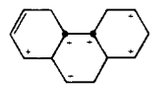
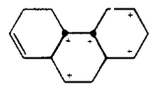
Table I
(Continued)

No.	Structure	Position of double bond	ΔH_f° (25 °C)	ΔH	ΔS	ΔG (80 °C)
24		2,3	8.49	8.49		
25		1,2	11.25	11.25		

[a] The values for ΔH_f° are the relative (to 7) values for the individual conformations. The values for ΔS allow for symmetry and mixing, and together with ΔG, these are for *compounds* rather than *conformations*. All for the gas phase. [b] The symbol (+) [or (−)] means that the carbon indicated is above (or below) the general place of the molecule. The symbols (++) and (−−) mean the same thing to a greater degree.

shown: **8**, 40%; **7**, 30%; **3**, 30%. They obtained the same mixture in several different ways, and hence concluded that it represented equilibrium. Their identification of the isomers was by gas phase chromatography, and structure determination with the aid of infrared, NMR (proton only), and Raman sepctroscopy.

Our calculations are in moderate agreement with the experimental work of the French workers. We agree that isomers **7** and **8** are the most stable, but find that isomer **3** is quite unstable, and therefore not likely to contribute significantly to the equilibrium mixture. We believe that isomer **10** or isomer **14**, or possibly a mixture of the two, was the third component which they obtained in the mixture. An unambiguous distinction between isomers **10**, **14**, and **3** does not seem possible on the basis of only infrared, Raman spectra, and ^1H NMR.

The starting coordinates were generated in each case from Fieser models by projection onto graph paper. About 3–6 min of computer time (IBM 360/65) was required for each calculation.

Registry No.—**1**, 16041-60-4; **2**, 17002-05-0; **3**, 20480-70-0; **4**, 62076-17-9; **5**, 62075-58-5; **6**, 62075-59-6; **7**, 20480-69-7; **8**, 20480-68-6; **9**, 62046-20-2; **10**, 62046-21-3; **11**, 62406-22-4; **12**, 62046-23-5; **13**, 62046-24-6; **14**, 39142-79-5; **15**, 62046-25-7; **16**, 62046-26-8; **17**, 62046-27-9; **18**, 62046-28-0; **19**, 62046-29-1; **20**, 62046-30-4; **21**, 62046-31-5; **22**, 62046-32-6; **23**, 62046-33-7; **24**, 62046-34-8; **25**, 62046-35-9.

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Phthalide Components of Celery Essential Oil

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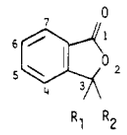
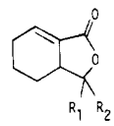
The characteristic odor of celery essential oil is due to a series of phthalide derivatives, of which 3-*n*-butyl phthalide (**1**) and sedanolide (**4**)[1,2] are reported to be the major odor components. Several other phthalides (**2**, **3**, **6**–**8**)[2–4] occur in





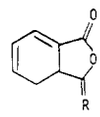
1 R_1 = H, R_2 = $CH_2CH_2CH_2CH_3$

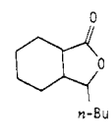
2 R_1, R_2 = $CHCH(CH_3)_2$

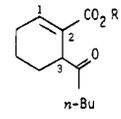
3 R_1, R_2 = $CHCH_2CH(CH_3)_2$

4 R_1 = H, R_2 = *n*-Bu

5 R_1, R_2 = $CH(CH_2)_2CH_3$







6 R = $CHCH(CH_3)_2$

7 R = $CHCH_2$-$CH(CH_3)_2$

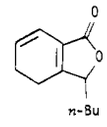
8

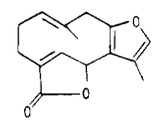
9 R = H

10 R = Me

trace quantities along with an additional major component which on base hydrolysis yields sedanonic acid (**9**). The suggested identity of this secondary component, sedanonic anhydride (**5**), was proposed by Ciamician and Silber[1] based on their classical work with celery constituents. More recent reports continue to suggest that sedanonic anhydride is a major odor component of celery and other oils.[5–7]

Our work with certain biologically active components of celery oil[8] has resulted in the isolation of the two major phthalide compounds: the well-characterized 3-*n*-butyl phthalide (**1**) and a second material which yields sedanonic acid on treatment with aqueous base. We wish to report the results of our work, which indicate that this secondary material is not sedanonic anhydride, but an unreported compound, 3-*n*-butyl 4,5-dihydrophthalide (sedanenolide) (**11**).





11 12

Chromatographic separation of the essential oil components of celery seed led to the isolation of 3-*n*-butyl phthalide (**1**) and sedanenolide in approximately equal quantities. Sedanenolide (**11**), $C_{12}H_{16}O_2$ (high-resolution mass spectrum), $[\alpha]^{24}_D$ −43.2°, shows absorption at λ_{max} 280 nm (ϵ 3790) in agreement with the cross-conjugated 3,4-dihydrophthalide system.[9] The

IR spectrum shows intense absorption at 1750 cm^{-1} in agreement with the α,β-unsaturated, γ,δ-saturated, γ-lactone. The ^1H NMR spectrum displays a one-proton doublet at 6.12 ppm (J = 10 Hz) and a one-proton multiplet at 5.85 ($W_{1/2}$ = 8 Hz) for the vinyl protons, H-7 and H-6, respectively,[10] and a one-proton multiplet at 4.86 ($W_{1/2}$ = 8 Hz) for H-3.

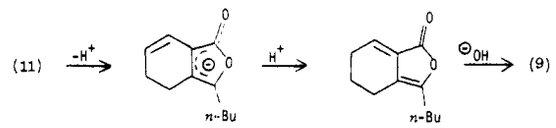
The ^{13}C NMR spectrum of sedanenolide is in accord with the proposed structure and played a key role in positional assignment of double bonds. Of primary importance in this regard is the appearance in the off-resonance decoupled spectrum of a doublet at 82.6 ppm, indicating saturation at C-3. Double bond assignments of the type indicated in compounds **13** and **5** are thus ruled out. Also appearing are two doublets (128.4 and 116.8) and a singlet (124.5) consistent with disubstituted and tetrasubstituted double bonds composed of C-6 and C-7, and C-1a and C-3a, respectively. In addition, signals appear for the side chain (C-1′ thru C-4′) as a series of four multiplets in the range 13.8–22.4, for C-4 and C-5 as two triplets (31.9 and 26.7, respectively), and for C-1 as a singlet (161.5).

Catalytic hydrogenation of sedanenolide in acetic acid over platinum oxide led to the formation of the known 3-*n*-butyl hexahydrophthalide (**8**) (IR, NMR, MS, and mp).

Treatment of sedanenolide with aqueous base gives, in quantitative yield, sedanonic acid (**9**) (IR, UV, NMR, MS, and mp),[11] which was readily converted to the corresponding methyl ester **10** (IR, UV, MS, NMR) by treatment with diazomethane. Similar facile keto ester formation from a substituted Δ^2-butenolide has been observed by Takeda et al.[12] in their work with linderalactone (**12**).

A reasonable mechanism for formation of sedanonic acid from sedanenolide (Scheme I) requires an initial proton ab-

Scheme I



(13)

straction from C-3 with formation of the delocalized furanoid system, followed by double bond rearrangement and hydrolysis.

It is of interest to note that no evidence was obtained in the present investigation for the presence of sedanolide in celery essential oil. Barton and DeVries[11] have also made this observation and they have suggested that 3-*n*-butyl phthalide has been confused with sedanolide in the relatively recent literature. Several reports have also appeared of the occurrence of sedanonic acid or sedanonic anhydride in various plant extracts.[4,5] These reports describe characterizations based on treatment of crude extracts with aqueous base or phthalazone formation. These procedures would not distinguish between sedanonic anhydride and sedanenolide. The natural product may very well be the latter compound in these cases.

Experimental Section

Melting points were taken in capillaries and are uncorrected. IR sepctra were measured in chloroform on a Perkin-Elmer 137 spectrometer; UV spectra were measured in ethanol using Bausch and Lomb Spectronic 505 and Cary Model 14 spectrometers; ^1H NMR spectra were taken in CCl_4 (unless otherwise indicated) on a Varian T-60 spectrometer; ^{13}C NMR spectra were determined in $DCCl_3$ at 25.144 MHz in the Fourier mode using a Nicolet TT-23 spectrometer with Brucker 40 console in conjunction with a 8K memory computer; chemical shifts are reported in δ units from internal Me_4Si, and when followed by parentheses give multiplicity of signal, coupling constant if applicable, and assignment. Spin multiplicity is given by s = singlet, d = doublet, t = triplet, m = multiplet. Mass spectra were obtained on a CEC 103 (low resolution) or CEC 21-110B (high resolution] instrument. Optical rotations were measured on solutions in 95% EtOH; column chromatography was performed on Merck silica gel 60 (>230 mesh). Thin-layer chromatography was carried out on silica gel precoated 60 F-254 chromatoplates (5 × 10 cm, 0.25-mm thick, EM Laboratories, Inc.).

Isolation of Phthalides from Celery Seed. Steam distillation at atmospheric pressure of ground celery seed (1 kg) produced 27 L of aqueous distillate, which was extracted consecutively with petroleum ether (bp 30–60 °C, 18 L), ethyl ether (18 L), and chloroform (18 L). Evaporation of the organic extracts in vacuo gave a combined yield of 16.8 g of essential oil. This material was placed on a silica gel column and nine fractions were eluted with 4.5 L of hexane–diethyl ether (1:1, v/v). A tenth fraction was eluted with 500 mL of methanol. Solvents were removed in vacuo and the oily residues were assayed for sedative activity as described by Brodie.[13] Significant activity resided only in the phthalide-containing fractions. 3-*n*-Butyl phthalide and sedanenolide were isolated from fractions 5 and 6 by gas chromatography under the following conditions: aluminum column (20 ft × ⅜ in.), packed with 15% S.E. 30 on dimethylchlorosilane (DMCS)-treated 60/80 mesh gas Chromosorb W, helium flow rate of 100 mL/min; and column, injector, and detector temperatures, 200, 218, and 235 °C, respectively. 3-*n*-Butyl phthalide and sedanenolide had retention times of 57 and 75 min, respectively, under these conditions.

3-*n*-Butyl phthalide (**1**) was obtained as a pale yellow oil with a distinct odor of celery oil: UV absorptions at 228, 275, and 282 nm (ϵ 8190, 1480, and 1480, respectively); IR band at 1750 cm^{-1} (γ-lactone); NMR signals at δ 7.23–7.84 (m, H-4, 5, 6, 7) and 5.41 (m, H-3), in accord with published data.[11]

Sedanenolide (**11**) is a colorless oil with a distinct celery odor: $[\alpha]^{24}_D$ −43.2°; IR bands at 1750 (γ-lactone), 1650, 1460, 1430, 1310, 1270, 1040, 960, and 915 cm^{-1}; UV spectrum λ_{max} 280 nm (ϵ 3790). The high-resolution mass spectrum displayed the molecular ion peak (22.9%); other major peaks were at *m/e* (composition, %) 163 ($C_{11}H_{15}O$, 3.6), 135 ($C_8H_7O_2$, 5.3), 108 (C_7H_8O, 21.7), 107 (C_7H_7O, 100.0), 85 (C_5H_9O, 9.7), 79 (C_6H_7, 24.3), 77 (C_6H_5, 24.2), and 57 (C_4H_9, 14.4).

Anal. Calcd for $C_{12}H_{16}O_2$: mol wt, 192.1150. Found: mol wt, 192.1158 (MS).

3-*n*-Butyl Hexahydrophthalide (8). A solution of sedanenolide (20 mg) in glacial acetic acid (5 mL) was hydrogenated over 50 mg of PtO_2 at atmospheric pressure for 48 h and filtered. The residue obtained after evaporation of solvent was purified by gas chromatography under the conditions described for the parent compound. The reduced product (rentention time, 35 min) was obtained as a low melting solid (mp 39–41 °C, lit,[11] 48–49 °C): IR bands at 1765 (γ-lactone), 1440, 1180, 1165, 1125, 980, and 735 cm^{-1}; NMR signals at 4.12 (m, $W_{1/2}$ = 10 Hz, H-3), and 2.61 (m, $W_{1/2}$ = 12 Hz, H-7a); UV spectrum showed only end absorption. The high-resolution mass spectrum exhibited the molecular ion (4.3%); other major peaks were at *m/e* 180 ($C_{12}H_{20}O$, 4.3), 165 ($C_{11}H_{17}O$, 3.1), 152 ($C_{11}H_{20}$, 18.2), 139 ($C_8H_{11}O_2$, 37.6), 111 ($C_7H_{11}O$, 9.2), and 109 (C_7H_9O, 34.8).

Anal. Calcd for $C_{12}H_{20}O_2$: mol wt, 196.1463. Found: mol wt, 196.1450 (MS).

Sedanonic Acid (9). Sedanenolide (50 mg) was treated with aqueous potassium hydroxide and sodium carbonate solutions as described by Barton and DeVries[11] for isolation of sedanonic acid from celery oil. Crystallization of the acidic reaction product from benzene/hexane afforded sedanonic acid (38 mg) as colorless needles: mp 109–110 °C (lit.,[11] 110–111 °C); IR bands at 2500–3400 (–OH), 1710 (acyclic ketone), 1695 (α,β-unsaturated carboxyl), 1650 (conjugated double bond), 1530, 1420, and 1260 cm^{-1}; NMR ($DCCl_3$) signals at 7.34 (t, J = 4 Hz, H-1) and 3.62 (m, $W_{1/2}$ = 10 Hz, H-3). The high-resolution mass spectrum revealed a molecular ion peak (1.3%); other major peaks were at *m/e* (composition, %) 125 ($C_7H_9O_2$, 2.7), 108 (C_7H_8O, 59.3), 97 (C_6H_9O, 3.0), 85 (C_5H_9O, 57.2), 79 (C_6H_7, 21.6), and 57 (C_4H_9, 100.0).

Anal. Calcd for $C_{12}H_{18}O_3$: mol wt, 210.1256. Found: mol wt, 210.1243 (MS).

Sedanonic Acid Methyl Ester (10). Methylation of 20 mg of **9** with excess diazomethane in the usual way and purification of the crude product by preparative TLC (silica gel, solvent chloroform) yielded 15 mg of **10** as a colorless oil: IR bands at 1710 (α,β-unsaturated ester and acyclic ketone), 1430, 1250, and 1080 cm^{-1}; UV spectrum λ_{max} 215 nm (ϵ 15 300); NMR signals at 7.02 (m, $W_{1/2}$ = 5 Hz, H-1) and 3.64 (s, OMe). The high-resolution mass spectrum afforded the molecular ion peak 4.7% and other major peaks at *m/e* 192 ($C_{12}H_{16}O_2$, 6.1), 140 ($C_8H_{12}O_2$, 22.9), 108 (C_7H_8O, 15.5), 86 (C_4H_9O, 7.5), 85 (C_5H_9O, 100.0), 79 (C_6H_7, 22.8), and 57 (C_4H_9, 85.3).

Anal. Calcd for $C_{13}H_{20}O_3$: mol wt, 224.1412. Found: mol wt, 224.1392 (MS).

Registry No.—**1**, 6066-49-5; **8**, 3553-34-2; **9**, 6697-07-0; **10**, 62006-38-6; **11**, 62006-39-7.

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Some 1-Pentacyanobutadienyl Derivatives[1]

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In 1972 reactions of polycyanovinyl halides with metal carbonyl anions were first reported[3] to give good yields of stable polycyanovinyl transition metal derivatives.[4] Subsequent work[5,6] showed that further reactions of these polycyanovinyl transition metal derivatives gave a variety of unusual and interesting cyanocarbon transition metal complexes including compounds containing terminal[7,8] and bridging[3,4] dicyanovinylidene ligands, dicyanoketeneimmonium derivatives,[9] novel types of chelates,[9] and new polycyano olefin complexes.[10]

This extensive new area of transition metal chemistry created by the discovery of polycyanovinyl transition metal derivatives made of interest the preparation and reactions of similar transition metal polycyanobutadienyl derivatives. This suggested an investigation of reactions of halopolycyanobutadienes with metal carbonyl anions. However, since halopolycyanobutadienes were completely unknown at that time, it was first necessary to develop methods for their preparation. This paper describes the methods for the preparation of 1-halopentacyanobutadienes that we first developed in 1972 as well as their reactions with certain metal carbonyl anions to give pentacyanobutadienyl transition metal derivatives.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 621 spectrometer with grating optics. Mass spectra were determined using a Perkin-Elmer Hitachi RMU-6 mass spectrometer. Relative intensities are given in parentheses with the indicated relative intensities for the ions containing chlorine and bromine being the sums of the ions containing the two major isotopes (i.e., ^{35}Cl and ^{37}Cl for chlorine and ^{79}Br and ^{81}Br for bromine). Melting points are taken in capillaries and are uncorrected.

Tetracyanoethylene was purchased from Kay-Fries Chemicals Inc., New York, N.Y., and converted to tetraethylammonium pentacyanobutadien-1-olate via tetracyanoethane[11] and disodium hexacyanobutenediide[12] by the published procedure.[13] Metal carbonyl derivatives were obtained by procedures similar to those used in previous work.[4]

Preparation of 1-Chloropentacyanobutadiene. A solution of 10.0 g (30.8 mmol) of tetraethylammonium pentacyanobutadien-1-olate in 150 mL of redistilled 1,2-dimethoxyethane was added to a solution of 7.7 g (5.2 mL, 60.8 mmol) of redistilled oxalyl chloride in 50 mL of redistilled 1,2-dimethoxyethane. After stirring for 34 h at room temperature, the reaction mixture was filtered to remove a tan precipitate. Solvent was then removed at ~25 °C (40 mm). The residue was extracted with dichloromethane. Excess diethyl ether was added to the filtered dichloromethane extract to precipitate 3.22 g of unreacted tetraethylammonium pentacyanobutadien-1-olate (32% recovery), identified by its infrared spectrum. After removal of this precipitate by filtration followed by evaporation of the filtrate at ~25 °C (40 mm), sublimation of the residue at 110–125 °C (0.2 mm) gave 1.91 g (29% conversion, 42% yield) of white, crystalline 1-chloropentacyanobutadiene: mp 195 °C dec; infrared spectrum (KBr) 2245 (w), 1540 (m), 1524 (m), 1399 (vw), 1378 (vw), 1357 (m), 1315 (sh), 1277 (w), 1234 (m), 1226 (m), 1208 (w, sh), 1028 (w), 1000 (m), 978 (w), 924 (vw), 900 (m), 806 (vw), 778 (m), 771 (w, sh), 654 (vw), 623 cm^{-1} (vw); ultraviolet spectrum (CH_3CN) 329 nm (ϵ 4700), 315 (6400), 264 (9200), 253 (11 400); mass spectrum $C_9N_5Cl^+$ (100), $C_8N_4Cl^+$ (6), $C_9N_5^+$ (13), $C_8N_4^+$ (9), $C_7N_3^+$ (15), $C_5N_3^+$ (7), $C_6N_2^+$ (16), C_3NCl^+ (15), $C_4N_2^+$ (33), C_4N^+ (10), C_3N^+ (7), C_2N^+ (9).

In repeat experiments the yields of 1-chloropentacyanobutadiene were erratic.

Anal. Calcd for C_9ClN_5: C, 50.5; H, 0.0; N, 32.8. Found: C, 49.4, 51.2; H, 0.3, 0.8; N, 33.1; 32.6.

Preparation of 1-Bromopentacyanobutadiene. A. From $[(C_2H_5)_4N][C_4(CN)_5O]$ and Oxalyl Bromide. A solution of 10.0 g (308 mmol) of tetraethylammonium pentacyanobutadien-1-olate in 100 mL of redistilled 1,2-dimethoxyethane was added to a solution of 7.2 g (3.0 mL, 33.3 mmol) of oxalyl bromide in 150 mL of 1,2-dimethoxyethane. After stirring for 22 h at room temperature solvent was removed at 40 °C (40 mm). The residue was extracted with two 250-mL portions of benzene. Evaporation of the filtered benzene extracts at ~40 °C (40 mm) gave a pale brown residue. Fractional sublimation of this residue first gave 0.33 g of an unidentified substance at 110–125 °C (0.2 mm) which was not investigated further since its infrared spectrum showed the absence of cyano groups. After removal of this substance, further vacuum sublimation at 130–135 °C (0.2 mm) gave 0.56 g (7% conversion, 12% yield) of 1-bromopentacyanobutadiene, identified by its infrared spectrum (see below). The residue remaining from the benzene extraction was crystallized from a mixture of dichloromethane and diethyl ether to give 4.1 g (41% recovery) of unreacted tetraethylammonium pentacyanobutadien-1-olate.

B. From $Na_2C_4(CN)_6$ and Bromine. A mixture of 10.1 g (~40 mmol) of disodium *trans*-hexacyanobutenediide [dried at 110 °C (0.1 mm) for 20 h], 4.0 mL (11.7 g, 73.1 mmol as Br_2) of bromine, and 80 mL of hexane was stirred for 25 h at room temperature. The reaction mixture was then evaporated to dryness at 40 °C (40 mm). Excess bromine was removed by pumping at 25 °C (0.1 mm) for 12 h. The dark brown residue was extracted with two 150-mL portions of benzene followed by one portion of 1,2-dichloroethane. Evaporation of the combined extracts at ~40 °C (40 mm) followed by vacuum sublimation at 135 °C (0.2 mm) gave 0.9 g (9% yield) of 1-bromopentacyanobutadiene: mp 228 °C dec; infrared spectrum (KBr) 2251 (w), 1549 (m), 1531 (m), 1401 (w), 1375 (m), 1348 (vw), 1276 (w), 1265 (m), 1220 (m), 1211 (vw), 1199 (vw), 1030 (vw), 1021 (w), 1002 (vw), 925 (vw), 911 (w), 872 (vw), 809 (vw), 784 (m), 777 cm^{-1} (w); ultraviolet spectrum (CH_3CN) 333 nm (ϵ 3700), 313 (4400), 265 (9600), 253 (9700); mass spectrum $C_9N_5Br^+$ (100), $C_9N_5^+$ (95), $C_8N_4^+$ (5), $C_7N_3^+$ (40), $C_5N_3^+$ (19), $C_6N_2^+$ (20), $C_4N_2^+$ (42), C_4N^+ (13), C_3N^+ (7), C_2N^+ 12).

Anal. Calcd for C_9BrN_5: C, 41.8; H, 0.0; N, 27.1; Br, 31.0. Found: C, 41.9; H, 0.3; N, 27.1; Br, 30.6.

Preparation of 1-Ethoxypentacyanobutadiene. A mixture of 0.30 g (1.4 mmol) of 1-chloropentacyanobutadiene, 10 mL of absolute ethanol, and 50 mL of tetrahydrofuran was boiled under reflux for 24 h. Removal of solvent at ~40 °C (40 mm) followed by crystallization from a mixture of dichloromethane and hexane gave a total of 0.30 g (96% yield) of 1-ethoxypentacyanobutadiene. Sublimation of the crude product at 110 °C (0.15 mm) gave the analytical sample as white crystals: mp 130–132 °C; infrared ν(CN) 2245 (w), ν(C=C) 1570 (m) and 1535 cm^{-1} (m); ^1H NMR spectrum CH_2 at τ 5.28 (quartet, J = 7 Hz), CH_3 at τ 8.44 (triplet, J = 7 Hz); ultraviolet spectrum (CH_3CN) 347 nm (ϵ 7500), 337 (6600), 270 (10 200).

Anal. Calcd for $C_{11}H_5N_5O$: C, 59.2; H, 2.2; N, 31.4. Found: C, 59.7; H, 2.4; N, 30.4.