## Synthesis of 1,3-(Dicyanomethylene)croconate Salts. New Bond-Delocalized Dianion, "Croconate Violet"

Sir:

The chemistry and the unique molecular properties of the croconate salts (e.g., 1 dipotassium salt) were first seriously investigated when a symmetrical, delocalized structure for the dianion 1 was proposed.[1] A few years later,[2,3] the dianion 1 and the related deltate,[4] squarate, rhodizonate, and tetrahydroxyquinone anions were recognized[3] as members of a new class of the aromatic oxocarbons $C_nO_n{}^{m-}$.
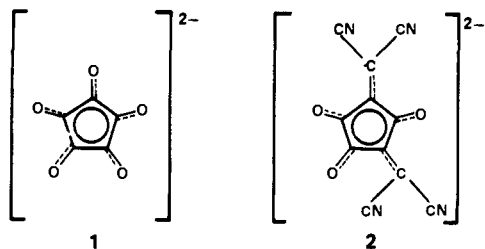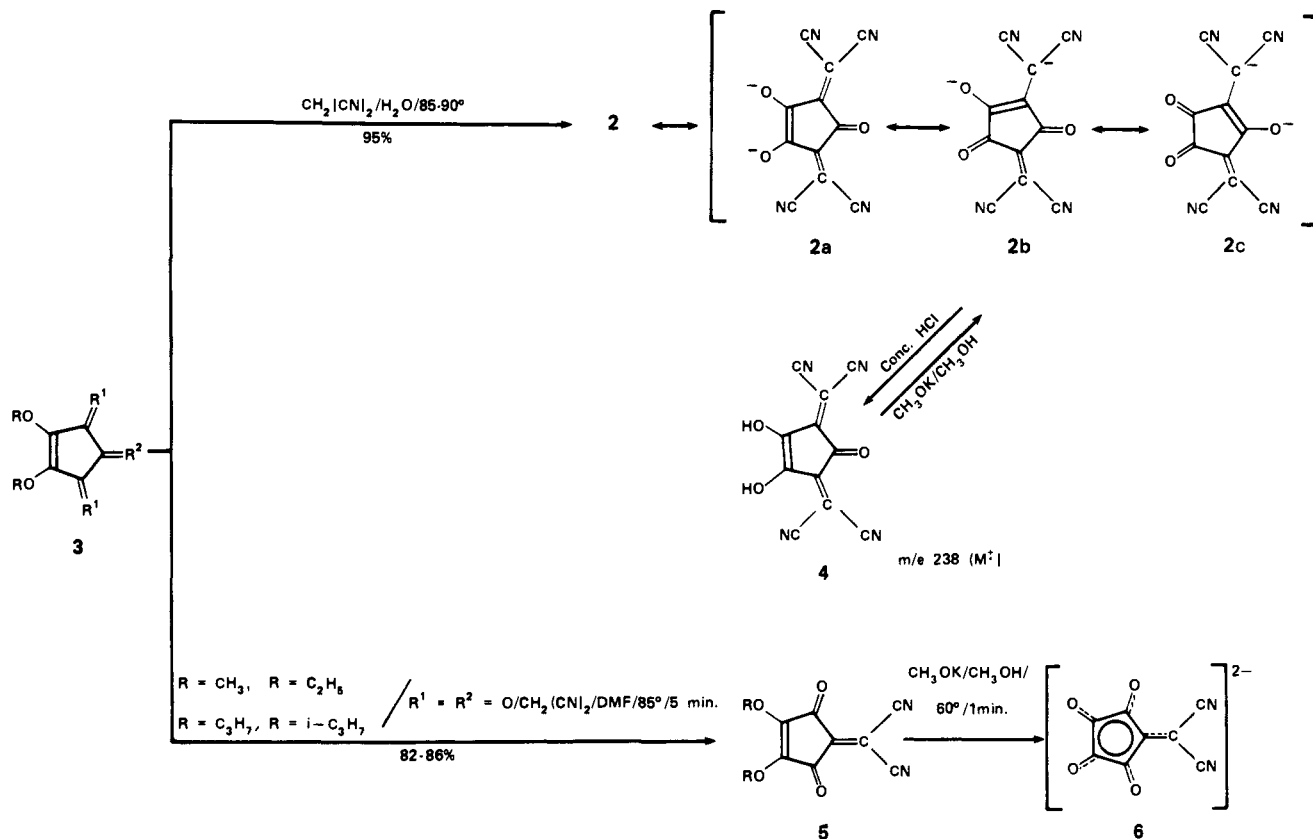

Studies pertinent to the aromatic oxocarbon dianions in which the original carbonyl oxygen atoms in $C_nO_n{}^{2-}$ are either partially or completely replaced have been made; these included the nitrogen,[5] sulfur,[6,7] selenium,[8] and dicyanomethylene[9,10] analogues of the squarate dianion, a sulfur analogue of the croconate dianion,[11] and the trimethylenecyclopropane dianions.[12] Here, the preparation and some of the properties of the croconate dianion analogue in which two of the carbonyl oxygen atoms are replaced by dicyanomethylene groups are described.

Treatment of dipotassium croconate (3, R = K, $R^1 = R^2 =$ O) (also 1 dipotassium salt) or other alkali croconates (3, R = Cs⁺, Li⁺, Na⁺, NH₄⁺, Rb⁺; $R^1 = R^2 = $ O)[13] with a 1 to 2 molar excess of malononitrile in aqueous solution at 85–90 °C yields the dipotassium salt of 1,3-(dicyanomethylene)-2-oxo-5-cyclopentene-4,5-diol, e.g., the salt of 2, e.g., 3 (R = K, R^1 = C(CN)₂, R^2 = O) (95% yield). Recrystallization from hot

water gives the salt of 2 as deep blue, metallic needles; it crystallizes as the dihydrate. The nearly planar dianion 2 is assigned a symmetrical, bond-delocalized structure; the resonance forms 2a–c are three of several possible forms contributing to the ground state of 2, and their real effects on the planarity of the dianion 2 will be discussed separately.[14]

The dipotassium salt of 2 is a dye,[15] termed "Croconate Violet" because of its intense color in solution. The electronic spectrum of the dianion 2 in an aqueous solution shows peaks at 534 (ϵ 87 700), 448 (sh) (ϵ 13 100), 313 (ϵ 5750), 282 (sh, ϵ 7900), 252 (ϵ 17500), 238 (sh, ϵ 14400), 227 (sh, ϵ 9800) nm. The IR spectrum ν_{max}^{KBr} (cm⁻¹), of the dipotassium salt of 2 shows bands at 2195 (s), 2004 (w, C≡N), 1680 (s, C=O), 1640 (w), 1620 (s), 1575 (s), and 1522 (s, C=O + C=C + CC(CN)₂), indicating possible contributions from the resonance forms 2a ↔ 2c, and, also, bands at 820 (m) and 760 (m). The strong band observed at 1430 cm⁻¹ can be ascribed to the skeletal vibration of the dianion.[12] The highly absorbing salt showed a poorly resolved Raman spectrum. In the ¹³C NMR spectrum (D₂O, Me₄Si salt), 2 exhibited peaks at δ 121.7 (nitrile), 112.9 (ring), and 33.8 ppm (methylene) which support the symmetrical structure of the dianion. Cyclic voltammetry of the salt (in water) (0.01 M potassium nitrate as the supporting electrolyte, and a glassy carbon electrode) revealed an irreversible oxidation potential (at a scan rate of 20 mV s⁻¹ and a current sensitivity of 5 µA/fs) at +0.55 V vs. AgCl as the reference electrode, as compared to dipotassium croconate (+0.72 V, also irreversible). In addition, for the salt of 2, an irreversible reduction process occurs at −0.65 V. The x-ray analysis was particularly helpful in determination of the 1,3 positions for the dicyanomethylene groups in the dipotassium salt of 2; the salt is a semiconductor with an electrical conductivity 2 × 10⁻⁴ Ω⁻¹ cm⁻¹ (compressed pellet, 300 K).

Heating of the dipotassium salt of 2 with concentrated hydrochloric acid for 3–5 min at 85 °C yielded orange crystals of a new oxocyanocarbon acid 4 (1,3-dicyanomethylene)-2-oxo-4-cyclopentene-4,5-diol) (mp 260–270 °C dec, m/e 238 (M⁺), ¹H NMR (Me₂SO-d_6) δ 9.53 (s, 1 H)) termed "Cro-

2a   2b   2c

4   m/e 238 (M⁺)

R = CH₃, R = C₂H₅
R = C₃H₇, R = i-C₃H₇

R¹ = R² = O/CH₂(CN)₂/DMF/85°/5 min.

82–86%

CH₃OK/CH₃OH/ 60°/1min.

5   6

conic Acid Violet": UV (H_2O) 534 (ϵ 89 200), 447 (sh, ϵ 13 000), 314 (ϵ 5900), 281 (sh, ϵ 8200), 254 (ϵ 17 800), 238 (sh, 13 100), 228 (sh, ϵ 10 800) nm. Aqueous solutions of either the salt or the acid **4** absorb at the same region in the visible spectrum. Cyclic voltammetry (water) of **4** gave an irreversible oxidation potential at +0.3 V and an irreversible reduction potential at −1.1 V. The IR spectrum (KBr) showed strong bands at 1774 and 1720 (C=O), 1662, 1608 (C=O + C=C), and 1570 and 1512 cm^{-1} (CC(CN)$_2$), indicating possible existence of a hybrid structure. The acid **4** is one of the strongest oxocyanocarbon acids ($pK_1 = 0.32 \pm 0.02$, $pK_2 = 1.02 \pm 0.02$) thus far discovered; it is twice as strong as acid as croconic acid (**3**, R = H; R^1 = R^2 = O[13](($pK_1 = 0.80 \pm 0.01$, $pK_2 = 2.24 \pm 0.01$[16]). The high acidity constant of the oxocyanocarbon acid **4** is considered to be due to the considerable delocalization of π electrons in the substantially planar ring of its dianion **2,** as is also observed for the oxocarbon acids and their anions.[2] The acid **4** was readily reconverted into the dipotassium salt of **2** by careful neutralization (CH$_3$OK–CH$_3$OH or aqueous K$_2$CO$_3$ at 60–70 °C for 5–15 min), and this procedure is the best way found for preparing the other alkali salts of type **2** Cs, Li, Na, Rb); the lithium salt, extremely soluble in water, was recrystallized from methanol–ether. The acid **4** is a potential electron acceptor.

The direct interaction of croconic acid (**3**, R = H, R^1 = R^2 = O) with malononitrile in warm water gives another oxocyanocarbon acid.[17]

Treatment of dimethyl, diethyl, or dipropyl croconates (**3,** R = CH$_3$, R^1 = R^2 = O;[18] R = C$_2$H$_5$, R^1 = R^2 = O;[18] R = C$_3$H$_7$, R^1 = R^2 = O) (mp 54–56 °C, m/e 226 (M$^+$) (75% yield), or diisopropyl croconate R = i-C$_3$H$_7$, R^1 = R^2 = O) (mp 215–225 °C dec, m/e 226 (M$^+$) (80% yield)[19]) in N,N-dimethylformamide with malononitrile produces golden plates of **5** (R = CH$_3$) (2-(dicyanomethylene)-4,5-dimethoxy-4-cyclopentene-1,3-dione: mp 183–184 °C; m/e 213 (M$^+$); UV (CH$_3$OH) 482 (sh), 410, 320, 258 nm; 86% yield) or the corresponding 4,5-dialkyl derivatives of **5**: R = C$_2$H$_5$, mp 124–125 °C, m/e 246 (M$^+$) (85% yield); R = C$_3$H$_7$, mp 114–115 °C, m/e 274 (M$^+$) (82% yield); R = i-C$_3$H$_7$, mp 145–146 °C, m/e 274 (M$^+$) (86% yield).[20] 2-Dicyanomethylene)alkyl croconates **5** are efficient electron acceptors (e.g., in regard to the formation of salts with tetrathiafulvalene, TTF); chemically, they react readily with aniline in warm alcohol to give deep red dyes of structure similar to that described for the product of reaction of 2-(dicyanomethylene)-1,3-indandione with the reagent.[21]

Careful alkaline hydrolysis (CH$_3$OK–CH$_3$OH, 60 °C, 1 min) of **5** (R = CH$_3$, R = C$_2$H$_5$, or R = C$_3$H$_7$) caused a substantial change in color, to give a new, violet dianion (**6**) (UV (CH$_3$OH), 540 (ϵ 82 500), 444 (sh, ϵ 11 500)), to which a bond-delocalized structure is assigned.

The dianions **2** and **6** and the dianions reported[5-11] may be regarded as members of a new class of nonbenzenoid, aromatic, pseudooxocarbons with the general formula C$_n$O$_{n-m}$X$_m^{l-}$ where X = N, S, Se, P, =C-.

References and Notes

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(14) The complete, x-ray crystal structure of the dipotassium salt of **2** will be described in a separate publication.
(15) Aqueous or alcoholic solutions of salts of **2** or acid **4** impart adherent stains to the skin; consequently, all operations require the use of rubber or plastic gloves.
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(17) A. J. Fatiadi, *Synthesis*, 165 (1978). Unlike the reaction of the croconic salts (e.g., their dianions) with malononitrile (to give Croconate Violet of type **2**), the direct interaction of croconic acid (**3**, R = H, R^1 = R^2 = O) with malononitrile in warm water gives another oxocyanocarbon acid, a new, solvatochromic dye (caution: strongly skin-staining) called "Croconic Acid Blue", the intense color of which is dependent on the polarity of the solvent; for example, its solution in alcohol or acetone is red (UV (Me$_2$CO) 475 nm); in water, it is deep blue (UV (H$_2$O) 595–600 nm).
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(19) Prepared by stirring silver croconate[18] with propyl or isopropyl iodide in ether (or ether–tetrohydrofuran) for 18–20 h. The esters of croconic acid (**3**, R = CH$_3$, C$_2$H$_5$, C$_3$H$_7$, i-C$_3$H$_7$; R^1 = R^2 = O) form conducting salts following reaction with tetrathiafulvalene.
(20) All new compounds gave satisfactory elemental analyses. Calcd for C$_{11}$H$_4$N$_4$O$_5$K$_2$, **3** (R = K, R^1 = C(CN)$_2$, R^2 = O) (2H$_2$O): C, 37.71; H, 1.15; N, 15.99; K, 22.32; 2H$_2$O, 10.28. Found: C, 37.51; H, 1.25; N, 15.88; K, 22.10; 2H$_2$O, 10.12. Calcd for C$_{11}$H$_6$N$_4$O$_8$Na$_2$, **3** (R = Na, R^1 = C(CN)$_2$, R^2 = O) (3H$_2$O): C, 39.30; H, 1.80; N, 16.66; Na, 13.68. Found: C, 39.22; H, 1.64; N, 16.78; Na, 13.48. Calcd for C$_8$H$_4$N$_2$O$_6$K$_2$, **6** (**3**, R = K, R^1 = O, R^2 = C(CN)$_2$) (2H$_2$O): C, 31.78; H, 1.33; N, 9.27. Found: C, 31.59; H, 1.15; N, 9.18. Calcd for C$_{11}$H$_2$N$_4$O$_3$, **4** (**3**, R = H, R^1 = C(CN)$_2$, R^2 = O): C, 55.47; H, 0.84; N, 23.52. Found: C, 55.35; H, 0.77; N, 23.44. Calcd for C$_{11}$H$_{14}$O$_5$, **3** (R = i-C$_3$H$_7$, R^1 = R^2 = O): C, 58.42; H, 6.23. Found: C, 58.36; H, 6.12. Calcd for C$_{14}$H$_{14}$N$_2$O$_4$, **3** (R = i-C$_3$H$_7$, R^1 = O, R^2 = C(CN)$_2$): C, 61.13; H, 5.14; N, 10.21. Found: C, 61.07; H, 5.02; N, 10.10.
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Alexander J. Fatiadi

Institute for Materials Research
National Bureau of Standards, Washington, D.C. 20234
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On the Mechanism of the Rubrene-Enhanced Chemiluminescence of α-Peroxylactones[1]

Sir:

A few years ago we reported[2] that the mechanism of the rubrene-enhanced chemiluminescence of α-peroxylactones involved energy transfer by the triplet donor (chemienergized carbonyl product from the α-peroxylactone) producing a triplet acceptor (rubrene), followed by triplet–triplet annihilation to afford singlet excited rubrene which emits efficiently. This mechanism was defended on the facts that rubrene gave rise to a ~100-fold greater light intensity than DPA (9,10-diphenylanthracene), but the decay rate constants of the enhanced chemiluminescence intensities were within the experimental error, the same as those for the direct chemiluminescence. That is, up to enhancer concentrations of ~5×10^{-4} M no induced decomposition of the α-peroxylactone by the enhancer could be detected.

This mechanistic interpretation was recently criticized on energetic grounds.[3] We also were alarmed by the fact that the triplet excited-state yield from the dimethyl α-peroxylactone