Table I. α-Alkylation of Dimethyl (Trifluoromethyl)malonate (1)

entry	RX	product	yield,[a] %
1	MeI	**3a**	80 (60)[b]
2	*n*-BuI	**3b**	39 (0)
3	$PhCH_2Br$	**3c**	63 (45)[c]
4	p-$NO_2C_6H_4CH_2Br$	**3d**	70
5	p-$NO_2C_6H_4CH_2Cl$	**3d**	31
6	CH_2=$CHCH_2Br$	**3e**	70 (47)[c]

[a] Figures in parentheses show yields obtained by use of CsF as a base.[6] [b] Reacted at room temperature overnight. [c] Reacted with 2.5 equiv of halides at 70–75 °C.

ester enolate by using EGB with a quaternary ammonium cation.

We report herein successful generation of a stable enolate **2** derived from (trifluoromethyl)malonate **1**, which is a useful starting material for various trifluoromethylated aliphatic and heterocyclic compounds,[11] and its efficient alkylation with alkyl halides (Scheme III).

The enolate **2** was generated by treatment of **1** with electrogenerated α-pyrrolidone anion[8,12] with tetraethylammonium as the countercation. When the reaction mixture was quenched with deuteriated trifluoroacetic acid, α-deuterio **1** [65% deuterium content (determined by NMR) 30 min after the generation of **2** at 0 °C] could be recovered in 88% yield. In contrast, **1** was recovered in extremely low yield when α-pyrrolidone anion with sodium as the countercation was used as a base.

Thus, as expected, the enolate **2** with a quaternary ammonium countercation would appear stable. Most recently, Smart et al. also reported extremely stable perfluoroalkyl carbanion salts with tris(dimethylamino)sulfonium cation (TAS).[14]

As shown in Table I, the electrogenerated enolate **2** reacted smoothly with various alkyl halides to provide the corresponding alkylated malonates **3** without any defluorination in good to reasonable yields.

Ishikawa and Yokozawa reported the successful alkylation of **1** in the presence of a large excess of CsF.[6] However, as indicated in Table I, their alkylation procedure is very sensitive to the reactivity of the alkyl halides. Methyl iodide can alkylate **1** at room temperature, whereas the alkylation with slightly less reactive benzyl and allyl bromides requires higher temperatures (Table I, entries 3 and 6). Furthermore, long-chain alkyl halides such as butyl iodide do not give any alkylated products (entry 2).[15]

In contrast, our method requires milder conditions and is less dependent upon the reactivity of the alkylating reagents.

Experimental Section

^1H NMR spectra were recorded at 60 MHz on a Hitachi R-24B NMR spectrometer using $CDCl_3$ and Me_4Si as solvent and internal standard, respectively. ^{19}F NMR spectra were recorded at 60 MHz on a Hitachi R-24F NMR spectrometer using CF_3COOH as external standard. IR spectra were obtained with a Hitachi 295 infrared spectrometer. Mass spectra were obtained with a JEOL JMS-D100 mass spectrometer.

General Procedure for α-Alkylation of Dimethyl (Trifluoromethyl)malonate (1). Using an undivided cell equipped with two platinum electrodes, cathodic reduction of α-pyrrolidone (4 mmol) was carried out in 8 mL of DMF containing Et_4NOTs (1.2 M) at room temperature under a nitrogen atmosphere. After 1.2 faradays mol^{-1} of electricity was passed at 0.58 A dm^{-2} of current density,[16] an aliquot (2.4 mL) of the catholyte was added dropwise to a stirred solution of **1** (1 mmol) in 1 mL of DMF at 0 °C under a nitrogen atmosphere. After the resultant mixture was stirred for 0.5 h at 0 °C, alkyl halide (1.2 mmol) was added, and the mixture was allowed to stand overnight. After addition of water to the reaction mixture, the resulting solution was extracted repeatedly with ether. The extracts were washed with brine and dried over anhydrous sodium sulfate. After removal of ether under reduced pressure, the residue was chromatographed on silica gel. Elution with hexane–AcOEt (8:1) provided alkylated products **3**.

The products other than **3b** and **3d** were identified by spectroscopic comparison with the authentic samples.[6]

Dimethyl butyl(trifluoromethyl)malonate (3b): ^1H NMR, δ 0.67–1.57 (m, 7 H, C_3H_7), 1.93–2.30 (m, 2 H, CH_2), 3.79 (s, 6 H, OCH_3); ^{19}F NMR, δ −11.5 (s); IR, 1772 cm^{-1} ($\nu_{C=O}$); MS, m/e 228 ($M^+ - C_2H_4$), 226 ($M^+ - C_2H_6$), 200 ($M^+ - CH_3CH_2CH$=CH_2), 159 ($M^+ - C_2H_4CF_3$). Anal. Calcd for $C_{10}H_{15}F_3O_4$: C, 46.88; H, 5.90. Found: C, 46.64; H, 5.92.

Dimethyl (*p*-nitrobenzyl)(trifluoromethyl)malonate (3d): mp 62–63 °C; ^1H NMR, δ 3.62 (s, 2 H, CH_2), 3.82 (s, 6 H, OCH_3), 7.23–8.08 (m, 4 H, C_6H_4); ^{19}F NMR, δ −12.8 (s); IR, 1775 cm^{-1} ($\nu_{C=O}$); MS, m/e 335 (M^+), 226 ($M^+ - CF_3$), 136 (p-$NO_2C_6H_4CH_2^+$). Anal. Calcd for $C_{13}H_{12}NF_3O_6$: C, 46.56; H, 3.61. Found: C, 46.30; H, 3.88.

Acknowledgment. We are grateful for valuable suggestions from Profs. T. Nonaka, N. Ishikawa, and T. Kitazume and Dr. T. Yokozawa of the Tokyo Institute of Technology.

Registry No. **1**, 5838-00-6; **1**-α-*d*, 110315-68-9; **3a**, 86311-85-5; **3b**, 110315-66-7; **3c**, 86311-86-6; **3d**, 110315-67-8; **3e**, 86317-58-0; MeI, 74-88-4; BuI, 542-69-8; $PhCH_2Br$, 100-39-0; p-$NO_2C_6H_4CH_2Br$, 100-11-8; p-$NO_2C_6H_4CH_2Cl$, 100-14-1; H_2C=$CHCH_2Br$, 106-95-6; α-pyrrolidone, 616-45-5; α-pyrrolidone(1^-)·tetraethylammonium, 39510-70-8.

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(12) Shono and Kashimura et al. found that a base electrogenerated from α-pyrrolidone possesses intriguing reactivity in promoting various reactions with high selectivity.[13] We also found that EGB from α-pyrrolidone effectively catalyzed polymerization of *N*-carboxy anhydrides of amino acids.[8]
(13) (a) Shono, T.; Kashimura, S.; Ishizaki, K.; Ishige, O. *Chem. Lett.* **1983**, 1311. (b) Shono, T.; Kashimura, S.; Nogusa, H. *J. Org. Chem.* **1984**, *49*, 2043. (c) Shono, T.; Ishige, O.; Ueyama, H.; Kashimura, S. *J. Org. Chem.* **1986**, *51*, 546. (d) Shono, T.; Kashimura, S.; Nogusa, H. *Chem. Lett.* **1986**, *425*.
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(15) Private information from Prof. N. Ishikawa and Dr. T. Yokozawa.
(16) The EGB from α-pyrrolidone generated by cathodic reduction at higher current density was found to be ineffective for alkylation of **1**.

Electrochemical Oxidation of the 2,3-Diphenylindole System. Elucidation of the Coupling Position and Analogous Behavior for the N-Substituted System

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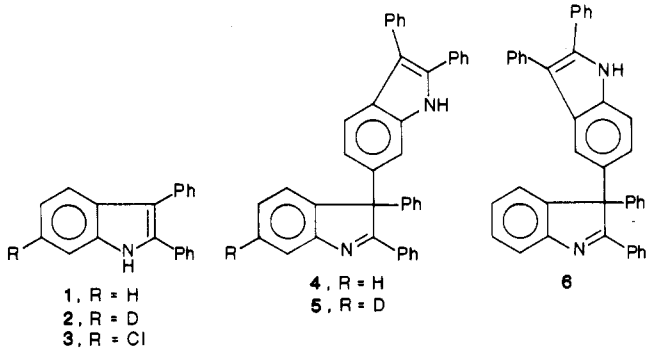
In our previous investigations, we studied the electrochemical oxidation of 2,3-diphenylindole (**1**) and reported

that the oxidative coupling gave the 3,5′ coupling product **6** in good yield.[2] In the light of subsequent work with deuteriated indole derivatives, we now revise **6** to the 3,6′ coupling product **4**. In addition, we report new work on the oxidation of *N*-methyl-2,3-diphenylindole (**7**), the electrochemical oxidation of which gives the indoleninium salt **8**.



The structure of **4** is based upon the fact that the oxidative coupling of 6-deuterio-2,3-diphenylindole (**2**) gives a product **5** containing only one deuterium rather than two as required by **6**. This structure proof is similar to our work on the oxidative coupling of 1,2,3,4-tetrahydrocarbazole to give the corresponding dimer[3] and relies on ^{13}C and ^{2}D NMR as well as mass spectrometry of the relevant compounds. In the present case, the deuteriated monomer **2** was prepared by catalytic deuteriation of the known 6-chloro-2,3-diphenylindole (**3**)[4] in $CH_3OD/KOCH_3$ over 5% palladium on carbon.[5] It was observed that the highest aromatic C–H ^{13}C resonance (122.6 ppm for **1**) is missing in the ^{13}C NMR spectrum of **2** and is replaced by the typical C–D coupling triplet, thereby assigning the 122.6 ppm resonance to the indole C-6 position. Our data for the 2,3-diphenylindole system and the related tetrahydrocarbazole series[3] is in accord with that of Gribble,[6] thus reversing the assignments in our original work[2] as well as that of Wenkert and his co-workers[7] and Roberts and his co-workers.[8] The resonance due to the corresponding carbon (C-6) in **5** (oxidation product of **2**) cannot be clearly seen because of the large number of carbons in the region 126–130 ppm. The ^{2}D NMR spectrum of **5**, however, clearly shows a single peak at δ 7.15, corresponding closely with the peak at δ 7.26 seen in the ^{2}D NMR spectrum of **2**. For comparison, the corresponding tetrahydrocarbazole coupling product shows a deuterium resonance at δ 7.21.[3] From these results, it is clear that **5** contains only one deuterium atom, indicating that coupling has occurred at the 6-position. Mester and co-workers have also shown that the analogous linkage is involved in the tetrahydrocarbazole series.[9]

The mass spectra of **4** and **5** in the region of M^+ are virtually identical except that the peaks are shifted 1 unit higher for **5**, as expected for a monodeuteriated dimer. The M^+ peak is the parent ion in each case. These mass spectral data, then, also indicate that the coupling occurs at the indole 6-position, leading to the incorporation of only one deuterium atom in **5**. The structures of **4** and **5** are also in accord with the corresponding tetrahydrocarbazole dimers.[3] This structure proof depends, of course, on the ipso substitution of chlorine by deuterium; however, this has been shown to be the case in the tetrahydrocarbazole work[3] and in other cases.[5a,5b] The ^{13}C NMR spectrum of the electrolysis product **8** of *N*-methyl-2,3-diphenylindole also suggests a structure similar to that of **4**, the resonances at 186.9 and 74.1 ppm being assigned to the 2 and 3 indoleninium ring carbons, respectively. Similar values were observed for the indolenine system in **4**[2] and for C-2 in the *N*-methyl-2,3,3-trimethylindoleninium system.[10] As given in the Experimental Section, resonances due to indole ring carbons are also present in the spectrum. Compound **8**, however, must be a salt (ClO_4^- or BF_4^-, depending on supporting electrolyte used) as inferred from the infrared spectra of the products. Mass spectral data clearly indicate a coupling product of molecular mass 565, with fragments due to loss of methyl and phenyl groups as well as cleavage of the parent molecule. The structure **8** shown for the electrolysis product is consistent with this spectral information. The coupling position on the indole ring is inferred from the present work on the coupling product from 2,3-diphenylindole oxidation and from similar studies of 1,2,3,4-tetrahydrocarbazole.[3]

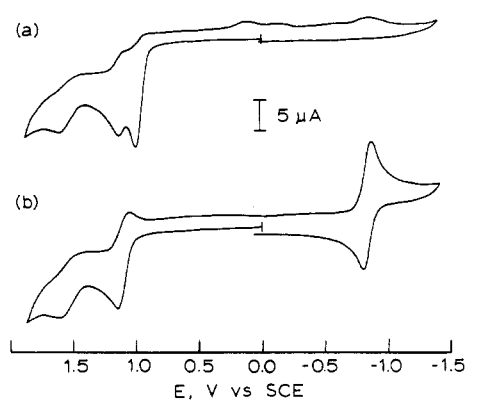
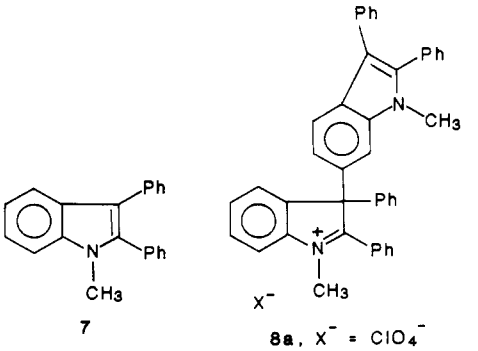


Figure 1. (a) Cyclic voltammogram of *N*-methyl-2,3-diphenylindole (1.7×10^{-3} M). (b) Cyclic voltammogram of **8a** (1.8×10^{-3} M). Voltammograms were obtained in acetonitrile/0.1 M TEAP solutions, at platinum (area = 2.0×10^{-2} cm^2), with a scan rate of 150 mV/s.



Formation of the product **8** requires passage of one electron per molecule of *N*-methyl-2,3-diphenylindole (**7**)

(1) Present address: Gates Energy Corp., Denver, CO 80207.
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during oxidation, as is observed by coulometry. The cyclic voltammogram in Figure 1b shows an oxidation peak at +1.14 V, also evident in Figure 1a following oxidation of **7**. This behavior was observed for the 2,3-diphenylindole system,[2] the peak for the product being attributed to oxidation of the indolic portion of the coupling product. The reversible couple at −0.84 V in Figure 1b depicts the redox behavior of the indoleninium center of the coupling product, similar to that seen for other phenyl-substituted immonium salts.[11] That these cyclic voltammetric features arise from electrochemical activity of electronically isolated parts of the molecule is clear since the same voltammogram is obtained regardless of initial scan direction. From these results and these spectral data, it is evident that the oxidative coupling pathway for *N*-methyl-2,3-diphenylindole is analogous to that for 2,3-diphenylindole, with the difference that the methyl group in the former compound causes the formation of an indoleninium salt instead of a neutral indolenine product.

Experimental Section[12]

6-Chloro-2,3-diphenylindole (3). Concentrated HCl (3.3 mL) was added to a mixture of 3-chloroaniline (26.3 mL, 0.25 mol) and benzoin (10.6 g, 0.05 mol). The mixture was heated under reflux for 35 min and then distilled to remove about 5 mL of a cloudy distillate, presumably mostly H_2O from the initial condensation. The temperature was then raised to 175–185 °C for 1 h to complete the indole formation. The mixture was cooled and triturated in ether, whereupon 3-chloroaniline hydrochloride crystallized. The salt was removed by filtration, and the filtrate was washed with 10% HCl (4 × 50 mL), H_2O (4 × 20 mL), and saturated NaCl (20 mL) and evaporated to yield 18.1 g of a purple oil. TLC (hexane/ether, 8:2, on silica gel GF_{254}) showed the presence of two major compounds, presumably **3** and its 4-chloro isomer. The oil was dissolved in hexane/ethyl acetate (8:2) and passed through a short column of silica gel 60 (15 × 1.5 cm from EM Reagents) until no more indoles eluted. The eluate was evaporated to 8.0 g of a brown oil, which was separated by preparative TLC (0.2 g per 1 mm × 20 × 20-cm layer of silica gel GF_{254} developed once with hexane/ether, 8:2). The top band was removed and eluted with ether to give, after evaporation, an oil, which crystallized from ether/hexane to give 3.2 g (21%) of **3**: mp 113–115 °C, lit.[4] mp 116–118 °C; ^{13}C NMR ($CDCl_3$): δ 110.7 (C-7) 115.1 (C-3) 120.6 (C-4) 121.1 (C-5), other peaks uncertain. The second major band yielded about the same amount of the 4-chloro isomer: mp 165–166 °C, lit.[13] mp 168–170 °C.

6-Deuterio-2,3-diphenylindole (2). Freshly cut potassium metal (0.5 g) was dipped in benzene and added to 25 mL of CH_3OD at 0 °C. After the evolution of D_2 was complete, the solution was diluted with 25 mL more of CH_3OD[14] and poured on 1.0 g of 5% Pd on C. Compound **3**, 1.2 g, was added, and the mixture was deuteriated in a Parr low-pressure apparatus at 13 psi for 53 h. The catalyst was removed by filtration, the CH_3OD was evaporated, and the residue was partitioned between ether and water. The water layer was acidified (HCl) to pH 6, the layers were separated, and the aqueous phase was washed several times with ether. The combined ether layers were washed (H_2O), dried (saturated NaCl and Na_2SO_4), and evaporated to a glass, which crystallized from ether/hexane to give 1.0 g of **2**: mp 113–115 °C; high-resolution MS, *m/z* 270.1285, calcd for $C_{20}H_{14}ND$, 270.1268. The ^{13}C spectrum was identical with that of **1**[2] except that the peak at 122.6 ppm was replaced by a small CD triplet centered at 122.3 ppm, thus reversing our earlier assignments[2] of C_5 and C_6.

Electrochemical Dimerization of 2. The electrochemical oxidation of **2** was carried out by a method similar to our previous work.[2] The oxidation mixture consisted of 135 mL of CH_3CN, 4.2 g of tetraethylammonium perchlorate (TEAP), and 300 mg of **2** placed in a divided cell separated by a Nafion membrane.[15] The reaction was carried out under nitrogen at +0.97 V vs SCE until starting material was gone (TLC developed by hexane/ethyl acetate, 8:2). The solvent was evaporated, and the residue was partitioned between ether and saturated aqueous $NaHCO_3$. The ether layer was separated, dried (saturated NaCl and Na_2SO_4), and evaporated to a residue which, on TLC, showed several spots, one with the same R_f as **4**. Extensive preparative TLC using benzene and hexane/ethyl acetate (8:2) finally yielded 120 mg (40%) of **5**, mp 160–165 °C[16] from ethanol/ether. **5**: MS (direct probe, 180 °C), *m/z* (% base peak, which is M^+) 539 (9, M + 2), 538 (46, M + 1), 537 (100, M^+); high-resolution MS, *m/z* (M^+) 537.2272, calcd for $C_{40}H_{27}ND$, 537.2318. These results can be compared with those for **4**: 538 (7, M + 2), 537 (42, M + 1), 536 (100, M^+). ^2D NMR ($CHCl_3$, with CD_3SOCD_3 as internal standard but given in δ units as shifted from $(CH_3)_4Si$) for **5**: 7.15. Compound **5** had a ^{13}C spectrum that was essentially identical with that of **4** since the deuterium-containing carbon C_6 is buried in the diphenyl carbon region.

***N*-Methyl-2,3-diphenylindole (7).** This compound was prepared from *N*-methylaniline and benzoin by using a similar procedure to that given for 6-chloro-2,3-diphenylindole above.[4] The crude product, dissolved in benzene, was chromatographed on silica gel, yielding 30% of **7** on the basis of the initial amount of benzoin. Recrystallization from ethanol gave crystals with melting point 137.5–138 °C (lit.[17] mp 137 °C): ^{13}C NMR ($CDCl_3$) δ 30.7 (NCH_3), 114.9 (C-3), 120.0 (C-4), other peaks uncertain.

Electrochemical Oxidation of 7. The conditions were the same as those used in our earlier work;[2] that is, a platinum gauze was used as the working electrode with a carbon rod, placed in a porous clay cup, as the counter electrode. The electrolysis mixture consisted of 80 mL of acetonitrile, 50 mg of **7**, and 1.72 g of TEAP or 1.55 g of tetraethylammonium tetrafluoroborate ($TEABF_4$), giving 0.1 M supporting electrolyte concentration. As seen in Figure 1, **7** undergoes oxidation at +1.00 V (peak potential vs SCE), and preparative electrolyses were carried out just beyond this potential at +1.04 V. In the initial stage of electrolysis, a light green color was observed in solution, changing rather soon to an orange color, which remained to the end of electrolysis. The electrolyses were terminated when the current reached a steady, low value, corresponding to the passage of 1.05 electrons per molecule of **7**. At this point, cyclic voltammograms of the solution showed that **7** had been completely oxidized (absence of oxidation peak at +1.00V), causing the appearance of a proton reduction peak at −0.30 V. Coulometric reduction at −0.60 V (proton reduction) gave charge values corresponding to approximately 0.45 of those for **7** oxidation. The color of the solution remained the same after reduction. After solvent removal on a rotary evaporator, the resulting orange solid was partitioned between water and benzene, and the water layer was washed until the benzene extracts were colorless. The benzene was evaporated, and the residue was separated by flash chromatography (Baker silica gel 7024-5) with benzene as the initial eluent (giving 1–2% of starting material) and gradually changing to acetonitrile/benzene (3:7), which yielded two small fluorescing bands, each corresponding

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(12) Melting points were measured on a Kofler block and are corrected. High-resolution mass spectra were measured on an AEI MS-9 instrument, and an LKB 9000 mass spectrometer was employed for other mass spectra. ^{13}C NMR spectra were obtained on a Bruker WH-90 or a JEOL JNM-PS-100 instrument. Resonances are reported in ppm from TMS as an internal standard. ^2D NMR spectra were measured on the Bruker instrument against a CD_3SOCD_3 internal standard, but shift values are given in ppm from TMS. A Beckman DU-7 spectrophotometer was used to acquire UV–Vis spectra. All evaporations were carried out on a rotary, vacuum evaporator.

(13) Ockenden, D. W.; Schofield, K. *J. Chem. Soc.* **1957**, 3175.

(14) It is essential that the CH_3OD have a minimum of air and moisture. We used a previously unopened bottle.

(15) The Nafion film was a gift of the Fluorocarbon Division of E.I. Du Pont Co., Wilmington, DE.

(16) When an identical experiment was carried out on **1**, a product, **4**, was obtained with the same melting point as **5**. The recorded melting point of **4** is 225–226 °C;[2] however, subsequent work has shown that the melting point of **4** is very dependent upon recrystallization conditions. ^{13}C NMR spectra of our **4** with the lower melting point and of known samples with the higher melting point are absolutely identical. Electrochemical experiments have also shown that these forms are identical. Attempts to dry the lower melting form of **4** to the higher melting form were not fruitful, and attempts to cross-seed the forms were sometimes successful and sometimes not.

(17) Richards, M. B. *J. Chem. Soc.* **1910**, 977.

to less than 1% of the crude material and then a large red-orange band of the major product. From the infrared spectra, the product was either a perchlorate salt (**8a**) or a tetrafluoroborate salt (**8b**) (bands at 1097 and 1084 cm^{-1}, respectively, depending upon whether the electrolyte had been TEAP or $TEABF_4$. The yield of 8 was found to be significantly better from the BF_4 medium: **8a**, 60%; **8b**, 80%. These products were recrystallized from ethanol/benzene (1:1), giving crystals that melted to red liquids over a rather wide temperature range: **8a**, red crystals, 180–189 °C; **8b**, orange crystals, 177–184 °C.

Although **8a** and **8b** show different colors in the solid state, their UV–Vis spectra (in acetonitrile) are identical: λ_{max} (log ϵ, ϵ in L/mol cm) 415 (3.16); 297 (4.34); 255 (4.53) nm; MS for **8b** (direct probe, 250 °C), *m/z* (% base peak) 567 (17, M + 2), 566 (42, M + 1), 565 (54, M^+), 564 (100), 563 (29), 562 (55), 552 (16), 551 (49), 550 (100), 490 (11), 489 (48), 488 (100), 486 (10), 485 (20), 284 (6), 283 (24). The MS for **8a** is similar; however, peaks due to loss of phenyl and product cleavage (283) are much less prominent (less than 5%). An additional peak at 580 (35) may indicate decomposition of the perchlorate salt. **8a**: ^{13}C NMR ($CDCl_3$) δ 31.3 (NCH_3), 114.8 (C-3), 110.3 (C-7), 37.7 ($N'CH_3$), 186.9 (C-2′), 74.1 (C-3′), 141.6, 142.5 (C-8′, C-9′), 117.4 (C-7′), other peaks uncertain. Primed numbers refer to positions on the indolenine ring. Anal. (**8a**) Calcd for $C_{42}H_{33}N_2 \cdot ClO_4$: C, 75.84; H, 5.00; N, 4.21. Found: C, 75.77; H, 5.35; N, 4.11. (**8b**) Calcd for $C_{42}H_{33}N_2 \cdot BF_4$: C, 77.31; H, 5.10; N, 4.29. Found: C, 77.40; H, 5.35; N, 4.14.

Acknowledgment. This work was sponsored, in part, by Grant CA 33195 from the National Cancer Institute of the National Institutes of Health to the University of Connecticut. We thank Dr. Thomas Leipert and Marvin Thompson of the Department of Chemistry at Connecticut for help with the NMR and MS, respectively, and S. Longchamp[18] of the Faculte des Sciences et des Techniques de Rouen, France, for a sample of **4** with the higher melting point. Grateful acknowledgment is also made to William Comstock of the National Heart, Lung, and Blood Institute, Bethesda, MD, for obtaining the mass spectra of the *N*-methyl-2,3-diphenylindole oxidation products.

Registry No. **2**, 110417-94-2; **3**, 66785-53-3; **5**, 110417-95-3; **7**, 6121-45-5; **8a**, 110417-97-5; **8b**, 110417-98-6; 3-chloroaniline, 108-42-9; benzoin, 119-53-9; 4-chloro-2,3-diphenyl-1*H*-indole, 81303-08-4; *N*-methylaniline, 100-61-8.

(18) Longchamp, S.; Caullet, C. *Electrochim. Acta* **1984**, *29*, 1074.

A Convenient Preparation of 4- and 5-Substituted Cyclopentenones: A Short Synthesis of Methylenomycin B

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Methods for the preparation of substituted cyclopentenones have been the subject of much attention, given the ubiquitous nature of this structural unit in both natural and unnatural products. Classical approaches have rested largely on 1,4-dicarbonyl condensations,[2] molecular rearrangements,[3] Friedel–Crafts reactions,[4] and the Nazarov cyclization.[5] All of these methods have been useful in preparing 2- and/or 3-substituted cyclopentenones. However, 4- and 5-substituted cyclopentenones have proven more difficult to prepare. Stork resolved the problem by protecting the enone double bond as its cyclopentadiene adduct.[6] More recently, the heteroatom-directed Nazarov cyclization developed by Denmark,[7a–d]

Scheme I

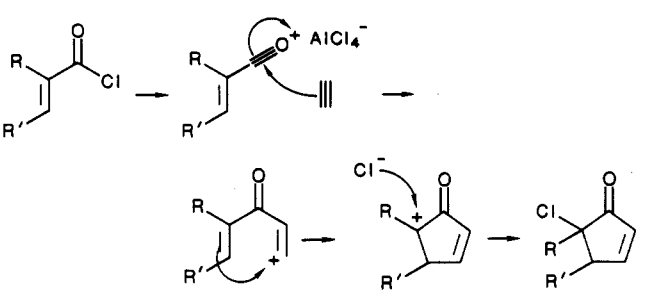
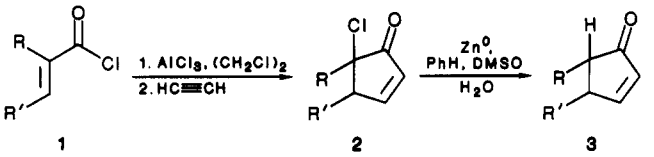


Table I[a]



			yield, %		
entry	R	R′	chlorocyclopentenone	cyclopentenone	overall yield, %
a	H	H	45[9c]	71[16]	32
b	H	Me	69[9c]	74[17]	51
c	Me	H	67[9c]	65[19]	44
d	Me	Me	66[9c]	75[18]	50
e	H	Ph	30	91[4d,7b,6h]	27
f	Me	Ph	50	84	42
g	$-(CH_2)_3-$		72	68[7b,7h,8h]	49
h	$-(CH_2)_4-$		68	92[7b,7d,8h]	63
i	$-(CH_2)_5-$		68	90[7b,7d]	61

[a] References are for previous preparations.

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