was already apparent in TLC after some minutes. This compound could be separated by chromatography, but a substantial amount could be recovered in pure state by cooling the reaction mixture overnight at 0 °C. The radical **16** slowly degrades in solution mainly yielding an unidentified brown material, but the decomposition was not complete even after 1 month at room temperature. Beside the experiments mentioned in Table I the reactions of the heteropentalenes **1a-c** were conducted in other conditions, viz., at different temperatures, in different solvents (chloroform or benzene), or quenching the reaction at a lower conversion, in the presence or in the absence of oxygen. In every case no large variation in the product distribution was observed.

Catalytic Hydrogenation of Compounds 3, 5, 6, 17, and 18. 0.050 g of compound **3** dissolved in 25 mL of ethanol was hydrogenated at room temperature and atmospheric pressure in the presence of Pd/C (10%). The solution turned from yellow to colorless while 1 mol equiv of hydrogen was absorbed. Evaporation of the solution afforded a pale yellow oil, which was crystallized from cyclohexane to yield 0.043 g (95%) of colorless needles of dimethyl 2-(pyrazolo[1,2-*a*]benzotriazol-1-yl)succinate (**8**).

The hydrogenation of compounds **5, 6, 17,** and **18** was similarly carried out to give (70-120 min, 80-90% yield) respectively compounds **9** and **20** (see Table II and Schemes I and IV).

1-(2-Aminophenyl)pyrazole. 0.285 g (15 mM) of 1-(2-nitrophenyl)pyrazole in 20 mL of ethanol was hydrogenated at room temperature and atmospheric pressure in the presence of Pd/C 10%. In 3 h the theoretical amount of hydrogen was absorbed. The solution was evaporated and the residue (0.23 g, 96%) was recrystallized from cyclohexane to yield pure 1-(2-aminophenyl)pyrazole, colorless crystals melting at 47-47.5 °C and correctly analyzing for $C_9H_9N_3$. NMR ($CDCl_3$) 6.45 (1 H, t), 7.72 (2 H, t), 4.6 (NH_2, br) δ.

Hydrolysis of Compound 7. A solution of 0.05 g of **7** in 2 mL of acetone containing 0.3 mL of 1:1 hydrochloric acid was refluxed for 10 min. After cooling and neutralization with solid sodium carbonate, the solution was filtered and evaporated. The usual workup of the residue and crystallization from cyclohexane afforded a quantitative yield of 1-(2-aminophenyl)pyrazole identical (admixed melting point and spectral properties) with the product obtained as reported above.

Addition of DMAD to Dimethyl 2-(Pyrazolo[1,2-*a*]-benzotriazol-1-yl)maleate (3). To a solution of 0.09 g (0.3 mM) of **3** in 5 mL of carbon tetrachloride was added 0.057 g (0.4 mmol) of DMAD. The gradual formation of compound **4** was monitored by TLC. After 5 days at room temperature the starting material was consumed and the solution was evaporated. Chromatography of the residue eluting with benzene-ethyl acetate (9:1) yielded 0.1 g (73%) of product **4**.

Addition of DMAD to Dimethyl Pyrazolo[1,2-*a*]benzotriazole-1,2-dicarboxylate (11). A solution of 0.055 g (0.2 mmol) of **11** and 0.142 g (1 mmol) of DMAD in 20 mL of carbon tetrachloride was refluxed for 2 days. TLC showed that a partial conversion to the bis adduct **12** had taken place. The solution was evaporated and the residue chromatographed, eluting with a benzene-ethyl acetate (9:1) mixture, to yield 0.025 g (30%) of compound **12**.

Acknowledgment. This work was supported in part by the Italian Ministry of Education.

Registry No. **1a**, 1738-57-4; **1b**, 15285-01-5; **1c**, 84681-22-1; **2**, 90460-12-1; **3**, 90460-13-2; **4**, 90460-14-3; **5**, 90481-23-5; **6**, 90460-15-4; **7**, 90460-16-5; **8**, 90460-17-6; **9**, 90460-18-7; **11**, 90460-19-8; **12**, 90460-20-1; **13**, 90460-21-2; **14**, 90460-22-3; **15**, 90460-23-4; **16**, 90460-24-5; **17**, 90460-25-6; **18**, 90460-26-7; **19** (isomer 1), 90460-27-8; **19** (isomer 2), 90460-28-9; **20**, 90460-29-0; DMAD, 762-42-5; 1-(2-nitrophenyl)-1*H*-pyrazole, 25688-17-9; 1-(2-aminophenyl)-1*H*-pyrazole, 54705-91-8.

Enamines from Iodine Oxidation of Trialkylamines. 1. Electrophilic Capture by Cationic Heterocyclic Rings

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Simple enamines derived from acetaldehyde, acetone, and propionaldehyde were generated in situ by iodine oxidation of triethylamine, *N,N*-diisopropylmethylamine, and tri-*n*-propylamine, respectively. The enamines were captured by a variety of cationic substrates including trityl, indolizinium, dithiolium, pyrylium, thiapyrylium, selenapyrylium, and tellurapyrylium cations. The use of a second equivalent of iodine (or excess) oxidized the initial products of enamine capture to various iminium dyes. These dyes were easily hydrolyzed to heterocyclylidene aldehydes and ketones. Cyclic amines such as *N*-methylpyrrolidine gave enamines derived from ring oxidation. 2-Cyano-*N,N*-dimethylethylamine generated a cyano-substituted enamine under the reaction conditions.

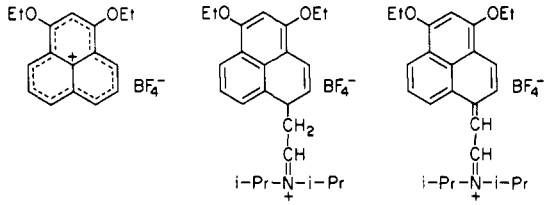
Tertiary amines have been oxidized to enamines or iminium salts by a variety of methods including photochemical transformations in the presence of suitable electron acceptors,[1] neutral permanganate,[2] iodine pentafluoride,[3] alkoxyaryltrifluoroperiodinanes,[4] trifluoroacetic anhydride,[5] hexachloroacetone,[6] and a variety of biochemical redox reagents.[7] Hydrolysis of the intermediate iminium salts or enamines to the corresponding aldehydes and ketones has been the major synthetic utility of such reactions.[8]

Capture of enamine species in the oxidation of tertiary amines has found limited success.[5,6] One example perti-

(1) (a) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141. (b) Markarian, S. A.; Fischer, H. *J. Chem. Soc., Chem. Commun.* **1979**, 1055.
(2) Rawalay, S. S.; Shechter, H. *J. Org. Chem.* **1967**, *32*, 3129.
(3) Olah, G. A.; Welch, J. *Synthesis* **1977**, 419.
(4) Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5294.
(5) Schreiber, S. L. *Tetrahedron Lett.* **1980**, *21*, 1027.
(6) Talley, J. J. *Tetrahedron Lett.* **1981**, *22*, 823.
(7) Boyer, P. D., Ed., "The Enzymes"; Academic Press: New York, 1975; Vol. 11.
(8) For a recent review, see: Bohme, H.; Viehe, H. G. "Iminium Salts in Organic Chemistry"; Wiley: New York, 1976; Vol. 9, Parts 1 and 2.

0022-3263/84/1949-2676$01.50/0

nent to our research interests was a reaction reported by Elwood[9] in which phenalenium cation 1 reacted with *N,N*-diisopropylethylamine in acetonitrile to give iminium dye 3. Presumably, 3 was formed by oxidation of 2, which would form from the reaction of 1 with *N,N*-diisopropylaminoethene.



1 2 3

This particular transformation suggested a more general reaction in which enamines produced as products in tertiary amine oxidations might be successfully trapped by highly electrophilic species such as heterocyclic or hydrocarbon cations. Obviously, further oxidation would lead to iminium dye species, and hydrolysis would lead to aldehydes and ketones.

In the Elwood reaction, cation 1, which was the most precious component of the reaction mixture, functioned as oxidant for both the amine and the initial iminium salt 2. If an inexpensive oxidant compatible with the electrophilic substrates were found to be efficient for enamine generation from tertiary amines as well as for further oxidation to iminium dyes, then such reactions would be useful for the preparation of iminium dyes and dye intermediates.

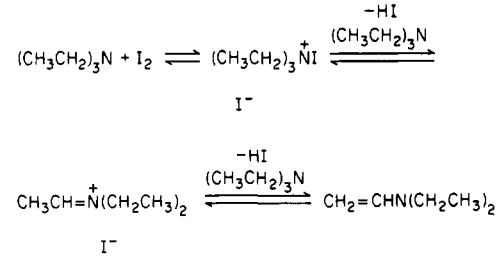
Two detailed analyses of the triethylamine–bromine complex and its chemistry have appeared recently.[10] Intermediate enamine products reacted rapidly with bromine to give dibromo- and tribromo-*N,N*-diethylacetamides, showing the ability of bromine to oxidize tertiary amines.

The ability of iodine to form complexes with tertiary amines has been recognized for many years.[11] Although such complexes have been well studied spectroscopically, they have found scant synthetic utility even though the potential for amine oxidation is quite apparent. Herein, we report the generation of enamines from tertiary amines and iodine and their reaction in situ with various cationic substrates to give iminium dyes and aldehydes and ketones.

Results and Discussion

The Iodine–Trialkylamine Complex. Conductance studies of iodine–trialkylamine complexes have shown that ionic species are present,[11] and spectroscopic studies have suggested that I_3^- is the anionic species in solution.[11b] We examined, by ^1H NMR spectroscopy, solutions of triethylamine in CD_3CN and C_5D_5N with various concentrations of I_2. Interestingly, as I_2 was added to either a CD_3CN or C_5D_5N solution of triethylamine, the only changes observed were in the methylene and methyl chemical shifts of the triethylamine. Thus, in C_5D_5N, the methylene and methyl signals shifted from δ 2.37 and 0.93, respectively, to δ 3.40 and 1.40, respectively, as up to 2 molar equiv of iodine was added. Additional iodine gave no further change. In CD_3CN, the shifts were from δ 2.50 and 1.05 for the methylene and methyl signals, respectively, to δ 3.10 and 1.30. No other signals were detected. The ^1H NMR data suggested rapidly equilibrating species, since an averaged signal was all that was observed during the addition of incremental amounts of iodine.

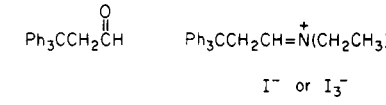
Scheme I



The spectral data gave no evidence for formation of enamines or iminium salts. However, if a small amount of water was added to the mixture of amine and iodine in CH_3CN, acetaldehyde in 20% yield and propionaldehyde in 25% yield could be isolated from triethylamine and tripropylamine, respectively, by nitrogen-purged distillation into a cold receiver. This suggested the intermediacy of iminium species or enamines. Although traces of trialkylamine in the distillate initiated rapid polymerization, the aldehydes could be identified by ^1H NMR and IR spectroscopy before polymerization.

The formation of both iminium salts and enamines can be rationalized as shown in Scheme I. The initial triethylamine–iodine complex (written in ionic form) could be dehydrohalogenated to give the iminium iodide directly. In the presence of excess base, a second deprotonation would give the enamine. Hydrolysis of either intermediate would give the appropriate aldehyde.

Enamine Capture. The capture of enamine species by electrophiles in situ would give synthetic utility to the trialkylamine–iodine complexes. Our initial attempts to capture the enamines with methyl iodide and benzyl bromide were unsuccessful. Greater success was found with a more electrophilic substrate, trityl chloride. With this substrate, reaction with triethylamine and iodine in CH_3CN followed by bicarbonate hydrolysis gave 3,3,3-triphenylpropionaldehyde (4) in about 20% yield. Presumably, addition to the enamine gave iminium salt 5, which was then hydrolyzed to 4.



4 5

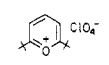
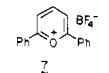
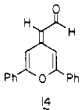
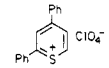
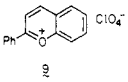
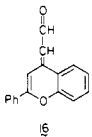
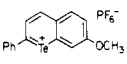
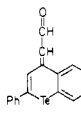
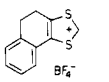
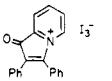
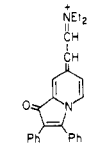
The successful addition of a carbocation to an enamine generated from triethylamine–iodine suggested that a variety of heterocyclic cations might also be useful substrates. The resulting iminium salts could be further oxidized to iminium dyes, which could then be hydrolyzed to heterocyclylidene acetaldehydes, important dye intermediates. In fact, a variety of cationic heterocyclic nuclei gave enamine addition products with triethylamine–iodine (Table I).

The yields in these reactions varied from 10% to 82%, depending upon the substrate. If reduction potential is considered to be a measure of electrophilicity, then a fairly good correlation exists between the yield of the reaction and the electrophilicity of the substrate (Table I).

Substituted Enamines. The generality of the reaction was next investigated to see if other enamines could be generated and captured. *N,N*-Diisopropylethylamine offered the possibility of generating enamines derived from

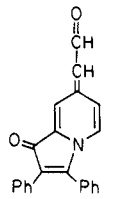
(9) Elwood, J. K. *J. Org. Chem.* **1973**, *38*, 2425.
(10) (a) Bellucci, G.; Berti, G.; Bianchini, R.; Orsini, L. *Tetrahedron Lett.* **1982**, *23*, 3635. (b) Isaacs, N. S.; Hodgson, M.; Tumi, S. O. *Ibid.* **1981**, *22*, 4139.
(11) (a) Schmulbach, C. D.; Hart, D. M. *J. Am. Chem. Soc.* **1964**, *86*, 2347. (b) Toyoda, K.; Person, W. B. *Ibid.* **1966**, *88*, 1629.

Table I. Reaction of Heterocyclic Cations with Triethylamine-Iodine

substrate	product	%yield[a]	mp, °C	E_0,V(red)[b]
 6	 13	10	oil[c]	-0.72
 7	 14	19	87-89[d]	-0.35
 8	 15	59[e]	oil	-0.21
 9	 16	38	110-111[f]	-0.16
 10	 17	37	140-141	-0.10
 11	 18	42[g]	oil	---
 12	 19	89	257.5-258	+0.04

[a] Isolated yield. [b] Platinum electrode (vs. SCE) in CH_3CN with 0.1 N tetrabutylammonium fluoroborate. [c] Reported as an air-sensitive solid in ref 13. [d] Lit.[14] mp 89–90 °C. [e] A 55:45 mixture of isomers (^1H NMR). [f] Lit.[14] mp 110–111 °C. [g] Mixture of isomers.

either a primary or secondary alkyl group. Interestingly, only products derived from reaction on the ethyl group were isolated. Thus, **10** and **12**[12] upon treatment with *N,N*-diisopropylethylamine and iodine in CH_3CN followed by hydrolysis gave aldehydes **17** and **20**, respectively.



20

When **8** was treated with *N,N*-diisopropylmethylamine[15] and iodine followed by hydrolysis, a bright yellow, crystalline solid, identified as **21**, was isolated in 47% yield. The formation of **21** can be rationalized as shown in Scheme II. Initial reaction of **8** with the enamine would give iminium salt **22**. Subsequent iodine oxidation would generate an active methyl species **23**. Deprotonation of **23** would generate a new enamine **24**, which would attack a second molecule of **8**. Iodine oxidation would give **25**, which would then be hydrolyzed to **21**.

Alternatively, the initially formed iminium salt **22** might deprotonate to generate a new enamine and add a second molecule of **8** before oxidation to **25**. Although **21** was the only isolated product when iodine was the limiting reagent in this reaction, evidence for this possibility was obtained by using **9** as the electrophilic substrate. Enamine generation and capture by 2 equiv of benzopyrylium **9** gave ketone **26**, isolated as a colorless oil in 71% yield.

Scheme II

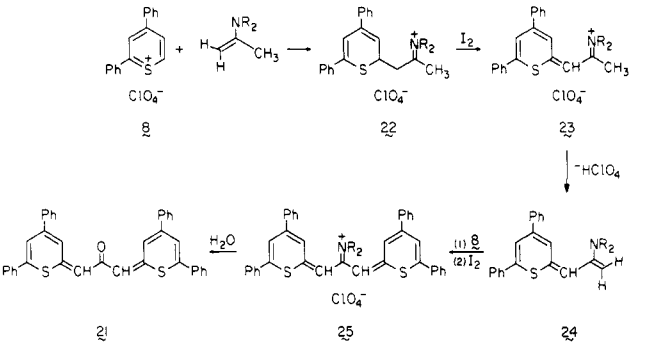
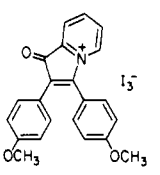
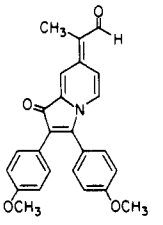
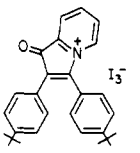
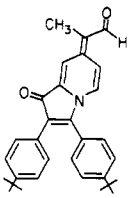
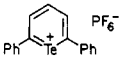
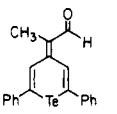
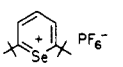
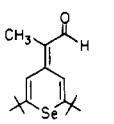
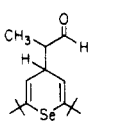
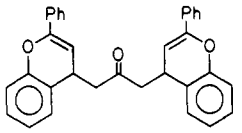


Table II. Reaction of Heterocyclic Cations with Tripropylamine-Iodine

substrate	product	%yield[a]	mp, °C
 27	 31	68	115-118
 28	 32	56	197-199
 29	 33	74	138-140
 30	 34	35	OIL
	 35	50	OIL

[a] Isolated yield.

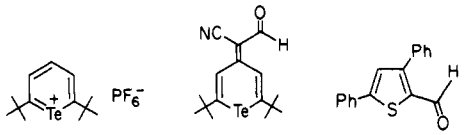
(12) Full details of indolizinium salt preparation will be reported elsewhere: Wadsworth, D. H.; Weidner, C. H., manuscript in preparation.
(13) Wilt, J. R.; Reynolds, G. A.; Van Allen, J. A. *Tetrahedron* **1973**, *29*, 795.
(14) Reynolds, G. A.; Van Allan, J. A. *J. Org. Chem.* **1969**, *34*, 2736.
(15) Krishnamurthy, S. *Tetrahedron Lett.* **1982**, *23*, 3315.



26

Enamine generation in the tri-*n*-propylamine–iodine system would place a substituent at the site of electrophilic attack. As shown by the examples in Table II, reaction with electrophilic substrates gave 2-heterocyclidenepropionaldehydes. The most interesting feature of Table II is the reluctance of the iminium salt of **35** to oxidize further.

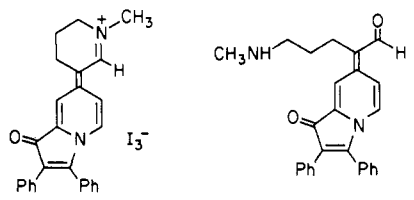
Electron-withdrawing substituents attached to the trialkylamine greatly reduced the efficiency of the reaction. Thus, 2-cyanoethyl-*N*,*N*-dimethylethylamine gave poor yields of enamine addition products upon treatment with iodine and an electrophilic substrate. In fact, the only substrate that gave isolable amounts of product was 2,6-di-*tert*-butyltellurapyrylium hexafluorophosphate (**36**), which gave cyano aldehyde **37** in 6% yield as an orange, crystalline solid.



36 37 38

Other substrates such as trityl chloride, **6**, **7**, **9**, and **11** did not react. 2,4-Diphenylthiapyrylium perchlorate (**8**) underwent a deep-seated structural rearrangement to give aldehyde **38** in quantitative yield upon treatment with iodine, 2-cyano-*N*,*N*-dimethylethylamine, and aqueous sodium carbonate in aceonitrile. Product **38** was detected in other product mixtures from the reaction of **8** with other amines, but in very small amounts.

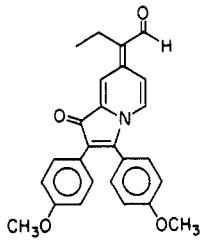
The use of cyclic amines offers some intriguing synthetic possibilities. The reaction of *N*-methylpiperidine and iodine with indolizinium salt **12** gave iminium dye **39**.



39 40

In a typical enamine reaction, the piperidine group is the dialkyl portion of the enamine with the olefinic group as a side chain. The *N*-methylpiperidine–iodine procedure gives facile entry to piperidine-based enamines. *N*-Methylpyrrolidine should behave similarly. In these systems, hydrolysis introduces both an aldehyde and an amine functionality as in **40**, which was susceptible to aminal formation and dehydration back to the iminium species.

Given the success of the trialkylamine–iodine reaction with electrophilic substrates, the actual capture of a preformed enamine by the electrophilic substrates would help substantiate the supposition that enamines are formed with trialkylamine–iodine complexes. 1-Butenylpiperidine[16,17] was added to **27** in pyridine. Hydrolysis of the initial reaction mixture and workup gave aldehyde **41**,

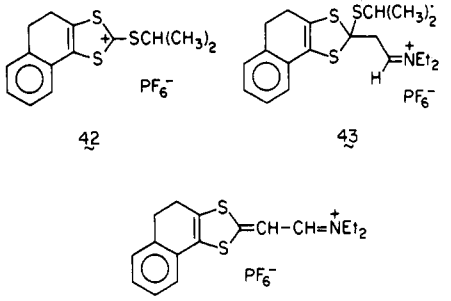


41

the expected product from enamine capture. The triiodine anion would oxidize the initial iminium salt to the fully conjugated iminium dye.

Modification and Extensions. One of the secondary reactions in this procedure is the oxidation of the initial iminium salt to the iminium dye. Excess iodine is used for this transformation. A leaving group (i.e., alkylthio) attached to the electrophilic center would allow a base-induced elimination reaction after enamine capture to give the iminium dye. In many substrates, these substituted materials are in fact intermediates used to prepare the more highly electrophilic species.[18]

The (2-isopropylthio)-substituted dithiolium salt **42** was



42 43

44

converted to aldehyde **18** in 60% yield upon treatment with triethylamine and 2 equiv of iodine. The second equivalent of iodine was consumed in converting isopropyl mercaptan to diisopropyl disulfide. Initial capture of the enamine would give iminium salt **43**. Elimination of isopropyl mercaptan to give iminium dye **44** would then give **18** upon hydrolysis. Other examples of this reaction are being investigated.

Summary and Conclusions

The complexes formed between trialkylamines and iodine can be driven to form enamines in the presence of excess base and electrophilic substrates, particularly cationic substrates. The enamines formed can bear alkyl substituents in the α or β positions and can be constrained in nitrogen-containing rings. Electron-withdrawing substituents on the olefin of the enamine diminish the reactivity of the electrophilic attack by substrates under the conditions of reaction. The initially formed iminium salts can oxidize further to iminium dyes. The iminium compounds can be hydrolyzed to aldehydes and ketones.

This reaction procedure is particularly useful for the generation of simple enamines such as those based on acetone, acetaldehyde, and propionaldehyde. These carbonyl compounds are not readily converted to enamines.

(16) Mannich, C.; Davidson, H. *Chem. Ber.* **1936**, *69*, 2106.

(17) Hellerman, L.; Garner, R. L. *J. Am. Chem. Soc.* **1946**, *68*, 819.

(18) For instance, **11** is prepared from **42** in two steps: reduction followed by elimination of isopropyl mercaptan.

The appropriate *N,N*-dialkylisopropyl-, -ethyl-, and -propylamines are readily available and allow in situ generation of the enamines. Work is in progress to expand the scope of the reaction to include the capture of alkyl halides and the use of appropriate leaving groups at the electrophilic center to allow stoichiometric use of iodine.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Boiling points are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM-390 instrument. Infrared spectra were recorded on a Beckman 4250 spectrophotometer. UV–vis spectra were recorded on a Cary 17 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer C, H, and N analyzer. Tellurium analyses were performed by atomic absorption spectroscopy. Acetonitrile was distilled from phosphorus pentoxide and stored over 3-Å molecular sieves. Tetrahydrofuran (THF) was distilled from benzophenone ketyl before use. Other solvents and reagents were used as received from Kodak Laboratory Chemicals or Aldrich.

Preparation of 3,3,3-Triphenylpropionaldehyde (4). Trityl chloride (0.50 g, 1.8 mmol) and iodine (0.91 g, 3.6 mmol) in 20 mL of CH_3CN were heated to reflux on a steam bath. Triethylamine (0.72 g, 7.2 mmol) was added in one portion. The mixture was heated at reflux for 1 min, and 5 mL of 10% aqueous sodium carbonate was added. After 5 min, the reaction mixture was poured into cold 5% hydrochloric acid (200 mL), and the products were extracted with methylene chloride (3 × 40 mL). The combined organic extracts were washed with cold 5% HCl (2 × 50 mL) and water (50 mL), dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel eluted with 2:1 (v/v) hexane/ether to give 0.10 g (16%) of **4**: mp 99–100 °C (lit.[17] mp 101 °C); ^{1}H NMR δ 9.37 (t, 1 H, J = 2.5 Hz), 7.10 (m, 15 H), 3.50 (d, 2 H, J = 2.5 Hz); mass spectrum, m/e 286 ($C_{21}H_{18}O$).

Preparation of (2,6-Di-*tert*-butylpyran-4-ylidene)acetaldehyde (13). Triethylamine (0.70 g, 7.0 mmol) was added dropwise to a boiling solution of 2,6-di-*tert*-butylpyrylium perchlorate (0.29 g, 1.0 mmol) and iodine (0.64 g, 2.5 mmol) in 10 mL of acetonitrile. The addition was isothermic. The resulting mixture was heated for 5 min on a steam bath. A solution of 2 g of K_2CO_3 in 10 mL of water was added. The mixture was heated for 0.5 h and then diluted with 100 mL of ice water. The products were extracted with ether (2 × 50 mL). The combined ether extracts were washed with water (50 mL) and cold 10% HCl (3 × 50 mL), dried over sodium sulfate, and concentrated. The residue was purified by chromatography on silica gel, eluting with 1:1 (v/v) hexane/ethyl acetate to give 0.020 g (10%) of the aldehyde as an air-sensitive oil that rapidly turned blue: ^{1}H NMR ($CDCl_3$) δ 9.78 (d, 1 H, J = 6 Hz), 6.50 (overlapping doublets, 2 H), 5.33 (d, 1 H, J = 6 Hz), 1.3 (s, 18 H); IR (CH_2Cl_2) 1670 cm^{-1}; field desorption mass spectrum, m/e 234 ($C_{15}H_{22}O_2$).

Preparation of (2,6-Diphenylpyran-4-ylidene)acetaldehyde (14). The procedure described for **13** was followed with 0.32 g (1.0 mmol) of 2,6-diphenylpyrylium fluoroborate, 0.64 g (2.5 mmol) of iodine, and 0.70 g (7.0 mmol) of triethylamine. The product was isolated in 19% yield (0.050 g) as an off-white solid: mp 87–89 °C; ^{1}H NMR ($CDCl_3$) δ 9.86 (d, 1 H, J = 6 Hz), 7.8 (m, 4 H), 7.5 (m, 6 H), 6.55 (br s, 2 H); field desorption mass spectrum, m/e 274 ($C_{19}H_{14}O_2$).

Preparation of (2,4-Diphenylthiapyran-6-ylidine)acetaldehyde (15). The procedure described for **13** was followed with 0.35 g (1.0 mmol) of **8**, 0.64 g (2.5 mmol) of iodine, and 0.70 g (7.0 mmol) of triethylamine. The product was isolated in 59% yield (0.17 g) as a yellow oil that ^{1}H NMR showed to be a 55:45 mixture of isomers: ^{1}H NMR ($CDCl_3$) δ 9.45 (d, 1 H, J = 7.7 Hz), 7.1–7.8 (m, 12 H), 6.50 (d, 1 H (major component), J = 7.7 Hz), 6.33 (d, 1 H (minor component), J = 7.7 Hz); IR (CH_2Cl_2) 1665, 1603 cm^{-1}; mass spectrum, m/e 290 ($C_{19}H_{14}OS$), 261 (M^+ – CHO). Anal. Calcd for $C_{19}H_{14}OS$: C, 78.6; H, 4.9; S, 11.0. Found: C, 78.5; H, 5.0; S, 11.2.

Preparation of (2-Phenylbenzo[*e*]pyran-4-ylidene)acetaldehyde (16). The procedure described for **13** was followed with 0.61 g (2.0 mmol) of **9**, 1.28 g (5.0 mmol) of iodine, and 2.53 g (25 mmol) of triethylamine. The crude product from chromatography was recrystallized from methanol to give 0.18 g (38%) of **16**: mp 110–111 °C; ^{1}H NMR ($CDCl_3$) δ 10.05 (d, 1 H, J = 7.5 Hz), 7.81 (s, 1 H), 7.8 (m, 3 H), 7.1–7.6 (m, 6 H), 6.20 (d, 1 H, J = 7.5 Hz); IR (KBr) 1665 cm^{-1}; mass spectrum, m/e 248 ($C_{17}H_{12}O_2$).

Preparation of (2-Phenyl-7-methoxybenzo[*e*]telluropyran-4-ylidene)acetaldehyde (17). The procedure described for **13** was followed with 0.51 g (1.0 mmol) of **10**, 0.51 g (2.0 mmol) of iodine, and 0.50 g (5.0 mmol) of triethylamine. The crude product from chromatography was recrystallized from methanol to give 0.15 g (37%) of **17**: mp 140–141 °C; ^{1}H NMR ($CDCl_3$) δ 11.43 (d, 1 H, J = 6 Hz); 8.30 (s, 1 H), 7.90 (d, 1 H, J = 9 Hz), 7.50 (m, 5 H), 7.23 (d, 1 H, J = 2.5 Hz), 7.00 (dd, 1 H, J = 2.5, 9 Hz), 6.41 (d, 1 H, J = 6 Hz), 3.92 (s, 3 H); IR (KBr) 1600, 1580, 1555 cm^{-1}; field desorption mass spectrum, m/e 392 ($C_{18}H_{14}O_2Te$). Anal. Calcd for $C_{18}H_{14}O_2Te$: C, 55.6; H, 3.6; Te, 32.7. Found: C, 55.3; H, 3.7; Te, 32.8.

Preparation of (2,3-Diphenyl-1-oxo-1*H*-indolizin-7-ylidene)acetaldehyde *N,N*-Diethyliminium Iodide (19). Diphenylcyclopropenone (2.0 g, 9.7 mmol) was dissolved in 30 mL of dioxane under an argon atmosphere. Pyridine (0.62 g, 7.8 mmol) was added, and the solution was heated for 30 min on a steam bath. Iodine (6.05 g, 0.024 mol) in pyridine was added, generating **12**. Triethylamine (7.55 g, 0.075 mol) was added. The mixture was heated for 15 min on a steam bath. The solution was diluted with methylene chloride and washed with cold, dilute HCl and then water. The organic phase was dried over $MgSO_4$ and concentrated. The product was triturated from CH_2Cl_2 solution with ligroin to give 3.25 g (82%) of **19** as a dark blue solid: mp 257.5–258 °C; UV max (CH_2Cl_2) 600 nm (ϵ 24 500). Anal. Calcd for $C_{26}H_{25}IN_2O$: C, 61.4; H, 4.9; N, 5.5. Found: C, 61.2; H, 5.0; N, 5.4.

Preparation of Bis(2,4-diphenylthiapyran-4-ylidene)-acetone (21). The procedure described for **13** was followed with 0.70 g (2.0 mmol) of **8**, 0.65 g (2.5 mmol) of iodine, and 2.5 g (22 mmol) of diisopropylmethylamine. The crude product from chromatography (silica gel eluted with 1:1 (v/v) ethyl acetate/hexane) was recrystallized from CH_3CN to give 0.26 g (47%) of **21**: mp 262–264 °C; ^{1}H NMR ($CDCl_3$) δ 7.86 (d, 2 H, J = 16 Hz), 7.8–7.2 (m, 24 H), 6.83 (d, 1 H, J = 16 Hz); IR (KBr) 1595 cm^{-1}; UV max (CH_2Cl_2) 437 nm; mass spectrum, m/e 500 ($C_{37}H_{26}OS_2$). Anal. Calcd for $C_{37}H_{26}OS_2$: C, 80.6; H, 4.8. Found: C, 80.3; H, 4.9.

Preparation of Bis(2-phenylbenzo[*e*]-4-pyranyl)acetone (26). The procedure for **13** was followed with 0.31 g (1.0 mmol) of **9**, 0.25 g (1.0 mmol) of iodine, and 0.68 g (5.0 mmol) of diisopropylmethylamine. The product (0.17 g, 71%) was isolated as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.50 (m, 4 H), 7.2 (m, 6 H), 7.4–6.8 (m, 8 H), 5.45 (dd, 2 H, J = 2.5 Hz), 4.0 (m, 2 H), 2.60 (d, 4 H, J = 7 Hz); IR (CH_2Cl_2) 1700 cm^{-1}; mass spectrum, m/e 470 ($C_{33}H_{26}O_3$), 207 ($C_{15}H_{10}O$, flavylium cation). Anal. Calcd for $C_{33}H_{26}O_3$: C, 84.2; H, 5.6. Found: C, 84.1; H, 5.6.

Preparation of Diisopropylmethylamine. Borane–dimethyl sulfide complex (10 M, 35 mL, 0.35 mol) was added dropwise to a 0 °C solution of diisopropylformamide in 75 mL of THF under nitrogen. The reaction was then warmed to reflux, and 50 mL of THF was added. After 1 h, the reaction mixture was cooled to 0 °C, 50 mL of methanol was added (vigorous evolution of gas), and the mixture was stirred for 0.5 h at ambient temperature. The reaction mixture was then acidified with gaseous HCl, and the solution was heated at reflux for 1 h. The reaction mixture was concentrated. The residue was taken up in ice water and made basic with sodium hydroxide. The amine was separated from the aqueous phase. The aqueous phase was extracted with 20 mL of ether. The combined organics were dried over sodium sulfate and filtered. Distillation gave 13.6 g (79%) of diisopropylmethylamine: bp 106–112 °C; ^{1}H NMR ($CDCl_3$) δ 2.87 (heptet, 2 H, J = 6.8 Hz), 2.10 (s, 3 H), 1.0 (d, 12 H, J = 6.8 Hz).

Preparation of 2-(2,3-Di-*p*-anisyl-1-oxo-1*H*-indolizin-7-ylidene)propionaldehyde (31). The procedure described for the preparation of **19** was followed with 2.0 g (7.5 mmol) of di-*p*-anisylcyclopropenone, 10 mL of pyridine, 10.75 g (75 mmol) of tri-*n*-propylamine, and 5.73 g (22.5 mmol) of iodine to give 3.1 g (68%) of the corresponding dipropyl iminium iodide. The iminium salt was hydrolyzed to aldehyde **31** by stirring for 0.5 h in 5 mL of pyridine and 5 mL of water. The reaction mixture was diluted with CH_2Cl_2. The organic phase was washed 3 times

with water, dried over $MgSO_4$, and filtered into ligroin. The blue solid was collected by filtration to give the aldehyde in quantitative yield: mp 115–118 °C; ^1H NMR ($CDCl_3$, mixture of cis and trans isomers) δ 10.28, 10.10 (2 s, 1 H), 8.11 (d, 1 H, J = 2 Hz), 7.40–6.65 (m, 9 H), 6.10 (dd, 1 H, J = 8, 2 Hz), 3.88 (s, 3 H), 3.78 (s, 3 H), 2.0 and 1.90 (2 s, 3 H); IR (KBr) 3010 (w), 1745 (m), 1654 (s), 1590 (s), 1505 (m), 1403 (m), 1326 (s), 1250 (s), 1166 (s), 1106 (m), 1061 (m), 1011 cm^{-1} (m); field desorption mass spectrum, m/e 399 ($C_{25}H_{21}NO_4$).

Preparation of 2-(2,3-Bis(*p*-*tert*-butylphenyl)-1-oxo-1*H*-indolizin-7-ylidene)propionaldehyde (32). The procedure for the preparation of **19** was followed with 1.0 g (3.1 mmol) of bis(*p*-*tert*-butylphenyl)cyclopropenone, 0.26 g (3.3 mmol) of pyridine, 4.50 g (31 mmol) of tri-*n*-propylamine, 2.40 g (9.5 mmol) of iodine, and 10 mL of dioxane. The reaction mixture was diluted with 250 mL of 1,2-dichloroethane, and 250 mL of 1 N $NaHCO_3$ was added. The reaction mixture was stirred for 2 h at ambient temperature. The organic phase was washed with water and dilute HCl, dried over $MgSO_4$, concentrated to 10–15 mL, and diluted with 1 L of ligroin, which precipitated a blue solid. The solid was collected by filtration and dried to give 0.80 g (56%) of **32**: mp 197–199 °C; ^1H NMR ($CDCl_3$, mixture of cis and trans isomers) δ 10.30, 10.14 (2 s, 1 H), 8.13 (d, 1 H, J = 2 Hz), 7.58–7.19 (m, 9 H), 6.10 (dd, 1 H, J = 8, 2 Hz) 1.99, 1.90 (2 s, 3 H), 1.39 (s, 9 H), 1.28 (s, 9 H); IR (KBr) 2990 (m), 1684 (m), 1615 (s), 1501 (s), 1463 (w), 1370 (m), 1312 (s), 1190 (m), 1110 (m), 1070 cm^{-1} (m); field desorption mass spectrum, m/e 451 ($C_{31}H_{33}NO_2$).

Preparation of 2-(2,6-Diphenyltellurapyran-4-ylidene)-propionaldehyde (33). 2,6-Diphenyltellurapyrylium hexafluorophosphate (**29**, 0.98 g, 2.0 mmol) and iodine (1.02 g, 4.0 mmol) in 30 mL of propionitrile were heated to near boiling. Tri-*n*-propylamine (1.45 g, 8.0 mmol) was added dropwise. The reaction mixture was heated at reflux for 2 min, diluted with a solution of 5.6 g of $NaHCO_3$ in 90 mL of water, and heated at 80 °C for 2 min. The products were extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel eluted with CH_2Cl_2 to give 0.28 g (35%) of **33** as a yellow solid: mp 138–140 °C; ^1H NMR ($CDCl_3$) δ 10.5 (s, 1 H), 8.10 (s, 1 H), 7.20 (s, 1 H), 7.33 (s, 10 H); IR (KBr) 1640, 1540 cm^{-1}; field desorption mass spectrum, m/e 402 ($C_{20}H_{16}OTe$). Anal. Calcd for $C_{20}H_{16}OTe$: C, 60.1; H, 4.0; Te, 31.9. Found: C, 60.4; H, 4.0; Te, 31.4.

Preparation of 2-(2,6-Di-*tert*-butylselenapyran-4-ylidene)propionaldehyde (34). The procedure for the preparation of **33** was followed with 3.1 g (7.7 mmol) of 2,6-di-*tert*-butylselenapyrylium hexafluorophosphate (**30**), 2.89 g (11.4 mmol) of iodine, and 4.32 g (30 mmol) of tri-*n*-propylamine. Chromatography on silica gel eluted with 10% ethyl acetate/methylene chloride gave 1.37 g (50%) of a higher R_f fraction identified as **35** and 0.83 g (35%) of **34** as a yellow oil. For **35**: ^1H NMR ($CDCl_3$) δ 9.8 (ill-defined t, 1 H, J < 1 Hz), 5.7 (t, 2 H, J = 4.5 Hz) 2.9 (m, 2 H), 1.4 (d, 3 H, J < 1 Hz), 1.2 (s, 18 H); IR (neat) 1700 cm^{-1}; field desorption mass spectrum, m/e 314 ($C_{16}H_{26}OSe$). For **34**: ^1H NMR ($CDCl_3$) δ 10.4 (s, 1 H), 7.90 (s, 1 H), 6.93 (s, 1 H), 1.83 (s, 3 H), 1.37 (s, 18 H); IR (neat) 1640, 1600 cm^{-1}; field desorption mass spectrum, m/e 312 ($C_{16}H_{24}OSe$).

Preparation of Cyano Aldehyde 37. Salt **36** (2.0 g, 4.1 mmol), iodine (3.1 g, 13 mmol), and 3-(dimethylamino)propionitrile (4.0 g, 41 mmol) were heated at 100 °C under nitrogen for 0.5 h. Sodium bicarbonate solution (3.4 g in 100 mL of water) was added, and the mixture was stirred for 0.5 h at 70 °C. The reaction mixture was cooled, and the products were extracted with CH_2Cl_2 (200 mL). The organic phase was washed with water (100 mL) and 3% HCl (2 × 100 mL), dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel, eluting with 2% acetone/CH_2Cl_2 to give 0.14 g (5%) of **37** as a yellow solid: mp 185–186 °C; ^1H NMR ($CDCl_3$) δ 9.73 (s, 1 H), 9.01 (s, 1 H), 7.60 (s, 1 H), 1.35 (s, 18 H); IR (KBr) 2210, 1760, 1670, 1600 cm^{-1}; UV max (CH_2Cl_2) 472 nm (ε 36 800), 488 (39 300); field desorption mass spectrum, m/e 385 ($C_{16}H_{21}NOTe$). Anal. Calcd for $C_{16}H_{21}NOTe$: C, 51.8; H, 5.7; N, 3.8. Found: C, 51.4; H, 5.7; N, 3.5.

Preparation of Aldehyde 18. Method A. Fluoroborate **11** (0.292 g, 1.0 mmol), iodine (0.50 g, 2.0 mmol), and triethylamine (0.60 g, 6.0 mmol) were treated as described for the preparation of **13**. Chromatography on silica gel gave the aldehyde in 42% yield as a mixture of isomers (^1H NMR).

Method B. Thiolium salt **42** (4.2 g, 10 mmol) and iodine (5 g, 20 mmol) were slurried in 75 mL of CH_3CN. Triethylamine (10 mL) was added. The mixture was stirred for 18 h at ambient temperature. The reaction mixture was concentrated, and the residue was stirred with water (100 mL), K_2CO_3 (10 g), and ethyl ether (100 mL) for 5 h. The organic phase was separated, washed with 1 N HCl, dried over $MgSO_4$, and concentrated to give a mixture of isomers (^1H NMR) of **18** (60%) and diisopropyl disulfide. For **18**: ^1H NMR ($CDCl_3$) δ 9.43, 9.40 (d, 1 H, J = 8 Hz), 7.20 (m, 4 H), 6.75, 6.77 (d, 1 H, J = 1.8 Hz), 2.80 (m, 4 H).

The aldehydes **18** were analyzed as the 2,4-dinitrophenylhydrazone, mp 194–196 °C. Anal. Calcd for $C_{19}H_{14}N_4O_4S_2$: C, 53.5; H, 3.3; N, 13.2. Found: C, 53.2; H, 3.0; N, 12.9.

Reaction of Butenylpiperidine with 27. 1-Butenylpiperidine was prepared by adding butyraldehyde (18.0 g, 0.25 mol) dropwise to a stirred mixture of piperidine (42.5 g, 0.5 mol) and K_2CO_3 (15.0 g, 0.108 mol). The reaction mixture was filtered, and the filtrate was distilled to give 16.0 g (55%) of butenylpiperidine, bp 90–91 °C (45 torr).

Di-*p*-anisylcyclopropenone (0.50 g, 1.9 mmol) and 10 mL of pyridine were heated on a steam bath for 15 min. Iodine (1.0 g, 3.9 mmol) in 5 mL of pyridine and 1.9 g (12 mmol) of butenylpiperidine were added. The reaction mixture was diluted with CH_2Cl_2 and washed with cold 1 N HCl and water. The organic phase was dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (eluted with 1:1 (v/v) ethyl acetate/CH_2Cl_2) to give 0.20 g (25%) of **41** as a mixture of isomers: mp 97–101 °C; ^1H NMR ($CDCl_3$) δ 10.1, 9.93 (br s, 1 H), 8.0 (s, 1 H), 7.3–6.5 (Ar, 10 H) 6.0 (d, 1 H), 3.80 (s, 3 H), 3.67 (s, 3 H), 2.35 (q, 2 H, J = 7 Hz), 0.90 (t, 3 H, J = 7 Hz); IR (KBr) 1690, 1610, 1550 cm^{-1}; mass spectrum, m/e 413 ($C_{26}H_{23}NO_4$).

Registry No. **4**, 90461-31-7; **6**, 35770-52-6; **7**, 15696-48-7; **8**, 30235-02-0; **9**, 6272-41-9; **10**, 84790-99-8; **11**, 90461-33-9; **12**, 86194-06-1; **13**, 41857-75-4; **14**, 20399-89-7; (*E*)-**15**, 90461-34-0; (*Z*)-**15**, 90461-62-4; **16**, 20399-90-0; **17**, 90461-35-1; (*E*)-**18**, 90461-36-2; (*Z*)-**18**, 90461-66-8; **18** (dinitrophenylhydrazone), 90461-67-9; **19**, 90461-37-3; **21**, 90461-38-4; **26**, 90461-39-5; **27**, 90461-41-9; **28**, 90461-43-1; **29**, 90461-45-3; **30**, 90461-47-5; (*E*)-**31**, 90461-48-6; (*Z*)-**31**, 90461-69-1; (*E*)-**31** (dipropyliminium iodide), 90461-63-5; (*Z*)-**31** (dipropyliminium iodide), 90461-64-6; (*E*)-**32**, 90461-65-7; (*Z*)-**32**, 90461-49-7; **33**, 90461-50-0; **34**, 90461-51-1; **35**, 90461-52-2; **36**, 90461-54-4; **37**, 90461-55-5; **38**, 20965-10-0; **39**, 90461-57-7; **40**, 90461-58-8; (*E*)-**41**, 90461-59-9; (*Z*)-**41**, 90461-68-0; **42**, 90461-61-3; Ph_3CCl, 76-83-5; Et_3N, 121-44-8; I_2, 7553-56-2; *i*-Pr_2NMe, 10342-97-9; *i*-Pr_2NCHO, 2700-30-3; *n*-Pr_3N, 102-69-2; $Me_2N(CH_2)_2CN$, 1738-25-6; pyridine, 110-86-1; di-*p*-anisylcyclopropenone, 25361-94-8; bis(*p*-*tert*-butylphenyl)cyclopropenone, 28480-27-5; diphenylcyclopropenone, 886-38-4; butanal, 123-72-8; piperidine, 110-89-4.