Formylation of 2,5-dimethoxyaniline in the presence of sodium hydride or sodium amide. To a solution of 2,5-dimethoxyaniline (12.1 g.) in 150 ml. of dimethylformamide (under nitrogen) was added 6.8 g. of a 53% dispersion of sodium hydride in oil.[12] The mixture was heated at reflux for 20 min., cooled (ice-bath) and then cautiously treated with water. After hydrolyzing the remaining sodium hydride, the mixture was diluted to *ca.* 1 l. with water and refrigerated for 16 hr. The crystalline 2,5-dimethoxyformanilide weighed 10.3 g. (62%), m.p. 78–79.5° (*cf.*, Table I).

When an equivalent quantity of commercial (Fisher Scientific Co.) sodium amide was substituted for sodium hydride and the reaction repeated exactly as described above, 8.7 g. (52%) of 2,5-dimethoxyformanilide, m.p. 79–80°, was isolated.

Each of the following formamides was prepared using the general sodium methoxide-dimethylformamide procedure. N-Phenyl-p-aminoformanilide. The crude product prepared from 27.6 g. of *p*-aminodiphenylamine recrystallized from methanol-water as purple crystals (18.7 g., 59%), m.p. 170–171°. Two additional recrystallizations from methanol-water (Norit-A) gave pure colorless leaflets melting at 174.5–175°.

Anal. Calcd. for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.66; H, 5.75; N, 13.12.

4,4′-Diformamidodiphenylsulfone (II). Conversion of 4,4′-diaminodiphenylsulfone (I, 40 g.) to the crude light brown diformyl derivative, m.p. 242–250° (48 g., 98%), was accomplished in the usual manner. Repeated recrystallization from methanol-water (Darco) led to a colorless crystalline analytical sample, m.p. 273–273.5° (lit.,[13] m.p. 260.5°).

Anal. Calcd. for $C_{14}H_{12}N_2O_4S$: C, 55.26; H, 3.97; N, 9.21; S, 10.53. Found: C, 55.22; H, 3.92; N, 9.10; S, 10.59.

α-Formamidonaphthalene. The crude formamide derivative prepared from 20 g. of α-naphthylamine weighed 19.7 g. (82.5%) and melted at 131–135°. Recrystallizing the reddish-brown product from benzene (Norit-A) gave colorless needles (19.0 g., 79.5%), m.p. 138.5–139.5° (lit.,[14] m.p. 138.5°).

8-Formamido-2-naphthol. Before collecting the formamide (8.8 g., 73%) derived from 10 g. of 8-amino-2-naphthol, the reaction mixture was cooled and adjusted to *p*H 5 with hydrochloric acid. Two recrystallizations from methanol-water (Darco) gave colorless needles melting at 205.5–207° dec. (lit.,[15] m.p. 205–207° dec.).

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4-(4-Dimethylaminostyryl)quinolines with a Methyl Group on the Styryl Ring[1]

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A series of 4-(4-dimethylaminostyryl)quinolines carrying a methyl group on the quinoline ring has been reported.[2] The series has been extended to include compounds carrying methyl groups on the ring in the styryl group. These compounds are of especial interest because of indications that the hydroxylation of certain positions of such compounds as *p*-aminodiphenyl *in vivo* is involved in their carcinogenetic effects.[3] It seemed that the methyl groups might modify the biological effects of the styrylquinolines by blocking or increasing hydroxylation at certain positions, or by steric effects. Melting points and analyses of the new compounds are shown in Table I.

The substituted 4-dimethylaminobenzaldehydes required were prepared from the corresponding substituted *N,N*-dimethylanilines by the method of Campaigne and Archer[4] or the method of Vilsmeier and Haack.[5] Attempts to prepare 4-dimethylamino-3,5-dimethylbenzaldehyde by these methods and by the method of Adams and Coleman[6] were unsuccessful.

The compounds have been tested against Walker 256 tumors by Professor Alexander Haddow and

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TABLE I

4-(4-Dimethylaminostyryl)quinolines

Substituent	M.P.	Method	Reaction Time	Reaction Temp.	Yield, %	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
2′-Methyl-[a]	163.5–164.5	$ZnCl_2$[2]	30 hr.	120	20	83.29	6.99	9.71	83.2 83.1	6.6 6.8	9.60[b]
3′-Methyl-	191.0–193.0	Leese[7]	1 hr.	140–160	4	83.30	6.99	9.71	83.26 83.56	6.85 6.70	[c]
2′,6′-Dimethyl-	140.6–141.9	Leese	40 min.	155–165	50	83.40	7.33	9.26	83.27	7.29	9.03[b]
2′,6′-Dimethyl-3-methyl-	130	Leese	3 hr.	155–170		83.50	7.64	8.85	83.82	7.35	8.91[b]

[a] Positions marked by a (′) are on the benzene ring of the styryl group. [b] Analyses by Burroughs Wellcome Laboratories. [c] Analyses by Galbraith Laboratories.

his associates at the Chester Beatty Research Institute. Several of them exhibited antitumor activity. The effects of the different locations of the alkyl groups are to be discussed in a later paper.

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Sodium Hypochlorite Oxidation of *p*-Methylacetophenone

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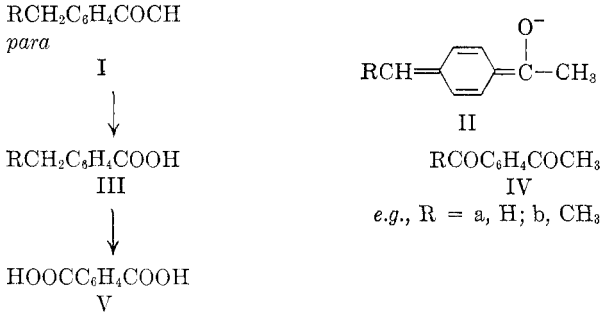
The recently proposed mechanism for sodium hypochlorite oxidations of *para*-methylene groups in acetophenone systems[1] (I), expressed in terms of the *a priori*-unlikely[2] enolization through the *para*-methylene group (e.g. II) and imputing a vital role to the acetyl group[1], is not supported by experimental evidence.



The experiment described below, under identical conditions, in which *p*-toluic acid (IIIa) was isolated in 77% yield after seven minutes, and was oxidized further to terephthalic acid (V) upon continuation of this treatment, demonstrates that in fact the vulnerable[2] acetyl group does not survive to give IV, and thus cannot participate in the oxidation of the aryl methyl or methylene group. The steps involved therefore are I → III → V, and the oxidation of the aryl methyl or methylene must be explained in terms of the effects of the first-formed carboxyl or carboxylate group.

EXPERIMENTAL

Oxidation of p-methylacetophenone (Ia). (A) A mixture of 5.0 g. of Ia and 800 ml. of commercial 5% sodium hypochlorite solution was refluxed gently under vigorous stirring and a nitrogen atmosphere.[1] After 7 min., a 100-ml. aliquot upon cooling and treatment with sodium bisulfite and acidification, precipitated 0.48 g. (77%) of pure *p*-toluic acid (m.p. 176–178°, identified as its amide and anilide). From the remainder of the reaction mixture after 28 hr., 2.9 g. of solid (m.p. >250°) was similarly obtained which upon washing with ether to remove *p*-toluic acid yielded 1.6 g. (30%) of pure terephthalic acid (V, subl. >300°, identified as its dimethyl and diethyl esters). Evaporation of the ether washings produced 1.3 g. (26%) of *p*-toluic acid containing chlorinated impurities (identified by infrared spectrum) which on oxidation under the above conditions gave only pure V (65% by weight).

(B) In a similar oxidation with added base (4.1 g. of sodium hydroxide), after 10 min., a 100-ml. aliquot yielded 0.62 g. (98%) of pure *p*-toluic acid, and the remainder of the reaction mixture after 44 hr. gave 1.26 g. (23%) of pure terephthalic acid and 2.34 g. (53%) of pure *p*-toluic acid.

Oxidation of p-toluic acid (IIIa, 4.3 g.) under the above conditions without adjusting for reagent changes entailed in the primary and rapid destruction of the acetyl group starting from Ia (24 hr.), gave 2.95 g. of solid (m.p. >240°) which was purified by washing with ether [1.65 g. (32%)] and identified as V by infrared spectrum. Evaporation of the ether washings produced 1.3 g. of impure IIIa.

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Reactions of *N,N*-Dichloroamines

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N-Chlorinated derivatives of amines can be prepared by a number of methods involving hypochlorous acid or its derivatives.[1,2,3] *N*-Chloro-*prim*-alkylidenimines have been prepared by the reaction of aldehydes with chloroamine[4] and *N*-chloro-*sec*-alkylidenimines have been postulated as intermediates in the preparation of α-aminoketones from *N,N*-dichloro-*sec*-alkylamines.[3] The preparation of *N*-chlorocyclohexanimine has been claimed by the reaction of cyclohexanone with chloramine.[5]

We have found that *N*-chloro-*sec*-alkylidenimines can be prepared from *N,N*-dichloro-*sec*-alkylamines by the action of bases. For example, *N,N*-dichlorocyclohexylamine yields *N*-chlorocyclohexanimine.[6] Such widely different bases as tertiary amines and

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