(one proton), and the aromatic multiplet at δ 6.8–7.2 (four protons). Compound **5** was also prepared by dissolving **1h** in methanol and evaporating to dryness.

(2-Chlorohexafluoro-2-propyl)benzene (6).—A mixture of (2-hydroxyhexafluoro-2-propyl)benzene[10] (100 g, 0.41 mol), thionyl chloride (100 g, 0.83 mol), and pyridine (5 ml) was refluxed with stirring for 48 hr. After cooling to room temperature, 500 ml of ice water and 500 ml of 1 *N* potassium hydroxide were added. The lower organic layer was separated and the aqueous layer was extracted with 100 ml of methylene chloride. The organic layers were combined, dried over anhydrous magnesium sulfate, and distilled at atmospheric pressure to give 69.5 g (65%) of **6**, bp 159°.

Anal. Calcd for $C_9H_5F_6Cl$: Cl, 13.5. Found: Cl, 13.7.

Attempted Reaction of 6 with Sodium Methoxide.—A mixture of **6** (16 g, 0.061 mol), sodium methoxide (6.5 g, 0.12 mol), and 120 ml of absolute methanol was heated at reflux for 24 hr with stirring, cooled to room temperature, acidified with concentrated hydrochloric acid, and diluted with 1 l. of water. The lower organic layer was separated. The aqueous layer was extracted with 50 ml of methylene chloride and the two organic layers were combined. After drying over anhydrous magnesium sulfate, the solution was distilled at atmospheric pressure to give 9.6 g of unchanged **6**, bp 158–160°, with no evidence for the formation of the desired methoxyl compound.

Registy No.—**1h**, 16878-48-1; **5**, 16878-49-2; **6**, 16878-50-5.

Acknowledgment.—The author wishes to express his gratitude to Dr. E. E. Gilbert and Professors J. Meinwald and M. Litt for helpful discussions and to Dr. B. B. Stewart for his help in interpreting the nmr data.

(10) B. S. Farah, E. E. Gilbert, and J. P. Sibilia, *J. Org. Chem.*, **30**, 998 (1965).

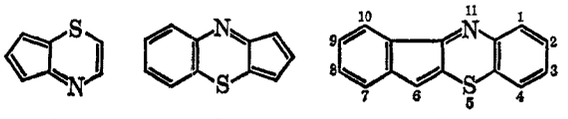
Derivatives of Indeno[2,1-*b*]-1,4-benzothiazine

F. G. BORDWELL, T. W. CUTSHALL, AND T. S. RINDERSPACHER

Chemistry Department, Northwestern University, Evanston, Illinois 60201

Received September 21, 1967

Inasmuch as the applicability of the Hückel $(4n + 2)$ π-electron rule[1] to fused heterocyclic systems is still unpredictable, synthesis of systems such as **1**, **2**, and **3**,

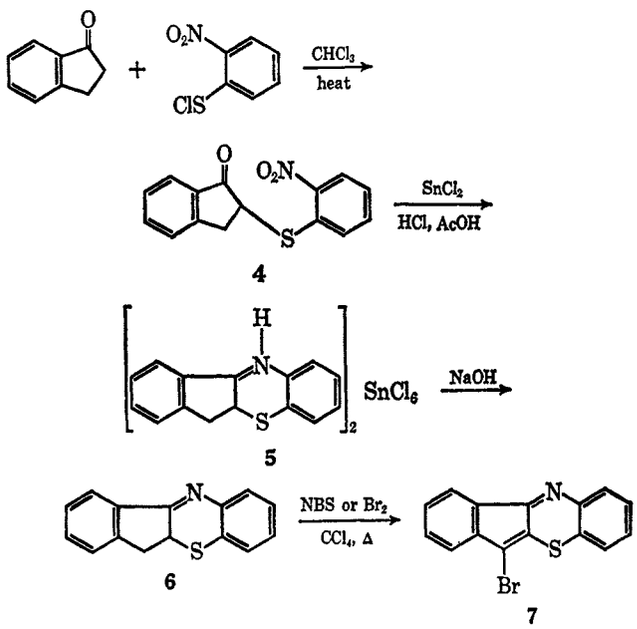


1 **2** **3**

which obey the rule and may show nonclassical aromaticity, is of interest. Neither **1** nor **2** has been prepared to date. Recently, indeno[2,1-*b*]-1,4-benzothiazine (**3**) has been prepared[2] by the condensation of 1,2-indandione with *o*-mercaptoaniline, followed by dehydration. The present paper describes the preparation and properties of some derivatives of **3**.

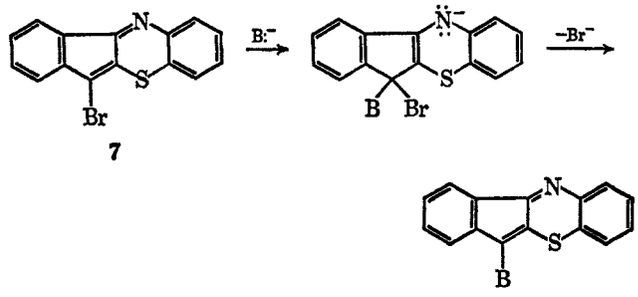
Initially, the goal of this work was the preparation of the parent compound **3** by a different synthetic route. The approach, which used in part the Zincke procedure,[3] is outlined in Scheme I. Condensation of *o*-nitrophenylsulfenyl chloride with 1-indanone gave 2-(*o*-nitrophenylthio)indanone (**4**) in 66.3% yield. Treatment of **4** with stannous chloride in concentrated hydrochloric acid and glacial acetic acid resulted in reduction and condensation to form bis(5a,6-dihydroindeno-[2,1-*b*]-1,4-benzothiazinium) hexachlorostannate(IV) (**5**), in 80.1% yield. The tin complex salt **5**, when shaken with a 10% sodium hydroxide solution, gave a 94.2% yield of 5a,6-dihydroindeno[2,1-*b*]-1,4-benzothiazine (**6**). Dehydrogenation of **6** was effected by treatment with either bromine or N-bromosuccinimide in refluxing carbon tetrachloride. However, instead of obtaining the parent compound **3**, an 84.8% yield of the monobromo derivative, 6-bromoindeno[2,1-*b*)-1,4-benzothiazine (**7**), was obtained as a deep purple solid. This result also occurred using limited amounts of bromine or N-bromosuccinimide, **7** being obtained along with unreacted **6**.

SCHEME I



4 **5** **6** **7**

The location of the bromine atom in **7** was established by the ease with which it underwent nucleophilic aromatic substitution reactions and by the products obtained from these reactions. The 6 position should be activated toward nucleophilic aromatic substitution and a bromine atom located there should be easily replaced by typical nucleophiles. This was found to be the case.



7

8a, B = SC_6H_5
b, B = CN
c, B = COOH

(1) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 412–419.
(2) D. Leaver, J. Smolicz, and W. H. Stafford, *J. Chem. Soc.*, 740 (1962).
(3) T. Zincke and H. Rose, *Ann.*, **406**, 103 (1914); T. Zincke and J. Baeumer, *ibid.*, **416**, 86 (1918).

TABLE I

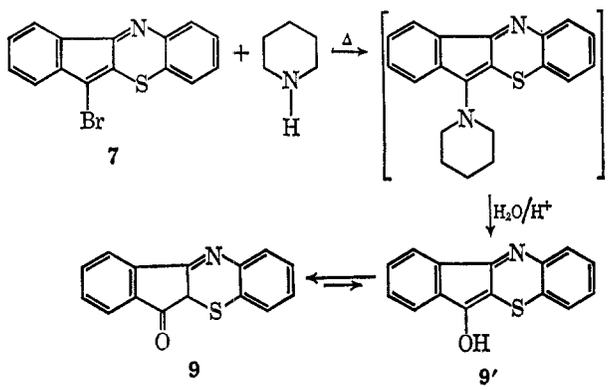
ULTRAVIOLET AND VISIBLE SPECTRA OF INDENO[2,1-*b*]-1,4-BENZOTHIAZINES[a]

Compd	(substituent)	Maxima, mμ (log ε)							
3[b]	H		250 (4.35)	257 (4.37)	292 (4.66)	357 (4.07)	374 (3.97)	519 (3.35)	
3'[b]	−H			276 (4.69)	299 (4.69)	365 (4.43)	381 (4.45)	514 (3.37)	572 (3.75)
6	2H	207 (4.38)			266 (4.34)	322 (3.92)		490 (2.00)	
9	=O	206 (4.42)	229 (4.45)		288 (3.00)				628 (3.00)
7	Br	214 (4.51)	250 (4.30)	257 (4.34)	297 (4.59)	357 (4.08)	373 (4.00)	515 (3.46)	
8a	SC_6H_5	205 (4.62)			301 (4.51)	363 (4.15)		534 (3.45)	
8b	CN	205 (4.30)	228 (4.34)	261 (4.11)	303 (4.34)		377 (3.97)	525 (3.36)	

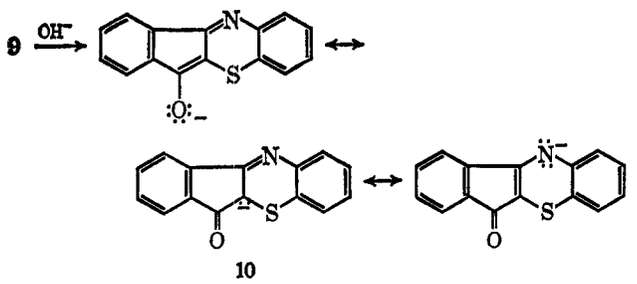
[a] Spectra of 6, 7, 8a, 8b, and 9 taken in 95% ethanol using a Beckman DB-G spectrophotometer. [b] Reference 2.

By refluxing **7** with sodium thiophenoxide in ethanol, a 73% yield of 6-phenylthioindeno[2,1-*b*]-1,4-benzothiazine (**8a**) was obtained. By refluxing **7** with cuprous cyanide in dimethylformamide,[4] a 96% yield of 6-cyanoindeno[2,1-*b*]-1,4-benzothiazine (**8b**) was obtained. The nitrile **8b** was converted, in low yield, into the carboxylic acid **8c** by acid hydrolysis. All of these compounds had the same deep purple color as **7** (and as **3**),[2] this color apparently being characteristic of this heterocyclic system.

When **7** was refluxed in a large excess of piperidine, the product isolated after the usual aqueous acid–base extraction techniques was not the expected 6-piperidino derivative, but was the hydrolysis product, 6-oxo-5a,6-dihydroindeno[2,1-*b*]-1,4-benzothiazine (**9**), a bluish green solid, obtained in 25% yield. The infrared spectrum of **9** showed no O–H or N–H absorption, but had a



strong carbonyl peak at 5.91 μ and a strong C=N peak at 6.10 μ. Compound **9** was soluble in dilute acid, giving a light blue solution, and in dilute base, giving a deep blue solution, presumably owing to the formation of the highly conjugated anion (**10**). The fact that this com-



pound exists in the keto (**9**) rather than the enol (**9'**) form indicates that the 5a,6 double bond provides very little (less than 5.5 kcal/mol)[5] stabilization energy to the aromatic system of **3** and its derivatives. This is not unusual for a centrally located double bond in a polycyclic aromatic system, however.

The location of the bromine atom in **7** at the 6 position would be expected by analogy with similar aromatic systems. Probably the bromine is incorporated *via* electrophilic substitution on the unsubstituted **3**, which is very likely formed by dehydrogenation of **6** during the reaction with bromine. The 6 position of the indeno-[2,1-*b*]-1,4-benzothiazine (**3**) ring system corresponds to the favored position in azulene and its heterocyclic analogs for electrophilic substitution.[6]

Since the dehydrogenation of **6** with bromine or N-bromosuccinimide led to the bromo derivative **7** instead of the desired parent compound **3**, another dehydrogenation procedure was attempted, in hope of obtaining pure **3**. This consisted of treating the dihydro derivative **6** with an equimolar quantity of benzoyl peroxide in a chloroform solution under ultraviolet radiation.[7] The product obtained was a dark reddish purple solid of questionable purity (mp up to 342°). Further examination indicated that this product was similar to that obtained[2] by Leaver, Smolicz, and Stafford, which they have shown[2] to be a mixture of **3** and its dimer (**3'**). Likewise, dehydrogenation of **6** with chloranil in refluxing xylene or with palladium on charcoal in refluxing xylene or reduction of bromo derivative **7** by zinc in acetic acid or by sodium borohydride in ethanol all led to similar products that appeared to be mixtures of **3** and **3'**.

Ultraviolet and visible spectra of the derivatives of **3** are compared with the published[2] spectral data for **3** and **3'** in Table I.

In summary, the indeno[2,1-*b*]-1,4-benzothiazine ring system, an 18-π-electron system, has been synthesized and shown to have some degree of aromaticity. However, the aromaticity must not be large, since the hydroxy derivative prefers the keto (**9**) rather than the enol (**9'**) form.

Experimental Section[8]

2-(*o*-Nitrophenylthio)indanone (4).—A solution of 42.0 g (0.222 mol) of *o*-nitrophenylsulfenyl chloride[9] and 29.3 g (0.222 mol) of

(4) L. Friedmann and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).

(5) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp 286 and 287.

(6) W. Keller-Schierlein and E. Heilbronner, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, pp 310–134 and references cited therein.

(7) These conditions are similar to bromine and N-bromosuccinimide dehydrogenation conditions.

(8) All melting points are uncorrected. Microanalyses were by Miss H. Beck. Infrared spectra were taken in potassium bromide pellets and measured on a Baird spectrophotometer. We wish to thank Dr. G. P. Hinds of the Shell Oil Co., Deer Park, Texas, for determination of the mass spectra.

(9) M. H. Hubacher, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 455.

1-indanone[10] in 400 ml of dry chloroform was refluxed for 1.5 hr. After removal of the solvent *in vacuo*, the solid product was recrystallized from chloroform–hexane to give 42.0 g (66.3%) of **4**, mp 130–131°, as a yellow solid: ir, 5.88 (C=O), 6.28 (phenyl), 6.65, and 7.52 μ (NO_2).

Anal. Calcd for $C_{15}H_{11}NO_3S$: C, 63.16; H, 3.89. Found: C, 63.32; H, 3.73.

5a,6-Dihydroindeno[2,1-*b*]-1,4-benzothiazine (6).—To a boiling solution of 56.4 g (0.198 mol) of **4** in 500 ml of glacial acetic acid was slowly added with stirring a hot solution of 140 g (0.521 mol) of stannous chloride dihydrate in 150 ml of concentrated hydrochloric acid. After the addition was completed (about 15 min), the solution was boiled an additional 30 min before cooling. The golden yellow solid which had crystallized was washed with 95% ethanol followed by ether, then dried to give 64.0 g (80.1%) of bis(5a,6-dihydroindeno[2,1-*b*]-1,4-benzothiazinium) hexachlorostannate (**5**), mp 170° dec. As **5** was only sparingly soluble in water and organic solvents, it was not further purified but used directly in the next step: ir, ν 6.12 μ (C=N).

A mixture of 30.4 g (0.0376 mol) of **5** in 500 ml of 10% sodium hydroxide solution was shaken intermittently for 1 hr. The yellow-tan solid which formed was washed with dilute sodium hydroxide until free of tin salts, then with water until free of base. After drying, 16.8 g (94.2%) of **6** was obtained as a light tan solid. Recrystallization of a small portion of this solid from chloroform gave pure **6**: mp 100–105° dec; ir, 3.30 and 3.52 (C–H), 6.12 μ (C=N).

Anal. Calcd for $C_{15}H_{11}NS$: C, 75.93; H, 4.67. Found: C, 75.56; H, 4.81.

6-Bromoindeno[2,1-*b*]-1,4-benzothiazine (7).—To a solution of 16.0 g (0.0675 mol) of **6** in 200 ml of carbon tetrachloride was added slowly with swirling a solution of 21.6 g (0.135 mol) of bromine in 50 ml of carbon tetrachloride. A brown precipitate formed initially, but after one-third of the bromine was added, the mixture turned dark green. Hydrogen bromide evolution did not begin until over half of the bromine was added. The mixture was warmed and allowed to stand overnight at room temperature. The dark green solid (hydrobromide of **7**) which had precipitated was dried and added to 500 ml of 10% sodium hydroxide. After intermittent shaking for 1 hr, a deep purple solid formed. This was washed with water and dried to give 18.0 g (84.8%) of **7**, mp 205–206°. Compound **7** was soluble in concentrated hydrochloric acid, giving a green solution: ir, 3.37 (C–H), 6.26, 6.58, 7.01, 8.01, 8.17, 10.60, 13.1 (broad), and 13.3 μ (broad). The analytical sample was purified by sublimation, mp 205–206°.

Anal. Calcd for $C_{15}H_8BrNS$: C, 57.34; H, 2.57; N, 4.46. Found: C, 57.12; H, 2.59; N, 4.18.

The **hydrobromide of 7** had mp 155° dec.

Anal. Calcd for $C_{15}H_9Br_2NS$: C, 45.57; H, 2.28; N, 3.54. Found: C, 45.58; H, 2.33; N, 3.28.

Nucleophilic Substitution Reactions of 7. A. 6-Phenylthioindeno[2,1-*b*]-1,4-benzothiazine (8a).—A solution of sodium thiophenoxide was prepared by adding a solution of 0.36 g (3.3 mmol) of thiophenol in 5 ml of absolute ethanol to a solution of 0.18 g (3.3 mmol) of sodium methoxide in 10 ml of absolute ethanol. To this solution was added a solution of 1.0 g (3.2 mmol) of **7** in 10 ml of absolute ethanol, and the mixture was refluxed overnight under nitrogen. Water was added to the cooled mixture to precipitate a purple solid, which was recrystallized from ethanol–water to give 0.8 g (73%) of **8a**: mp 114–116°; ir, 3.38 (C–H), 6.26, 6.36, 6.68, 6.81, 6.88, 7.01, 7.68, 8.01, 8.17, 13.4 (very broad), and 14.58 μ; mass spectrum (low ionizing voltage), 343.

Anal. Calcd for $C_{21}H_{13}NS_2$: C, 73.46; H, 3.82; N, 4.08. Found: C, 73.21; H, 3.85; N, 4.19.

B. 6-Cyanoindeno[2,1-*b*]-1,4-benzothiazine (8b).—A mixture of 1.0 g (3.2 mmol) of **7**, 0.35 g (3.9 mmol) of cuprous cyanide, and 10 ml of dimethylformamide was refluxed for 4 hr.[4] After cooling, the mixture was poured into a ferric chloride–hydrochloric acid solution and warmed for 30 min. The precipitated solid was washed successively with dilute hydrochloric acid, dilute sodium hydroxide, and water, then dried to give 0.8 g (96%) of **8b**, mp 215–220°, as a deep purple solid: ir, 3.43 (C–H), 4.63 (C≡N), 6.29, 6.68, 6.92, 7.06, 7.68, 7.93, 8.12, 8.99, 13.1 (broad), and 13.3 μ (broad); mass spectrum, 260. The analytical sample was purified by sublimation, mp 215–220°.

Anal. Calcd for $C_{16}H_8N_2S$: C, 73.84; H, 3.10; N, 10.77. Found: C, 74.18; H, 3.17; N, 10.93.

C. 6-Oxo-5a,6-dihydroindeno[2,1-*b*]-1,4-benzothiazine (9).—A solution of 1.0 g (3.2 mmol) of **7** in 30 ml (303 mmol) of piperidine was refluxed under nitrogen for 5 days. The excess piperidine was removed *in vacuo* and the residue was taken up in ether. The precipitated piperidinium bromide was removed by filtration (recovered 0.4 g, 75% of theoretical). The ethereal filtrate was extracted with dilute hydrochloric acid to give a blue aqueous solution. The purple ether layer containing unreacted **7** was discarded. The aqueous acidic solution was extracted with ether until all unreacted **7** was removed. When the solution was made basic with dilute sodium hydroxide, a deep blue solution was obtained, from which no organic material could be extracted with ether. However, when the solution was carefully neutralized by adding dilute hydrochloric acid, a greenish blue substance precipitated, which was extracted with ether. The ether solution was washed with water and dried over anhydrous sodium sulfate, and the ether was removed *in vacuo*. Recrystallization of the residue from ether–ethanol gave 0.2 g (25%) of **9**, mp 210–212°, as a blue-green solid. Compound **9** was readily soluble in dilute acid, giving a blue solution, and in dilute base, giving a deep blue solution: ir, 3.24 and 3.43 (C–H), 5.91 (C=O), 6.10 (C=N), 6.27, 6.35, 6.61, 6.83, 7.02, 7.32, 7.78, 8.26, 11.7, and 13.5 μ.

Anal. Calcd for $C_{15}H_9NOS$: C, 71.71; H, 3.61; N, 5.57. Found: C, 71.97; H, 3.71; N, 5.67.

Indeno[2,1-*b*]-1,4-benzothiazinyl-6-carboxylic Acid (8c).—A mixture of 0.50 g (1.9 mmol) of **8b** in 15 ml of glacial acetic acid, 15 ml of concentrated hydrochloric acid, and 5 ml of water was refluxed for 4 hr. The solvents were removed *in vacuo* and the residue was taken up in ether. The ether solution was extracted with dilute hydroxide until the extracts were colorless. The ether solution containing unreacted **8b** was discarded. The combined basic extracts were acidified with dilute hydrochloric acid, and the product was extracted with ether. After the ether washing layer was washed with water and dried over anhydrous sodium sulfate, the ether was removed *in vacuo* to give less than 0.1 g of **8c**, mp >250°, as a dark purple solid. Compound **8c** was soluble in dilute base: ir, 3.3–3.7 (COOH), 6.07 (conjugated C=O), 6.64, 6.85, 7.04, 7.63, 7.98, 8.13, 13.12, and 13.44 μ.

Anal. Calcd for $C_{16}H_9NO_2S$: N, 5.02. Found: N, 4.82.

Registry No.—**4**, 16888-88-3; **6**, 16888-89-4; **7**, 16888-90-7; **7** HBr, 16888-91-8; **8a**, 16888-92-9; **8b**, 16888-93-0; **8c**, 16888-94-1; **9**, 16888-95-2.

Acknowledgment.—This investigation was supported by Public Health Research Grant No. CA-07351 from the National Cancer Institute.

(10) K. L. Rinehart, Jr., and D. H. Gustafson, *J. Org. Chem.*, **25**, 1836 (1960).

Tishchenko Reaction of Chloral by Aluminum Haloalcoholates

TAKEO SAEGUSA AND TAKASHI UESHIMA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

Received February 9, 1968

The Tishchenko reaction of trichloroacetaldehyde (chloral) by the usual aluminum alcoholate catalyst is very sluggish.[1,2] In this communication, we report our finding that some aluminum haloalcoholates cause a rapid Tishchenko reaction of chloral to produce trichloroethyl trichloroacetate. The results are sum-

$$Cl_3CCHO \longrightarrow Cl_3CCOOCH_2CCl_3 \quad (1)$$

(1) I. Lin and A. R. Day, *J. Amer. Chem. Soc.*, **74**, 5133 (1952).
(2) R. Dworzak, *Monatsch.*, **47**, 11 (1927).