

Salicylaldehyde

In subject area: [Chemistry](#)

Salicylaldehyde is a compound that can react with amino groups and form stable coordination bonds with metal ions. It is widely used in the research of metal complexes.

AI generated definition based on:

[Coordination Chemistry Reviews, 2023](#)

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Chapters and Articles

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Six-membered Rings with One Heteroatom, and their Fused Carbocyclic Derivatives

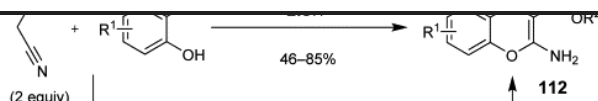
M.A. Brimble, ... J. Sperry, in

[Comprehensive Heterocyclic Chemistry III](#), 2008

7.08.5.2 Formation of More than One Bond

Salicylaldehydes usually react with activated methylene groups to afford coumarins; however, when activation of the methylene group is brought about by a nitrile group, 2-amino-4*H*-chromenes are formed. In this manner, salicylaldehydes react with two equivalents of ethyl 2-cyanoacetate in the presence of 3 Å molecular sieves to form 2-amino-4*H*-chromenes **112** in moderate yield (**Scheme 35**) <2000TL6993>. The reaction proceeds via an initial Knoevenagel condensation of the aromatic aldehyde with the activated methylene group, followed by cyclization to form the 2-imino-2*H*-chromene-3-carboxylate intermediate **113**. Michael addition of a second molecule of ethyl 2-cyanoacetate then affords 4*H*-chromenes **112** (**Scheme 35**) <2000TL6993>.

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Asymmetric Cycloadditions

Qiuyuan Tan, Ohyun Kwon, in
[Comprehensive Chirality \(Second Edition\)](#), 2024

6.11.2.4 Salicylaldehyde Derivatives– Allenes/Alkynes

Salicylaldehyde derivatives are great four-atom units because they feature a nucleophilic OH (or other pronucleophilic) unit and an electrophilic aldehyde (or its [imine](#) derivative) functionality.

Scheme 28 demonstrates the general mechanism for the phosphine-catalyzed [4+2] annulation of salicylaldehyde derivatives and [allenes](#). Initially, the prototypical zwitterionic intermediate **A** undergoes γ -addition to the electrophilic aldehyde **2–98**, producing intermediate **B**. Subsequent [proton transfer](#) facilitates [deprotonation](#) of the pronucleophile, forming **C**, which undergoes [intramolecular Michael addition](#) and β -elimination to release the phosphine and afford the corresponding [4+2] cycloadduct **2–100** featuring an exocyclic *E*-double bond. When γ -substituted allenoates are employed, an equilibrium is established between the β -phosphonium [enolate](#) **A** and the vinylogous [ylide](#) **D**, with the latter adding preferably to the aldehyde (or its equivalent) to form the intermediate **E**.

Subsequent proton transfer and intramolecular γ -umpolung addition leads to the eventual formation of the chiral product

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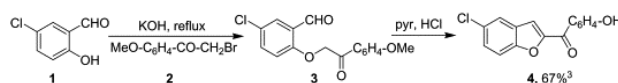
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RAMBERG–BACKLUND Olefin Synthesis to RUZICKA–FUKUSHIMA Ketosteroid Rearrangement

A. Hassner, I. Namboothiri, in
[Organic Syntheses Based on Name Reactions \(Third Edition\)](#),
2012

RAPP–STOERMER Benzofuran Synthesis

[Benzofuran](#) synthesis from salicylaldehydes **1** and α -haloketones
2 via intramolecular [aldol reaction](#) of intermediate of **3**.



Benzofuran (4).³ A mixture of **1** (15 g, 0.096 mol), **2** (22 g, 0.096 mol) and KOH (5.3 g, 0.096 mol) in EtOH (150 mL) was heated to reflux to give 10 g of crude **3** (35%). **3** was heated with pyridine hydrochloride for 30 min, cooled, stirred with water, filtered, and crystallized as its [sodium](#) salt from aq EtOH to afford 6 g of **4** (67%), mp 238 °C.

1	Rap E	<i>Gazz Chim Ital</i>	1895	25	285
2	Stoermer R	<i>Liebigs Ann</i>	1900	312	237
3	Buu Hoi, Ng P	<i>J Chem Soc</i>	1957		2593
4	Rao MLN	<i>Tet Lett</i>	2007	48	431
5	Giampaolo G	<i>Curr Med Chem</i>	2009	16	1
6	Wang Z	<i>Syn Comm</i>	2009	39	4079

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Light Activated Processes with Zeolites: Recent Developments

2.2 Organic Photochemistry within Zeolites

Fundamental studies on the formation of photochemically generated charge separated and metastable species within [zeolites](#) are of interest, and the reader can also find relevant information in several review articles [8,9]. The influence of the [zeolite](#) on guest molecules is evident in many ways. A good recent example is salicylaldehyde [azine](#) (SAA), shown in Figure 2.2, a molecule 14 Å in length and 5 Å in width which can exist in various forms. Upon inclusion of this molecule in the 13 Å supercages of zeolite X (Figure 2.1a), several changes are observed both in ground and excited state properties [10]. The form that [SAA](#) acquires in the zeolite cages is that of the zwitterionic structure consistent with previous studies of salicylideneaniline, the parent molecule of SAA [11]. Stabilization of the zwitterionic structure is promoted by the polar zeolite framework, with the [phenolate](#) O⁻ interacting with framework cations, and the positively charged ⁺NH interacting with the anionic framework.



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A critical review of the 2005 literature preceded by two chapters on current heterocyclic topics

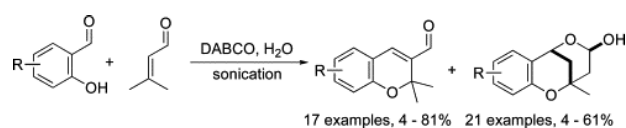
John D. Hepworth, B. Mark Heron, in [Progress in Heterocyclic Chemistry](#), 2007

6.4.2.2 [1]Benzopyrans and Dihydro[1]benzopyrans (Chromenes and Chromans)

The reaction of salicylaldehydes with α,β -unsaturated aldehydes in aqueous dioxane and under sonification affords a mixture of 2H-[1]benzopyran-3-carboxaldehydes and a tricyclic hemiacetal. The former is considered to arise from the 1,4-addition of a

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<05ASC555>.



The reaction of resorcinols with α,β -unsaturated aldehydes and ketones catalysed by ethylenediamine diacetate has been used to

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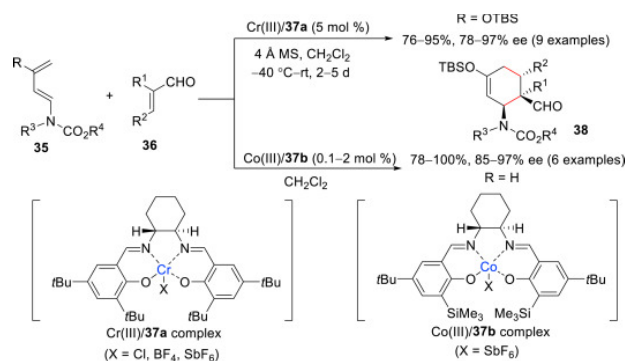
Asymmetric Cycloadditions

X.-X. Yang, ... Y.-C. Chen, in

[Comprehensive Chirality \(Second Edition\)](#), 2024

6.08.2.1.3 Other Lewis acid complexes

Salens, condensed from salicylaldehyde derivatives and diamines, can form complexes with suitable metals, which have been applied to asymmetric Diels–Alder reaction as well. The Rawal group found that both chiral Cr(III)/salen **37a** complex³⁸ and Co(III)/salen **37b** complex³⁹ promoted the highly enantioselective Diels–Alder reaction between 1-carbamate-3-siloxybutadienes **35** and α -substituted [acroleins](#) **36** (Scheme 11).



Scheme 11. Enantioselective Diels–Alder reaction of 1-amino-3-siloxy-dienes **35** and α -alkyl substituted acroleins **36**.

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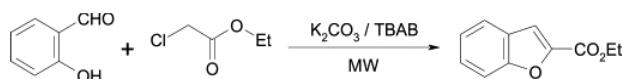
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Microwave-assisted Organic Synthesis

Dariusz Bogdal, in [Tetrahedron Organic Chemistry Series](#), 2005

7.3.3 Benzofuran-2-carboxylic acid ethyl ester

CAUTION! Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, lab coat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



Equipment


Single-mode microwave reactor equipped with a pyrometer (300W)

Reaction vessel (Figure 4.2b)

[Adapter](#) (Figure 4.2f)

Cold finger

Materials

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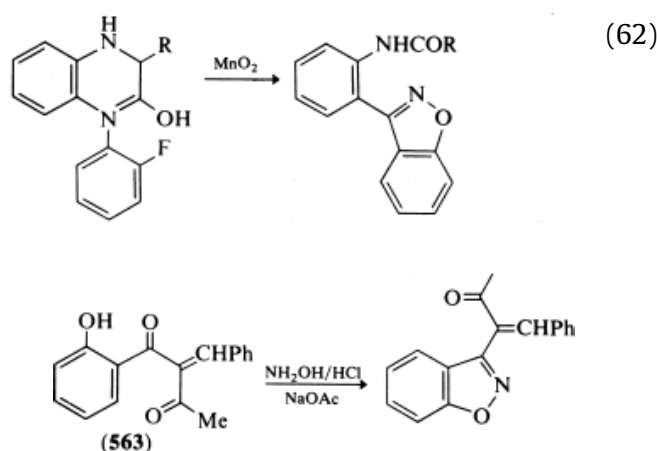
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Isoxazoles and their Benzo Derivatives

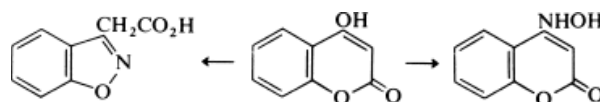
4.16.4.19.1.(ii) Other methods

The utilization of azidyl ion with salicylaldehyde gave 1,2-benzisoxazole accompanied by up to 15% of 2-aminobenzoxazole (67AHC(8)277) . Nitrile oxide addition to benzyne gave 3-substituted 1,2-benzisoxazole. Nitrile oxide addition to ketone enamines gave reduced derivatives which were brominated with NBS, and subsequent loss of HBr also generated 3-substituted 1,2-benzisoxazoles (67AHC(8)277, 80IJC(B)571) .

1,2-Benzisoxazoles were obtained from quinazolin-3-ols in an ArF displacement activated by MnO₂ (equation 62) (74JHC885) . The 1,2-benzisoxazole was produced as a minor side product in the reaction of (563) with hydroxylamine (73MI41600) .



The literature had reported the preparation of a coumarin hydroxylamine by the reaction of 4-hydroxycoumarin with hydroxylamine. A reinvestigation of the reaction showed the product to be 1,2-benzisoxazole-3-acetic acid (Scheme 172) (69JHC279) .



Scheme 172.

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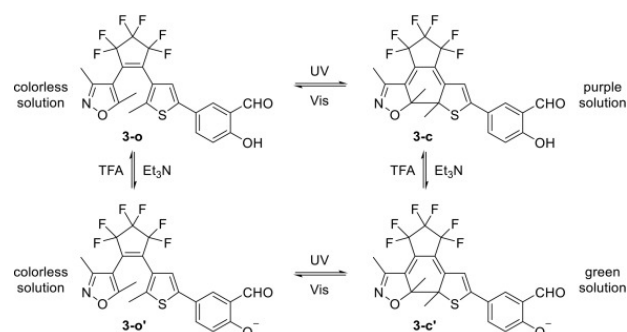
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FIVE-MEMBERED RINGS WITH TWO Heteroatoms, and Their Fused Carbocyclic Derivatives

Franca M. Cordero, ... Fabrizio Machetti, in *Comprehensive Heterocyclic Chemistry IV*, 2022

4.03.4.3 Isomerism

A photochromic diarylethene, bearing a salicylaldehyde group, showed multi-responsive photochromism with distinguishable color change due to open-chain/closed-ring [photoisomerization](#), under the stimuli of acid/base and light. In fact, this phenomenon was observed in MeCN for either **3-o** and **3-c** or the deprotonated forms **3-o'** and **3-c'**, upon [light irradiation](#) (Scheme 3). A fluorescent switching for the species **3-o** and **3-o'**, even related to the conversion from the open-ring isomer to the non-fluorescent closed-ring one, was also evidenced by photoirradiation in [acetonitrile](#). The electrochemical properties of open-ring and closed-ring isomers were also investigated with [cyclic voltammetry](#) (CV).¹⁷



Scheme 3. Open-chain/closed-ring photoisomerization in compound **3**.

The same behavior was observed for a series of diarylethene derivatives, bearing different substituents on the [thiophene](#) ring, and their photochromic and fluorescent properties have been systematically investigated through the stimulus of light, [metal ions](#), and anions. These results were then exploited to build highly selective and sensitive fluorescent and colorimetric [chemosensors](#) for recognition of metal ions (Zn^{2+} , Cd^{2+} , Al^{3+} , Cu^{2+} , Mg^{2+}), as well as different anions (F^- , Cl^- , I^- , Br^- , CO_3^{2-} , HCO_3^- , NO_3^- , CN^- , etc.).^{18–33}

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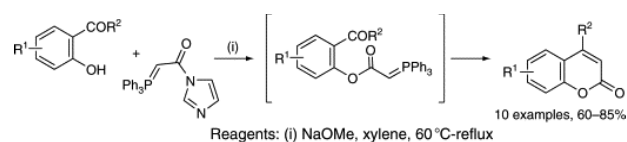
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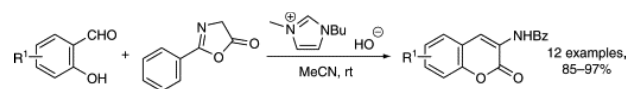
John D. Hepworth, B. Mark Heron, in
[Progress in Heterocyclic Chemistry](#), 2011

6.4.2.6 Coumarins

Several new approaches to [coumarins](#) use salicylaldehydes as the starting point, as for example in two one-pot processes. Reaction of the derived [oxyanion](#) with the [ylide](#) triphenyl(α -carboxymethylene)phosphorane [imidazolide](#) is followed by an intramolecular [Wittig reaction](#) (Scheme 52) <09TL236> and reaction with 2-phenyl-1,3-oxazolan-5-one in an [ionic liquid](#) proceeds through a [Knoevenagel reaction](#) and yields 3-benzamidocoumarins (Scheme 53) <09TL2208>.



Scheme 52.



Scheme 53.

High yields of 3-arylbenzopyran-2-thiones result from reaction

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