Tetrahedron. Vol. 25, pp. 5941 to 5951. Pergamon Press 1969. Printed in Great Britain

A NOVEL SYNTHESIS OF INDENO[1.2.3-*DE*]QUINOLIN-2-ONES

T. VAN Es[1] and B. STASKUN

Department of Chemistry including Biochemistry, University of the Witwatersrand, Johannesburg, South Africa

(*Received in the UK* 23 *July* 1969; *Accepted for publication* 25 *August* 1969)

Abstract—Cyclization of 2,2-dichlorobenzoylacetanilides in sulfuric acid gave indeno[1.2.3-*de*]quinolin-2-ones.

AS PART of our study[2] of the effect of concentrated sulfuric acid on dichloroacetoacetanilides and on dichlorobenzoylacetanilides **1** we have further examined the latter reaction and have now established unequivocally that the products are indeno-[1.2.3-*de*]quinolin-2-ones **2**. The high-melting, yellow product derived from 2,2,4'-trichlorobenzoylacetanilide (**1a**) and concentrated sulfuric acid was sparingly soluble in the usual organic solvents but could be recrystallized from dimethylformamide. Elemental and mass spectral analysis established a molecular formula $C_{15}H_7Cl_2NO$[2] whilst the IR spectrum indicated an amide CO group. The compound's structure as 1,6-dichloro-indeno[1.2.3-*de*]quinolin-2(3*H*)-one (**2a**) was elucidated from the following observations: Catalytic hydrogenation in the presence of Raney nickel under pressure gave a dehalogenated derivative, $C_{15}H_{11}NO$, which was assigned structure **3a**, i.e. 1,11-dihydro-indeno[1.2.3-*de*]quinolin-2(3*H*)-one, on the basis of its NMR spectrum (aromatic multiplet at 2·67, seven protons; quartet at 5·85, one (methine) proton; quartet at 6·85, one (methylene) proton; triplet at 7·85 τ, one (methylene) proton). The spectrum was rationalized in terms of an ABX system, the 11-(methine) proton being designated X, the two (non-equivalent) methylene protons as A and B, and J_{AB}, J_{AX}, J_{BX} = 15, 15 and 6·7 Hz respectively. In support was the spectrum of 3,4-dihydro-4-phenyl-2(1*H*)-quinolone[3] which revealed the methine proton as a triplet at 5·7 and the (equivalent) methylene protons as a doublet at 7·25 τ.

Finally, the dihydro indenoquinolone **3a** was dehydrogenated with PdC to give yellow crystals, $C_{15}H_9NO$, m.p. 276–277°, which were identical (mixture m.p. and IR spectrum) with those of indeno[1.2.3-*de*]quinolin-2(3*H*)-one (**2b**) prepared from 1-aminofluorene.[4]

In the case of the product ($C_{17}H_{11}Cl_2NO$)[2] derived from 2,2,4'-trichloro-N-ethylbenzoylacetanilide (**1b**), its indenoquinolone structure **2c** was confirmed more directly by NMR. The spectrum (aromatic multiplet at 2·0–3·25, six protons; quartet centered at 5·83, two protons; and triplet centered at 8·67 τ, three protons) was in keeping with formula **2c**. Compound **2c** was catalytically hydrogenated to a dihydro derivative ($C_{17}H_{15}NO$) assigned structure **3b**. The NMR spectrum was of a similar type to that of **3a**: aromatic multiplet at 2·23–3·26, seven protons; quartet at 6·03, three protons; quartet at 6·80, one proton: triplet at 7·84, one proton; triplet at 8·72 τ, three protons. This was consistent with and supported a structure **3b** in terms of an ABX system and with the absorptions of the 11-(methine) proton and the two (Et)

methylene protons superimposed as a quartet centered at 6·03 τ. Reduction of **2c** with Raney alloy in alcoholic sodium hydroxide afforded two other indenoquinolone derivatives, viz., **2d** and **2e**, as evidenced by elemental and spectral analysis. The latter product **2e**, was formed (in 84% yield) when the dichloroindenoquinolone **2c** was refluxed in ethanol with sodium ethoxide.

Various other substituted 2,2-dichlorobenzoylacetanilides (**1**) on warming with concentrated sulfuric acid were likewise converted into the corresponding indenoquinolones (Table 1).

2,2-Dichloroacetanilides which arose by hydrolysis of **1** during reaction were on occasion isolated as side products.

Of particular interest was the action of sulfuric acid on 2,2,4'-trichloro-2',5'-dimethylbenzoylacetanilide (**1c**);[5] the product ($C_{17}H_{11}Cl_2NO$) has been assigned structure **4a** in keeping with the evidence available at present. A similar compound, viz. **4b** was obtained from anilide **1f**.*

Brominated indenoquinolones resulted on conducting the cyclization of **1** in a mixture of concentrated sulfuric acid and bromine. Thus 2,2,4'-trichlorobenzoylacetanilide (**1a**) was converted into a bromo derivative, $C_{15}H_6BrCl_2NO$, assigned structure **5a** in view of the following: The same product **5a** was obtained (i) from reaction of 1,6-dichloro-indeno[1.2.3-*de*]quinolin-2(3*H*)-one (**2a**) with the acid mixture, and also (ii) by cyclization of 3''-bromo-2,2,4'-trichlorobenzoylacetanilide (**1d**) with concentrated sulfuric acid.

2,2-Dichloro-N-ethylbenzoylacetanilide (**1e**) was converted by sulfuric acid and bromine into a dibromo indenoquinolone formulated as **5c**. 2,2,4'-Trichloro-N-ethylbenzoylacetanilide (**1b**) and the indenoquinolone **2c** each gave the same product viz. **5b**.

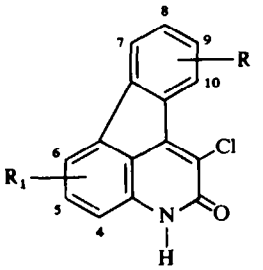
The study was extended to the cyclization of various 2,4'-dichloro-2-alkyl-benzoylacetanilides **6** in concentrated sulfuric acid. When the 2-substituent was ethyl the acid solution of the anilide **6b** did not develop a green color as was usual in indenoquinolone formation† and the product proved to be 1,6-dichloro-4-phenyl-2(1*H*)-quinolone (in 50% yield). Smaller yields (20–25%) of the same quinolone resulted from the 2-n-propyl- and the 2-benzyl- substituted anilides (**6c** and **6d**). In the case of 2,4'-dichloro-2-methylbenzoylacetanilide (**6a**) an indenoquinolone derivative ($C_{16}H_9Cl_2NO$, by analysis) was obtained and assigned structure **7**. The mass spectrum of **7** however showed a base peak at *m/e* 335 whilst the intensities of the chlorine isotope peaks were indicative of three Cl atoms in the molecule, i.e. $C_{16}H_8Cl_3NO$. An (M + 34) peak was exhibited also in the mass spectra of other indenoquinolones **2** but was relatively much less intense. This is probably due to impurities.

Various aspects of the synthesis, for example the mode of formation of indenoquinolones **2a** and **2c** from anilides **1g** and **1e**, respectively,[2] remain to be clarified. However, other observations may be accounted for, tentatively, in terms of an intermediate entity such as **8** which could originate from the anilide **1** and sulfuric acid

* The NMR spectra of these compounds were recorded in concentrated sulfuric acid and are not readily interpreted in terms of structures **4a** and **4b**. A migration of a methyl group may have occurred during the cyclization of anilides **1e** and **1f** and this reaction is being studied further.

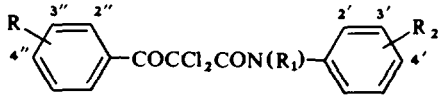
† It was noted that a dark-red rather than green solution resulted from anilide **1e** and sulfuric acid in forming **4a**.

TABLE 1. INDENO[1.2.3-*de*]QUINOLIN-2(3*H*)-ONES



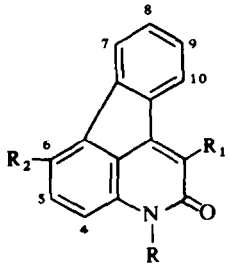
				Calcd, %				Found, %			
R	R_1	Yield, %	Formula	C	H	N	Mol. wt[a]	C	H	N	Mol. wt[b]
H	4-Br	12	$C_{15}H_7BrClNO$	54·15	2·11	4·21	331	53·51	2·09	4·31	331
H	6-Br	70	$C_{15}H_7BrClNO$	54·15	2·11	4·21	331	53·77	2·15	4·23	331
H	5-Br-6-Cl	60	$C_{15}H_6BrCl_2NO$	49·06	1·65	3·81	365	48·74	1·69	3·78	365
H	4-Cl	20	$C_{15}H_7Cl_2NO$	62·50	2·45	4·86	287	61·88	2·30	4·96	287
H	6-Cl-4-CH_3	24	$C_{16}H_9Cl_2NO$[c]	63·58	2·98	4·63		62·80	2·79	4·53	
H	4,6-diCl-5-CH_3	10	$C_{16}H_8Cl_3NO$	57·06	2·38	4·16	336	57·34	2·64	4·38	336
9(or 7)-Br	6-Cl	30	$C_{15}H_6BrCl_2NO$	49·06	1·65	3·81		49·00	1·51	3·88	
H	4,6-diBr	<5[d]	$C_{15}H_6Br_2ClNO$	43·76	1·46	3·40	409	43·67	1·35	3·42	409

[a] Cl = 35, Br = 79. [b] Mass spectrum. [c] NMR (conc H_2SO_4) 1·9–2·8 (m, 5, aromatic) and 7·45 τ (broad peak, 3, CH_3). [d] The main product (69%) was 2,2-dichloro-2′,4′-dibromoacetanilide, m.p. 118° (dilute EtOH). Found: C, 26·69; H, 1·34; N, 3·74. $C_8H_5Br_2Cl_2NO$ requires: C, 26·50; H, 1·38; N, 3·86%.



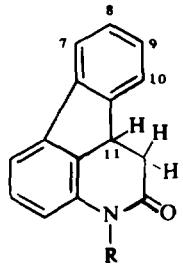
1

a: R = R_1 = H; R_2 = 4′-Cl
b: R = H; R_1 = Et; R_2 = 4′-Cl
c: R = R_1 = H; R_2 = 2′,5′-diMe-4′-Cl
d: R = 3″-Br; R_1 = H; R_2 = 4′-Cl
e: R = R_2 = H; R_1 = Et
f: R = R_1 = H; R_2 = 2′-Br-5′-Me-4′-Cl
g: R = R_1 = R_2 = H



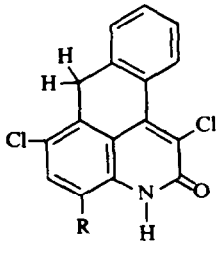
2

a: R = H; R_1 = R_2 = Cl
b: R = R_1 = R_2 = H
c: R = Et; R_1 = R_2 = Cl
d: R = Et; R_1 = H; R_2 = Cl
e: R = Et; R_1 = OEt; R_2 = Cl



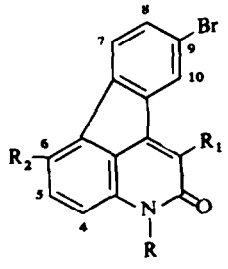
3

a: R = H
b: R = Et



4

a: R = Me
b: R = Br

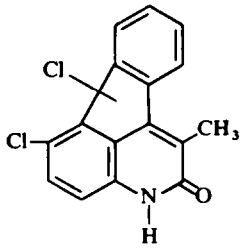


5

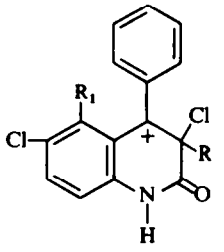
a: R = H; R_1 = R_2 = Cl
b: R = Et; R_1 = R_2 = Cl
c: R = Et; R_1 = Cl; R_2 = Br

6

a: R = Me
b: R = Et
c: R = n-Pr
d: R = $PhCH_2$



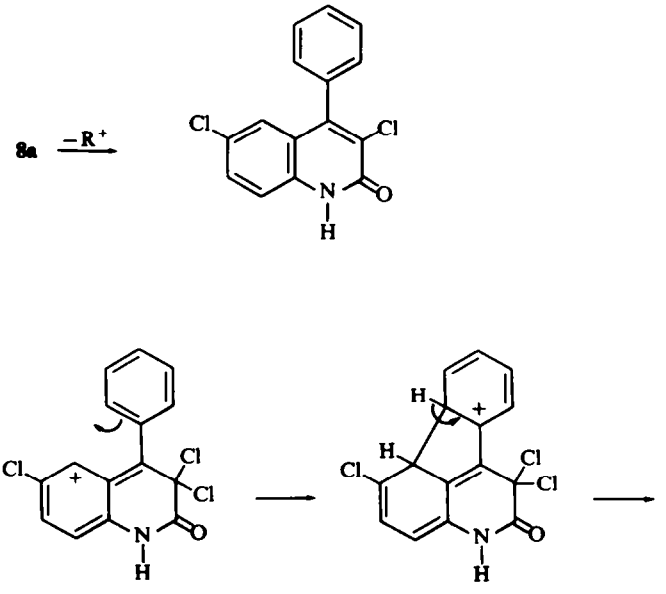
7

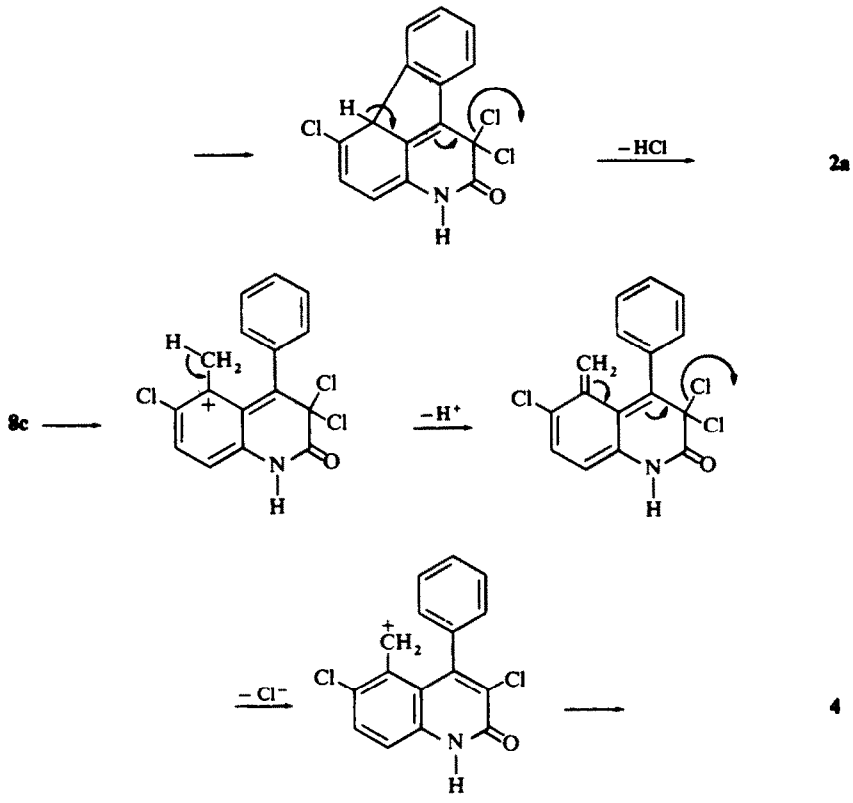


a: R = alkyl; R_1 = H
b: R = Cl; R_1 = H
c: R = Cl; R_1 = Me

8

SCHEME 1





as before.[2] Some possible subsequent transformations of **8** are outlined in Scheme 1, and may well occur in a concerted manner.

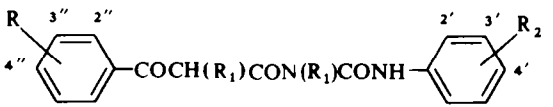
EXPERIMENTAL*

Preparation of benzoylacetanilides (Table 2). The appropriate arylamine (0·1 mole) and ethyl benzoylacetate (0·13 mole) were stirred together at 140–145° for 2 hr. After cooling somewhat the reaction mixture was extracted with warm 0·1M NaOH (200 ml) and the filtered (charcoal) alkaline soln acidified with glacial AcOH to precipitate the anilide. It should be noted that the anilides derived from N-substituted arylamines were isolated by high-vacuum distillation of the reaction mixture in order to remove unreacted β-keto ester; the respective residues (and also the other products in Table 2) were recrystallized from EtOH or aqueous EtOH. *2-Alkylbenzoylacetanilides* were prepared by adding the appropriate alkyl bromide (0·10 mole) to a refluxing soln of benzoylacetanilide (0·10 mole) in EtOH (150 ml) containing Na (2·30 g, 0·10 g-atom) over a period of 1 hr and heating for a further 3 hr. The main bulk of the EtOH was removed, the residue diluted with water, and the resulting solid was recrystallized from the appropriate solvent.

The nature of each product was confirmed, after purification, by elemental analysis. New anilides are listed in Table 2.

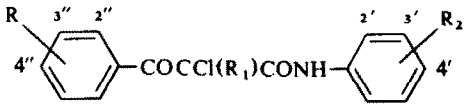
* M.ps are uncorrected. IR spectra were obtained for all new compounds and were recorded on a Perkin–Elmer Infracord Model 137 spectrophotometer (1 mg/300 mg KBr). Mass spectra were determined from an AEI Model MS9 spectrometer (70 eV). NMR spectra were recorded on a Varian A-60 spectrometer with TMS as internal reference.

TABLE 2. BENZOYLACETANILIDES



						Calcd, %			Found, %		
R	R_1	R_1	M.p., C	Yield, %	Formula	C	H	N	C	H	N
3″-Br	H	H	123–124	12	$C_{15}H_{12}BrNO_2$	56·60	3·81	4·40	56·59	3·74	4·45
4″-Br	H	H	146–147	12	$C_{15}H_{12}BrNO_2$	56·60	3·81	4·40	56·83	3·71	4·03
H	H	2′,5′-diCH_3	145–146	36	$C_{17}H_{17}NO_2$	76·38	6·41	5·24	76·5	6·29	5·24
H	H	2′-Br-5′-CH_3	145–146	28	$C_{16}H_{14}BrNO_2$	57·83	4·25	4·22	57·64	4·24	4·35
H	H	2′,4′-diBr	162	11	$C_{15}H_{11}Br_2NO_2$	45·35	2·80	3·53	45·28	2·65	3·33
H	C_2H_5	4′-Cl	131–132	84	$C_{17}H_{16}ClNO_2$	67·64	5·34	4·64	67·70	5·31	4·76
H	CH_3	H	139	69	$C_{16}H_{15}NO_2$	75·86	5·97	5·53	76·1	6·06	5·59
H	CH_3	4′-Cl	155	59	$C_{16}H_{14}ClNO_2$	66·76	4·90	4·87	66·7	4·95	4·91
H	*i*-C_3H_7	H	157–158	59	$C_{18}H_{19}NO_2$	76·84	6·79	4·98	76·2	6·77	4·60
H	*n*-C_3H_7	H	160	64	$C_{18}H_{19}NO_2$	76·84	6·79	4·98	76·6	6·84	5·08
H	$C_6H_5CH_2$	H	158–159	85	$C_{22}H_{19}NO_2$	80·22	5·80	4·25	80·3	5·65	4·35

TABLE 3. 2,2-DICHLORO- AND 2-ALKYL-2-CHLORO-BENZOYLACETANILIDES



R	R_1	R_2	M.p., °C	Yield, %	Formula	Calcd, %			Found, %		
						C	H	N	C	H	N
3''-Br	Cl	Cl	not purified								
4''-Br	Cl	Cl	not purified								
H	Cl	2'-Br	107–108	93	$C_{15}H_{10}BrCl_2NO_2$	46·51	2·61	3·62	46·53	2·50	3·88
H	Cl	3'-Br-4'-Cl	130–132	76	$C_{15}H_9BrCl_3NO_2$	42·71	2·13	3·32	43·44	2·15	3·42
H	Cl	4-Br	138–140	87	$C_{15}H_{10}BrCl_2NO_2$	46·51	2·61	3·62	46·80	2·54	3·68
H	Cl	2'-Cl	78–80	70	$C_{15}H_{10}Cl_3NO_2$	52·54	2·95	4·09	52·57	2·79	4·18
H	Cl	2'-CH_3-4'-Cl	96–97	71	$C_{16}H_{12}Cl_3NO_2$	53·84	3·39	3·93	53·46	3·21	4·04
H	Cl	2',4'-diBr	not purified								
H	Cl	2',5'-diCH_3-4'Cl	116–117	91	$C_{17}H_{14}Cl_3NO_2$	55·05	3·81	3·78	55·34	3·74	4·03
H	Cl	2'-Br-5-CH_3	not purified								
H	CH_3	4'-Cl	120–121	80	$C_{16}H_{13}Cl_2NO_2$	59·61	4·07	4·35	59·8	4·11	4·33
H	CH_3	2',4'-diCl	79	79	$C_{16}H_{12}Cl_3NO_2$	53·84	3·39	3·92	54·4	3·62	3·83
H	C_2H_5	4'-Cl	106–107	84	$C_{17}H_{15}Cl_2NO_2$	60·70	4·49	4·17	60·7	4·43	4·01
H	n-C_3H_7	4'-Cl	100	92	$C_{18}H_{17}Cl_2NO_2$	61·70	4·88	4·00	61·2	4·93	4·12
H	$C_6H_5CH_2$	4'-Cl	not purified								

2,2-Dichloro- and 2-chloro-2-alkyl-benzoylacetanilides (Table 3). The appropriate benzoylacetanilide (0·10 mole) and SO_2Cl_2 (1·0 mole) were refluxed for 15 min. The excess SO_2Cl_2 was removed under vacuum, the residue diluted with water, and the product recrystallized from EtOH or aqueous EtOH.

Elemental analysis, supplemented on occasion by IR and NMR spectra, served to characterize the products. New compounds are listed in Table 3.

Chlorination of 2-methylbenzoylacetanilide led to a mixture of **6a** and 2,2',4'-trichloro-2-methylbenzoylacetanilide which was separated by chromatography; the NMR spectrum of each product showed an intact Me group at τ 2·10; the other protons were aromatic. Alkaline hydrolysis gave 4-chloroaniline and 2,4-dichloroaniline, respectively. Compound **1c**, (0·5 g) (derived from 2',5'-dimethylbenzoylacetanilide) was heated with NaOH (2M, 10 ml) on a steam bath for 1 hr. Extraction with benzene followed by recrystallization from dil MeOH gave 4-chloro-2,5-dimethylaniline, m.p. 91° (lit.[6] m.p. 93°); the acetyl derivative was crystallized from dil MeOH, m.p. 181–183° (lit.[6] m.p. 176°). (Found: C, 60·67; H, 6·07; N, 6·67. $C_{10}H_{12}ClNO$ requires: C, 60·72; H, 6·12; N, 7·03%).

Synthesis of indeno[1.2.3-de]quinolin-2-ones (**2**). Table 1. The appropriate **1** (1·0 g) and conc H_2SO_4 (2 ml) were heated on a steam bath for 15 min; a green color formed immediately but faded on heating. After pouring into water the insoluble yellow product was extracted with hot EtOH and the residue **2** recrystallized from DMF. From the EtOH extracts a quantity of the corresponding 2,2-dichloroacetanilide[2] (identified by its IR spectrum) was recovered. The new, yellow **2** are listed in Table 1 and all the compounds had not melted at 330°.

1,11-Dihydroindeno[1.2.3-de]quinolin-2(3H)-one (**3a**). Compound **2a** (0·60 g), DMF (100 ml), Raney Ni (~ 1 g) and H_2 (140 lbs/sq in) in an hydrogenator were stirred at 40° overnight. The mixture was filtered and the solvent evaporated to afford **3a** (0·45 g, 97%) m.p. 215–216° (from EtOH); IR (KBr) 3·1 (NH), and 5·90 μ (amide CO); NMR (DMSO-d_6) 2·67 (m, 7, aromatic), 5·85 (q, 1, J_{AX} = 15 Hz; J_{BX} = 6·7 Hz, 11-H), 6·85 (q, 1, J_{AB} = 15 Hz; J_{BX} = 6·7 Hz, 1-H), and 7·85 τ (t, 1, J_{AB} = 15 Hz; J_{AX} = 15 Hz, 1-H). (Found: C, 81·64; H, 5·08; N, 6·26; mol. wt. 221 (mass spectrum). $C_{15}H_{11}NO$ requires: C, 81·41; H, 5·02; N, 6·33%; mol. wt. 221).

Indeno[1.2.3-de]quinolin-2(3H)-one (**2b**). Compound **3a** (100 mg) was heated with PdC (10%, 100 mg) at 250° in a stream of CO_2. A yellow sublimate of **2b** was collected (35 mg; m.p. 273–275°) and was recrystallized from dil AcOH, m.p. 276–277°. A mixture m.p. with authentic **2b** prepared by the method of Koelsch[4] was not depressed; moreover the IR and mass spectra of the two compounds were identical. (Found: N, 6·28; mol. wt. 219 (mass spectrum). $C_{15}H_9NO$ requires: N, 6·39%; mol. wt., 219).

1,6-Dichloro-3-ethylindeno[1.2.3-de]quinolin-2-one (**2c**).[2] The NMR spectrum ($DCCl_3$) of **2c** (m.p. 198–201°) was determined: 2·0–3·25 (m, 6, aromatic), 5·83 (q, 2, $\underline{CH_2}$) (CH_2), and 8·67 τ (t, 3, CH_2 $\underline{CH_3}$). NMR (conc H_2SO_4) 2·0–2·8 (m, 6, aromatic), 5·25 (broad peak, 2, $\underline{CH_2}CH_3$), and 8·35 τ (broad peak, 3, $CH_2\underline{CH_3}$). NMR (CF_3COOH) 1·9–2·8 (m, 6, aromatic), 6·17 (q, 2, $\underline{CH_2}CH_3$) and 9·0 τ (t, 3, $CH_2\underline{CH_3}$).

1,11-Dihydro-3-ethylindeno[1.2.3-de]quinolin-2-one (**3b**). Compound **2c** (1·0 g), EtOH (200 ml), Raney Ni (5 g), and H_2 (140 lb/sq in) were stirred at 45° overnight. The mixture was filtered and the solvent evaporated to give a syrup (0·75 g, 95%) which was purified by chromatography on silica gel using 7% MeOH in benzene; NMR ($DCCl_3$) 2·75 (m, 7, aromatic), 6·03 (q, 3, 11-H and $\underline{CH_2}CH_3$), 6·80 (q, 1, 1-H), 7·84 (t, 1, 1-H), and 8·72 τ (t, 3, $CH_2\underline{CH_3}$). (Found: C, 82·0; H, 6·02; N, 5·52. $C_{17}H_{15}NO$ requires: 81·89; H, 6·06; N, 5·62%).

7-Chloro-3-ethylindeno[1.2.3-de]quinolin-2-one (**2d**) *and 7-chloro-1-ethoxy-3-ethylindeno[1.2.3-de]quinolin-2-one* (**2e**). Raney alloy (5 g) was added in small portions over a period of 30 min to a stirred mixture of **2c** (0·5 g), EtOH (75 ml), and NaOH (2M, 15 ml). The mixture was filtered and concentrated and the residue was chromatographed on silica gel using 10% MeOH in benzene to give (i) **2d**, m.p. 178–180° (from EtOH, 17%). (Found: C, 72·4; H, 4·30; N, 4·78; mol. wt., 281 (mass spectrum). $C_{17}H_{12}ClNO$ requires: C, 72·44; H, 4·30; N, 4·97%; mol. wt., 281 (Cl = 35), and (ii) **2e**, m.p. 148–149° (from EtOH, 39%); NMR ($DCCl_3$) 1·80–3·13 (m, 6, aromatic), 5·37 (q, 2, $O\underline{CH_2}CH_3$), 5·76 (q, 2, $N\underline{CH_2}CH_3$), 8·52 (t, 3, $OCH_2\underline{CH_3}$), and 8·67 τ (t, 3, $NCH_2\underline{CH_3}$). (Found: C, 70·2; H, 4·83; N, 4·35; mol. wt. 325 (mass spectrum). $C_{19}H_{16}ClNO_2$ requires: C, 70·02; H, 4·94; N, 4·30%; mol. wt., 325 (Cl = 35)).

Compound **2e** was formed also when **2c** (0·20 g) was refluxed with EtOH (20 ml) containing Na (0·25 g) for 0·5 hr; the soln was cooled and **2e** separated out (0·17 g, 84%, m.p. 148–149°).

Cyclization of 2,2,4'-trichloro-2',5'-dimethylbenzoylacetanilide (**1c**). Conc H_2SO_4 (5 ml) was added to **1c** (1 g) and heated on a water bath at 95° for 30 min when HCl was evolved; on addition of the acid a dark-red soln was obtained. The soln was cooled and poured into ice-water, but no solid separated out. A water-soluble sulphonated product could have been formed but was not investigated. However, when the above

anilide (1 g) was treated with conc H_2SO_4 (2 ml) at 95° for 5 min and poured into water a solid was obtained;[5] yellow crystals of **4a** (from DMF, 40% yield, not melted at 330°). NMR (conc H_2SO_4) 1·9–2·8 (m, aromatic, integral 23), and 7·5 τ (broad doublet, CH_3?, integral 44). (Found: C, 64·16; H, 3·42; N, 4·62; mol. wt. 315 (mass spectrum). $C_{17}H_{11}Cl_2NO$ requires: C, 64·56; H, 3·41; N, 4·44%; mol. wt. 315 (Cl = 35)).

The above **4a** was reduced with H_2 and Raney Ni as described above. The product crystallized from dil AcOH, m.p. >300°. (Found: C, 72·40; H, 4·29; N, 5·00; mol. wt., 281 (mass spectrum). $C_{17}H_{12}ClNO$ requires: C, 72·50; H, 4·27; N, 4·98%; mol. wt., 281 (Cl = 35)).

Compound **1f** (1 g) and conc H_2SO_4 (2 ml) at 95° for 10 min likewise furnished **4b** (yellow crystals from DMF, m.p. > 330°) in 18% yield; NMR (conc H_2SO_4) 1·7–2·7 (m, aromatic, integral 26), and 7·35 τ (s, CH_3?, integral 24). (Found: C, 50·8; H, 2·21; N, 4·02; mol. wt., 379 (mass spectrum). $C_{16}H_8BrCl_2NO$ requires: C, 50·39; H, 2·12; N, 3·67%; mol. wt. 379 (Br = 79, Cl = 35)).

9- (*or* 7-) *Bromo*-1,6-*dichloroindeno*[1.2.3-de]*quinolin*-2(3H)-*one* (**5a**). Compound **1d** (1 g) was warmed (95°) with conc H_2SO_4 (1·5 ml) for 15 min and poured into ice-water as for **2**; yellow crystals (from DMF, 30% yield), m.p. >330°. (Found: C, 49·00; H, 1·51; N, 3·88. $C_{15}H_6BrCl_2NO$ requires: C, 49·06; H, 1·64; N, 3·81%).

The same **5a** was formed (identified by elemental analysis and its IR spectrum) when 1 g of either **2a** or **1a** was reacted with conc H_2SO_4 (5 ml) containing Br_2 (1 ml) for 5 min on the steam bath (95°); the reaction mixture was poured into water and **5a** recrystallized from DMF (40% yield).

9- (*or* 7-) *Bromo*-1,6-*dichloro*-3-*ethylindeno*[1.2.3-de]*quinolin*-2-*one* (**5b**). Compound **1b** (1·0 g) was stirred with a mixture of conc H_2SO_4 (1·5 ml) and Br_2 (1 ml) for 15 min at 95°; after pouring into ice-water the solid was collected and recrystallized from DMF to give yellow crystals, m.p. 228–230° (65% yield). (Found: C, 51·67; H, 2·56; N, 3·52. $C_{17}H_{10}BrCl_2NO$ requires: C, 51·64; H, 2·56; N, 3·54%).

The same **5b** was formed (identified by mixture m.p., and IR spectrum) from similar treatment of **2c** with the acid mixture. Compound **5b** was converted into the more soluble (for NMR purposes) 1-ethoxy derivative by refluxing in EtOH containing NaOEt; yellow crystals, m.p. 193–195° (from glacial AcOH, 70% yield). NMR ($DCCl_3$) 1·82–3·02 (m, 5, aromatic), 5·30 (q, 2, $O\underline{CH_2}CH_3$), 5·71 (q, 2, $N\underline{CH_2}CH_3$), 8·48 (t, 3, $OCH_2\underline{CH_3}$), and 8·60 τ (t, 3, $NCH_2\underline{CH_3}$). (Found: C, 56·59; H, 3·81; N, 3·44. $C_{19}H_{15}BrClNO_2$ requires: C, 56·37; H, 3·73; N, 3·46%).

Cyclization of **1e** with H_2SO_4 and Br_2 as for **1b** afforded a yellow **5c** m.p. 263–270° (from DMF, 25% yield). (Found: C, 46·08; H, 2·32; N, 3·18; mol. wt., 437 (mass spectrum). $C_{17}H_{10}Br_2ClNO$ requires: C, 46·43; H, 2·30; N, 3·19%; mol. wt., 437 (Br = 79, Cl = 35)).

6,X-*Dichloro*-1-*methylindeno*[1.2.3-de]*quinolin*-2(3H)-*one* (**7**). Compound **6a** (1·0 g) was warmed (95°) with conc H_2SO_4 (2 ml) for 15 min and the mixture then poured into ice-water. The product was filtered, washed with hot EtOH, and recrystallized from DMF to give yellow **7** (not melted at 330°), in 15% yield; NMR (conc H_2SO_4) 2·1–2·8 (m, 5, aromatic) and 7·3 τ (broad peak, 3, CH_3). (Found: C, 63·69; H, 2·90; N, 4·85; mol. wt. 301. The mass spectrum showed peaks at *m/e* 301 and 335 (base peak), indicative of **7** and of a trichloro derivative, respectively. ($C_{16}H_9Cl_2NO$ requires: C, 63·56; H, 3·01; N, 4·63%; mol. wt., 301 (Cl = 35)). The compound **7** (100 mg) was reduced in DMF with Raney Ni and H_2 (140 lbs/sq in) as described above. The reduction product was recrystallized from AcOH (40 mg, 57%; m.p. 224–226°). (Found: C, 81·96; H, 5·65; N, 5·85; mol. wt. 235 (mass spectrum). $C_{16}H_{13}NO$ requires: C, 81·68; H, 5·57; N, 5·95%; mol. wt. 235).

From the hot EtOH washings of **7** a compound suspected of being 6-chloro-3-hydroxymethyl-4-phenyl-2(1*H*)-quinolone was recovered (70 mg, ~7%), m.p. 200° (from dil EtOH). The IR (KBr) showed a weak OH absorption. (Found: C, 66·94; H, 4·07; N, 4·72. $C_{16}H_{12}ClNO_2$ requires: C, 67·20; H, 4·20; N, 4·90%).

When **6b** was similarly reacted with H_2SO_4 the product (colorless crystals from glacial AcOH, m.p. 285–286° (lit.[2] m.p. 288–290°), 50% yield) proved to be (mixture m.p. and IR spectrum) 3,6-dichloro-4-phenyl-2(1*H*)-quinolone. (Found: C, 62·07; H, 3·13; N, 4·75; mol. wt. 289 (mass spectrum). $C_{15}H_9Cl_2NO$ requires: C, 62·04; H, 3·14; N, 4·82%; mol. wt., 289 (Cl = 35)).

The same quinolone was isolated also after H_2SO_4 treatment of **6c** (2 hr heating, 25% yield) and **6d** (15 min heating, 20% yield).

Acknowledgement—We wish to thank the South African Council for Scientific and Industrial Research for measurement of NMR and mass spectra, and Dr. S. H. Eggers for helpful discussion in connection with some of the mass spectra.

REFERENCES

[1] Department of Biochemistry, Rutgers State University, New Brunswick, New Jersey.
[2] A. J. Hodgkinson and B. Staskun, *J. Org. Chem.* **34**, 1709 (1969).
[3] R. T. Conley and W. N. Knopka, *Ibid.* **29**, 496 (1964).
[4] C. F. Koelsch and A. F. Steinhauer, *Ibid.* **18**, 1516 (1953).
[5] A. J. Hodgkinson, M.Sc. Thesis, This University (1967).
[6] A. S. Wheeler and M. Morse, *J. Am. Chem. Soc.* **46**, 2572 (1924).