under argon for 40 min (or until IR indicated complete reaction of **1a**). Four equivalents of iodine or 2.2 equiv of bromine dissolved in the reaction solvent were added dropwise at room temperature, and the resulting solution was stirred for 1 h, or until the product precipitated. The triiodide salt was filtered off and washed with an acetonitrile, methanol, water mixture or recrystallized from an appropriate solvent to furnish pure product. The bromides, which occasionally proved to be hygroscopic, were dissolved in methanol directly after filtration and were treated with excess 48% fluoboric acid to furnish pure fluoborate salts.

B. Method 2. A sample of an appropriate indolizinol was dissolved in chlorobenzene, pyridine, THF, or DMF and was treated with 2 equiv of bromine. The solution was stirred for 30 min at room temperature, and the resulting solid was filtered off. Since bromine analyses of the isolated bromides were often high due to the presence of tribromide ion, fluoborates were prepared by treating water or DMF–water solutions of crude bromides with excess 48% fluoboric acid.

C. Method 3. An appropriate indolizinol was dissolved in acetone (10% w/v) and was treated with 1 equiv of pyridine. Four equivalents of iodine dissolved in acetone were added in one portion, and the mixture was stirred at room temperature for 1 h. If no precipitate was formed, the solution was treated with water until the product precipitated. The resulting triiodide salt was recrystallized from an appropriate solvent.

D. Method 4. An indolizinol and 3.1 equiv of 48% aqueous HBF_4 were dissolved in a minimum of dioxane and were treated with 1 equiv of chloranil. The resulting red solution was stirred at room temperature until the product precipitated. Filtration and washing with hot dioxane furnished pure oxoindolizinium fluoborate.

Attempted Preparation of 1,7-Dihydro-2,3-diphenyl-7-methyl-1-oxoindolizinium Bromide. A 5% solution of 0.41 g (2 mmol) of 2,3-diphenylcyclopropenone and 0.37 g (4 mmol) of 4-picoline in chlorobenzene was heated on the steam bath for 30 min. Treatment of the cooled solution with 0.35 g (2.2 mmol) of Br_2 gave a bright magenta solution that rapidly deposited a red solid. Filtration and other washing furnished 0.55 g of a crude product. Mass spectrometry (FDMS) of the crude material revealed a complex mixture containing none of the desired product.

Attempted Preparation of 3-Oxoindolizinium Salts. A. Method 1. All attempts to isolate 7-H- or 7-Me-3-oxoindolizinium salts have been unsuccessful, furnishing only dimers.

1. A 5% solution of 0.41 g (2 mmol) 2,3-diphenylcyclopropenone in 4-picoline was stirred under argon for 15 min at room temperature. The greenish solution was treated with 0.36 g (2.2 mmol) of Br_2, and the resulting red solution was allowed to stir for several minutes at room temperature. Filtration of the reaction mixture in air and washing the precipitate with isopropyl alcohol gave 0.41 g of **3a** (68% yield).

2. A 5% solution of 0.21 g (1 mmol) of 2,3-diphenylcyclopropenone in pyridine was stirred at room temperature under argon for 15 min. Bromine (0.16 g, 2 mg-atoms) dissolved in pyridine was added rapidly at room temperature, and the reaction mixture was stirred at room temperature for 10 min. The resulting solid was removed by filtration, washed with several portions of ether, and dried to furnish 0.30 g of **2a**.

B. Method 2. 3,7-Dihydro-7-*tert*-butyl-1,2-diphenyl-3-oxoindolizinium Bromide (21). A solution of 0.21 g (1 mmol) of 2,3-diphenylcyclopropenone in 5 mL of deoxygenated 4-*tert*-butylpyridine was heated under argon at 120 °C/0.5 h, cooled, and diluted with 25 mL of chlorobenzene. Bromine (0.18 g, 1.1 mmol) was added rapidly, and the solution was allowed to stand at room temperature for 2 h. The resulting orange-red precipitate was filtered off and dried to give 0.15 g (18% yield) of product: mp 283–5 °C dec; ^1H NMR (CD_3CN + 2 drops CF_3SO_3H, Me_4Si as internal standard) δ 8.97 (d, 1 H, J = 6 Hz), 8.06 (dd, 1 H, J = 6 Hz, 1.5 Hz), 7.72 (d, 1 H, J = 1.5 Hz), 7.70–7.20 (m, 10 H), 1.40 (s, 9 H); IR (KBr) 3045, 3020, 2965–2560 (broad, strong), 1710, 1620, 1375, 1205, 1160, 700 cm^{-1}; FDMS m^+/e 340 ($C_{24}H_{22}BrNO$) – (Br). Unable to obtain satisfactory analyses for C. Anal. Calcd for $C_{24}H_{22}BrNO$: C, 68.6; H, 5.3; N, 3.3. Found: C, 65.5; H, 5.4; N, 3.2.

Reduction of 1-Oxoindolizinium Ions. A. Method 1. A dilute solution of 0.10 g of **25** in methanol was treated with 0.10 g of L-ascorbic acid and several drops of water. After warming for several minutes, the yellow solution was flooded with water and filtered, furnishing 0.08 g of product. Spectral data were consistent with authentic 7-cyano-2,3-diphenyl-1-indolizinol.

B. Method 2. A solution of 0.2 g (0.5 mmol) of **20** (BF_4^-) in 2 mL of pyridine was thoroughly flushed with argon and 0.2 g (1.1 mmol) of L-ascorbic acid was added. After heating at 100 °C for 15 min, 0.2 g (2 mmol) acetic anhydride was added, and heating was continued an additional 5 min. The solution was flooded with water and was stirred to give a crude solid that was filtered and dried. Chromatography on Woelm silica gel, eluting with CH_2Cl_2, gave 0.08 g (45%) of bright yellow solid identical with authentic 2,3-diphenyl-1-indolizinyl acetate (NMR, IR).

Supplementary Material Available: X-ray diffraction data for **2a** and **3a** and analyses for **2, 3,** and **21–31** (11 pages). Ordering information is given on any current masthead page.

Indolizines. 4. Dyes Derived from Oxoindolizinium Ions and Active Methylene Compounds

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Received January 12, 1989

Dyes of a new class, incorporating the dihydro-1-oxoindolizine structural unit, have been synthesized. Oxoindolizinium ions react with active methylene compounds to give dyes (λ_{max} 560–630 nm) in high yield. The syntheses of the dihydro-1-oxoindolizinium ions and representative dyes from their reactions with active methylene compounds, along with the spectral and physical properties of the intermediates and the dyes, are presented. One example of the preparation of an isomeric dihydro-3-oxoindolizine dye is also described. The preparation of several 5-substituted indolizinols and their coupling reactions with active methylenes is described.

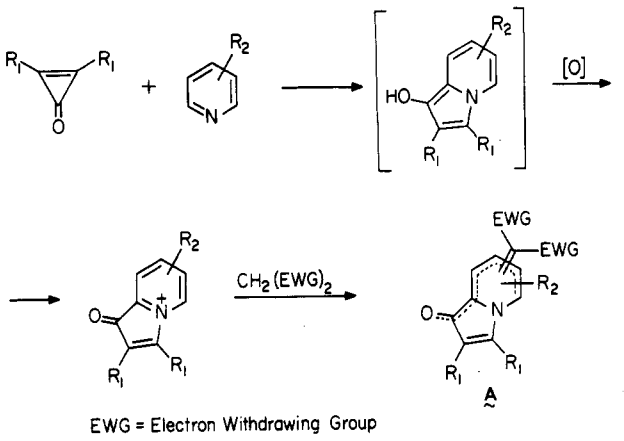
As previously reported,[1] a variety of stable oxoindolizinium salts can be prepared from appropriate cyclopropenones and pyridines. These reactive molecules can be oxidatively coupled in high yield with active methylene compounds to form a new class of dye A (Scheme I).

The dyes absorbed at unexpectedly long wavelengths, as compared with corresponding pyridinium and pyrylium analogues, leaving their structures in some doubt. Since legitimate dye structures can be drawn for substitution at **5**, **6**, **7**, or **8** on A, it was necessary to demonstrate unam-

(1) Wadsworth, D. H.; Weidner, C. H.; Nuttall, R. H.; Bender, S. L. *J. Org. Chem.*, preceding paper in this issue.

0022-3263/89/1954-3660$01.50/0

Scheme I



EWG = Electron Withdrawing Group

biguously the correct structure, as summarized in Scheme II.

Sequential treatment of **3** with Meldrum's acid, decomposition of adduct B in HCO_2H/HBF_4,[2] reduction of the resulting methyl derivative **4** with dimethylamineborane, and esterification of the methylindolizinol with pivaloyl chloride gave the identical **3** as formed from 4-picoline, diphenylcyclopropenone, and pivaloyl chloride. Dyes were assigned analogous structures based on spectral comparison.

Dyes formed from the reaction of the dihydro-1-oxoindolizinium ions with active methylene couplers gave λ_{max} between 570 and 630 nm. The choice of base used to remove a proton from the active methylene compound is of considerable importance. Pyridine consistently gave the best yields and purities, whereas bases such as triethylamine, tripropylamine, and diisopropylethylamine gave substantial amounts of byproducts in addition to the desired dyes.[3]

It was not necessary to isolate the reactive oxoindolizinium intermediates before coupling; however, the best yields and highest purity products were obtained from the purified salts. Either the triiodides (which contain the stoichiometric amount of oxidant necessary for oxidative coupling) or the fluoborates in combination with *p*-benzoquinine furnished high yields of nearly pure products.

Somewhat surprisingly, the indolizinol precursors and appropriate active methylenes, when treated with 2 equiv of benzoquinone, also furnished good yields of the corresponding dyes. In a previous publication, we showed that benzoquinone only oxidizes the indolizinol to the radical.[1] Given the observation that the addition of radicals to ions is an unlikely occurrence (see ref 4 for a discussion of this phenomenon), it must be surmised that a redox equilibrium of the radical, cation, and anion (Scheme III) provides a minute amount of cation as the reactive species.

Although we had previously reported the inability to form 5-substituted indolizinols from the corresponding 2-substituted pyridines (based on our failure to condense cyclopropenones with 2-picoline or 2-chloropyridine[5]), it has been found that pyridines with sterically small 2-substituents, when used as the reaction solvent, will react with diphenylcyclopropenone upon prolonged heating to form the corresponding 5-substituted indolizinols. Quinoline, 2-formylpyridine, and 2-cyanopyridine, for instance, all gave good yields of the corresponding indolizinols. The addition of their oxoindolizinium ions to active methylenes was accomplished by the previously described standard procedures to give **23**, **22**, and **21**.

The substituent groups in the 5-membered ring of the indolizinol were easily changed by selection of the desired cyclopropenone. Thus, **19** could be formed from pyridine, dimesitylcyclopropenone, and Meldrum's acid. Similarly, **17** was prepared from bis(2,5-dimethoxyphenyl)cyclopropenone, pyridine, and indandione. Both 6- and 8-substituted dyes were formed if 3-substituted pyridines were used for preparation of the indolizinol intermediate.[5] The less soluble 6-isomers could often be solvent separated; however, the 8-isomers could only be purified chromatographically. Table I summarizes the properties of several representative compounds.

In addition to the variety of dihydro-1-oxoindolizine dyes obtained by the above method, it is also possible to make the isomeric dihydro-3-oxoindolizine dyes.[5,6] Although isolation of dihydro-3-oxoindolizinium ions was not feasible because of extensive dimerization during oxidation, good yields of the dihydro-3-oxoindolizine dyes could be realized (Scheme IV) if the indolizinols were oxidized in the presence of the desired active methylene compound. The products were contaminated with ~10% of the corresponding 1-isomer, however, often requiring difficult chromatographic separations due to similar elution rates with a variety of solvents. Compounds **5** and **6**, however, had remarkably different solubilities in methanol, hence a slurry of the crude dye mixture in methanol could be merely filtered to give pure **5** as the precipitate with **6** in the filtrate.

Conclusions

A variety of novel dyes can be easily prepared from 1- and 3-oxoindolizinium ions and active methylenes. The method is very versatile for analogue formation, given the wide variety of cyclopropenone, pyridine, and active methylene starting materials. The dyes show exceptionally long wavelength absorptions for their chromaphore size, have good heat and light stability, and can be tailored for many desired physical and spectral properties. Dyes **6** and **5** are the basis of the corresponding 7-methyl-1- and -3-oxoindolizinium ions, which are themselves useful dye intermediates. The oxoindolizinium ions react with many photographic couplers to form interesting long-wavelength dyes.[6]

Experimental Section

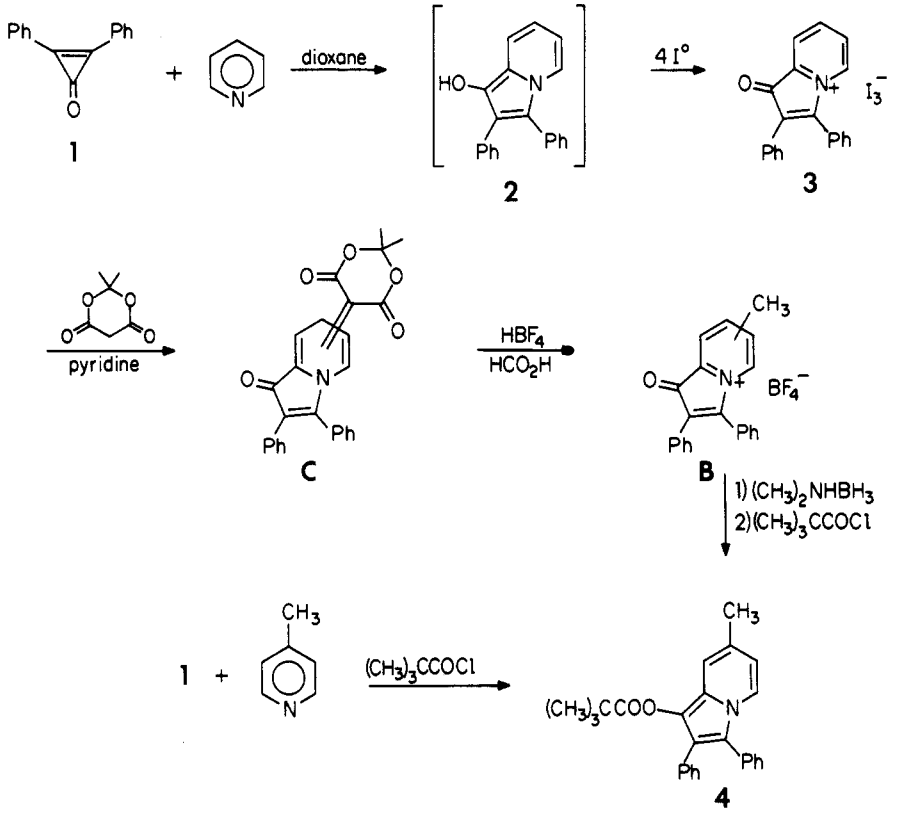
Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were run on a Varian EM-390 90-MHz spectrometer with Me_4Si as internal reference. UV–visible spectra were run on a Carey 17 spectrophotometer, with CH_2Cl_2 as solvent. Infrared spectra were taken on a Beckman IR 4250 spectrophotometer. Field-desorption mass spectra were obtained on a Varian MAT-731 mass spectrometer. Microanalyses were done by the Analytical Sciences Division of Kodak's Research Laboratories.

I. Preparation of Dye Intermediates. A. Oxoindolizinium Ions. Except as noted, all oxoindolizinium ions were prepared by methods described in ref 5.

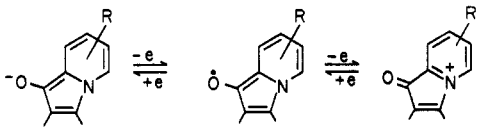
B. Preparation of 5-Substituted Indolizinols. 1. Preparation of 5-Cyano-2,3-diphenyl-1-indolizinol. A solution of 2.04 g of **1** in 5 mL of 2-cyanopyridine was heated at 95 °C for 18 h and poured with rapid stirring into a large excess of water acidified with ascorbic acid. The resulting precipitate was filtered

(2) Van Allen, J. A.; Reynolds, G. A. *J. Heterocycl. Chem.* **1971**, *8*, 803.
(3) Wadsworth, D. H.; Detty, M. R.; Murray, B. J.; Weidner, C. H.; Haley, N. F. *J. Org. Chem.* **1984**, *49*, 2676.
(4) Pross, A. *J. Am. Chem. Soc.* **1986**, *108*, 3537.
(5) Wadsworth, D. H.; Bender, S. L.; Weidner, C. H.; Smith, D. L.; Luss, H. R. *J. Org. Chem.* **1986**, *51*, 4639.
(6) Wadsworth, D. H.; Bender, S. L.; Luss, H. R. *Tetrahedron Lett.* **1981**, *22*, 3569.
(7) Fletcher, G. L.; Bender, S. L.; Wadsworth, D. H. US 4577024 U.S.

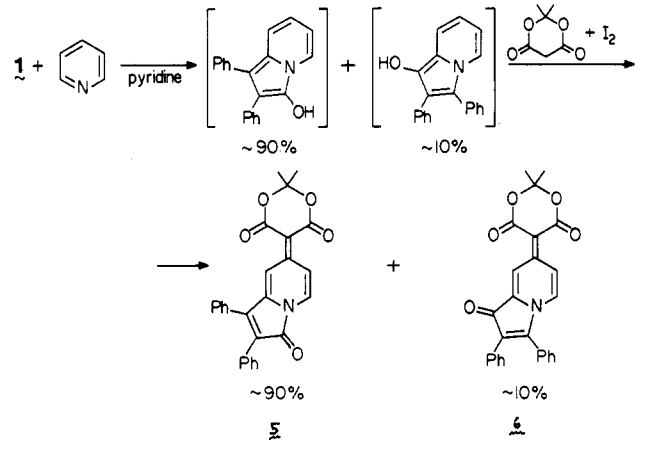
Scheme II



Scheme III



Scheme IV



off, washed with water/ascorbic acid, and air-dried to furnish 2.9 g of crude product. Crystallization from methanol gave 2.4 g of pure product (69% yield).

2. Preparation of 2,3-Diphenyl-5-formyl-1-indolizinol. A solution of 6.18 g (0.015 m) of 1 was dissolved in 20 mL of distilled, deoxygenated 2-pyridinecarboxaldehyde and heated on the steam bath under argon for 3 h. The reaction mixture was poured into 30 mL of glacial acetic acid, stirred until precipitation was complete, filtered, and washed with acetic acid to furnish 4.6 g (50%) of chromatographically pure product.

II. Compounds Used in Structure Proof of Dyes (Scheme II). A. 1,7-Dihydro-2,3-diphenyl-7-methyl-1-oxoindolizinium Tetrafluoroborate (C) (Methyl in 7-Position). A mixture of 6 (0.5 g, 1.17 mmol) and 10 mL of HCO_2H was heated at 100 °C for 30 min. The reaction mixture was allowed to cool, and 0.5 g of 50% aqujeous HBF_4 (excess) was added. The volatiles were removed on a rotary evaporator, and the solid remaining was triturated with Et_2O and filtered. This was used in the next reaction without further purification: yield 0.45 g (98%); mp 190 °C dec; ^1H NMR (TFA) δ 8.60 (d, 1 H, J = 6 Hz), 8.26 (d, 1 H, J = 1.5 Hz), 8.07 (dd, 1 H, J = 6, 1.5 Hz), 7.68 (m, 5 H), 7.40 (s, 5 H), 2.88 (s, 3 H); IR (KBr) 1740, 1650, 1470, 1150–1000 (BF_4^-) cm^{-1}; field-desorption mass spectrum, m/e 298 ($C_{21}H_{16}BF_4NO - BF_4$).

Anal. Calcd for $C_{21}H_{16}BF_4NO$: C, 65.4; H, 4.2; N, 3.6. Found: C, 64.9; H, 4.4; N, 3.6.

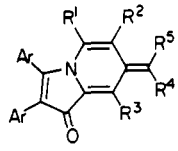
B. 2,3-Diphenyl-7-methyl-1-indolizinyl Pivalate (4). From 4-Picoline/Diphenylcyclopropenone. A solution of *p*-dioxane (15 mL) and 2,3-diphenylcyclopropenone (0.21 g, 1 mmol) was thoroughly flushed with argon. 4-Picoline (0.1 g, 1.07 mmol) was added, and the mixture was refluxed under argon for 40 min. The mixture was cooled, pivaloyl chloride (0.24 g, 2 mmol) was added, and the mixture was stirred under argon for 15 min. Evaporation of volatiles and chromatography on Woelm silica gel, eluting with CH_2Cl_2, was used for purification. Collection of the pale yellow, front-running fraction and evaporation of volatiles gave 0.30 g (77%) of product. An analytical sample was recrystallized from hexanes: mp 188.5–189.5 °C; ^1H NMR ($CDCl_3$) δ 8.74 (d, 1 H, J = 7.5 Hz), 7.34 (s, 5 H), 7.22 (s, 5 H), 6.80 (d, 1 H, J = 1.5 Hz), 6.19 (dd, 1 H, J = 7.5, 1.5 Hz), 2.29 (s, 3 H), 1.37 (s, 9 H); IR (KBr) 1760, 1610, 1345, 1101, 768, 739, 700 cm^{-1}; field-desorption mass spectrum, m/e 383 ($C_{26}H_{25}NO_2$).

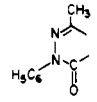
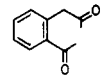
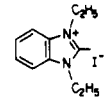
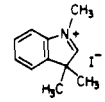
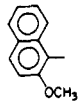
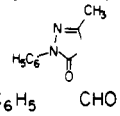
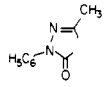
Anal. Calcd for $C_{26}H_{25}NO_2$: C, 81.4; H, 6.6; N, 3.7. Found: C, 81.7; H, 6.8; N, 3.7.

From Indolizinium Ion C. A mixture of C (0.2 g, 0.78 mmol) and 1,2-dichloroethane (15 mL) was flushed thoroughly with argon. Dimethylamineborane (0.09 g, 1.6 mmol) was added in one portion, and the mixture was stirred at room temperature for 1.5 h under argon. Pivaloyl chloride (0.19 g, 1.6 mmol) and sodium bicarbonate (~m0.2 g) were added, and the mixture was stirred for 0.5 h at room temperature. Washing with H_2O (3 × 25 mL), drying the organic layer over $MgSO_4$, and evaporation gave a crude product, which was purified by column chromatography as above: yield 0.21 g (70%); mp 187–188 °C; spectral data as above.

Anal. Calcd for $C_{26}H_{25}NO_2$: C, 81.4; H, 6.6; N, 3.7. Found: C, 81.3; H, 6.8; N, 3.5.

Table I. Active Methylene Dyes



no.	Ar	R^1	R^2	R^3	R^4	R^5	visible $\lambda_{max}(CH_2Cl_2)$, nm/log E	yield, %	mp, °C/solvent
6	C_6H_5	H	H	H			560/4.28	97	268-70/toluene
7	C_6H_5	H	H	H	CH_3CO	CH_3CO	600/4.19	93	177-8/toluene
8	C_6H_5	H	H	H	CN	CN	590/4.24 555/4.25	54	228-9/cyclohexane
9	C_6H_5	H	H	H	CN	COO*t*-Bu	590/4.28 553/4.27	95	191-2/cyclohexane
10	C_6H_5	H	H	H	CF_3CO	CO*t*-Bu	603/4.27 570/4.26	95	116-8/cyclohexane
11	C_6H_5	H	H	H	*t*-BuCO	$CONHC_6H_5$	570/4.22	92	210-1/cyclohexane
12	C_6H_5	H	H	H			580/4.38	94	>300/pyridine
13	C_6H_5	H	H	H			630/4.20	91	261-2/toluene
14	C_6H_5	H	H	H			590/4.40	89	279-80/pyridine
15	C_6H_5	H	H	H	H		630/4.66	100	dec
16	C_6H_5	H	H	H	H		640/4.45	100	dec
17	$2,5-(CH_3O)_2C_6H_3$	H	H	H			615/4.23	85	
18		H	H	H	CH_3CO	CH_3CO	566 600/4.17	91	
19	$2,4,6-(CH_3)_2C_6H_3$	H	H	H			598/4.24	100	dec
20	$4-CH_3OC_6H_4-$	H	H	H			570/4.22	90	
21	C_6H_5	CN	H	H	CH_3CO	CH_3CO	580/4.37	71	
22	C_6H_5	CHO	H	H	CH_3CO	CH_3CO	570/4.22	70	
23	C_6H_5	$-C_6H_4-$		H	CH_3CO	CH_3CO	710/		>300/CH_2Cl_2 C_6H_{14}
24	C_6H_5	H	CH_3	CH_3			625/4.01	100	
25	C_6H_5	H	CH_3	H	C_6H_5	CHO	598/4.23	80	dec
26	C_6H_5	H	H	CH_3	C_6H_5	CHO			
27	C_6H_5	$-C_6H_4-$		H			605/4.18	100	>300/CH_2Cl_2 C_6H_{14}
28	C_6H_5	CHO	H	H	C_6H_5	CHO	570/4.24	23	

III. Dihydro-1-oxoindolizine Dyes. A. General Method 1. An appropriate active methylene compound dissolved in pyridine was treated with a pyridine solution of an equimolar amount of the desired triiodide B. The brightly colored solution was stirred at room temperature for 1 h and poured into water. The resulting precipitate was filtered off, washed with water, and air-dried to furnish good yields of product of good purity. In general, the use of other convenient solvents is not detrimetnal to the reaction if sufficient pyridine is present to react with the HI generated in the reaction. If the solvent is not water miscible, product is precipitated in ether or ligroin, filtered off, and washed with water to remove the pyridinium iodide.

If oxoindolizinium ions other than triiodides were used, an equivalent of benzoquinone or iodine was necessary to complete the reaction, although up to 50% yields of dye could be formed without additional oxidant.

B. General Method 2. The desired indolizinol, prepared by one of the previously described methods, was mixed with an equimolar amount of an appropriate active methylene compound and an excess of pyridine. The resulting solution was mixed with a dioxane solution of a molar equivalent of benzoquinone or iodine, stirred at room temperature for 1 h, and poured into water. The resulting dye was filtered off, washed thoroughly with water to remove hydroquinone or pyridinium hydroiodide, and air-dried to furnish 90–100% yields of product of good purity, as determined by thin-layer chromatography/silica gel.

C. A 20% solution of 2.06 g (10 mmol) of diphenyllcyclopropenone in 11 mL of quinoline was heated at 80 °C under argon for 50 min until IR indicated all of the cyclopropenone had reacted. The heat was removed, and the reaction mixture was treated sequentially with a 2-fold excess of Meldrum's acid and 4 equiv of iodine/12 mL of pyridine. After 40 min (590-nm absorption stops increasing) the reaction mixture was diluted with CH_2Cl_2 and washed five times with 1 N HCl. Evaporation of the organic layer furnished 5.8 g (>100% yield) of a crude blue solid shown by NMR to contain approximately 50% of the desired adduct. Crystallization from methanol gave pure product, as determined by microanalysis or thin-layer chromatography, as noted below.

IV. Dihydro-3-oxoindolizine Dyes. A. 5-(3,7-Dihydro-1,2-diphenyl-3-oxoindolizin-7-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (5). Pyridine (10 mL) was thoroughly purged with argon, 2,3-diphenylcyclopropenone (0.41 g, 2 mmol) was added, and the mixture was stirred under argon for 0.5 h at room temperature. Addition of 2,2-dimethyl-1,3-dioxane-4,6-dione (0.32 g, 2.2 mmol) followed by a solution of I_2 (1.01 g, 4 mmol) in 10 mL of pyridine gave a red solution. The solution was poured into 200 mL of 1 N HCl, which precipitated the crude dye: 0.73 g (86%) after filtration, washing, and drying. This crude mixture of **5** and **6** was dissolved in a minimum of CH_2Cl_2 and poured into 100 mL of MeOH. The CH_2Cl_2 was boiled off, and 0.55 g (65%) of **5** was obtained after filtration and drying: mp 275–277 °C dec; $\lambda_{max}^{CH_2Cl_2}$ 442 nm; $\epsilon_{max}^{CH_2Cl_2}$ 4.30. Thin-layer chromatography indicated a trace of **6** as the only contaminant.

Acceptable micro analytical data were difficult to obtain on many of the tabulated compounds because of their tendency to tenaciously retain solvent. All materials gave correct m/z results and **6–14**, **19**, **20**, **25**, and **26** gave microanalytical results within 0.5% C, 0.2% H, N. Missing melting points and spectral properties for several compounds were not available since compounds were used as intermediates without obtaining the analytical data. The compounds were included in the table for comparative purposes.

Registry No. **1**, 886-38-4; **4**, 105019-60-1; **5**, 86193-36-4; **6**, 86222-47-1; **7**, 86222-48-2; **8**, 86222-46-0; **9**, 121030-45-3; **10**, 86193-12-6; **11**, 86193-10-4; **12**, 86193-08-0; **13**, 121030-46-4; **14**, 121030-47-5; **15**, 121030-48-6; **16**, 121030-49-7; **17**, 121030-50-0; **18**, 121030-51-1; **20**, 86193-13-7; **21**, 121030-52-2; **22**, 121030-53-3; **23**, 121030-54-4; **24**, 121030-55-5; **25**, 121030-56-6; **26**, 121030-57-7; **27**, 121030-58-8; **28**, 121030-59-9; 5-cyano-2,3-diphenyl-1-indolizinol, 121030-41-9; 2-cyanopyridine, 100-70-9; 2,3-diphenyl-5-formyl-1-indolizinol, 121030-42-0; 2-pyridinecarboxaldehyde, 1121-60-4; 2,3-diphenyl-7-methyl-1-oxo(1*H*)-indolyimium tetrafluoroborate, 121030-44-2; 4-picoline, 108-89-4; pyridine, 110-86-1; 2,2-dimethyl-1,3-dioxane-4,6-dione, 2033-24-1.

Reaction of Carbamoyl-*S*-benzylcarbodithiolate with Dipolarophiles

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Received June 30, 1988

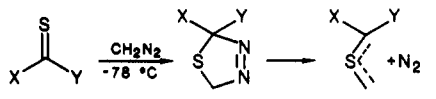
Tetrahydrothiophenes are obtained when dithiooxamide *S*-methylide is allowed to react with dipolarophiles. The reaction mechanism probably involves a nonconcerted pathway.

Introduction

Thiocarbonyl ylides can be successfully used in the synthesis of tetrahydrothiophenes.[1] There are several methods for obtaining thiocarbonyl ylides;[2] however, the mildest conditions are the ones used by Huisgen[3] in which a thiocarbonyl compound is treated with diazomethane to yield a thiadiazoline; this extrudes N_2 to yield the desired thiocarbonyl ylide (Scheme I).

However, only a few thioketones or thioaldehydes are readily available materials, owing to the instability of the C=S double bond. We have been searching for different stable thiocarbonyl compounds.

Scheme I



The easiest way to obtain stable thiocarbonyl compounds is to conjugate the C=S bond with heteroatoms. In fact, many of these compounds are stable, as thioesters or trithiocarbonates. However, conjugation of the C=S bond with the nonbonding electrons of the heteroatoms raises the LUMO of the thiocarbonyl compound, which turns the reaction with the diazoalkane into a slow process, and the rate of extrusion of N_2 is considerably enhanced. Under these conditions dithiolanes are the reaction products,[4] because the ylide undergoes cycloaddition with the

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