acetate. Removal of the solvent left a residue which on crystallization from alcohol gave 4-acetyl-3-hydroxy-6-methylxanthone as long shiny needles, m.p. and m.m.p. 243–244°, 1.94 g. yield.

Employing the same sequence of reactions and identical experimental conditions as given for the preparation of 4′-methylfurano(3′,2′:4,3)xanthone, 4-acetyl-3-hydroxy-6-methylxanthone has been converted into the 3-O-carbethoxy ester which has been subsequently hydrolyzed and allowed to undergo internal cyclization. The physical constants of the intermediates, as well as the final compound, and the analysis values are recorded in Table I.

Acknowledgment.—Our thanks are due to Professor S. Siddappa for his kind interest. We also record our thanks to the Government of India, Ministry of Scientific Research and Cultural Affairs, for the award of a Research Training Scholarship to G. S. Puranik.

Seven-Membered Heterocycles. III. Homoallylic Resonance and a Unique Sulfur Extrusion Reaction in Seven-Membered Sulfur Heterocycles[1-3]

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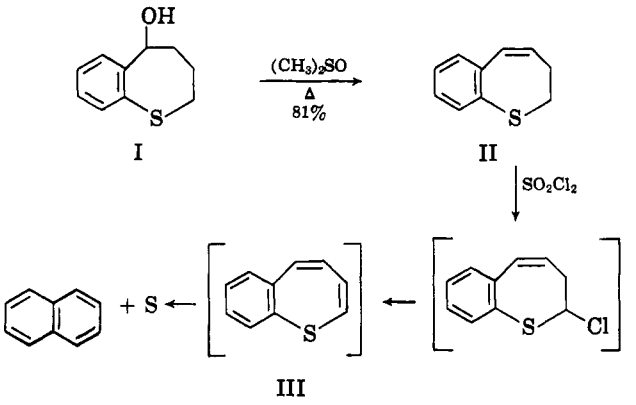
Received October 28, 1963

This paper describes some observations made during a study directed toward the synthesis of benzo[*b*]thiepin. The synthesis and structure of 5-hydroxy-2-chloro-4,5-dihydrobenzo[*b*]thiepin (VII) and its acetate (VIII) are reported. Treatment of VII with *p*-toluenesulfonic acid produced an ester (XI). In rationalizing the origin of XI, homoallylic resonance stabilization of the intermediate carbonium ion becomes important. Since carbonium ions appeared to promote a ring contraction, the pyrolysis of VIII was studied. The pyrolysis products were α-chloronaphthalene and 1,1′-naphthyl disulfide, which suggested the intermediate formation of 2-chlorobenzo[*b*]thiepin. A reaction of extruded sulfur and 2-chloronaphthalene is reported.

A number of papers dealing with the preparation and properties of thiepin derivatives have appeared during the past decade; however, the synthesis of benzo[*b*]thiepin remains to be accomplished. In previous reports we have reviewed the known thiepin derivatives,[5] described the synthesis of benzo[*b*]thiepin 1,1-dioxide,[5] and discussed its chemical properties.[1] This paper presents some unexpected reactions encountered in work directed toward the synthesis of benzo[*b*]thiepin.

In the initial synthetic approach toward benzo[*b*]thiepin, the introduction of the 4,5-double bond preceded the 2,3-double bond. The key material for this scheme, 2,3-dihydrobenzo[*b*]thiepin (II), was available readily by dehydration in dimethyl sulfoxide[6] of the known 5-hydroxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin (I).[5] Attempts to introduce the 2,3-double bond by dehydrogenation or *via* allylic bromination with N-bromosuccinimide, followed by reaction with base, were unsuccessful.[7] When II was subjected to chlorination with sulfuryl chloride,[8] sulfur (2.5%, expt. 2 4.5%), naphthalene (9.6%, expt. 2 5.3%), and a dichlorination product of II (22%, the structure of this material has not been established) were isolated. The appearance of sulfur and naphthalene in similar amounts leads one to suspect the presence of benzo[*b*]thiepin (III) which suffered sulfur extrusion.[9] The origin of benzo[*b*]thiepin could be rationalized by a thermal elimination of hydrogen chloride from the 2-chloro derivative of II, the expected product of the chlorination reaction.



These results suggested a limited thermal stability for benzo[*b*]thiepin and the need for an alternate synthetic approach. In this alternate pathway the 2,3-double bond was introduced first, followed by attempts to insert the 4,5-double bond. The compounds utilized in these studies were 5-substituted 2-chloro-4,5-dihydrobenzo[*b*]thiepins. The chloro group in the 2-position was a consequence of the synthetic method employed to introduce the 2,3-double bond.

The reaction sequence which conveniently led to the preparation of the desired starting materials is outlined in Scheme 1.

When IV was subjected to the chlorination procedure of Truce, Birum, and McBee[8] using at least 2 moles of sulfuryl chloride, substitution proceeded, in good yield, α to the sulfur and gave 5-(*p*-nitrobenzoyloxy)-2,2-dichloro-2,3,4,5-tetrahydrobenzo[*b*]thiepin (V) as a white crystalline product. Attempts to monochlorinate IV produced amorphous solids which could not be crystallized and purified. During the melting point determination of V, the evolution of a gas was evident

(1) For part II in this series, see V. J. Traynelis and R. F. Love, *J. Org. Chem.*, **29**, 366 (1964).

(2) Presented before the Organic Division at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962.

(3) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

(4) Smith Kline and French Foundation Fellow, 1959–1960; Eastman Kodak Fellow, 1960–1961. Abstracted from part of the Ph.D. dissertation of J. R. Livingston, Jr., March, 1962.

(5) V. J. Traynelis and R. F. Love, *J. Org. Chem.*, **26**, 2728 (1961).

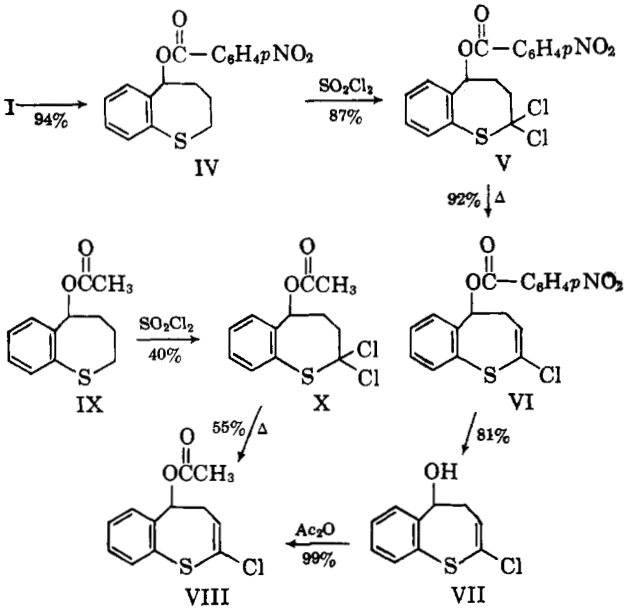
(6) V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *ibid.*, **27**, 2377 (1962).

(7) R. F. Love, Ph.D. dissertation, University of Notre Dame, 1960.

(8) (a) W. E. Truce, G. H. Birum, and E. T. McBee, *J. Am. Chem. Soc.*, **72**, 3594 (1952); (b) F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955).

(9) For a review of sulfur extrusion reactions, see J. D. Loudon, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p. 299; also, see ref. 1.

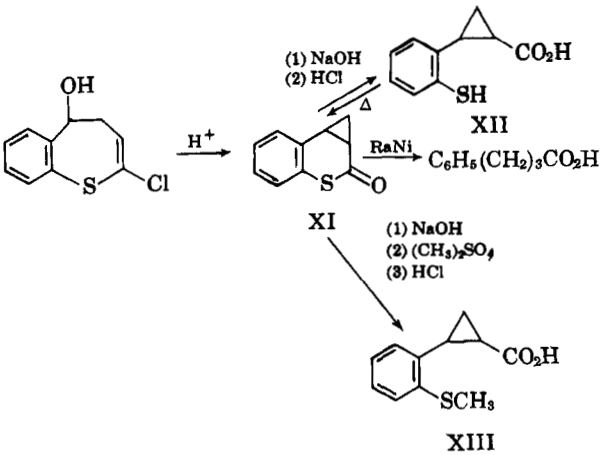
SCHEME I



and, when V was heated in refluxing xylene for a few hours, 1 mole of hydrogen chloride was lost and 5-(*p*-nitrobenzoyloxy)-2-chloro-4,5-dihydrobenzo[*b*]thiepin-(VI) was isolated in good yield. Alkaline hydrolysis of VI in aqueous *t*-butyl alcohol produced the first key intermediate, 5-hydroxy-2-chloro-4,5-dihydrobenzo[*b*]-thiepin (VII), and a simple acetylation of VII afforded the second key intermediate, 5-acetoxy-2-chloro-4,5-dihydrobenzo[*b*]thiepin (VIII). An alternate approach to the preparation of VIII involved the acetylation of I to 5-acetoxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin (IX); dichlorination with sulfuryl chloride gave X followed by the pyrolytic elimination of hydrogen chloride to give VIII. The structural assignments for compounds VII and VIII were based on elemental analysis, infrared (in particular the observation of functional group changes as one proceeds through the reaction scheme), ultraviolet, and n.m.r. spectra. The n.m.r. spectral data, along with proton assignments, are recorded in the Experimental section.

The initial experiments to introduce the final double bond in the sulfur ring involved a dehydration study of VII. When VII was heated with a trace of *p*-toluenesulfonic acid in benzene, some water distilled as an azeotrope with benzene and also hydrogen chloride was formed. A white crystalline product was isolated in 30% yield and was assigned the structure of 2-oxo-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran[10] (XI) on the basis of the following chemical and physical evidence.

(1) Compound XI was dissolved in hot aqueous sodium hydroxide solution and upon acidification gave the acid XII. When XII was heated under reduced pressure, the starting cyclic ester (XI) was recovered as a sublimate. Treatment of a solution of XI in aqueous sodium hydroxide with methyl sulfate produced the methylmercapto acid (XIII). These data are rationalized conveniently by the presence of a cyclic thiol ester function.



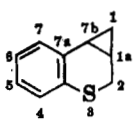
(2) The infrared spectrum of XI had a strong absorption at 6.05 μ which is attributed to the thiol ester carbonyl. Hurd and Kreuz[11] have prepared 2-thienol and reported a carbonyl absorption at 6.0 μ, which may arise from one of two tautomeric structures.[11] In considering the structural effects in XI such as the conjugative effect of a cyclopropyl ring, the presence of a benzo fused ring and the ring size, the appearance of the carbonyl band for XI at 6.05 μ is compatible with the carbonyl band in 2-thienol at 6.0 μ. The infrared spectra of XII and XIII were consistent with the assigned structures for these compounds.

(3) A Raney nickel desulfurization of XI gave γ-phenylbutyric acid, identified by spectral comparison and mixture melting points of the free acid and its amide with authentic samples.

(4) The strongest support for the presence of a cyclopropane ring comes from the n.m.r. spectra of XI, XII, and XIII. These spectra showed complex multiplets in the region of τ 7–9 and were similar to the n.m.r. spectra of *cis*- and *trans*-2-phenylcyclopropanecarboxylic acids. Compounds XI and XII showed complex multiplets in three regions which centered at τ 8.72, 8.25, and 7.45 (determined in deuteriochloroform) and 8.78, 8.27, and 7.36 (determined in trifluoroacetic acid), respectively. However, compound XIII, *cis*- and *trans*-2-phenylcyclopropanecarboxylic acids (each measured in trifluoroacetic acid solution), had complex multiplets in only two regions centered at τ 8.19 and 7.50 (τ 7.60 S–CH_3 absorption), 8.40 and 7.16, and 8.49 and 7.35, respectively. The absence of olefinic protons excluded consideration of a seven-membered thiol ester with a double bond in the hetero ring in XI.[12]

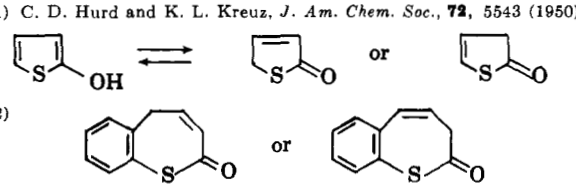
(5) Some confirmatory evidence in favor of the cyclopropane ring in preference to a double bond was the failure of XI to add hydrogen catalytically or decolorize bromine in carbon tetrachloride.

(10) For the numbering of XI according to A. M. Patterson, L. T. Capell, and D. F. Walter, "The Ring Index," 2nd Ed., American Chemical Society, Washington, D. C., 1960, see p. 275.

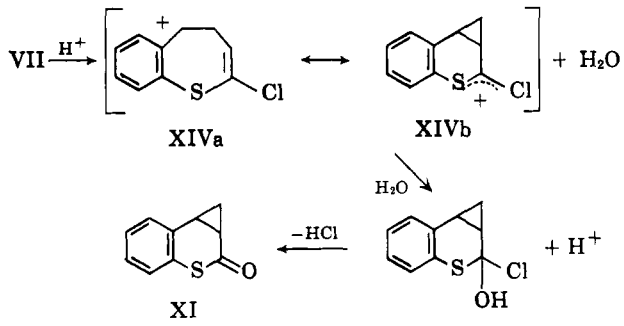


(11) C. D. Hurd and K. L. Kreuz, *J. Am. Chem. Soc.*, **72**, 5543 (1950).

(12)



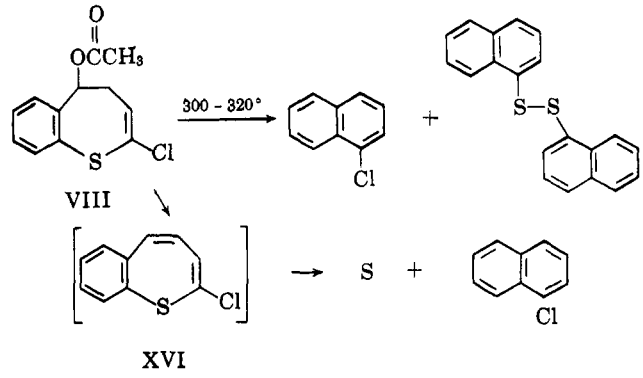
The origin of the cyclic ester XI can be nicely rationalized by application of carbonium ions stabilized by homoallylic resonance. In this case the contribution of structure XIVb to the resonance hybrid of the carbonium ion XIV becomes appreciable because of the presence of two electron-releasing atoms (sulfur and chlorine) which help delocalize the positive charge from C-2. This effect is reflected in the isolation of the cyclopropyl ester (XI) in 30% yield. The remaining 70% for the reaction is still under investigation.



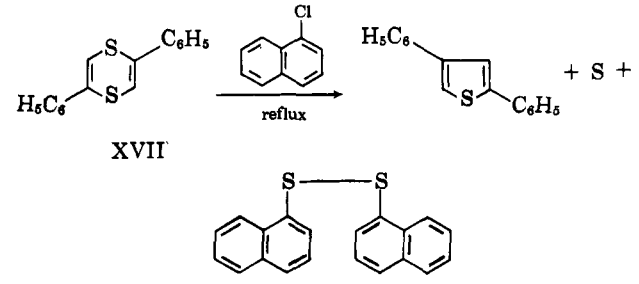
Since elimination reactions which proceed *via* carbonium ions would be prone to the above homoallylic resonance, the next approach to introduce the 4,5-double bond of benzo[*b*]thiepin utilized an acetate pyrolysis which involves a *cis* cyclic elimination. Thus, VIII was distilled into a tube heated to about 300° and the pyrolysis products were separated by column chromatography. The first compound eluted was α-chloronaphthalene (10%), identified by comparison of its infrared and ultraviolet spectra with that of an authentic sample, and by a mixture melting point of its picrate with an authentic sample. A second fraction was recovered as a yellow viscous oil from which was isolated 1,1′-naphthyl disulfide (11%) as a yellow crystalline solid. The remaining oil possessed infrared and ultraviolet spectra identical with 1,1′-naphthyl disulfide and most likely was a mixture of 1,1′-naphthyl disulfide and 1,1′-naphthyl polysulfides. The yield based on the initial yellow viscous oil being 1,1′-naphthyl disulfide was 20%.

The identity of 1,1′-naphthyl disulfide was established by analysis, molecular weight determination, comparison of infrared and ultraviolet spectra with an authentic sample, and melting point and mixture me'ting point with an authentic sample. A reduction of the disulfide was accomplished by zinc and hydrochloric acid and was followed by conversion of the mercaptan to the known α-napthylthioacetic acid. A mixture melting point with an authentic sample was not depressed. Evidence for the presence of some 1,1′-napthyl polysulfides was found when hydrogen sulfide was liberated during reduction of the liquid mixture containing this compound with zinc and hydrochloric acid. The resulting mercaptan was converted to α-naphthylthioacetic acid.

In order to rationalize the products isolated, one can picture the expected pyrolysis of the acetate VIII leading to 2-chlorobenzo[*b*]thiepin (XVI). Since these seven-membered sulfur systems are known to extrude sulfur,[9,13,14] such a reaction proceeding with XVI would form sulfur and α-chloronaphthalene. In a recent report Parham and Koncos[13] suggested the formation of 3-chlorobenzo[*b*]thiepin as an intermediate which under reaction conditions was converted to the isolated product, β-chloronaphthalene.



Such an extrusion of sulfur nicely accounts for α-choronaphthalene. As for the formation of 1,1′-naphthyl disulfide, one possibility may involve a reaction of sulfur with α-chloronaphthalene. A mixture of elemental sulfur and pure α-chloronaphthalene was refluxed; however, only starting materials were recovered. This failure of reaction could be attributed to the different nature of sulfur, as extruded in the pyrolysis, and elemental sulfur. Another compound known to extrude sulfur at a temperature which would permit pyrolysis in refluxing α-chloronaphthalene is 1,4-dithiadiene (XVII).[15] When XVII was added to refluxing α-chloronaphthalene, about 4% of 1,1′-naphthyl disulfide was isolated. Identification was by comparison of its infrared spectrum with an authentic sample. The nature of this reaction is under further investigation.



In conclusion, the pyrolytic method of introducing a double bond suffers from the disadvantage (as a method for making benzo[*b*]thiepin) of requiring temperatures at which the desired product loses sulfur and is converted to a more stable naphthalene system. Other pathways toward benzo[*b*]thiepin are now being studied.

Experimental[16]

5-Hydroxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin (I).—This starting material was prepared by the sequence of reactions described

(13) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

(14) G. P. Scott, *ibid.*, **75**, 6332 (1953); K. Dimroth and G. Lenke, *Chem. Ber.*, **89**, 2608 (1956); J. D. Loudon, A. D. B. Sloan, and L. A. Summers, *J. Chem. Soc.*, 3814 (1957).

(15) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **76**, 4960 (1954).

(16) All melting points and boiling points are uncorrected. The microanalyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind., and Schwartzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were determined on a Baird Associates infrared spectrophotometer by J. R. L., Jr.; ultraviolet spectra were recorded by Mr. Fred Klebacher on a Perkin-Elmer Spectracord; the n.m.r. spectra were determined by Dr. M. Gianni and Mr. B. Nowak with a Varian Associates 60-Mc. high resolution n.m.r. spectrometer, Model V-4300B.

by Traynelis and Love.[5] Thiophenol (0.50 mole) and butyrolactone (0.50 mole) were converted in 86% yield to γ-phenylmercaptobutyric acid which was cyclodehydrated with polyphosphoric acid to 5-oxo-2,3,4,5-tetrahydrobenzo[*b*]thiepin (85% yield); reduction with sodium borohydride gave 5-hydroxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin (96%), m.p. 69–70.5°, lit.[5] m.p. 70–71°.

2,3-Dihydrobenzo[*b*]thiepin (II).—Dehydration of the preceding alcohol in dimethyl sulfoxide was described previously[6] and supplied the material used in this work.

Reaction of 2,3-Dihydrobenzo[*b*]thiepin with Sulfuryl Chloride.—Following the procedure of Bordwell and Pitt,[8] a solution of sulfuryl chloride (8.4 g., 0.062 mole) in 20 ml. of petroleum ether (b.p. 30–60°) was added dropwise over a period of 45 min. to 2,3-dihydrobenzo[*b*]thiepin (10.0 g., 0.062 mole) in 20 ml. of petroleum ether. After the solution was refluxed 55 min., sodium bicarbonate (5.0 g., 0.055 mole) was added, and the solution refluxed 1 hr. The reaction mixture was dried over anhydrous magnesium sulfate and distilled rapidly under nitrogen. Chromatography of the distillate (9.35 g.) on Alcoa F-20 alumina (450 g.) using dry petroleum ether as eluent gave 0.05 g. (2.5%) of elemental sulfur, m.p. 111–112°. Recrystallization from ethyl acetate produced 0.025 g. (1.2%) of sulfur, m.p. 118–119°, which showed no depression in melting point when mixed with an authentic sample recrystallized in the same manner. Naphthalene (0.77 g., 9.6%), m.p. 72–78°, was eluted next and upon recrystallization from ethanol gave 0.34 g. (4.3%) of pure naphthalene, m.p. 79–80.5°, lit.[17] m.p. 79–80°. A mixture melting point with an authentic sample was not depressed, and the infrared spectra of the two samples were identical. The third compound eluted from the column was 2,3-dihydrobenzo[*b*]thiepin (0.09 g., 1%), identified by its infrared spectrum. A final component (3.25 g.) was eluted with ether–petroleum ether (20:80) and contained chlorine. Distillation of this material gave a mixture, b.p. 83–86° (0.02 mm.), $n^{20}D$ 1.6329–1.6345, which appeared to be primarily a dichlorination product. The structure of this material has not been established.

In a second experiment the reaction mixture was heated under nitrogen at 85° for 24 hr. and gave sulfur (4.5%) and naphthalene (5.3%).

5-(*p*-Nitrobenzoyloxy)-2,3,4,5-tetrahydrobenzo[*b*]thiepin (IV).—Solid *p*-nitrobenzoyl chloride (23.0 g., 0.124 mole) was added in one portion to a solution of 5-hydroxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin (19.0 g., 0.105 mole) in 60 ml. of pyridine, and the mixture refluxed for 15 min. after all the solid dissolved. The reaction mixture was poured into water and the solid was collected, triturated with saturated sodium bicarbonate solution, washed with water, dried, and crystallized from a benzene–petroleum ether (b.p. 60–70°) mixture. The yield of 5-(*p*-nitrobenzoyloxy)-2,3,4,5-tetrahydrobenzo[*b*]thiepin as pale yellow needles, m.p. 149–150°, lit.[5] m.p. 149–150°, was 32.3 g. (94%).

2,2-Dichloro-5-(*p*-nitrobenzoyloxy)-2,3,4,5-tetrahydrobenzo[*b*]thiepin (V).—Sulfuryl chloride (22.0 g., 0.17 mole) was added dropwise with stirring to a solution of 5-(*p*-nitrobenzoyloxy)-2,3,4,5-tetrahydrobenzo[*b*]thiepin (25.0 g., 0.076 mole) in 100 ml. of methylene chloride at a rate sufficient to keep the solution refluxing gently. After addition was complete, the solution was refluxed for an additional 40 min. and then one-third of the solvent was removed under reduced pressure. Petroleum ether (b.p. 30–60°, 200 ml.) was added, and the precipitate was filtered and washed with petroleum ether (b.p. 30–60°). The yield of 2,2-dichloro-5-(*p*-nitrobenzoyloxy)-2,3,4,5-tetrahydrobenzo[*b*]thiepin, m.p. 112°, was 26.2 g. (82%).

Anal. Calcd. for $C_{17}H_{13}Cl_2NO_4S$: C, 51.27; H, 3.29; Cl, 17.81; N, 3.52. Found: C, 51.21; H, 3.17; Cl, 17.91; N, 3.79.

2-Chloro-5-(*p*-nitrobenzoyloxy)-4,5-dihydrobenzo[*b*]thiepin (VI).—A solution of 2,2-dichloro-5-(*p*-nitrobenzoyloxy)-2,3,4,5-tetrahydrobenzo[*b*]thiepin (5.0 g., 0.0125 mole) in 20 ml. of sodium-dried xylene was refluxed vigorously for 4 hr. and cooled to 0°; the precipitate of 2-chloro-5-(*p*-nitrobenzoyloxy)-4,5-dihydrobenzo[*b*]thiepin, 4.15 g. (92%), m.p. 199–201°, was collected. An analytical sample was prepared by repeated recrystallization from benzene, m.p. 201–202°.

Anal. Calcd. for $C_{17}H_{12}ClNO_4S$: C, 56.43; H, 3.34; Cl, 9.80; N, 3.87. Found: C, 56.67; H, 3.47; Cl, 10.02; N, 3.96.

2-Chloro-5-hydroxy-4,5-dihydrobenzo[*b*]thiepin (VII).—A mixture of potassium hydroxide (5.0 g., 0.088 mole), water (10 ml.), 2-chloro-5-(*p*-nitrobenzoyloxy)-4,5-dihydrobenzo[*b*]thiepin (25.2 g., 0.069 mole), and *t*-butyl alcohol (100 ml.) was refluxed until all materials dissolved and then for an additional 15 min. After the reaction mixture was poured into water, the solid was isolated, and recrystallization from petroleum ether (b.p. 60–70°) gave 11.6 g. of white needles of 2-chloro-5-hydroxy-4,5-dihydrobenzo[*b*]thiepin, m.p. 98–99°; $\lambda_{max}^{heptane}$ 217, 240, and 273 mμ (ε 8800, 3640, and 4200). Concentration of the mother liquor followed by treatment with Norit gave an additional 0.45 g. of alcohol, m.p. 97.5–98.5°, for a total yield of 12.0 g. (81%).

Anal. Calcd. for $C_{10}H_9ClOS$: C, 56.47; H, 4.27; Cl, 16.67; S, 15.08. Found: C, 56.51; H, 4.26; Cl, 16.89; S, 14.90.

The n.m.r. spectrum[18] had the following peaks: multiplet, τ 3.00 center, wt. of 4 (aromatic protons); triplet,[19] 4.31 center, wt. of 1 (C_3–H olefinic proton); quartet,[19] 4.51 center, wt. of 1 (C_5–H, benzylic proton); singlet, 6.75, wt. of 1 (OH proton); and multiplet, 7.44 center, wt. of 2 (C_4–H allylic protons).

2-Chloro-5-acetoxy-4,5-dihydrobenzo[*b*]thiepin (VIII). Method A.—A solution of 2-chloro-5-hydroxy-4,5-dihydrobenzo[*b*]thiepin (4.70 g., 0.022 mole), acetic anhydride (10 g., 0.098 mole), and pyridine (20 ml.) was refluxed for 20 min. and after cooling poured into water. Recrystallization of the resulting solid from petroleum ether (b.p. 60–70°) gave 5.55 g. (99%) of 2-chloro-5-acetoxy-4,5-dihydrobenzo[*b*]thiepin, m.p. 110–111°. An analytical sample, m.p. 111–112°, obtained by recrystallization from the same solvent, had $\lambda_{max}^{heptane}$ 240 mμ (ε 3570) and 274 (5250).

Anal. Calcd. for $C_{12}H_{11}ClO_2S$: C, 56.57; H, 4.34. Found: C, 56.29; H, 4.54.

The n.m.r. spectrum had the following peaks: multiplet, τ 2.64 center, wt. of 4 (aromatic protons); quartet, 3.30 center, wt. of 1 (C_5–H, benzylic proton); triplet, 4.03 center, wt. of 1 (C_3–H, olefinic proton); multiplet 7.15 center, wt. of 2 (C_4–H, allylic protons); and singlet, 7.83, wt. of 3 (methyl protons).

Method B.—Sulfuryl chloride (7.30 g., 0.054 mole) was added dropwise to a well-stirred solution of 5-acetoxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin[5] (5.45 g., 0.0245 mole) in methylene chloride (10 ml.). After the solution was refluxed until the evolution of hydrogen chloride ceased, the methylene chloride was removed and petroleum ether (b.p. 30–60°) was added. The resulting solid was isolated and recrystallization from petroleum ether (b.p. 60–70°) gave 3.0 g. (40%) of 2,2-dichloro-5-acetoxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin, m.p. 75–77°.

A solution of the above dichloro derivative (2.30 g., 0.0079 mole) in xylene (10 ml.) was refluxed 2.5 hr.; then most of the xylene was removed under reduced pressure. Petroleum ether (b.p. 30–60°) was added and the precipitate was collected. Recrystallization from a mixture of benzene petroleum ether (b.p. 60–70°) after a Norit treatment gave 1.1 g. (55%) of 2-chloro-5-acetoxy-4,5-dihydrobenzo[*b*]thiepin, m.p. 110–111°.

2-Oxa-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran (XI).—A solution of 2-chloro-5-hydroxy-4,5-dihydrobenzo[*b*]thiepin (2.0 g., 0.0094 mole), *p*-toluenesulfonic acid (0.2 g.), and anhydrous benzene (15 ml.) was allowed to reflux for 3 hr. during which time hydrogen chloride was evolved. The benzene was removed, 20 ml. of petroleum ether (b.p. 60–70°) was added, and, after a Norit treatment, 0.54 g. (30%) of colorless plates of 2-oxa-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran, m.p. 79–80°, was isolated. Further recrystallization from petroleum ether (b.p. 60–70°) produced an analytical sample, m.p. 80.5–81°, $\lambda_{max}^{heptane}$ 255 mμ (ε 4450) and 280 infl. (1635).

Anal. Calcd. for $C_{10}H_8OS$: C, 68.15; H, 4.58; S, 18.19. Found: C, 68.21; H, 4.58; S, 17.83.

A solution of 2-oxa-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran in 10 ml. of dioxane and 33 mg. of 10% palladium on charcoal were stirred at atmospheric pressure in a semimicro hydrogenation apparatus[20] for 5 hr. Since no significant uptake of hydrogen occurred, the reaction mixture was transferred to a Paar hydrogenation apparatus and kept at 50 p.s.i. of hydrogen for 2 hr. When the solvent was removed, starting material with m.p. 80–81° was recovered.

When 2-oxo-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran was treated with an excess of bromine in carbon tetrachloride for 2

(17) G. Egloff, "Physical Constants of Hydrocarbons," Vol. IV, Reinhold Publishing Corp., New York, N. Y., 1947, p. 77.

(18) The n.m.r. spectrum was determined in deuteriochloroform solution with tetramethylsilane as an internal standard.

(19) One band of the C_3–H triplet was superimposed on one band of the C_5–H quartet.

(20) For a diagram of the apparatus, see A. A. Baldoni, Ph.D. dissertation, University of Notre Dame, 1951, p. 54.

hr., no decolorization of bromine took place and only unchanged starting material was recovered.

2-(2-Mercaptophenyl)cyclopropanecarboxylic Acid (XII).—2-Oxo-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran (100 mg., 0.568 mmole) and 10 ml. of 10% sodium hydroxide solution were heated until the solid dissolved. After the solution was acidified, the resulting solid was crystallized from ethanol–water to give 78 mg. (71%) of 2-(2-mercaptophenyl)cyclopropanecarboxylic acid, m.p. 146–150°.

Anal. Calcd. for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19. Found: C, 61.71; H, 5.23.

Ring Closure of 2-(2-Mercaptophenyl)cyclopropanecarboxylic Acid.—2-(2-Mercaptophenyl)cyclopropanecarboxylic acid (100 mg., 0.52 mmole) was sublimed slowly and gave 62 mg. (69%) of 2-oxo-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran, m.p. 75–80°. The infrared spectrum was identical with that of an authentic sample, and a mixture melting point with an authentic sample was 77–79.5°.

2-(2-Methylthiophenyl)cyclopropanecarboxylic Acid (XIII).—Dimethyl sulfate (700 mg., 5.5 mmoles) was added to a solution of 2-oxo-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran (200 mg., 1.4 mmoles) in 10 ml. of sodium hydroxide (2.0 g., 0.05 mole), and the resulting solution was heated for 5 min. The solution was cooled, strongly acidified with sulfuric acid, and the precipitate was collected. The yield of 2-(2-methylthiophenyl)cyclopropanecarboxylic acid, m.p. 165–166°, was 210 mg. (89%). Recrystallization from benzene–petroleum ether (b.p. 60–70°) produced an analytical sample, m.p. 168–169°.

Anal. Calcd. for $C_{11}H_{12}O_2S$: C, 63.42; H, 5.80; S, 15.39. Found: C, 63.45, 63.27; H, 5.92, 5.83; S, 15.51, 15.23.

Desulfurization of 2-Oxa-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran.—To a solution of 2-oxo-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran (200 mg., 1.2 mmoles) in 30 ml. of 6.7% sodium hydroxide solution was added slowly and with stirring 2.0 g. of Raney nickel alloy. The mixture was heated for 2 hr. on a steam bath and filtered through Celite; the filtrate strongly was acidified with concentrated hydrochloric acid. A precipitate of 93 mg. (50%) of γ-phenylbutyric acid, m.p. 50–52°, was collected and an additional 54 mg. (30%), m.p. 50–52°, was obtained by extraction of the acidic filtrate with methylene chloride. A mixture melting point with an authentic sample was not depressed.

The amide was prepared in the usual manner[21] and melted at 84–86°. A mixture melting point with an authentic sample was undepressed. The infrared spectra of both the acid and the amide were identical with those of authentic samples.

γ-Phenylbutyric Acid.—Addition of 200 g. of crushed Dry Ice to the Grignard reagent prepared from γ-phenylpropyl chloride (15.5 g., 0.10 mole), magnesium (3.0 g., 0.12 g.-atom), and 40 ml. of ether produced 7.6 g. (44%) of γ-phenylbutyric acid, m.p. 48–51.5°, lit.[22] m.p. 51°, isolated by ether extraction of the acidified reaction mixture.

The amide was prepared in the usual manner and after recrystallization from benzene–petroleum ether (b.p. 60–70°) melted at 84–86°, lit.[23] m.p. 84.5°.

2-Phenylcyclopropanecarboxylic Acid.—Employing the procedure of Burger and Yost,[24] the reaction of ethyl diazoacetate[25] (18.3 g., 0.161 mole) and styrene (16.7 g., 0.161 mole plus 8.35 g., 0.08 mole) produced 19.4 g. (63% based on ethyl diazoacetate) of ethyl 2-phenylcyclopropanecarboxylate, b.p. 91–93° (0.4 mm.), $n^{20}D$ 1.5192, lit.[24] b.p. 103–105° (0.5–0.7 mm.). Saponification of a portion of the above ester followed by fractional crystallization according to the procedure of Burger and Yost[24] gave *trans*-2-phenylcyclopropanecarboxylic acid, m.p. 92–93°, lit.[24] m.p. 93°, and *cis*-2-phenylcyclopropanecarboxylic acid, m.p. 106–107°, lit.[24] m.p. 106–107°.

Pyrolysis of 2-chloro-5-acetoxy-4,5-dihydrobenzo[*b*]thiepin.—After 2-chloro-5-acetoxy-4,5-dihydrobenzo[*b*]thiepin (5.55 g., 0.022 mole) was distilled slowly at 0.05-mm. pressure into a jacketed, electrically heated, 13 × 2.3 mm. glass tube packed loosely with glass wool and maintained at 300–320°, the apparatus was cooled and the pyrolysis tube and condenser were washed with carbon tetrachloride. Removal of the solvent left 5.2 g. of a black residue which was redissolved in carbon tetrachloride, placed on 70 g. of Alcoa F-20 activated alumina, and washed with 500 ml. of petroleum ether (b.p. 30–60°). When the eluate was concentrated, 0.70 g. (12.6%) of starting material with m.p. 109–111° crystallized. An infrared spectrum was identical with that of an authentic sample. The remainder of the solvent was removed and the 2.1 g. of residue was chromatographed on 120 g. of Alcoa F-20 activated alumina. Elution with petroleum ether (b.p. 30–60°) gave 350 mg. (10%) of α-chloronaphthalene. The infrared spectrum was identical with that of authentic material.

The picrate was prepared by the method of Vogel[26] and had m.p. 133–136°, and a mixture melting point with an authentic sample was not depressed.

A second substance eluted with petroleum ether (b.p. 30–60°) was a viscous yellow oil which, when mixed with acetic acid, gave a yellow crystalline solid (1st crop, m.p. 88–89.5°; 2nd crop, m.p. 79–82°; 3rd crop, m.p. 80–85°) in 387-mg. total yield. An analytical sample, m.p. 88.5–91°, was prepared by recrystallization from methanol.

Anal. Calcd. for $C_{20}H_{14}S_2$: C, 75.43; H, 4.42; mol. wt., 318. Found: C, 75.72; H, 4.72; mol. wt., 332.

The ultraviolet spectrum determined in *n*-heptane showed λ_{max} 299 mμ (ϵ_{max} 11,950).

The infrared and ultraviolet spectra of the solid were identical with those of 1,1′-naphthyl disulfide, and a mixture melting point of the first crop of crystals with an authentic sample was not depressed. Removal of the solvent from the mother liquors left 300 mg. of yellow oil which had infrared and ultraviolet spectra identical with 1,1′-naphthyl disulfide. The total yield of oil plus solid was 687 mg. (32% considering this as 1,1-naphthyl disulfide).

1,1-Naphthyl Disulfide.—Employing the procedure of Taboury,[27] the α-mercaptonaphthalene resulting from α-bromonaphthalene (12.5 g., 0.061 mole), magnesium (1.47 g., 0.061 g.-atom), and sulfur (1.94 g., 0.061 mole) was extracted into 20% sodium hydroxide that had been freed of dissolved air. This solution was treated with 30% hydrogen peroxide (5.0 ml.), and the precipitate (3.5 g.) was collected after 1 hr. Recrystallization from ethanol gave 2.8 g. (29%) of 1,1′-naphthyl disulfide, m.p. 88.5–90°, lit.[28] m.p. 91°.

α-Naphthylthioacetic Acid.—Zinc dust (2.0 g., 0.03 g.-atom) was added in small portions to a slurry of 1,1′-naphthyl disulfide (1.0 g., 0.0031 mole) in ethanol (30 ml.) and concentrated hydrochloric acid (10 ml.). After the mixture was heated on a steam bath until solution was complete and the color was discharged, the solution was made basic with potassium hydroxide, and chloroacetic acid (1.5 g., 0.016 mole) was added. The mixture was heated 1 hr. on a steam bath, cooled, and acidified; the resulting solid was crystallized from benzene–petroleum ether (b.p. 60–70°). The yield of α-naphthylthioacetic acid, m.p. 102–104°, lit.[29] m.p. 111–112°, was 600 mg. (45%).

When the yellow oil (300-mg. fraction) from the above pyrolysis experiment was treated as above, some hydrogen sulfide was evolved (trapped as lead sulfide), and the yield of α-naphthylthioacetic acid, m.p. 102–104°, was 147 mg. (37%). A mixture melting point with an authentic sample was not depressed.

Attempted Reaction of α-Chloronaphthalene with Elemental Sulfur.—Sulfur (0.20 g., 0.0063 g.-atom) and α-chloronaphthalene (1.0 g., 0.0062 mole) were refluxed for 5 min. and cooled; 5 ml. of petroleum ether (b.p. 30–60°) was added. The solid isolated was 140 mg. of sulfur. The mother liquor was placed on 60 g. of Alcoa F-20 activated alumina and washed with petroleum ether (b.p. 30–60°). The first fraction contained 10 mg. of sulfur (total sulfur, 150 mg., 75%), and fractions 2 and 3 contained 900 mg. (90%) of α-chloronaphthalene identified by its infrared spectrum.

2,5-Diphenyl-1,4-dithiadiene.—This material was prepared according to the procedure of Barker and Barkenbus.[30]

Pyrolysis of 2,5-Diphenyl-1,4-dithiadiene in α-Chloronaphthalene.—A suspension of 2,5-diphenyl-1,4-dithiadiene (1.50 g., 5.6 mmoles) in α-chloronaphthalene (3.00 g.) was added to refluxing

(21) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 200.

(22) E. Fischer and W. Schmitz, *Ber.*, **39**, 2208 (1906).

(23) C. Willgerodt and F. H. Merk, *J. prakt. Chem.*, [2]**80**, 197 (1909).

(24) A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).

(25) F. B. LaForge, W. A. Gersoff, N. Green, and H. S. Schechter, *J. Org Chem.*, **17**, 381 (1952).

(26) A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longmans Green and Co., New York, N. Y., 1957, p. 578.

(27) M. F. Taboury, *Compt. rend.*, **138**, 982 (1904).

(28) R. Leuckart, *J. prakt. Chem.*, [2]**41**, 217 (1890).

(29) German Patent 414,853; *Chem. Zentr.*, **96** II, 774 (1925).

(30) R. H. Barker and C. Barkenbus, *J. Am. Chem. Soc.*, **58**, 262 (1936).

α-chloronaphthalene (0.50 g.) over a 5-min. period. After allowing the mixture to cool, 2.0 g. of α-chloronaphthalene was removed by distillation and had b.p. 125° (12 mm.). The residue was triturated with petroleum ether (b.p. 30–60°), and the resulting solution was chromatographed on 120 g. of Alcoa F-20 activated alumina. The materials to come off the column were 10 mg. (5.8%) of sulfur, m.p. 119–120°; 835 mg. of α-chloronaphthalene (a total recovery of α-chloronaphthalene was 2.84 g., 81%); 200 mg. (15.2%) of 2,4-diphenylthiophene, m.p. 118–119°, lit.[15] m.p. 121.5–123°; and 31.2 mg. (3.7%) of a yellow oil–crystal mixture which had an infrared spectrum identical with that of authentic 1,1-naphthyl disulfide.

2-Hydroxycyclohexylhydrazines. I.[1] Synthesis, Acylation, Acyl Migration, and Dihydrooxadiazine Ring Formation

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Received August 6, 1963

DL-*trans*- and DL-*cis*-2-hydroxycyclohexylhydrazines (*trans*- and *cis*-I) were prepared. The *trans* isomer was correlated with DL-*trans*-2-aminocyclohexanol in two ways, confirming the configuration of *trans*-I and accordingly of *cis*-I. N-Monobenzoyl, N_1,N_2-dibenzoyl, and N_1,N_2,O-tribenzoyl derivatives were derived from I. The N-benzoylated derivatives were treated with hydrogen chloride in anhydrous ethanol (method A) and in water (method B). Method A converted both forms of DL-2-benzoyl-1-(2-hydroxycyclohexyl)hydrazine (VI) and DL-*cis*-1,2-dibenzoyl-1-(2-hydroxycyclohexyl)hydrazine (*cis*-V) to dihydrooxadiazine derivatives (*trans*-X, *cis*-X, and *cis*-IX) with retention. On the same treatment, each form of DL-1-benzoyl-1-(2-hydroxycyclohexyl)hydrazine (IV) was converted to DL-4a,5,6,7,8,8a-hexahydro-3-phenyl-1H-4,1,2-benzoxadiazine (X) with retention, which was identical with the product from VI. This indicated that the reaction involved $N_1 \rightarrow N_2$ acyl migration followed by cyclization reaction to X. This new mode of acyl migration from N_1 to N_2 was found and confirmed in treatments of IV by method B and also with 10% anhydrous ethanolic hydrogen chloride for less time than in method A.

A few studies[2] have been carried out on 2-hydroxyalkyl hydrazines, mainly for synthetic purposes, but nothing appears to be reported concerning the stereochemistry of diastereomeric 2-hydroxyalkyl hydrazines. This prompted us to investigate the stereochemical behavior of DL-2-hydroxycyclohexylhydrazines (I) in comparison with that of the DL-2-aminocyclohexanols which have been widely studied.

DL-*trans*-2-Hydroxycyclohexylhydrazine (*trans*-I) was prepared by the action of hydrazine on *meso*–*cis*-cyclohexene oxide in ethanol. The *trans* assignment was established by correlating it with DL-*trans*-2-aminocyclohexanol[3] in three ways, of which two are described below and the other will appear in the next paper.[4] Treatment with hydroxylamine O-sulfonic acid[2g] converted DL-*trans*-2-aminocyclohexanol to a hydrazine derivative which was identical with *trans*-I. *trans*-I was condensed with acetone to give the N_2-isopropylidene derivative (*trans*-II), the structure of which was supported by the ultraviolet and the infrared spectra: λ_{max}^{EtOH} 227 mμ (ε 8092) (C=N), ν_{max}^{Nujol} 1634 cm.$^{-1}$ (C=N). The Schotten–Baumann benzoylation converted *trans*-II to the N_1-benzoyl, N_2-isopropylidene derivative (*trans*-III) which gave DL-*trans*-2-benzamidocyclohexanol on treatment with sodium amalgam in acetic acid. Thus the results confirmed the configuration of *trans*-I.

Benzoyl derivatives of *trans*-I were prepared and characterized as follows. The N_1-benzoyl, N_2-isopropylidene compound (*trans*-III) underwent deacetonization to give DL-*trans*-1-benzoyl-1-(2-hydroxycyclohexyl)hydrazine hydrochloride (*trans*-IV·HCl) by adding ether as soon as dissolved in 20% anhydrous ethanolic hydrogen chloride in the cold.[5] Support for the structure of *trans*-IV was presented when the compound reverted to *trans*-III by condensation with acetone. Moreover, the infrared spectrum also supported the structure: ν_{max}^{Nujol} 1647 (–CON<) and 1610 cm.$^{-1}$ (–NH_2). *trans*-IV was further treated with benzoyl chloride in aqueous sodium hydroxide to afford a dibenzoyl derivative which was identified as DL-*trans*-1,2-dibenzoyl-1-(2-hydroxycyclohexyl)hydrazine (*trans*-V) by infrared spectrum determination (lack of the ester carbonyl bands). *trans*-V was converted to the N_1,N_2,O-tribenzoate (*trans*-VII) on heating with benzoyl chloride in pyridine; ν_{max}^{Nujol} 1692, 1292, and 1120 (ester), and 1684 and 1664 cm.$^{-1}$ (amide). On the other hand, acylation of *trans*-I with boiling ethyl benzoate gave rise to a monobenzoyl derivative which was identified as DL-*trans*-2-benzoyl-1-(2-hydroxycyclohexyl)hydrazine (*trans*-VI) because of nonidentity with the N_1-benzoyl derivative (*trans*-IV) and also with the O-benzoate (see below) by mixture melting point and infrared comparison. An alternative preparation of *trans*-VI concerns application of the acyl migration reaction described later. In the Schotten–Baumann benzoylation of *trans*-I with 1 equiv. of benzoyl chloride, reaction temperature was found to govern product formation. Room temperature favored the formation of *trans*-V, while chilling at 0–5° resulted in the formation of *trans*-IV accompanied by a small amount of *trans*-VI.

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(4) T. Taguchi, J. Ishibashi, T. Matsuo, and M. Kojima, *J. Org. Chem.*, **29**, 1104 (1964). The correlation was achieved by the conversion of *trans*-I to DL-*trans*-2-aminocyclohexanol through the deamination reaction.

(5) Treatment for a prolonged time or hot caused $N_1 \rightarrow N_2$ benzoyl migration affording *trans*-VI and the use of 10% anhydrous ethanolic hydrogen chloride hot caused ring closure to *trans*-X, as discussed later.