is one of very few cyclobutenedione crystal structures that have been reported[11]. The amino nitrogen is flat and with its two attached CH_2 groups is coplanar with the ring. It is conjugated with the vinylogous ring ketone as shown by the short C_4-N_2 and C_2-C_3 bond lengths, while the carboxamide group is twisted completely out of conjugation with the ring. This product apparently results from a benzilic acid type rearrangement to a 4-membered ring under very mild conditions. A related rearrangement of leuconic acid trihydrate to squaric acid has been observed[12].

FIGURE 3 ORTEP diagram of 4 showing 30% probability ellipsoids, with selected structure data.

Selected Bond Lengths (Å)

O(1)-C(1)	1.189(5)
O(2)-C(2)	1.189(6)
C(1)-C(2)	1.549(7)
C(2)-C(3)	1.457(6)
C(3)-C(4)	1.398(6)
C(1)-C(4)	1.525(7)
N(1)-C(5)	1.303(7)
N(2)-C(4)	1.308(6)
C(3)-C(5)	1.516(6)
O(3)-C(5)	1.233(6)
N(1)-C(11)	1.476(6)
N(1)-C(13)	1.486(6)
N(2)-C(23)	1.490(7)
N(2)-C(21)	1.482(6)



Selected Bond Angles (deg.)

C(5)-N(1)-C(11)	117.5(4)	C(5)-N(1)-C(13)	125.2(4)
C(11)-N(1)-C(13)	117.1(4)	C(4)-N(2)-C(21)	120.3(4)
C(4)-N(2)-C(23)	121.1(4)	C(21)-N(2)-C(23)	117.9(4)
O(1)-C(1)-C(2)	137.2(4)	O(1)-C(1)-C(4)	136.1(4)
C(2)-C(1)-C(4)	86.5(3)	O(2)-C(2)-C(1)	134.8(4)
O(2)-C(2)-C(3)	137.6(4)	C(1)-C(2)-C(3)	87.6(4)
C(2)-C(3)-C(4)	95.1(4)	C(2)-C(3)-C(5)	132.8(4)
C(4)-C(3)-C(5)	132.0(4)	N(2)-C(4)-C(1)	132.0(4)
N(2)-C(4)-C(3)	137.3(4)	C(1)-C(4)-C(3)	90.7(4)
O(3)-C(5)-N(1)	125.7(4)	O(3)-C(5)-C(3)	117.2(4)
N(1)-C(5)-C(3)	117.1(4)		

When an excess of H_2O is added to a solution of the dication 3 in acetonitrile, the cyclobutenedione 4 is still formed but the major product is the known[13] cyclopentenetrione derivative 5, identified by preparation of an authentic sample. Thus the dication 3 is unstable to hydrolysis, but is reductively and thermally stable. Its further reactions, aimed at the production of stabilized cyclopentadienyl cations, will be reported elsewhere.

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3. ^{1}H-NMR(d_8-toluene, 100°C): δ 4.19 (m, 2H), 3.39 (s, 1H), 3.11 (m, 6H), 2.64 (m, 4H), 0.99 (t, 6H), 0.90 (t, 6H), 0.88 (t, 6H). ^{13}C-NMR(CDCl$_3$): δ 203.2, 181.5, 165.4, 139.5, 61.0, 46.6, 44.3, 13.9, 13.6. IR (KBr, cm^{-1}): 2965, 2930, 2872, 1738, 1660, 1542, 1452. m.p. 87–88.5°C (pentane). MS m/e = 309 (M+). UV-VIS (CH$_3$CN, nm): 500(ε 515), 355(ε 8200), 255(ε 8300). Anal. calcd. for $C_{17}H_{31}N_3O_2$: C, 65.98; H, 10.10. Found: C, 65.66; H, 9.96.
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5. ^{1}H-NMR(CD$_3$CN): δ 1.38 (t, 24H), 3.69 (q, 8H), 3.93 (q, 8h). ^{13}C-NMR(CD$_3$CN): δ 200.5, 152.2, 148.0, 49.7, 49.4, 13.9, 12.0. IR (KBr, cm^{-1}): 1780, 1733, 1620(ClO$_4$-), 1454. UV-VIS (CH$_3$CN,nm): 572.
6. $C_{21}H_{40}N_4O\cdot 2ClO_4$, Monoclinic, space group C2/c, a = 14.959(3) Å, b = 9.815(3) Å, c = 18.927(3) Å, β = 103.82(1)°, Z = 4. 2113 unique reflections with $I > 2\sigma(I)$ used in the analysis, R = 0.056. Crystallographic data (for both structures) can be obtained from Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Requests should include a complete citation of this communication.
7. ^{1}H-NMR of $\underline{3}\cdot 2PF_6$ identical to that of the perchlorate. IR (KBr, cm^{-1}): 1725, 1583, 1508, 1458, 1435.
8. 0.1 M n-Bu$_4$NClO$_4$ in freshly distilled CH$_3$CN, Pt button working electrode. At slower scan rates, waves became irreversible.
9. ^{1}H-NMR(CDCl$_3$): δ 1.19 (t, 3H), 1.21 (t, 3H), 1.25 (t, 3H), 1.31 (t, 3H), 3.51 (q, 4H), 3.63 (q, 2H), 3.86 (q, 2H). ^{13}C-NMR(CD$_3$CN): δ 13.0, 13.2, 14.8, 15.2 (CH$_3$); 40.2, 43.7, 46.3, 46.7 (CH$_2$); 159.9, 162.8, 180.4, 186.4, 195.7. IR (KBr, cm^{-1}): 1783, 1741, 1634. m.p. 82.5–83°C (benzene/pentane). MS m/e = 252(M+). UV (CH$_3$CN, nm): 253, 305.
10. $C_{13}H_{20}N_2O_3$, Orthorhombic, space group Pna2$_1$, a = 24.650(6) Å, b = 9.099(3) Å, c = 6.266(1) Å, Z = 4. 1733 unique reflections with $I > 2\sigma(I)$ used in the analysis, R = 0.054.
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13. Yamakazi, T.; Oohama, T.; Doiuchi, T.; Takazawa, T. Chem. Pharm. Bull., 1972, 20, 238, report ^{1}H-NMR(CDCl$_3$): δ 3.62, 1.17; IR (KBr, cm^{-1}): 1714, 1682, 1626. We find ^{1}H-NMR(CDCl$_3$): δ 3.72, 1.22; IR (KBr, cm^{-1}): 1715, 1624.

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