

reaction was refluxed for 2 hr. No 9-chloroanthracene was detected by vpc analysis.

A mixture of 2 ml of chlorobenzene, 0.5 g (0.0016 mol) of 9-iodoanthracene, and 2.0 g (0.015 mol) of copper(II) chloride was refluxed and stirred for 2 hr. Within 30 min a strong iodine color developed in the reaction. At the end of the reaction period no 9-iodoanthracene remained; vpc analysis (3 ft \times 0.25 in. 3% Dowfax, 215°, 100 ml/min) showed two product peaks at 4.9 min (71%) and 14.8 min (29%). Work-up of the reaction mixture gave 0.3 g of yellow-green crystals (74%). Recrystallization from ethanol and subsequently from acetone gave yellow needles: mp 211–213° (lit. 209–210°);^{20b} retention time, 4.9 min. *Anal.* Calcd for C₁₄H₉Cl₂: C, 68.04; H, 3.26; Cl, 28.70. Found: C, 66.36; H, 3.38; Cl, 28.20.

Catalysts for the Synthesis of Aryl Iodides.—Into 70 ml of xylene were placed 12.7 g (0.05 mol) of iodine, 14.7 g (0.11 mol) of copper(II) chloride, and 0.38 g (0.001 mol) of iron(II) iodide tetrahydrate. The reaction was stirred and refluxed for 1.5 hr. After the normal work-up, an 87% yield of iodoxyene was isolated. A control experiment containing no iron(II) iodide gave a 23% yield under identical conditions.

Registry No.—Benzene, 71-43-2; toluene, 108-88-3; *m*-xylene, 108-38-3; *o*-xylene, 95-47-6; *p*-xylene, 106-42-3; mesitylene, 108-67-8; durene, 95-93-2; *tert*-butylbenzene, 98-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1.

Synthesis of Two Benzothiacyclanones via a Novel Two-Carbon Ring Expansion of Thiolactones with Vinylolithium

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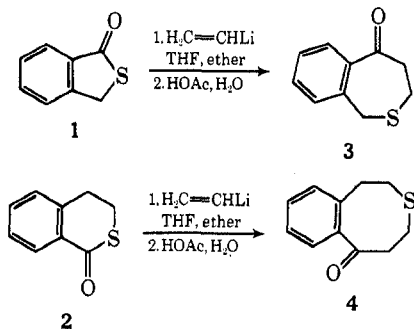
The thiolactones thiophthalide (1) and 2-thiochroman-1-one (2) react with 1 equiv of vinylolithium in ether-tetrahydrofuran followed by acetic acid to form, respectively, seven- and eight-membered ring γ -keto sulfides by a novel two-carbon ring expansion. This method is an improvement on existing, inefficient Friedel-Craft acylation routes to such ketones. Syntheses of 2-thiochroman-1-one and a much improved synthesis of thianaphthen-2-one are reported.

In the course of our studies of organic sulfur chemistry, we required pure samples of 4,5,6,7-tetrahydro-2H-benzo[*c*]thiepin-5-one (3) and 3,4,7,8-tetrahydro-2H-benzo[*e*]thiocin-4-one (4). These ketones had pre-

viously been obtained as impure oils in low yield by the AlCl₃-catalyzed cyclization of acid chlorides 5a and b, respectively.¹ We decided to attempt the addition of 1 equiv of vinylolithium to the readily available thiophthalide (1), in anticipation that the initial tetrahedral adduct 6 might be stable toward vinylolithium, but ring open to the vinyl ketone 7 upon hydrolysis. The latter should then cyclize by conjugate addition of the mercaptan to form 3. As expected, a 51% yield of crystalline 3 was obtained from treatment of a cold ether solution of 1 with a 2 *M* solution of vinylolithium in tetrahydrofuran, followed by acidification with glacial acetic acid, vacuum distillation, and sublimation. Analogous reaction of thiolactone 2 at -70° gave 19% crystalline 4.

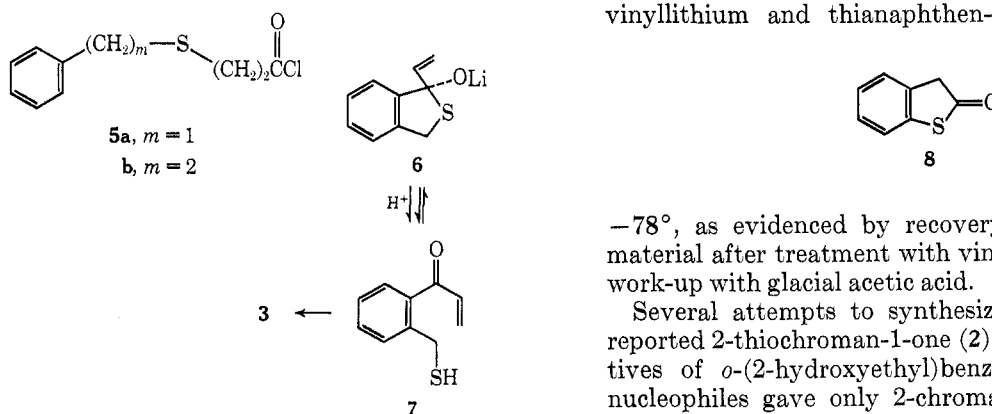
The crude ketones 3 and 4 were contaminated with polymeric material, variable amounts of recovered starting material, and a volatile, pungent oil which has not been identified.

Recovery of thiolactones implies that they undergo either enolate formation or competing addition of 2 equiv of vinylolithium to form divinylcarbinols, which may be responsible for polymer formation. Enolate formation was the predominant reaction between vinylolithium and thianaphthen-2-one (8), at 25 to



–78°, as evidenced by recovery of 84–95% of this material after treatment with vinylolithium followed by work-up with glacial acetic acid.

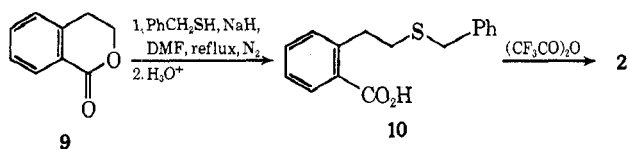
Several attempts to synthesize the previously unreported 2-thiochroman-1-one (2) by reaction of derivatives of *o*-(2-hydroxyethyl)benzoic acid with sulfur nucleophiles gave only 2-chroman-1-one (9). It was found, after considerable experimentation, that lactone 9 reacted with sodium benzylmercaptide in dimethylformamide at reflux to give the carboxylic acid 10 in



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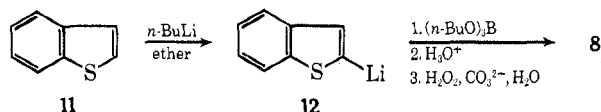
(1) P. Cagniant and D. Cagniant, *Bull. Soc. Chim. Fr.*, 1998 (1959).

81% yield. The latter was recovered from polyphosphoric acid at 120° but reacted exothermically at room



temperature with trifluoroacetic anhydride to afford a mixture of recovered starting material and **2** in 48% yield. This transformation presumably involves an acid-catalyzed debenylation with concomitant or subsequent lactonization, analogous to the transformation of phthalide to thiophthalide.²

An attempt to synthesize thianaphthen-2-one (**8**) from *o*-nitrotoluene³ was unsuccessful. Thianaphthene (**11**), however, could be oxidized to **8** in good yield by the sequence **11** to **12** to **8**. This procedure was adapted from the method of Hornfeldt and Gronowitz for the oxidation of thiophenes to the tautomers of 2-hydroxythiophenes.⁴



Experimental Section

Melting points and boiling points are uncorrected and the former were measured in an electrically heated Thiele-Dennis tube. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer and nmr spectra on a Varian HA-100 instrument in the frequency sweep mode. Chemical shifts are reported in δ units. Vpc analyses and isolations were performed on a 5 ft \times $\frac{3}{8}$ in., 10% SE-30 on Anakrom ABS (70–80 mesh) using a Varian Model A-90-P3 instrument with thermal conductivity detector (He carrier at 80 ml min⁻¹). Microanalyses were performed by Galbraith Laboratories, Inc.

Materials.—Commercially available materials were used without purification. A solution of $\sim 2 M$ vinylolithium in tetrahydrofuran, previously available from Alpha Inorganics, Inc., was standardized by double titration and used in this work.⁵

4,5,6,7-Tetrahydro-2H-benzo[*c*]thiepin-5-one (3).—A magnetically stirred solution of thiophthalide (**1**), 3.00 g, 20.0 mmol, in 100 ml of anhydrous ether in a side-arm flask fitted with serum cap and nitrogen inlet, was cooled under a slight positive pressure of nitrogen in a Dry Ice-acetone bath until crystallization began. The mixture was then warmed until homogeneous and treated during 5 min with 12.0 ml of 1.68 *M* solution of vinylolithium in tetrahydrofuran from a syringe. A copious precipitate formed after a few minutes.

The mixture was warmed to room temperature, treated with glacial acetic acid (1.7 ml) and 25 ml of water, and then stirred until two nearly clear layers had formed. The layers were separated and the water layer was extracted with an equal volume of ether. The combined ether layers were washed with saturated sodium bicarbonate solution (10 ml), dried over MgSO₄ (anhydrous), filtered, and evaporated *in vacuo* leaving 3.91 g of a cloudy, two-phase residue. Distillation of this material gave 2.64 g of a partially crystalline oil, bp 100–130° (0.01 mm). Vpc analysis of this fraction (8 ft \times $\frac{1}{4}$ in., 20% SE-30 on 60–80 mesh Chromosorb P at 210°, He carrier 80 ml min⁻¹) showed one major peak for the desired ketone **3** (>98 area %). Trituration of this material with pentane-ether gave a crude white solid which was sublimed (50°, 0.01 mm) to give 1.81 g (51%) of

crystalline **3**: mp 50–51°; $\nu_{\text{max}}^{\text{CCl}_4}$ 2925, 1680, 1600 cm⁻¹; nmr (CDCl₃) 7.65 (1 H, q, *J* = 7, 2 Hz), 7.4 (3 H, complex), 3.85 (2 H, s), 2.94 (4 H, A₂B₂).

Anal. Calcd for C₁₀H₁₀OS: C, 67.38; H, 5.66; S, 17.98. Found: C, 67.18; H, 5.70; S, 18.12.

The oxime melted at 168–169° dec (recrystallized from benzene-pentane).

Anal. Calcd for C₁₀H₁₁NOS: C, 62.14; H, 5.74; N, 7.25; S, 16.59. Found: C, 62.06; H, 5.83; N, 7.05; S, 16.82.

3,4,7,8-Tetrahydro-2H-benzo[*e*]thiocin-4-one (4).—A stirred solution of 2.69 g (16.4 mmol) of 2-thiochroman-1-one (**2**) in 350 ml of anhydrous ether was cooled to –70° under N₂ and treated with 11.0 ml of an $\sim 1.6 M$ solution of vinylolithium in tetrahydrofuran. The resulting mixture was warmed, treated with 1.7 ml of glacial acetic acid, and worked up as for **3** to give 0.59 g (19%) of **4**: mp 58–60°; $\nu_{\text{max}}^{\text{CCl}_4}$ 3070, 3020, 2925, 1708, 1675, 1597, 1447, 1418, 1320, 1287, 1035, 915, 848 cm⁻¹ (the carbonyl doublet in the ir is not due to ring opening to a vinyl ketone since the nmr is devoid of vinyl absorption; this doublet is either due to the presence of unaveraged conformers of **4** or to Fermi resonance of the true frequency of the C=O stretch, *e.g.*, with the first overtone of the weak 848-cm⁻¹ band); nmr (CDCl₃) 7.3 (4 H, complex), 3.1 (4 H, A₂B₂), 2.9 (4 H, A₂B₂).

Anal. Calcd for C₁₁H₁₂OS: C, 68.71; H, 6.30; S, 16.68. Found: C, 68.68; H, 6.44; S, 16.72.

***o*-(2-Benzylmercaptoethyl)benzoic Acid (10).**—Sodium hydride (12.0 g of a 60% dispersion in Nujol, 0.3 mol) was washed free of Nujol with hexane by decantation under nitrogen. To the residue was added dropwise under nitrogen 37.2 g (0.300 mol) of benzyl mercaptan in 100 ml of dimethylformamide with magnetic stirring. Initial hydrogen evolution was exothermic and cooling was required to prevent foaming. The resulting mixture was treated with a solution of 18.0 g (0.12 mol) of isochroman-1-one (**9**) in 100 ml of dimethylformamide, and the mixture was stirred and refluxed vigorously for 24 hr under N₂. The resulting dark mixture was poured on ice and 100 ml of 20% hydrochloric acid and extracted with ether. The combined ether extracts were washed with at least five portions of 10% aqueous potassium carbonate. (Extraction of the acid **10** was inefficient with aqueous sodium bicarbonate or carbonate and it was only slowly soluble in aqueous potassium carbonate.) Acidification of the carbonate washings with 20% hydrochloric acid at 0° gave 30 g (81%) of crude, crystalline, desired acid, mp 88–94°. Recrystallization from aqueous methanol and then twice from ether-hexane gave off-white prisms: mp 100–101°; $\nu_{\text{max}}^{\text{CHCl}_3}$ 3500–2500 (broad), 1680, 1601, 1570, 1485, 1445, 1390, 1295, 1123, 1067 cm⁻¹; nmr (CDCl₃) 11.0 (1 H, broad), 7.94 (1 H, q, *J* = 8, 2 Hz), 7.35–6.95 (8 H, complex), 3.50 (2 H, s), 2.8 (4 H, 8 lines, $\Delta\nu$ = 56 Hz).

Anal. Calcd for C₁₆H₁₆O₂S: C, 70.55; H, 5.92; S, 11.78. Found: C, 70.68; H, 5.88; S, 11.82.

2-Thiochroman-1-one (2).—To 25.0 g (0.092 mol) of powdered *o*-(2-benzylmercaptoethyl)benzoic acid (**10**) in round-bottomed flask fitted with a reflux condenser was added 30 ml of trifluoroacetic anhydride dropwise to moderate the very exothermic reaction. After standing 0.5 hr the resulting mixture was refluxed 0.5 hr, cooled, and poured on ice. The mixture was extracted with two equal volumes of ether and the dark ether layers were combined and washed with water and then 5% potassium carbonate solution until the washings were basic.

The ether layer was then dried over MgSO₄, filtered, and evaporated *in vacuo* giving 9.0 g of a dark orange oil which was distilled to give 5.0 g of a yellow oil, bp 104–110° (0.02 mm), which crystallized. Sublimation of this material gave yellow crystals, mp 59–61°. The yield of sublimed material, based on recovered acid **10** from the acidified aqueous layer, was 48%. Recrystallization of sublimed **2** from aqueous methanol gave white needles: mp 60–61.5°, after drying *in vacuo*; $\nu_{\text{max}}^{\text{CCl}_4}$ 3070, 3030, 2938, 2840, 1715 (weak), 1655, 1601, 1485, 1450, 1430, 1280, 1205, 1105, 945 (very strong), 880 (doublet) cm⁻¹; nmr (CDCl₃) 7.92 (1 H, q, *J* = 7, 2 Hz), 7.5–7.1 (3 H, complex), 3.23 (4 H, s, accidental equivalence).

Anal. Calcd for C₉H₈OS: C, 65.82; H, 4.91; S, 19.53. Found: C, 65.67; H, 4.85; S, 19.25.

Thianaphthen-2-one (8).—Benzothiophene (26.8 g, 0.200 mol) in 100 ml of anhydrous ether was metalated with 130 ml of commercial solution of 1.6 *M* *n*-butyllithium in hexane accord-

(2) M. Protiva, M. Rajsner, E. Adlerova, V. Seidlova, and Z. Vejdecke, *Coll. Czech. Chem. Commun.*, **29**, 2161 (1964).

(3) C. Marshalk, *J. Prakt. Chem.*, **88** [2], 237 (1913).

(4) A. B. Hornfeldt and S. Gronowitz, *Ark. Kemi*, **21**, 239 (1963).

(5) For a recent summary of preparations of this reagent and methods for standardization, see J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).

(6) P. Maite, *Colloq. Int. Cent. Nat. Rech. Sci. (Paris)*, No. 64, 197 (1955); *Chem. Abstr.*, **55**, 10426.

ing to the procedure of Shirley and Cameron.⁷ The resulting magnetically stirred solution of 2-lithiobenzothiophene was cooled in a Dry Ice-acetone bath and treated with 64.5 g (0.280 mol) of tributylborate giving a gelatinous precipitate. Hydrochloric acid (1 *N*, 200 ml) was added to the stirred mixture at 0°. After stirring 1 hr at 0–25°, the layers were separated and the aqueous phase extracted with ether. The combined ether layers were extracted with 200 ml of 1 *N* NaOH and the basic aqueous layer was backwashed with ether. Acidification of the aqueous layer with ice cold 3 *N* hydrochloric acid gave a pink-yellow odiferous precipitate of crude boronic acid which was collected and washed with water by suction. The crude boronic acid was dissolved in a small volume of ether and the stirred solution treated with 96 ml of 10% hydrogen peroxide containing 2 ml of saturated aqueous sodium carbonate. The resulting mixture was refluxed and stirred for 1 hr and then stirred overnight at room temperature. The layers were separated; the aqueous layer was extracted with ether. The combined ether extracts were washed with water until free of H₂O₂ by the ferrous ion test. The ether layer was then washed with saturated NaCl solution, dried over MgSO₄, filtered, and evaporated *in vacuo* giving 21.7 g

(7) D. A. Shirley and M. D. Cameron, *J. Amer. Chem. Soc.*, **72**, 2788 (1950).

(72%) of crystalline thianaphthen-2-one, mp 32–34°. Recrystallization from hot aqueous methanol by cooling to –20° gave pale yellow needles: mp 34–35° (lit. mp 33–34°, 44–45°^{3,8}); $\nu_{\text{max}}^{\text{C=O}}$ No–OH absorption, 1723, 1595, 1460 (doublet), 1390, 1130, 1088, 1010 cm⁻¹; nmr (CDCl₃) 7.24 (4 H, m), 3.92 (2 H, s).

Registry No.—1, 1194-57-6; 2, 25606-96-6; 3, 25606-97-7; 3 oxime, 25606-98-8; 4, 25606-99-9; 8, 496-31-1; 10, 25607-01-6; vinyl lithium, 917-57-7.

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(8) Two crystalline forms "stout prisms," mp 44–45°, and "fine needles," mp 33–34°, of **8** have been isolated.³ The lower melting form is reported to be the more stable. In our laboratory sublimation of the low melting form at 0.005 mm gave nearly colorless, stout prisms, mp 46–48°. Recrystallization from aqueous methanol gave either form, with the high melting form being the more frequent. Infrared spectra of both materials in CCl₄ were identical and consistent only with the ketotautomer **8**.

N,N-Dialkylamino-1,2,3-triazole- α -diazamidine Tautomers from Substituted Benzenesulfonyl Azides and Ynamines

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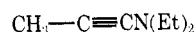
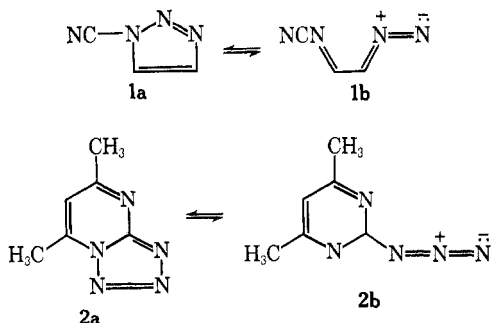
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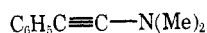
The 1,3 dipolar additions of a number of substituted benzenesulfonyl azides to *N,N*-diethylaminoprop-1-yne yielded 1,2,3-triazoles and α -diazamidines which, in solution, were shown by nmr and ir spectroscopy to exist in a tautomeric equilibrium. The structure and stereochemistry of one of the products were proved by chemical degradation. The 1,3 dipolar additions of all the substituted benzenesulfonyl azides to *N,N*-dimethylaminophenylacetylene afforded only α -diazamidines.

During the last few years, several interesting examples of ring-chain tautomerism involving a variety of functional groups have been reported.^{1–3} For instance, in 1967, Hermes and Marsh⁴ reported the existence of ring-chain equilibrium between 1-cyano-1,2,3-triazole (**1a**) and α -diaz-*N*-cyanoethylideneimine (**1b**). A similar type of equilibrium between 5,7-dimethyltetrazole[1,5-*a*]pyrimidine (**2a**) and 2-azido-4,6-dimethylpyrimidine (**2b**) was also recently reported by Huisgen, *et al.*⁵ From the reaction of substituted benzenesulfonyl azides and *N,N*-diethylaminoprop-1-

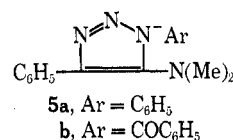
yne (**3**), we have obtained strong evidence for the existence of a ring-chain equilibrium between *N,N*-diethylamino 1,2,3-triazole and α -diazamidine functions. A number of 1,3 dipolar additions to ynamines have been reported to produce a series of five-membered heterocycles.^{6–8} For example, the additions of both aryl and aroyl azides to *N,N*-dimethylaminophenylacetylene (**4**) gave only the corresponding 1,2,3-triazoles **5a** and **5b**, respectively. As an extension of this reaction, we studied the 1,3 dipolar additions of a number of substituted benzenesulfonyl azides (**6**) to ynamines **3** and **4**. The reactions were conducted by adding equimolar



3



4



5a, Ar = C₆H₅

5b, Ar = COC₆H₅

solutions of **6** to either **3** or **4** in tetrahydrofuran at 0 to –78°. Removal of the solvent by evaporation under reduced pressure afforded the corresponding crystalline *N,N*-dialkylamino-1,2,3-triazoles **7a–d**, and the diazamidines **8e–f** and **9a–e**. The infrared (ir) spectra of compounds **8e–f** and **9a–e** in chloroform solutions or as KBr pellets showed strong peaks around 2060 cm⁻¹,

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