tuted product: IR ν 2220 cm^{-1} (CN); NMR δ 1.13 (d, 6 H), 3.91 ppm (t, 1 H); mass spectrum *m/e* (rel intensity) 111 (M^+ − 27, 43), 96 (M^+ − 42, 100). Picrate: yellowish leaflets from ethanol–acetone, mp 106–111 °C dec. Anal. Calcd for $C_{14}H_{17}N_5O_7$: C, 45.77; H, 4.67; N, 19.07. Found: C, 45.6; H, 4.6; N, 18.8.

***N*-Isopropylpiperidine (Expt 14).** The ether extracts were distilled. Unchanged amine (1.3 g) was recovered at about 55–60 °C (24 mm) and then 9.4 g of *N*-isopropyl-2-cyanopiperidine was obtained at 108–110 °C (24 mm): IR ν 2210 cm^{-1} (CN); NMR δ 1.10 (double d, 6 H, J = 6 Hz), 3.94 ppm (t, 1 H); mass spectrum *m/e* (rel intensity) 125 (M^+ − 27, 33), 110 (M^+ − 42, 100). Picrate: yellowish leaflets from ethanol–acetone, mp 105.5–109 °C dec. Anal. Calcd for $C_{15}H_{19}N_5O_7$: C, 47.24; H, 5.02; N, 18.37. Found: C, 47.0; H, 5.0; N, 18.0.

***N*-*tert*-Butylpyrrolidine (Expt 15).** The distillation gave 2.0 g of starting amine and 9.6 g of *N*-*tert*-butyl-2-cyanopyrrolidine [bp 98 °C (13 mm)]: IR ν 2225 cm^{-1} (CN); NMR δ 1.09 (s, 9 H), 1.95 (broad, 4 H), 2.75 (broad, 2 H), 3.73 ppm (broad, 1 H); mass spectrum *m/e* (rel intensity) 152 (M^+, 3), 137 (M^+ − 15, 85), 125 (M^+ − 27, 40), 110 (M^+ − 42, 100), 68 (74). Picrate: yellowish prisms from ethanol–acetone, mp 177–179 °C dec. Anal. Calcd for $C_{15}H_{19}N_5O_7$: C, 47.24; H, 5.02; N, 18.37. Found: C, 47.4; H, 5.0; N, 18.0.

Registry No.—**3a,** 62842-25-5; **3a** picrate, 62842-26-6; **4b,** 62842-27-7; **4b** picrate, 62842-28-8; **5a,** 62842-29-9; **5a** picrate, 62842-30-2; **6a,** 62842-31-3; **6a** picrate, 62842-32-4; **8a,** 20297-37-4; **8a** picrate, 18747-97-2; **8b,** 29134-29-0; **8b** picrate, 62842-33-5; **9a,** 18747-95-0; **9a** picrate, 18747-96-1; **9b,** 3010-03-5; **9b** picrate, 25283-66-3; **10a,** 62842-34-6; **10a** picrate, 62842-35-7; **11a,** 62842-36-8; **11a** picrate, 62842-37-9; **11b,** 62842-38-0; **11b** picrate, 62842-39-1; **12a,** 62842-40-4; **12a** picrate, 62842-41-5; **13a,** 62842-42-6; **13a** picrate, 62842-43-7; **14a,** 62842-44-8; **14a** picrate, 62842-45-9; **15a,** 62842-46-0; **15a** picrate, 62842-47-1; α-dimethylaminoacetamide, 6318-44-1; NaCN, 143-33-9; *N,N*-diisopropylaminoacetonitrile, 54714-49-7.

References and Notes

(1) H. Schmidt and H. Meinert, *Z. Anorg. Allg. Chem.*, **295,** 174 (1958).
(2) (a) K. Koyama, T. Susuki, and S. Tsutsumi, *Tetrahedron Lett.*, **No. 11,** 627 (1965); (b) K. Koyama, T. Susuki, and S. Tsutsumi, *Tetrahedron*, **23,** 2675 (1966); (c) T. Susuki, K. Koyama, and S. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **41,** 2663 (1968); (d) S. Tsutsumi and K. Koyama, *Discuss. Faraday Soc.*, **45,** 247 (1968).
(3) L. Eberson and S. Nilsson, *Discuss. Faraday Soc.*, **45,** 242 (1968).
(4) S. Andreades and E. W. Zahnow, *J. Am. Chem. Soc.*, **91,** 4181 (1969).
(5) K. Yoshida and T. Fueno, *J. Org. Chem.*, **37,** 4145 (1972).
(6) General discussion, *Discuss. Faraday Soc.*, **45,** 269 (1968).
(7) V. D. Parker and B. E. Burgert, *Tetrahedron Lett.*, **No. 45,** 4065 (1965).
(8) K. Yoshida and T. Fueno, *J. Org. Chem.*, **36,** 1523 (1971).
(9) (a) C. K. Mann, *Anal. Chem.*, **36,** 2424 (1964); (b) K. K. Barnes and C. K. Mann, *J. Org. Chem.*, **32,** 1474 (1967); (c) P. J. Smith and C. K. Mann, *ibid.*, **34,** 1821 (1969); (d) L. C. Portis, V. V. Bhat, and C. K. Mann, *ibid.*, **35,** 2175 (1970); (e) L. C. Portis, J. T. Klug, and C. K. Mann, *ibid.*, **39,** 3488 (1974).
(10) M. Masui and H. Sayo, *J. Chem. Soc. B*, 1593 (1971); see also M. Masui, H. Sayo, and Y. Tsuda, *ibid.*, 973 (1968).
(11) T. Takamura and F. Mochimaru, *J. Electrochem. Soc. Jpn.*, 233 (1968).
(12) (a) N. L. Weinberg and T. B. Reddy, *J. Am. Chem. Soc.*, **90,** 91 (1968); (b) N. L. Weinberg, *J. Org. Chem.*, **33,** 4326 (1968).
(13) G. Spielberger in Houben-Weyl, "Methoden der Organischen Chemie", Vol. XI/1, Georg Thieme Verlag, Stuttgart, 1957, p 24.
(14) L. Spialter and J. A. Pappalardo, *J. Org. Chem.*, **22,** 840 (1957).
(15) J. V. Braun, C. Müller, and E. Beschke, *Ber.*, **39,** 4347 (1906).
(16) Einem Autorenkollektiv, "Organish-Chemishes Grundpraktikum", VEB Deutscher Verlag der Wissenschaften, Berlin, 1965, p 480.
(17) D. B. Luten, Jr., *J. Org. Chem.*, **3,** 588 (1938–1939).
(18) R. A. Turner, *J. Am. Chem. Soc.*, **68,** 1607 (1946).
(19) A. Lespagnol, E. Cuingnet, and M. Debaert, *Bull. Soc. Chim. Fr.*, 2, 383 (1960).
(20) C. F. H. Allen and J. A. Van Allen, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 275.
(21) C. A. Grob and A. Sieber, *Helv. Chim. Acta*, **50,** 2520 (1967).
(22) T. D. Stewart and V. Cook, *J. Am. Chem. Soc.*, **50,** 1973 (1928).
(23) R. H. Reitsema and J. H. Hunter, *J. Am. Chem. Soc.*, **70,** 4009 (1948).
(24) H. Najer, R. Giudicelli, and J. Sette, *Bull. Soc. Chim. Fr.*, 556 (1962).
(25) E. Knoevenagel, *Ber.*, **37,** 4073 (1904).
(26) C. Malen and J. R. Boissier, *Bull. Soc. Chim. Fr.*, 923 (1956).
(27) E. Knoevenagel, *Ber.*, **37,** 4078 (1904).

The Mechanism of Indeno[1,2,3-*de*]quinolin-2-one Formation

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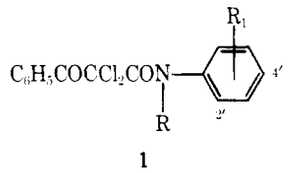
The unambiguous synthesis of 1,6-dichloro-3-ethylindeno[1,2,3-*de*]quinolin-2(3*H*)-one (**7**) was undertaken. Product **7** was found to be identical with that derived by sulfuric acid catalyzed cyclization of 2,2,4′-trichloro-*N*-ethylbenzoylacetanilide (**4**). This is evidence that **7** arises from **4** via a "direct" cyclization intermediate. A convenient modification of the Cook and Koelsch indenoquinolinone synthesis, which afforded **7** by a shorter route, is reported. The diagnostically useful anisotropic deshielding of the C-7 and C-10 protons by the halogen at C-1 and C-6 in the ^1H NMR spectrum of **7** is described.

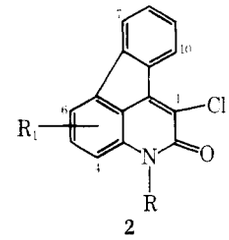
We report further developments relating to the mode of cyclization of 2,2-dichlorobenzoylacetanilides **1** to indeno[1,2,3-*de*]quinolin-2-ones **2.** In our earlier work,[1] a "direct" ring closure was tacitly assumed. The recent findings of Harcourt and Taylor[2] with 4′-methoxybenzylaminoacetonitrile prompted us to consider the intervention of a similar, appropriately modified "spiro" intermediate during the cyclization of **1,** in helping to explain the migrations encountered with certain methyl-substituted substrates.[1]

It is evident (Scheme I) that closure of the relatively uncomplicated **4** via a "spiro" intermediate i in which bond a breaks would lead to the 5-chloroindenoquinolinone **6,** whereas rearrangement of i to the "direct" intermediate ii,[3] and/or closure in a "direct" fashion, would result in the 6-chloroindenoquinolinone **7.** Competitive cleavage of both carbon and nitrogen bonds in related "spiro" species has been described by Hey; for example, treatment of the spirodienol **8** with acid gave a mixture of benzophenanthridinones in which the product of nitrogen migration, **9,** predominated.[4] The sole indenoquinolinone product derived from **4** has now been unequivocally identified as **7,** and accordingly, pathway 1 (Scheme I) for this cyclization can be discounted.



1

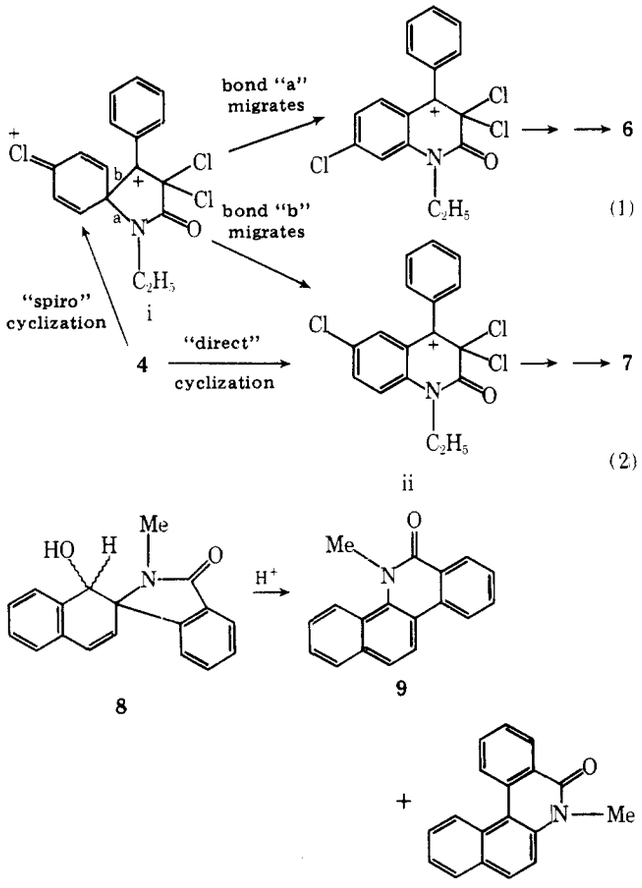
3, R = H; R_1 = 4′-Cl
4, R = C_2H_5; R_1 = 4′-Cl



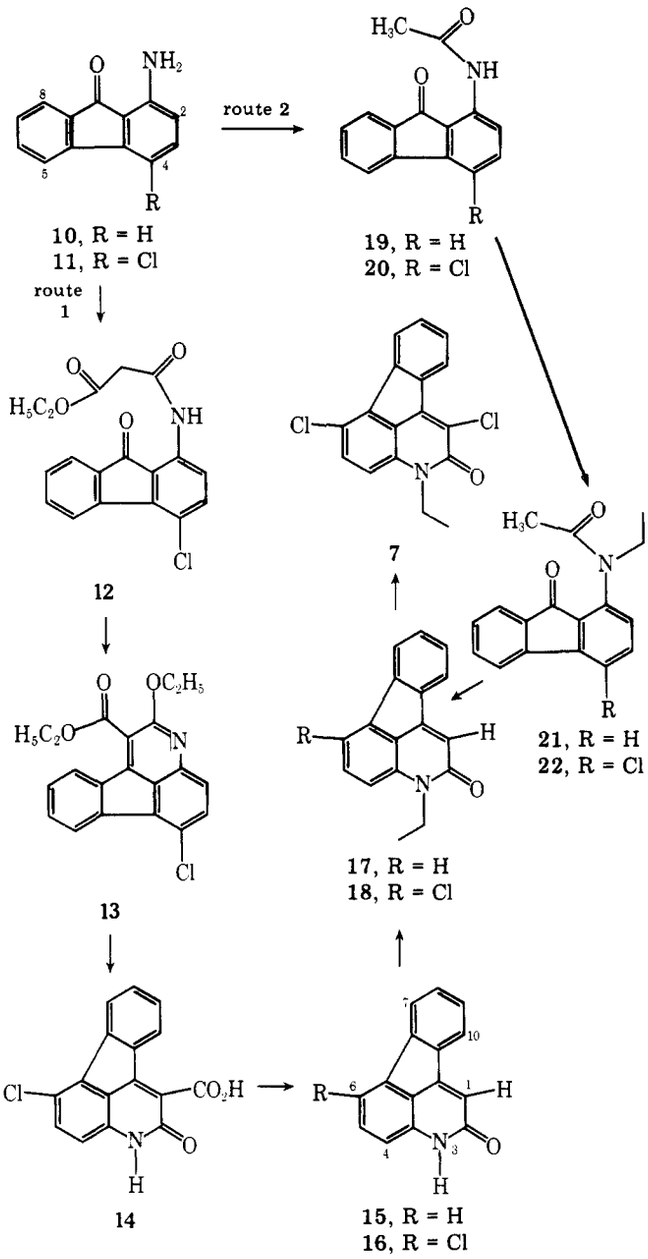
2

5, R = H; R_1 = 6-Cl
6, R = C_2H_5; R_1 = 5-Cl
7, R = C_2H_5; R_1 = 6-Cl

Scheme I



Scheme II

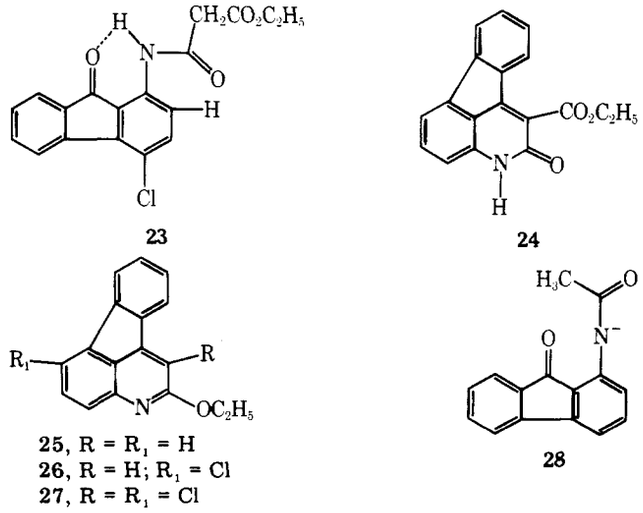


Anilides **3** and **4** were treated with concentrated sulfuric acid to afford the supposed **5** (60%) and **7** (88%), respectively. The structural relationship between these products was established by alkylating **5** with sodium hydride and ethyl bromide, to produce a mixture of *N*- and *O*-ethyl derivatives, which were separated and characterized from their spectral properties. The 3-ethylindenoquinolinone, **7**, so obtained proved to be identical with that derived from **4**, and confirmed a similar mode of cyclization for the substrates **3** and **4**.

In the absence of suitable crystals of either **5** or **7** for x-ray crystal structure determination, the preparation of authentic (chloroform-soluble) **7** was undertaken. Application of the unambiguous method of Koelsch and Steinhauer[5] furnished the intermediate product 6-chloroindeno[1,2,3-*de*]quinolin-2(3*H*)-one (**16**), and the complete synthesis of **7** is outlined in Scheme II (route 1). A modified and shorter approach (route 2) to **7** was subsequently developed.

Preparation of 7 via Route 1 (Scheme II). Chlorination of 1-aminofluoren-9-one (**10**) gave the 4-chloro derivative **11**.[6] The identity of this product, being central to the problem, was unequivocally confirmed from its NMR spectrum. The C-5 proton was anisotropically deshielded by the neighboring 4-Cl substituent and resonated downfield at δ 8.09 as a double doublet. The C-2 proton, shielded by the amino group, appeared as a doublet at δ 6.42; indeed, the spectrum was well resolved and the remaining protons could be assigned with confidence. In comparison, the NMR spectrum of **10** showed no deshielded protons.

Amine **11** was condensed with diethyl malonate to yield amide **12**. Hydrogen bonding in **12** may occur as indicated in **23**. In support,[7] **12** displayed a broad band near 3190 cm^{-1}. An interesting consequence of this suggested hydrogen bonding was revealed in the NMR spectrum of **12**. The deshielded proton ortho to the amide was further affected since it falls within the ambit of the deshielding cone of the amide carbonyl function; it thus appeared as a sharp doublet (J = 9 Hz) at δ 8.29. The NMR spectrum displayed the anisotropic deshielding of the C-5 proton as a broad doublet (J = 7.5 Hz) at δ 8.02.



Treatment of **12** with sodium ethoxide in ethanol gave the 1-carbethoxy-2-ethoxy derivative **13**. In contrast, Koelsch[5] obtained **24** from the corresponding amide, on neutralization of the reaction mixture with hydrochloric acid. Assignment **13** was supported by the IR spectrum [strong peak at 1730 cm^{-1} (ester CO); amide CO absent] and the mass spectrum, which showed the parent ion at *m/e* 353 and the expected fragmentations for **13**.

Hydrolysis of **13** to yield the corresponding 1-carboxyindenoquinolinone **14** was affected by refluxing with aqueous sodium hydroxide. In the final step of the Koelsch synthesis, thermal decarboxylation, by heating at 310 °C, gave the new 6-chloroindenoquinolinone **16** as a yellow sublimate. Spectral properties were in accord with structure **16**. A parallel series of reactions starting from **10** provided the known[5] parent indenoquinolinone **15**.

Sodium hydride abstraction of the amidic proton in **16**, followed by treatment of the ambident anion with ethyl bromide, yielded the desired 6-chloro-3-ethylindenoquinolinone **18** (51%) as well as the *O*-ethyl derivative **26** (11%). These were separated by chromatography and characterized from their spectra. Compound **15** was likewise alkylated and gave **17** (73%) and **25** (17%).

Completion of the synthesis (route 1) was effected by chlorination of the respective substrates, **17** and **18**, in chloroform with sulfuryl chloride. The two separate products proved to be the same, viz., the 1,6-dichloroindenoquinolinone **7**. The preferential electrophilic substitution at sites C-1 and C-6 in **17** was thus demonstrated.

Finally, comparison of this **7** with the product of cyclization of **4** showed them to be identical in all respects (IR, NMR, MS, mixture melting point, R_f). This finding supports the belief that **7** arises from **4** via a "direct" intermediate of type ii (Scheme I), notwithstanding the origin of the latter being in question.[3]

^1H NMR spectra were of particular diagnostic value in substantiating the various structural assignments. The protons at C-7 and C-10 in **7** were anisotropically deshielded by the chlorine substituents at C-6 and C-1, and this resulted in a two-proton multiplet (two juxtapositioned double doublets) centered at δ 7.95 ($CDCl_3$). In comparison, the monochloro compound **18** displayed only one deshielded proton (7-H) as a four-line multiplet (J_o = 7 and J_m = 2 Hz) centered at δ 8.06, while the unsubstituted **17** showed no deshielded protons. Closely related deshielding phenomena have been noted with certain 9,10-dihalogenated anthracenes.[8]

Synthesis of 7 via Route 2 (Scheme II). The acetyl derivatives **19** and **20** were readily obtained from the appropriate aminofluorenone and acetic anhydride. Cook[9] and Koelsch[5] had been unable to cyclize **19** using either sodium ethoxide or sodium hydroxide. This lack of success is here attributed to the monoanion **28**, formed by these relatively weak bases, being unable to cyclize. Alkylation of **19** and **20** with sodium hydride and ethyl bromide gave the *N*-ethyl derivatives **21** and **22**, respectively. This was evidence for the intermediacy of the anion **28**. Infrared analysis of **21** and **22** served to confirm that N-ethylation had occurred in preference to O-ethylation. Both compounds displayed the $\nu_{C=O}$ (amide) at 1650 cm^{-1}, while $\nu_{C=O}$ (keto) was near 1700 cm^{-1}. The mass spectra revealed (minor) McLafferty loss of C_2H_4, major elimination of ketene, and other fragmentations expected from the structures. Treatment of **21** and **22** with sodium hydride proved successful, and led to the cyclized products **17** (69%) and **18** (50%), respectively. This modification of the Koelsch[5] synthesis thus allowed for a more convenient approach to these heterocyclics.

Experimental Section

All melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer using KBr disks (w = weak, m = medium, s = strong). Mass spectra were recorded on a Varian CH-5 spectrometer at 70 eV. Relative abundances, particularly in mixtures, were temperature dependent. In all cases, the correct isotope abundance ratios were observed in the MS of the various halogen-containing compounds reported. ^1H NMR spectra, taken on an Hitachi Perkin-Elmer R-20 spectrometer, are recorded in δ units relative to $(CH_3)_4Si$. Chemical shifts are reported as δ (multiplicity, coupling constant, number of protons, assignment). Silica gel 60 (particle size 0.063–0.2 mm, E. Merck) was used as adsorbent for column chromatography. The petroleum ether eluent had bp 60–80 °C. Organic solvents used for extraction of aqueous solutions were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure.

1,6-Dichloroindeno[1,2,3-*de*]quinolin-2(3*H*)-one (5) was obtained in 60% (crude) yield from **3** (1 g) and concentrated H_2SO_4 (2 mL) at 95 °C for 15 min:[10] yellow crystals (from DMF); mp > 350 °C; mass spectrum *m/e* 286.992 (M^+, calcd for $C_{15}H_7Cl_2NO$, 286.991).

1,6-Dichloro-3-ethylindeno[1,2,3-*de*]quinolin-2-one (7) was similarly prepared from **4** (1 g) in 88% (crude) yield as yellow needles (from DMF): mp 204–205 °C (lit.[10] mp 198–201 °C); IR 2975 (m), 2850 (w), 1650 (s), 1630 (s), 1595 (m), 1480 (m), 1440 (m), 1120 (m), 1000 (m), 750 cm^{-1} (m); NMR ($CDCl_3$) δ 1.34 (t, J = 7 Hz, 3 H, CH_2CH_3), 4.18 (q, J = 7 Hz, 2 H, CH_2CH_3), 6.91 (d, J = 9 Hz, 1 H, ArH), 7.2–7.4 (m, 3 H, ArH), 7.84–8.06 (m, 2 H, 7-H and 10-H); mass spectrum *m/e* (rel intensity) 319 (M + 4, 7), 317 (M + 2, 41), 315 (M^+, 62), 289 (69), 287 (M − C_2H_4, 100).

Anal. Calcd for $C_{17}H_{11}Cl_2NO$: C, 64.58; H, 3.51; N, 4.43. Found: C, 64.29; H, 3.35; 4.39.

N- and O-Ethylation of 5. A mixture of **5** (0.421 g, 1.47 mmol) and NaH (0.168 g, 7.0 mmol, washed free of mineral oil) in dry DMF (15 mL) was stirred under a N_2 atmosphere for 30 min at 20 °C. Ethyl bromide (1.6 mL, 21 mmol) was added in one portion and stirring was continued for 3 h. After addition of water, extraction with $CHCl_3$ afforded a yellow solid. This was chromatographed on silica gel using petroleum ether–EtOAc (1.5:1) to give two products: (1) **1,6-Dichloro-3-ethylindeno[1,2,3-*de*]quinolin-2-one (7)**, mp 204–205 °C (0.164 g, 35.5%), identical (IR, NMR, MS, R_f, mixture melting point) with **7** derived from **4**, and (2) **1,6-dichloro-2-ethoxyindeno[1,2,3-*de*]quinoline (27)**, yellow crystals (from EtOH) [mp 153–154 °C (0.155 g, 33.6%); IR 2900 (w), 1620 (w), 1440 (s), 1370 (m), 1320 (s), 1280 (w), 1160 (w), 1060 (w), 810 (m), 740 cm^{-1} (s); NMR (CF_3COOD) δ 1.79 (t, J = 7 Hz, 3 H, CH_2CH_3), 4.89 (q, J = 7 Hz, 2 H, CH_2CH_3), 7.4–7.6 (m, 4 H, ArH), 8.04–8.35 (m, 2 H, 7-H and 10-H); mass spectrum *m/e* (rel intensity) 317 (M + 2, 38), 315 (M^+, 58), 300 (M − CH_3, 88), 287 (M − C_2H_4, 100), 271 (M − C_2H_4 − O, 52), 259 (M − C_2H_4 − CO, 12), 232 (M − C_2H_4 − CO − HCN, 10)].

1-Amino-4-chlorofluoren-9-one (11).[6] Dry Cl_2 was bubbled through a stirred solution of **10**[9] (2.0 g, 10 mmol) in glacial HOAc (100 mL). The reaction was monitored by TLC (petroleum ether–EtOAc, 6:1) and was terminated at the first sign of 1-amino-2,4-dichlorofluorenone. During the course of reaction **11** separated from solution. Filtration, followed by crystallization from EtOH, gave orange **11** (0.85 g, 36%): mp 178–179 °C (lit.[6] mp 186–187 °C); IR 3450 (s), 3340 (s), 1685 (s), 1640 (w), 1605 (w), 1570 (s), 1480 (m), 1450 (m), 1410 (w), 1290 (m), 1245 (m), 1190 (s), 1120 (s), 945 (m), 805 (m), 765 (m), 730 cm^{-1} (s); NMR ($CDCl_3$) δ 5.57 (bs, 2 H, NH_2), 6.42 (d, J = 9 Hz, 1 H, 2-H), 7.07 (d, J = 9 Hz, 1 H, 3-H), 7.28 (dt, J_o = 7.5, J_m = 1 Hz, 1 H, 6-H), 7.46 (dt, J_o = 7.5, J_m = 1.5 Hz, 1 H, 7-H), 7.62 (dd, J_o = 7.5, J_m = 1 Hz, 1 H, 8-H), 8.09 (dd, J_o = 7.5, J_m = 1.5 Hz, 1 H, 5-H); mass spectrum (65 °C) *m/e* (rel intensity) 231 (M + 2, 53), 229 (M^+, 100), 202 (54), 139 (36).

Anal. Calcd for $C_{13}H_8ClNO$: C, 67.99; H, 3.51; N, 6.10. Found: C, 67.71; H, 3.27; N, 6.00.

1-Carbethoxyacetamido-4-chlorofluoren-9-one (12). A mixture of **11** (0.723 g, 3.15 mmol) and diethyl malonate (10 mL, 65.5 mmol) was refluxed for 30 min. Excess ester was distilled under reduced pressure, and the resultant oil was triturated with 96% EtOH (6 mL) to yield **12**: yellow needles (from EtOH); mp 137–138 °C (0.619 g, 57%); IR 3230 (w), 3190 (w), 2981 (w), 2920 (w), 1730 (s), 1705 (s), 1690 (m), 1630 (w), 1605 (s), 1595 (m), 1575 (m), 1285 (m), 1185 (m), 930 (m), 820 (m), 770 (m), 745 cm^{-1} (m); NMR ($CDCl_3$) δ 1.31 (t, J = 7 Hz, 3 H, CH_2CH_3), 3.52 (s, 2 H, CH_2), 5.0 (q, J = 7 Hz, 2 H, CH_2CH_3), 7.25–7.59 (m, 4 H, ArH), 8.02 (bd, J = 7.5 Hz, 1 H, 5-H), 8.29 (d, J = 9 Hz, 1 H, 2-H); mass spectrum (110 °C) *m/e* (rel intensity) 345 (M + 2, 16), 343 (M^+, 47), 298 (M − OC_2H_5, 17), 256 (M − $CH_2CO_2C_2H_5$, 12), 229 (M − $C_2H_5CO_2CH{=}C{=}O$, 100).

Anal. Calcd for $C_{18}H_{14}ClNO_4$: C, 62.89; H, 4.10; N, 4.08. Found: C, 63.19; H, 4.10; N, 4.16.

1-Carbethoxy-6-chloro-2-ethoxyindeno[1,2,3-*de*]quinoline

(13). To a refluxing solution of 12 (0.568 g, 1.65 mmol) in absolute EtOH (20 mL) was added a solution of sodium ethoxide in EtOH (6 mL of 1.1 M, 6.6 mmol), and heating was continued for 45 min. Filtration of the cooled mixture afforded 13 (0.54 g, 93%): mp >200 °C; IR 1730 (s), 1645 (m), 1600 (s), 1580 (s), 1480 (s), 1440 (s), 1250 (m), 1155 (m), 1090 (s), 1075 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 355 (M + 2, 35), 353 (M^+, 100), 325 (M − C_2H_4, 12), 308 (M − C_2H_5O, 25).

1-Carboxy-6-chloroindeno[1,2,3-*de*]quinolin-2(3*H*)-one (14). A mixture of 13 (0.575 g, 1.63 mmol) and 5% aqueous NaOH (100 mL) was refluxed for 3 h. The solution was filtered and added to boiling 6 M HCl to precipitate 14 as a yellow solid (0.267 g, 55%): mp >350 °C; IR 1740 (s), 1640 (w), 1630 (s), 1585 (w), 1475 (m), 1435 (s), 1400 (m), 1380 (m), 1150 (m), 1090 (m), 965 (w), 815 (w), 780 (m), 745 (m), 675 cm^{-1} (m); mass spectrum (223 °C) *m/e* (rel intensity) 299 (M + 2, 14), 297 (M^+, 37), 253 (M − CO_2, 100), 225 (M − CO_2 − CO, 33), 198 (M − CO_2 − CO − HCN, 44).

6-Chloroindeno[1,2,3-*de*]quinolin-2(3*H*)-one (16). Acid 14 (0.236 g, 0.794 mmol) was heated on a sand bath at 310 °C under a N_2 atmosphere. The product 16 was collected as a yellow sublimate (0.150 g, 74.6%): mp >300 °C; IR 3150 (w), 3010 (w), 2850 (w), 1660 (s), 1600 (m), 1585 (m), 1450 (m), 1435 (m), 1320 (m), 850 (m), 805 (m), 780 (m), 745 cm^{-1} (m); mass spectrum (165 °C) *m/e* (rel intensity) 255 (M + 2, 32), 253 (M^+, 100), 225 (M − CO, 8), 218 (M − Cl, 13), 198 (M − CO − HCN, 11).

Anal. Calcd for $C_{15}H_8ClNO$: C, 71.02; H, 3.18; N, 5.52. Found: C, 70.86; H, 3.00; N, 5.32.

The parent indenoquinolinone 15 was prepared in a parallel series of reactions starting from 10, and obtained as yellow crystals (from DMF): mp 275–278 °C (lit.[5] mp 277–279 °C); mass spectrum (157 °C) *m/e* (rel intensity) 219 (M^+, 100), 191 (M − CO, 16), 164 (M − CO − HCN, 31).

N- and O-Ethylation of 16. Alkylation of 16 (0.145 g, 0.572 mmol) with NaH (0.047 g, 1.95 mmol) and ethyl bromide (0.36 mL, 4.8 mmol) and subsequent chromatography, as for 6, afforded two products. (1) **6-Chloro-3-ethylindeno[1,2,3-*de*]quinolin-2-one (18),** yellow crystals (from DMF): mp 186–187 °C (lit.[11] mp 178–180 °C); 0.082 g (51%); IR 2970 (w), 1655 (s), 1610 (s), 1580 cm^{-1} (s); NMR ($CDCl_3$) δ 1.32 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 4.21 (q, *J* = 7 Hz, 2 H, CH_2CH_3), 6.95 (s, 1 H, 1-H), 7.04–7.74 (m, 5 H, ArH), 8.06 (dd, J_o = 7, J_m = 2 Hz, 1 H, 7-H); mass spectrum (195 °C) *m/e* (rel intensity) 283 (M + 2, 27), 281 (M^+, 59), 253 (M − C_2H_4, 100). (2) **6-Chloro-2-ethoxyindeno[1,2,3-*de*]quinoline (26),** yellow needles (from petroleum ether): mp 128–130 °C; 0.018 g (11%); IR 2980 (w), 1630 (w), 1600 (w), 1440 (s), 1420 (w), 1370 (m), 1320 (s), 1200 (s), 1040 (w), 770 (m), 735 cm^{-1} (m); mass spectrum (150 °C) *m/e* (rel intensity) 283 (M + 2, 17), 281 (M^+, 42), 266 (M − CH_3, 94), 253 (M − C_2H_4, 100), 237 (M − C_2H_4 − O, 52), 225 (M − C_2H_4 − CO, 25), 198 (M − C_2H_4 − CO − HCN, 42).

The ethylation of 15 was similarly conducted and gave two products. (1) **3-Ethylindeno[1,2,3-*de*]quinolin-2-one (17):** 73% yield; yellow needles (from petroleum ether); mp 116–117 °C; IR 2970 (w), 1655 (s), 1620 (m), 1595 (s), 775 (s), 755 cm^{-1} (s); NMR ($CDCl_3$) δ 1.31 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 4.19 (q, *J* = 7 Hz, 2 H, CH_2CH_3), 6.87 (s, 1 H, 1-H), 7.11 (dd, J_o = 7.5, J_m = 2 Hz, 1 H, ArH), 7.2–7.7 (m, 6 H, ArH); mass spectrum (162 °C) *m/e* (rel intensity) 247 (M^+, 95), 232 (M − CH_3, 17), 219 (M − C_2H_4, 100). (2) **2-Ethoxyindeno[1,2,3-*de*]quinoline (25)** (17%): yellow crystals (from EtOH); mp 72–74 °C (lit.[5] mp 76.5–77.5 °C); NMR ($CDCl_3$) δ 1.47 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 4.56 (q, *J* = 7 Hz, 2 H, CH_2CH_3), 7.2–7.9 (m, 8 H, ArH); mass spectrum (33 °C) *m/e* (rel intensity) 247 (M^+, 43), 232 (M − CH_3, 100), 219 (M − C_2H_4, 84), 203 (M − C_2H_4 − 0, 78), 191 (M − C_2H_4 − CO, 21), 164 (M − C_2H_4 − CO − HCN, 40).

Chlorination of 17 and 18 to 7. Substrate 17 (0.134 g, 0.54 mmol) was refluxed with SO_2Cl_2 (0.16 g, 1.2 mmol) in dry $CHCl_3$ (8 mL) for 4 h. Excess reagent and $CHCl_3$ were removed under reduced pressure and the residue was purified on a silica gel column using petroleum ether–EtOAc (1.5:1) as eluent. Crystallization from DMF gave yellow needles (90 mg, 53%), mp 204–205 °C, identical (IR, NMR, MS, R_f, mixture melting point) with the product derived from cyclization of 4. Compound 18 with a 2.2 molar proportion of SO_2Cl_2 gave the identical 7 in 74% yield.

1-Acetamido- (19) and 1-Acetamido-4-chlorofluoren-9-one (20). A mixture of 11 (0.05 g, 0.22 mmol) and acetic anhydride (2 mL) was refluxed for 1 h. Excess reagent was evaporated and the residue was extracted with Et_2O and crystallized (from EtOH) to give yellow 20 (0.046 g, 78%): mp 194–196 °C; mass spectrum (75 °C) *m/e* (rel intensity) 273 (M + 2, 11), 271 (M^+, 32), 229 (M − CH_2=C=O, 100).

Anal. Calcd for $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found: C, 65.98; H, 3.52; N, 5.06.

Amide 19 was likewise formed from 10 in 36% yield: mp 139–140 °C (lit.[5] mp 136–137 °C); mass spectrum (88 °C) *m/e* (rel intensity) 238 (M + 1, 22), 237 (M^+, 67), 195 (M − CH_2=C=O, 100).

1-(*N*-Acetyl-*N*-ethyl)- (21) and 1-(*N*-Acetyl-*N*-ethyl)-4-chloroaminofluoren-9-one (22). The alkylation of 19 (0.100 g, 0.422 mmol) with NaH (0.030 g, 1.3 mmol) and ethyl bromide (0.20 mL, 2.6 mmol) was conducted as for 6. Chromatography on silica gel with petroleum ether–EtOAc (6:1) as eluent gave 21 (0.068 g, 61%): mp 99–100 °C; IR 2970 (w), 2930 (w), 1715 (s), 1710 (s), 1650 (s), 1615 (m), 1600 (s), 920 (s), 820 (m), 760 (s), 750 (m), 690 cm^{-1} (s); mass spectrum (84 °C) *m/e* (rel intensity) 266 (M + 1, 14), 265 (M^+, 71), 237 (M − C_2H_4, 5), 223 (M − CH_2CO, 100), 208 (M − CH_2CO − CH_3, 97). Product 22 was similarly obtained from 20 in 52% yield: mp 125–130 °C; IR 1700 (s), 1650 cm^{-1} (s); mass spectrum (86 °C) *m/e* (rel intensity) 301 (M + 2, 19), 299 (M^+, 43), 271 (M − C_2H_4, 4), 257 (M − CH_2CO, 71), 242 (M − CH_2CO − CH_3, 97).

3-Ethyl- (17) and 6-Chloro-3-ethylindeno[1,2,3-*de*]quinolin-2-one (18). A mixture of 21 (0.050 g, 0.19 mmol) and NaH (0.020 g, 0.83 mmol) in dry DMF(25 mL) was stirred at 18 °C for 2 h. Dilution with water (50 mL) and extraction into Et_2O yielded an orange oil (0.041 g) which was chromatographed on silica gel with petroleum ether–EtOAc (1.5:1) to afford 17 (32 mg, 69%), mp 116–117 °C, identical (IR, NMR, MS, mixture melting point, and R_f) with 17 derived from 15.

Compound 18 was likewise obtained from 22 in 50% yield, mp 185–188 °C, identical with the product from 16.

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Registry No.—3, 19359-40-1; 4, 19359-44-5; 5, 19359-53-6; 7, 19359-54-7; 10, 6344-62-3; 11, 5358-50-9; 12, 62743-42-4; 13, 62778-03-4; 14, 62743-43-5; 15, 25559-71-1; 16, 62743-44-6; 17, 62743-45-7; 18, 25559-79-9; 19, 6954-57-0; 20, 16304-68-0; 21, 62743-46-8; 22, 62743-47-9; 25, 62743-48-0; 26, 62743-49-1; 27, 62743-50-4; ethyl bromide, 74-96-4; diethyl malonate, 510-20-3.

References and Notes

(1) B. Staskun, *J. Org. Chem.*, **39**, 3494 (1974).
(2) D. N. Harcourt and N. Taylor, *J. Chem. Soc., Chem. Commun.*, 643 (1972).
(3) (a) We thank a referee for helpful suggestions concerning the behavior of i. (b) An attempt to isolate a spirocyclodienone intermediate from 4′-methoxy-2,2-dichlorobenzoylacetanilide and sulfuric acid afforded instead a small yield of 3-chloro-6-methoxy-4-phenylquinolin-2(1*H*)-one and chlorinated derivatives (unpublished results). There is no compelling evidence at this stage for persevering with "spiro" intermediate i, and the simpler, "direct" pathway to ii is preferred.
(4) D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc., Perkin Trans. 1*, 1162 (1972).
(5) C. F. Koelsch and A. F. Steinhauer, *J. Org. Chem.*, **18**, 1516 (1953).
(6) O. Hromatka, K. A. Maier, and K. Knollmüller, *Monatsh. Chem.*, **98**, 1567 (1967).
(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London, 1958.
(8) "Varian High Resolution NMR Spectra Catalog", Vol. 2, 1963.
(9) J. W. Cook and J. S. Moffat, *J. Chem. Soc.*, 1160 (1950).
(10) A. J. Hodgkinson and B. Staskun, *J. Org. Chem.*, **34**, 1709 (1969).
(11) T. van Es and B. Staskun, *Tetrahedron*, **35**, 5941 (1969).