1-Azidoadamantane (1) with Dipolarophiles. A mixture of 1-azidoadamantane (1, 1.00 mmol) and an appropriate dipolarophile (0.81–7.35 mmol) in toluene (2 mL) was stirred at 25–110 °C. After removal of the solvent, the residue was purified by recrystallization, or on a silica gel (Mallinckrodt, 100 mesh) column eluted with CH_2Cl_2–CH_3OH or CH_2Cl_2–$CH_3CO_2C_2H_5$ (Tables I and II).

Conversion of 1-(1-Adamantyl)-4-(hydroxymethyl)-1*H*-1,2,3-triazole (31) to 1-(1-Adamantyl)-4-(methoxycarbonyl)-1*H*-1,2,3-triazole (28). A mixture of the triazole **31** (175 mg, 0.751 mmol), potassium permanganate (255 mg, 1.61 mmol), and sodium hydroxide (23 mg, 0.575 mmol) in water (3.5 mL) was stirred for 15 h at room temperature. The mixture was decolorized by addition of 5% aqueous sodium thiosulfate, and the precipitates were filtered and washed with 5% aqueous sodium hydroxide (2 mL). The combined filtrate and washings were acidified (20% aqueous hydrochloric acid). The resulting precipitates were filtered, washed with water, and dried to afford crude carboxylic acid (93 mg, 50.1%). Treatment of the acid with diazomethane (ca. threefold excess) in ether for 12 h at room temperature and removal of the solvent and excess diazomethane gave crude methyl ester which was purified by preparative TLC (silica gel, CH_2Cl_2–CH_3OH) to afford **28** (78 mg, 39.7% overall), identified by having the same IR and ^1H NMR spectra as those of the sample obtained from the cycloaddition.

1-(1-Adamantyl)-5-(methoxycarbonyl)-1*H*-1,2,3-triazole (29) from 32. A mixture of triazole **32** (80 mg, 0.34 mmol), potassium permanganate (148 mg, 0.94 mmol), Aliquat 336 (50 mg) in benzene (5 mL), and water (5 mL) was stirred vigorously for 12 h at room temperature and decolorized by addition of 5% aqueous thiosulfate. The resulting precipitates were filtered and washed with 5% hydrochloric acid and benzene. The organic layer of combined filtrate and washings was separated, and the water layer was extracted with benzene (5 × 5 mL). The combined organic layer and benzene extracts were extracted with 10% aqueous sodium hydroxide (5 × 5 mL). Acidification of the combined alkaline extracts with 20% hydrochloric acid gave crude acid product as colorless precipitates (50 mg, 58.9%) which on treatment with an excess of diazomethane in ether for 12 h afforded the **methyl ester 29** as colorless crystals after chromatography on a silica gel column (CH_2Cl_2); mp 137–138 °C. For analytical and spectral data, see Tables II and III.

Lithium Aluminum Hydride Reduction of 1-(1-Adamantyl)-4-(ethoxycarbonyl)-1*H*-1,2,3-triazole (34) to 31. A mixture of triazole **34** (50 mg, 0.18 mmol) and lithium aluminum hydride (100 mg, 2.64 mmol) in ether (10 mL) was heated under reflux for 2 h. The cooled mixture was treated with water, the organic layer was separated, and the water layer was extracted with ether (5 × 5 mL). The combined organic layer and extracts were dried (Na_2SO_4). Removal of the solvent gave an oily residue which on sublimation at 130–150 °C (0.2 mmHg) afforded the **(hydroxymethyl)triazole 31** as colorless crystals (40 mg, 94.2%). The IR and ^1H NMR spectra were superimposable on those of the specimen obtained from the cycloaddition of 1 with **30**.

Oxidation of 4-(Ethoxycarbonyl)-1-(1-adamantyl)-Δ^2-1,2,3-triazoline (16) to the Corresponding Triazole 34. A mixture of the triazoline **16** (49 mg, 0.18 mmol) and potassium permanganate (100 mg, 0.64 mmol) in acetone (5 mL) was stirred for 3 days at room temperature. The mixture was decolorized by addition of ethanol (2 mL), and the resulting precipitates were removed by filtration. Removal of the solvent gave a solid residue which was purified on a silica gel column eluted with CH_2Cl_2–AcOEt to afford the **triazole 34** as colorless crystals after recrystallization from *n*-hexane (35 mg, 70.6%). The melting point and IR and ^1H NMR spectra were identical with those of the specimen obtained by the cycloaddition of 1 with **33**.

4-(Acetoxymethyl)-1-(1-adamantyl)-1*H*-1,2,3-triazole (44). This compound was prepared by acetylation of the 4-(hydroxymethyl)triazole **31** with acetic anhydride in pyridine. The usual workup afforded the acetate **44** in 76.3% yield as colorless crystals, mp 96–97 °C (*n*-hexane). For spectral and analytical data, see Tables II and III.

Registry No. **1**, 24886-73-5; **2**, 498-66-8; **3**, 121-46-0; **4**, 7350-72-3; **5**, 573-57-9; **6**, 76599-30-9; **7**, 76599-30-9; **8**, 76599-32-1; **9**, 76599-33-2; **10**, 76599-34-3; **11**, 3638-64-0; **12**, 20451-53-0; **15**, 140-88-5; **16**, 76599-35-4; **17**, 76599-49-0; **18**, 102-96-5; **21**, 76599-36-5; **22**, 76599-37-6; **23**, 536-74-3; **24**, 40430-66-8; **25**, 76599-38-7; **27**, 922-67-8; **28**, 76599-39-8; **29**, 76599-40-1; **30**, 107-19-7; **31**, 76599-41-2; **32**, 76599-42-3; **33**, 623-47-2; **34**, 76599-43-4; **36**, 762-42-5; **37**, 110-65-6; **38**, 501-65-5; **39**, 78-66-0; **40**, 76599-44-5; **41**, 76599-45-6; **42**, 76599-46-7; **43**, 76599-47-8; **44**, 76599-48-9.

Structure of Anhydroacetylsalicylamide

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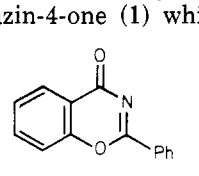
Anhydroacetylsalicylamide, previously reported[3] as 2-methyl-4*H*-1,3-benzoxazin-4-one (**2**), has been shown by chemical and spectroscopic analysis to be 2-[2-(2-hydroxybenzamido)propenyl]-4*H*-1,3-benzoxazin-4-one (**8**) or its simple tautomer **9**. The product of the reaction of this substance with ammonia has been shown to be 2-(2-hydroxyphenyl)-4-methyl-6-(2-hydroxybenzamido)pyrimidine (**4**).

In 1910 Titherley reported the acid-catalyzed dehydration of *O*- or *N*-benzoylsalicylamide to 2-phenyl-4*H*-1,3-benzoxazin-4-one (**1**) which is driven by removal of a



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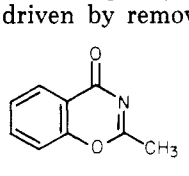

2

water-containing azeotrope.[2] In his hands other acylsalicylamides failed to give identifiable dehydration products under similar conditions. Forty-eight years later, Hanada reported that a modification of Titherley's conditions converts the acetylsalicylamides to a yellow substance, X (mp 217 °C), to which he assigned the structure 2-methyl-4*H*-1,3-benzoxazin-4-one (**2**).[3] This structural assignment has been accepted in a number of reports.[4] In this paper we demonstrate that anhydroacetylsalicylamide (X) is not **2** but has a more complex and interesting structure.

An examination of the UV spectra of anhydroacetylsalicylamide (X) and anhydrobenzoylsalicylamide reveals that the former has a more complex chromophore with a

(1) On faculty fellowship from the College of the Holy Cross.
(2) Titherley, A. W. *J. Chem. Soc.* **1910**, *97*, 200.
(3) Hanada, T. *Nippon Kagaku Kaishi* **1958**, *31*, 1024.
(4) (a) Brunetti, H.; Lüthi, C. E. *Helv. Chim. Acta* **1972**, *55*, 1566. (b) Ryabukhin, Y. I.; Dorofeenko, G. N.; Mezheritskii, V. V. *Khim. Geterotsikl. Soedin.* **1975**, 280. (c) *Ibid.* **1975**, 460. (d) Dorofeenko, G. N.; Ryabukhina, O. Y.; Mezheritskii, V. V.; Ryabukhin, Y. I. *Ibid.* **1977**, 47.

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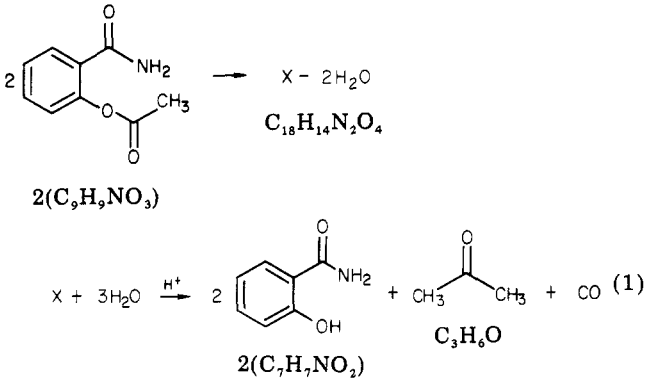
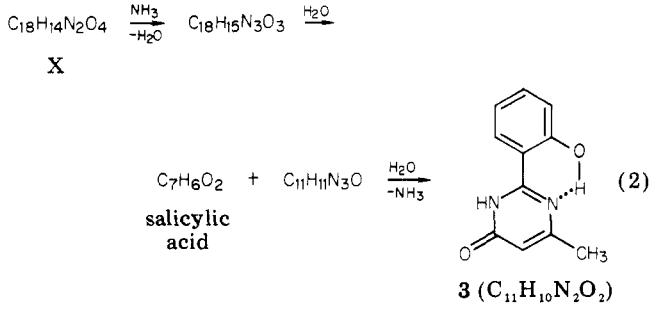
long-wavelength absorption maximum at roughly 100 nm longer wavelength [H_2O–dioxane; λ_{max} (1) = 245 nm (log ϵ 4.2), λ_{max} (X) = 352 nm (log ϵ 4.4)]. This result is inconsistent with Hanada's structural assignment of **2** for X, as is its mass spectrum, which shows a molecular ion at m/e 322, corresponding to a molecular formula of $C_{18}H_{14}N_2O_4$.

The hydrolysis behavior of **1** and X also differs significantly. Substance **1** is relatively inert to aqueous bases but very labile toward acids ($t_{1/2}$ ca. 4 min at pH 3 and 25 °C) and is hydrated to form *N*-benzoylsalicylamide quantitatively. Substance X is reported by Hanada to form salicylamide upon alkaline hydrolysis; we also observe the formation of a simple hydration product, $C_{18}H_{16}N_2O_5$, under these conditions. Acidic hydrolysis of X provides a significant structural clue. When X is heated to reflux for 3 min in 6 N HCl and a portion of the solvent is allowed to distill from the reaction flask and is treated with an excess of 2,4-dinitrophenylhydrazine reagent, 37% of 1 equiv of acetone 2,4-dinitrophenylhydrazone (80% crude yield) was isolated; rapid cooling of the pot contents allowed recovery of 67% of 2 equiv of salicylamide (90% crude yield). From eq 1 it is clear that all of the atoms

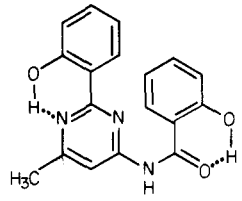


of X are accounted for if the remaining product is 1 equiv of carbon dioxide, most reasonably formed by decarboxylation of an acetoacetic acid moiety that is contained in X. From this result, it is clear that a Claisen-type condensation involving the acetyl function occurred during the formation of X.

Further evidence in support of this conclusion was obtained by examination of the product of formula $C_{18}H_{15}N_3O_3$ which is formed by reaction of X with aqueous ammonia, as reported without structural assignment by Hanada. Although much more stable toward hydrolysis than X itself, this substance can be hydrolyzed by aqueous base to salicylic acid and a substance of formula $C_{11}H_{11}N_3O$, which can in turn be hydrolyzed with aqueous acid to 2-(2-hydroxyphenyl)-6-methyl-4-pyrimidone ($C_{11}H_{10}N_2O_2$, **3**), independently synthesized from ethyl acetoacetate and *o*-hydroxybenzamidine (eq 2).



This reaction sequence as well as the spectroscopic properties of the ammonia product is in complete accord with its formulation as 2-(2-hydroxyphenyl)-4-methyl-6-(2-hydroxybenzamido)pyrimidine (**4**). Possible structures



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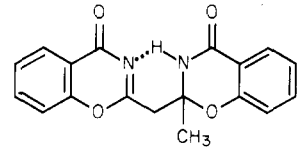
for $C_{18}H_{14}N_2O_4$ isomers which contain salicylamide and acetoacetate moieties and which can be expected to form **4** are **5**–**9**. Of these, **8** and **9** are simple tautomers which



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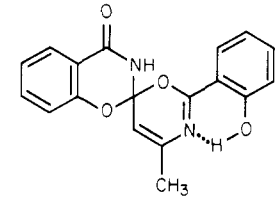

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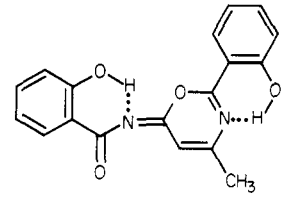

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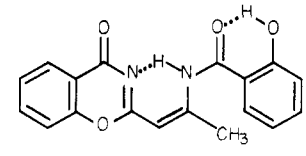

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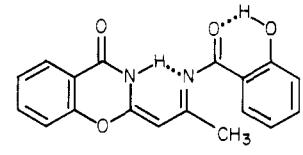


9

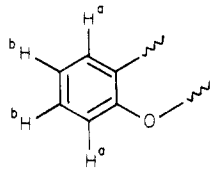
are likely to be difficult to distinguish, and **5** and **6** can be rejected as inconsistent with the UV spectrum observed for X. Since **5** can be seen to result from a simple Claisen-type condensation of **2** and its enamide tautomer and **6**–**9** are envisaged as readily interconvertable under acidic or basic conditions, distinguishing between structures **7** and **8** or **9** must proceed from spectroscopic evidence.

The proton-noise-decoupled pulse Fourier transform ^{13}C NMR spectra of X in $CDCl_3$ confirmed, but did not distinguish between, structures **7**–**9** by establishing the presence of six deshielded carbons that do not bear protons (δ 154.5, 158.4, 162.9, 164.7, 165.3, 170.2; 2 CO, 2 C=O, OC=N or OCN, C=N or =CNCO), one *C*-methyl (δ 23.4), and one =CH (δ 97.3, singlet in the decoupled spectrum which becomes a doublet in the coupled spectrum). The chemical shift of the latter resonance could be argued to be more in accord with that expected for the vinyl C of **9**, which has β-enol ether character,[5] than for that of **8**. If a pyrimidine C-5 is an acceptable model for the vinyl H–C of structure **7**, then a resonance in the range of δ 110–130[6] would be expected (compare with δ 113 observed for the C-5 of the pyrimidine of **4**).

Although the 60-MHz ^1H NMR spectrum of substance X confirmed the presence of vinyl H, CH_3C, and aromatic H, it was weak and uninformative since the solubility of X in suitable solvents is quite small. The 250-MHz ^1H

(5) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.
(6) Reference 5, 245.

NMR spectrum in $CDCl_3$ revealed resonances corresponding to the following features: intramolecularly H bonded OH and NH at δ 13.8 (s, 1) and 11.9 (s, 1), eight aromatic protons [δ 8.39 (dd, J = 7.5, 1.6 Hz, 1 H), 8.16 (dd, J = 7.5, 1.5 Hz, 1 H), 7.71 (td, J = 7.2, 1.5 Hz, 1 H), 7.53–7.46 (pair of overlapping t, 2 H), 7.33 (dd, J = 7.7, 1.0 Hz, 1 H), 7.14 (td, J = 7.3, 1.0 Hz, 1 H), 7.01 (dd, J = 8.5, 1.3 Hz, 1 H)], a vinyl proton at δ 5.34, and three methyl protons at δ 2.69 (s). The aromatic protons correspond to the two ortho-substituted phenyl functions of X and are clearly divided into triplets corresponding to b-type protons and doublets corresponding to a-type protons, as in part structures **10** or **11**.



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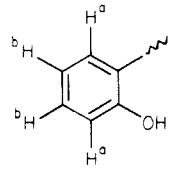
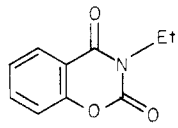


11

The striking feature of the aromatic resonances of X is that only two protons, one type a and one type b, can be assigned to the shielded range of δ 6.8–7.1 which is characteristic of aromatic hydrogens ortho or para to a hydroxyl function, as in partial structure **11**.[7] This pair must clearly belong to one *o*-hydroxyphenyl function, which is common to structures **7–9**. Structure **8**, which has two such functions, is therefore incompatible with the proton NMR spectrum and can be excluded on this basis. The availability of 250-MHz ^1H spectra for **1**, **4**, and **7** allows confirmation of this conclusion. Thus **4**, with two *o*-hydroxyphenyl functions, exhibits phenyl resonances at δ 8.37 (dd, 1 H), 7.65 (dd, 1 H), 7.53 (td, 1 H), 7.38 (td, 1 H), and 7.09–6.91 (m, 4 H), corresponding to the expected four shielded hydrogens ortho or para to an OH group. By contrast, **1** and **12**, which approximate the environment



12

of the benzoxazinones of **8** and **9**, show aromatic resonances at δ 8.41 (dd, 2 H), 8.38 (dd, 1 H), 8.20 (td, 1 H), and 7.80–7.27 (m, 5 H) and at 8.08 (dd, 1 H), 7.70 (td, 1 H), 7.34 (td, 1 H), 7.30 (dd, 1 H), respectively. It may be noted that all protons in these two spectra are deshielded relative to those of benzene, and protons in each approximate the chemical shift of the most deshielded aromatic proton seen in X, which is clearly that ortho to the heterocyclic carbonyl.

The spectroscopic evidence cannot be used to distinguish between the tautomers **8** and **9**; however, the conjugation pattern of **9** can be argued to partition electron-withdrawing and -donating character less equally between the left and right sides of the molecule, and for this reason we regard **8** as the more stable and likely structure.

Experimental Section

Reagents and solvents were reagent grade and used without further purification. All melting points are uncorrected. The C^{13} and ^1H NMR spectra were obtained with a Bruker 250-MHz FT NMR spectrometer. Ultraviolet spectra were determined with a Bausche and Lomb Spectronic 505. Infrared spectra were recorded on a Perkin-Elmer Infracord, Model 2378. Mass spectra were measured courtesy of Dr. I. Lengyel and Dr. K. Biemann. Microanalyses were performed by either Scandinavian Microanalytical Laboratories or Galbraith Laboratories, Inc.

2-[2-(2-Hydroxybenzamido)propenyl]-4*H*-1,3-benzoxazin-4-one (8 or 9; Anhydroacetylsalicylamide). The procedure described by Hanada[3] was followed: IR ($CHCl_3$) 1685 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 322 (65.9), 161 (20.2), 121 (100), 120 (82.8), 127 (m, 202 → 106); decoupled ^{13}C NMR ($CDCl_3$) δ 23.4, 97.3, 114.6, 116.9, 118.1, 118.6, 120.0, 126.7, 127.7, 128.1, 135.3, 135.8, 154.5, 158.4, 162.9, 164.7, 165.3, 170.2; ^1H NMR ($CDCl_3$) δ 2.69 (s, 3 H), 5.34 (d, 1 H), 7.01 (dd, J = 8.5, 1.3 Hz, 1 H), 7.14 (td, J = 7.3, 1.0 Hz, 1 H), 7.33 (dd, J = 7.7, 1.0 Hz, 1 H), 7.53–7.46 (pair of overlapping t, 2 H), 7.71 (td, J = 7.2, 1.5 Hz, 1 H), 8.16 (dd, J = 7.5, 1.5 Hz, 1 H), 8.39 (dd, J = 7.5, 1.6 Hz, 1 H), 11.9 (s, 1 H), 13.8 (s, 1 H); UV (H_2O–dioxane) λ_{max} 245 nm (log ϵ 4.21), 352 (4.4).

Alkaline Hydrolysis of 8. A mixture of 1.0 g of anhydrosalicylamide **8** (3.1 mM) and dioxane (40 mL) was heated, and 0.24 N NaOH (30 mL, 7.2 mM) was added. This bright yellow solution was stirred at room temperature for 5 h. The mixture was then acidified with dilute HCl to pH 1, and a pink solid precipitated. This was taken up in a small amount of ethyl acetate. Repeated scratching of the flask side yielded 29 mg (29%) of crystals, mp 188.5–189.5 °C.

Anal. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.53; H, 4.71; N, 8.23; O, 23.53. Found: C, 63.42; H, 4.83; N, 8.15.

Acidic Hydrolysis of 8. A solution of **8** (375 mg, 1.1 mmol) in 6 N HCl (10 mL) was placed in the pot of a microdistillation apparatus and was heated to boiling in 1.5 min and then alllowed to boil an additional 2 min. At this time liquid distilled into the receiver in which had previously been placed 2,4-dinitrophenylhydrazine (300 mg) in ethanol (10 mL). The contents of the receiver were then heated to boiling, allowed to cool, and diluted with water. A precipitate consisting of yellow needles and a dark red solid came out of solution: 257 mg; mp 121–160 °C. The theoretical yield of the DNP of acetone is 298 mg. The precipitate was dissolved in ethyl acetate and passed through an alumina column. Evaporation of the effluent yielded 112 mg (37%) of a yellow-orange solid (mp 119.5–122.5 °C) identical with a prepared sample of the DNP of acetone.

The pot contents were poured onto $NaHCO_3$ (7 g), and the resulting slurry was extracted with ethyl acetate. Evaporation yielded 313 mg (100%) of a yellow solid, mp 127–131 °C. Recrystallization from ethyl acetate–cyclohexane yielded 212 mg (67%) of crystals identical with salicylamide.

2-(2-Hydroxyphenyl)-4-methyl-6-(2-hydroxybenzamido)-pyrimidine (4). The procedure described by Hanada[3] for the reaction of **8** with aqueous ammonia was followed: IR ($CHCl_3$) 3100, 1655 cm^{-1}; decoupled C^{13} NMR ($CDCl_3$) δ 24.2, 107.1, 113.8, 118.2, 119.0, 119.4, 119.6, 126.2, 129.0, 133.5, 136.1, 157.2, 161.1, 162.4, 164.6, 167.1, 169.5; ^1H NMR ($CDCl_3$) δ 2.63 (s, 3 H), 6.91–7.09 (m, 4 H), 7.38 (td, 1 H), 7.53 (td, 1 H), 7.65 (dd, 1 H), 8.03 (s, 1 H), 8.37 (dd, 1 H), 8.73 (s, 1 H), 11.5 (s, 1 H), 13.49 (s, 1 H); UV (H_2O dioxane) λ_{max} 260 (log ϵ 4.33), 313 (4.23).

2-(2-Hydroxyphenyl)-6-methyl-4-pyrimidone (3). A mixture of 2-hydroxybenzamidine (2.2 g, 16 mmol) and ethyl acetoacetate (2.5 g, 25 mmol) in ethanol (8 mL) was refluxed overnight. The resulting precipitate was collected, washed with a small portion of ethanol, and dried to yield 2.3 g (70%) of a powder that exhibits an intense green fluorescence. Recrystallization from dioxane afforded 1.95 g (61%) of the pyrimidone: mp 243.0–245.0 °C; decoupled C^{13} NMR ($CDCl_3$) δ 23.4, 111.0, 112.2, 119.1, 119.5, 126.3, 134.8, 157.4, 161.8, 163.2, 164.1.

Anal. Calcd for $C_{11}H_{10}O_2N_2$: C, 65.33; H, 4.99; N, 13.86; O, 15.82. Found: C, 65.57; H, 5.07; N, 13.85.

Basic Hydrolysis of 4. Pure **4** (350 mg, 1.1 mmol) was dissolved in 1 N NaOH (5 mL) and refluxed for 24 h. After cooling, the mixture was acidified to pH 10.5 and extracted twice with 10 mL portions of ethyl acetate. The water layer was then acidified to pH 1 and reextracted twice with 10-mL portions of ethyl acetate. The pH 1 extract after evaporation yielded 105 mg (90%) of salicylic acid, mp 153–156 °C. Recrystallization from water yielded 59 mg of product that had a mixed melting point

(7) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; p 202.

of 156.5–159.5 °C upon mixture with salicylic acid.

The pH 10.5 extract after evaporation yielded 191 mg (75%) of a solid that exhibited an intense blue-green fluorescence. Recrystallization from chloroform–petroleum ether afforded 100 mg of crystals, mp 153.5–155.5 °C.

For analysis the substance was recrystallized twice from chloroform–petroleum ether and dried in vacuo at 60 °C for 3 h; mp 157–157.5 °C.

Anal. Calcd for $C_{11}H_{11}ON_3$: C, 65.64; H, 5.52; N, 20.88; O, 7.95. Found: C, 65.76; H, 5.61; N, 20.88.

This product ($C_{11}H_{11}ON_3$; 100 mg, 4.7 mmol) was dissolved in 6 N HCl (20 mL) and refluxed for 48 h. The solution was then brought to pH 14 with 6 N NaOH and extracted twice with 10-mL portions of ethyl acetate. Evaporation of the ethyl acetate layer yielded 35 mg (35%) of a solid identical with **3** prepared by the reaction of 2-hydroxybenzamidine and ethyl acetoacetic ester as described in this paper. Acidification of the base layer to pH 10 and extraction with ethyl acetate followed by evaporation yielded 50 mg of the starting material.

2-Phenyl-4*H*-1,3-benzoxazin-4-one (1). The procedure described by Titherley[2] was followed: decoupled C^{13} NMR ($CDCl_3$) δ 117.0, 118.3, 127.1, 128.0, 129.0, 129.9, 134.2, 135.4, 154.9, 164.0, 166.9; ^1H NMR ($CDCl_3$) δ 7.27–7.80 (m, 5 H), 8.20 (td, 1 H), 8.38 (dd, 1 H), 8.41 (dd, 2 H).

Benzo[1,3]oxazin-2,4-dione 12. The procedure described by Kemp and Woodward[8] was followed: decoupled C^{13} NMR ($CDCl_3$) δ 1.32 (t, 3 H), 4.13 (q, 2 H), 7.30 (dd, 1 H), 7.34 (td, 1 H), 7.70 (td, 1 H), 8.08 (dd, 1 H).

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Registry No. 1, 3084-52-4; 2, 54789-69-4; 3, 76467-22-6; 4, 3605-06-9; 8, 76467-23-7; 12, 2038-01-9; 2-hydroxybenzamidine, 45744-18-1; ethyl acetoacetate, 141-97-9.

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Studies toward Practical Thioxanthene-Derived Protective Groups. 9,10-Propanothioxanthylium Salts

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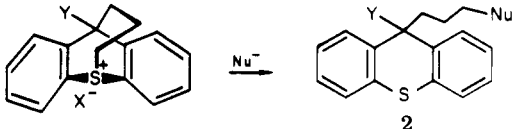
The preparation of 9,10-propanothioxanthylium salts **1** is described. The novel bridged ring system of these salts is readily cleaved by nucleophiles to yield the open-chain derivatives **2**. These readily undergo rapid solvolysis when substituted in the 9-position with an electronegative group. The potential use of a 9-oxygenated-9,10-propanothioxanthylium salt as a protective group is discussed.

Elsewhere,[2,3] we have described a general strategy for the design of new protective groups involving analogues of benzyl esters or urethanes for which an electron-withdrawing function attached to the benzyl ring can be converted selectively, under mild conditions, into a para-oriented electron-donating substituent. This conversion results in protective group removal, since the heterolytic cleavage of the benzylic C–O bond is retarded by electron-withdrawal and greatly accelerated by ortho or para electron donation.[4]

Among the reagents that can be envisaged to effect this conversion are the nucleophiles iodide and phenyl selenide ions; their high reactivity toward alkyl carbon,[5] together with their lack of basicity and inertness to the functional groups of peptides, renders them very promising candidates for orthogonal deprotection under exceptionally gentle reaction conditions that would be unlikely to damage even the most vulnerable peptide or protein.

Drawn by the analogy of **1** with triptycene, we were attracted to the transformation **1** → **2** as a means of realizing an iodide or phenyl selenide labile protective group. An ester of **1** (Y = $R'CO_2$) is expected to resist heterolytic C–O cleavage reactions (bridgehead tertiary alkyl) and to undergo attack by nucleophiles at acyl carbon slowly (hindered tertiary ester). However, the alkyl–sulfur bond is expected to be cleaved readily by good nucleophiles, by analogy with the reactivity of alkyldiphenylsulfonium salts. The cleaved species, **2**, is a thioxanthene that should undergo rapid solvolysis if Y is an electronegative group.



2

1a, Y = H; X = BF_4^-
b, Y = H; X = $CF_3SO_3^-$

In this paper we report the first preparation of the novel ring system of **1** together with a study of its properties. Although we do not envisage that a practical protective group can result from this study, we note that the anticipated properties of **1** and **2** have been confirmed in all respects.

Preparation of **1a** was achieved by reaction of silver tetrafluoroborate with 9-(3-iodopropyl)thioxanthene (**3**), prepared from 9-(3-chloropropyl)thioxanthene[6] and NaI.

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