

NOVEL INTRAMOLECULAR TWO-SUBSTITUENT MIGRATION ACCOMPANYING INDENOQUINOLONE FORMATION

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(Received in UK 30 May 1972; Accepted for publication 23 June 1972)

Abstract. Treatment of 2,2,4'-trichloro-2',5'-dimethylbenzoylacetanilide (**2c**) with H_2SO_4 gave 1,5-dichloro-4,6-dimethylindeno[1,2,3-*de*]quinolin-2(3H)-one (**3a**) which was identified by spectral (IR) comparison with various isomeric **3**. Product **3a** may arise via concerted, intramolecular 1,2-shifts of two substituents during cyclization. Substrate 2,2,2',4'-tetrachloro-3',5'-dimethylbenzoylacetanilide (**2e**), in which this rearrangement is not feasible, was converted into 1,4,6-trichloro-5-methyl-7H-dibenz[*f, ij*]isoquinolin-2(3H)-one (**5b**).

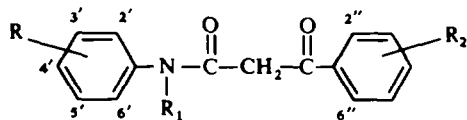
In previous papers^{1,2} we described a new synthesis of indeno[1,2,3-*de*]quinolin-2-ones **3** by cyclization of 2,2-dichlorobenzoylacetanilides **2** with conc H_2SO_4 . Further developments are now reported.

Generally, acceptable yields (40–60%) of **3** resulted from those anilides **2** bearing a 4'-Cl substituent, as in **2a** (60%), **2g** (42%), and **2h** (53–60%). In contrast was the relatively poor production (5–20%) of **3** from the substrate **2** possessing a 4'-CH₃ group,* as in **2b** (15%), **2f** (15–19%), and **2n** (<5%). Indeed, the principal cyclization product from **2** was the corresponding 4-phenylquinolone **7**; in addition, the reaction furnished chlorinated **3** and **7**. By way of illustration, 2,2,3'-trichloro-2',4'-dimethylbenzoylacetanilide (**2f**, **3g**) with H_2SO_4 (6 ml) at 90–95° for 6 min yielded, on pouring into water, indenoquinolones **3a** and **3b** (15–19%) together with 4-phenylquinolones **7a** and **7b** (~30%). Product **7** presumably arises by loss of Cl⁺ from an intermediate² carbonium ion such as **8**; subsequent attack by the chlorinium ion (or an equivalent species) on a susceptible substrate (such as **3**) leads to the chlorinated derivative. In some instances the yield of the latter material was quite substantial. Thus, 2,2-dichloro-N-methylbenzoylacetanilide (**2l**) gave an indenoquinolone mixture (~30% yield) comprising chiefly 1,6-dichloro-N-methylindeno[1,2,3-*de*]quinolin-2-one (**3i**) together with a smaller proportion of the normal product **3h**. The N-ethyl anilide **2m** likewise furnished a mixture of **3k** and **3j** in which the former base predominated; previously the presence of **3k** only had been reported.¹

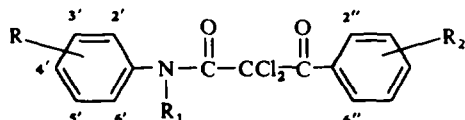
Anilide **2** in which the arylamino moiety was substituted at a "blocking" position (as in **2d**, **2i**), or was deactivated towards electrophilic substitution by the presence of a NO₂ group (as in **2j**, **2o**, **2p**), failed to yield either **3** or **7** on warming with acid; **2d** and **2i** were recovered largely unchanged, but the other **2** suffered extensive hydrolytic cleavage† to the corresponding dichloroacetanilide, CHCl₂CONHAr.

* This substituent effect is compatible with electrophilic attack by ring A upon nucleus B, rather than *vice versa*, as in Scheme 1.

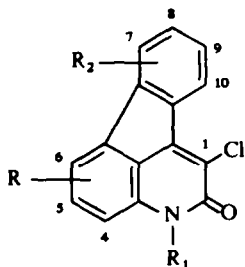
† Anilides **1j** and **1k** when similarly reacted yielded 2-methyl-5-nitroaniline and 2,5-dichloroaniline, respectively; the products may well have arisen *via* an analogous acetanilide intermediate.



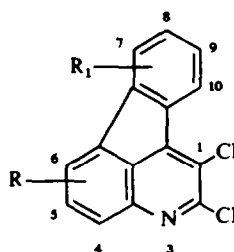
- 1a:** $R_1 = R_2 = H$; $R = 2',3'\text{-diCH}_3$
1b: $R_1 = R_2 = H$; $R = 2',4'\text{-diCH}_3$
1c: $R_1 = R_2 = H$; $R = 2',5'\text{-diCH}_3$
1d: $R_1 = R_2 = H$; $R = 2',6'\text{-diCH}_3$
1e: $R_1 = R_2 = H$; $R = 3',5'\text{-diCH}_3$
1f: $R_1 = R_2 = H$; $R = 3'\text{-Cl-}2',4'\text{-diCH}_3$
1g: $R_1 = H$; $R_2 = 3''\text{-CH}_3$; $R = 4'\text{-Cl-}2'\text{-CH}_3$
1h: $R_1 = R_2 = H$; $R = 4'\text{-Cl-}2'\text{-CH}_3$
1i: $R_1 = R_2 = H$; $R = 2',6'\text{-diC}_2\text{H}_5$
1j: $R_1 = R_2 = H$; $R = 2'\text{-CH}_3\text{-}5'\text{-NO}_2$
1k: $R_1 = R_2 = H$; $R = 2',5'\text{-diCl}$
1l: $R = R_2 = H$; $R_1 = \text{CH}_3$
1m: $R = R_2 = H$; $R_1 = \text{C}_2\text{H}_5$
1n: $R_1 = R_2 = H$; $R = 4'\text{-CH}_3$
1o: $R_1 = R_2 = H$; $R = 2',5'\text{-diCH}_3\text{-}4'\text{-NO}_2$
1p: $R_1 = R_2 = H$; $R = 4'\text{-NO}_2$



- 2a:** $R_1 = R_2 = H$; $R = 4'\text{-Cl-}2',3'\text{-diCH}_3$
2b: $R_1 = R_2 = H$; $R = 2',4'\text{-diCH}_3$
2c: $R_1 = R_2 = H$; $R = 4'\text{-Cl-}2',5'\text{-diCH}_3$
2d: $R_1 = R_2 = H$; $R = 4'\text{-Cl-}2',6'\text{-diCH}_3$
2e: $R_1 = R_2 = H$; $R = 2',4'\text{-diCl-}3',5'\text{-diCH}_3$
2f: $R_1 = R_2 = H$; $R = 3'\text{-Cl-}2',4'\text{-diCH}_3$
2g: $R_1 = H$; $R_2 = 3''\text{-CH}_3$; $R = 4'\text{-Cl-}2'\text{-CH}_3$
2h: $R_1 = R_2 = H$; $R = 4'\text{-Cl-}2'\text{-CH}_3$
2i: $R_1 = R_2 = H$; $R = 4'\text{-Cl-}2',6'\text{-diC}_2\text{H}_5$
2j: $R_1 = R_2 = H$; $R = 2'\text{-CH}_3\text{-}5'\text{-NO}_2$
2k: $R_1 = R_2 = H$; $R = 2',5'\text{-diCl}$
2l: $R = R_2 = H$; $R_1 = \text{CH}_3$
2m: $R = R_2 = H$; $R_1 = \text{C}_2\text{H}_5$
2n: $R_1 = R_2 = H$; $R = 4'\text{-CH}_3$
2o: $R_1 = R_2 = H$; $R = 2',5'\text{-diCH}_3\text{-}4'\text{-NO}_2$
2p: $R_1 = R_2 = H$; $R = 4'\text{-NO}_2$



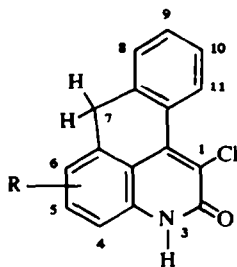
- 3a:** $R = 5\text{-Cl-}4,6\text{-diCH}_3$; $R_1 = R_2 = H$
3b: $R = 5\text{-Cl-}4,6\text{-diCH}_3$; $R_1 = H$; $R_2 = 9\text{-Cl}$
3c: $R = 6\text{-Cl-}4,5\text{-diCH}_3$; $R_1 = R_2 = H$
3d: $R = 6\text{-Cl-}4\text{-CH}_3$; $R_1 = H$; $R_2 = \text{X-CH}_3$
3e: $R = 6\text{-Cl-}4\text{-CH}_3$; $R_1 = R_2 = H$
3f: $R = 4,6\text{-diCH}_3$; $R_1 = R_2 = H$
3g: $R = 4,6\text{-diCH}_3$; $R_1 = H$; $R_2 = \text{X-Cl}$
3h: $R = R_2 = H$; $R_1 = \text{CH}_3$
3i: $R = 6\text{-Cl}$; $R_1 = \text{CH}_3$; $R_2 = H$
3j: $R = R_2 = H$; $R_1 = \text{C}_2\text{H}_5$
3k: $R = 6\text{-Cl}$; $R_1 = \text{C}_2\text{H}_5$; $R_2 = H$



- 4a:** $R = 5\text{-Cl-}4,6\text{-diCH}_3$; $R_1 = H$
4b: $R = 5\text{-Cl-}4,6\text{-diCH}_3$; $R_1 = 8\text{-Cl}$
4c: $R = 5\text{-Cl-}4,6\text{-diCH}_3$; $R_1 = 9\text{-Cl}$
4d: $R = 6\text{-Cl-}4,5\text{-diCH}_3$; $R_1 = H$
4e: $R = 6\text{-Cl-}4\text{-CH}_3$; $R_1 = \text{X-CH}_3$
4f: $R = 6\text{-Cl-}4\text{-CH}_3$; $R_1 = H$

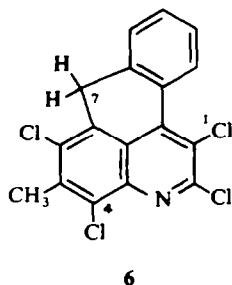
The most significant results in this paper pertain to the effect of conc H_2SO_4 on the substrates **2c** and **2e**. As previously² mentioned, 2,2,4'-trichloro-2',5'-dimethylbenzoylacetanilide (**2c**) with a 5'-methyl group positioned to prevent indenoquinolone formation, nevertheless underwent ready reaction with liberation of HCl to furnish a product (hereafter referred to as "A"), which analyzed as $\text{C}_{17}\text{H}_{11}\text{Cl}_2\text{NO}$, and was formulated tentatively as **5a**. This unexpected result motivated the present study.

The structure of **2c**, derived^{1,2} from anilide **1c** and SO_2Cl_2 , was verified by alkaline

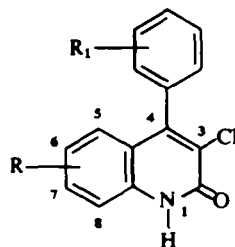


5a: R = 6-Cl-4-CH₃

5b: R = 4,6-diCl-5-CH₃



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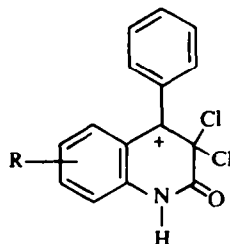
7a: R = 7-Cl-6,8-diCH₃; R₁ = H

7b: R = 7-Cl-6,8-diCH₃; R₁ = X-Cl

7c: R = 6,8-diCH₃; R₁ = H

7d: R = 6,8-diCH₃; R₁ = X-Cl

7e: R = 6-CH₃; R₁ = H



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hydrolysis to give 4-chloro-2,5-dimethylaniline, identified from its NMR spectrum, elemental analysis, and conversion to known derivatives. An NMR spectrum (in CF₃COOH-H₂SO₄) of "A", with a better resolution than that previously² obtained, showed two overlapping singlets (6H) near δ 2.7, attributed to two methyl moieties, and a multiplet (\sim 4H) at δ 7.2–8.3. This evidence and the absence of other absorption peaks conclusively disproved the proposed² structure **5a**; the methylene protons of **5a** would be expected to absorb near δ 5, as found for the comparable protons of anthrone.*

Just as indenoquinolone **3** on reaction with SOCl₂/DMF was transformed into a chloroform-soluble derivative (**4**), "A" gave a product (referred to as "B") of molecular formula C₁₇H₁₀Cl₃N, established from elemental and mass spectral analysis. The NMR spectrum of "B" (in CDCl₃) exhibited two distinct singlets (6H) near δ 2.6, which unequivocally established the presence in the molecule of two methyl groups, and an aromatic multiplet (4H) at δ 7.2–8.3.

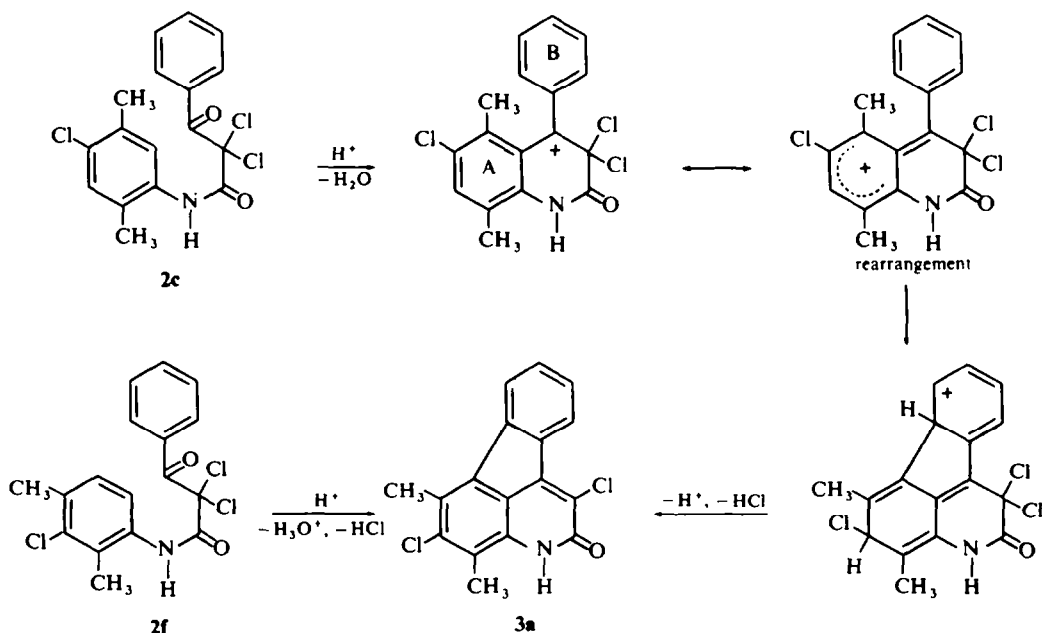
With the elimination of **5a**, the alternative isomeric structures **3c** and **3d** were contemplated for "A"; of these, the former, with its implication of a Jacobsen-like methyl migration,³ seemed the more plausible. Compound **3c** was readily available from 2,2,4'-trichloro-2',3'-dimethylbenzoylacetanilide (**2a**) and H₂SO₄. A comparison of the IR spectra of **3c** and "A" showed that these were different substances. This finding was confirmed with the corresponding trichloro derivatives (i.e. **4d** and "B").

* The methylene protons of compound **5b** (see below) gave a peak near δ 5.

The possibility of an internuclear methyl migration during the formation of "A" from **2c**, and the representation of "A" as **3d** ($X = 7$) also merited consideration. The assignments **3d** ($X = 8$) and **3d** ($X = 9$) were less plausible on account of the strong absorption peak near 750 cm^{-1} in the IR spectra of "A" and "B" (present also in **3c** and **4d**), indicative of three or four adjacent hydrogen atoms in an aromatic ring,⁴ while **3d** ($X = 10$) seemed unlikely on steric grounds. 4'-Chloro-2',3''-dimethylbenzoylacetanilide (**1g**), derived from 4-chloro-2-methylaniline and ethyl 3-toluoylacetate, was chlorinated with SO_2Cl_2 to give the 2,2,4'-trichloroanilide **2g**. It was anticipated that reaction of **2g** with H_2SO_4 in the usual manner would provide both **3d** ($X = 7$) and **3d** ($X = 9$). But the indenoquinolone product obtained (42% yield, molecular ion, m/e 315) was entirely devoid of "A", as revealed from its IR spectrum. The corresponding 2-chloro derivative, **4e**, moreover contained no "B". As the product from **2g** was thought unlikely to be constituted exclusively of either **3d** ($X = 7$) or **3d** ($X = 9$) alone, the possibility of "A" having been derived *via* the aforementioned migration was discounted. Subsequently, evidence against the feasibility of the envisaged methyl transfer was provided from the observations with anilide **2e** (see below).

The seemingly remote possibility of "A" having structure **3a** as a result of an extraordinary two-substituent (Cl and CH_3) displacement accompanying cyclization (Scheme 1) was examined. Compound **3a**, together with **3b**,* was derived from anilide

Scheme 1



2f as already mentioned. In this connection the structure of the 3-chloro-2,4-dimethylaniline, employed in the synthesis of **2f**, was unequivocally substantiated from its NMR spectrum.

Gratifyingly, the IR absorption peaks of "A" were all present in the spectrum of

* The allocation of the Cl substituent to the 9-position in **3b** is discussed below.

the above indenoquinolone mixture. In support, "B" was similarly indicated in the mixture of the corresponding 2-chloro-derivatives (**4a** and **4c**). More convincingly, column chromatography of the latter product provided a specimen of **4a** identical (IR spectrum) with "B".

In another approach, "A" in H_2SO_4 soln was treated with Cl_2 to yield a trichloro derivative, $\text{C}_{17}\text{H}_{10}\text{Cl}_3\text{NO}$ (IR absorption near 750 cm^{-1} absent; molecular ion at m/e 349, and negligible ($M + 34$) impurity); this material was also obtained on passage of Cl_2 into a soln of **2c** in H_2SO_4 which had been kept at $90\text{--}95^\circ$ for 5 min. The aforementioned indenoquinolone mixture derived from **2f** on similar chlorination, was converted into the identical (IR spectrum) product **3b**; in this instance, component **3a** underwent nuclear chlorination to **3b** to supplement the material already present. It is noteworthy that **3b** (essentially free of **3a** impurity) was formed, albeit in negligible yield, on treatment of **2f** with H_2SO_4 at $20\text{--}90^\circ$.

From the above observations, it was concluded that "A" was indeed 1,5-dichloro-4,6-dimethylindeno[1,2,3-*de*] quinolin-2(3H)-one (**3a**). Finally, the aforementioned trichloro derivative from "A" was refluxed with SOCl_2/DMF and converted into a tetrachloro indenoquinoline, $\text{C}_{17}\text{H}_9\text{Cl}_4\text{N}$ [amide $\text{C}=\text{O}$ absorption absent; molecular ion at m/e 367, and negligible ($M + 34$) impurity; NMR ($\text{CF}_3\text{COOH-H}_2\text{SO}_4$) δ 2.94 (2s, 6H, CH_3 ; the superimposed singlets were resolved into two distinct peaks in C_6H_6 soln), 7.65 (q, 1H, $J = 7$ and 2 Hz, 8-H), 7.92 (d, 1H, $J = 7$ Hz, 7-H), 8.35 (d, 1H, $J = 2$ Hz, 10-H)]. The identical (IR spectrum) material (**4c**) was formed on similar conversion of **3b** derived from **2f**.

The NMR splitting pattern and coupling shown in the aromatic multiplet could be reconciled with either structure **4b** or **4c**, but it excluded other isomeric possibilities. The aromatic proton at δ 8.35 on account of its relatively low downfield position, was correlated tentatively with a proton neighbouring two Cl substituents; structure **4c** is accordingly preferred for the tetrachloroindenoquinoline product. The trichloro derivative from "A" (**3a**) and Cl_2 consequently is **3b**.

In the synthesis of **3a** from **2c**, the product, contaminated only to a minor extent with **3b**, was produced in substantial ($> 50\%$) yield. More significantly, the **3a** was free of detectable (IR spectrum) amounts of isomeric impurities such as **3c** and **3d**, and of demethylated and dechlorinated material (**3e** and **3f** respectively). Sulfonation and disproportionation such as occur in the Jacobsen³ reaction, apparently play no role in this particular rearrangement.

A tentative suggestion at this stage is that formation of **3a** from **2c** is attended by electrophilic attack of ring A upon ring B, inducing concerted, intramolecular 1,2-shifts of two substituents (CH_3 and Cl), as outlined in Scheme 1. The mechanistic aspects, as well as the synthetic potential of this rearrangement, are currently under study.

In the case of 2,2,2',4'-tetrachloro-3',5'-dimethylbenzoylacetanilide (**2e**), treatment with H_2SO_4 likewise gave a novel product. The arylamino moiety of this substrate, it should be noted, offers no scope for a group migration of the type indicated immediately above, as it does for an internuclear methyl transfer. The structure of **2e**, derived from anilide **1e** and SO_2Cl_2 , was substantiated by alkaline hydrolysis to give 2,4-dichloro-3,5-dimethylaniline.

Elemental and spectral analysis of the yellow, high-melting material obtained (42%) from **2e** and acid established a molecular formula $\text{C}_{17}\text{H}_{10}\text{Cl}_3\text{NO}$, and showed

it to be a cyclic amide (multiple NH absorption near 3000, strong C=O peak at 1650 cm^{-1}). This substance is regarded as 1,4,6-trichloro-5-methyl-7H-dibenz- $[f,i,j]$ isoquinolin-2(3H)-one (**5b**) on the basis of its NMR spectrum ($\text{CF}_3\text{COOH-H}_2\text{SO}_4$): δ 2.90 (s, 3H, CH_3), 5.0 (s, 2H, CH_2), 7.2–8.5 (m ~ 4H, aromatic). To substantiate this proposed assignment the product was converted by reaction with SOCl_2/DMF into a tetrachloro derivative, $\text{C}_{17}\text{H}_9\text{Cl}_4\text{N}$ (**6**) (amide NH and C=O absorptions absent), in which the presence of two methylene protons and only one methyl moiety in the structure was again revealed from the NMR spectrum (CF_3COOH): δ 2.97 (s, 3H, CH_3), 5.0 (s, 2H, CH_2), 7.2–8.5 (m, 4H, aromatic).

The above cyclization which constitutes a new synthesis of the dibenz- $[f,i,j]$ isoquinolone system, **5**, may involve intermediates of the type previously² indicated, and is being further investigated.

EXPERIMENTAL

All m.ps are uncorrected. Solvent (CHCl_3) extracts were dried over Na_2SO_4 and evaporated by rotary evaporator.

IR spectra were recorded on a Perkin-Elmer Infracord model 137 spectrophotometer (1 to 1.3 mg per 300 mg KBr), and in some instances, on a Perkin-Elmer 521 instrument. Mass spectra were determined with an AEI model MS9 spectrometer (70 eV). NMR spectra were recorded on an Hitachi Perkin-Elmer R-20 spectrometer with TMS as internal reference.

Spots due to **1** and **2** on silica gel TLC (5–10% EtOAc in benzene) were visualized by quenching of fluorescence; those due to **4** and **6** were revealed (on conventional plates) under UV radiation.

Starting materials. Commercial xylydines and arylamines were used directly without purification for condensation with ethyl benzoylacetate. These included 2,3-dimethylaniline (Schuchardt, Munich), 2,4-dimethylaniline (Fluka AG), 2,5-dimethylaniline [(Schuchardt, Munich); IR (neat) identical with standard (Sadtler) spectrum; N-formyl derivative, m.p. 118–119° (lit.⁵ m.p. 116–117°), N-acetyl derivative, m.p. 141–142° (lit.⁶ m.p. 140.5–141°)], 2,6-dimethylaniline (Astra, Copenhagen), 3,5-dimethylaniline (Schuchardt, Munich), 2,6-diethylaniline (Ethyl Corporation, New York). 2,5-dimethyl-4-nitroaniline was prepared by nitration¹¹ of acet-2,5-dimethylanilide [yellow crystals (from EtOH), m.p. 142–145° (lit.⁷ m.p. 145.5–146°)]. 3-Chloro-2,4-dimethylaniline was prepared from 2,6-dimethylaniline by the following route: Sandmeyer reaction of the latter amine (26 g) yielded 1-chloro-2,6-dimethylbenzene [10 g, b.p. 175–177° (627 mm)], which was nitrated at ~20° with a mixture of conc HNO_3 (d. 1.40; 7 ml) and conc H_2SO_4 (9 ml) over a period of 1 hr with stirring and appropriate cooling; the reaction mass was stirred for an additional hr and poured into water to give chiefly 3-chloro-2,4-dimethylnitrobenzene [8 g, crude yield; yellow crystals (from MeOH), m.p. 45–47° (lit.⁸ m.p. 46–47°)]. This was reduced with granulated Sn and HCl to the desired amine, which was obtained, after steam distillation of the alkaline reaction mixture, as an orange oil (6–7 g, crude yield); the product was purified by dissolving in 2M HCl and precipitating from the charcoaled acid soln with 2M NaOH [colorless needles (from dil MeOH), m.p. 48–49° (lit.⁸ m.p. 48–49°); * NMR (CCl_4) δ 2.16 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.33 (broad s, 2H, NH_2), 6.27 (d, $J = 8\text{ Hz}$, one aromatic proton), 6.70 (d, $J = 8\text{ Hz}$, one aromatic proton, coupled to an ortho proton). (Found: C, 62.19; H, 6.58; N, 9.10. $\text{C}_8\text{H}_9\text{ClN}$ requires: C, 61.74; H, 6.48; N, 9.00%). N-acetyl derivative, colorless crystals (from dilute EtOH), m.p. 157–158°. (Found: C, 60.59; H, 5.97; N, 7.19. $\text{C}_{10}\text{H}_{11}\text{ClNO}$ requires: C, 60.76; H, 6.12; N, 7.09%).

Benzoylacetanilides **1**

General procedure. A mixture of ethyl benzoylacetate (BDH: 0.11 mol) and the appropriate arylamine (0.1 mol) was stirred at 145–150° for 1 hr. The reaction mass was cooled and triturated with light petroleum (b.p. 40–60°)–benzene (1:1, v/v) to dissolve undesirable material, and filtered. The residue of sparingly soluble anilide **1** was crystallized from aqueous EtOH or, in some instances, from aqueous EtOH-DMF.

In the case of the nitrobenzoylacetanilides **1a** and **1p**, the (light petroleum-benzene) triturated material was freed of unchanged nitroamine impurity by extraction into warm 1M NaOH; acidification of the filtered alkaline extract with glacial AcOH precipitated the crude anilide.

* M.p. 58–59° quoted in Ref. 5, p. 696, pertains to 4-chloro-3,5-dimethylaniline.

Relevant data of new **1** are given in Table 1.

TABLE 1. BENZOYLACETANILIDES **1**

Compound	Formula	M.p., °C	Calculated, %			Found, %		
			C	H	N	C	H	N
1a	C ₁₇ H ₁₇ NO ₂	174–175	76.38	6.41	5.24	76.29	6.42	5.14
1b	C ₁₇ H ₁₇ NO ₂	156–158	76.38	6.41	5.24	76.31	6.28	5.35
1d	C ₁₇ H ₁₇ NO ₂	151–152	76.38	6.41	5.24	76.35	6.37	5.27
1e	C ₁₇ H ₁₇ NO ₂	103–104	76.38	6.41	5.24	76.64	6.44	5.38
1f	C ₁₇ H ₁₆ ClNO ₂	154–156	67.66	5.34	4.64	67.61	5.38	4.68
1g	C ₁₇ H ₁₆ ClNO ₂	152–153	67.66	5.34	4.64	67.86	5.42	4.71
1h	C ₁₆ H ₁₄ ClNO ₂	165–166	66.79	4.90	4.87	66.87	4.81	4.73
1i	C ₁₉ H ₂₁ NO ₂	141–142	77.25	7.17	4.74	77.03	7.17	4.58
1j	C ₁₆ H ₁₄ N ₂ O ₄	198–199	64.43	4.73	9.39	64.45	4.68	9.61
1k	C ₁₅ H ₁₁ Cl ₂ NO ₂	167–168	58.46	3.60	4.57	57.97	3.43	4.32
1o	C ₁₇ H ₁₆ N ₂ O ₄	198–200	65.37	5.16	8.97	65.31	5.06	8.92

2,2-Dichlorobenzoylacetanilides **2**

General procedure. A 5–6 molar proportion of SO₂Cl₂ (0.1–0.12 mol) was added portion-wise over 1–2 min to the appropriate benzoylacetanilide **1** (0.02 mol), dissolved or suspended in CHCl₃ (~ 10 ml) contained in a flask plugged with cotton wool; the chlorination proceeded readily with vigorous evolution of HCl and SO₂. The reaction was only slightly exothermic. The resulting soln was kept at room temp for 15–20 min with intermittent swirling. CHCl₃ (~ 30 ml) was added and excess reagent and solvent removed under reduced pressure at <40°. The residue of crude **2** was washed with water and crystallized from aqueous EtOH.

Under these conditions several of the anilides **1** also underwent nuclear chlorination. Thus the substrates **1a**, **1c**, and **1e** yielded **2a**, **2c**, and **2e**, respectively. Anilide **1d** furnished 2,2-dichloro-2',6'-dimethylbenzoylacetanilide as the main product; reaction of **1d** with a 6-molar proportion of SO₂Cl₂, in the absence of CHCl₃, at 50° for 30 min provided the 4'-chloro derivative **2d**. 2,2,4'-Trichloro-2',6'-diethylbenzoylacetanilide (**2i**) was prepared as for **2d**. The IR spectra, supplemented in some instances by NMR and mass spectra, served to substantiate the structures of the respective products. Relevant details of new **2** are collected in Table 2.

TABLE 2. 2,2-DICHLOROBENZOYLACETANILIDES **2**

Compound	Formula	M.p., °C	Calculated, %			Found, %		
			C	H	N	C	H	N
2a	C ₁₇ H ₁₄ Cl ₂ NO ₂	125–126	55.09	3.81	3.78	54.88	3.66	3.59
2b	C ₁₇ H ₁₅ Cl ₂ NO ₂	107–109	60.73	4.50	4.17	60.38	4.41	3.97
2d	C ₁₇ H ₁₄ Cl ₂ NO ₂	136–138	55.09	3.81	3.78	54.69	3.65	3.69
2e	C ₁₇ H ₁₃ Cl ₄ NO ₂	105–106	50.40	3.23	3.46	50.25	3.20	3.19
2f	C ₁₇ H ₁₄ Cl ₂ NO ₂	152–153	55.09	3.81	3.78	54.64	3.59	3.76
2g	C ₁₇ H ₁₄ Cl ₂ NO ₂	95–97	55.09	3.81	3.78	54.81	3.62	3.75
2h	C ₁₆ H ₁₂ Cl ₂ NO ₂	103–104	53.89	3.39	3.93	53.95	3.37	3.82
2i	C ₁₉ H ₁₆ Cl ₂ NO ₂	141–142	57.24	4.55	3.51	57.52	4.54	3.40
2j	C ₁₆ H ₁₂ Cl ₂ N ₂ O ₄	131–133	52.34	3.30	7.63	52.45	3.22	7.68
2k	C ₁₅ H ₉ Cl ₄ NO ₂	73–74	47.78	2.41	3.72	47.21	2.27	3.54
2l	C ₁₆ H ₁₃ Cl ₂ NO ₂	91–92	59.65	4.07	4.35	59.64	4.01	4.27
2n	C ₁₆ H ₁₃ Cl ₂ NO ₂	126–127	59.65	4.07	4.35	59.71	4.01	4.10
2o	C ₁₇ H ₁₄ Cl ₂ N ₂ O ₄	125–126	53.56	3.70	7.35	53.22	3.63	7.46
2p	C ₁₅ H ₁₀ Cl ₂ N ₂ O ₄	119–120	51.02	2.85	7.93	51.11	2.78	7.88

Compound **2c** (1 g) was refluxed with 2M NaOH (10 ml) for 1 hr to provide 4-chloro-2,5-dimethylaniline [colorless crystals (from dilute EtOH), m.p. 92–93° (lit.⁹ m.p. 92–93°); NMR (CCl₄) δ 2.02 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 3.30 (broad s, 2H, NH₂), 6.29 (s, one aromatic proton), 6.80 (s, one aromatic proton, coupled to a *para* proton). (Found: C, 61.61; H, 6.46; N, 8.58. C₈H₁₀ClN requires: C, 61.74; H, 6.48; N, 9.00%); N-benzoyl derivative, m.p. 164–165° (lit.⁹ m.p. 163°).

A mixture of **2c** (0.5 g) and 2M NaOH (5 ml) was kept at ~20° for 10 min with intermittent shaking; water (~5 ml) was added and the crude dichloroacet-4-chloro-2,5-dimethylaniline was collected by filtration; colorless, woolly crystals (from dilute EtOH), m.p. 216–217°. (Found: C, 45.63; H, 3.74; N, 5.59. C₁₀H₁₀Cl₂NO requires: C, 45.07; H, 3.78; N, 5.26%).

Compound **2e** (1 g) was refluxed with 2M NaOH (10 ml) for 1 hr to give 2,4-dichloro-3,5-dimethylaniline [colorless crystals (from dilute EtOH), m.p. 76–77° (lit.¹⁰ m.p. 71–72°). (Found: C, 51.11; H, 4.78; N, 7.76. C₈H₈Cl₂N requires: C, 50.55; H, 4.77; N, 7.37%); N-acetyl derivative, m.p. 149–150°; N-benzoyl derivative, m.p. 158–159° (lit.¹⁰ m.p. 158°).

1,5-Dichloro-4,6-dimethylindeno[1,2,3-de]quinolin-2(3H)-one (**3a**)

(i) From 2,2',4'-Trichloro-2',5'-dimethylbenzoylacetanilide² (**2c**). Conc H₂SO₄ (8 ml) was added to anilide **2c** (4 g) contained in a conical flask protected from extraneous moisture by a plug of cotton wool. The mixture was heated on a steam bath (~90–95°) for 5 min with intermittent swirling; reaction occurred with copious evolution of HCl and a trace of Cl₂ (detected with KI-starch paper). The orange soln was poured into cold water (~100 ml) with stirring, and the yellow solid which precipitated was washed with water and warmed with EtOH (2 × 50 ml) to dissolve impurities (such as unchanged **2c** and dichloroacet-4-chloro-2,5-dimethylaniline). The sparingly soluble residue ("A") consisted of crude **3a** [(1.8 g, ~53%); yellow crystals (from DMF), m.p. >300°; IR 3200–2800 (H-bonded NH), 1650 (amide C=O), 820, 750, 735, 700 cm⁻¹; NMR (CF₃COOH-H₂SO₄, ca 5:1) δ 2.66 and 2.70 (overlapping 2s, 6H, CH₃), 7.2–8.3 (m, ~4H, aromatic). (Found: C, 64.65; H, 3.43; N, 4.29; mol wt, 315. C₁₇H₁₁Cl₂NO requires: C, 64.58; H, 3.51; N, 4.43%; mol wt, 315 (Cl = 35)]. The presence in the crystallized **3a** of some trichloro (M + 34 peak) impurity was revealed from the mass spectrum.

Treatment of **2c** (5 g) with a smaller proportion of H₂SO₄ (5 ml) for 10 min at 90–95° led to a decreased yield (1.3 g crude, 31%) of **3a**; evaporation of the ethanolic extract gave more (1.4 g) dichloroacet-4-chloro-2,5-dimethylaniline and unchanged **2c**.

Cyclization of **2c** (1 g) with H₂SO₄ (2 ml) at ~20° for 5 hr resulted in a poor yield (0.15 g) of crude **3a**.

1,2,5-Trichloro-4,6-dimethylindeno[1,2,3-de]quinoline (**4a**)

A mixture of crystallized indenquinolone **3a** (0.3 g), redistilled SOCl₂ (8 ml), and DMF (0.05 g) was refluxed for 3–4 hr; the solid **3a** gradually dissolved to give a yellow soln. To this was added CHCl₃ (~20 ml) and the excess reagent and solvent removed under reduced pressure. The residue was treated with water and extracted into CHCl₃ (~200 ml) to separate sparingly soluble unchanged **3a**. Evaporation of the dried CHCl₃ soln yielded crude **4a** ("B") [(0.2–0.25 g); yellow crystals (from DMF), soluble in benzene, and giving one spot on TLC [silica gel, benzene-petroleum ether (b.p. 60–80°) (1:3)], m.p. 230–250°; IR 816, 750 cm⁻¹; NMR (CDCl₃) δ 2.59 and 2.64 (2s, 6H, CH₃), 7.2–8.3 (m, 4H, aromatic), NMR (CF₃COOD) δ 2.88 and 2.90 (2s, 6H, CH₃), 7.3–8.7 (m, 4H, aromatic). (Found: C, 61.17; H, 2.91; N, 4.12; mol wt, 333. C₁₇H₁₀Cl₃N requires: C, 61.02; H, 3.01; N, 4.19%; mol wt, 333 (Cl = 35)].

The preparation of **4a** was also accomplished with POCl₃ in place of SOCl₂.

1,5,9-Trichloro-4,6-dimethylindeno[1,2,3-de]quinolin-2(3H)-one (**3b**)

Dry Cl₂ was passed (rate: ca 2–3 bubbles/sec) through a soln of "A" (i.e. **3a**) (40 mg) in conc H₂SO₄ (2 ml) at ~20° for 15 min. The dark red soln was poured into water to precipitate the chlorinated derivative **3b** [25 mg; virtually free of **3a** and (M + 34) impurity, as evidenced from the IR and mass spectra]; yellow crystals (from DMF), m.p. >300°; IR 3200–2800 (H-bonded NH), 1650 (amide C=O), 825, 782, 728 cm⁻¹. [Found: C, 58.37; H, 2.78; N, 3.76; mol wt, 349. C₁₇H₁₀Cl₃NO requires: C, 58.24; H, 2.87; N, 3.96%; mol wt, 349 (Cl = 35)].

Compound **3b** was also obtained by passage of Cl₂ into a soln of anilide **2c** (0.5 g) in conc H₂SO₄ (1 ml) which had been reacted at 90–95° for 5 min, cooled rapidly to 20°, and diluted with conc H₂SO₄ (10 ml); after chlorination for $\frac{1}{2}$ hr the soln was poured into water to give **3b** (0.1 g) free of **3a**, as evidenced by the IR spectrum.

1,2,5,9-Tetrachloro-4,6-dimethylindeno[1,2,3-de]quinoline (**4c**)

A mixture of **3b** (0.2 g), SOCl₂ (9 ml), and DMF (50 mg) was refluxed for $\frac{3}{4}$ hr and treated as for **4a**, to

yield 0.15 g crude **4c**; [yellow crystals (from DMF), shown from its mass spectrum to be virtually free of impurity; m.p. 260–280°; IR 828, 798, 690 cm^{-1} ; NMR ($\text{CF}_3\text{COOH}-\text{H}_2\text{SO}_4$, ca 10:1) δ 2.94 (s, 6H, CH_3), 7.65 (q, 1H, $J = 7$ and 2 Hz, 8-H), 7.92 (d, 1H, $J = 7$ Hz, 7-H), 8.35 (d, 1H, $J = 2$ Hz, 10-H); the superimposed singlet at δ 2.94 was resolved into two distinct CH_3 singlets in benzene solution. [Found: C, 54.85; H, 2.29; N, 3.56; mol wt, 367. $\text{C}_{17}\text{H}_{10}\text{Cl}_4\text{N}$ requires: C, 55.33; H, 2.46; N, 3.80%; mol wt, 367 ($\text{Cl} = 35$)]. Compounds **4a** and **4c** had similar R_f values (silica gel TLC with benzene-petroleum ether (b.p. 40–60°), 1:3), and a mixture of the two was separated with difficulty (see below).

1,5-Dichloro-4,6-dimethylindeno[1,2,3-de]quinolin-2(3H)-one (3a) and related compounds

(ii) From 2,2,3'-Trichloro-2',4'-dimethylbenzoylacetylacetanilide (**2f**). Conc H_2SO_4 (6 ml) was added to **2f** (3 g) as in preparation (i), and the permanganate-colored mixture was heated on a steam-bath (90–95°) for 6 min with intermittent swirling, when HCl was evolved. The orange soln was poured into cold water with stirring to give a substantial amount of a yellow solid. This product was filtered and extracted, initially with CHCl_3 (2×100 ml), and finally with warm (50–55°) EtOH (3×50 ml), to give a sparingly soluble residue "R" (0.4–0.5 g), which was a mixture of **3a** and **3b**. (The IR spectrum was a composite of the absorption peaks of "A" and **3b**, while the mass spectrum showed molecular ion peaks at m/e 315 and 349.)

Residue "R" (30 mg) in conc H_2SO_4 (2 ml) was chlorinated by passage of Cl_2 at 20° for 15 min. Addition of water precipitated crude **3b**, identical (IR spectrum) with the trichloroquinolone obtained on similar halogenation of "A". Moreover, **3b** (20 mg), derived from "R", gave, with SOCl_2 -DMF, the same (IR spectrum) **4c** described above.

Residue "R" (200 mg) was refluxed with SOCl_2 (8 ml) and DMF (50 mg) for 6 hr. The CHCl_3 -soluble yellow product (~200 mg) (isolated as for **4a**) was a mixture of **4a** and **4c**. (The IR spectrum was a composite of the absorption peaks of "B" and **4c**, while the mass spectrum revealed molecular ion peaks at m/e 333 and 367.)

The mixture (80 mg) was chromatographed over alumina [Brockmann, Merck; 30 g; benzene-light petroleum (b.p. 60–80°), 1:4]; selected 5 ml fractions were evaporated and the respective residues examined by IR. The appropriate faster-moving residues were combined to afford ~3 mg of **4a** virtually free of **4c**; the residues from the slower-moving fractions were enriched in component **4c**. The IR spectra of "B" and fraction **4a** were virtually identical.

The aforementioned CHCl_3 and EtOH extracts of "R" were combined, and evaporated to furnish a yellow solid [0.8 g; colorless crystals (from EtOH, charcoal)] as the major product of reaction. From the (IR and mass) spectral evidence this was a mixture of **7a** (molecular ion, m/e 317) as chief component, and **7b** (molecular ion m/e 351), and was not further studied.

Conc H_2SO_4 (1.4 ml) and **2f** (0.7 g) were allowed to react at 20° for 30 min; the temp was gradually raised to 90° over 1 hr. Addition of water gave a solid (0.6 g), which was extracted into warm EtOH. The sparingly soluble residue [ca 1 mg; yellow crystals (from DMF)] was identified (IR spectrum) as **3b**.

Evaporation of the EtOH extract gave as the main reaction product a mixture of **7a** (molecular ion, m/e 317) and **7b** (molecular ion, m/e 351).

1,6-Dichloro-4,5-dimethylindeno[1,2,3-de]quinolin-2(3H)-one (3c)

Conc H_2SO_4 (5 ml) and **2a** (2.5 g) were reacted as for **3a** to give EtOH-insoluble **3c** [1.3 g, ~60% crude yield; yellow crystals (from DMF), m.p. > 300°; IR (different from that of **3a**), 3200–2800 (H-bonded NH), 1650 (amide $\text{C}=\text{O}$), 750, 680 cm^{-1} . (Found: C, 64.39; H, 3.41; N, 4.43; mol wt, 315. $\text{C}_{17}\text{H}_{11}\text{Cl}_2\text{NO}$ requires: C, 64.58; H, 3.51; N, 4.43%; mol wt, 315 ($\text{Cl} = 35$)).

1,2,6-Trichloro-4,5-dimethylindeno[1,2,3-de]quinoline (4d)

Crude **3c** (0.4 g) was refluxed with SOCl_2 (9 ml) and DMF (100 mg) for 3 hr. The product **4d** (80% crude yield) was isolated as for **4a** and chromatographed over silica gel (30 g, 0.05–0.2 mm; benzene). Fractions were examined by TLC (silica gel, benzene) and appropriate ones giving one spot were combined and evaporated to provide **4d** (0.2 g) free of impurity [yellow crystals (from DMF), m.p. 230–260°; IR 755 cm^{-1} ; NMR (CF_3COOH) δ 2.62 and 2.72 (2s, 6H, CH_3), 7.3–8.5 (m, 4H, aromatic). (Found: C, 61.14; H, 2.78; N, 3.91; mol wt, 333. $\text{C}_{17}\text{H}_9\text{Cl}_3\text{N}$ requires: C, 61.02; H, 3.01; N, 4.19%; mol wt, 333 ($\text{Cl} = 35$)).

1,6-Dichloro-4,X-dimethylindeno[1,2,3-de]quinolin-2(3H)-one (3d)

Compound **2g** (1.1 g) and conc H_2SO_4 (2 ml) at 90–95° for 10 min furnished EtOH-insoluble **3d** [0.4 g; yellow crystals (from DMF), m.p. > 300°; IR (spectrum revealed complete absence of "A") 3200–2800

(H-bonded NH), 1650 (amide C=O), 828, 782, 692 cm^{-1} ; molecular ion, m/e 315 ($\text{C}_{17}\text{H}_{11}\text{Cl}_2\text{NO}$ requires mol wt, 315 ($\text{Cl} = 35$)). It was not established whether the product was 1,6-dichloro-4,7-dimethylindeno[1,2,3-*de*]quinolin-2(3H)-one, the 4,9-dimethyl isomer, or a mixture of the two (as seemed likely).

1,2,6-Trichloro-4-X-dimethylindeno[1,2,3-*de*]quinoline (4e)

This was obtained from **3d** (0.3 g), SOCl_2 (8 ml), and DMF (50 mg), refluxed for 7 hr, in high yield [yellow crystals (from DMF), IR (spectrum revealed total absence of "B") 835, 800, 760, 710 cm^{-1} ; molecular ion, m/e 333 ($\text{C}_{17}\text{H}_9\text{Cl}_3\text{N}$ requires mol wt, 333 ($\text{Cl} = 35$); the mass spectrum showed negligible impurity ($M + 34$ peak); NMR (CF_3COOH) δ 2.48 and 2.70 (2s, 6H, CH_3), and 7.2–8.0 (m, 4H, aromatic)]. The product gave one spot on TLC (silica gel, light petroleum (b.p. 40–60°)—benzene, 2:1), but the possibility of it being a mixture was not excluded.

1,4,6-Trichloro-5-methyl-7H-dibenzo[f, ij]isoquinolin-2(3H)-one (5b)

Conc H_2SO_4 (12 ml) was added to **2e** (6 g), giving a permanganate-colored mixture. This was kept at 90–95° for 6 min with intermittent swirling: reaction occurred with copious evolution of HCl and a trace of Cl_2 . The orange soln was poured into cold water (~200 ml) with stirring and the precipitated solid was washed with water and extracted with warm (~50°) EtOH (2 \times 100 ml) to afford a residue of sparingly soluble **5b** (1.7 g); the ethanolic extract was chilled and deposited an additional 0.5 g of product [total crude yield, 2.2 g, ~42%; yellow crystals (from DMF), m.p. > 300°; IR 3200–2900 (H-bonded NH), 1650 (amide C=O), 758, 720 cm^{-1} ; NMR ($\text{CF}_3\text{COOH}-\text{H}_2\text{SO}_4$, ca 10:1) δ 2.90 (s, 3H, CH_3), 5.0 (s, 2H, CH_2), 7.2–8.5 (m, ~4H aromatic). (Found: C, 58.75; H, 2.83; N, 4.10; mol wt, 349. $\text{C}_{17}\text{H}_9\text{Cl}_3\text{NO}$ requires: C, 58.24; H, 2.87; N, 3.96%; mol wt, 349 ($\text{Cl} = 35$)).

The presence in the crystallized product of a small amount of an impurity was shown by the NMR (doublet near δ 2.6) and mass spectra (molecular ion peak at m/e 315).

1,2,4,6-Tetrachloro-5-methyl-7H-dibenzo[f, ij]isoquinoline (6)

A mixture of crystallized **5b** (0.4 g), SOCl_2 (8 ml) and DMF (100 mg) was refluxed for 3½ hr. The CHCl_3 —soluble product **6** (0.3 g crude yield) was isolated as for **4a** and purified by chromatography (Kieselgel, 0.05–0.2 mm, 50 g; benzene). The appropriate fractions giving one spot on TLC (R_f ~ 0.7) were combined and evaporated to provide **6** [0.15 g, free of impurity; yellow crystals (from DMF, or 95% AcOH), m.p. 215–218°; IR 760, 740 cm^{-1} ; NMR (CF_3COOH) δ 2.97 (s, 3H, CH_3), 5.0 (s, 2H, CH_2), 7.4–8.5 (m, 4H, aromatic). (Found: C, 54.95; H, 2.22; N, 4.09; mol wt, 367. $\text{C}_{17}\text{H}_9\text{Cl}_4\text{N}$ requires: C, 55.33; H, 2.46; N, 3.80%; mol wt, 367 ($\text{Cl} = 35$)).

1,2,6-Trichloro-4-methylindeno[1,2,3-*de*]quinoline (4f)

Cyclization of **2h*** (2 g) with conc H_2SO_4 (4 ml) at 90–95° for 15 min gave EtOH-insoluble, crude **3e** (0.9–1.05 g, 53–60%). The crude product (0.4 g) was refluxed with SOCl_2 (8 ml) and DMF (50 mg) for 5 hr to give CHCl_3 —soluble quinoline **4f** [0.35 g; yellow crystals (from DMF), m.p. 260–270°; IR 800, 752, 704 cm^{-1} ; NMR (CF_3COOH) δ 2.80 (s, 3H, CH_3), 7.4–8.4 (m, 5H, aromatic). (Found: C, 59.63; H, 2.35; N, 4.44; mol wt, 319. $\text{C}_{16}\text{H}_8\text{Cl}_3\text{N}$ requires: C, 59.94; H, 2.51; N, 4.37%; mol wt, 319 ($\text{Cl} = 35$)).

Action of concentrated sulfuric acid on miscellaneous anilides 2

General procedure. A mixture of compound **2** (1 g) and H_2SO_4 (2 ml) contained in a conical flask protected with a plug of cotton wool was kept on a steam bath (90–95°) with intermittent shaking for a specified time, and poured into cold water with stirring. The precipitated acid-insoluble product was collected by filtration, washed with water, and stirred with warm (50–60°) EtOH (3 \times 15 ml) to separate the sparingly soluble indenoquinolone **3**. Evaporation of the EtOH extract gave other reaction products and/or unchanged **2**.

2,2-Dichloro-2',4'-dimethylbenzoylacetanilide (2b) (10 min). The EtOH-insoluble residue [0.13 g, ~15% crude yield, yellow crystals (from DMF), insoluble in CHCl_3], appeared to be a mixture of indenoquinolones **3g** (molecular ion, m/e 315) and **3f** (molecular ion, m/e 281), and was not further examined. The major product (~0.4 g, soluble also in CHCl_3) was a mixture mainly of the quinolones **7d** (molecular ion, m/e 317) and **7c** (molecular ion, m/e 283).

* 2-Amino-5-chlorotoluene (N-benzoyl derivative, m.p. 172–174°) was purchased from L. Light and Co. Limited, Colnbrook, England. A specimen of alleged isomeric 5-chloro-o-toluidine (2-amino-4-chlorotoluene) supplied by British Drug Houses Limited, Poole, England, was in fact identical (IR spectrum).

2,2-Dichloro-4'-methylbenzoylacetanilide (**2m**) (15 min). This gave a negligible yield (<5%) of indenoquinolone which was not characterized. The chief product was **7e** [colorless crystals (0.5 g, 60%) from EtOH, m.p. 286–288°, identified by comparison (IR spectrum) with **7e** from 2-chloro-4'-methylbenzoylacetanilide¹¹ (1 g) and H₂SO₄ (2 ml) at 90–95° for 1 hr]. The mass spectrum of the crude chief product revealed the presence also of some 3,X-dichloroquinolone [molecular ion, *m/e* 303 (Cl = 35)].

2,2-Dichloro-N-methylbenzoylacetanilide (**2l**) (10 min). The acid-insoluble reaction product (0.6 g) dissolved completely in warm EtOH; TLC (silica gel, benzene-acetone, 10:1) showed the presence of a number of substances. Separation on a column (Kieselgel, 30 g; benzene-acetone, 10:1) gave a yellow solid (0.3–0.35 g, one spot on TLC) which, however, proved to be a mixture of **3i** and **3h**, with the former predominating, as evidenced from the NMR [(CDCl₃) singlets at δ 5.57 and 3.52] and mass spectra (molecular ions at *m/e* 301 and 267).

2,2-Dichloro-N-ethylbenzoylacetanilide² (**2m**) (15 min). This likewise gave (after chromatography) a mixture (0.3–0.4 g, one spot on TLC; molecular ions at *m/e* 315 and 281) of **3k** and **3j**, with the former,^{1,2} in excess.

2,2-Dichloro-2',5'-dimethyl-4'-nitrobenzoylacetanilide (**2o**) (5 min). The reaction product consisted of dichloroacet-2,5-dimethyl-4-nitroanilide together with unchanged **2o** (molecular ions at *m/e* 276 and 380).

2,2-Dichloro-4'-nitrobenzoylacetanilide (**2p**) (15 min). This was converted in high yield to dichloroacet-4-nitroanilide [pale yellow needles (from dilute EtOH), m.p. 128–129° (lit.¹¹ m.p. 128–130°), identified from its IR spectrum].

2,2-Dichloro-2'-methyl-5'-nitrobenzoylacetanilide (**2j**) (1 hr). This gave dichloroacet-2-methyl-5-nitroanilide [crystals from dilute EtOH, m.p. 159–160° (Found: C, 41.19; H, 3.03; N, 10.77. C₉H₈Cl₂N₂O₃ requires: C, 41.09; H, 3.06; N, 10.65 %)].

2,2,2',5'-Tetrachlorobenzoylacetanilide (**2k**) (1 hr). This yielded dichloroacet-2,5-dichloroanilide [colorless crystals from dilute EtOH, m.p. 146–147° (Found: C, 34.96; H, 1.76; N, 4.73. C₈H₃Cl₄NO requires: C, 35.21; H, 1.85; N, 5.13 %)].

2,2,4'-Trichloro-2',6'-dimethylbenzoylacetanilide (**2d**) (30 min), and 2,2,4'-trichloro-2',6'-diethylbenzoylacetanilide (**2l**) (1 hr). These were recovered largely unchanged. In contrast, **1j** and **1k** when similarly reacted with conc H₂SO₄ for 1 hr, gave 2-methyl-5-nitroaniline and 2,5-dichloroaniline, respectively.

Acknowledgement—The author is grateful to the S.A. Council for Scientific and Industrial Research, Pretoria, for financial assistance.

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