and benzyl azide (0.2 mol) was heated at 100° until gas evolution ceased (72 hr). Addition of ether furnished **18** (55%) which was crystallized from ether–petroleum ether, mp 151–153°, ir (KBr) 1610 cm^{-1}.

Acknowledgment. We thank Dr. E. Van Loock for having carried out some preliminary experiments in this field. We are also indebted to the F. K. F. O. (Belgium) for financial support.

Registry No.—**1**, 42770-61-6; **6a**, 54999-84-7; **6b**, 54999-85-8; **7a**, 54999-86-9; **7b**, 54999-87-0; **7c**, 54999-88-1; **7d**, 54999-89-2; **7e**, 54999-90-5; **8a**, 54999-91-6; **8b**, 54999-92-7; **8c**, 54999-93-8; **9a**, 54999-94-9; **9b**, 54999-95-0; **9c**, 54999-96-1; **9d**, 54999-97-2; **9e**, 54999-98-3; **9f**, 54999-99-4; **10**, 55000-00-5; **11**, 55000-01-6; **12**, 53016-96-9; **13**, 7475-56-1; **14**, 55000-02-7; **15** (R = *n*-Bu), 55000-03-8; **15** (R = Ph), 55000-04-9; **16**, 55000-05-0; **17**, 21494-82-6; **18**, 55000-06-1; diphenylketene, 525-06-4; *tert*-butyl cyanoketene, 29342-22-1; ethyl isocyanate, 109-90-0; *n*-butyl isocyanate, 111-36-4; phenyl isocyanate, 103-71-9; *p*-methoxyphenyl isocyanate, 5416-93-3; *p*-chlorophenyl isocyanate, 104-12-1; dicyclohexylcarbodiimide, 538-75-0; dibenzylcarbodiimide, 6721-03-5; diphenylcarbodiimide, 622-16-2; methyl isothiocyanate, 556-61-6; *n*-butyl isothiocyanate, 592-82-5; benzyl isothiocyanate, 622-78-6; phenyl isothiocyanate, 103-72-0; *p*-tolyl isothiocyanate, 622-59-3; *p*-chlorophenyl isothiocyanate, 2131-55-7; benzyl azide, 622-79-7.

References and Notes

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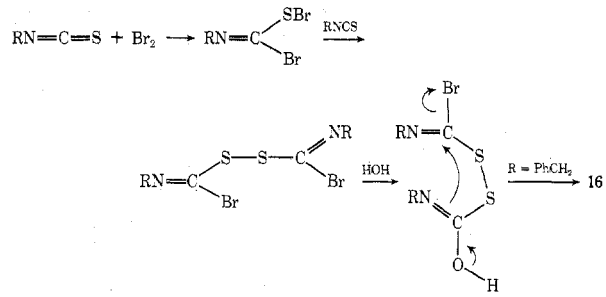
(7) Over 80 years ago, Freund[6] reported the reaction of isothiocyanates with bromine in the presence of some water to give a product of empirical formula $(RNCS)_2O$. Only very recently its correct structure (e.g., **16**) was elucidated,[8] but the mechanism of this unusual reaction remains to be resolved. Based on the work of Ottmann and Hooks,[5] we propose the following mechanism.



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2-Dialkylphosphonyl- and 2-Alkylidene-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazines

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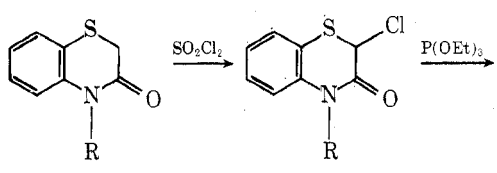
2-Chloro-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazines have been shown to react with triethyl phosphite in a Michaelis–Arbuzov manner to give the 2-phosphonates. These latter compounds react readily with aldehydes and ketones to give the 2-alkylidene derivatives. The olefins from aldehydes are assigned the *Z* stereochemistry on the basis of NMR data.

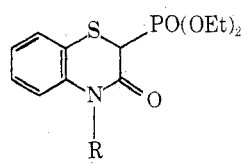
The reaction of various α-halocarbonyl systems with phosphorus nucleophiles has been well investigated. α-Haloamides normally react with trialkyl phosphites in a Michaelis–Arbuzov fashion to give phosphonates unless special structural requirements are met.[1-6] Although the possible influence of an α-thioether group in this reaction has not been reported previously, an α-thioether group generally is believed to enhance SN2 reactivity,[7] which is the usual mechanism of the Michaelis–Arbuzov reaction.

We now wish to report on the reaction of triethyl phosphite with 2-chloro-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazines (**2**), a cyclic α-haloamide system bearing an α-thioether linkage, and on the utility of the products of this reaction in a new general route to alkylidene benzothiazines.



1 **2**

a, R = H
b, R = Me
c, R = CH_2CO_2Et



3

Results and Discussion

Reaction of 2 with Triethyl Phosphite. The three chlorobenzothiazinones **2a–c** were obtained from treatment of the corresponding **1** with 1 equiv of sulfuryl chloride. Reaction of **2** with neat, excess, refluxing triethyl phosphite gave the analogous phosphonate (Michaelis–Arbuzov product) in good yield. The structure of **3** is confirmed in each case by the observation of an infrared band for the amide carbonyl group at 1660–1675 cm^{-1} and a ^1H NMR signal for the 2-H as a doublet at δ 4.57–4.35 with J_{H-P} = 21.2–22.6 Hz.

Thus, in this case the presence of an α-thioether group

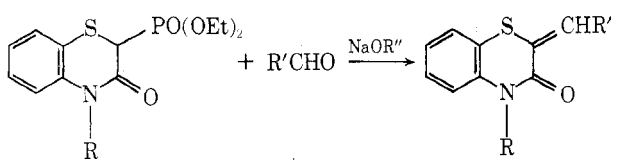
Table I
2-Alkylidene-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazines (4)[a,b]

Compd	R	R′	Yield, %	Mp, °C	NMR ($CDCl_3$), δ =CHR′	NMR ($CDCl_3$), δ NCH_3	NMR ($CDCl_3$), δ Other
4a	H	C_6H_5	90	202–204[c]	7.90		
4b	Me	C_6H_5	68	86–87.5[d]	7.93	3.54	
4c	Me	p-MeC_6H_4	72	139–140	7.85	3.50	2.35 (p-CH_3)
4d	Me	3,4-$(OCH_2O)C_6H_3$	85	151–152	7.79	3.52	6.00 (OCH_2O)
4e	Me	2-Thienyl[e]	64	90–91	8.02	3.48	
4f	H	3,4-$(OCH_2O)C_6H_3$	86	216–218[f]	7.82		6.03 (OCH_2O)
4g	H	p-$MeOC_6H_4$	94	208–210[g]	7.76		3.84 (p-OCH_3)
4h	CH_2CO_2Et	m-$F_3CC_6H_4$	76	131–131.5	7.90		4.80 (NCH_2)
4i	Me	o-FC_6H_4	50	94–95	7.99	3.53	
4j	Me	o-$O_2NC_6H_4$	82	107–108	8.18	3.58	
4k	Me	9-Anthryl	87	173–174	8.65[h]	3.60	
4l	Me	PhCH=CH	55	110–111	[i]	3.47	
4m[j]	H	H	85	>260 dec	6.47 5.69		

[a] Satisfactory analytical data (±0.30% for C, H, and S) were obtained for all new compounds and have been made available to the editors. [b] New *N*-methyl compounds exhibited an infrared band in $CHCl_3$ at ca. 1645 cm^{-1}. [c] Lit.[13i] mp 202–204°. [d] Lit. mp 85–86°: H. Kugita, H. Inoue, M. Ikezaki, M. Konda, and S. Takeo, *Chem. Pharm. Bull.*, **18**, 2284 (1970). [e] Crude product was an oil which crystallized after 1 day. [f] Lit.[13d] mp 212–214°. [g] Lit.[13d] mp 207–208°. [h] This assignment is not unambiguous. An additional singlet at δ 8.44 is assigned to the 10-H of the anthracene ring, since this signal is broader than the one at δ 8.65. The broadening is assumed to be due to long-range coupling with the other aromatic protons. [i] Vinyl proton absorption obscured in aromatic region (δ 7.68–6.65). The predicted values, based on the values observed for **4m** (see text), would be δ 7.71 for the *Z* isomer and δ 6.93 for the *E* isomer. [j] Product obtained using 37% aqueous formaldehyde; crude product analytically pure. This compound is white; **4a–l** are yellow to orange.

does not alter the usual mode of reaction of monohaloamides with trialkyl phosphites.[8] It does allow the preparation of some novel heterocyclic phosphonates which are useful synthetic intermediates, however.

Reaction of 3 with Aldehydes. The phosphonates **3** should undergo Wadsworth–Emmons reaction[9] readily, since the intermediate carbanion can be stabilized by both α-thioether and α-carbamoyl groups. In fact, addition of sodium alkoxide to an alcohol solution of equivalent amounts of **3** and an aromatic aldehyde, cinnamaldehyde, or formaldehyde results in the almost immediate separation of the olefins **4**. Crude products are obtained in fair to

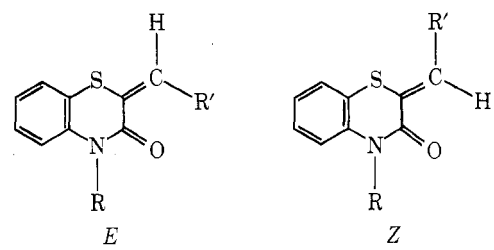


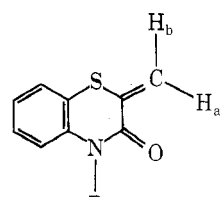
3 **4**

good yields (50–94%), regardless of the steric or electronic nature of the aldehyde, and they are of quite good chemical and geometrical purity as judged by their NMR spectra and melting points.

The scope of the reaction and the physical properties of the products are summarized in Table I.

The products from reaction with aromatic aldehydes are assigned the *Z* stereochemistry on the basis of the chemical shift of the vinyl proton. Application of substituent shielding constants for vinyl proton absorption[10] to compound **4m** gives predicted δ values in $CDCl_3$ for H_a and H_b of 6.15 and 5.47, respectively. The observed values are 6.47 and 5.69, respectively. The differences between the calculated and observed values are somewhat greater than the standard deviation of 0.17 ppm associated with the additivity calculations.[10b] The differences can be attributed to the fact that the RS group here is an arylthio group rather than an alkylthio group[11] and/or the fact that the fixed geometry of the amide carbonyl group in relation to the vinyl protons in **4m** probably causes these protons to be abnormally deshielded.[10a]





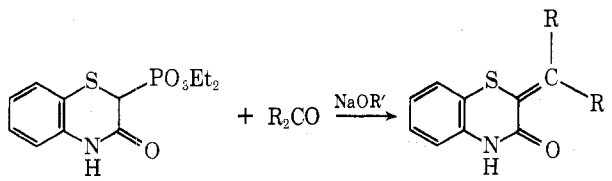
4m

Whatever the source of the deviation, the observed chemical shifts of H_a and H_b in **4m** serve as models for predicting chemical shifts in **4a–l** and therefore for establishing the stereochemistry of these compounds. The substituent shielding constant[10b] for replacing a geminal proton in an olefin with an aromatic group is 1.38 ppm. For an ortho-substituted aromatic group the value of 1.65 ppm is used. The predicted δ values for **4a–h** then are 7.07 for the *E* isomer and 7.85 for the *Z* isomer, and the predicted values for **4i–k** are 7.34 for the *E* isomer and 8.12 for the *Z* isomer. The data in Table I show that the observed δ value for each of these compounds except **4k** (R′ = 9-anthryl) falls within ±0.17 ppm of the predicted value for the *Z* isomer. In **4k**, the anthryl group is probably of great enough steric bulk that it is significantly distorted from coplanarity with the rest of the olefinic system, and therefore the *gem*-vinyl proton would be expected to be abnormally deshielded.[10d]

The reaction of phosphonates **3** with aldehydes thus shows the normal high stereoselectivity associated with the Wadsworth–Emmons reaction but does not appear to exhibit complete stereospecificity. Both TLC on silica gel–20% silver nitrate and NMR spectroscopy of reaction

mixtures in some cases indicate the presence of small amounts of *E* isomers.

Reaction of 3 with Ketones. The reaction of phosphonates **3** with ketones has not been as thoroughly investigated, but **3a** does react readily with diethyl ketomalonate and more slowly with the enolizable ketone, acetone. No reaction was observed with acetophenone.



3a **5a**, R = CO_2Et; **b**, R = Me

At least seven previous methods[13] have been reported for the preparation of various 2-alkylidene-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazines, including one[13i] of scope generally comparable to that of the present method, but geometrical isomerism in this system has been considered only briefly in one example.[13h] Where comparison is possible, the melting points reported for previous examples agree with those now assigned to the *Z* isomers.

Experimental Section

General. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian T-60 or EM-360 spectrometer. Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Inc.

3,4-Dihydro-4-methyl-3-oxo-2*H*-1,4-benzothiazine (1b). This compound was obtained in 73% yield from 3,4-dihydro-3-oxo-2*H*-1,4-benzothiazine[14] (**1a**) and methyl iodide by the general procedure of Pachter and Kloetzel[15] for the alkylation of amides with potassium hydroxide in acetone: mp 50–53° (lit.[16] mp 55°); NMR ($CDCl_3$) δ 7.17 (m, 4), 3.37 (s, 3), and 3.43 (s, 2).

3,4-Dihydro-3-oxo-2*H*-1,4-benzothiazine-4-acetic Acid Ethyl Ester (1c). This compound was obtained similarly from **1a** and ethyl bromoacetate in 88% yield: mp 54–55° [recrystallized from ethanol, mp 57–58° (lit.[17] mp 48.5–50.5°)]; NMR ($CDCl_3$) δ 7.50–6.72 (m, 4), 4.63 (s, 2), 4.22 (q, 2, *J* = 7 Hz), 3.43 (s, 2), and 1.27 (t, 3, *J* = 7 Hz).

Anal. Calcd for $C_{12}H_{13}NO_3S$: C, 57.35; H, 5.21; N, 5.57. Found: C, 57.37; H, 5.17; N, 5.30.

Chlorination of 1 with Sulfuryl Chloride. General Procedure. A stirred mixture of **1** in methylene chloride (ca. 0.1 mol/100 ml) was treated dropwise in 0.5 hr with 1 equiv of sulfuryl chloride. The mixture was stirred for 2–5 hr more and then was concentrated to a solid or viscous liquid residue. The residue was stirred for a few minutes with petroleum ether, and the resulting mixture was filtered to give solid product.

2-Chloro-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazine (2a). Crude product (mp 202–207°) obtained in 86% yield from **1a** by the above procedure was suitable for subsequent reaction with triethyl phosphite but could be recrystallized twice from acetone to give purified material: mp 221–223° (lit.[18] mp 215°); NMR (DMSO-d_6) δ 11.17 (broad s, 1), 7.60–6.90 (m, 4), and 6.23 (s, 1).

Anal. Calcd for C_8H_6ClNOS: C, 48.12; H, 3.03; Cl, 17.76. Found: C, 48.20; H, 3.05; Cl, 17.93.

2-Chloro-3,4-dihydro-4-methyl-3-oxo-2*H*-1,4-benzothiazine (2b). Crude product from **1b** was obtained in 91% yield and was used without further purification: mp 95–97°; NMR ($CDCl_3$) δ 7.55–6.95 (m, 4), 5.68 (s, 1), and 3.51 (s, 3).

Anal. Calcd for C_9H_8ClNOS: Cl, 16.59. Found: Cl, 16.26.

2-Chloro-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazine-4-acetic Acid Ethyl Ester (2c). This material was obtained from **1c** in 84% yield and also was used without additional purification: mp 76–78°; NMR ($CDCl_3$) δ 7.45–6.81 (m, 4), 5.60 (s, 1), 5.03 (asymmetrical d, 1, *J* = 17 Hz), 4.38 (asymmetrical d, 1, *J* = 17 Hz), 4.18 (q, 2, *J* = 7 Hz), and 1.27 (t, 3, *J* = 7 Hz).

Anal. Calcd for $C_{12}H_{12}ClNO_3S$: Cl, 12.41; S, 11.22. Found: Cl, 12.45; S, 11.22.

2-Diethylphosphonyl-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazine (3a). A stirred mixture of **2a** (26.5 g, 0.13 mol) and triethyl phosphite (101 ml, 0.58 mol) was heated to ca. 100°. A vigorous exothermic reaction began, and soon a clear orange solution was obtained. The solution was stirred under reflux for 1.5 hr more and then was cooled to ca. 60° and diluted with 100 ml of petroleum ether (bp 30–75°). Cooling of the mixture to room temperature and filtration gave 31.2 g (78%) of pale yellow solid, mp 131–133.5°. Recrystallization from 250 ml of benzene–petroleum ether (2:3) gave 29.8 g of product: mp 134–136°; NMR (DMSO-d_6) δ 10.80 (broad s, 1), 7.44–6.90 (m, 4), 4.35 (d, 1, J_{H-P} = 21.2 Hz), 4.27–3.54 (m, 4), 1.17 (t, 3, *J* = 7.2 Hz), and 1.00 (t, 3, *J* = 7.2 Hz); ir ($CHCl_3$) 3400, 3000, 1675, 1590, 1480, 1370, 1250, 1160, 1050, 1020, and 975 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}NO_4PS$: C, 47.84; H, 5.35; S, 10.64. Found: C, 47.94; H, 5.38; S, 10.77

2-Diethylphosphonyl-3,4-dihydro-4-methyl-3-oxo-2*H*-1,4-benzothiazine (3b). A mixture of **2b** (64.0 g, 0.30 mol) and triethyl phosphite (112 ml, 0.64 mol) was refluxed for 19 hr. After standing for 1.5 hr, the resulting mixture was filtered to give a pale yellow solid. Recrystallization from 175 ml of benzene–petroleum ether (4:3) gave 61.2 g (65%) of white product: mp 127–129°; NMR (DMSO-d_6) δ 7.50–6.89 (m, 4), 4.50 (d, 1, J_{H-P} = 22.2 Hz), 4.20–3.45 (complex, 4), 3.35 (d, 3, *J* = 1.1 Hz), 1.13 (t, 3, *J* = 7.2 Hz), and 0.98 (t, 3, *J* = 7.2 Hz); ir ($CHCl_3$) 3000, 1660, 1590, 1480, 1445, 1360, 1250, 1050, 1020, and 975 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}NO_4PS$: C, 49.52; H, 5.75; S, 10.17. Found: C, 49.73; H, 5.88; S, 10.31.

2-Diethylphosphonyl-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazine-4-acetic Acid Ethyl Ester (3c). A mixture of **2c** (40.0 g, 0.14 mol) and triethyl phosphite (51.0 g, 0.31 mol) was refluxed for 28 hr. Volatile materials were removed from the resultant solution by heating it on a rotary evaporator at 100° for 0.5 hr at 0.1 Torr. The residue was treated with 20 ml of warm ethanol and then 200 ml of petroleum ether. Cooling (Dry Ice) of the solution gave separation of an oil which crystallized upon trituration to give 32.0 g of tan solid, mp 65–68°. Evaporation of the filtrate gave an additional 18.0 g of brown solid, mp 60–65°, combined crude yield 50.0 g (92%). Chromatography of 43.0 g of this material on alumina (20% chloroform–carbon tetrachloride to 100% chloroform) gave 24.0 g of solid. Recrystallization from benzene–petroleum ether gave 18.5 g white product: mp 73–75°; NMR (DMSO-d_6) δ 7.58–6.95 (m, 4), 4.92 (asymmetrical d, 1, *J* = 18.0 Hz), 4.59 (asymmetrical d, 1, *J* = 18.0 Hz), 4.57 (d, 1, J_{H-P} = 22.6 Hz), 4.34–3.60 (complex, 6), and 1.32–0.88 (complex, 9); ir ($CHCl_3$) 1750, 1665, 1390, 1255, 1190, 1050, and 1025 cm^{-1}.

Anal. Calcd for $C_{16}H_{22}NO_6PS$: C, 49.61; H, 5.72; N, 3.62; S, 8.28. Found: C, 49.78; H, 5.83; N, 3.63; S, 8.41.

2-Alkylidene-3,4-dihydro-4-methyl-3-oxo-2*H*-1,4-benzothiazines. General Procedure. To a stirred solution of the aldehyde (0.010 mol) and **3** (0.010 mol) in alcohol (50 ml of 80% aqueous ethanol for **3a**, 30 ml of methanol for **3b**, and 30 ml of ethanol for **3c**) was added 5.0 ml of a 2.0 *N* solution of base (sodium ethoxide in ethanol for **3a** and **3c**, sodium methoxide in methanol for **3b**). If a solid product did not separate immediately, the reaction flask was cooled in an ice bath after 5 min and the inside wall of the flask was scratched with a glass rod. Product then crystallized readily. In all cases, after the appearance of solid material, the mixture was stirred for 10 min more and then filtered to obtain product, which was judged by its melting point and NMR spectrum to be of good chemical and geometrical purity. The melting point of the product normally increased less than 3° upon purification. Analytical samples were obtained in the following manner. The crude product was dissolved in 20 ml of chloroform, and this solution was washed with two 10-ml portions of water, dried ($MgSO_4$), and concentrated to a residue. The residue was recrystallized one or two times from 30 ml of 2:1 or 1:1 carbon tetrachloride–petroleum ether. The properties of the products are summarized in Table I.

3,4-Dihydro-3-oxo-$\Delta^{2\alpha}$-2*H*-1,4-benzothiazine-2-malonic Acid Diethyl Ester (5a). To a stirred mixture of **3a** (6.02 g, 0.020 mol) and diethyl ketomalonate (3.5 g, 0.020 mol) in 50 ml of ethanol was added 20 ml of a 1.0 *N* solution of sodium ethoxide. A clear solution was obtained, and after approximately 1 min a yellow precipitate occurred. An additional 100 ml of ethanol was added to the mixture, and stirring was continued for 0.5 hr. Filtration then gave 6.3 g (98%) of bright yellow solid, mp 162–163°. Recrystallization from ethanol gave the analytical sample: mp 163–163.5°; NMR (DMSO-d_6) δ 7.50–6.90 (complex, 4), 4.24 (q, 4, *J* = 7 Hz), 1.23 and 1.20 (two triplets, 6, *J* = 7 Hz).

Anal. Calcd for $C_{15}H_{15}NO_5S$: C, 56.06; H, 4.71; S, 9.98. Found: C, 56.11; H, 4.77; S, 10.05.

3,4-Dihydro-2-isopropylidene-3-oxo-2*H*-1,4-benzothiazine (5b). To a stirred solution of **3a** (4.5 g, 0.015 mol) and 10 ml of acetone in 20 ml of methanol was added 7.5 ml of a 2.0 *N* sodium methoxide solution. The solution was stirred for 48 hr. The mixture was then diluted with 5 ml of water and subsequently filtered to obtain 2.0 g (65%) of white product: mp 217–219° (lit.[13c] mp 213–215°); NMR (DMSO-d_6) δ 7.42–6.84 (complex, 4), 2.22 (s, 3), and 2.05 (s, 3).

Registry No.—**1a,** 5325-20-2; **1b,** 37142-87-3; **1c,** 6376-75-6; **2a,** 55043-49-7; **2b,** 55043-50-0; **2c,** 55043-32-8; **3a,** 55043-33-9; **3b,** 55043-34-0; **3c,** 55043-35-1; **4a,** 55043-20-4; **4b,** 55043-21-5; **4c,** 55043-22-6; **4d,** 55043-23-7; **4e,** 55043-24-8; **4f,** 55043-25-9; **4g,** 55043-26-0; **4h,** 55043-27-1; **4i,** 55043-28-2; **4j,** 55043-29-3; **4k,** 55043-30-6; **4l,** 55043-31-7; **4m,** 55043-51-1; **5a,** 55043-52-2; **5b,** 55043-53-3; SO_2Cl_2, 7791-25-5; $P(OEt)_3$, 122-52-1; methyl iodide, 74-88-4; ethyl bromoacetate, 105-36-2; benzaldehyde, 100-52-7; *p*-methylbenzaldehyde, 104-87-0; 3,4-methylenedioxybenzaldehyde, 120-57-0; 2-thiophenecarboxaldehyde, 98-03-3; formaldehyde, 50-00-0; *p*-methoxybenzaldehyde, 123-11-5; *m*-trifluoromethylbenzaldehyde, 454-89-7; *o*-fluorobenzaldehyde, 446-52-6; *o*-nitrobenzaldehyde, 552-89-6; 9-anthracenecarboxaldehyde, 642-31-9; cinnamaldehyde, 104-55-2; acetone, 67-64-1; diethyl ketomalonate, 609-09-6.

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$$PhSCHClCONEt_2 + P(OEt)_3 \longrightarrow PhSCH(PO_3Et_2)CONEt_2 + PhSPO_3Et_2 + Et_2O_3PCH_2CONEt_2$$
i ii iii

are secondary products derived from attack of triethyl phosphite on thioether sulfur of the primary product i. Such a process would be less favored in the benzothiazinone system since there it would require opening of the ring.
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Benzopyranopyridine Derivatives. 2. Reaction of Azaxanthones with Hydroxylamine[1]

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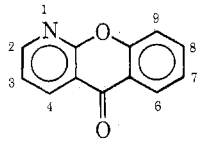
5*H*-[1]Benzopyrano[2,3-*b*]pyridin-5-one, referred to throughout this series as 1-azaxanthone (**1**), reacted in an anomalous manner with an alcoholic KOH solution of $HONH_2$·HCl to give a mixture of 3-(2-1*H*-pyridinon-3-yl)-1,2-benzisoxazole (**2**) and 3-*o*-hydroxyphenyl(2-1*H*-pyridinon-3-yl) ketoxime (**3**). The structure of **2** was established by the usual spectral analyses as well as total synthesis from 3-*o*-chlorobenzoylpyridine. It was shown that **3** is not the intermediate necessary for the formation of **2** and that **2** is formed by a direct attack of the $HONH_2$ anion on 1-azaxanthone.

5*H*-[1]Benzopyrano[2,3-*b*]pyridin-5-one, **1**, referred to throughout this series as 1-azaxanthone,[2] failed to form an oxime under the usual conditions, i.e., $HONH_2$·HCl in pyridine and EtOH. In contrast, the 2- and 4-azaxanthones were readily converted into oximes.



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Under forcing conditions,[3] excess KOH in EtOH, ketone-**1** reacted with $HONH_2$·HCl to give a mixture of two products, 3-(2-1*H*-pyridinon-3-yl)-1,2-benzisoxazole (**2**) and 3-*o*-hydroxyphenyl-(2-1*H*-pyridinon-3-yl) ketoxime (**3**). These compounds were separated by column chromatography on silica gel.