The oxazolines **3a–3e** were recovered in yields of 53–71% (Table I) by dropwise addition of the acid solution into excess, rapidly stirring aqueous sodium bicarbonate with continuous ether extraction.[1a] Each oxazoline was identified unequivocally by comparison with an authentic sample.[1a,24]

Proton Exchange Studies.—The exchange of the nitrogen proton of ions **2a–2e** in 65% sulfuric acid solution was determined by diluting solutions of the ions to the proper concentration and observing the disappearance of the previously observed nmr signal. The H–D exchange studies required monitoring of the nmr spectra and using peak integration as the measuring device.

Protonation of 1-Acylaziridine.—The aziridine derivatives **1a–1c** were each dissolved in sulfur dioxide and the resulting solutions were added to 1:1 fluorosulfonic acid–antimony pentafluoride at −70°. Their individual spectra were recorded at −55° (Table II).

Registry No.—**2a**, 23704-69-0; **2b**, 23704-70-3; **2c**, 23704-71-4; **2d**, 23704-72-5; **2e**, 23704-73-6; **4a**, 23402-58-6; **4b**, 23402-59-7; **4d**, 23402-60-0.

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Nenitzescu Indole Synthesis with 2-Chloro-5-methylbenzoquinone

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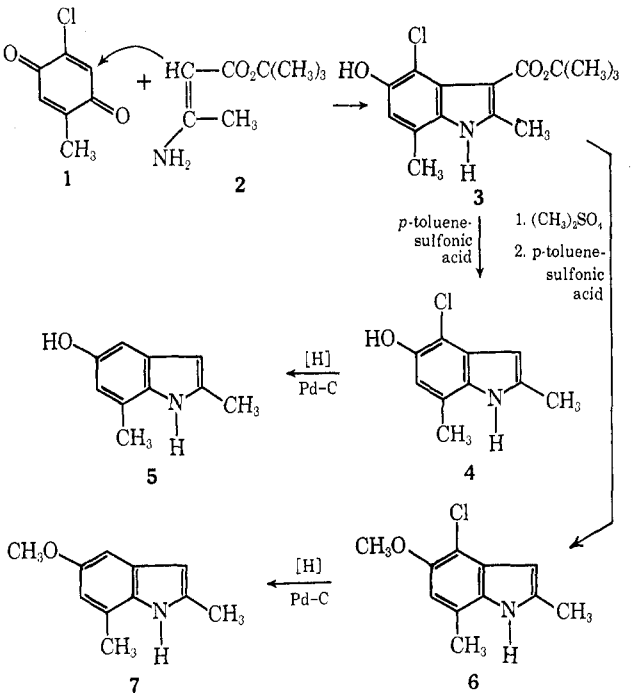
The reaction of aminocrotonate esters (*e.g.*, **2**) with *p*-quinones (*e.g.*, **1**) to form 5-hydroxy-3-carbalkoxyindoles (*e.g.*, **3**) proceeds *via* condensation of the terminal carbon of the enamine triad and one of the C=C carbons of the quinone system.[1,2] With unsymmetrically substituted quinones, the isomeric 5-hydroxyindole that is ultimately produced depends on which of the available double-bond carbons participates in this condensation. In the case of monosubstituted quinones, a 4-substituted 5-hydroxyindole product has been reported only with trifluoromethyl[3] and carbethoxy[4] qunone substituents. Such a product implies condensation of the enamine carbon at the *ortho* position in the quinone ring. With substituents such as alkyl,[1] halogen,[3] and alkoxy,[1] condensation occurs at the *para* or *meta* positions, and leads to 6-substituted and in some cases also 7-substituted 5-hydroxyindoles.

Since neither methyl nor chlorine leads to *ortho* condensation when substituted on the quinone ring, it was of some interest to investigate a Nenitzescu reaction with 2-chloro-5-methylbenzoquinone. In this case condensation would have to take place at an *ortho* position. From this condensation we have been able to detect only one isomer, the product of enamine condensation *ortho* to the chlorine substituent (namely, the 4-chloro-7-methyl isomer **3**), which was obtained in 51% yield. Proof of structure was provided by decarbalkoxylation and dechlorination (hydrogenolysis with Pd–C catalyst) to the known[1] 2,7-dimethyl-5-hydroxyindole (**5**). Although in this instance the dechlorination yield was low, a satisfactory yield (74%) was obtained with the 5-methoxy derivative **6** to give 2,7-dimethyl-5-methoxyindole (**7**). Thus, this procedure appears to offer a potentially useful synthetic method for the preparation of 2,7-dialkyl-5-oxyindoles.



Experimental Section[5]

***t*-Butyl 4-Chloro-5-hydroxy-2,7-dimethylindole-3-carboxylate (3).**—To a hot solution of 5-chloro-2-methyl-1,4-*p*-benzoquinone (**1**)[6] (3.12 g, 0.0199 mol) in glacial acetic acid (15 ml), *t*-butyl 3-aminocrotonate (**2**)[3] (3.14 g, 0.02 mol) was added. After 30 min without application of heat, the solution was cooled, and the resulting pink precipitate was filtered and washed with chilled acetic acid to give 2.99 g (51%) of **3**, mp 178–180° dec.

An analytical sample was obtained by elution from Florisil[7] (magnesia–silica gel adsorbent), followed by recrystallization from methylene chloride: mp 177–179°; λ_{max} 218, 248, 288 mμ (ε 27,300, 15,300, 885); ir 3.08, 6.0, 6.3, 7.05, 8.64, 8.9 μ; nmr, δ 1.53 [s, 9, C(CH$_3$)$_3$], 2.37 (s, 3, 7-CH$_3$), 2.47 (s, 3, 2-CH$_3$), 6.62 (broadened s, 1, 6-H), 8.97 (s, 1, OH), and 11.2 (broadened s, 1, NH) ppm.

Anal. Calcd for $C_{15}H_{18}ClNO_3$: C, 60.91; H, 6.13; Cl, 11.98; N, 4.73. Found: C, 61.14; H, 6.60; Cl, 11.78; N, 4.80.

4-Chloro-5-hydroxy-2,7-dimethylindole (4).—A magnetically stirred solution of *t*-butyl 4-chloro-5-hydroxy-2,7-dimethylindole-3-carboxylate (**3**) (2.99 g, 0.0101 mol) and *p*-toluenesulfonic acid (250 mg) in 250 ml of toluene was heated at reflux for 1 hr. The solution was cooled, filtered, and evaporated to dryness. The residue was dissolved in ethyl acetate and washed with dilute sodium bicarbonate solution and then with water. The organic

(1) G. R. Allen, Jr., C. Pidacks, and M. J. Weiss, *J. Amer. Chem. Soc.*, **88**, 2536 (1966).

(2) D. Raileanu and C. D. Nenitzescu, *Rev. Roum. Chem.*, **10**, 339 (1965); *Chem. Abstr.*, **63**, 9903 (1965).

(3) R. Littell and G. R. Allen, Jr., *J. Org. Chem.*, **33**, 2064 (1968).

(4) G. R. Allen, Jr., and M. J. Weiss, *ibid.*, **33**, 198 (1968).

(5) Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. Ultraviolet spectra were determined in methanol solution with a Cary recording spectrophotometer, and infrared spectra were determined in potassium bromide disks with a Perkin-Elmer Model 21 spectrophotometer. The proton magnetic resonance spectrum was determined with a Varian A-60 spectrometer in dimethyl sulfoxide-d_6, using tetramethylsilane as an internal standard. Evaporations were done under reduced pressure.

(6) H. H. Hodgson and F. H. Moore, *J. Chem. Soc.*, 2036 (1926).

(7) Florisil is the trademark of the Floridin Co. for a magnesia–silica gel adsorbent.

phase was dried over magnesium sulfate and concentrated to a red oil. The oil was chromatographed on Celite[8] and the product, eluted with 10% ether–benzene, was recrystallized from ether–petroleum ether (bp 30–60°) to give 1.23 g (63%) of **4** as pink crystals: mp 111–113°; λ_{max} 218, 275 mμ (ε 22,500, 10,500); ir 2.9, 3.02, 6.5, 6.67, 8.15, 8.5 μ.

Anal. Calcd for $C_{10}H_{10}ClNO$: C, 61.34; H, 5.11; Cl, 18.14; N, 7.16. Found: C, 61.80; H, 5.46; Cl, 18.29; N, 7.34.

2,7-Dimethyl-5-hydroxyindole (5).—4-Chloro-5-hydroxy-2,7-dimethylindole (**4**) (392 mg, 2 mmol) and 40 ml of 0.1 *N* aqueous sodium hydroxide were shaken in a Parr low pressure hydrogenation apparatus with 500 mg of 10% palladium-on-charcoal catalyst, at an initial hydrogen pressure of 30 psi, until hydrogen uptake ceased. The reaction mixture was filtered, and the filtrate was acidified with dilute hydrochloric acid and then extracted with ethyl acetate. The combined extracts were dried over magnesium sulfate and concentrated to an oil, which was chromatographed on silica gel. The product was eluted with 5% ether–benzene. Recrystallization from methylene chloride–petroleum ether (bp 30–60°) gave near-white crystals, 58 mg (18%), mp 145–147°, undepressed on admixture of this substance with authentic **5**[1] and identical in ultraviolet and infrared spectrum.

***t*-Butyl 4-Chloro-2,7-dimethyl-5-methoxyindole-3-carboxylate.**—To a stirred solution of 15.5 g (0.0523 mol) of *t*-butyl 4-chloro-5-hydroxy-2,7-dimethylindole (**3**) in 96.3 ml of ethyl alcohol and 193 ml of 2 *N* sodium hydroxide solution was added dropwise over 1 hr 31.6 g (23.4 ml, 0.251 mol) of dimethyl sulfate. The mixture was heated at reflux temperature for 1.5 hr, cooled, diluted with water, and filtered, to give 13.1 g (80%) of product, mp 175–180°. A sample was recrystallized from ether to give crystals: mp 182–184° (gas evol); λ_{max} 221, 285 (shoulder), 285 mμ (ε 40,000, 17,100, 11,800); ir 3.05, 3.35, 6.00, 6.25, 6.85, 8.25, 8.6, 9.25 μ.

Anal. Calcd for $C_{16}H_{20}ClNO_3$: C, 62.03; H, 6.50; Cl, 11.47; N, 4.51. Found: C, 61.94; H, 6.65; Cl, 11.18; N, 4.32.

4-Chloro-2,7-dimethyl-5-methoxyindole (6).—A solution of 8.2 g (0.0266 mol) of *t*-butyl 4-chloro-2,7-dimethyl-5-methoxyindole-3-carboxylate and 600 mg of *p*-toluenesulfonic acid monohydrate in 900 ml of toluene was heated at reflux for 1 hr. The solution was cooled, filtered, and evaporated to dryness. The residue was chromatographed on silica gel, and elution of product with benzene gave 4.13 g (74.5%) of product melting at 132–136°. A sample was recrystallized from ether–petroleum ether (bp 30–60°) to give crystals: mp 139–140°; λ_{max} 221, 278 mμ (ε 28,800, 10,300); ir 2.9, 3.44, 6.26, 7.3 μ.

Anal. Calcd for $C_{11}H_{12}ClNO$: C, 62.99; H, 5.76; Cl, 16.92; N, 6.67. Found: C, 62.81; H, 5.64; Cl, 16.65; N, 6.98.

2,7-Dimethyl-5-methoxyindole (7).—4-Chloro-2,7-dimethyl-5-methoxyindole (**6**) (419.4 mg, 2 mmol), 392 mg (4 mmol) of potassium acetate and 480 mg of 10% palladium-on-charcoal in 50 ml of ethyl alcohol was shaken in a Parr low pressure hydrogenation apparatus at an initial hydrogen pressure of 30 psi until hydrogen uptake ceased. The reaction mixture was filtered and concentrated. The residue was partitioned between methylene chloride and water. The organic phase was separated, and washed several times with water, dried, and evaporated. The residue was crystallized from ether–petroleum ether (bp 30–60°) to give 257 mg (73.5%) of crystals, mp 73–75°, undepressed on admixture of this substance with authentic 2,7-dimethyl-5-methylindole (**7**), prepared as described below, and identical in ultraviolet and infrared spectrum.

2,7-Dimethyl-5-methoxyindole (7).—To a stirred solution of 26.4 g (0.163 mol) of 2,7-dimethyl-5-hydroxyindole (**5**),[1] 297 ml of ethanol and 595 ml of 2 *N* sodium hydroxide solution was added dropwise, under nitrogen, 73.3 ml of dimethyl sulfate (0.785 mol) over a period of 1 hr. The reaction mixture was then heated at reflux for 1 hr, cooled, diluted with water, and extracted with ethyl acetate. The combined extracts were washed with saline, dried over magnesium sulfate, and concentrated. The residue was dissolved in benzene and passed through a magnesia–silica column using benzene as the eluting solvent. The initial 1200 ml of eluate was evaporated to give 23 g (78%) of yellow oil, which crystallized on standing. A sample was recrystallized from ether–petroleum ether (30–60°) to give near white crystals: mp 76–77°; λ_{max} 215, 272 mμ (ε 19,200, 8570); ir 3.0, 3.45, 6.25, 6.73, 8.36, 9.55 μ.

(8) Celite is the trademark of the Johns–Manville Corp. for diatomaceous earth.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.10; H, 7.31; N, 7.67.

Registry No.—**1**, 19832-87-2; **3**, 23386-23-4; **4**, 23386-24-5; **6**, 23386-25-6; **7**, 23386-26-7; *t*-butyl 4-chloro-2,7-dimethyl-5-methoxyindole-3-carboxylate, 23386-27-8.

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Reductive Cleavage of Ferrocene Derivatives

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Ferrocene (**1**) and a number of ferrocene derivatives have been subjected to reduction by solutions of metals in amines.[1] As part of our research in ferrocene chemistry, we were interested in studying factors influencing the ease of reduction of substituted ferrocenes and in identifying the isomers of substituted cyclopentadienes obtainable by reductive cleavage of 1,1′-dialkylferrocenes. We subjected three symmetrically substituted dialkylferrocenes, 1,1′-dimethyl- (**2**), 1,1′-diethyl- (**3**), and 1,1′-dibenzylferrocene (**4**), and two ferrocenophanes, [3]ferrocenophane (**5**) and [3][3]-1,3-ferrocenophane (**6**), as well as **1**, to reduction by Li in propylamine (Scheme I). We assumed originally that reduction of each dialkyl compound would lead to three alkylcyclopentadienes and that these could be identified as 1-, 5-, or 7-substituted norbornene derivatives by preparing Diels–Alder adducts with maleic anhydride. However, we found no 7-substituted norbornenes and, in the case of 1,1′-dibenzylferrocene, only the 1-benzylnorbornene derivative, which arises from 2-benzylcyclopentadiene, was found. After reduction and quenching, **1** gave cyclopentadiene which was converted into N-phenyl-5-norbornene-2,3-dicarboximide (**7**) by treatment with maleic anhydride and then acetyl chloride, followed by aniline. Similarly, **2** gave a mixture of 2- and 3-methylcyclopentadienes which were characterized as 1- and 5-methyl-N-phenyl-5-norbornene-2,3-dicarboximides (**8** and **9**). The reduction of **3** and subsequent treatment of the reaction product with maleic anhydride led to 1-ethyl-5-norbornene-2,3-dicarboxylic anhydride (**10**), the corresponding dicarboxylic acid (**11**), and a lactonic acid, mp 157.5–158°, which proved to be 5-ethyl-5-hydroxynorbornane-2,3-dicarboxylic acid γ-lactone (**12**) indicating the formation of 2- and 3-ethylcyclopentadiene only. The preparation of 5-ethyl-5-norbornene-2,3-dicarboxylic acid (**13**), mp 156°, has been reported,[2] but, since its structure was not proved and since the

(1) (a) D. S. Trifan and L. Nichols, *J. Amer. Chem. Soc.*, **79**, 2746 (1957). (b) J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 4604 (1961). (c) A. N. Nesmeyanov, *et al.*, *Dokl. Akad. Nauk SSSR*, **160**, 137 (1965); **177**, 586 (1967). (d) G. W. Watt and L. J. Baye, *J. Inorg. Nucl. Chem.*, **26**, 2099 (1964). (e) D. W. Slocum and W. E. Jones, *J. Organometal. Chem.*, **15**, 262 (1968).

(2) K. Alder and H.-J. Ache, *Chem. Ber.*, **95**, 503 (1962).