layer chromatography on kieselgel G with 4% methanol in benzene as developer and concentrated sulfuric acid as a spray reagent revealed the presence of two components with R_f 0.14 and 0.46. The faster moving component was identified as 2,3,4-tri-*O*-acetyl-1-*N*-(*p*-tolyl)-5-thio-D-xylosylamine by comparison with authentic material. After a similar reaction sequence on 2.5 g. of *N*-*p*-tolyl-5-thio-D-xylosylamine the residue was taken up in 10 ml. of benzene containing 4% methanol, the mixture was cooled, and the undissolved 2,3,4-tri-*O*-acetyl-1-*N*-(*p*-tolyl)-5-thio-D-xylosylamine was removed by filtration. The filtrate was applied to a column of 200 g. of silica gel, the column was eluted with benzene containing 4% methanol, and the fractions were examined by a thin layer chromatography. The total amount of solid acetate recovered was 2.44 g. or 65%. A further 1.33 g. (35% yield) of a dark sirup was decolorized by stirring for 4 hr. with an equal weight of activated charcoal in 25 ml. of methanol. It was filtered through Celite, and the filter was washed twice with 10 ml. of methanol. Evaporation of the filtrate gave a yellow sirup which was rechromatographed on silica gel using 4% methanol in benzene. The fraction with R_f 0.14 was concentrated and dried over phosphorus pentoxide, $[\alpha]^{20}D$ $-1°$ (*c* 0.79, methanol).

Anal. Calcd. for $C_{18}H_{23}NO_6S$: C, 56.6; H, 6.04; N, 3.69. Found: C, 56.3; H, 6.15; N, 3.62.

Attempted deacetylation of this sirup with barium hydroxide, sodium methoxide, sodium hydroxide, or acid led to complex mixtures. Examination of these reaction mixtures by thin layer chromatography showed the absence of an Amadori product.

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Furano Compounds. II[1a]

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The greater ease of synthesis of simple or condensed furanopyrones carrying a β-methyl substituent in the furan ring over similar compounds lacking such a substituent is discussed. Further, the significance of the presence of a C-methyl group in a number of simple or condensed benzo-γ-pyrone derivatives of plant origin and that of a β-methyl substituent in the furan ring of a few naturally occurring benzofurans has been stressed. This is illustrated by a typical synthesis of 4′-methylfurano(3′,2′:4,3)xanthone and 4′,6-dimethylfurano-(3′,2′:4,3)xanthone.

In part I[1b] of this series, the occurrence of a furan nucleus in a number of related natural products, *viz.*, furanocoumarins, -chromones, -flavones, -isoflavones, and -xanthones, was discussed, and the synthesis of furano(3′,2′:4,3)xanthone, the xanthone analog of the well-known furanoflavone Karanjin, was recorded. This synthesis employs one of the typical methods for the preparation of benzofuran derivatives, *viz.*, a mixed Claisen-type condensation or internal aldol condensation using the appropriately substituted aldehyde or ketone and bromoacetic or bromomalonic ster. Thus, 4-formyl-3-hydroxyxanthone obtained rom 3-hydroxyxanthone was submitted to such a condensation employing bromomalonic ester which effected simultaneous esterification and internal aldol condensation (cyclization).

On the other hand, the corresponding ketones, *viz.*, 4-acetyl-3-hydroxyxanthones, which can also be submitted to a similar internal Claisen condensation leading to the formation of a furan skeleton, can be more easily prepared and in better yields from the hydroxyxanthones through a Friedel–Crafts–Fries reaction. However, while aldehydo esters give rise to furano compounds unsubstituted in the furan ring, the use of substituted ketones for such an internal Claisen condensation results in furano compounds carrying a methyl substituent in the β-position. It may be pointed out that the occurrence in nature of furano compounds carrying a methyl substituent is not uncommon. Thus menthofuran,[2] the chemical constituent of various peppermint oils, and Evodon,[3] a crystalline ketone from the essential oil of *Evodia hortensis*, are β-methylbenzofurans. It could also be expected that a methyl substituent in the β-position may affect the physiological properties of the furano compounds concerned. Further, the presence of a C-methyl group in the benzenoid ring of a number of related, naturally occurring, simple or condensed benzo-γ-pyrone derivatives[4] and its significance in the biogenetic evolution of such compounds made us attempt the synthesis of two typical examples of furanoxanthones, *viz.*, 4′-methylfurano(3′,2′:4,3)xanthone and 4′,6-dimethylfurano(3′,2′:4,3)xanthone, carrying a methyl substituent in the furan ring alone or with such substituents both in the furan ring and in the benzenoid nucleus. The first step in such synthesis, *viz.*, the preparation of the 4-acetyl derivatives from 3-hydroxyxanthone and 3-hydroxy-6-methylxanthone, is based on the valuable observations of Mustafa and Hishmat[5] and of Davies, Scheinmann, and Suschitzky.[6]

Thus, 3-hydroxyxanthone and 3-hydroxy-6-methylxanthone on treatment with acetyl chloride in the presence of aluminum chloride yield the appropriate 4-acetyl derivatives. These have been condensed with bromoacetic ester in presence of potassium carbonate to yield the 3-O-carbethoxy derivatives which on hydrolysis with aqueous potassium hydroxide give the corresponding carboxylic acids. The internal Claisen condensation (cyclization) of the acids has been effected by sodium acetate and acetic anhydride to yield 4′-methylfurano(3′,2′:4,3)xanthone (IIa) and 4′,-

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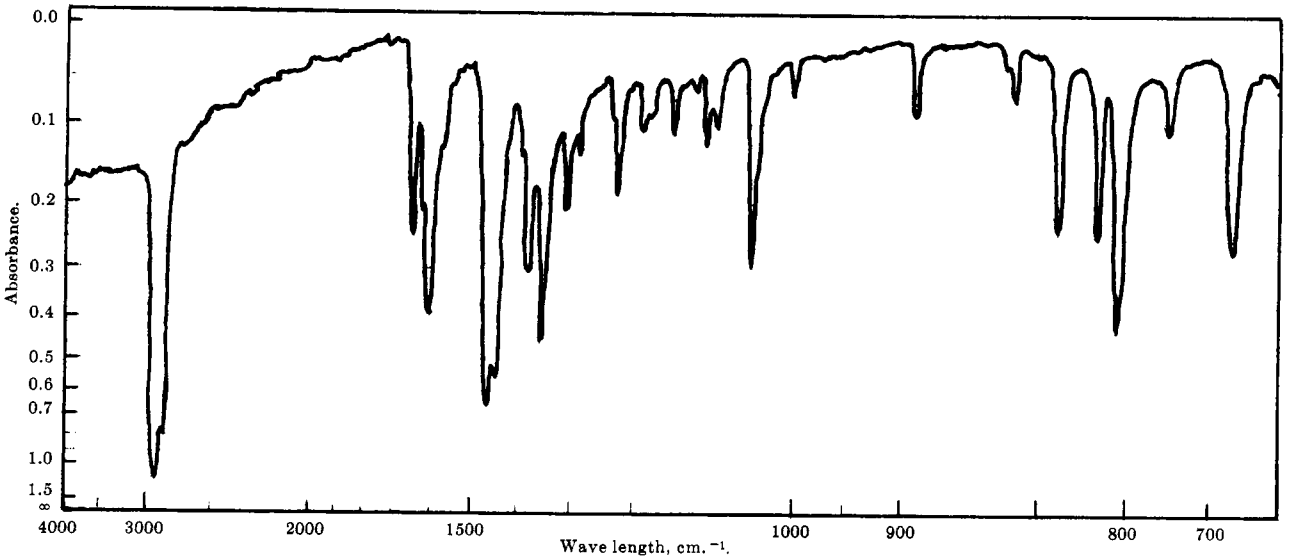


Fig. 1.—Infrared spectrum of 4′-methylfurano(3′,2′:4,3)xanthone (IIa) in Nujol.

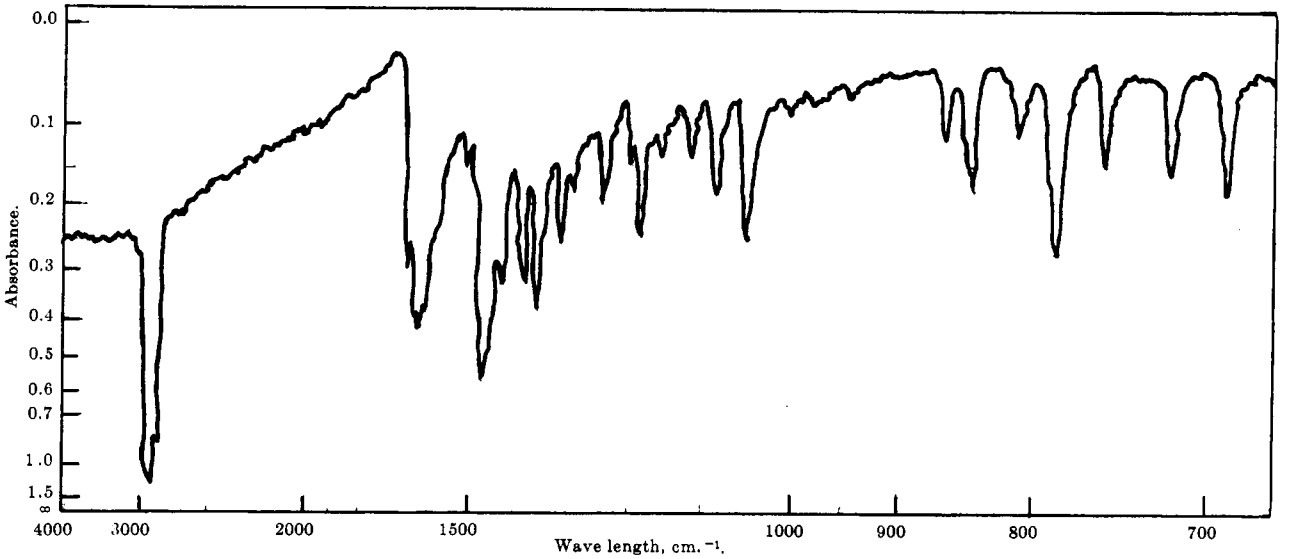
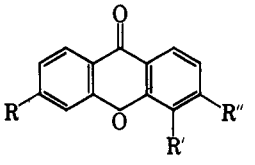


Fig. 2.—Infrared spectrum of 4′,6-dimethylfurano(3′,2′:4,3)xanthone (IIb) in Nujol.

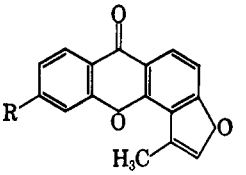
6-dimethylfurano(3′,2′:4,3)xanthone (IIb), cyclization and decarboxylation having occurred simultaneously.

It may be pointed out that 3-hydroxy-6-methylxanthone has been prepared earlier by Shah, *et al.*,[7] by condensing *m*-cresotic acid with resorcinol in the presence of fused zinc chloride and phosphorus oxychloride and subsequently heating the resulting benzophenone with water under pressure. The present procedure involves the modified Ullmann condensation of 2-chloro-4-methylbenzoic acid[8] with *m*-methoxyphenol and subsequent cyclization of the phenoxybenzoic acid and demethylation of the resulting 3-methoxy-6-methylxanthone, thereby dispensing with any reaction under pressure.

The infrared absorption spectra (Fig. 1 and 2) of these furanoxanthenes (IIa and IIb) show the following characteristics (the values in parentheses refer to compound IIb while the other ones refer to compound IIa): strong bands at (a) 1645, 1600 (1645, 1625)



Ia, R = R′ = R″ = H
b, R = H; R′ = $COCH_3$; R″ = H
c, R = H; R′ = $COCH_3$; R″ = $CH_2COOC_2H_5$
d, R = H; R′ = $COCH_3$; R″ = CH_2COOH
e, R = CH_3; R′ = R″ = H
f, R = CH_3; R′ = $COCH_3$; R″ = H
g, R = CH_3; R′ = $COCH_3$; R″ = $CH_2COOC_2H_5$
h, R = CH_3; R′ = $COCH_3$; R″ = CH_2COOH



IIa, R = H
b, R = CH_3

characteristic of xanthone carbonyl[9-12]; (b) 1460 (1460) characteristic of C–C and C–O stretching in

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TABLE I

Compound	Recrystn. solvent	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
4-Acetyl-3-acetoxy-6-methylxanthone	Ethanol	167	$C_{18}H_{14}O_5$	69.68	69.72	4.51	4.82
Ethyl 4-acetyl-6-methyl-9-oxo-3-xanthyloxyacetate (Ig)	Ethanol	154	$C_{20}H_{18}O_6$	67.79	67.48	5.09	5.21
4-Acetyl-6-methyl-9-oxo-3-xanthyl-oxyacetic acid (Ih)	Acetic acid	260	$C_{18}H_{14}O_6$	66.27	66.51	4.29	4.61
4',6-Dimethylfurano(3',2':4,3)-xanthone (IIb)	Ethanol	227	$C_{17}H_{12}O_3$	77.27	77.32	4.55	4.62

derivatives of furan[13-17]; (c) 1044 (1044) characteristic of C–H out-of-plane deformation of furan derivatives[13-17]; and (d) 889 (840) due to "furan ring breathing".[13-17]

Experimental

All melting points are corrected and were determined in open capillary tubes.

4-Acetyl-3-hydroxyanthone (Ib).—A mixture of 3-hydroxyxanthone (Ia, 2.12 g.) in redistilled nitrobenzene (25 ml.) and acetyl chloride (1.6 g.) was treated with aluminum chloride (3.5 g.) in portions as rapidly as it dissolved. The reaction mixture was heated for 3 hr. (steam bath) and kept at room temperature overnight. It was poured into ice–water (150 ml.) containing concentrated hydrochloric acid (25 ml.) and then was steam distilled. The solid residue in the flask then was extracted with hot ethyl acetate. Concentration of the ethyl acetate extract by slow evaporation gave the 4-acetyl-3-hydroxyxanthone, which crystallized from alcohol as pale yellow needles, m.p. 205–206°, 1.4 g. yield. It gave a scarlet-red color with ethanolic ferric chloride.

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 70.87; H, 3.94. Found: C, 70.58; H, 4.12.

Its 2,4-dinitrophenylhydrazone, which was obtained as orange needles from acetic acid, had m.p. 267°.

Anal. Calcd. for $C_{21}H_{14}N_4O_7$: N, 12.90. Found: N, 12.62.

4-Acetyl-3-acetoxyanthone.—This was prepared by heating 4-acetyl-3-hydroxyxanthone (0.1 g.) with acetic anhydride (2 ml.) and few drops of pyridine for 2 hr. and working up in the usual manner. On crystallization from alcohol, it was obtained as colorless needles, m.p. 145°; it gave no color with ethanolic ferric chloride.

Anal. Calcd. for $C_{17}H_{12}O_5$: C, 68.92; H, 4.05. Found: C, 68.67; H, 4.05.

Ethyl 4-Acetyl-9-oxo-3-xanthyloxyacetate (Ic).—4-Acetyl-3-hydroxyxanthone (Ib, 0.64 g.) in acetone (120 ml.) was treated with bromoacetic ester (1.3 g.) and anhydrous potassium carbonate (2.5 g.), and the mixture refluxed vigorously for 20 hr. The reaction product was filtered from the potassium salts and the solvent was removed from the filtrate. The residual oily product on crystallization from alcohol gave ethyl 4-acetyl-9-oxo-3-xanthyloxyacetate as colorless shiny rectangular plates, m.p. 165°, 0.82 g. yield.

Anal. Calcd. for $C_{19}H_{16}O_6$: C, 67.05; H, 4.71. Found: C, 67.21; H, 4.62.

4-Acetyl-9-oxo-3-xanthyloxyacetic Acid (Id).—Ethyl 4-acetyl-9-oxo-3-xanthyloxyacetate (Ic, 0.68 g.) was macerated with potassium hydroxide (10%, 15.0 ml.) and left overnight at room temperature. The orange solution was filtered and chilled and then acidified carefully with dilute hydrochloric acid when a precipitate was obtained. This was filtered and washed with small amount of water. 4-Acetyl-9-oxo-3-xanthyloxyacetic acid crystallized from acetic acid as colorless shiny rods, m.p. 249° dec., 0.58 g. yield.

Anal. Calcd. for $C_{17}H_{12}O_6$: C, 65.37; H, 3.85. Found: C, 65.42; H, 3.92.

4'-Methylfurano(3',2':4,3)xanthone (IIa).—4-Acetyl-9-oxo-3-xanthyloxyacetic acid (Id, 0.31 g.) in acetic anhydride (2 ml.) and sodium acetate (1.0 g.) were heated under reflux for 2 hr. The reaction product was diluted with water, and the precipitate thus obtained was filtered and treated with hot sodium hydrogen carbonate. It was filtered and washed with water. On crystallization from alcohol 4'-methylfurano(3',2':4,3)xanthone was obtained as rectangular shiny plates, m.p. 216°, 0.20 g. yield.

Anal. Calcd. for $C_{16}H_{10}O_3$: C, 76.81; H, 4.00. Found: C, 76.92; H, 4.21.

3-Hydroxy-6-methylxanthone (Ie). A. 2-Carboxy-5-methyl-3'-methoxydiphenyl Ether.—2-Chloro-4-methylbenzoic acid (17.5 g.), potassium carbonate (34 g.), *m*-methoxyphenyl (16.5 g.), copper bronze (0.2 g.), cuprous iodide (0.2 g.), and nitrobenzene (175 g.) were stirred at 160° for 6 hr. The mixture was cooled and diluted with water, the solvent was removed in steam, and the residual aqueous solution was filtered from tar. Acidification to pH 6 precipitated more tar, after removal of which the filtrate was adjusted to pH 2 and the carboxydiphenyl ether was collected. It crystallized from benzene–petroleum ether (b.p. 40–60°) as colorless needles, m.p. 124°, 10.2-g. yield.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.77; H, 5.43. Found: C, 69.48; H, 5.61.

B. 3-Methoxy-6-methylxanthone (Cyclization).—2-Carboxy-5-methyl-3'-methoxydiphenyl ether (7.5 g.) was dissolved in acetyl chloride (75 ml.) and cooled in ice. Concentrated sulfuric acid (1.5 ml.) was added, and the reaction mixture was left for an hour at room temperature. Then acetyl chloride was removed by distillation and the reaction product was poured in ice. The resulting precipitate was collected and crystallized from alcohol when 3-methoxy-6-methylxanthone was obtained as needles, m.p. 132°, 5.80 g. yield.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.01; H, 5.00. Found: C, 74.87; H, 5.12.

C. Demethylation.—3-methoxy-6-methylxanthone (4.5 g.) dissolved in xylene (100 ml.) was treated with aluminum chloride (9.0 g.) and kept on a boiling water bath for 2 hr. The reaction mixture, after decomposition with ice, was steam distilled to remove the solvent. The solid residue thus obtained was dissolved in sodium hydroxide (10%) and, after treatment with animal charcoal, was acidified to get the hydroxyxanthone. It crystallized from acetic acid in small yellow needles, m.p. 318–319°, 4.2 g. yield (Shah, *et al.*,[7] report the same melting point).

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.33. Found: C, 74.52; H, 4.51.

4-Acetyl-3-hydroxy-6-methylxanthone (If). A.—3-Hydroxy-6-methylxanthone (Ie, 2.26 g.) in redistilled nitrobenzene (25 ml.) and acetyl chloride (1.6 g.) was treated with aluminum chloride (3.5 g.) in portions as rapidly as it dissolved. The reaction mixture was heated for 3 hr. (steam bath) and kept at room temperature overnight. Subsequent work-up of the reaction product as in the case of 4-acetyl-3-hydroxyxanthone gave the crude 4-acetyl-3-hydroxy-6-methylxanthone and If on crystallization from alcohol was obtained as shiny needles, m.p. 243°, 1.68 g. yield. It gave a scarlet-red color with ethanolic ferric chloride.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.48. Found: C, 71.91; H, 4.51.

Its 2,4-dinitrophenylhydrazone which was obtained as orange needles from acetic acid had m.p. 276°.

Anal. Calcd. for $C_{22}H_{16}N_4O_7$: N, 12.50. Found: N, 12.32.

B.—Redistilled acetic anhydride (5.0 g.) in *sym*-tetrachloroethane (30.00 ml.) was added dropwise to a stirred suspension of powdered aluminum chloride (13.3 g.) and 3-hydroxy-6-methylxanthone (4.1 g.) in *sym*-tetrachloroethane (90.00 ml.). The dark mixture was heated with stirring on a steam bath for 3 hr. and then poured onto crushed ice and concentrated hydrochloric acid (50.00 ml.). The resulting mixture was steam distilled to remove *sym*-tetrachloroethane, and the residue was taken up in ethyl

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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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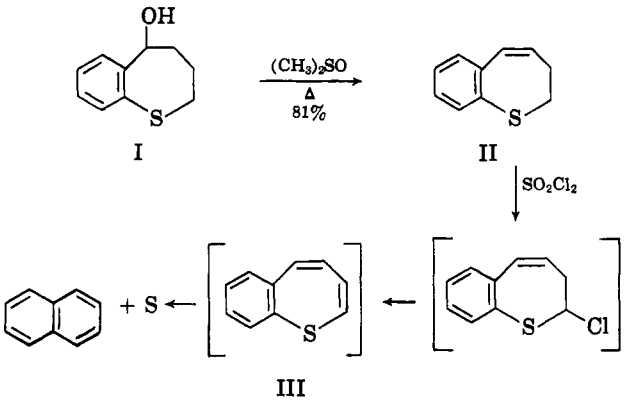
This paper describes some observations made during a study directed toward the synthesis of benzo[*b*]thiepin. The synthesis and structure of 5-hydroxy-2-chloro-4,5-dihydrobenzo[*b*]thiepin (VII) and its acetate (VIII) are reported. Treatment of VII with *p*-toluenesulfonic acid produced an ester (XI). 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.

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