methylcyclopropane (ret. time, 7.8 min.), 2-methyl-1-butene (ret. time, 11.6 min.) and 2-methyl-2-butene (ret. time, 14.6 min.). The latter three compounds were present in ratios of 69:18:13.

For further identification the reaction mixture was fractionated. After three distillations 1,1-dimethylcyclopropane was obtained 94% pure (b.p. 20–20.5°) and showed an infrared spectrum identical to that of an authentic sample (prepared from 1-chloro-2,2-dimethylcyclopropane by reduction with sodium and methanol in tetrahydrofuran[8]. The two methylbutenes could not be separated by distillation and were trapped from the vapor phase chromatogram. Identification was achieved by their infrared spectra. The total yield of C_5-hydrocarbons was determined by v.p.c. of the various distillation fractions to be 29%.

2-Methylbutan *p*-Toluenesulfonylhydrazone.—To a solution of 2-methylbutanal[20] (5.0 g., 0.058 mole) in methanol (20 ml.) was added a solution of *p*-toluenesulfonylhydrazide (16.5 g., 0.058 mole) in 60° methanol (40 ml.). The mixture was cooled at once with an ice-bath and the product was allowed to crystallize at −20° for 2 hours. The precipitate was filtered off and washed with cold (−20°) methanol and dried *in vacuo* (9.2 g., 45%). A sample, recrystallized from methanol for analysis, melted at 73–74°.

Anal. Calcd. for $C_{12}H_{18}N_2O_2S$ (354.8): C, 40.62; H, 5.11. Found: C, 40.36; H, 5.26.

Decomposition of 2-Methylbutanal *p*-Toluenesulfonylhydrazone with Sodium Methoxide.—A three-neck flask was equipped with stirrer, dropping funnel, thermometer and a 1-ft. uninsulated Vigreux column which was connected with a receiving flask cooled to −70°. Sodium methoxide (2.7 g., 0.05 mole) was suspended in diethylene glycol dimethyl ether (50 ml.). The mixture was heated to 160° and a solution of 2-methylbutanal *p*-toluenesulfonylhydrazone (8.0 g., 0.022 mole) in diethylene glycol dimethyl ether (75 ml.) was added dropwise. The heating of the mixture was regulated so as to permit the olefins, cyclopropanes and the methanol to distill into the receiving flask. After addition was complete (70 min.) the apparatus was flushed with nitrogen for 10 min. to drive all the volatile products into the receiver. To the contents of the receiver heptane (20 ml.) was added and the mixture was washed with ice-water to remove the methanol; v.p.c. analysis established the composition. The following compounds were identified by their retention times: *trans*-dimethylcyclopropane (ret. time at 24°, 35 ml. helium/min., 14.08 min.) 2-methyl-1-butene (ret. time, 16.02 min.) ethylcyclopropane (ret. time, 19.65 min.) and *cis*-dimethylcyclopropane (ret. time, 20.52 min.). The compounds were present in concentration ratios of 12:63:20:5. The peak of *cis*-dimethylcyclopropane was separated only incompletely from ethylcyclopropane. The concentration ratio of these compounds was determined by comparison of the shape of the curve with those of synthetic mixtures of the two cyclopropanes. All compounds were further identified by their infrared spectra after trapping the fractions from the vapor phase chromatogram.

Distillation of the product mixture over a short Vigreux column separated the C_5-hydrocarbons from higher boiling (mainly small amounts of diethylene glycol dimethyl ether). The fraction distilling from 30 to 40° (1.25 g., 0.18 mole, 82%) was collected and consisted entirely of the above-mentioned C_5H_{10} hydrocarbons.

Stability of *n*-Butyllithium in the Presence of 1-Chloropentane.—To a solution of *n*-butyllithium (0.053 mole) in diethyl ether (100 ml.) at −30° was added 1-chloropentane (6.2 g., 0.058 mole). After 1 hour an aliquot was withdrawn and and the concentration of *n*-butyllithium was determined by the double titration method[21] (0.047 mole, 89%).

Acknowledgment.—The author gratefully acknowledges partial financial support by a grant from Research Corporation.

---

[20] Z. Csuros, K. Zech and T. Pfliegel, *Hung. Acta Chim.*, **1**, 31 (1946).

[21] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN.]

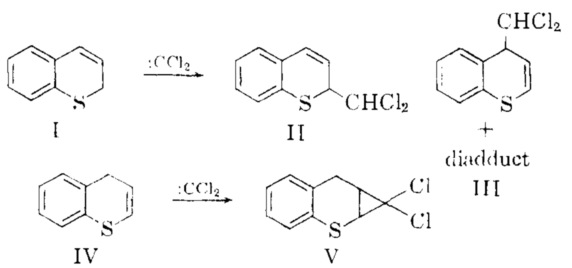
The Reaction of Dichlorocarbene with 2,3-Chromene and 3,4-Chromene[1]

BY WILLIAM E. PARHAM AND LAURENCE D. HUESTIS

RECEIVED OCTOBER 5, 1961

The reaction of dichlorocarbene with 2,3- and 3,4-chromene affords cyclopropyl adducts in high yield. No insertion products, as found for the analogous 2,3-thiochromene, were evident. The derived cyclopropyl adducts are thermally quite stable and unlike 2-oxa-7,7-dichloronorcarane, which readily loses hydrogen chloride to give 3-chloro-dihydroöxepine, they do not afford derivatives of benzoxepine when decomposed in the presence of hot quinoline.

A previous study[2] of the reaction of dichlorocarbene with the thiochromenes I and IV established that the course of reactions was dependent upon the position of the double bond in the olefin. Thus, 3,4-thiochromene (I) reacted with dichlorocarbene to give two isomeric insertion products (II and III) and a diadduct of undetermined structure. However, none of the dichlorocyclopropane adduct was formed. By contrast, 2,3-thiochromene (IV) reacted with dichlorocarbene to give only a high yield of 1,1-dichlorocyclopropa(b)(1)thiobenzopyran (V). In view of these results, it was considered of particular interest to determine the course of reaction of the corresponding oxygen analogs (XIII and XVII) with dichlorocarbene.



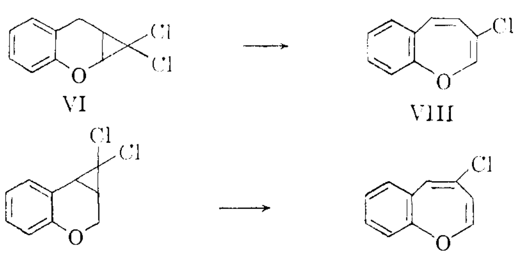
Interest in the chromenes was also stimulated by the possibility that the derived cyclopropane adducts might serve as starting material for the preparation of chlorobenzoxepines, since it had been shown[3] that the dichlorocyclopropane adduct of dihydropyran could be readily converted to 2,3-dihydro-6-chloroöxepine by pyrolysis in quinoline at 140°. The b and c isomers of 1,1-dichlorocylopropa(1)benzopyran (VI and VII, respectively) might, therefore, be expected to form 3- and 4-chlorobenzoxepine (VIII and IX, respectively) by a similar reaction.

---

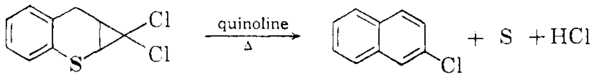
[1] This work was supported by a grant from the National Science Foundation (GSF-G14458).

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

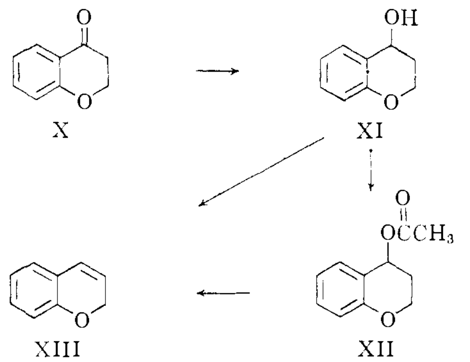
[3] E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960).



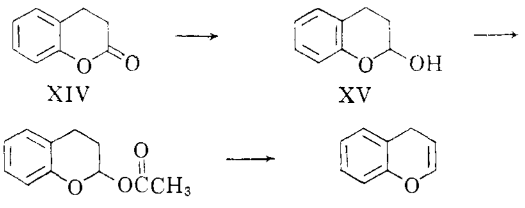
A study of the thermal rearrangement of VI and VII was of further interest since it had been shown[2] that V, which is the sulfur analog of VI, eliminated sulfur upon heating in quinoline to give 2-chloronaphthalene as the only recognizable product.



Both the isomeric chromenes were known,[4] but their synthesis was accomplished more easily by the procedures summarized in the accompanying formulas.

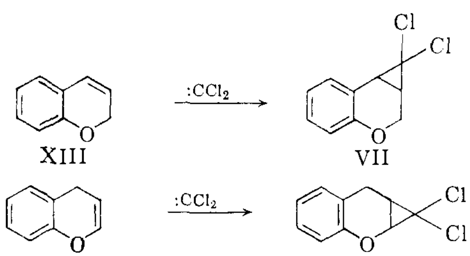


It was found that 3,4-chromene (XIII) could be formed in 58% yield by dehydration of 4-chromanol (XI) with dimethyl sulfoxide,[5] or in 89% yield by a two-step conversion involving a Kraft pyrolysis of 4-chromanyl acetate (XII).

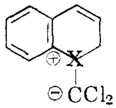


The reduction of dihydrocoumarin (XIV) to the known 2-chromanol (XV) is of interest since this is believed to be the first example of a reduction of a lactone to a hemiacetal by the use of lithium tri-*t*-butoxyaluminohydride.[6,7] The structure of XV was confirmed by the absence of a carbonyl band in the infrared spectrum and by the formation of the 2,4-dinitrophenylhydrazone of 3-(*o*-hydroxyphenyl)-propanal by treatment of XV with 2,4-dinitrophenylhydrazine.

The reaction of dichlorocarbene with the two chromenes was carried out in the usual manner using the ethyl trichloroacetate–sodium methoxide method[8] for generation of dichlorocarbene. In both cases, solid dichlorocarbene monoadducts were formed in high yields. Thus, XIII gave 1,1-dichlorocyclopropa(c)(1)benzopyran (VII) in 92% yield as a colorless low melting solid. A combination of chemical, ultraviolet and infrared data (see Experimental) showed that VII could not be a dichlorocarbene insertion product. The nuclear magnetic resonance spectrum of the product confirmed this conclusion, and further indicated that the product could have only the cyclopropane structure. By a similar combination of methods, it was established that the product (83% yield) obtained by reaction of dichlorocarbene with XVII was 1,1-dichlorocyclopropa(b)(1)benzopyran (VI).



It is of interest to note that of the two chromenes (XIII and XVII) and two analogous thiochromenes (I and II) studied, only one, 3,4-thiochromene (I), reacts with dichlorocarbene by insertion. While the difference noted is subject to considerable speculation as to mechanism, we feel that rationalization is provided by the difference in nucleophilicity of the hetero atom and the double bond[2] which are in competition for the electrophilic carbene. It is concluded that only I reacts with dichlorocarbene to give XVIII, a type of intermediate presumed to form prior to insertion.



XVIII

As noted with V, the cyclopropane adducts VI and VII show unusual thermal stability as compared with 2-oxa-7,7-dichloronorcarane. A capillary sample of VII does not begin to decompose until 240°, and a similar sample of VI shows no decomposition until 210°. This thermal stability is also evident in the presence of amine solvents as shown by the recovery of VII unchanged after prolonged refluxing in triethylamine, and the absence of any important amounts of dibenzylammonium chloride after heating VII for one hour at temperatures less than 200°. At temperatures above 220°, hydrogen chloride is readily eliminated as evidenced by high yields of dibenzylammonium chloride.

The pyrolysis of VI and VII also provides a contrast to that of the cyclopropane adduct V.

---

(4) P. Maitte, *Ann. Chim.*, **9**, 431 (1954).

(5) Private communication from V. J. Traynelis, University of Notre Dame.

(6) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958).

(7) H. C. Brown, *J. Chem. Educ.*, **38**, 173 (1961).

(8) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 17 (1959).

Whereas V eliminates sulfur to give 2-chloronaphthalene, neither VI nor VII gave 2-chloronaphthalene upon pyrolysis. Pyrolysis of VI in quinoline gave no distillable products at all, while pyrolysis of VII in quinoline gave a low yield of a yellow liquid which boiled near the expected boiling point of 4-chlorobenzoxepine. However, a nuclear magnetic resonance spectrum indicated that the product could not be 4-chlorobenzoxepine since the spectrum showed a characteristic splitting arising from three methyl hydrogens being split by an adjacent hydrogen. The identity of this material was not established.

Experimental

4-Chromanone (X).—A mixture of 100 g. (0.60 mole) of β-phenoxypropionic acid and 350 g. of polyphosphoric acid was heated to a maximum of 75° for 1.25 hours. After allowing to stand at room temperature for 4 hours, the red mixture was poured into 1 liter of water and the resulting mixture was cooled. The solid was filtered and dissolved in ether. The aqueous red filtrate was extracted with three 200-ml. portions of ether. The combined ether fractions were extracted with 200 ml. of water followed by 200 ml. of 10% sodium carbonate solution. After drying the solution (Na_2SO_4), the ether was removed and the dark red product was distilled through a spiral wire column. The yield of colorless 4-chromanone was 77.6 g. (89%), b.p. 78–80° (0.30 mm.). This distillate solidified to a white solid, m.p. 39° (lit.[9] b.p. 160° (50 mm.), m.p. 38.5°).

4-Chromanol (XI).—A solution of 145 g. (0.98 mole) of 4-chromanone in 200 ml. of anhydrous ether was added over a period of 1.25 hours to a mixture of 15 g. (0.40 mole) of lithium aluminum hydride in 500 ml. of anhydrous ether. After refluxing the mixture for an additional hour, a saturated solution of ammonium chloride was cautiously added to the stirred product. The ether was decanted and the inorganic salts were extracted with ether. Ether was removed from the dry (Na_2SO_4) extract, and the product was crystallized from cyclohexane which contained about 5% benzene. The yield of colorless needles was 138 g. (94%), m.p. 40–41.5°. This 4-chromanol was used in subsequent reactions without further purification.

Anal. Calcd.[10] for $C_9H_{10}O_2$: C, 71.97; H, 6.72. Found: C, 72.29; H, 6.82.

4-Chromanyl Acetate (XII).—A solution of 115 g. (0.77 mole) of 4-chromanol, 370 ml. (3.9 moles) of acetic anhydride and 45 ml. of anhydrous pyridine was refluxed for 5 hours. The acetic acid, acetic anhydride and pyridine were removed by distillation at 2 mm. The residue was distilled through a spiral wire column to give 143 g. (97%) of nearly colorless ester, b.p. 79–83° (0.02–0.06 mm.), n^{25}_{D} 1.5302; analytical sample: b.p. 81–82° (0.03 mm.), n^{27}_{D} 1.5296; infrared spectrum: 3030w, 2970m, 2880w, 1733s, 1615m, 1592m, 1500s, 1465m, 1438w, 1378m, 1320w, 1280w, 1250–1235s, 1205w, 1160w, 1125m, 1100w, 1064s, 1025s, 975m, 935w, 887m, 860w, 763s, 735w, cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.59; H, 6.45.

3,4-Chromene (XIII). A. By Dehydration of 4-Chromanol (XI) with Dimethyl Sulfoxide.—A solution of 15.0 g. (0.10 mole) of 4-chromanol and 55 g. (0.70 mole) of dimethyl sulfoxide (purified by drying over sodium hydroxide for a week and then distilling)[5] was heated at 170–175° for 12 hours (under N_2). The yellow solution was extracted with three 100-ml. portions of petroleum ether (30–60°). After drying the solution (Na_2SO_4), the petroleum ether was removed and the residual liquid distilled. A yield of 7.6 g. (58%) of colorless liquid was obtained, b.p. 51–53° (1.2 mm.), n^{25}_{D} 1.5883.

B. By Kraft Pyrolysis of 4-Chromanyl Acetate (XII).—A total of 88.0 g. (0.458 mole) of 4-chromanyl acetate was dropped over 155 minutes onto a vertical 28-cm. glass helice packed column which was heated to 410° by an automatically controlled electric furnace. Nitrogen was used as carrier gas and it was set at a flow rate of 25 ml./minute. After addition of the ester, the hot column was flushed with 50 ml. of benzene. The resulting orange solution was washed with 100 ml. of water and 100 ml. of saturated sodium bicarbonate solution and then dried (Na_2CO_3). After removal of the benzene, the residue was distilled to give 55.4 g. (92%) of colorless 3,4-chromene, b.p. 49–51° (0.9 mm.), n^{25}_{D} 1.5882; analytical sample: b.p. 49.5–50.0° (1.0 mm.), n^{25}_{D} 1.5879 (lit.[4] b.p. 91° (13 mm.), n^{16}_{D} 1.5923); infrared spectrum: 3040w, 2970w, 2840m, 1644m, 1613m, 1480m, 1495s, 1470s, 1400m, 1380m, 1315w, 1285w, 1230s, 1210s, 1165w, 1125s, 1052m, 935m, 860w, 790w, 760s, 685m, cm.$^{-1}$. The ultraviolet spectrum showed $_{\max}^{95\%\ \mathrm{EtOH}}$ 263 mμ (log ε 3.60).

Anal. Calcd. for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.57; H, 6.41.

2-Chromanol (XV).—A solution of 20.7 g. (0.140 mole) of dihydrocoumarin in 100 ml. of dry redistilled tetrahydrofuran was cooled to about −60° in a acetone–Dry Ice-bath (under N_2). A solution of 35.4 g. (0.140 mole) of lithium tri-*t*-butoxyaluminohydride (Metal Hydrides, Inc.) in 300 ml. of tetrahydrofuran was added to the stirred solution over a period of 75 minutes. The mixture was allowed to warm to room temperature (1.5 hours), and was poured into 400 ml. of ice-water. The resulting white mush was filtered (Filter-cel) and the nearly colorless filtrate was extracted with four 100-ml. portions of ether. After drying the combined extracts (Na_2SO_4), the ether was removed and the residue fractionated. A total of 10.3 g. (49%) of colorless, viscous distillate was obtained, b.p. 90–91° (0.10 mm.). The distillate solidified to a white solid upon cooling; analytical sample: b.p. 88–89° (0.05 mm.), n^{21}_{D} 1.5620, m.p. 28° (lit.[4] b.p. 139° (12.5 mm.)); infrared spectrum: 3400m, 3020w, 2930w, 1613w, 1588m, 1497s, 1465m, 1360w, 1307w, 1280w, 1230s, 1195w, 1175w, 1140w, 1120m, 1100m, 1065a, 1030w, 1005m, 960s, 940vw, 915w, 873m, 835vw, 820w, 760s, 708w, cm.$^{-1}$.

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.97; H, 6.72. Found: C, 71.99; H, 6.89.

2,4-Dinitrophenylhydrazone of 3-(*o*-Hydroxyphenyl)-propanal.—A solution of 2.0 g. (0.0145 mole) of dihydrocoumarin in 15 ml. of tetrahydrofuran was treated with 3.4 g. (0.014 mole) of lithium tri-*t*-butoxyaluminohydride in 25 ml. of tetrahydrofuran as before. The resulting filtrate was added to an acidic aqueous ethanol solution of 2,4-dinitrophenylhydrazine. The orange solid weighed 3.3 g. (75%) and melted at 179–182°. Three crystallizations of this product from aqueous ethanol gave a crystalline orange solid, m.p. 182–183° (lit.[4] m.p. 185°).

Anal. Calcd. for $C_{15}H_{14}N_4O_5$: C, 54.56; H, 4.27. Found: C, 54.88; H, 4.33.

2-Chromanyl Acetate (XVI).—The method of preparation was similar to that for the other isomer XII. From 31.0 g. (0.206 mole) of 2-chromanol (reflux time 1.25 hours), there was obtained 31.5 g. (79%) of a fragrant, colorless ester, b.p. 86–88° (0.06 mm.), n^{25}_{D} 1.5249; analytical sample: b.p. 88–89° (0.10 mm.), n^{25}_{D} 1.5268, m.p. 36.5° (solidifies upon standing to a white solid); infrared spectrum: 3020vw, 2900w, 1742s, 1610w, 1585m, 1495s, 1400m, 1375m, 1335w, 1308w, 1250w, 1210s, 1180s, 1125m, 1110w, 1055m, 1010s, 960s, 920m, 895w, 825w, 755s, cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.91; H, 6.53.

2,3-Chromene (XVII).—A total of 31.2 g. (0.162 mole) of 2-chromanyl acetate was dropped onto a glass helice packed column (410°) over a period of 90 minutes. The flow rate of nitrogen gas was set at 26 ml./minute. After flushing the column with 30 ml. of benzene, the resulting orange solution was extracted once with 50 ml. of water and once with 50 ml. of saturated sodium bicarbonate solution. After drying the solution (Na_2CO_3), the benzene was removed and the residue fractionated to give 15.4 g. (72%) of a colorless, mobile liquid, b.p. 43–45° (1.3 mm.), n^{25}_{D} 1.5551; redistilled sample: b.p. 44° (1.3 mm.), n^{25}_{D} 1.5551 (lit.[4] b.p. 77° (9 mm.), $n^{12.5}_{\mathrm{D}}$ 1.5641); infrared spectrum: 3010w, 2800w, 1665s, 1610vw, 1580m, 1490s, 1460m, 1440vw, 1385vw, 1343w, 1302m, 1273s, 1250s, 1203w, 1180s, 1115s, 1050s, 1035w, 955vw, 930vw, 900vw, 800vw, 755s, 740w, cm.$^{-1}$.

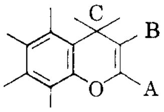
The nuclear magnetic resonance spectrum of 2,3-chromene run as a 10% solution in carbon tetrachloride with 1% tetramethylsilane as reference gave: 6.66τ, singlet, weight 2.17, assigned to hydrogens at C; 5.17τ, multiplet, weight

---

[9] S. G. Powell, *J. Am. Chem. Soc.*, **45**, 2708 (1923).

[10] Analytical sample prepared by S. Mierzwa; m.p. 41.5–43°.

0.83, assigned to hydrogen at B; 3.62τ, doublet, weight 0.76, assigned to hydrogen at A; 3.09τ, singlet, weight 4.00, assigned to the aromatic hydrogens.

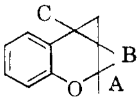


Compound XVII reduced a methanolic solution of potassium permanganate immediately, and gave a red-orange precipitate with 2,4-dinitrophenylhydrazine (consistent with a vinyl ether).

Reaction of 3,4-Chromene with Dichlorocarbene. A. Ethyl Trichloroacetate–Sodium Methoxide Method.[8]—A mixture of 20 g. (0.37 mole) of sodium methoxide, 25.4 g. (0.192 mole) of 3,4-chromene and 150 ml. of dry olefin-free petroleum ether (30–60°) was cooled (under N_2) in an ice–Dry Ice-bath. After 1 hour, 67 g. (0.35 mole) of ethyl trichloroacetate was added all at once to the cold orange mixture. Within 10 minutes, a rather exothermic reaction occurred and it was necessary to use a Dry Ice condenser to prevent loss of material. The mixture was stirred in the cold for 7 hours and then allowed to warm up overnight. After adding 100 ml. of water, the layers were separated and the aqueous layer was extracted with 100 ml. of petroleum ether (30–60°) and 100 ml. of ethyl ether. After drying the combined organic layers (Na_2SO_4), the ethers were removed by evaporation. The dark red residue was distilled to give 37.9 g. (92%) of nearly colorless distillate, b.p. 89–91° (0.15 mm.). This distillate soon solidified to a white solid which was crystallized from petroleum ether (30–60°) to give colorless needles, m.p. 46–47°; analytical sample: m.p. 46.5–47.5°; Infrared spectrum: 3020w, 2950w, 2860w, 1615w, 1590m, 1500s, 1475m, 1460w, 1370w, 1340w, 1312m, 1270m, 1232s, 1213w, 1195w, 1125m, 1105m, 1082w, 1068w, 1042w, 1000w, 980m, 940w, 830m, 802w, 758s, cm.$^{-1}$. A capillary sample of this 1,1-dichlorocyclopropa[c][1]benzopyran (VII) darkened about 240° and decomposed with evolution of gas about 265°; VII does not decolorize a methanol solution of potassium permanganate.

Anal. Calcd. for $C_{10}H_8Cl_2O$: C, 55.83; H, 3.77. Found: C, 55.79; H, 4.01.

The nuclear magnetic resonance spectrum, run as before had: 7.77τ, multiplet, weight 1.05, assigned to hydrogen at B; 7.30τ, doublet, weight 1.06, assigned to the hydrogen at C; 5.72τ, doublet, weight 2.25, assigned to the hydrogens at A; 3.08τ, multiplet, weight 4.00, assigned to the aromatic hydrogens.

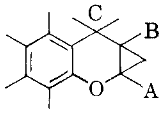


B. Sodium Trichloroacetate Method.[11]—A mixture of 20.9 g. (0.113 mole) of sodium trichloroacetate, 10.1 g. (0.076 mole) of 3,4-chromene and 50 ml. of dry 1,2-dimethoxyethane was refluxed under nitrogen for 8.5 hours. The mixture was filtered and the 1,2-dimethoxyethane was removed. The residue was then fractionated to give two turbid main fractions (A, b.p. 40–43°, and B, b.p. 91–92° at 0.06 mm.). Both fractions were dissolved in ether. After removal of the ether from the dried solution (Na_2SO_4), A and B were again distilled. Fraction A gave 3.9 g. (39% recovery) of 3,4-chromene, b.p. 44–46° (0.25 mm.), $n^{25}D$ 1.5883, and fraction B gave 4.0 g. (24% or 40% based on starting material consumed) of VII, b.p. 95–96° (0.35 mm.). The colorless distillate VII solidified as before and after one crystallization from petroleum ether (30–60°) it appeared as colorless needles, m.p. 46–47°. The infrared spectrum was identical with the product prepared by the ethyl trichloroacetate–sodium methoxide method. A mixed melting point with a sample prepared by the other method showed no depression.

Reaction of 2,3-Chromene with Dichlorocarbene.—The ethyl trichloroacetate–sodium methoxide method was used and the procedure was identical to that described for 3,4-chromene. A total of 28.5 g. (0.150 mole) of ethyl trichloroacetate was added all at once to a cold mixture of 8.5 g. (0.158 mole) of sodium methoxide, 5.0 g. (0.038 mole) of 2,3-chromene and 80 ml. of dry, olefin-free petroleum ether (30–60°). The product was processed as previously described and 6.8 g. (83%) of 1,1-dichlorocyclopropa(b)(1)benzopyran (VI) was obtained by distillation, b.p. 90–91° (0.29 mm.). The distillate soon solidified to a white solid whereupon it was crystallized twice from petroleum ether (30–60°) to give colorless compact crystals, m.p. 66–67°; infrared spectrum: 2995w, 2870w, 1612w, 1585s, 1520w, 1500m, 1490s, 1460s, 1435w, 1335m, 1305w, 1265s, 1255w, 1205s, 1135w, 1108m, 1060m, 1048m, 968m, 933w, 865s, 800m, 775w, 755vs cm.$^{-1}$. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ EtOH}$ 273 mμ (log ε $3\rightleftarrows 26$), 280 mμ (log ε 3.18). A capillary sample of VI darkened about 210° and decomposed with evolution of gas about 255°; VI did not decolorize a methanol solution of potassium permanganate.

Anal. Calcd. for $C_{10}H\ Cl_2O$: C, 55.83; H, 3.77. Found: C, 55.78, H, 3.95.

The nuclear magnetic resonance spectrum of this product showed the peaks: 7.95τ, multiplet, weight 0.94, assigned hydrogen at B; 6.99τ, doublet, weight 1.70, assigned to hydrogens at C; 5.94τ, doublet, weight 0.96, assigned to hydrogen at A; 3.10τ, singlet, weight 4.00, assigned to aromatic hydrogens.



Attempted Ring Expansion of 1,1-Dichlorocyclopropa[c]-[1]benzopyran (VII). A. Pyrolysis in Quinoline.—A mixture of 10.0 g. (0.046 mole) of VII was refluxed in 30 ml. of practical grade quinoline for 45 minutes (under N_2). The resulting black tarry liquid was extracted with petroleum ether (30–60°). This solution was then extracted with 1 *M* hydrochloric acid until the washings were acidic (*p*H 2, *p*H paper). After drying the organic layer (Na_2CO_3) and removing the petroleum ether, the residue was distilled from a Koelsch flask to give 1.7 g. of an orange liquid. A total of 7.24 g. of this orange distillate was fractionated in a spiral wire column at 0.10 mm. However, separation into pure fractions proved impossible. Most of the yellow distillate boiled over a range of 48–55° (0.10 mm.). Spectra were taken on one fraction, b.p. 53.5–54°, $n^{25}D$ 1.5890: infrared spectrum: 3010m, 2940w, 2900w, 1630m, 1602m, 1575m, 1510w, 1488s, 1458s, 1370m, 1360m, 1320m, 1255m, 1235s, 1205s, 1188w, 1155w, 1125m, 1088m, 1055s, 1035w, 1005w, 990m, 940w, 910s, 877m, 852m, 818m, 795w, 760s, cm.$^{-1}$. A nuclear magnetic resonance spectrum showed: 8.56τ, doublet, weight 3.00; 7.55τ, singlet (?), weight 0.83; 5.16τ, quadruplet, weight 1.00: 3.61τ, singlet, weight 0.86; 3.21τ, singlet (?), weight 4.41. No satisfactory analysis could be obtained for any fraction. If allowed to stand in diffuse light at room temperature, the product turned black within a few days.

B. Pyrolysis in Dibenzylamine.—A mixture of 5.0 g. (0.023 mole) of VII in 15 ml. (0.076 mole) of dibenzylamine was heated to 220–240° for 1.5 hours (under N_2). The resulting dark red crystalline mass was mixed with ether and filtered to give 5.2 g. (96%) of crude dibenzylammonium chloride. The crude product was crystallized from hot water to give colorless plates, m.p. 261–263° (lit.[12] m.p. 256°). This product did not depress the melting point of an authentic sample made from dibenzylamine and hydrochloric acid.

Distillation of the filtrate gave almost no product other than dibenzylamine. Several grams of material remained in the distillation flask. Upon cooling, this material set to a red polymeric glass.

Pyrolysis of 1,1-Dichlorocyclopropa[b][1]benzopyran (VI) in Quinoline.—The procedure was identical with that described for the pyrolysis of VII. No distillable product was obtained.

---

(11) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

(12) K. Kindler, von W. Dehn and W. Peschke, *Ann.*, **485**, 113 (1931).