Experimental Section

Caution: HFTA dimer and HFA are toxic!

HFTA Dimer (1). A 500-mL, three-necked flask was fitted with a mechanical stirrer, thermometer, a water-cooled condenser, and a gas inlet tube. The outlet of the condenser was attached to a −78 °C cold trap. Under an atmosphere of nitrogen, the flask was charged with 200 mL of dry DMF, 23 g (0.72 mol) of sulfur, and 5.0 g of KF. The mixture was warmed to 40 °C, the heat source removed, and HFP bubbled in at a rate of about 1 g/min. The temperature rose and leveled off in the range of 52–57 °C. After 96 g of HFP had been added, an additional 23 g of sulfur was added (total sulfur charged 1.44 mol). Hexafluoropropene was added until a total of 199.5 g (1.33 mol) was used (2.3 h). The whole mixture was cooled to −20 °C and filtered. The solid was washed with cold DMF. After allowing the solid to melt, it was filtered, and the lower layer was washed twice with 50 mL of H_2O. This gave 199.7 g of pale yellow product (82.5% yield) of 98% purity by GC.

Hexafluoroacetone. From KIO_3. In an apparatus like that described above except for the gas inlet tube was charged 1 g of anhydrous KF, 30 g (0.14 mol) of KIO_3, 20.0 g of HFTA dimer (distilled, bp 110 °C, 0.055 mol), and 100 mL of dry DMF (water content 0.004%). The mixture was then heated to 140 °C over 20 min. The temperature rose gradually to 149 °C during an additional 100 min. The mixture turned dark brown as iodine was formed. In the cold trap 16.3 g (0.098 mol) of HFA (95% by GC) was collected (89% yield).

From NO_2. A 250-mL, three-necked flask was equipped with a thermometer, stirrer, gas inlet tube, and a cold-finger condenser containing acetone held to −10 to −20 °C. A dry ice and acetone trap (−78 °C) was connected to the −20 °C condenser. The flask was charged with 125 g of HFTA dimer (85% purity, 0.29 mol), 3.5 g of KF, and 100 mL of dry DMF. The mixture was heated to 100–120 °C and 70 g (1.52 mol) of NO_2 was passed subsurface into the liquid over a period of 5.5 h. At the end of this period, the −20 °C condenser was allowed to warm to room temperature and the apparatus flushed with nitrogen. The −78 °C trap contained 113.5 g, which after distillation, afforded 77.3 g (0.466 mol, 80% yield from 1) of HFA (bp −28 °C) and 36 g of NO_2 (bp 21 °C).

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Registry No. 1, 791-50-4; hexafluoropropene, 116-15-4; hexafluoroacetone, 684-16-2.

Anomalous Course of Leuckart Reduction of Anthraquinones by Formamide

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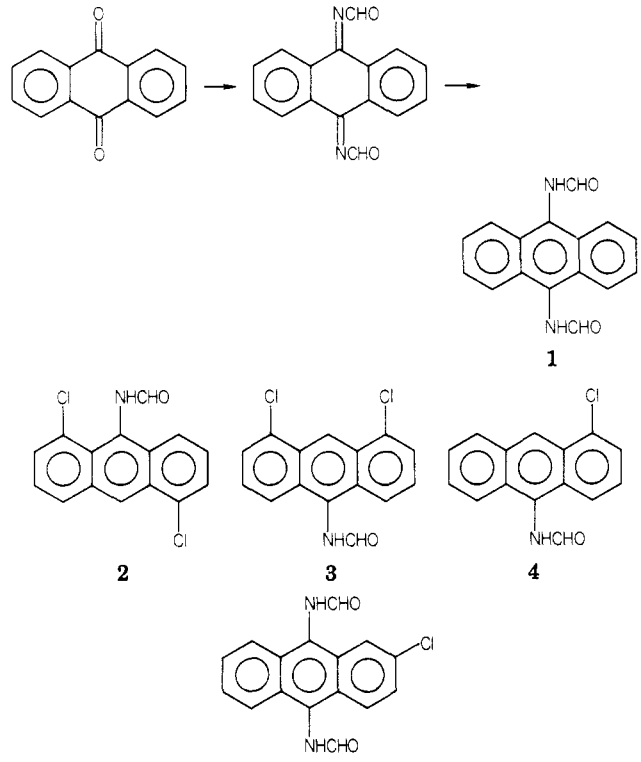
Reactions of such alkyl- and dialkylamides as methylformamide, dimethylformamide, and hexamethylphosphoric triamide with a variety of chloroanthraquinones have been described;[1,2] these give (methylamino)- and (dimethylamino)anthraquinones, depending on the reagent and conditions. Formamide, presumably because of its demonstrated capacity for reacting with the carbonyl groups in the parent anthraquinone,[3] has apparently not been used in comparable experiments. It has, however, been known for some time that aminoanthraquinones can be produced from chloroanthraquinones by reaction with *p*-toluenesulfonamide[4] or phthalimide,[5] followed in each case by hydrolysis.

Schiedt[3] had originally reported 1 as the product obtained from reaction of anthraquinone with formamide. This was unfortunately misquoted on review as the 9,10-dihydro derivative, i.e., the compound anticipated from a double Leuckart reaction of anthraquinone.[6] We have now confirmed (microanalysis, IR, and mass spectroscopy) Schiedt's original formulation. Evidently, two molecules of formamide have condensed, one at each carbonyl group, with anthraquinone and a third molecule of formamide (or formic acid) has effected 9,10 reduction (or, equivalently, a single Leuckart reaction followed by proton shift) to produce an aromatic central ring.



We now report our results on the reaction of formamide with chloroanthraquinones. The symmetrical 1,5-dichloroanthraquinone gave, after 3-h reflux with formamide, a mixture containing **2** and 1,5-dichloroanthracene, together with some unreacted quinone. The course of reaction was thus following that noted by Schiedt (reaction at carbonyl)[3] rather than that observed with methylformamide and dimethylformamide (displacement of chlorine),[1,2] but further stages of reduction were apparent. The yield of 1,5-dichloroanthracene increased with lengthening reaction time. With the assumption that **2** is derived from the product of an initial Schiedt-type sequence, these observations may be rationalized as a conversion of the Schiedt-type intermediate by formamide (or formic acid) to the 9,10-dihydro derivative, a reduction equivalent to tautomerization and Leuckart reduction. The dihydro derivative then eliminates a molecule of formamide.

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Repetition of these steps permits reductive removal of the remaining nitrogen function as formamide.

Similar treatment of 1,8-dichloroanthraquinone with formamide gave 1,8-dichloro-10-formamidoanthracene **3**. We assign this structure rather than that of the 9-isomer since the mass spectrum shows no transition corresponding to loss of HCl from the molecular ion. By contrast, the mass spectrum of **2** (which contains chloro and formamido substituents proximate to each other) shows a base peak at *m/e* 253, corresponding to loss of HCl from its molecular ion. 1,8-Dichloroanthracene appeared as a significant reaction product as the reflux time was extended, but this compound was better prepared by reaction of **3** with formamide, with optional addition of formic acid.

Similarly, 1-chloroanthraquinone reacted with formamide (8-h reflux) to give the amide **4** formulated on the basis of the mass spectrum; this amide could be slowly reduced by further reaction with formamide, with optional addition of formic acid, to 1-chloroanthracene. The isomeric 2-chloroanthraquinone was reduced to the diamide **5** under these conditions; prolonged treatment of **5** with formamide, with or without added formic acid, caused slight reduction to monoamide(s) and 2-chloroanthracene (mass spectrum) but in insufficient quantities to encourage attempts at isolation.

The successive reductive stages in anthraquinone/formamide reactions are thus, depending on substituents, quinone → diamide (e.g., **1**, **5**) → monoamide (e.g., **2**, **3**, **4**) → anthracene. The ease of progression beyond the diamide stage in cases of 1-chloro substitution probably results from anthrol/anthrone type isomerization (tautomerization) relieving 1,9 steric compression, allowing Leuckart reduction to proceed at the 10-position. Elimination of formamide then occurs to give the monoamide. Analogous processes convert the monoamide (more slowly) to the anthracene.

It is interesting to compare these findings with those from Meerwein-Ponndorf reductions of anthraquinones with various aluminum alkoxide/alkanol systems,[7,8] in which recognized stages from anthraquinone are 9,10-dihydroxyanthracene, 9,10-dihydro-9,10-dihydroxyanthracene, and anthracene; reduction has not been observed beyond the second stage with 1-chloro- and 1,5-dichloroanthraquinones. The two reductive sequences are thus in some measure complementary, the extent of reduction depending on the substituents present in the anthraquinone.

Experimental Section

Mass spectra were determined with an AEI MS-30 double-beam spectrometer; *m/e* values are quoted for the lowest isotopic species and relative intensities are noted in parentheses.

Commercial samples of anthraquinones were crystallized, and formamide was distilled before use.

Reactions with Formamide. General Procedure. Reactions were carried out by heating the substrate (ca. 12 mmol) under reflux in formamide (30 mL) with stirring; the volume of formamide was increased for less soluble substrates and formic acid was added in approximately equal volume where noted. When cool, the reaction mixture was diluted with water and the precipitated solid was filtered off and dried. Products were separated by chromatography or crystallization, the process being monitored by thin-layer chromatography (TLC). Reactions are listed by substrate used.

a. 1,5-Dichloroanthraquinone. This quinone (3.4 g, 12.3 mmol) gave, after 3-h reflux, a solid which was extracted with chloroform, a small amount of insoluble material being discarded. Evaporation and chromatography (Florisil; benzene/light petroleum) gave 1,5-dichloroanthracene (0.6 g, 20%) and compound **2** (0.95 g, 27%), in addition to recovered quinone (1.35 g, 40%).

1,5-Dichloroanthracene formed pale-yellow plates: mp 186.5–187 °C (lit.[9] mp 187 °C); mass spectrum, *m/e* 246 (M^+, 100).

Anal. Calcd for $C_{14}H_8Cl_2$: C, 68.02; H, 3.23. Found: C, 67.97; H, 3.32.

Compound **2** formed pale-yellow needles: mp 273–274 °C (from benzene); IR (KBr) 1645 cm^{-1} (C=O); mass spectrum, *m/e* 289 (M^+, 29), 261 ($C_{14}H_9Cl_2N$, 32), 253 ($C_{15}H_8ClNO$, 100), 233 ($C_{13}H_7Cl_2$, 17), 226 ($C_{14}H_9ClN$, 17).

Anal. Calcd for $C_{15}H_9Cl_2NO$: C, 62.07; H, 3.10; N, 4.83. Found: C, 62.65, H, 3.20; N, 4.81.

b. 1,8-Dichloroanthraquinone. This quinone (8.3 g, 30 mmol) gave, after 3-h reflux, a solid which was extracted with acetone, a small amount of insoluble material being discarded. Evaporation gave crude **3** (8.3 g, 96%), mp 307–310 °C, containing two minor impurities. Sublimation (twice) in vacuo gave an analytical sample: mp 319–320 °C; IR 1645 cm^{-1} (C=O); mass spectrum, *m/e* 289 (M^+, 100), 261 (87), 233 (35), 226 (53).

Anal. Calcd for $C_{15}H_9Cl_2NO$: C, 62.07; H, 3.10; N, 4.83. Found: C, 62.07; H, 3.02; N, 4.87%.

c. Compound 3. This compound (1.5 g, 5.2 mmol) gave, after 16-h reflux, a solid product. This was leached with benzene to give a solution and unchanged **3** (1.28 g, 85%). Chromatography of the dissolved material (Florisil/benzene) gave 1,8-dichloroanthracene (174 mg, 14%) as pale-yellow needles: mp 185 °C (lit.[9] mp 185 °C); mass spectrum, *m/e* 246 (M^+, 100).

From a similar experiment with added formic acid (48-h reflux), the yield of 1,8-dichloroanthracene was 18%.

d. 1-Chloroanthraquinone. This quinone (4.0 g, 16.5 mmol) gave, after 16-h reflux, a very dark product. This was continuously extracted with chloroform (Soxhlet) to give a soluble fraction (1.33 g) and a black residue (3.10 g), which was discarded. The extracted solid was crystallized from 1-propanol to give compound **4**, mp 276–280 °C, slightly contaminated with impurities (TLC): IR 1645 cm^{-1} (C=O).

An analytically pure sample, mp 279.5–280 °C, was obtained by sublimation in vacuo, further crystallization, and final sublimation: mass spectrum, *m/e* 255 (M^+, 100), 227 (79), 199 (28), 192 (38).

Anal. Calcd for $C_{15}H_{10}ClNO$: C, 70.45; H, 3.91; N, 5.48. Found: C, 70.54; H, 3.82; N, 5.42.

e. Compound 4. This compound (1.6 g, 6.3 mmol) gave, after 16-h reflux, a solid product which was treated essentially as in part c above. This gave unreacted **4** (1.2 g, 75%) and 1-chloroanthracene (120 mg, 9%): yellow plates, mp 83–84 °C (lit.[10] mp 81 °C); mass spectrum, *m/e* 212 (M^+, 100).

From a similar experiment with added formic acid (9-h reflux), the yield of 1-chloroanthracene was 20%.

f. 2-Chloroanthraquinone. This quinone (9.0 g, 37.2 mmol) gave, after 8-h reflux, a solid which when crystallized from benzene gave **5** as yellow needles (9.3 g, 92%): mp 360 °C; IR (KBr) 1645 cm^{-1} (C=O); mass spectrum, *m/e* 298 (M^+, 100), 241 (54).

Anal. Calcd for $C_{16}H_{11}ClN_2O_2$: C, 64.32; H, 3.69. Found: C, 64.14; H, 3.90.

In separate experiments, compound **5** was refluxed with formamide (16 h), and with formamide/formic acid (9 h). In both cases, **5** was recovered (94–97%), contaminated with trace amounts of compounds showing (mass spectrum) *m/e* 255 and 212; these peaks were not present in the mass spectrum of the starting material.

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Registry No. **2**, 79917-74-1; **3**, 79917-75-2; **4**, 79917-76-3; **5**, 79917-77-4; 1,5-dichloroanthraquinone, 82-46-2; 1,5-dichloroanthracene, 6406-96-8; 1,8-dichloroanthraquinone, 82-43-9; 1,8-dichloroanthracene, 14381-66-9; 1-chloroanthraquinone, 82-44-0; 1-chloroanthracene, 4985-70-0; 2-chloroanthraquinone, 131-09-9; formamide, 75-12-7.

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