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Telluropyrylium Dyes. 1. 2,6-Diphenyltelluropyrylium Dyes

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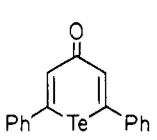
Methine and polymethine dyes containing at least one 2,6-diphenyltelluropyrylo group as well as another 2,6-diphenylchalcogenopyrylo group have been prepared by the condensation of 2,6-diphenyl-4-methylchalcogenopyrylium salts with 4*H*-2,6-diphenyltelluropyran-4-one or (4*H*-2,6-diphenyltelluropyran-4-ylidene)acetaldehyde or by the reaction of 2,6-diphenyl-4-methyltelluropyrylium tetrafluoroborate with bisaldehyde equivalents. Similarly, various *N*,*N*-dialkylamino-containing telluropyrylium dyes have also been prepared. The telluropyrylium dyes absorb at longer wavelengths than their oxygen, sulfur, or selenium counterparts. This shift can be empirically correlated with an increase in electropositive character of the heteroatom.

The preparation of dyes that show electronic absorptions at lower energies than existing dyes has been of increasing interest to chemists.[1] Cyanine dyes have been shown to be exceptionally useful in this respect.[2] Pyrylium,[3] thiapyrylium,[4] and selenapyrylium[5] nuclei give large bathochromic shifts when incorporated in methine and polymethine dyes, much larger than with other heterocyclic nuclei.

Within the pyrylo methine and polymethine dyes, sequential bathochromic shifts are observed as the pyrylium nucleus is replaced with a thiapyrylium nucleus, which in turn is replaced with a selenapyrylium nucleus (Table I). This trend can be correlated with an increase in electropositive character as one goes down the group 6a elements. The corresponding telluropyrylium dyes would be expected to continue this trend, as tellurium is more electropositive than the lighter group 6a elements. Although two telluroxanthylium compounds have been prepared, this is the first report of telluropyrylium dyes to appear in the literature.

This paper describes the successful preparation of mono-, tri-, penta-, and heptamethine dyes containing at least one telluropyrylo group and the preparation of various *N*,*N*-dialkylamino-substituted telluropyrylium dyes. The syntheses were dependent on several factors: the ability of 4*H*-2,6-diphenyltelluropyran-4-one (1) to condense with 2,6-diphenyl-4-methylchalcogenopyrylium salts, the conversion of 1 to 2,6-diphenyl-4-methyltelluropyrylium tetrafluoroborate (2); the conversion of 2 to (4*H*-2,6-diphenyltelluropyran-4-ylidene)acetaldehyde (3); and the successful condensation of 2 with various aldehydes.



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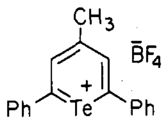

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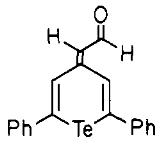

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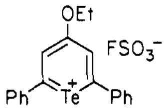
Results and Discussion

Telluropyrylo Methine and Polymethine Dyes. Telluropyrone 1 was converted to pyrylium salt 2 in four steps. Ethylation of 1 with ethyl fluorosulfate gave the 4-ethoxytelluropyrylium salt 4. The reaction of 4 with Meldrum's acid in pyridine gave telluropyranylidene 5, which rapidly lost carbon dioxide upon treatment with formic acid. The formate salt of 2 was then treated with fluoroboric acid to give 2.



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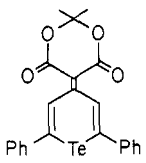

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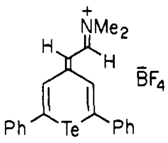

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The aldehyde 3 was easily prepared from 2 in two steps. The reaction of 2 with *N*,*N*-dimethylthioformamide in acetic anhydride gave imminium salt 6. Hydrolysis of 6

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(1) Reynolds, G. A.; Drexhage, K. H. *J. Org. Chem.* **1977**, *42*, 885.

(2) Brooker, L. G. S. In "Chemistry of Natural and Synthetic Colouring Matters and Related Fields"; Gore, T. S., Joshi, B. S., Sunthanker, S. V., Tilak, B. D., Eds.; Academic Press: New York, 1962; p 573.

(3) Reynolds, G. A.; Van Allan, J. A. U.S. Patent 3417083, 1972. Williams, J. L. R.; Reynolds, G. A. *J. Appl. Phys.* **1968**, *39*, 5327.

(4) Wizinger, R.; Angliker, H. J. *Helv. Chim. Acta* **1966**, *49*, 2046.

(5) Tolmachev, A. I.; Kudinova, M. A. *Khim. Geterotsikl. Soedin.* **1974**, 49.

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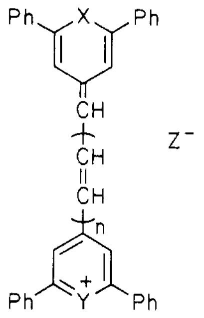
Table I. Bis(chalcogenopyrylo) Methine and Polymethine Dyes of Structure:



compd	X	Y	Z	n	λ_{max} (CH_2Cl_2), nm	log ϵ
10[a]	O	O	ClO_4	0	545	
11[a]				1	686	
12[b]	O	S	ClO_4	0	585	
13[b]				1	725	
14[b]	O	Se	ClO_4	0	605	
15[b]				1	743	
16	O	Te	BF_4	0	650	5.14
17				1	780	5.35
18[c]	S	S	ClO_4	0	622	
19[c]				1	751	
20[c]				2	879[d]	
21[e]	S	Se	ClO_4	0	643	
22				1	782	
23	S	Te	ClO_4	0	690	5.11
24				1	820	5.30
25[e]	Se	Se	ClO_4	0	667	
26[e]				1	795	
27[e]				2	910[d]	
28	Se	Te	ClO_4	0	722	5.00
29				1	843	5.26
30	Te	Te	BF_4	0	759	5.20
31				1	885	5.45
32				2	1010	5.18

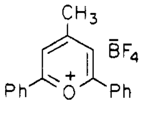
[a] Reference 8. [b] Reference 9. [c] Reference 4. [d] In CH_3CO_2H. [e] Reference 7.

Table II. *N,N*-Dialkylamino-Substituted Telluropyrylium Dyes

compd	mp, °C	λ_{max} (CH_2Cl_2), nm	log ϵ
6	135-140	525	4.85
		370	4.03
39	200-202	653	4.83
40	248-250	790	4.97
41	foam	795	5.08
		415	4.16
42	172 (dec)	818	5.02
		745	4.88
		410	3.92
45	149-152	870	5.19
		440	4.08

with saturated sodium bicarbonate gave **3**.

The telluropyrylo mono- and trimethine dyes listed in Table I were easily prepared by condensation of the 4-methylpyrylium salts **2**, **7**,[3] **8**,[4] and **9**[5] with telluropyrone **1** and aldehyde **3**, respectively, in acetic anhydride. Table I lists the long-wavelength absorption maxima for all possible chalcogenopyrylo mono- and trimethine dyes (excluding polonium). The bistelluropyrylo pentamethine dye **32** was prepared in 17% yield by the reaction of **2** with 1,3,3-trimethoxypropene and sodium acetate in acetic anhydride. In solution, this dye was unstable to light and oxygen. The bis(telluropyrylo)heptamethine dye (**32**, n = 3) was neither isolable nor detectable in all attempts to prepare it.



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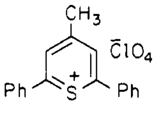

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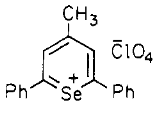

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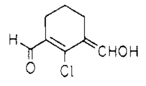
A stable bis(telluropyrylo)heptamethine dye was prepared by the condensation of 2 equiv of **2** with 1 equiv of bisaldehyde **33**.[1] The dye isolated from this reaction was **34** with a long-wavelength absorption maximum at 1190 nm (log ϵ 5.43), much longer than that of the related thiapyrylium dye **35** (1017 nm) or the selenapyrylium dye **36** (1050 nm).[5]



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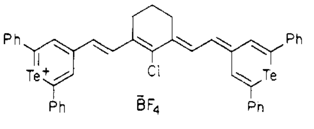

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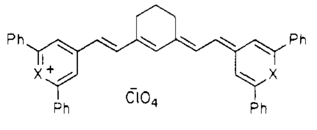
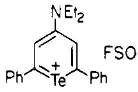


35, X=S

36, X=Se

***N,N*-Dialkylamino-Substituted Telluropyrylium Dyes.** We initially attempted the preparation of 4-(diethylamino)-2,6-diphenyltelluropyrylium fluorosulfate **37** by the reaction of diethylamine with **4** in ethanol. Instead of substitution, dealkylation of **4** occurred to give **1** and triethylammonium fluorosulfate.



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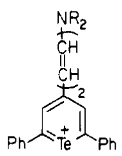

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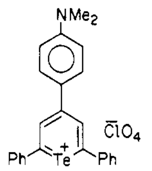

39

The next higher homologue in this series is represented by **6**, whose preparation is described above. The spectral properties of **6** are described in Table II.

The next higher homologue in this series would be the 4-(4-(dialkylamino)-1,3-butadienyl)-2,6-diphenyltelluropyrylium salts (**38**). Instead of preparing such salts, which might offer synthetic and stability problems, we prepared 4-(*p*-dimethylanilino)-2,6-diphenyltelluropyrylium perchlorate (**39**). The benzene ring should be similar to the butadiene fragment in that the longest chromophore through the aromatic ring would include two conjugated double bonds.

The dye **39** was prepared by the addition of the Grignard reagent from *p*-bromo-*N,N*-dimethylaniline to **1** to give the intermediate alcohol. Dehydration of the alcohol with acetic acid followed by anion exchange with perchloric acid gave **39** (Table II).

The styryl dye **40** (Chart I) was prepared by the condensation of **2** with *p*-(dimethylamino)benzaldehyde in acetic anhydride (Table II).

Constraining the alkyl groups of *N,N*-dialkylanilino groups gives longer wavelength absorption maxima.[6] This

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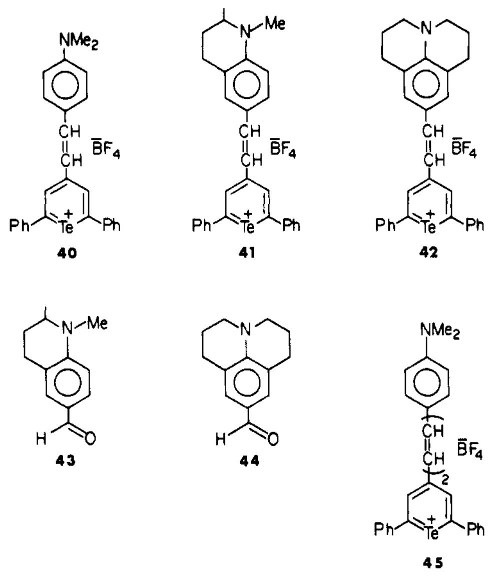
(6) (a) Barker, C.; Hallas, G. *J. Chem. Soc. B* **1969**, 1068. (b) Smith, P.; Yu, T.-Y. *J. Org. Chem.* **1952**, *17*, 1281. (c) Castelino, R.; Hallas, G. *J. Chem. Soc. B* **1971**, 793. (d) Reynolds, G. A.; Van Allan, J. A. *J. Heterocycl. Chem.* **1975**, *12*, 367.

Chart I



effect has been attributed to enforced conjugation of the nitrogen lone pair of electrons with the aromatic ring[6c] as well as steric shielding of the nitrogen lone pair of electrons.[6d] If this effect were operative with the telluropyrylium dyes, one would expect bathochromic shifts in absorption for **41** and **42** relative to **40** by constraining the nitrogen in these systems. The condensation of **2** with aldehydes **43** and **44** in acetic anhydride gave **41** and **42**, respectively (Table II).

The highest member in this series was prepared by the condensation of **2** with *p*-(dimethylamino)cinnamaldehyde in acetic anhydride to give **45** (Table II).

Dye Absorption Properties. In the bispyrylomethine and polymethine dyes, sequential bathochromic shifts were observed as the chalcogen atoms became heavier. This trend can be empirically correlated to increasing electropositive character in the heteroatoms. The trend is continued in the dialkylamino-substituted chalcogenopyrylium dyes, as shown in Table III.

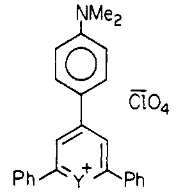
In both series of dyes, each additional ethylene of separation between the two ends of the dye gives approximately a 100-nm bathochromic shift (Tables I and II). The magnitude of this shift appears to be independent of the heteroatoms in the dye framework.

Constraining the amino group of the *N*,*N*-dialkylanilino-substituted dyes by the formation of one or two six-membered rings attached to the anilino aromatic ring causes bathochromic shifts.[6] A 5-nm shift is observed between **40** and **41**, and **42** is shifted 23 nm more bathochromic than **41**.

Conclusions

Various telluropyrylium dyes have been prepared and have longer wavelength absorption maxima than their oxygen, sulfur, and selenium counterparts. The observed bathochromic shifts can be empirically correlated with increasing electropositive character of the heteroatom. Separating the two heteroatom ends of these dyes gives approximately 100-nm bathochromic shifts for each ethylene of separation. Constraining the nitrogen atom of *N*,*N*-dialkylanilino groups also gives bathochromic shifts.

Table III. Absorption Maxima for 4-(*p*-Dimethylanilino)-2,6-diphenylchalcogenopyrylium Perchlorates



Y	λ_{max} (CH_2Cl_2), nm	electronegativity of Y
O	550[a]	3.5
S	592[a]	2.5
Se	620[a]	2.4
Te	653	2.1

[a] Reference 10.

Experimental Section

^1H NMR spectra were run on a Varian EM-390 instrument. Absorption spectra were run on a Cary 17 instrument. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer. Solvents were reagent grade materials from Kodak Laboratory Chemicals. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Aldehyde **43** was obtained from Tennessee Eastman Co. Aldehyde **44** was obtained from the Synthetic Chemicals Division of Eastman Kodak Co. Tellurium analyses were performed by atomic absorption spectroscopy.

Preparation of 2,6-Diphenyltelluropyrone (1). A 1 M solution of lithium triethylborohydride in tetrahydrofuran (120 mL) was added to tellurium powder (7.65 g, 0.06 mol) under a nitrogen atmosphere. The resulting mixture was stirred at ambient temperature for 4 h. A 1 M solution of sodium ethoxide in ethanol was prepared by the reaction of sodium metal (5.52 g, 0.24 mol) with 240 mL of absolute ethanol. The resulting solution was added to the dilithium telluride, giving a deep purple color. 1,5-Diphenyl-1,4-pentadiyn-3-one (13.8 g, 0.06 mol) was dissolved in a mixture of 150 mL of tetrahydrofuran and 150 mL of 1 M sodium ethoxide in ethanol (3.45 g of sodium metal reacting with 150 mL of absolute ethanol). The solution of 1,5-diphenyl-1,4-pentadiyn-3-one was poured as rapidly as possible into the dilithium telluride solution. Immediately after addition, the reaction vessel was placed in a 50 °C water bath, and the temperature of the bath was increased until solvent began to reflux on the sides of the reaction flask, about 30 min after addition. The water bath was removed, and the mixture was stirred overnight at room temperature. The reaction mixture was dissolved in 400 mL of methylene chloride and washed with 800 mL of water. The organic phase was separated and concentrated to an oil. The oil was dissolved in 600 mL of methylene chloride and filtered through a pad of sand to remove a slight amount of black precipitate. The methylene chloride solution was washed with 200 mL of 2% aqueous sodium chloride, dried over $MgSO_4$, and concentrated to 20 g of brownish solid. Trituration with 40 mL of butyronitrile separated a fine, yellow solid. The solid was collected by filtration to give 10.9 g (51%) of **1**: mp 126–129 °C; ^1H NMR ($CDCl_3$) δ 7.47 (s, 10 H), 7.33 (s, 2 H); λ_{max} (CH_2Cl_2) 290 nm (ϵ 19 900), 365 (12 100); mass spectrum, *m/e* 362 (M^+, $C_{17}H_{12}OTe$).

Anal. Calcd for $C_{17}H_{12}OTe$: C, 56.7; H, 3.4. Found: C, 56.8; H, 3.5.

Preparation of 2,6-Diphenyl-4-ethoxytelluropyrylium Fluorosulfate (4). 2,6-Diphenyltelluropyrone (**1**, 0.98 g, 2.7 mmol) was added to 4 mL of freshly distilled ethyl fluorosulfate. The resulting mixture was heated under nitrogen on a steam bath until solution occurred, and then the reaction vessel was placed in a 60 °C water bath for 5 min. Upon cooling, the product crystallized. Trituration with 90 mL of anhydrous ethyl ether

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(7) Sadekov, I. D.; Ladatko, A. A.; Sadekova, E. I.; Minkin, V. I. *Khim. Geterotsikl. Soedin.* **1980**, 274.

(8) Tolmachev, A. I.; Kudinova, M. A. *Khim. Geterotsikl. Soedin.* **1971**, 924.

(9) Reynolds, G. A., unpublished results.

(10) Reynolds, G. A.; Haley, N. F., unpublished results.

and filtration gave 1.27 g (96%) of 4 as a yellowish solid. Recrystallization from acetonitrile gave an air- and moisture-sensitive yellow solid: mp 208–210 °C; λ_{max} (CH_2Cl_2) 295 nm (ϵ 17 900), 385 (15 700).

Anal. Calcd for $C_{19}H_{17}FO_4STe$: C, 46.76; H, 3.51; F, 3.89; S, 6.57; Te, 26.15. Found: C, 46.21; H, 3.11; F, 4.50; S, 6.65; Te, 28.21.

Preparation of Meldrum's Acid Adduct (5). Meldrum's acid (1.44 g, 0.01 mol) was dissolved in 25 mL of pyridine. The 4-ethoxy-2,6-diphenyltelluropyrylium fluorosulfate (4, 5.0 g, 0.01 mol) was added as a powder, giving a dark red solution. Immediately after addition, the solution was concentrated under vacuum. The residue was purified by chromatography on Florisil (100/200 mesh), eluted with methylene chloride, to give 4.0 g (80%) of the adduct as a red solid: mp 199–201 °C; ^1H NMR ($CDCl_3$) δ 9.35 (s, 2 H), 7.67–7.33 (m, 10 H), 1.68 (s, 6 H); IR (KBr) 1666, 1566, 1425, 1300, 1185, 925, 698 cm^{-1}; mass spectrum, *m/e* 488 (M^+, $C_{23}H_{18}O_4Te$).

Anal. Calcd for $C_{23}H_{18}O_4Te$: C, 56.8; H, 3.7; Te, 26.3. Found: C, 56.5; H, 3.8; Te, 25.2.

Preparation of 2,6-Diphenyl-4-methyltelluropyrylium Tetrafluoroborate (2). The Meldrum's acid adduct 5 (12.0 g, 0.0247 mol) was dissolved in 240 mL of 88% formic acid. The reaction mixture was stirred on a steam bath until gas evolution ceased (about 15 min). HBF_4 (49%, 5.30 g, 0.0296 mol) was added, and the reaction mixture was concentrated under vacuum. The residue was dissolved in 40 mL of acetonitrile and filtered through a medium sintered-glass funnel into 400 mL of ethyl ether, which caused a yellow solid to precipitate. Filtration yielded 9.6 g (87%) of yellow solid: mp 187–192 °C dec; IR (KBr) 1565, 1425, 1080 (br), 763 cm^{-1}.

Anal. Calcd for $C_{18}H_{15}BF_4Te$: C, 48.5; H, 3.4; Te, 28.6. Found: C, 48.3; H, 3.4; Te, 29.1.

Preparation of (2,6-Diphenyltelluropyranylidene)acetaldehyde (3). A solution of 1.7 mL of *N,N*-dimethylthioformamide in 10 mL of acetic anhydride was added to 2.95 g (6.6 mmol) of 2,6-diphenyl-4-methyltelluropyrylium tetrafluoroborate. The mixture was heated on a steam bath for 90 min and cooled to ambient temperature. An additional 10 mL of acetic anhydride and 70 mL of ethyl ether were added. After standing overnight at ambient temperature, the reaction mixture was filtered to give 3.14 g (94.9%) of 6 as a red solid.

Anal. Calcd for $C_{21}H_{20}BF_4NTe$: C, 50.4; H, 4.0; N, 2.8; Te, 25.5. Found: C, 49.9; H, 4.0; N, 3.1; Te, 24.8.

The imminium salt (2.90 g, 5.8 mmol) was dissolved in 40 mL of acetonitrile, and 40 mL of saturated $NaHCO_3$ was added. The reaction vessel was placed in a 55 °C water bath. The bath temperature was gradually raised to 80 °C over 15 min, at which time TLC showed the hydrolysis to be complete. The reaction mixture was cooled and extracted with 200 mL of methylene chloride. The methylene chloride solution was washed once with water, dried with $MgSO_4$, and concentrated under reduced pressure. Chromatography on a Woelm silica gel column, eluted with methylene chloride, followed by 10/1 (v/v) CH_2Cl_2/acetone gave 2.02 g (90%) of 3 as an oil. The oil was dissolved in hot acetonitrile. Upon standing overnight at ambient temperature, the oil crystallized to give 1.4 g (63%) of 3 as a yellow solid: mp 77–80 °C; ^1H NMR ($CDCl_3$) δ 10.25 (d, 1 H, J = 7 Hz), 8.30 (s, 1 H), 7.42 (s, 10 H), 6.97 (s, 1 H), 5.95 (d, 1 H, J = 7 Hz); IR (KBr) 1635, 1590, 1385, 1205, 1125, 755 cm^{-1}; mass spectrum, *m/e* 388 (M^+, $C_{19}H_{14}OTe$).

Anal. Calcd for $C_{19}H_{14}OTe$: C, 59.1; H, 3.7. Found: C, 58.9; H, 3.7.

Preparation of 16. Telluropyrone 1 (0.20 g, 0.55 mmol) and 7 (0.15 g, 0.45 mmol) were slurried in 3 mL of acetic anhydride and warmed on a steam bath for 15 min. The reaction mixture was chilled, precipitating the dye. The dye was collected by filtration and recrystallized from acetonitrile to give 0.11 g (37%) of 16 as copper-bronze crystals: mp 269–271 °C; λ_{max} (CH_2Cl_2) 415 nm (ϵ 24 300), 650 (138 000); IR (KBr) 1648, 1570, 1480, 1255, 1220, 1050 (br), 760 cm^{-1}.

Anal. Calcd for $C_{35}H_{25}BF_4OTe$: C, 62.2; H, 3.7; Te, 18.9. Found: C, 62.5; H, 3.9; Te, 19.2.

Preparation of 23. Telluropyrone 1 (0.18 g, 0.50 mmol) and 8 were slurried in 2 mL of acetic anhydride and warmed on a steam bath for 15 min. Upon cooling, the dye crystallized as copper needles, which were collected by filtration to give 0.27 g (77%) of 23. Recrystallization from acetonitrile gave 0.21 g (60%) of a copper-bronze solid: mp 213–215 °C dec; λ_{max} (CH_2Cl_2) 418 nm (ϵ 21 300), 690 (128 000); IR (KBr) 1605 (w), 1550, 1498, 1220, 1180, 755, 734 cm^{-1}.

Anal. Calcd for $C_{35}H_{25}ClO_4STe$: C, 59.6; H, 3.6. Found: C, 59.3; H, 3.5.

Preparation of 28. Telluropyrone 1 (0.18 g, 0.50 mmol) and 9 (0.20 g, 0.50 mmol) were slurried in 3 mL of acetic anhydride and warmed on a steam bath for 5 min. The reaction mixture was diluted with 2 mL of acetonitrile and chilled, precipitating 0.30 g of material. Recrystallization from acetonitrile gave 0.23 g (62%) of 28 as shiny copper needles: mp 208–209 °C dec; λ_{max} (CH_2Cl_2) 425 nm (ϵ 21 200), 722 (101 000); IR (KBr) 1550, 1495, 1220, 1090, 760, 715 cm^{-1}.

Anal. Calcd for $C_{35}H_{25}ClO_4SeTe$: C, 55.9; H, 3.4. Found: C, 55.7; H, 3.5.

Preparation of 30. Telluropyrone 1 (4.80 g, 0.0133 mol) and 2 (5.28 g, 0.0118 mol) were slurried in 24 mL of acetic anhydride. The resulting mixture was warmed with stirring on a steam bath for 2 min, and a copper-bronze solid formed. Upon cooling, the crystalline mass was collected by filtration and recrystallized from acetonitrile to give 8.5 g (91%) of 30 as a copper-bronze solid: mp 225–227 °C; λ_{max} (CH_2Cl_2) 455 nm (ϵ 21 000), 759 (157 000); IR (KBr) 1550, 1495, 1220, 1100 (br), 830, 760 cm^{-1}.

Anal. Calcd for $C_{35}H_{25}BF_4Te_2$: C, 53.4; H, 3.2; Te, 32.4. Found: C, 53.1; H, 3.3; Te, 31.1.

Preparation of 17. Aldehyde 3 (0.27 g, 0.72 mmol) and 8 (0.20 g, 0.60 mmol) were slurried in 1.5 mL of acetic anhydride and warmed on a steam bath for 10 min. The reaction mixture was cooled to room temperature, and 2 mL of acetonitrile was added. A dark, crystalline material precipitated, which was collected by filtration to give 0.13 g (30%) of 17: mp 155 °C dec; λ_{max} (CH_2Cl_2) 413 nm (ϵ 22 000), 780 (225 000); IR (KBr) 1630, 1490, 1180, 1080, 765 cm^{-1}. We could not obtain a satisfactory analysis on this material.

Preparation of 24. Aldehyde 3 (0.25 g, 0.66 mmol) and 8 (0.20 g, 0.55 mmol) were slurried in 1.5 mL of acetic anhydride and heated on a steam bath for 1.5 min. Acetonitrile (2 mL) was added, and the resulting mixture was allowed to stand at room temperature. The dye was collected by filtration to give 0.10 g (25%) of 24: mp 208 °C dec; λ_{max} (CH_2Cl_2) 418 nm (ϵ 20 000), 820 (198 000); IR (KBr) 1600 (w), 1475, 1150 (br), 867, 755 cm^{-1}.

Anal. Calcd for $C_{37}H_{27}ClO_4STe$: C, 60.8; H, 3.7. Found: C, 60.5; H, 3.5.

Preparation of 29. Aldehyde 3 (0.20 g, 0.52 mmol) and 9 (0.20 g, 0.49 mmol) were slurried in 1.5 mL of acetic anhydride and warmed on a steam bath for 1.5 min. Acetonitrile (2 mL) was added, and the resulting mixture was allowed to stand at room temperature. The crystalline mass was collected by filtration to give 0.28 g (74%) of 29 as a copper-bronze solid: mp 214 °C dec; λ_{max} (CH_2Cl_2) 425 nm (ϵ 22 200), 845 (257 000); IR (KBr) 1600 (w), 1455, 1260, 1155, 863, 757 cm^{-1}.

Anal. Calcd for $C_{37}H_{27}ClO_4SeTe$: C, 57.1; H, 3.5. Found: C, 56.9; H, 3.6.

Preparation of 31. Aldehyde 3 (0.20 g, 0.52 mmol) and 1 (0.20 g, 0.45 mmol) were slurried in 1.5 mL of acetic anhydride and warmed on a steam bath for 1.5 min. Acetonitrile (2 mL) was added. Upon standing at ambient temperature, 31 crystallized from solution and was collected by filtration to give 0.23 g (61%) of 31: mp 280–282 °C; λ_{max} (CH_2Cl_2) 430 (ϵ 23 300), 885 (285 000); IR (KBr) 1495, 1450, 1255, 1150 (br), 860, 755 cm^{-1}.

Anal. Calcd for $C_{37}H_{27}BF_4Te_2$: C, 54.6; H, 3.3. Found: C, 54.6; H, 3.5.

Preparation of 32. 1,3,3-Trimethoxypropene (0.07 g, 0.5 mmol), 2 (0.45 g, 1.0 mmol), and 50 mg of sodium acetate were slurried in 3 mL of acetic anhydride. The reaction mixture was warmed for 0.5 min on a steam bath and immediately chilled in a 10 °C water bath. The crystalline mass was collected by filtration and recrystallized from acetonitrile to give 0.07 g (17%) of a brown solid: mp 231–234 °C; λ_{max} (CH_2Cl_2) 1010 nm (ϵ 150 000); IR (KBr) 1580, 1510, 1420, 1210, 1100 (br), 755, 718 cm^{-1}.

Anal. Calcd for $C_{39}H_{29}BF_4Te_2$: C, 55.8; H, 3.5; Te, 30.4. Found: C, 55.9; H, 3.6; Te, 29.9.

Preparation of 34. 4-Chloro-2,6-diformylcyclohexene (0.08 g, 0.5 mmol) and 2 (0.46 g, 1.0 mmol) were slurried in 3 mL of acetic anhydride and warmed for 0.5 min on a steam bath. The dye precipitated as a copper-bronze solid: mp 233–235 °C; λ_{max} (CH_2Cl_2) 1190 nm (ϵ 270 000); IR (KBr) 1590 (w), 1515, 1430, 1220, 1150 (br), 830, 755, 718 cm^{-1}.

Anal. Calcd for $C_{44}H_{39}BClF_4Te_2$: C, 56.2; H, 3.6, Te, 27.1. Found: C, 55.9; H, 3.5; Te, 26.5.

Preparation of 39. A solution of *p*-bromo-*N*,*N*-dimethylaniline (1.00 g, 5.00 mmol) in 5 mL of dry THF was added to magnesium turnings (0.24 g, 10 mg-atom) under an argon atmosphere. A small crystal of iodine (~10 mg) was added, and the mixture was warmed at reflux for 2 h. Telluropyrone **1** (0.20 g, 0.56 mmol) in 5 mL of dry THF was added dropwise. The mixture was stirred at reflux for an hour more. The THF solution was decanted from the magnesium turnings and concentrated. The residue was taken up in 5 mL of acetic acid, and 1 mL of 70% perchloric acid was added. The solution was added dropwise to 20 mL of cold water. The precipitate was collected by filtration and recrystallized from acetonitrile to give 0.26 g (81%) of **39** as a copper-bronze solid: IR (KBr) 1610, 1545, 1400, 1086, 810, 685 cm^{-1}.

Anal. Calcd for $C_{25}H_{22}ClNO_4Te$: C, 53.3; H, 3.9; N, 2.5. Found: C, 53.1; H, 3.7; N, 2.1.

Preparation of 40. *p*-(Dimethylamino)benzaldehyde (0.24 g, 1.6 mmol) and **2** (0.67 g, 1.5 mmol) were slurried in 3 mL of acetic anhydride. The mixture was heated on a steam bath for 4 min. The reaction mixture was cooled to ambient temperature, and 3 mL of acetonitrile was added. Chilling the solution induced crystallization of **40**, which was collected by filtration, washed with ether, and dried to give 0.63 g (72%) of shiny green needles: field desorption mass spectrum, *m/e* 492 (M^+, $C_{27}H_{24}NTe$).

Anal. Calcd for $C_{27}H_{24}BF_4NTe$: C, 56.2; H, 4.2; N, 2.4. Found: C, 56.1; H, 4.3; N, 2.5.

Preparation of 41. Aldehyde **43** (1.0 g, 5.3 mmol) and **2** (1.0 g, 2.0 mmol) in 5 mL of acetic anhydride were heated on a steam bath for 1.5 min. The reaction mixture was poured into 300 mL of ether, causing a gummy solid to precipitate. The ether was decanted, and the residue was dissolved in 5 mL of acetonitrile. The solution was diluted with 300 mL of ether, precipitating a solid. This procedure was repeated. The residue was dried under vacuum to give **41** as a friable foam (1.20 g, 90%): field desorption mass spectrum, *m/e* 532 (M^+, $C_{30}H_{28}NTe$).

Preparation of 42. 9-Formyljulolidine (**44**, 0.32 g, 1.6 mmol) and **2** (0.67 g, 1.5 mmol) were slurried in 3 mL of acetic anhydride. The mixture was allowed to stand for 4 h at ambient temperature and chilled. After 48 h, the reaction mixture was filtered, giving 0.81 g (86%) of **42** as bright copper needles: IR (KBr) 1625, 1520, 1100 (br), 1035, 758, 692 cm^{-1}.

Anal. Calcd for $C_{31}H_{28}BF_4NTe$: C, 59.2; H, 4.5; N, 2.2; Te, 20.3. Found: C, 58.8; H, 4.6; N, 2.2; Te, 20.3.

Preparation of 45. *p*-(Dimethylamino)cinnamaldehyde (0.28 g, 1.6 mmol) and **2** (0.67 g, 1.5 mmol) in 3 mL of acetic anhydride were warmed on a steam bath for 4 min. The reaction mixture was diluted with 3 mL of acetonitrile and chilled. The dye was collected by filtration, washed with ether, and dried to give 0.20 g (22%) of **45** as a maroon solid: field desorption mass spectrum, *m/e* 518 (M^+, $C_{29}H_{26}NTe$).

Anal. Calcd for $C_{29}H_{26}BF_4NTe$: C, 57.8; H, 4.3; N, 2.3. Found: C, 57.3; H, 4.2; N, 2.1.

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Registry No. **1**, 80697-46-7; **2**, 83710-66-1; **3**, 83710-67-2; **4**, 83710-69-4; **5**, 83710-70-7; **6**, 83710-72-9; **7**, 2340-23-0; **8**, 13586-30-6; **9**, 49655-20-1; **16**, 83711-01-7; **17**, 83710-81-0; **23**, 83710-75-2; **24**, 83710-83-2; **28**, 83710-77-4; **29**, 83710-85-4; **30**, 83710-79-6; **31**, 83710-87-6; **32**, 83710-89-8; **34**, 83710-91-2; **39**, 83710-93-4; **40**, 83711-03-9; **41**, 83710-95-6; **42**, 83710-97-8; **43**, 76529-12-9; **44**, 33985-71-6; **45**, 83710-99-0; 1,5-diphenyl-1,4-pentadiyn-3-one, 15814-30-9; Meldrum's acid, 2033-24-1; 1-chloro-2,6-diformylcyclohexene, 83710-73-0; *p*-bromo-*N*,*N*-dimethylaniline, 586-77-6; *p*-(dimethylamino)benzaldehyde, 100-10-7; *p*-(dimethylamino)cinnamaldehyde, 6203-18-5.

Regioselective Functionalization.[1] β Substituent Effects on the Regioselectivity of Baeyer–Villiger Oxidations of 3-Substituted 2-Azabicyclo[2.2.2]octan-5-ones (Isoquinuclidin-5-ones)

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The regioselectivity of the Baeyer–Villager oxidation of *N*-carboalkoxy-2-azabicyclo[2.2.2]octan-5-ones **1** has been found to vary markedly as a function of the identity and stereochemistry of the substituent at the 3-position and the choice of peracid oxidant. With peracetic acid predominantly bridgehead (BH)-migrated lactones **2** were obtained from the ketones **1b** (R′ = *exo*-Me, 62% BH), **1e** (R′ = *exo*-CH_2OCOPh, 84% BH (TLC), and **1g** (R = *endo*-COOMe, 66% BH (TLC) and exclusively bridgehead migration from the ketones **1a** (R′ = H), **1c** (R′ = *exo*-Ph), and **1d** (R′ = *exo*-COOMe). The ketone **1f** (R = *endo*-Me) failed to undergo oxidation with peracetic acid. When *m*-chloroperbenzoic acid was used as the oxidant, greater amounts of methylene-migrated lactones **4** were obtained in every case examined. For ketones **1d** (R′ = *exo*-COOMe, 18% BH (TLC), and **1g** (R = *endo*-COOMe, 38% BH (TLC), methylene-migrated lactones **4** were the predominant lactones found. The change in migratory preference was especially notable with **1d** (R′ = *exo*-COOMe), which afforded 100% *bridgehead*-migrated lactone **2d** with peracetic acid but 82% *methylene*-migrated lactone **4d** with *m*-chloroperbenzoic acid. Migratory aptitudes for ketones **1** could not be correlated with ^{13}C NMR shifts of the carbonyl carbons of the ketones **1** when peracetic acid was used as the oxidant, but upfield shifts for the resonances of the ketone carbonyl carbons in **1d** (R′ = *exo*-COOMe) and **1g** (R = *endo*-COOMe) did correlate with a preference for methylene migration with *m*-chloroperbenzoic acid as the oxidant.

If regioselective insertion of oxygen between the methine and carbonyl carbon atoms of isoquinuclidin-5-ones **1** of known configuration at carbon 3 were to be effected, lactones **2**, the cyclized form of piperidines **3**, would be obtained (Scheme I). Such piperidines **3**, stereoselectively functionalized at positions 2, 3, and 6, are of potential use as synthons for elaboration of alkaloid natural products.[2–4]

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[2] Krow, G.; Johnson, C. *Synthesis* **1979**, 50–51.

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