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Radical Anion Stabilities in 1,6-Dioxa-6a-tellurapentalenes and Related Compounds. The Quantum Efficiency of Photoconduction as a Measure of $E°$

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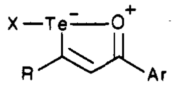
1,6-Dioxa-6a-tellurapentalenes have been prepared by the condensation reactions of 3-methyl-5-aryl-1,2-oxatellurolylium chlorides with acid chlorides in the presence of an amine base or pyridine. The scope of the reaction includes the use of imidoyl chlorides to prepare 1-aza-6-oxa-6a-tellurapentalenes and the use of 3-methyl-5-aryl-1,2-oxaselenolylium chloride to prepare 1,6-dioxa-6a-selenapentalenes. The reduction potentials for these compounds were determined by cyclic voltammetry. The relationship between $E°$ for the dioxatellurapentalene–dioxatellurapentalene radical anion couple and the rate of back electron transfer (hole-electron collapse) of photogenerated charges in thin films containing 30% tri-*p*-tolylamine–Lexan 145 films and 2% of a dioxatellurapentalene was developed. With a common donor and a related series of acceptors, A, a linear relationship is expected between $\ln [(1 - \Phi)/\Phi]$ and $-E°(A/A^{\bullet-})$, where Φ is the quantum efficiency for the photogeneration of charges at an electric field strength of 1×10^6 V/cm. Relative orderings for $E°$ can be made from such data for the acceptors even though the reduction waves may be irreversible by cyclic voltammetry. The magnitudes of the substituent effects suggest delocalized unpaired spin in the radical anions.

Introduction

In previous reports, we described the preparation and properties of 1,2-oxatellurolyl-1-ium halides (1)[1] and 1,2-oxaselenolyl-1-ium halides (2)[2] as well as their pertellurane (3) and perselenurane (4) analogues.[3] The bonding between Te or Se and the more electronegative ligand atoms is highly ionic and is perhaps best described as three-center, four-electron bonding with partial covalent bonding between atoms.[3]



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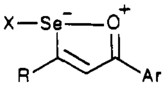

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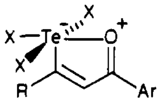

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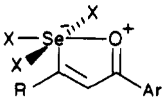

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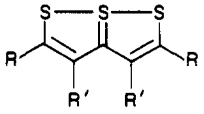
This bonding situation is quite similar to that found in thiathiophthenes (5)[4] and related compounds such as 6[5] and 7[6] in which three or more sulfur atoms are bonded in multicenter, multielectron bonds. Back-bonding or catanation is believed to be important in such molecules, leading to some π-bonding between sulfur atoms.



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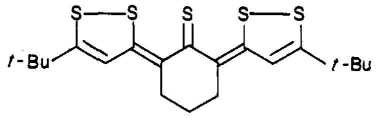

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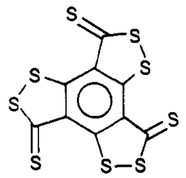

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The heavier chalcogen, selenium, has been incorporated into similar structures, like those represented by 8,[7] 9,[8] and

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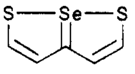
10.[9] No example of tellurium replacing one sulfur or more in thiathiophthenes has been reported.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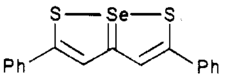
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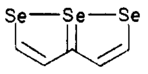
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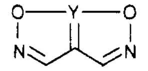
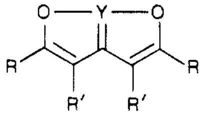
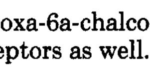
Sulfur,[10] selenium,[11] and tellurium[11c] analogues of 2,5-diaza-1,6-dioxa-6a-chalcogenapentalenes (**11**) have been prepared as have sulfur,[12] selenium,[12b] and tellurium[13] analogues of 1,6-dioxa-6a-chalcogenapentalenes (**12**). Although similar in structure to the thiathiophthenes, these compounds have highly electronegative ligands for the more electropositive central heteroatom, making bonding in these systems nearly identical with that in oxatellurolylium halides (**1**) and oxaselenolylium halides (**2**). Back-bonding between oxygen and the larger chalcogens Se and Te is not believed to be important in these systems.[3]


11, Y = S, Se, Te


12, Y = S, Se, Te

The dioxapentalenes **11** and **12** and halides **1** and **2** are hypervalent systems, which have central heteroatoms that are highly oxidized.[3] Consequently, these systems should be prone to reduction. The addition of one or more electrons to the dioxapentalene ring systems should be possible, perhaps leading to some unusual bonding. Pertellurane and perselenurane analogues of these systems are easily reduced, giving chalcogen–halogen bond cleavage.[3]

The oxatellurolylium and oxaselenolylium halides have been found useful as electron-accepting sensitizers for triarylamine photoconduction.[14] Since the central heteroatom has already expanded its valence octet in 10-Te-3 telluranes **1**[15] and 10-Se-3 selenuranes **2**,[15] the addition of an electron would be expected to lead to bond cleavage. As an example, the reduction of oxatellurolylium halides **1** would generate radical anions that should fragment either as in **13** to give a halide ion and a neutral radical or as in **14** to give the delocalized ketyl radical ion.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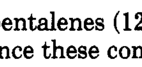
14

The 1,6-dioxa-6a-chalcogenapentalenes (**12**) function as electron acceptors as well.[16] Since these compounds also have a 10-electron valence shell for the central heteroatom, reduction should lead to cleavage of one ligand–heteroatom bond. However, both electronegative ligands are bound to the carbon π-framework, giving a delocalized ketyl radical anion by scission of either heteroatom–oxygen bond, as shown for **15** for a dioxatellurapentalene. It should be possible to evaluate the effects of substituents on the stability of such radical anions involving hypervalent main-group elements. In particular, the effect of remote substituents on the thermodynamic stabilities of the radical anions should reflect electron densities, delocalization, and bonding in the species.


15

Both the kinetic and thermodynamic stabilities of the intermediate ketyl radical anions should be influenced by substituents attached to the pentadienyl carbon framework. Steric blocking of the radical center can give kinetic stability. An electron-donating or an electron-accepting substituent can thermodynamically stabilize free radicals,[17] although incorporating two donor or two acceptor substituents can destabilize a radical center relative to the situation with one donor or one acceptor substituent.[18] A combination of electron-donating and electron-accepting substituents can stabilize the radical beyond an additive term.[18] Experimentally, stabilization of the dioxachalcogenapentalene radical anions should be reflected in less negative reduction potentials for the dioxachalcogenapentalenes. Ideally, the reduction potentials should be measured at high dilution in the gas phase or immobilized in the solid phase to prevent other radicals or reactive molecules from approaching the radical anion.[19] Cyclic voltammetry allows the determination of solution redox potentials. While values of $E°$ for reversible systems should give relative orderings of radical anion ground-state energies, peak potentials for irreversible systems (irreversible even at very fast scan rates) are not as reliable in assigning relative ground-state energies.[20]

In thin-film formats used for triarylamine photoconduction, the electron acceptor such as a dioxachalcogenapentalene is immobilized in a homgeneous film with the triarylamine donor, across which is applied a large potential.[14,16] Upon irradiation, donor radical cations and acceptor radical anions are formed. The quantum efficiency of photodecay at fixed electric field should be a function of the thermodynamic stability of the radical anion.[21] Increased stability of the acceptor radical anion would lead to decreased rates of hole-electron recombination and greater quantum efficiencies of photodecay and allow an ordering of radical/anion stabilities.

Herein, we report a general synthesis for 1,6-dioxatellurapentalenes and 1,6-dioxaselenapentalenes, the electrochemical redox potentials of such compounds as determined by cyclic voltammetry, and quantum efficiencies for photodecay at 1×10^6 V/cm of triarylamine films containing the pentalenes as electron acceptors. Substituent effects appear to be important in the stabilization of the radical anions and are pronounced in both the electrochemical redox potentials and quantum efficiencies of photodecay for the pentalene acceptors. Dioxachalcogenapentalenes containing a donor and an accepting sub-

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Table I. Physical and Spectral Properties of 1,6-Dioxa-6a-tellurapentalenes and 1,6-Dioxa-6a-selenapentalenes

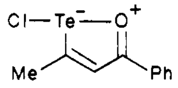
compd	% yield[a]	mp, °C	ν,[b] cm^{-1}	λ_{max},[c] nm	log ϵ	^{1}H NMR,[d] δ
17	39	169.5–170.5	1515	424	4.61	8.15
18	25	142–144	1560, 1590	399	4.48	7.96, 7.93, 3.0
19	25	183–185	1515, 1610	430	4.71	8.07, 3.88
20	27	202–206	1560, 1590	420	4.41	8.23, 8.05
24	12	184–186	1530, 1610	480	4.60	
25	34	186–189	1520, 1545, 2250	470	4.62	
26	80	253–255	1510, 1610	440	4.54	
27	39	250–251	1510, 1605	435	4.78	8.23, 3.90
28	34	163–165	1515, 1605	408	4.60	
29	27	207–209	1510, 1605	424	4.61	
30	66	227–228	1510, 1605	432	4.53	8.21, 8.13
31	58	214–217	1522, 1570, 2250	428	4.55	8.10, 8.03
32	33	224.5–225	1540, 1595	423	4.65	8.00
33	21	208.5–210.5	1515, 1605	430	4.68	
34	11	189–191	1523, 1542	420	4.57	8.25, 7.98
35	85	245 dec	1520, 1540	423	4.53	
36	49	112–114	1510, 1540	401	4.47	
37	15	200 dec	1510, 1605	460	4.66	
38	64	195–197 dec	1510, 1595	462, 440	4.69, 4.64	8.05
39	50	193–196 dec	1510, 1600	466, 444	4.65, 4.64	
41	40	244–247	1525, 1610	424	4.48	
42	10	251–253	1510, 1609	421	4.65	7.43, 3.85
43	15	250–251	1525, 1610	417	4.50	7.41, 7.33
46	71	166–167.5	1505	426	4.55	8.20
47	89	150.5–152.5	1520	427	4.56	8.20
49	11	72–77 dec	1610, 1480, 1400	471, 426	4.38, 4.60	8.03, 7.77, 3.60

[a] Isolated yield. [b] KBr pellet. ν for C≡N, C=C, C=O, and C=N stretches. [c] In CH_2Cl_2. [d] Chemical shifts of pentalene ring methine protons, methyl protons, and methoxy protons.

stituent appear to form thermodynamically more stable radical anions, perhaps indicative of the captodative effect.[18]

Results and Discussion

Preparative Studies. The base-induced condensation of 3-methyl-5-phenyl-1,2-oxatellurolyl-1-ium chloride (**16**) with benzoyl chloride gave dioxatellurapentalene **17** in 39% yield.[13] The condensation reaction of **16** with aliphatic acid chlorides (acetyl chloride to give **18**), with aroyl chlorides substituted with electron-donating substituents (p-methoxybenzoyl chloride to give **19**), and with aroyl chlorides substituted with electron-withdrawing substituents (p-nitrobenzoyl chloride to give **20**) also gave dioxatellurapentalenes. Various spectral and physical properties of the dioxatellurapentalenes are compiled in Table I.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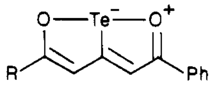
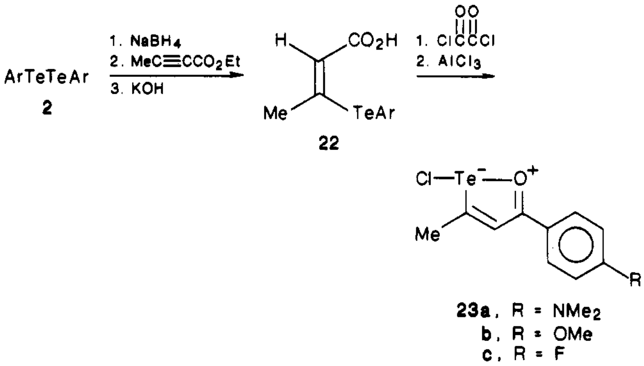

17, R = Ph
18, R = Me
19, R = p-MeOC$_6$H$_4$
20, R = p-O$_2$NC$_6$H$_4$

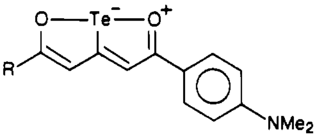
The preparation of 3-methyl-5-aryl-1,2-oxatellurolyl-1-ium chlorides with donor groups in the para position was straightforward, as indicated in Scheme I.[1] The appropriate diaryl ditelluride **21** was reduced with sodium borohydride in ethanolic tetrahydrofuran, and the sodium aryltelluride was added to ethyl tetrolate. The resulting (Z)-β-arylbutenoate ester was converted to the acid **22** with ethanolic potassium hydroxide. The acids gave the acid chlorides upon treatment with oxalyl chloride. The acid chlorides were rearranged to the oxatellurolylium chlorides **23** with aluminum chloride as catalyst.

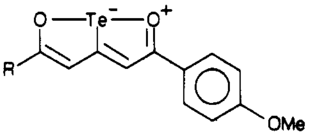
The oxatellurolylium chlorides **23** were condensed with benzoyl chloride, p-nitrobenzoyl chloride, p-anisoyl chloride, p-fluorobenzoyl chloride, p-cyanobenzoyl chloride, 2,4-dinitrobenzoyl chloride, 3,5-dinitrobenzoyl chloride, and acetyl chloride in the presence of an amine base to give dioxatellurapentalenes **24**–**36**. The physical and spectral properties of these dioxatellurapentalenes are compiled in Table I.

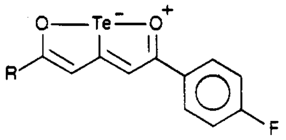
Scheme I



23a, R = NMe$_2$
b, R = OMe
c, R = F


24, R = p-O$_2$NC$_6$H$_4$
25, R = p-NCC$_6$H$_4$


26, R = p-O$_2$NC$_6$H$_4$
27, R = p-MeOC$_6$H$_4$
28, R = Me


29, R = Ph
30, R = p-O$_2$NC$_6$H$_4$
31, R = NCC$_6$H$_4$
32, R = p-FC$_6$H$_4$
33, R = p-MeOC$_6$H$_4$
34, R = 2,4-(O$_2$N)$_2$C$_6$H$_3$
35, R = 3,5-(O$_2$N)$_2$C$_6$H$_3$
36, R = Me

The spectroscopic properties of the dioxatellurapentalenes show some differences from their S and Se ana-

Table II. Physical and Spectral Properties of 12-Te-5 Pertelluranes Based on 1,6-Dioxa-6a-tellurapentalenes

compd	% yield[a]	mp, °C	ν,[b] cm^{-1}	λ_{max},[c] nm	log ϵ	^{1}H NMR,[d] δ
44	90	198–198.5	1600, 1550	555	4.57	7.83
45	57	186–192 dec	1590, 1550	598	4.58	7.92
48	30	212–215	1590, 1550	587	4.56	
50	56	202–205	1600, 1555	545	4.40	7.72
51	63	174–177 dec	1590, 1555	528	4.54	
52	46	192–192	1600, 1580, 1555	538	4.52	
53	60	195–196	1600, 1560	555	4.53	
54	65	212–215	1600, 1580, 1555	555	4.54	
55	63	>330	1605, 1555	590	4.52	
56	26	>330	2240, 1600, 1570, 1505	593	4.54	

[a] Isolated yield. [b] KBr pellet. ν for C≡N, C=C, and C=O stretches. [c] In CH_2Cl_2. [d] Chemical shifts in CD_2Cl_2 of pentalene ring methine protons.

Table III. Redox Potentials for Dioxatellurapentalenes and Dioxaselenapentalenes[a]

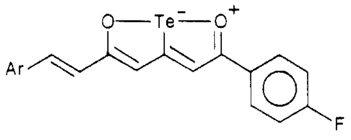
	red.				
	E_1		E_2		ox.
compd	E_p^c, V	E_p^a, V	E_p^c, V	E_p^a, V	E_p^a, V
17	−1.595				+1.36
18	−1.58				+1.31
19	−1.525				+1.24
20	−1.14				+1.46
24	−1.06	−0.98			+1.33
26	−0.99	−0.92	−1.29	−1.22	+1.33
27	−1.56				+1.18
28	−1.63				+1.24
29	−1.47		−1.88		+1.36
30	−0.96	−0.88	−1.23	−1.08[c]	+1.31
31	−1.39	−1.28[b]	−1.73		+1.50
32	−1.50				+1.35
33	−1.51		−1.94		+1.28
34	−0.77	−0.67	−1.035	−0.935[d]	+1.44
35	−0.825	−0.73	−1.205	−1.095[e]	1.52
36	−1.60				+1.50
41	−0.97	−0.90	−1.30		1.46
42	−1.58				+1.18
43	−0.96	−0.89	−1.25		+1.60
46	−1.35				+1.65
47	−1.28				+1.65

[a] All potentials are vs. SCE. Samples were run at ~5 × 10^{-4} M in CH_2Cl_2 with 0.1 M $Bu_4N^+BF_4^-$ as supporting electrolyte with a Pt disk working electrode at a scan rate of 0.1 V/s. [b] Partially reversible (i_c/i_a = 1.5). [c] Partially reversible (i_c/i_a = 1.4). [d] Partially reversible (i_c/i_a = 1.4). [e] Partially reversible (i_c/i_a = 1.5).

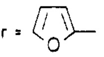
logues. The ^{1}H NMR spectrum of **17** shows a sharp singlet at δ 8.15 for the two ring protons which is at 1 ppm lower field than the corresponding S and Se analogues.[12b] The ^{13}C NMR spectrum of **17** showed the carbons bearing the heteroatoms to be at low field (δ 181.0 and 180.5) while the remaining two ring carbons were at quite high field (δ 107.7). These values suggest that the ring carbons are pentadienyl cation-like in their charge densities.[3] The IR spectra of all of the dioxachalcogenapentalenes are similar with a strong absorption around 1520 cm^{-1}. The UV-visible absorption spectrum of **17** displays a long-wavelength maximum at 424 nm (log ϵ 4.61). This value is more than 20-nm bathochromic from the absorption maxima of the S and Se analogues.

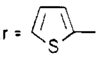
The incorporation of the dimethylamino substituent into dioxatellurapentalenes **24** and **25** gave long-wavelength absorption maxima at 480 and 470 nm, respectively.

We were interested in obtaining other dioxatellurapentalenes with longer wavelength maxima. Increasing the conjugation in the carbon π-framework would be one method of achieving longer wavelength absorption maxima. The condensation of **23b** with p-methoxycinnamoyl chloride gave dioxatellurapentalene **37** with the long-wavelength absorption now at 460 nm, which is 30 nm more bathochromic than the lower homologue **33**. 2-Furanacryloyl chloride and 2-thiopheneacryloyl chloride reacted with **23c** to give extended-chain dioxatellurapentalenes **38** and **39**, respectively, with absorption maxima at 462 nm for **38** and at 466 nm for **39**.

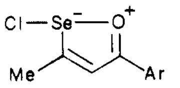


37, Ar = 4-MeOC$_6$H$_4$

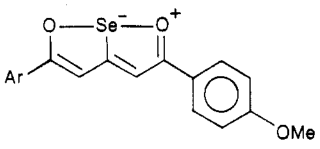
38, Ar =


39, Ar =


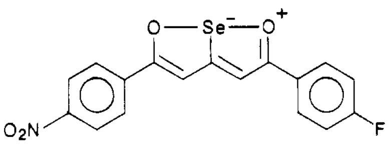
The condensation reactions could be extended to include the preparation of dioxaselenapentalenes. The oxaselenolylium chlorides **40**[2] react with p-nitrobenzoyl chloride and p-anisoyl chloride to give the dioxaselenapentalenes **41**–**43** in modest yield. The physical and spectral properties of these compounds are compiled in Table I.



40a, Ar = p-MeOC$_6$H$_4$
b, Ar = p-FC$_6$H$_4$



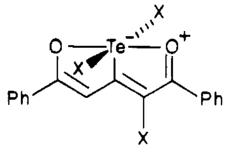
41, Ar = p-O$_2$NC$_6$H$_4$
42, Ar = p-MeOC$_6$H$_4$



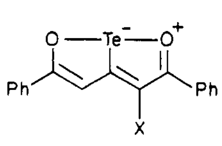
43

Functionalization of the dioxatellurapentalene ring system was also possible. The addition of bromine and chlorine to dioxatellurapentalene **17** gave 12-Te-5 pertelluranes **44** and **45**, respectively. Hydrazine reduction of the pertelluranes gave the 3-halogen-substituted dioxatellurapentalenes **46** and **47**.[13] The addition of chlorine to **32** gave 3,4-dichlorodioxatellurapentalene *Te*,*Te*-dichloride **48**, which was reduced to dioxatellurapentalene **49** in 30% overall yield.

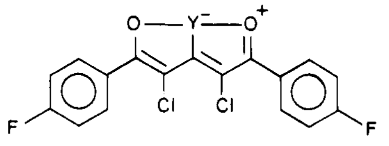
In general, the dioxatellurapentalenes could be monobrominated by the addition of 2 equiv of Br_2 to give the 12-Te-5 pertelluranes, incorporating one bromine into the ring. The products were quite insoluble, and the regiochemistry of bromination could not be unequivocally assigned. The physical and spectral properties of the 12-Te-5 pertelluranes **44**, **45**, **48**, and **50**–**56** are compiled in Table II. These 12-Te-5 pertelluranes absorb at much longer wavelengths than their dioxatellurapentalene counterparts.



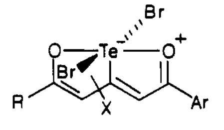
44, X = Br
45, X = Cl



46, X = Br
47, X = Cl

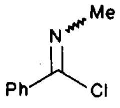


48, Y = TeCl$_2$
49, Y = Te

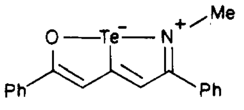


50, R = Ar = p-FC$_6$H$_4$, X = H
51, R = Me, Ar = Ph, X = Br
52, R = Me, Ar = p-MeOC$_6$H$_4$, X = Br
53, R = p-O$_2$NC$_6$H$_4$, Ar = p-FC$_6$H$_4$, X = Br
54, R = p-O$_2$NC$_6$H$_4$, Ar = p-MeOC$_6$H$_4$, X = Br
55, R = p-O$_2$NC$_6$H$_4$, Ar = p-Me$_2$NC$_6$H$_4$, X = Br
56, R = p-NCC$_6$H$_4$, Ar = p-Me$_2$NC$_6$H$_4$, X = Br

The substitution of nitrogen for one oxygen in the dioxatellurapentalene ring system was also possible. The condensation of **16** with imidoyl chloride **57** gave azaoxatellurapentalene **58** as a bright orange, crystalline solid. The ^{1}H NMR spectrum of **58** displayed two one-proton singlets at δ 8.03 and 7.77 for the two ring protons and a three-proton singlet at δ 3.60 for the *N*-methyl group.



57



58

Electrochemical Studies. The oxidation and reduction potentials for the dioxatellurapentalenes and dioxaselenapentalenes of this study as determined by cyclic voltammetry are compiled in Table III. All waves were irreversible for non-nitro-bearing pentalenes. Nitrophenyl-substituted dioxatellurapentalene **20** showed partially reversible reduction ($i_c/i_a \approx 1.5$) in dichloromethane on both platinum and glassy carbon electrodes. The other nitrophenyl- or dinitrophenyl-substituted dioxatellura- or dioxaselenapentalenes of this study gave reversible reductions ($i_c/i_a = 1$, ΔE_p approaching 60 mV with slower scan speeds), although reversibility lessened at scan rates slower than 0.05 V/s. A plot of i_c against the square root of the scan speed was linear for all compounds across a range of 0.05–0.5 V/s (correlation coefficient >0.99), as expected for a diffusion-controlled electrode process.

The first reduction wave of nitrobenzene is reversible with $E° = 1.15$ V (vs. SCE), whereas the second reduction is an irreversible wave with $E_p{}^c = -1.9$ V (vs. SCE).[22] The introduction of a nitro substituent into an aromatic ring of the dioxatellura- or dioxaselenapentalenes makes reduction less negative by 0.6 V relative to dioxatellurapentalene **17**. In the nitrophenyl-substituted compounds **24**, **26**, and **30**, the $E°$ is between 0.92 and 1.02 (vs. SCE). The second, irreversible reduction wave for these compounds falls in the range of −1.19 to −1.30 V (vs. SCE). The ΔE difference between the radical anion and dianion states of 0.23–0.30 V of the pentalenes relative to the 0.75-V difference between the radical anion and dianion states of nitrobenzene is indicative of increased delocalization in the dioxachalcogenapentalenes of the nitroaryl radical anions and dianions.

The increased delocalization is also apparent in a more subtle way in the dinitrophenyl-substituted dioxatellurapentalenes **34** and **35**. 1,3-Dinitrobenzene shows two reversible reduction waves with $E°$ of −0.90 and −1.25 V (vs. SCE).[22] In 3,5-dinitrophenyl derivative **35**, the dioxatellurapentalene is not capable of resonance interaction with the two nitro groups. The reversible reduction waves for **35** have $E°$ of −0.78 and −1.15 V (vs. SCE), quite similar to the values of $E°$ for the reduction of 1,3-dinitrobenzene. 2,4-Dinitrophenyl derivative **34** is capable of direct resonance interaction of the dioxatellurapentalene ring with the two nitro groups. The reversible reduction waves for **34** have $E°$ of −0.72 and −0.98 V (vs. SCE) which are less negative than the $E°$ values for **35** or 1,3-dinitrobenzene. In particular, the difference between $E°_1$ and $E°_2$ of 0.26 V in **34** is less than the 0.37- and 0.35-V differences between $E°_1$ and $E°_2$ for **35** and 1,3-dinitrobenzene, respectively. The narrowing of ΔE and the less negative potentials can be attributed to increased delocalization in **34** relative to **35**.

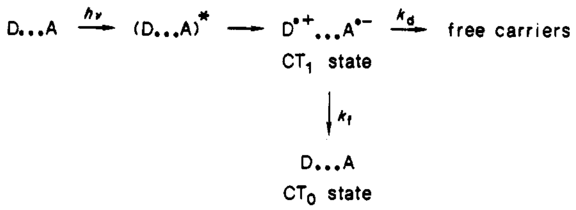
In the absence of the nitro group, all scans were irreversible, making comparison of substituent effects difficult. Substitution of the donor substituents F or OMe for one or both para hydrogens in the phenyl groups of **17** gave very small (<0.15 V) changes in $E_p{}^c$ relative to $E_p{}^c$ of **17**. The bromo and chloro groups made reduction markedly less negative in **46** and **47** relative to **17** ($E_p{}^c = -1.35$ V for **46** and $E_p{}^c = -1.28$ V for **47**).

Photodischarge Studies. Although relative groupings of the thermodynamic stabilities of the dioxatellura- and dioxaselenapentalene radical anions can be made from values of $E°$ and $E_p{}^c$ as determined by cyclic voltammetry, the irreversibility of most of the reduction waves prevents an accurate determination of $E°$. The irreversibility of reduction suggests some chemical transformation of the radical anions.

The formation of the dioxachalcogenapentalene radical anions in a polymer matrix should minimize radical anion dimerization, attack by electrophiles and rotation about the pentadienyl carbon framework. If values of $E°$ for the dioxachalcogenapentalenes or some other property dependent on $E°$ were to be measured in the polymer, then accurate substituent effects on the thermodynamic stabilities of the radical anions could be determined.

The theory associated with photoconduction in organic assemblies has developed rapidly in recent years in response to commercial development of electrophotography and organic photovoltaic devices.[23] A simplified general expression for photoconduction is shown in Scheme II for an arylamine donor (D) and a molecule acting as an ac-

Scheme II



$$\begin{tikzcd} D\ldots A \arrow[r, "h\nu"] & (D\ldots A)^{*} \arrow[r] & D^{\bullet+}\ldots A^{\bullet-} \arrow[r, "k_d"] \arrow[d, "k_f"] & \text{free carriers} \\ & & D\ldots A & \end{tikzcd}$$

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(22) Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* 1961, *83*, 1852.

(23) For reviews see: Perlstein, J. H.; Borsenberger, P. M. *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982; Vol. 2, Chapter 8. Perlstein, J. H. *Electrical Properties of Polymers*, Seanor, D., Ed.; Academic: New York, 1982; Chapter 2.

ceptor (A) in a binder in the presence of an electric field (E).[24]

Braun has developed a model for electric-field-assisted dissociation of charge-transfer states assuming that free charge carriers are photogenerated from a relaxed CT_1 state, where CT_1 represents the lowest lying excited state of the charge-transfer complex between D and A.[25] Some fraction (or perhaps all) of photons results in the formation of a relaxed CT_1, which can then decay to the ground state of the charge-transfer complex through radiative and nonradiative means (with rate constant k_f) or separate into charge carriers [with rate constant $k_d(E)$].

In the ground state, the charge-transfer interaction can be described in terms of eq 1. The products of the electron-transfer step ($D^{\bullet+}$ and $A^{\bullet-}$) are thermodynamically defined species for triarylamines (radical cation) and dioxatellura- or dioxaselenapentalenes (radical anion). The rate of black electron transfer, k_{21}, which is assumed to be completely reversible, will be a function of $\Delta G^{\ddagger}{}_{21}$, which in turn makes it a function of ΔG_{12} for the process in eq 1.[21,26]

$$\mathrm{D\cdots A} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{D^{\bullet +}\cdots A^{\bullet -}} \xrightarrow{k_d} \text{charge carriers} \qquad (1)$$

In the high-temperature limit, Marcus theory has been quite useful in describing the rates of electron transfer as a function of ΔG between the donor and acceptor.[26] Although the rate of back electron transfer (k_{21}) is predicted to follow a parabolic response over a large range of ΔG values, a linear response of k_{21} with respect to ΔG would be expected over a more narrow range.

The back-electron-transfer step of eq 1 can be described by eq 2 and 3, where $k_{21}{}^0$, $\Delta G^{\ddagger}{}_{21}$, ΔG_{12}, and k_{12} are the

$$k_{21} = k_{21}{}^0 e^{-\Delta G^{\ddagger}{}_{21}/RT} \qquad (2)$$

$$k_{21} = k_{12} e^{-\Delta G_{12}/RT} \qquad (3)$$

frequency factor, the standard free activation energy for back electron transfer, the standard free energy change of the electron transfer, and the rate constant for electron transfer in D···A, respectively. For a series involving the same triarylamine donor and closely related electron acceptors, K_{12} and $\Delta G^{\ddagger}{}_{21}$, k_{21} and ΔG_{12} would then be strongly influenced by the ground-state energy of $A^{\bullet -}$. For the purposes of this study involving triarylamines and dioxachalcogenapentalenes, interactions in the encounter complexes are assumed to be weak. The standard free-energy change (ΔG_{12}) for eq 1 will be proportional to the difference in standard potentials for the donor and acceptor redox couples[26,27]

$$\Delta G_{12} = E°(D/D^{\bullet +}) - E°(A/A^{\bullet -}) - (\text{Coulomb term}) \qquad (4)$$

Table IV. Quantum Efficiencies, Φ, for 30% Tri-*p*-tolylamine–Lexan 145 Films Containing 2% Dioxatellurapentalene or Dioxaselenapentalene Acceptors

compd	λ exposure, nm	E_0, V/cm	Φ_0	ln $[(1 - \Phi_0)/\Phi_0]$
none	350	1.6×10^6	0.0094 (0.0062)[a]	(5.08)
19	350	1.0×10^6	0.012	4.41
24	350	6.7×10^5	0.030 (0.045)[a]	(3.05)
26	350	9.9×10^5	0.067	2.63
27	350	1.0×10^6	0.0084	4.77
29	350	1.0×10^6	0.016	4.12
30	350	9.9×10^5	0.124	1.96
32	350	1.0×10^6	0.0097	4.62
41	350	9.9×10^5	0.11	2.09
42	350	1.0×10^6	0.0084	4.77
43	350	1.0×10^6	0.10	2.20
47	350	1.0×10^6	0.021	3.89

[a] Values in parentheses are corrected to E_0 of 1.0×10^6 V/cm.

where the Coulomb term results from the attractive interaction in the ion-pair state. Thus, k_{21} and $E°(A/A^{\bullet -})$ are related terms for a common triarylamine donor and a series of structurally related acceptors. The relationship of k_{21} and $E°(A/A^{\bullet -})$ to photoconduction can now be demonstrated.

It can be shown that the quantum efficiency for generation of charges, Φ, in a thin film is related to k_d and k_f by the expression[24]

$$\Phi \propto \frac{k_d(E)}{k_d(E) + k_f} \qquad (5)$$

The constant k_f is the summation of various terms including radiative and nonradiative ones in the form

$$k_f = k_{21} + \sum k_i \qquad (6)$$

where k_{21} is the nonradiative rate of back electron transfer to the ground state (eq 1) and the other k_i includes rates of intersystem crossing, internal conversion, fluorescence, and phosphorescence. The value of k_{21} would be expected to be much larger than $\sum k_i$, such that these terms could be neglected and k_f and k_{21} would be essentially identical.[26,28]

Substitution of eq 4 for ΔG_{12} and k_f for k_{21} in eq 3 gives

$$k_f = k_{12} e^{E°(D/D\bullet^+)/RT} e^{-E°(A/A\bullet^-)/RT} e^{-(\text{Coulomb term}/RT)} \qquad (7)$$

With a common donor and a series of related acceptors at the same temperatures, the factor $k_{12}e^{E°(D/D^+)/RT}$ will be a constant and eq 7 can be rewritten as

$$k_f = k e^{-E°(A/A\bullet^-)/RT} \qquad (8)$$

and

$$\ln k_f \propto -E°(A/A^{\bullet -}) \qquad (9)$$

The proportionality in eq 5 can be rewritten as

$$k_f \propto [(1 - \Phi)/\Phi]k_d \qquad (10)$$

which, since k_d should be constant with the same binder and donor, can be written as

$$\ln k_f \propto \ln [(1 - \Phi)/\Phi] \qquad (11)$$

which in turn gives

$$\ln [(1 - \Phi)/\Phi] \propto -E°(A/A^{\bullet -}) \qquad (12)$$

Although the approximations are somewhat crude, one would expect a linear relationship between ln $[(1 - \Phi_0)/\Phi_0]$ and $-E°(A/A^{\bullet -})$. In Marcus theory, this relationship would correspond to a plot of ln k for back electron transfer

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(24) Goliber, T. E.; Perlstein, J. H. *J. Chem. Phys.* **1984**, *80*, 4162.

(25) Braun, C. J. *J. Chem. Phys.* **1984**, *80*, 4157.

(26) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(27) Strictly defined, the encounter complex D···A has eliminated W_p and W_r (the work required to bring reactants together and the corresponding term for the products, respectively) from the expression

$$\Delta G_{12} = \Delta G + W_p - W_r$$

such that

$$\Delta G_{12} = \Delta G$$

where

$$\Delta G = E°(D/D^{\bullet +}) - E°(A/A^{\bullet -}).$$

(28) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

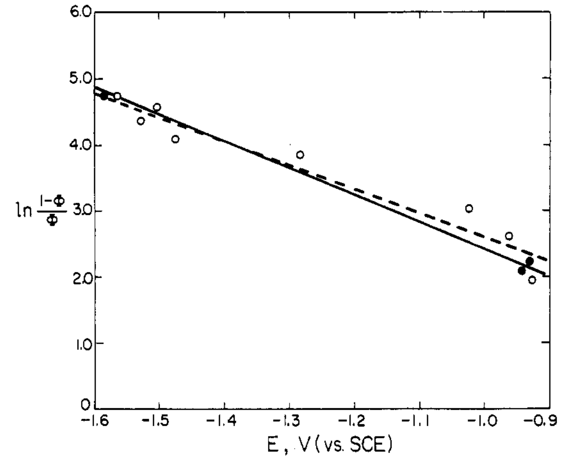

Figure 1. Plot of ln [(1 − Φ)/Φ] vs. $-E°$ (V vs. SCE) for the dioxatellurapentalene–dioxatellurapentalene radical anion couple (○, ---) and the dioxaselenapentalene–dioxaselenapentalene radical anion couple (●, —).

against ΔG between the donor and acceptor.[26] Over a narrow range, both of these relationships would be expected to give a linear regression. Furthermore, the thermodynamic stability of the acceptor radical anion has a direct influence on the quantum efficiency of the triarylamine photoconductor.

Thin films were prepared containing 30% by weight of tri-*p*-tolylamine and 2% by weight of a dioxatellura- or dioxaselenapentalene in a polycarbonate (Lexan 145) binder. The films were then charged to a surface potential of 1.0×10^6 V/cm. The slope of the initial discharge curve upon exposure to 350-nm light was determined. The calculated values of Φ are compiled in Table IV and represent averages determined from two or more runs. The formula used for calculating Φ is described in eq 13, where

$$\Phi = \frac{\kappa\epsilon_0}{elI}\frac{\mathrm{d}V}{\mathrm{d}t} \qquad (13)$$

κ is the film dielectric constant (= 3 for polycarbonate), ϵ_0 is the permittivity of free space, e is the electronic charge, l is the film thickness, I is the photon intensity incident on the film surface, and V is the surface potential. All of the terms are constant in eq 13 except for $\mathrm{d}V/\mathrm{d}T$, which is the slope of the discharge curve immediately after exposure.

A plot of ln [(1 − Φ)/Φ] for the tri-*p*-tolylamine–Lexan 145 films vs. $-E°$ or $-E_p{}^c$ for the dioxatellura- or dioxaselenapentalene acceptors is shown in Figure 1. In Figure 1, the dioxaselenapentalene points describe a line with a correlation coefficient of 0.9997, a slope of 4.071 V^{-1}, and an intercept of −1.662. The dioxatellurapentalene points describe a line with correlation coefficient of 0.974, a slope of 3.61 V^{-1}, and an intercept of −0.974.

The values of Φ and $E°$ or $E_p{}^c$ appear to give the same orderings for the thermodynamic stabilities of the dioxatellura- and dioxaselenapentalene radical anions. The most stable radical anions have an electron-withdrawing group ($-NO_2$) on one and an electron-donating group (–F, –OMe, $-NMe_2$) on the other as substituents on the phenyl rings of **24**, **26**, **30**, **41**, and **43**. The least stable radical anions have two electron-donating groups (–F, –OMe) as substituents (one on each phenyl ring) on **27**, **32**, and **42**. Both of these observations are predicted by MO theory[17,18] with the more stable radical anions illustrating the captodative effect.[18]

Obviously, one could predict the relative quantum efficiencies for photoconduction of a series of related electron acceptors with a common donor if one could determine the values of $E°$ for the acceptors. The converse of this statement is also true. More importantly, the relationship of $E°$ and thermodynamic stability allows very reactive radical anions of hypervalent main-group organometallic species to be studied. The design of electron acceptors for photoconduction or related photochemical electron-transfer processes is also made more facile. Appropriate choice of substituents to give the thermodynamically most stable radical anions should produce the slowest rates of back electron transfer and might produce species with long enough lifetimes for study by other methods. The large substituent effects suggest that the radical-anions have an extensively delocalized unpaired spin in the carbon framework.

Experimental Section

Melting points were determined on a Thomas-Hoover melting-point apparatus and are corrected. ^1H NMR spectra were recorded on a Varian EM 390 or a GE NMR QE-300 instrument. Infrared spectra were recorded on a Beckman IR 4250 instrument. UV–visible spectra were recorded on a Cary 17 spectrophotometer. Solvents were obtained from Kodak Laboratory Chemicals and were stored over 3A molecular sieves prior to use. Microanalyses were performed at Kodak on a Perkin-Elmer C, H, and N analyzer. Tellurium analyses were performed by atomic absorption spectroscopy with ±1% accuracy. Oxatellurolylium chlorides **16**, **23b**, and **23c** were prepared by the literature procedure.[1] Oxaselenolylium chlorides **40a** and **40b** were prepared by the literature procedure.[2] Compounds **46** and **47** were prepared by the literature procedure.[13]

Electrochemical Procedures. A Princeton Applied Research Model 173 potentiostat/galvanostat and a Model 175 Universal programmer were used for the electrochemical measurements. The working electrode for cyclic voltammetry was a platinum disk obtained from Princeton Applied Research. All samples were run in J. T. Baker HPLC-grade dichloromethane that had been stored over 3A molecular sieves prior to use. Electrometric-grade tetra-*n*-butylammonium fluoroborate, obtained from Southwestern Analytical Chemicals, Inc., recrystallized from ethyl acetate–pentane and dried at 80 °C overnight, was used as supporting electrolyte at 0.1 M concentration. Argon was used for sample deaeration. Tri-*p*-tolylamine was used as a known 1e couple.

Photodischarge Procedures. Films were prepared by dissolving the arylamine, sensitizer, and Lexan 145 in dichloromethane and coating the resulting solutions onto a polyethylene terephthalate support containing a 0.4 optical density evaporated nickel layer. The films were dried in an oven at 40 °C for at least 24 h. Dry thickness of the films were determined from 2500X photomicrographs of cross sections. Film spectra were determined with a Varian Superscan 3 recording spectrophotometer.

A typical photodischarge was performed as follows: a 5-cm × 5-cm film sample was mounted in an apparatus designed so that either a corona charger or a Monroe Electronics Model 144S-4 electrostatic voltmeter could be positioned in front of it. The film was then charged to a desired surface potential with a corona supplied by a Universal Voltronics high voltage supply. After the electrostatic voltage detector was moved in front of the film, the film was exposed to light passing through a Bausch and Lomb monochromator (having a bandwidth of 10 nm) while the resulting discharge was recorded on a Hewlett-Packard chart recorder. The intensity of the exposing radiation was measured with Optronics Laboratories, Inc., Model 730A radiometer. Two or three film samples were run for each sensitizer.

Preparation of 2,5-Diphenyl-1,6-dioxa-6a-tellurapentalene (17). Benzoyl chloride (0.42 g, 3.0 mmol) and **9** (0.50 g, 1.6 mmol) were slurried in 10 mL of acetonitrile. Triethylamine (0.51 g, 5.0 mmol) in 5 mL of acetonitrile was added, and the resulting mixture was warmed 10 min on a steam bath. The reaction mixture was concentrated. The residue was purified by chromatography on silica gel with methylene chloride as eluent (R_f 0.9). The yellow crystalline product was recrystallized from methanol to give 0.23 g (39%) of **17** as yellow needles. FDMS: m^+/e 378 ($C_{17}H_{12}O_2{}^{130}Te$). Anal. Calcd for $C_{17}H_{12}O_2Te$: C, 54.3; H, 3.2; Te, 33.9. Found: C, 54.0; H, 3.3; Te, 33.5.

Preparation of 2-Methyl-5-phenyl-1,6-dioxa-6a-tellurapentalene (18). Acetyl chloride (1.6 g, 0.020 mmol) and **9** (1.0 g, 3.2 mmol) were slurried in 5 mL of pyridine. The resulting mixture was heated until solution occurred. The reaction mixture was purified on a Florisil column with CH_2Cl_2 as eluent to give 0.25 g (25%) of **18** as a yellow solid. FDMS: m^+/e 316 ($C_{12}H_{10}O_2{}^{130}Te$). Anal. Calcd for $C_{12}H_{10}O_2Te$: C, 45.9; H, 3.2. Found: C, 45.8; H, 3.2.

Preparation of 2-(*p*-Methoxyphenyl)-5-phenyl-1,6-dioxa-6a-tellurapentalene (19). Benzoyl chloride (0.64 g, 4.6 mmol) and **23b** (0.32 g, 0.95 mmol) were slurried in 1.0 g of triethylamine. The resulting mixture was heated on a steam bath for 5 min. The reaction mixture was purified on Florisil with methylene chloride as eluent to give 0.11 g (27%) of **19** as a yellow solid. FDMS: m^+/e 408 ($C_{18}H_{14}O_3{}^{130}Te$). Anal. Calcd for $C_{18}H_{14}O_3Te$: C, 53.3; H, 3.5; Te, 31.4. Found: C, 53.2; H, 3.5; Te, 29.5.

Preparation of 2-(*p*-Nitrophenyl)-5-phenyl-1,6-dioxa-6a-tellurapentalene (20). *p*-Nitrobenzoyl chloride (0.40 g, 2.1 mmol) and **16** (0.62 g, 2.0 mmol) were slurried in 10 mL of CH_3CN. Triethylamine (0.51 g, 5.0 mmol) in 5 mL of CH_3CN was added. The resulting slurry was warmed on a steam bath for 2 min, giving a dark red solution. The reaction mixture was diluted with 200 mL of CH_2Cl_2. The resulting solution was washed with 10% HCl (2 × 50 mL), dried over sodium sulfate, and concentrated. The residue was dissolved in boiling 3/1 (v/v) CH_3CN/THF. Cooling gave 0.23 g (27%) of **20** as a yellow solid. FDMS: m^+/e 423 ($C_{17}H_{11}NO_4{}^{130}Te$). Anal. Calcd for $C_{17}H_{11}NO_4Te$: C, 48.5; H, 2.6; N, 3.3; Te, 30.3. Found: C, 48.9; H, 2.8; N, 3.2; Te, 29.9.

Preparation of (*Z*)-3-(*p*-(Dimethylamino)phenyltelluro)butenoic Acid (22a). Bis(*p*-(dimethylamino)phenyl) ditelluride (3.00 g, 6.05 mmol) was dissolved in 10 mL of THF. Ethanol (10 mL) was added followed by 0.3 g of sodium borohydride. When the color of the ditelluride faded, ethyl tetrolate (1.32 g, 11.8 mmol) in 5 mL of ethanol was added. The resulting mixture was stirred 1 h at ambient temperature and was then diluted with 50 mL of CH_2Cl_2 and 150 mL of 10% HCl. The organic phase was separated, and the aqueous phase was extracted with methylene chloride (2 × 25 mL). The combined organics were dried over sodium sulfate and concentrated. The residue was recrystallized from ethanol to give 1.84 g (47%) of the ethyl ester, mp 94–96 °C. Anal. Calcd for $C_{14}H_{19}NO_2Te$: C, 46.6; H, 5.3; N, 3.9. Found: C, 46.6; H, 5.3; N, 4.1. The ester was dissolved in 25 mL of hot ethanol, and 25 mL of 10% aqueous KOH was added. The resulting mixture was stirred on a steam bath for 1 h. The reaction mixture was acidified with 10% HCl and was then neutralized with saturated sodium bicarbonate precipitating the acid. The acid was recrystallized from CH_3CN to give 1.03 g (26%) of **22a** as a pale yellow solid which quickly began to darken.

Preparation of 3-Methyl-5-(*p*-(dimethylamino)phenyl)-1,2-oxatellurol-1-ium Chloride (23a). Acid **22a** (0.33 g, 1.0 mmol) was added to a solution of 10 mL of oxalyl chloride in 10 mL of CH_2Cl_2. The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated, and the residue was dissolved in 10 mL of methanol. The solution was made basic by the addition of 10 mL of saturated sodium bicarbonate solution precipitating a brick-orange solid. The solid was collected by filtration, washed with methanol, and dried to give 0.11 g (31%) of **23a**: mp 208–210 °C; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 460 nm (4.61); FDMS, m^+/e 353 ($C_{12}H_{14}ClNO^{130}Te$). Anal. Calcd for $C_{12}H_{14}ClONTe$: C, 41.0; H, 4.0; N, 4.0. Found: C, 41.2; H, 4.0; N, 3.9.

Preparation of 2-(*p*-(Dimethylamino)phenyl)-5-(*p*-nitrophenyl)-1,6-dioxa-6a-tellurapentalene (24). *p*-Nitrobenzoyl chloride (0.070 g, 0.38 mmol) and **23a** (0.070 g, 0.20 mmol) were slurried in 3 mL of CH_3CN. Triethylamine (0.20 g, 2.0 mmol) was added. The resulting mixture was stirred under nitrogen at ambient temperature for 1 h. The reaction mixture was concentrated. The residue was purified by chromatography on silica gel with CH_2Cl_2 as eluent (R_f 0.8) to give 0.011 g (12%) of **24**: FDMS, m^+/e 466 ($C_{19}H_{16}N_2O_4{}^{130}Te$). Anal. Calcd for $C_{19}H_{16}N_2O_4Te$: C, 49.2; H, 3.5; N, 6.0. Found: C, 49.3; H, 3.5; N, 6.1.

Preparation of 2-(*p*-(Dimethylamino)phenyl)-5-(*p*-cyanophenyl)-1,6-dioxa-6a-tellurapentalene (25). *p*-Cyanobenzoyl chloride (2.10 g, 0.013 mol) and **23a** (1.05, 3.0 mmol) were heated to melting, and triethylamine (3.0 g, 0.030 mol) was added. The resulting mixture was slurried for 1 min and cooled. The residue was recrystallized from CH_3CN to give 0.40 g (34%) of **25** as a brick-red solid. Anal. Calcd for $C_{20}H_{16}N_2O_2Te$: C, 54.1; H, 3.6; N, 6.3. Found: C, 53.8; H, 3.6; N, 6.2.

Preparation of 2-(Methoxyphenyl)-5-(*p*-nitrophenyl)-1,6-dioxa-6a-tellurapentalene (26). *p*-Nitrobenzoyl chloride (0.96 g, 5.2 mmol) and **23b** (0.32 g, 0.95 mmol) were added to 2.0 g (20 mmol) of triethylamine. The resulting mixture was heated on a steam bath for 5 min. Acetonitrile (5 mL) was added, precipitating the product. Recrystallization from methanol gave 0.34 g (80%) of **26**: FDMS, m^+/e 453 ($C_{18}H_{13}NO_5{}^{130}Te$). Anal. Calcd for $C_{18}H_{13}NO_5Te$: C, 47.9; H, 2.9; N, 3.1; Te, 28.3. Found: C, 47.9; H, 3.0; N, 2.8; Te, 30.9.

Preparation of 2,5-Bis(*p*-methoxyphenyl)-1,6-dioxa-6a-tellurapentalene (27). *p*-Anisoyl chloride (0.30 g, 1.8 mmol) and **23b** (0.20 g, 0.59 mmol) were heated together on a steam bath to form a homogenous melt. Pyridine (1 mL) was poured onto the hot melt. The reaction mixture was heated at reflux for 1 min. Chromatography on Florisil with methylene chloride as eluent gave 0.10 g (39%) of **27**: FDMS, m^+/e 438 ($C_{19}H_{16}O_4{}^{130}Te$). Anal. Calcd for $C_{19}H_{16}O_4Te$: C, 52.3; H, 3.7; Te, 29.3. Found: C, 52.0; H, 3.9; Te, 29.1.

Preparation of 2-Methyl-5-(*p*-methoxyphenyl)-1,6-dioxa-6a-tellurapentalene (28). Acetyl chloride (1.3 g, 16.6 mmol) and **23b** (1.0 g, 3.0 mmol) were heated together on a steam bath to form a melt. Pyridine (5 g) was added, and the resulting mixture was heated 30 s on a steam bath. Chromatography on Florisil with CH_2Cl_2 as eluent gave 0.35 g (34%) of **28** as a yellow solid: FDMS, m^+/e 346 ($C_{13}H_{12}O_3{}^{130}Te$). Anal. Calcd for $C_{13}H_{12}O_3Te$: C, 45.4; H, 3.5; Te, 37.1. Found: C, 45.4; H, 3.6; Te, 36.6.

Preparation of 2-(*p*-Fluorophenyl)-5-phenyl-1,6-dioxa-6a-tellurapentalene (29). Benzoyl chloride (2.6 g, 18.5 mmol) and **23c** (1.2 g, 3.7 mmol) were heated together to form a melt, and 10 mL of pyridine was added. The reaction was heated 1 min at reflux. Chromatography on Florisil with methylene chloride as eluent gave 0.43 g (27%) of **29** as shiny yellow needles: FDMS, m^+/e 396 ($C_{17}H_{11}FO_2{}^{130}Te$). Anal. Calcd for $C_{17}H_{11}FO_2Te$: C, 51.8; H, 2.8; Te, 32.4. Found: C, 51.7; H, 3.0; Te, 31.1.

Preparation of 2-(*p*-Fluorophenyl)-5-(*p*-nitrophenyl)-1,6-dioxa-6a-tellurapentalene (30). *p*-Nitrobenzoyl chloride (1.14 g, 6.13 mmol) and **23c** (1.0 g, 3.1 mmol) were heated to reflux in 20 mL of CH_3CN. 2,6-Lutidine (2.0 mL, 17 mmol) was added, and the resulting mixture was warmed 1 h at reflux. The reaction mixture was diluted with 100 mL of CH_2Cl_2. The resulting solution was washed with 5% HCl (2 × 100 mL), dried over sodium sulfate, and concentrated. Chromatography on Florisil with CH_2Cl_2 as eluent gave 0.89 g (66%) of **30** as an orange solid: FDMS, m^+/e 441 ($C_{17}H_{10}FNO_4{}^{130}Te$). Anal. Calcd. for $C_{17}H_{10}FNO_4Te$: C, 46.5; H, 2.3; N, 3.2; Te, 29.1. Found: C, 46.5; H, 2.4; N, 3.0; Te, 29.0.

Preparation of 2-(*p*-Fluorophenyl)-5-(*p*-cyanophenyl)-1,6-dioxa-6a-tellurapentalene (31). *p*-Cyanobenzoyl chloride (0.71 g, 4.3 mmol) and **23c** (0.70 g, 2.1 mmol) were slurried in 20 mL of CH_3CN. 2,6-Lutidine (1.5 mL) was added. The resulting mixture was stirred at ambient temperature for 5 days, after which it was concentrated. The residue was dissolved in 200 mL of CH_2Cl_2. The resulting solution was filtered through a pad of Celite, washed with 10% HCl (2 × 100 mL), dried over Na_2SO_4, and concentrated. The residue was recrystallized from CH_3CN to give 0.52 g (58%) of **31** as a yellow solid: FDMS, m^+/e 421 ($C_{18}H_{10}FNO_2{}^{130T}eF$). Anal. Calcd for $C_{18}H_{10}FNO_2{}^{130}TeF$: C, 51.6; H, 2.4; N, 3.3. Found: C, 51.6; H, 2.4; N, 3.2.

Preparation of 2,5-Bis(*p*-fluorophenyl)-1,6-dioxa-6a-tellurapentalene (32). *p*-Fluorobenzoyl chloride (0.60 g, 3.4 mmol) and **23c** (0.60 g, 1.8 mmol) were dissolved in 5 mL of hot CH_3CN. Triethylamine (0.5 g, 5 mmol) in 1 mL of CH_3CN was added dropwise. The resulting solution was heated 1 min on a steam bath and then cooled to ambient temperature. The product crystallized and was collected by filtration. The crystalline mass was redissolved in hot CH_3CN and filtered through Celite to remove Te metal. The mother liquors produced bright gold, chunky crystals of **32** which were collected by filtration to give 0.25 g (33%): FDMS, m^+/e 414 ($C_{17}H_{10}F_2O_2{}^{130}Te$). Anal. Calcd for $C_{17}H_{10}F_2O_2Te$: C, 49.6; H, 2.4; Te, 31.0. Found: C, 49.3; H, 2.5; Te, 29.9.

Preparation of 2-(*p*-Fluorophenyl)-5-(*p*-methoxyphenyl)-1,6-dioxa-6a-tellurapentalene (33). *p*-Anisoyl chloride (1.90 g, 11.1 mmol) and **23c** (1.00 g, 3.07 mmol) were heated together to form a melt. Pyridine (5 mL) was added, and the resulting mixture was warmed 1 min at reflux. Chromatography on Florisil with CH_2Cl_2 as eluent gave 0.27 g (21%) of **33** as a yellow solid: FDMS, m^+/e 426 ($C_{18}H_{13}FO_3{}^{130}Te$). Anal. Calcd for $C_{18}H_{13}FO_3Te$: C, 51.0; H, 3.1; Te, 30.1. Found: C, 51.0; H, 3.3; Te, 29.4.

Preparation of 2-(2,4-Dinitrophenyl)-6-(fluorophenyl)-1,6-dioxa-6a-tellurapentalene (34). Freshly prepared 2,4-dinitrobenzoyl chloride (1.41 g, 6.13 mmol) and **23c** (1.0 g, 3.1 mmol) were dissolved in 20 mL of CH_3CN. 2,6-Lutidine (2.0 mL) in 5 mL of CH_3CN was added dropwise. The resulting mixture was stirred at ambient temperature for 4 days. The reaction mixture was concentrated, and the residue was dissolved in 300 mL of CH_2Cl_2. The resulting solution was washed with 10% HCl (2 × 100 mL) and saturated $NaHCO_3$ (3 × 100 mL) and was concentrated. Chromatography of the residue on silica gel with CH_2Cl_2 as eluent gave 0.16 g (11%) of **34** as a red solid: FDMS, m^+/e 486 ($C_{17}H_9FN_2O_6{}^{130}Te$). Anal. Calcd for $C_{17}H_9FN_2O_6Te$: C, 42.2; H, 1.9; N, 5.8. Found: C, 42.6; H, 2.1; N, 5.7.

Preparation of 2-(3,5-Dinitrophenyl)-6-(*p*-fluorophenyl)-1,6-dioxa-6a-tellurapentalene (35). Recrystallized 3,5-dinitrobenzoyl chloride (0.36 g, 3.4 mmol) and **23c** (1.0 g, 3.1 mmol) were dissolved in 20 mL of CH_3CN. 2,6-Lutidine (2.0 mL) in 5 mL of CH_3CN was added. The reaction mixture was stirred for 4 days at ambient temperature. The product crystallized from solution and was collected by filtration. Recrystallization from chloroform gave 1.25 g (85%) of **35** as a brown solid: m^+/e 486 ($C_{17}H_9FN_2O_6{}^{130}Te$). Anal. Calcd for $C_{17}H9_FN_2O_6Te$: C, 42.2; H, 1.9; N, 5.8. Found: C, 42.6; H, 1.9; N, 5.8.

Preparation of 2-Methyl-5-(*p*-fluorophenyl)-1,6-dioxa-6a-tellurapentalene (36). Acetyl chloride (1.9 g, 24 mmol) and **23c** (1.00 g, 3.07 mmol) were heated to form a melt. Pyridine (5 mL) was added, and the resulting mixture was heated at reflux for 1 min. Chromatography on silica gel with CH_2Cl_2 as eluent gave 0.40 g (49%) of **36** as a yellow solid: FDMS, m^+/e 334 ($C_{12}H_9FO_2Te$). Anal. Calcd for $C_{12}H_9FO_2$: C, 43.4; H, 2.7; Te, 38.5. Found: C, 43.6; H, 2.8; Te, 38.2.

Preparation of 2-(*p*-Methoxyphenyl)-5-(*p*-nitrophenyl)-1,6-dioxa-6a-selenapentalene (41). *p*-Nitrobenzoyl chloride (1.50 g, 8.7 mmol) and **40a** (0.50 g, 1.7 mmol) were heated until a homogenous melt was formed. Triethylamine (4 mL) was added, and the resulting mixture was heated at 100 °C for 1 min. The reaction mixture was diluted with CH_2Cl_2 (100 mL). The organic phase was washed with 5% HCl (2 × 50 mL), dried over magnesium sulfate, and concentrated. The residue was recrystallized from acetonitrile to give 0.36 g (40%) of **41** as a yellow solid: mp 244–247 °C. IR (KBr) 1610, 1525, 1175, 805 cm^{-1}; FDMS, m^+/e 403 ($C_{18}H_{13}NO_5{}^{80}Se$). Anal. Calcd for $C_{18}H_{13}NO_5Se$: C, 53.7; H, 3.3; N, 3.5. Found: C, 53.7; H, 3.2; N, 3.6.

Preparation of 2,5-Bis(*p*-methoxyphenyl)-1,6-dioxa-6a-selenapentalene (42). *p*-Anisoyl chloride (4.8 g, 0.028 mol) and **40a** (1.6 g, 5.5 mmol) were heated together to form a melt. Diisopropylethylamine (6.4 g) was added, and the resulting mixture was heated 30 s at 100 °C. The reaction mixture was diluted with 100 mL of CH_2Cl_2. The resulting solution was washed with 5% HCl (2 × 50 mL), dried over magnesium sulfate, and concentrated. Chromatography on Florisil with CH_2Cl_2 as eluent gave the product (R_f 0.8). Recrystallization from CH_3CN gave 0.22 g (10%) of **42** as a yellow solid: mp 251–253 °C; IR (KBr) 1609, 1433, 1400, 1255, 1180, 1025 cm^{-1}; m^+/e 388 ($C_{19}H_{16}O_4{}^{80}Se$). Anal. Calcd for $C_{19}H_{16}O_4Se$: C, 58.9; H, 4.2. Found: C, 59.4; H, 4.5.

Preparation of 2-(*p*-Fluorophenyl)-5-(*p*-nitrophenyl)-1,6-dioxa-6a-selenapentalene (43). *p*-Nitrobenzoyl chloride (3.0 g, 16 mmol) and **40b** (1.0 g, 4.4 mmol) were heated together to form a melt. Triethylamine (5 mL) was added, and the resulting mixture was heated at 100 °C for 30 s. The reaction mixture was diluted with 100 mL of CH_2Cl_2. The resulting solution was washed with 5% HCl (2 × 50 mL), dried over magnesium sulfate, and concentrated. Chromatography on Florisil with CH_2Cl_2 as eluent gave 0.26 g (15%) of **43** as yellow crystals: mp 250–251 °C; IR (KBr) 1610, 1525, 1440, 1350, 1240 cm^{-1}; FDMS, m^+/e 391 ($C_{17}H_{10}FO_4N^{80}Se$). Anal. Calcd for $C_{17}H_{10}FO_4NSe$: C, 52.3; H, 2.6; N, 3.6. Found: C, 52.2; H, 2.3; N, 3.9.

Preparation of 2-[2-(2-Furanyl)ethene]-5-(*p*-fluorophenyl)-1,6-dioxa-6a-tellurapentalene (38). 2-Furanacryloyl chloride (0.75 g, 4.8 mmol) and **23a** (0.50 g, 1.5 mmol) in 2.5 mL of pyridine were heated on a steam bath for 2 min. The reaction mixture was diluted with 100 mL of CH_2Cl_2. The resulting solution was washed with 10% HCl (2 × 50 mL), dried over $MgSO_4$, and concentrated. Recrystallization from CH_3CN gave 0.39 g of a yellow solid: FDMS, m^+/e 412 ($C_{17}H_{11}FO_3{}^{130}Te$).

Preparation of 2-[2-(2-Thiophenyl)ethene]-5-(*p*-fluorophenyl)-1,6-dioxa-6a-tellurapentalene (39). The procedure described above for the preparation of **38** was followed using 2-thiopheneacryloyl chloride (0.75 g, 4.3 mmol) and **23c** (0.50 g, 1.5 mmol) in 2.5 mL of pyridine. Product yield was 0.32 g (50%) of **39** as a yellow solid: FDMS, m^+/e 428 ($C_{17}H_{11}FO_2S^{130}Te$).

Preparation of *N*-Methyl-2,5-diphenyl-1-aza-6-oxa-6a-tellurapentalene (58). Imidoyl chloride **57** (0.50 g, 3.2 mmol) and **16** (0.50 g, 1.6 mmol) were slurried in 10 mL of CH_3CN. 2,6-Lutidine (1.0 mL) was added. The resulting mixture was heated at reflux for 3 h. The reaction mixture was concentrated. The residue was dissolved in 100 mL of CH_2Cl_2. The resulting solution was filtered through a plug of Celite, washed with 10% HCl (3 × 60 mL) and water (60 mL), and concentrated. The residue was purified by chromatography on silica gel with CH_2Cl_2 as eluent to give 0.070 g (11%) of **58** (R_f 0.9) as a gummy red solid. Recrystallization from CH_3CN gave bright yellow crystals of **58**. FDMS, m^+/e 391 ($C_{18}H_{15}NO^{130}Te$). Anal. Calcd for $C_{18}H_{15}NOTe$: C, 55.6; H, 3.9; N, 3.6. Found: C, 55.5; H, 3.9; N, 3.7.

General Procedure for the Bromination of Dioxatellurapentalenes. The dioxatellurapentalenes were dissolved or slurried in CH_2Cl_2 (10 mg/mL). Bromine (2 molar equiv) in CH_2Cl_2 (100 mg/mL) was added dropwise with stirring. After being stirred 10 min at ambient temperature, the reaction mixture was concentrated. The residue was heated in boiling CH_3CN. Cooling precipitated the 12-Te-5 pertelluranes. Yields and melting points are given in Table II.

For **44**: ^1H NMR (CD_2Cl_2) δ 8.13 (m, 4 H), 7.83 (s, 1 H), 7.60 (m, 6 H); IR (KBr) 1600, 1550, 1450, 1355, 1150, 772 cm^{-1}; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 340 (4.28), 555 nm (4.57); FDMS, m^+/e 614 ($C_{17}H_{11}Br_3O_2{}^{130}Te$), 535 ($M^+ - Br$), 456 ($M^+ - 2\,Br$). Anal. Calcd for $C_{17}H_{11}Br_3O_2Te$: C, 33.2; H, 1.8. Found: C, 33.4; H, 1.9.

For **50**: ^1H NMR (CD_2Cl_2) δ 8.20 (d × d, 4 H, J = 6, 9 Hz), 7.72 (s, 2 H), 7.30 (d × d, 4 H, J = 6, 12 Hz); IR (KBr) 1600, 1555, 1375, 1225, 1175, 1150, 1095, 866, 847, 820 cm^{-1}; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 420 (4.00), 545 nm (4.40); FDMS, m^+/e 572 ($C_{17}H_{10}Br_2F_2O_2{}^{130}Te$), 493 ($M^+ - Br$), 414 ($M^+ - 2\,Br$). Anal. Calcd for $C_{17}H_{10}Br_2F_2O_2Te$: C, 35.7; H, 1.8; Te, 22.3; F, 6.6. Found: C, 35.3; H, 2.0; Te, 23.7; F, 6.9.

For **51**: IR (KBr) 1590, 1555, 1375, 1200, 1170, 1020, 950, 770 cm^{-1}; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 328 (4.28), 528 nm (4.54); FDMS, m^+/e 552 ($C_{12}H_9Br_3O_2{}^{130}Te$), 473 ($M^+ - Br$), 394 ($M^+ - 2\,Br$). Anal. Calcd for $C_{12}H_9Br_3O_2Te$: C, 26.1; H, 1.6. Found: C, 26.3; H, 1.6.

For **52**: IR (KBr) 1600, 1580, 1555, 1470, 1150, 1015, 950, 843, 800 cm^{-1}; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 538 nm (4.52); FDMS, m^+/e 582 ($C_{13}H_{11}Br_3O_3{}^{130}Te$), 503 ($M^+ - Br$), 424 ($M^+ - 2\,Br$). Anal. Calcd for $C_{13}H_{11}Br_3O_3Te$: C, 26.8; H, 1.9. Found: C, 27.1; H, 2.1.

For **53**: IR (KBr) 1600, 1560, 1520, 1410, 1345, 1190, 1150, 848 cm^{-1}; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 335 (4.23), 555 nm (4.53). Anal. Calcd for $C_{17}H_9Br_3FNO_4Te$: C, 30.1; H, 1.3; N, 2.1. Found: C, 30.0; H, 1.3; N, 2.1.

For **54**: IR (KBr) 1600, 1580, 1555, 1510, 1345, 1153, 848 cm^{-1}; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 405 (4.26), 555 nm (4.54); FDMS, m^+/e 689 ($C_{18}H_{12}Br_3NO_5{}^{130}Te$), 610 ($M^+ - Br$), 531 ($M^+ - 2\,Br$). Anal. Calcd for $C_{18}H_{12}Br_3NO_5Te$: C, 31.3; H, 1.8; N, 2.0. Found: C, 31.4; H, 1.8; N, 2.0.

For **55**: IR (KBr) 1605, 1555, 1505, 1360, 1340, 1150, 1040, 848, 821, 745 cm^{-1}; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 334 (4.11), 590 nm (4.52); FDMS, m^+/e 702 ($C_{19}H_{15}Br_3N_2O_4{}^{130}Te$), 504 ($M^+ - 2\,Br$). Anal. Calcd for $C_{19}H_{15}Br_3N_2O_4Te$: C, 32.5; H, 2.3; N, 4.0. Found: C, 32.8; H, 2.4; N, 4.2.

For **56**: IR (KBr) 2240, 1600, 1570, 1550, 1365, 1155, 1040, 820, 742 cm^{-1}; $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 593 nm (4.54); FDMS, m^+/e 524 ($M^+ - 2\,Br$). Anal. Calcd for $C_{20}H_{15}Br_3N_2O_2Te$: C, 35.2; H, 2.2; N, 4.1. Found: C, 35.3; H, 2.2; N, 4.0.

Chlorination of 32 To Give 48. Dioxatellurapentalene **32** (0.41 g, 1.0 mmol) was dissolved in 50 mL of CH_2Cl_2. The resulting solution was cooled to 0 °C, and chlorine gas was bubbled through the reaction mixture, giving a lavender solution. Chilling to −20 °C precipitated shiny green crystals of **48** (0.28 g, 50%): ^{1}H NMR ($CDCl_3$) δ 8.66 (m, 4 H), 7.20 (m, 4 H), 7.20 (m, 4 H); IR (KBr) 1605, 1555, 1500 cm^{-1}; $\lambda_{max}^{CH_2Cl_2}$ (log ϵ) 345 (4.24), 587 nm (4.56); FDMS, m^+/e 552 ($C_{17}H_8Cl_4F_2O_2{}^{130}Te$), 482 ($M^+$ − 2 Cl). Anal. Calcd for $C_{17}H_8Cl_4F_2O_2Te$: C, 37.0; H, 1.5. Found: C, 37.3; H, 1.6.

Registry No. **2a**, 108743-34-6; **9**, 34108-71-9; **16**, 87761-66-8; **17**, 87761-67-9; **18**, 108743-24-4; **19**, 91412-35-0; **20**, 108743-25-5; **22a**, 108743-33-5; **22a** ethyl ester, 108743-35-7; **23a**, 101009-47-6; **23b**, 91412-62-3; **23c**, 108743-36-8; **24**, 91412-33-8; **25**, 108743-26-6; **26**, 91412-34-9; **27**, 91412-35-0; **28**, 108743-27-7; **29**, 91412-37-2; **30**, 91412-38-3; **31**, 108743-28-8; **32**, 108743-29-9; **33**, 91412-39-4; **34**, 108743-30-2; **35**, 108743-31-3; **36**, 91412-40-7; **37**, 108743-32-4; **38**, 91412-45-2; **39**, 91412-46-3; **40a**, 84144-41-2; **40b**, 84144-47-8; **41**, 91412-42-9; **43**, 91412-43-0; **44**, 87761-70-4; **45**, 87761-71-5; **46**, 87761-72-6; **47**, 87761-73-7; **48**, 91412-54-3; **49**, 108772-63-0; **50**, 91412-53-2; **51**, 108743-37-9; **52**, 108743-38-0; **53**, 108743-39-1; **54**, 108743-40-4; **55**, 108743-41-5; **56**, 108743-42-6; **57**, 21737-87-1; **58**, 91412-48-5; PhC(O)Cl, 98-88-4; AcCl, 75-36-5; *p*-$NO_2C_6H_4CO)Cl$, 122-04-3; *p*-$CNC_6H_4C(O)Cl$, 6068-72-0; *p*–$FC_6H_4C(O)Cl$, 403-43-0; Ethyl tetrolate, 4341-76-8; *p*-anisoyl chloride, 100-07-2; 2,4-dinitrobenzoyl chloride, 20195-22-6; 3,5-dinitrobenzoyl chloride, 99-33-2; 2-furanacryloyl chloride, 20689-54-7; 2-thiopheneacryloyl chloride, 28424-61-5.

Mechanism of the Light-Assisted Nucleophilic Acylation of Activated Olefins Catalyzed by Vitamin B_{12}

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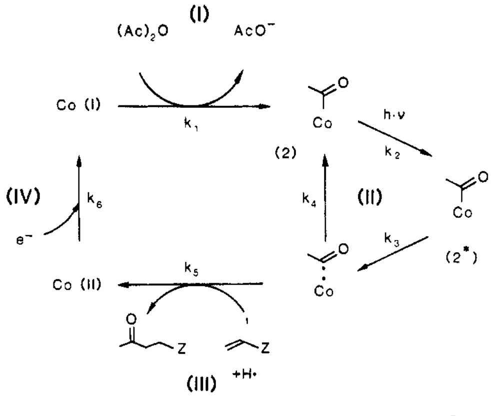
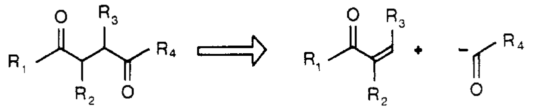
The conjugate addition of acyl groups to C–C double bonds, by a vitamin B_{12} catalyzed electrochemical reduction of acetic anhydride in the presence of Michael olefins and under visible light, is shown to involve sequential formation and cleavage of the Co–C bond in acetylcobalamin. Photolysis of this intermediate takes place efficiently only in the presence of the activated olefin. The rate constant of acylation of B_{12s} by acetic anhydride (k_1 = 0.017 M^{-1} s^{-1}), the quantum yield of the visible light induced cleavage of the Co–C bond ($\Phi \approx 0.35$), and the relative rate of acylation of a series of activated olefins were determined electrochemically from catalytic currents. These values are comparable with independently measured k values for the isolated reaction steps. The k values for the acetyl-transfer reaction correlate well with the reduction potentials of the activated olefins or with their σ_p^-, exhibiting a linear free energy relationship (ρ = 2.3). The transferred acyl moiety reacts as a Co-stabilized nucleophilic radical and not as a "free" radical.

Scheme I. Catalytic Cycle. B_{12}-Catalyzed Acetylation of Activated Olefins under Visible Light Illumination and Reducing Conditions



There exists a broad interest in simple and mild methods for the synthesis of 1,4-dioxo compounds. Their retrosynthetic disconnection, as shown in eq 1, leads to a Mi-



(1)

chael acceptor and an acyl anion. The associated chemical problem consists in stabilizing the negative charge on the C atom of the carbonyl function to the extent that side reactions are avoided but nucleophilic reactivity persists. Reagents with masked functionality[1] and acylmetallic compounds have been found to meet these conditions. In the latter case, limited synthetic use has been reported for group Ia, IIa, and IIIb derived acyl anions due to their uncontrollably high reactivity.[2a] Improved stability has recently been noted for acyl anions produced from acyl chlorides and SmI_2.[2b] Nucleophilic acylation of activated olefins by formal acyl anions bound to transition metals are reported for acylcuprates,[2c] acyltetracarbonyliron,[2d] and acylnickelates.[2e] Their preparation, by sequential insertion of CO and activated olefin into metal–carbon bonds, is not suited for catalytic applications. On the other hand, so-called "free" radicals are known to exhibit sufficient nucleophilic reactivity for Michael-type reactions.[3] Recently Scheffold and co-workers have shown that under mild reductive conditions vitamin B_{12} (1) is an excellent catalyst for the 1,4 addition of carboxylic anhydrides to activated olefins[4a] (eq 2). An intermediate acylcobalamin (2) is

$$R^2R^3C{=}CR^1Z + (R^4CO)_2O + H^\bullet + e^- \xrightarrow[-1.0\text{ V}, h\nu, \text{ or } -1.6\text{ V}]{\text{vitamin B}_{12}} (R^4CO)R^2R^3C{-}CHR^1Z + R^4CO_2^- \quad (2)$$

Z = electron-withdrawing group

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