spectrum (70 eV) *m/e* (rel intensity) 260 (0.85), 214 (48), 213 (79), 182 (10), 118 (11), 117 (14), 110 (9), 109 (100), 105 (44), 104 (39), 103 (115), 93 (10), 91 (7), 77 (10).

The residue after filtration was stripped of solvent and distilled to give a 3.48-g (16%) sample which was redistilled and a fraction of 1.27 g, bp 103–107 °C (0.07 mm), was taken: NMR ($CDCl_3$) δ 3.66 (doublet, 6, $POCH_3$), 5.75 and 6.26 (pair of doublets, 1.05, $PC{=}CH_2$), 7.30 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 214 (5), 213 (53), 212 (39), 118 (47), 117 (60), 116 (58), 115 (32), 110 (19). 109 (9), 105 (29), 104 (100), 103 (54), 102 (17), 93 (44), 91 (20), 77 (68).

Control with Diethyl α-Styrylphosphonate (2b). Triethyl phosphite (0.01 mol) and equimolar amounts of **2b** and **3b** were sealed in an NMR tube and heated at 50 °C for 2 h. The NMR spectrum was that of the individual components and remained unchanged after standing 1 month.

Control with 1-Dimethoxyphosphinyl-1-phenyl-2-nitroethane (5a). A 0.35-g sample of **5a** was mixed with 2 mL of trimethyl phosphite and 5 mL of DME and heated at 50 °C for 20 h. The solvent was removed under vacuum and the mixture solidified on standing. The solid was mixed with a small amount of ether and filtered to give 0.31 g (88%) of unchanged **5a**. There were no signals in the NMR spectrum for either **2a** or **6a**.[3]

Control with 2-Dimethoxyphosphinyl-2-methoxy-2-phenylacetaldehyde Oxime (6a). A 0.5-g sample of **6a** was mixed with 2 mL of trimethyl phosphite and 5 mL of DME and heated at 50 °C for 20 h. The low boiling materials were removed by vacuum distillation to leave a 0.55-g residue which on crystallization gave 0.35 g of unchanged **6a**. The remainder was shown by NMR to be free of **2a** and **5a**.

Synthesis of Diethyl α-Styrylphosphonate (2b). Diethyl α-styrylphosphonate (**2b**) was prepared from 3.68 g (20 mmol) of α-styrylphosphonic acid,[12] 7.15 g (43 mmol) of silver nitrate, and 2.24 g (40 mmol) of ethyl iodide according to the procedure of Werbel et al.[13] Distillation gave 3.25 g (67%) of **2b**, bp 108–112 °C (0.5 mm), whose IR and NMR spectra were identical in every respect with those of **2b** prepared from β-nitrostyrene.

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Registry No.—**1**, 102-96-5; **5a**, 37909-64-1; **5b**, 37909-65-2; ethyl nitrite, 109-95-5; propyl nitrite, 543-67-9; 1-nitropropane, 108-03-2; 1-propanol, 71-23-8.

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An Improved Procedure for the Addition of Dichloroketene to Unreactive Olefins[1]

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The cycloaddition of dichloroketene to hindered or unreactive olefins has, in the past, enjoyed only limited success. Not only are a large excess of the olefin or acid halide necessary, but the yields are often low. Most of these problems have now been overcome by dehalogenating trichloroacetyl chloride with activated zinc in the presence of the olefin and phosphorus oxychloride. Under these conditions, dichloroketene can even be added to tri- and tetrasubstituted olefins. An important feature of this procedure is that often only a small (5%) excess of acid chloride is necessary. The phosphorus oxychloride may function by complexing the zinc chloride produced in the reaction. Although styrene, which is normally polymerized by zinc salts, is transformed in good yield to the cyclobutanone adduct by this method, the very sensitive olefins dihydropyran and cyclopentadiene fail to yield isolable dichlorocyclobutanones.

Introduction

The cycloaddition of dichloroketene[2] to reactive olefins is a useful method for the synthesis of cyclobutanones. Certain of these dichlorocyclobutanones, for example, the adducts of indene[3] and various cyclopentadienes,[2a,4] are valuable precursors of tropolones. Many other synthetically useful transformations of cyclobutanones have been described[5] recently. Since dichloroketene is unstable and polymerizes readily, it is generated in situ in the presence of the olefin by (1) the dehydrohalogenation of a dichloroacetyl halide with an amine like triethylamine, or (2) the dehalogenation of a trichloroacetyl halide (usually trichloroacetyl bromide) with activated zinc (see eq 1 and 2). Both methods have certain

$$Cl_2CH\overset{O}{\overset{\|}{C}}X \xrightarrow{Et_3N} Cl_2C{=}C{=}O + Et_3\overset{+}{N}H\overset{-}{X} \quad (1)$$

$$Cl_3C\overset{O}{\overset{\|}{C}}X \xrightarrow{ZnCu} Cl_2C{=}C{=}O + ZnCl_2 \quad (2)$$

disadvantages. Tertiary amines and/or ammonium salts catalyze the decomposition of dichloroketene.[2b] The zinc dehalogenation method suffers from the fact that certain olefins, such as styrene, cyclopentadiene, or dihydropyran, are polymerized by zinc salts.[2b] With either method, a large excess of the olefin or acid halide is generally used.[2] Even with an excess

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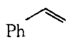
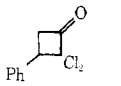
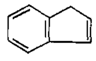
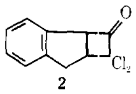
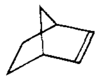
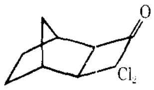
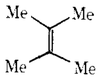
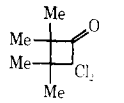
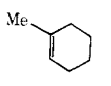
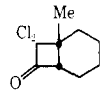
Table I. Generation of Dichloroketene from Trichloroacetyl Chloride and Activated Zinc in the Presence of Selected Olefins and Phosphorus Oxychloride

Olefin	Registry no.	Product	Registry no.	Yield, %[a]	Previous yield, %
	100-42-5	 1	13866-28-9	87	19[2b]
	95-13-6	 2	7316-61-2	81	12[3] 41[3c]
	498-66-8	 3	57774-86-4	70	10[2d]
	563-79-1	 4	66239-90-5	41	—
	591-49-1	 5	52809-65-1	79	(not reported)[11]
6	15910-23-3	7	26612-84-0	78	75[6]
8	66288-85-5	9	66239-91-6	72	—

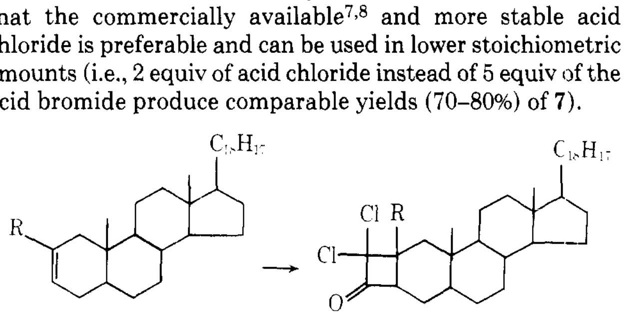
[a] Yield refers to purified product; yield of crude product was higher.

of reagent, however, yields of dichlorocyclobutanones from hindered olefins are often low or nil.

In cycloadditions to unreactive olefins, for example 2-cholestene (**6**) or 4-*tert*-butylcyclohexene, we[2e,6] have found it necessary to generate dichloroketene via the zinc dehalogenation procedure. The use of trichloroacetyl bromide, which fumes in the air and has to be freshly prepared and distilled at 135–136 °C, often gave irreproducible results.

Results and Advantages

Although most reports in the literature[2] in which the dichloroketene is generated by the zinc dehalogenation procedure have utilized trichloroacetyl bromide, we have now found that the commercially available[7,8] and more stable acid chloride is preferable and can be used in lower stoichiometric amounts (i.e., 2 equiv of acid chloride instead of 5 equiv of the acid bromide produce comparable yields (70–80%) of **7**).



6, R = H 7, R = H
8, R = CH$_3$ 9, R = CH$_3$

Our more notable finding is that the addition of phosphorus oxychloride to the reaction mixture of zinc, trichloroacetyl chloride, and the olefin facilitates product isolation in all cases and leads to a dramatic improvement in yield in several cases (see Table I). Some advantages derived from the presence of $POCl_3$ are enumerated below.

When trichloroacetyl chloride was added to a stirred suspension of activated zinc and an olefin in ether, the reaction was quite exothermic and the solution refluxed appreciably. With phosphorus oxychloride present, however, the reaction mixture did not exhibit exothermicity.

The isolation of volatile dichlorocyclobutanones can usually be carried out by distillation from the reaction mixture, but purification of solid dichlorocyclobutanones sometimes presents a problem. This was especially evident in the trichloroacetyl bromide-activated zinc reactions of 2-cholestene (**6**) or indene. Crude products were sometimes dark viscous oils which were difficult to crystallize. With the trichloroacetyl chloride–phosphorus oxychloride method, however, crude products were much cleaner, usually being off-white solids.

With many reactive olefins like styrene or indene, it was sufficient to employ a 5% excess each of trichloroacetyl chloride and phosphorus oxychloride and a 10% excess of activated zinc. This is in contrast to literature[2] procedures for dichloroketene additions by either the dehalogenation or dehydrohalogenation method, in which a large excess of either olefin or acid chloride is usually employed. Product yields are significantly better in the presence of phosphorus oxychloride; for instance, the adduct of styrene was obtained in 87% yield, even though this olefin reportedly[2b] polymerizes in the presence of zinc salts.

Dichloroketene adducts of trisubstituted olefins were obtained in good yields (see Table I) and the dichloroketene adduct (**4**) of 2,3-dimethyl-2-butene was isolated in fair yield (41%). This example apparently represents the first successful addition of dichloroketene to a tetrasubstituted olefin. Thus the trichloroacetyl chloride–phosphorus oxychloride-activated zinc procedure seems to be the method of choice for the reaction of dichloroketene with unreactive olefins although a longer reaction time (15–20 h) is required.

However, the method was not applicable to enol ethers prone to polymerization by Lewis acids, namely dihydropyran and ethyl vinyl ether, and for the very reactive cyclopentadiene. With these olefins, only dark tars were isolated from the reaction mixtures. Also, the very electrophilic olefin acrylonitrile yielded no isolable cycloadduct.

Discussion

The role of the phosphorus oxychloride in the dichloroketene reactions appears to be that of complexing the $ZnCl_2$ produced in the reaction. In fact, $POCl_3$ is known[9] to form addition complexes with $ZnCl_2$ as well as with many Lewis acids, such as $AlCl_3$, BBr_3, $SnCl_4$, $TiCl_4$, although the nature of these addition compounds is rather unclear. It is not known whether the oxygen or the chlorine atom is donating electrons to the metal involved in the adduct. Since tertiary phosphine oxides in general are known to form complexes with acids and with Lewis acids,[9] we tried to substitute triphenylphosphine oxide for phosphorus oxychloride but it offered no advantages in these reactions. In fact $Ph_3P{=}O$ is much more expensive than phosphorus oxychloride, and it is difficult to remove. Again, no dichlorocyclobutanones could be isolated from the reactions of dihydropyran or cyclopentadiene.

In addition to triphenylphosphine oxide, dimethyl sulfoxide and pyridine *N*-oxide are known[10] to form complexes with acids. These compounds were not found useful in replacing phosphorus oxychloride in the dichloroketene reactions since they reacted with trichloroacetyl chloride and unreacted olefins were isolated. Also, thionyl chloride, phosphorus tribromide, and phosphorus pentachloride were found to have no beneficial effect in the dichloroketene cycloadditions.

That phosphorus oxychloride has no inherent stabilizing effect toward ketene was evidenced by the quantitative recovery of olefin 6 when dichloroketene was generated from dichloroacetyl chloride, triethylamine, in the presence of phosphorus oxychloride.

In summary, dichlorocyclobutanones derived from hindered or unreactive olefins can be obtained in good yield by dehalogenating trichloroacetyl chloride with activated zinc in the presence of the olefin and phosphorus oxychloride.

Experimental Section

Melting points were determined on a Fisher-Johns block and are uncorrected. Infrared spectra were obtained of liquid films or carbon tetrachloride solutions as noted on a Perkin-Elmer 457 instrument. NMR spectra were recorded on a Varian A-60A or EM-360 spectrometer with Me_4Si as an internal standard. Mass spectra were determined on a Varian MAT CH5 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.

Trichloroacetyl Chloride. This procedure is a slight modification of the literature procedure.[8]

To a stirred mixture of 97.0 g (0.59 mol) of Cl_3CCO_2H and 3.0 mL of DMF at 85 °C was added 51.0 mL (84.5 g, 0.71 mol) of thionyl chloride dropwise. When addition was complete, heating at this temperature was continued for 2 h. The bath temperature was lowered to 60–65 °C and the product distilled (40–45 °C at 20–25 mm) and collected in an ice-cooled receiver. The first few milliters was discarded. The product was distilled one more time at reduced pressure and finally at atmospheric (625 mm) pressure (collected 180–110 °C) to yield 74.3 g (70%) of trichloroacetyl chloride.

Activation of Zinc. This procedure is a slight modification of the procedure of Brady.[2c] A stirred suspension of 10.0 g (0.15 m) of zinc dust in 40 mL of water was degassed by bubbling N_2 through it for 15 min. Then 750 mg (4.7 mmol) of $CuSO_4$ was added at once. The black suspension was stirred while N_2 was bubbled through it for an additional 45 min. The Zn–Cu couple was collected on a sintered glass funnel under a stream of N_2 and washed successively with 100 mL of degassed water and acetone. The Zn–Cu couple was transferred to a small flask under a stream of N_2 and dried at reduced pressure (0.2 mm) for 2 h. Nitrogen was admitted to the system when the vacuum was broken, and the Zn–Cu couple stored under N_2 in a tightly stoppered flask.

2,2-Dichloro-3-phenylcyclobutanone (1). The procedure for the addition of dichloroketene to styrene is illustrative: a 50-mL three-necked flask equipped with a condenser, addition funnel, magnetic stirrer, and N_2 inlet was flame dried while purged with N_2. When cool, the flask was charged with 1.1 mL (1.0 g, 9.6 mmol) of styrene, 0.69 g (10.5 mmol) of activated zinc, and 20 mL of anhydrous ether. The suspension was stirred under N_2 and a solution of 1.1 mL (1.83 g, 10.0 mmol) of Cl_3CCOCl and 0.92 mL (1.53 g, 10.0 mmol) of $POCl_3$ (distilled from K_2CO_3) in 10 mL of anhydrous ether was added dropwise over a 1-h period. When addition of the solution was complete, the mixture was refluxed with stirring for 2 h. The reaction mixture was then filtered through a pad of Celite and the unreacted zinc washed with 25 mL of ether. The ethereal solution was concentrated in vacuo to ca. 25% of its original volume, an equal volume of pentane added, and the solution stirred for a few minutes to precipitate the zinc salts. The solution was decanted from the residue, washed successively with water, a cold saturated $NaHCO_3$ solution and brine, and dried over Na_2SO_4, and the solvent was removed in vacuo to leave 1.93 g of crude 1. Bulb-to-bulb distillation (oven 90 °C, 0.02 mm) afforded 1.80 g (87%) of **1**:[2b] IR (CCl_4) 1810 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (s, 5 H), 4.18 (m, 1 H) and 3.56 (m, 2 H). The spectra of the crude and purified 1 were practically identical.

3,4-Benzo-6,6-dichlorobicyclo[3.2.0]hept-7-one (2). To a stirred mixture of 1.0 g (8.6 mmol) of indene and 0.62 g (9.5 mmol) of activated zinc in 25 mL of anhydrous ether was added a solution of 1.0 mL (1.65 g, 9.0 mmol) of Cl_3CCOCl and 0.83 mL (1.39 g, 9.0 mmol) of $POCl_3$ in 15 mL of anhydrous ether. After the solution was complete, the mixture was refluxed with stirring for 2 h. Workup afforded 1.78 g (92%) of a white solid which was purified by bulb-to-bulb distillation (oven 150 °C, 0.02 mm) to yield 1.57 g (81%) of **2**: IR (CCl_4) 1805 cm^{-1};[2d] NMR (CCl_4) δ 7.3 (m, 4 H), 4.50 (m, 2 H) and 3.3 (m, 2H). The spectra of crude and purified **2** were practically identical. When this reaction was repeated on a much larger scale (50 g of indene), the yield of purified **2** was slightly lower (71%).

4,4-Dichloro-*exo*-tricyclo[4.2.1.0^{2,5}]nonan-3-one (3). From 1.0 g (10.6 mmol) of norbornene, 0.76 g (11.7 mmol) of activated zinc in 30 mL of anhydrous ether, and addition of 1.22 mL (2.04 g, 11.2 mmol) of Cl_3CCOCl and 1.02 mL (1.72 g, 11.2 mmol) of $POCl_3$ in 15 mL of anhydrous ether, after 12 h of reflux, one obtained on bulb-to-bulb distillation (oven 120 °C, 0.02 mm) 1.15 g (70%) of **3**: IR (neat) 1802 cm^{-1}; NMR ($CDCl_3$) δ 3.55 (m, 3 H), 2.75 (m, 3 H) and 1.95– 0.95 (6 H).

2,2-Dichloro-3,3,4,4-tetramethylcyclobutanone (4). 2,3-Dimethyl-2-butene (1.0 g, 11.9 mmol), activated zinc (0.85 g, 13.0 mmol), Cl_3CCOCl (2.27 g, 12.5 mmol), $POCl_3$ (1.92 g, 12.5 mmol), after refluxing with stirring in 40 mL of anhydrous ether for 20 h, followed by bulb-to-bulb distillation (oven 120 °C, 0.02 mm), yielded 0.95 g (41%) of **4**: IR (CCl_4) 1795 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (s, 6 H) and 1.27 (s, 6 H); *m/e* (%) no M+, 131 (1.5), 95 (3.1), 93 (1.1), 91 (2.3), 89 (6.4), 84 (18.4), 81 (5.6), 79 (6.6), 77 (5.6), 70 (100), 69 (16.2), 53 (11.5), 41 (39.0), 40 (26.7), and 38 (21.1).

Anal. Calcd for $C_8H_{12}Cl_2O$: C, 49.52; H, 6.20. Found: C, 49.23; H, 6.20.

8,8-Dichloro-1-methylbicyclo[4.2.0]octan-7-one (5). Following the procedure described for 1, 1-methylcyclohexene (5.0 g, 52 mmol) and 3.7 g (57.2 mmol) of activated zinc in 100 mL of anhydrous ether was reacted with a solution of 6.0 mL (9.9 g, 54.6 mmol) of Cl_3CCOCl and 5.0 mL (8.37 g, 54.6 mmol) of $POCl_3$ in 50 mL of anhydrous ether. After 2 h of reflux and the usual workup, distillation afforded 8.5 g (79%) of **5**,[11] bp 62–63 °C (0.5 mm): IR (neat) 1800 cm^{-1}; NMR (CCl_4) δ 3.5 (broad, 1 H), 2.3–1.1 (8 H) and 1.5 (s, 3 H).

2a,2a-Dichloro-2α,3α-ethanocholestan-3a-one (7). To 10.0 g (27 mmol) of 2-cholestene[12] and 5.3 g (81 mmol) of activated zinc in 350 mL of anhydrous ether was added a solution of 5.9 mL (9.8 g, 54 mmol) of Cl_3CCOCl and 4.9 mL (8.2 g, 54 mmol) of $POCl_3$ in 50 mL of anhydrous ether. The mixture was refluxed with stirring for 15 h. The usual workup followed by recrystallization from ethyl formate yielded a first crop of 8.3 g and a second crop of 1.8 g (combined yield 78%) of **7**: IR (CCl_4) 1805 cm^{-1}; NMR (CCl_4) δ 4.2–3.6 (1 H) and 3.2–2.6 (1 H) as previously reported.[6]

2a,2a-Dichloro-2α,3α-ethano-2β-methylcholestan-3a-one (9). 2-Methyl-2-cholestene (8)[13] (2 g, 5.2 mmol) and 1.05 g (16 mmol) of activated zinc in 75 mL of anhydrous ether was refluxed with a solution of 1.14 mL (1.89 g, 10.4 mmol) of Cl_3CCOCl and 0.95 mL (1.59 g, 10.4 mmol) of $POCl_3$ in 35 mL of anhydrous ether. TLC (silica gel, pentane/benzene (3:1) eluent) indicated that olefin was consumed after 20 h. The usual workup afforded 2.50 g (97%) of a yellow solid. Recrystallization from ethyl formate–methanol gave 1.85 g (72%) of **9**, mp 128–129 °C: IR (CCl_4) 1800 cm^{-1}; CD ($CHCl_3$); NMR ($CDCl_3$) δ 3.60–3.33 (1 H) and 1.50 (2 β-methyl); MS *m/e* (%) M + 2 496 (15.0), M+ 494 (21.0), 468 (18.8), 466 (27.1), 383 (21.2), 329 (37.9), 287 (30.7), 119 (34.0), 107 (43.5), 95 (69.0), 105 (35.6), 81 (58.8), and 42 (100).

Anal. Calcd for $C_{30}H_{48}Cl_2O$: C, 72.70; H, 9.76. Found: C, 72.93; H, 9.88.

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Registry No.—Cl_3CCO_2H, 76-03-9; Cl_3CCOCl, 76-02-8; $Cl_2C{=}C{=}O$, 4591-28-0; $POCl_3$, 10025-87-3.

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Electrochemical Acetoxylation of *N*-Acetylindolines and *N*-Acetylindoles. A New Synthesis of Indigos

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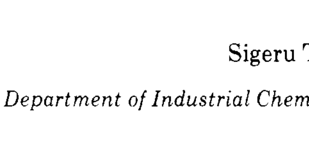
Electrochemical acetoxylation of *N*-acetylindolines **3** in AcOH–Et_3N at potentials 1.1–1.7 V vs. SCE, 4 faradays/mol of electricity, using platinum electrodes afforded the corresponding 2,3-diacetoxyindolines **5** in 70–77% yields. Likewise, *N*-acetylindoles **4** gave **5** in 76–82% yields. The acetate **5** could also be prepared from indoline (**2**) without isolating the intermediates **3** and **4**. Thermal decomposition of **5** at 140–145 °C gave *N*-acetylindoxyl acetates **7** in 81–87% yields and subsequent hydrolysis with 1 M aqueous sodium hydroxide provided indigos in 86–96% yields. Electrochemical bromination of **3a** (X = H) using various alkali bromides led to the corresponding bromide **3b** (X = Br) in 95–99% yields, which can be used as a precursor of bromoindigo synthesis.

Recent revival in the use of indigo dyes has stimulated new synthetic interest. Instead of the well-known preparative methods involving alkali fusion of phenylglycine[1] or phenylglycine-*o*-carboxylic acid,[2] we have examined the possibility of using an electrochemical reaction as a nonpolluting procedure for preparing indigos.[3]

We described herein electrochemical acetoxylation of *N*-acetylindolines **3** and *N*-acetylindoles **4** leading to the corresponding 2,3-diacetoxyindolines **5** as well as two-step conversion of the diacetates **5** into indigos **1** via *N*-acetylindoxyl



1a X=H
b X=Br

acetates **7** and also the electrochemical bromination of **3a** (X = H) leading to **3b** (X = Br) as a precursor of bromoindigo synthesis. Actually, we have succeeded in obtaining **5** directly from **2** without isolating **3** and **4** in a one-batch procedure.

A reverse synthetic pathway from indigos **1** to indoline (**2**) via the key intermediate **5** is outlined in Scheme I. Here, it can be seen that our novel indigo synthesis consists of three steps starting from either **2, 3,** or **4** via the intermediates **5** and **7.** Electrolysis of **3a** (X = H) in AcOH–Et_3N at potentials 1.1–1.7 V vs. SCE, applied voltages 2.0–2.9 V, current densities 3.3 mA/cm^2, using platinum foil electrodes consumed ca. 4 faradays/mol of electricity (over 80% of current efficiency) for 3 h (Table I, entry 1). All three products, 1-acetyl-2,3-diacetoxyindoline (**5a,** X = H, 77%), **4a** (X = H, 3%), and 1-acetylindoxyl acetate (**7a,** X = H, 2%) were separable and were

Scheme I