

Naphthol

Naphthols are also obtained from arylmethyleneketenes generated by FVP of derivatives of Meldrum's acid (304).

From: Comprehensive Organic Synthesis, 1991

Related terms:

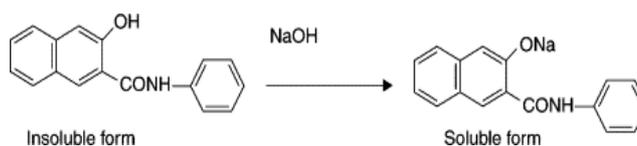
Phenol, Quinone, Ligand, Aldehyde, 2-Naphthol, Alkyne, Ring Formation, [Alpha]

Azoic dyeing

D.P. Chattopadhyay, in Handbook of Textile and Industrial Dyeing, 2011

19.3.1 Naphthols

The naphthols are insoluble in water. They are phenols, soluble in alkaline solution and substantive to cotton, particularly in the presence of salt. In the presence of strong alkali they are converted to the corresponding naphtholate ions and are water soluble (Fig. 19.1). The naphtholate ions are always coplanar and preferably have elongated molecular structures. These relatively small molecules are of low to moderate substantivity for cotton. The naphthols may be classified into four groups depending on their affinity for cotton (Shenai, 1993).



19.1. Solubilisation of naphthol (conversion of naphthol to naphtholate).

- Low substantivity naphthols: Naphthol AS, Naphthol ASD, Naphthol AS-OL, Naphthol AS-IRG, Naphthol AS-PH, etc.
- Medium substantivity naphthols: Naphthol AS-BG, Naphthol AS-LT Naphthol AS-RL, etc.
- High substantivity naphthols: Naphthol AS-BS, Naphthol AS-SW Naphthol AS-BI, Naphthol AS-BO, etc.
- Very high substantivity naphthols: Naphthol AS-BT, Naphthol AS-S Naphthol AS-BT, Naphthol AS-BR, etc.

In general, the higher the substantivity the better the rubbing fastness since less azo pigment forms on the fibre surfaces. The substantivity increases with increase in the molecular size of the naphtholate ion, but the diffusion rate in the fibres and solubility in dilute aqueous alkali decrease. Addition of salt promotes better exhaustion of the bath, more being needed for naphthols of lower substantivity. For the dissolution of naphthols usually caustic soda solution of 72°TW, i.e. 38°Be, is used. The first ACC, which was employed in the commercial synthesis of azoic colour, was the 2-hydroxy-naphthalene, i.e. Beta-naphthol. The same was later replaced by more substantive arylamides of 2-hydroxy-3-naphthoic acid discovered in 1911 in Germany. This product is known today as Naphthol AS. With different substitutions on the basic structure, several other substantive naphthols were subsequently developed in the following years which were named as members of the Naphthol AS series (Table 19.1).

Table 19.1. Examples of some naphthols (ACC)

Naphthol	Substantivity	Structure	C.I. constn. no.	ACC
β -Naphthol	—	—	—	—
Naphthol AS	Low		37505	2
Naphthol ASD	Low		37520	18
Naphthol AS-BG	Medium		—	19
Naphthol AS-OL	Low		37530	20
Naphthol AS-PH	Low		37558	14

Naphthol	Substantivity	Structure	C.I. constn. no.	ACC
Naphthol AS-SW	Higher		37565	7
Naphthol AS-BO	Higher		37560	4

A correlation between the chemical structures of ACCs and their affinity for cotton has been attempted. The theoretically computed correlation equations of the practical affinity with the van der Waals surface, the molecular volume and the hydrophobicity are reported in the literature (Dăescu and Hădă Ruga, 1999). Though reversing the position of amino groups in the conventional AS series of naphthols was found to enhance the brightness of the developed shade, significant advantages over conventional products were not achieved (Hall *et al.*, 1980).

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URL: <https://www.sciencedirect.com/science/article/pii/B978184569695500192>

Dyes

Christophe J. Le Coz, in [Encyclopedia of Toxicology](#) (Second Edition), 2005

Dye-Fixing and Dye-Coupling Agents

β -Naphthol (2-naphthol, azoic coupling component 1) (Figure 22) is no longer used.

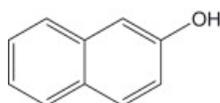


Figure 22. β -Naphthol.

Naphthol AS (3-hydroxy-2-naphthoic acid [anilide](#), azoic coupling component 2) (Figure 23), a coupling agent used for cotton dyeing, has replaced β -naphthol because of a stronger affinity for [cellulose](#). Naphthol AS first caused pigmented contact [dermatitis](#) in workers at a textile factory in Mexico in the 1970s, where it was widely used. It has been reported as an agent of pigmented contact dermatitis in several patients, generally due to non-European and non-North American textiles. Its presence in textile can be easily ascertained by [thin-layer chromatography](#).

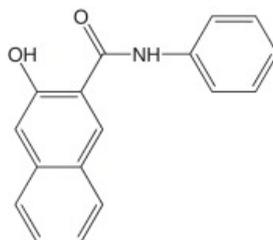


Figure 23. Naphthol AS.

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Dye–Fibre interaction

J.N. Chakraborty, in [Fundamentals and Practices in Colouration of Textiles](#), 2014

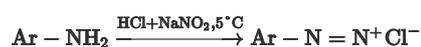
3.2.4 Dyeing of cellulose with insoluble azoic colour

Coupling components or naphthols are first solubilised with NaOH and then applied on cotton. When a base is diazotised and the naphtholated textile is treated in this base, coupling takes place between naphthol and base resulting in formation of coloured lake *in situ* cotton. The whole process passes through three different stages, *viz.*

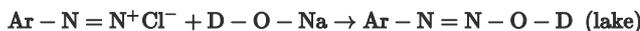
(a) solubilisation of naphthol:



(b) diazotisation of base



(c) reaction between naphthol and diazotised base to develop lake



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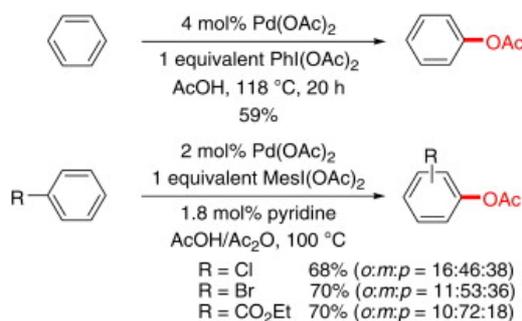
URL: <https://www.sciencedirect.com/science/article/pii/B9789380308463500030>

Oxidation

A. Lei, W. Liu, in *Comprehensive Organic Synthesis II (Second Edition)*, 2014

7.13.3.3 Simple Phenols

Phenol, naphthol, and other simple phenols are considered to be among the most basic chemical building blocks, and they can be produced by simple and cheap chemical processes. However, the direct aromatic C—H **oxygenation** of unactivated aromatic C—H bonds by **metal catalysts** is still a big challenge for chemists. Using Pd(OAc)₂/PhI(OAc)₂ conditions, simple **benzene** underwent C—H oxygenation to produce **phenyl acetate** in 59% yield at 120 °C (Scheme 19).²⁰ Other substituted **arene** substrates can be acetoxyated in good yields with MesI(OAc)₂ as the **oxidant**, although three **isomers** are obtained in the final products.²¹



Scheme 19.

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URL: <https://www.sciencedirect.com/science/article/pii/B9780080977423007151>

Synthesis: Carbon with Three or Four Attached Heteroatoms

Erich Kleinpeter, Kalevi Pihlaja, in *Comprehensive Organic Functional Group Transformations*, 1995

6.17.1.3.2.(i) From phenols and naphthols

Phenols and naphthols readily react with **thiophosgene** in the presence of a base to give aryl chlorothioformates in good yield (Equation (7)) <62JOC4509, 65CB2063, 65LA(681)64, 67AG(E)281, 83HOU(E4)407>. Aryl chlorothioformates (in addition to those given in <83HOU(E4)407>) which were synthesized in this way are listed in Table 2. Hydrocarbons and chlorohydrocarbons were used as solvents. Phenyl chlorothioformate is a yellow liquid boiling at 91 °C and 10 torr (mm Hg) <59ZOB3792>. In a number of cases, the aryl chlorothioformates were not isolated but used for the synthesis of thiocarbonic acid derivatives <81JA932, 82EUP62834, 83JA4059, 87USP4754072>. In some cases thiophosgene was produced directly in the reaction mixture (see above) (a) by **chlorination** of CS₂ <85JAP62120358, 90JAP03220173> from which the corresponding phenyl chlorothioformates were obtained in 93–96% yield; (b) by reduction of CCl₃CSCl <85JAP61229860, 85JAP61229861, 88JAP2009858>, the aryl chlorothioformates being obtained in 63% yield and the corresponding naphthyl derivatives in 74% yield; and (c) by reducing CCl₃SH with SO₂ <86GEP3616009>.

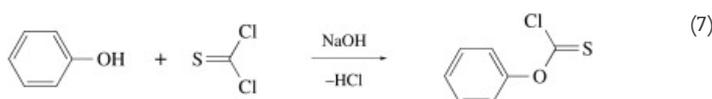


Table 2. Aryl chlorothioformates synthesized from thiophosgene and phenols or naphthols.

Aryl—OH	Base	Yield (%)	Ref.
Phenol	NaOH/H ₂ O	95.0	91JAP03218336

Aryl—OH	Base	Yield (%)	Ref.
			91JAP03193759
<i>m</i> -tert-butyl-phenol	NaOH/H ₂ O		93JAP05058990
<i>m</i> -tert-butyl-phenol	NaOH/H ₂ O	98.9	88JAP01301654
<i>m</i> -R ¹ - <i>p</i> -R-phenol	NaOH/H ₂ O		83JAP60155152
R ¹ = halogen; R = alkyl ≥ 2			
5,6,7,8-tetrahydro-naphthol-2	NaOH/H ₂ O	89.9	90JAP04066566
5,6,7,8-tetrahydro-naphthol-2	NaOH/H ₂ O	80.9	90JAP04128263
			90JAP05032616
			87JAP01102058
5,6,7,8-tetrahydro-naphthol-2	NaOH/H ₂ O/Na ₂ S ₂ O ₄	81.0	87JAP01075462
C ₆ Cl ₅ —OH	NaOH	99.0 ^a	85SUL61
2,4,6-Trimethyl-phenol	NaOH	81.0 ^b	85SUL61
2,6-di-OMe—C ₆ H ₃ ONa		48 ^c	90CL83

a
Colorless solid; m.p. 108–112 °C.

b
Oily product; m.p. 40–43 °C.

c
In THF at 0 °C.

The esters ROC(Cl)=S (R = succinimido, phthalimido, norborn-5-ene-2,3-dicarboximido) proved to be useful reagents for introducing the thiocarbonyl group into organic compounds <88EGP273832>.

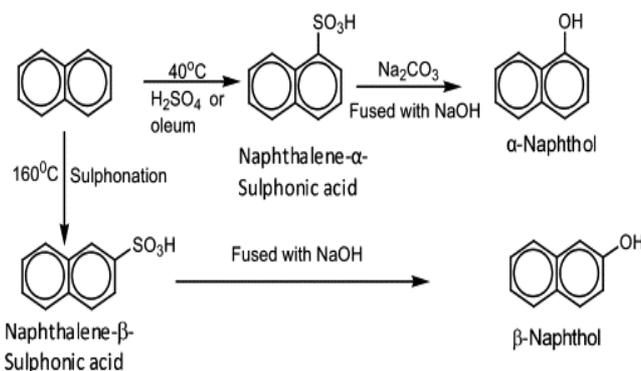
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Synthesis of dye intermediates

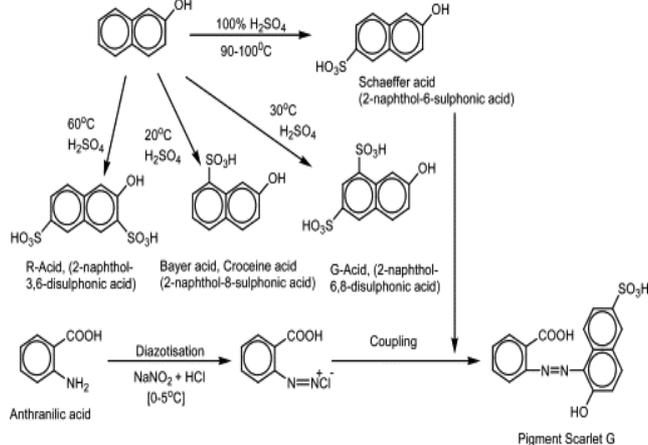
J.N. Chakraborty, in *Fundamentals and Practices in Colouration of Textiles*, 2014

32.2.2 β-naphthol



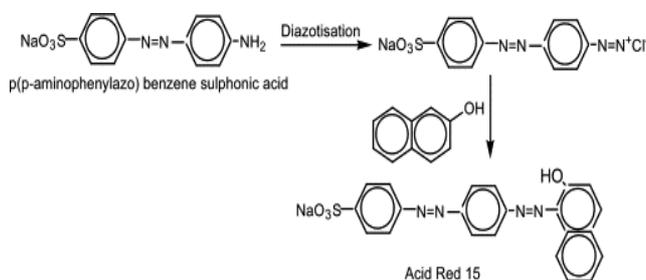
Application

Sulphonation of β-naphthol with H₂SO₄ at various concentrations as well as temperatures can form various types of mono- and polysulphonic acids as described below.



However – the first transition product – 2-naphthol 1-sulphonic acid is very unstable and rearranges by itself to croceine (or croceic acid (2-naphthol 1-sulphonic acid)), which in turn rearranges partially at cold but completely at higher temperature to Schaeffer acid. R acid and G acids are formed in presence of H_2SO_4 in too excess. The nomenclature of R and G acids is based on their ability to form red and yellow dyes when reacted with diazonium salts.

Coupling of β -naphthol with diazotised p (p-aminophenylazo) benzene sulphonic acid results a red pigment, viz. Acid Red 15.



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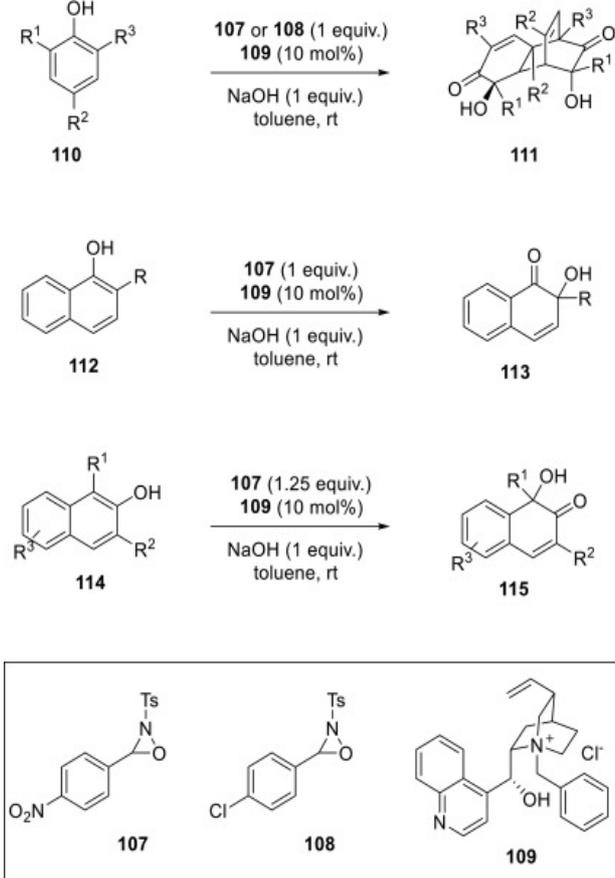
URL: <https://www.sciencedirect.com/science/article/pii/B9789380308463500327>

Oxaziridines and Oxazirines

Sang Kook Woo, in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, 2020

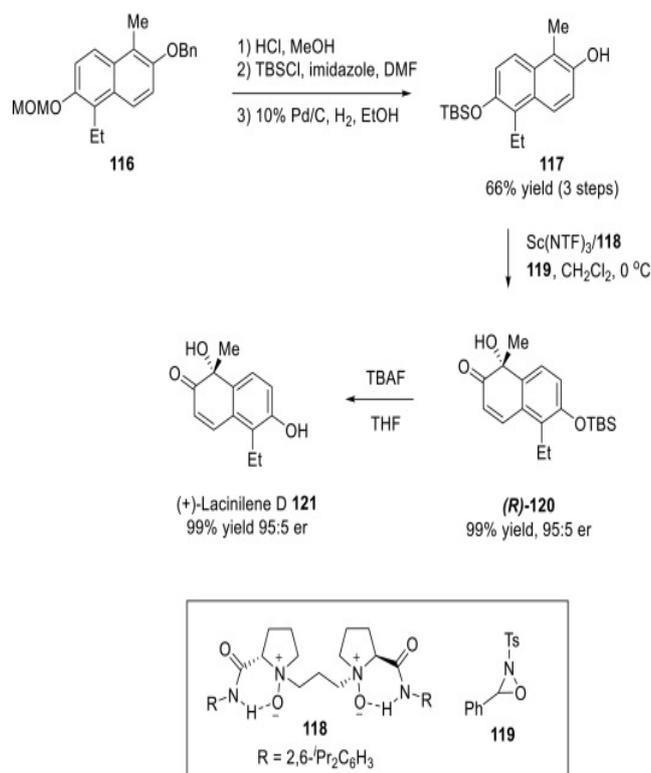
3.3.6.2 Hydroxylation of phenols and naphthols

The hydroxylation of phenols and naphthols produces hydroxycyclohexadienones by dearomatization in the presence of oxaziridines. Recently, Toullec and co-workers have developed the oxaziridine mediated hydroxylative dearomatization of phenols and naphthols in moderate to good yields. They used base and phase-transfer reagents to increase reactivity (Scheme 15).³⁹ The use of phenols **110** provided additional dimerization products **111** by a cycloaddition reaction. Additionally, 1-naphthols **112** and 2-naphthols **114** were converted to the corresponding hydroxylated products at room temperature.



Scheme 15. Hydroxylative dearomatization of phenols and naphthols.

Feng et al. reported the enantioselective hydroxylation of 2-naphthols using a chiral N,N' -dioxide-Sc(NF₂)₃ complex catalyst with oxaziridine as oxidant.⁴⁰ This method has been successfully applied to the catalytic asymmetric synthesis of the phytoalexins lacinilenes **121** (Scheme 16).



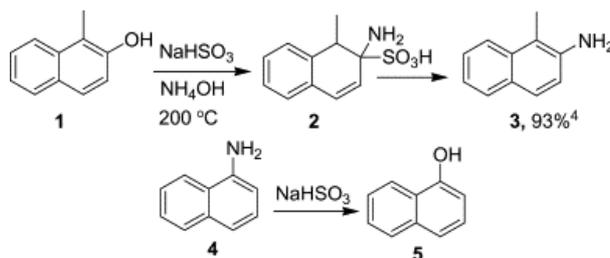
Scheme 16. Asymmetric synthesis of the phytoalexins lacinilene.

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BUCHERER–LE PETIT Naphthol (Naphthylamine) Synthesis

Synthesis of **naphthylamines 3** from naphthols **1** or of naphthols **5** from naphthylamines **4** by means of reversible bisulfite-ammonia addition to C=O or C=N.



1-Methyl-2-naphthylamine (3).⁴ 1-Methyl-2-naphthol **1** (78 g, 0.05 mol) and NaHSO₃ (10 g, 0.1 mol) in 40 mL 28% NH₄OH and 10 mL H₂O were heated to 200–205 °C for 48 h. After basification and ether extraction, HCl gas was passed into the organic phase. **2**·HCl was filtered and after treatment with NaOH was extracted with ether. Evaporation gave 72 g of **3** (93%), mp 46–50 °C; recrystallized (PE), mp 49–50 °C.

1	Le Petit R	<i>Bull Soc Ind Mulhouse</i>	1903	73	326
2	Bucherer HT	<i>J Prakt Chem</i>	1904	69	49(2)
3R	Drake NL	<i>Org React</i>	1942	1	105
4	Johnson WS	<i>J Am Chem Soc</i>	1944	66	210
5R	Weidon BCL	<i>Quart Rev</i>	1952	6	380
6	Seeboth H	<i>Angew Chem</i>	1958	70	312
7	Canete A	<i>Synth Commun</i>	2001	31	2143

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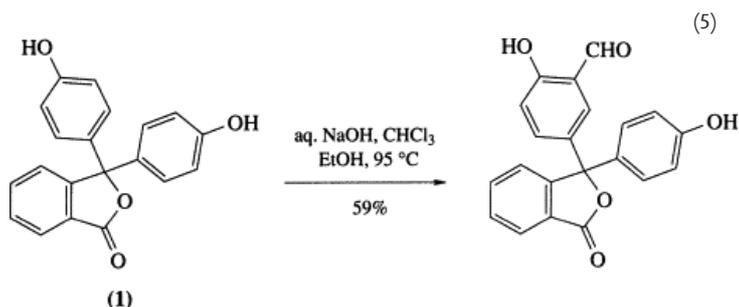
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Additions to CX π-Bonds, Part 2

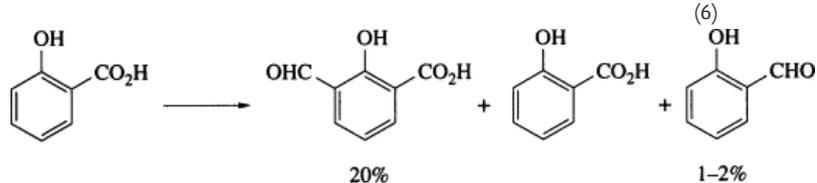
Hans Wynberg, in *Comprehensive Organic Synthesis*, 1991

3.4.3 Scope and Limitations

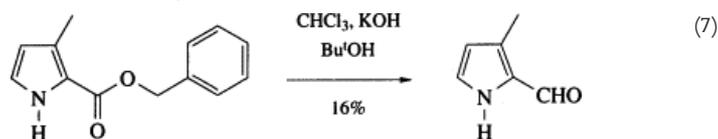
In addition to phenols, naphthols, their alkyl derivatives and the heterocyclic compounds mentioned above, a large variety of substituted monocyclic as well as condensed phenols have been subjected to the Reimer–Tiemann reaction. Although with a few exceptions the yields are only moderate, the facile reaction conditions, at least on a laboratory scale, have assured the reaction a permanent place among the variety of methods by which an aldehyde group can be attached to an aromatic nucleus. For example, phenolphthalein (1) has been formylated under standard Reimer–Tiemann conditions by van Kampen to yield the *o*-hydroxy aldehyde in 59% yield (equation 5).¹¹



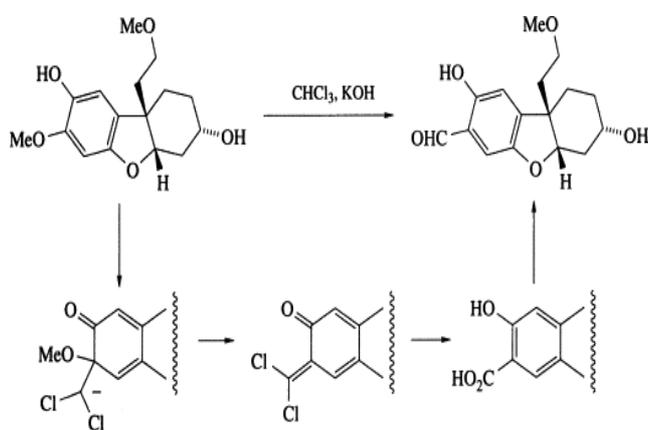
In addition to phenolphthalein, other carboxy-substituted phenols have been subjected to the Reimer–Tiemann reaction. Mixtures of compounds, some lacking the carboxyl group, result (equation 6).¹ Even though the nature of the reaction (*i.e.* the attack by the electrophilic dichlorocarbene on the nucleophilic phenolate carbanion) would seem to preclude successful substitution on phenols carrying such negative substituents as carboxyl and sulfonic acid groups, reports of such substitution can be found, albeit mostly in the patent literature.¹



A recent careful examination of the substitution pattern of a series of pyrrole-2-carboxylates established that loss of the carboxyl group occurs with simultaneous entry of the formyl group (equation 7).¹⁰



Another unusual observation concerns the replacement of a methoxy group by a formyl group under Reimer–Tiemann reaction conditions. The mechanism proposed by the authors (Scheme 1) seems reasonable¹² and supposes two consecutive replacements. First, the methoxy substituent is replaced by the dichlorocarbene to give an *o*-quinone methide. The latter is hydrolyzed to a carboxyl group by a mechanism involving conjugate addition of hydroxide. A second replacement occurs, the carboxyl group being displaced by the formyl (*via* the carbene) group. All-in-all, this is a strange, unsubstantiated, but not unreasonable sequence of events.



Scheme 1.

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