168–170°, pure according to nmr data. No other product could be eluted from the column.

The **nmr spectrum of 10** (100 Mc) showed the following signals: methyls, C-5 at 1.02 (d, J = 6 cps) and C-10 at 1.9 (s); ring methylenes between 1.72 and 2.3 (complex); ring methines, H_5 at 2.50, H_6 at 2.65, H_7 at 3.41 with $J_{H_5H_6}$ = 14 cps, $J_{H_6H_7}$ = 4.8 cps, and $J_{H_7H_8}$ = 7 cps; vinyl protons, exocyclic at 5.70 (s) and 6.58 (s), H_2 at 7.41, and H_3 at 5.90 ppm ($J_{H_2H_3}$ = 10 cps).

In double resonance experiments at 100 Mc, the protons at C-5 and C-6 gave partially overlapping, complex signals centered at 2.5 and 2.65, respectively, while H_7 appeared as a poorly resolved doublet at 3.41. Upon irradiation at H_7 the vinyl signals were not affected but H_6 was converted into a doublet with $J_{H_5H_6}$ = 14 cps. The area near the vinyl methyl at 1.90 was also affected, indicating the general location of the C-8 protons. The location of H_5 was ascertained by irradiating at 2.50, which converted the C-5 methyl doublet into a singlet. Conversely, irradiation at the C-5 methyl converted the complex H_5 signal into a doublet with $J_{H_5H_6}$ = 14 cps. Irradiation at H_6 sharpened H_7 into a peak with a half width of 7 cps, while irradiation at H_8 near 1.90 converted H_7 into a doublet with $J_{H_6H_7}$ = 4.8 cps. Finally, from the half width measurement of the H_7 signal (about 7 cps), one finds that $J_{H_7H_8}$ is not more than 7 cps.

Circular dichroism values in dioxane were as follows: 371 (+2.46), 353 (+4.06), 342 (+3.91), 298 (−14.90), 229 (−1.99), positive at shorter wavelengths; in ethanol, they were 344 (+5.65), 302 (−15.53), and 229 (−1.62), strongly positive at shorter wavelengths. The same solutions showed uv maxima at 298 and 230 (infl) in dioxane and at 304 and 230 nm (infl) in ethanol For comparison, in ethanol a sample of 4 containing about 20% 10 gave values of 344.5 (+4.98), 304 (−20.86), and 237 (−1.56), strongly positive at shorter wavelengths.

The methyl ester was obtained by diazomethane treatment and had mol wt 260 (mass spectroscopy). A rotation was determined on a mixture of 4 and 10 which was made 50% in each component by a preliminary treatment on a smaller column of silica gel. The observed value was $[\alpha]_D$ −383° (c 0.11, in $CHCl_3$), which corresponds to −325° for 10. The ir spectrum of 10 in $CHCl_3$ showed absorptions at 5.9, 6.2, 6.18, and 6.31 μ.

Acid Treatment of 4 and 10.—All the acid treatment experiments on 4 and 10 were performed in nmr sample tubes kept at the appropriate temperature. After the proper reaction time the nmr spectrum was recorded, the acidic products in the reaction mixture were isolated and they were also examined by nmr spectroscopy.

Adduct 14.—A solution of 0.629 g of 1 in 15 ml of methanol was treated with a few drops of 0.1 N sodium hydroxide. After 4 hr at room temperature, the solution was diluted with water and extracted with chloroform. A quantitative yield of adduct [mol wt 296 (mass spectroscopy)] was obtained upon recrystallization of the extract from methanol. The melting point (203–235°) was raised to 235–237°, $[\alpha]_D$ 23.8 ± 2° (c 0.3, dioxane), after several recrystallizations. The nmr spectrum showed prominent signals at 1.18 (s, C-5 methyl), 1.21 (d, J = 8 cps, C-10 methyl), 3.38 (s, $-OCH_3$), 3.67 (d, J = 5 cps, $-CH_2-O-$), 4.96 ppm (d, J = 9 cps, H_6). In addition to the broad melting range, the presence of a mixture of isomers (probably at C-11) was suggested by the lack of sharpness of the 1.21 and 4.96 ppm peaks, which could be due to almost superimposed signals from both isomers.

Acid Treatment of 14. A. In Acetic Acid–Sulfuric Acid.—Two drops of sulfuric acid was added to a solution of 0.047 g of 14 in 10 ml of acetic acid. The solution was heated to 80° for 30 min. After addition of water it was worked up as usual. The acidic fraction was crystallized from ether–hexane and yielded 0.009 g of 15: mp 176–177°; λ_{max} 212 nm (ϵ 7900), 243 (5300) and 306 (14,900). The nmr spectrum indicated two CH_3's at 1.8 ppm, characteristic for the coronopilic acidlike structure.

B. In Formic Acid.—A solution of 0.300 g of 14 in 5 ml of 97% acid was heated to 80° for 30 min. After the usual work-up, 0.064 g of acid was obtained. Its nmr spectrum and melting point were identical with those of the above products. Contrary to the results observed with 1, the dienone isomer was not detected.

Registry No.—1, 2571-81-5; **10a**, 16526-71-9; **15**, 16526-72-0.

Acknowledgments.—Part of this work was carried out at the University of Texas in the laboratory of Dr. T. J. Mabry, whom we sincerely thank. We are indebted to Drs. T. J. Mabry, W. Herz, and H. E. Miller for help and useful discussions during the course of this work, Dr. R. Wolff for mass spectral studies, Dr. G. Snatzke for the circular dichroisms and their interpretation, and Mrs. L. Lacombe for the decoupling experiments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. A NATO grant to H. B. K. and support from the Robert A. Welch Foundation are also gratefully acknowledged.

Preparation and Reactions of a 3-Chlorocoumarin Photodimer

J. WILLIAM HANIFIN AND ELLIOTT COHEN

Organic Chemical Research Section, Lederle Laboratories, A Division of American Cyanamid Company,
Pearl River, New York 10965

Received February 2, 1968

The preparation of a head-to-tail 3-chlorocoumarin photodimer is described. Attempts to convert this dimer into the corresponding cyclobutadienoid system are discussed.

Both the direct and sensitized photodimerization of coumarin have been reported in the literature. Anet[1] reported that direct irradiation of coumarin in ethanol solution produces the *cis* head-to-head dimer (1) while Schenck[2] showed that irradiation in the presence of benzophenone gives the *trans* head-to-head dimer (2) along with a trace of the *trans* head-to-tail dimer (3). Hammond[3] reinvestigated these reactions and concluded that the direct irradiation proceeds through interaction of excited coumarin singlet whereas the sensitized irradiation involves excited-triplet coumarin. The effect of various solvents on the direct, unsensitized dimerization was later studied by Morrison.[4] He found that in nonpolar solvents the *trans* head-to-head dimer (2) is formed to the virtual exclusion of the *cis* head-to-head dimer (1). The ratio of 2 to 1 decreases in polar solvents and is reversed in methanol. Morrison suggests that 1 is formed from a singlet excimer, whereas 2 arises *via* a monomeric triplet species. These solvent effects are similar to those found independently by

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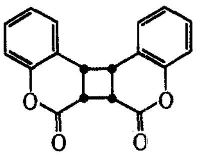
[1] R. Anet, *Can. J. Chem.*, **40**, 1249 (1962).

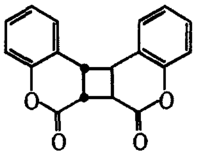
[2] G. O. Schenck, I. von Wilucki, and C. H. Krauch, *Ber.*, **95**, 1409 (1962).

[3] G. S. Hammond, C. A. Stout, and Angelo A. Lamola, *J. Amer. Chem. Soc.*, **86**, 3103 (1964).

[4] H. Morrison, H. Curtis, and T. McDonell, *ibid.*, **88**, 5415 (1966).

Krauch[5] who has also isolated the *cis* head-to-tail dimer (4) from the nonsensitized irradiation. This compound shows a solvent dependency analogous to 1.


1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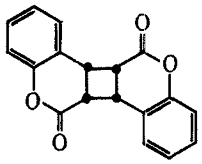
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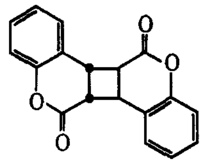
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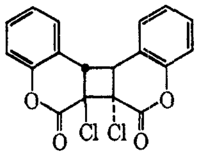
We have investigated the sensitized photodimerization of 3-chlorocoumarin in the hope of obtaining the *trans* head-to-head dimer (5) which might yield the cyclobutadienoid system 6 under the proper reaction conditions.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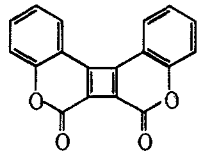
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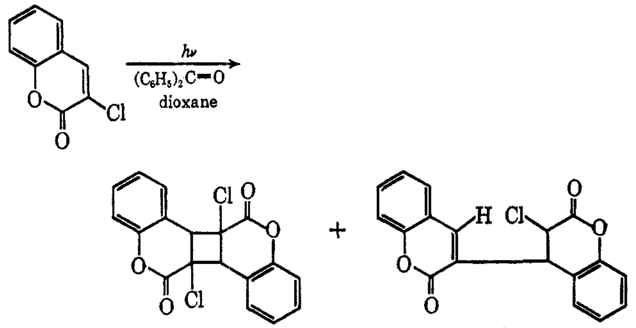
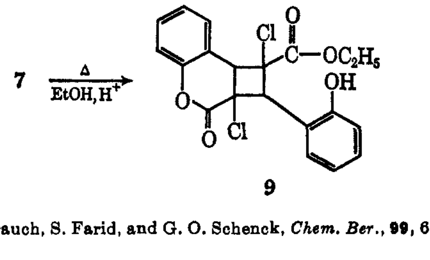
The irradiation of 3-chlorocoumarin was carried out in the presence of benzophenone. Two photolysis products were obtained from this sensitized reaction. The major product was shown to be the head-to-tail 3-chlorocoumarin dimer (7). The minor product was isolated and identified as 3′-chloro-3′,4′-dihydro-3,4′-bicoumarin (8).



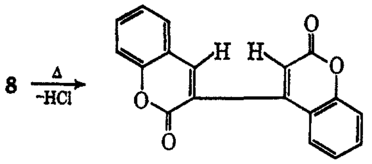
7 8

During the course of the separation of 7 and 8, it was found that, if the 3-chlorocoumarin dimer (7) is heated in ethanol in the presence of a trace amount of acid, one of the lactone rings undergoes ethanolysis to give 9. It was on the basis of the nmr spectrum of 9 that the dimer (7) was initially assigned the head-to-tail structure. The spectrum shows two cyclobutane hydrogens at τ 4.50 and 4.88, each as a singlet. Therefore, these hydrogens are uncoupled and most probably not on adjacent carbon atoms as they would have to be if the ethanolysis product were formed from a head-to-head dimer. Thus far attempts to determine whether the dimer is *cis* or *trans* head-to-tail have been inconclusive.[6,7]



9

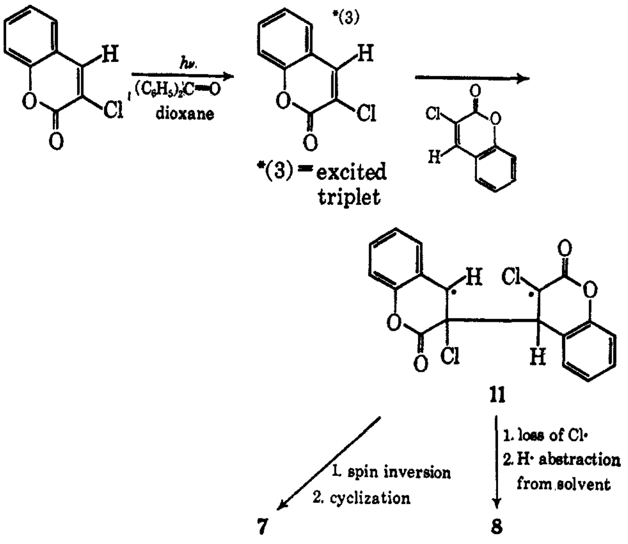
The structure of the minor product (8) was determined from its spectral data. The nmr spectrum of 8 showed one β-coumarin hydrogen at τ 2.20, and two ring hydrogens at 4.70 and 5.08, each as a doublet (J = 7 cps). Heating 8 beyond its melting point resulted in the evolution of hydrogen chloride and the formation of 3,4′-bicoumarin (10). The orientation of this bicoumarin, which can be established from its nmr spectrum, further verifies the structure assigned to the minor product (8). The nmr spectrum of 10 showed one β-coumarin hydrogen at τ 2.08 (singlet) and one α-coumarin hydrogen at 4.33 (singlet).



10

In an attempt to determine whether the minor product (8) is a primary or secondary photolysis product, the sensitized irradiation of the dimer (7) was carried out. One might consider the formation of 8 from 7 proceeding through an initial homolytic cleavage of the cyclobutane ring. No evidence was found for the formation of 8 from irradiation of the dimer (7). Thus, it appears that 8 is a primary photolysis product. A possible mechanism for its formation is shown in Scheme I. The diradical intermediate 11 may be a common precursor to both 7 and 8.

SCHEME I



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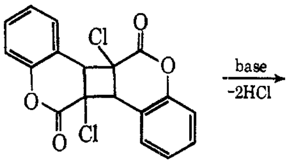
(5) C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, **99**, 625 (1966).

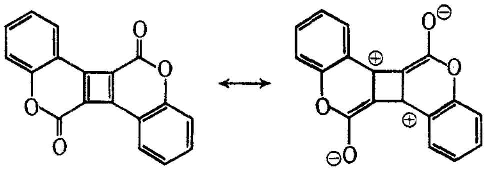
(6) The possibility of this photodimer (7) having *trans*-ring fusions is considered highly unlikely. No compounds of this type have been isolated from the photodimerization studies of coumarin.[1-5]

(7) An attempt to prepare the desired *trans* head-to-head dimer (5) by direct photolysis produced the same dimer (7) as obtained by photosensitization.

The chemical literature contains many examples of attempts to prepare substituted cyclobutadienes. The synthesis of cyclobutadienoid systems in which the instability of the four-membered system is diminished by some structural or electronic feature has been somewhat successful.[8] The head-to-tail 3-chlorocoumarin dimer (**7**) is a possible intermediate in the preparation of the cyclobutadienoid system (**12**). Treatment of the dimer with base under the proper conditions might yield **12** with the elimination of 2 mol of hydrogen chloride. It is possible that **12** would be stable owing to some contribution of structure **13** to the resonance hybrid.



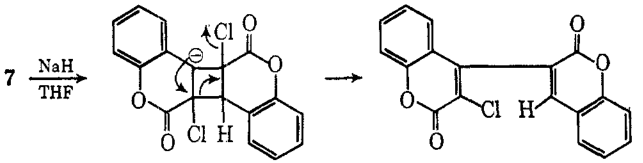
7



12 **13**

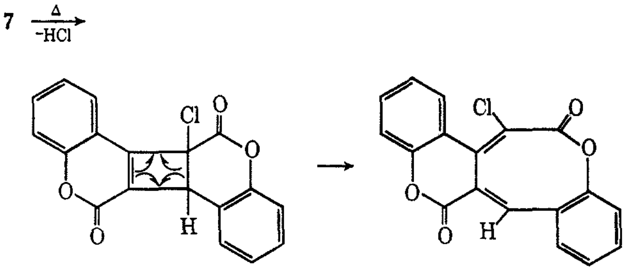
Several attempts were made to prepare **12** with different dehydrohalogenating agents as well as by pyrolysis. In no case was the synthesis of **12** accomplished; however, other interesting reaction products were obtained.

Treatment of the 3-chlorocoumarin dimer (**7**) with sodium hydride resulted in the elimination of 1 mol of hydrogen chloride to give 3′-chloro-3,4′-bicoumarin (**14**). The same product was also obtained by treatment of the dimer with triethylamine. The structure of the product was determined from its uv, ir, nmr, and mass spectrum. The uv spectrum of the product is quite similar to that of 3,4′-bicoumarin (**10**). The reaction most likely proceeds by the pathway



14

Another approach to the synthesis of **12** was by pyrolysis of **7**. On heating **7**, it was observed that the compound gave off hydrogen chloride at its melting point. Pyrolysis of **7** at 280° gave a new compound, however, with the elimination of only 1 mol of hydrogen chloride. This new material is believed to be the substituted eight-membered-ring lactone **16**. Again the structure of the product is based upon the analysis, nmr, ir, uv, and mass spectrum (see Experimental Section). The uv spectrum of the product (**16**) was quite significant. It showed uv max (CH_3OH) 291 mμ (ε 16,600) and 327 mμ (ε 18,800), while the 3′-chloro-3,4′-bicoumarin (**14**) gave uv max (CH_3OH) 284 (ε 20,000) and 315 mμ (ε 15,100). Thus the new material (**16**), compared with **14**, shows a shift to longer wavelengths for its uv maxima. In compound **14** there are two coumarin chromophores connected by an essential single bond and it appears that there is steric inhibition of coplanarity with essentially no interaction between the two chromophores.[9] In the case of **16**, it is expected that this molecule would have an extra double bond in conjugation with one of the carbonyl groups, thus giving rise to the longer wavelength absorption. The reaction probably proceeds by initial loss of hydrogen chloride to give a cyclobutene intermediate (**15**) which then rearranges to the product.



15 **16**

In conclusion, attempts to prepare the cyclobutadienoid system **12** have thus far been unsuccessful. However, the possibility remains that with the proper dehydrohalogenating agent the compound may be isolated or trapped.

Experimental Section[10]

Irradiation Apparatus.—Irradiations were carried out using an immersion apparatus supplied by the Hanovia Lamp Division of Englehard Industries. The lamp used was a 450-W, medium-pressure mercury arc, type no. 679A-10. Cylindrical glass filters were placed inside the lamp well.

Material.—Benzophenone from Eastman Organic Chemicals and 3-chlorocoumarin from Aldrich Chemical Co. were used without additional purification. Sodium hydride was supplied by Metal Hydrides, Inc. Dioxane and tetrahydrofuran from Matheson Coleman and Bell were used. The dioxane was purified by distillation from the sodium ketyl of benzophenone and stored frozen under nitrogen. Tetrahydrofuran was distilled from lithium aluminum hydride.

Irradiation of 3-Chlorocoumarin.—A solution of 4.2 g (0.023 mol) of 3-chlorocoumarin, 0.50 g (0.003 mol) of benzophenone, and 25 ml of dioxane was prepared in a Pyrex test tube. Nitrogen gas was bubbled through the solution and the test tube was sealed and taped to the outside of the cylindrical reaction well of the immersion apparatus. The test tube was then irradiated for 30 hr. The solvent was removed on the rotating evaporator and the residue was recrystallized from benzene to give 1.5 g (36%) of the head-to-tail 3-chlorocoumarin dimer (**7**), mp 266°. The infrared spectrum of the dimer contained strong carbonyl absorption at 1757 cm^{-1}. The nmr spectrum contained two cyclobutane hydrogens at τ 5.08 (single peak) and eight aromatic hydrogens at 2.63 (multiplet).

Anal. Calcd for $C_{18}H_{10}O_4Cl_2$: C, 59.9; H, 2.8; Cl, 19.6. Found: C, 60.1; H, 3.2; Cl, 19.6.

The minor reaction product (**8**) was isolated by stripping the benzene filtrate to a minimum volume and cooling. Using this procedure, 0.50 g (13%) of 3′-chloro-3′,4′-dihydro-3,4′-bicoumarin (**8**) was isolated. The material was recrystallized from ethanol to give pure product, mp 217°. The infrared spectrum contained strong carbonyl absorption at 1776 and 1712 cm^{-1}. The nmr spectrum showed the β-coumarin hydrogen at τ 2.20

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(8) For a review, see P. Cava and M. J. Mitchell, "Organic Chemistry. V. 10 Cyclobutadiene and Related Compounds," Academic Press Inc., New York, N. Y., 1967, pp 1–84.

(9) This conclusion is based on a comparison of the uv spectrum of **14** with those of coumarin and 3-chlorocoumarin.

(10) Nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer. Ultraviolet spectra were measured in methanol on a Cary Model 11 MS spectrophotometer. Mass spectra were determined on a AEIMS9 mass spectrometer. Melting points were determined in a capillary tube in a Mel-Temp apparatus and are uncorrected.

(singlet), two ring hydrogens at 4.70 and 5.08, each as a doublet (J = 7 cps), and eight aromatic hydrogens centered at 2.70 (multiplet). The uv spectrum showed uv max (CH_3OH) 280 mμ mμ (ε 14,300) and 314 mμ (ε 9400).

Anal. Calcd for $C_{18}H_{11}O_4Cl$: C, 66.2; H, 3.4; Cl, 10.8. Found: C, 65.9; H, 3.7; Cl, 10.8.

1,3-Dichloro-2,4-bis(O-hydroxyphenyl)-1,3-cyclobutanecarboxylic Acid Ethyl Ester δ-Lactone (9).—To 30 ml of ethanol was added 0.5 g (0.0015 mol) of the head-to-tail 3-chlorocoumarin dimer and 0.3 ml of 12 N HCl. This mixture was heated at reflux until all of the material went into solution. The ethanol was evaporated and the residue recrystallized from benzene to give 0.40 g (71%) of a white solid, mp 191–193°. The infrared spectrum showed hydroxyl absorption at 3448 cm^{-1} and carbonyl absorption at 1754 and 1727 cm^{-1}. The nmr spectrum contained two cyclobutane hydrogens at τ 4.50 and 4.88 (singlets), two methylene hydrogens at 5.97 (quartet), three methyl hydrogens at 9.02 (triplet), and eight aromatic hydrogens at 2.70 (multiplet).

Anal. Calcd for $C_{20}H_{16}O_5Cl_2$: C, 59.0; H, 4.0; Cl, 17.4. Found: C, 58.9; H, 4.2; Cl, 17.5.

3,4′-Bicoumarin (10).—In a Pyrex test tube was placed 1.0 g (0.003 mol) of 3′-chloro-3′,4′-dihydro-3,4′-bicoumarin (8). The test tube was then heated at 250° in a Wood's metal bath for 20 min. After cooling, the solid material in the test tube was removed and recrystallized from benzene. Approximately 300 mg (34%) of a solid white precipitate, mp 255–257°, was obtained. The infrared spectrum showed strong absorption at 1724, 1608, 1449, and 1376 cm^{-1}. Th uv spectrum of the material showed uv max (CH_3OH) 282 mμ (ε 18,400) and 313 mμ (ε 13,900). The nmr spectrum contained one β-coumarin hydrogen at τ 2.08 (singlet), one α-coumarin hydrogen at 4.33 (singlet), and eight aromatic hydrogens centered at 3.03 (multiplet).

Anal. Calcd for $C_{18}H_{10}O_4$: C, 74.5; H, 3.5. Found: C, 74.9; H, 3.6.

Sensitized Irradiation of the Head-to-Tail 3-Chlorocoumarin Dimer (7).—A solution containing 0.70 g (0.002 mol) of the head-to-tail 3-chlorocoumarin dimer, 0.20 g (0.001 mol) of benzophenone, and 150 ml of dioxane was prepared and added to the outside vessel of the 450-W, medium-pressure mercury arc irradiation apparatus. After flushing with nitrogen, the solution was irradiated for 45 hr. The solvent was then removed on the rotating evaporator. The infrared spectrum of the residue indicated that no amount of 3′-chloro-3′,4′-dihydro-3,4′-bicoumarin (8) was formed.

3′-Chloro-3,4′-bicoumarin (14).—In 15 ml of tetrahydrofuran was dissolved 1.0 g (0.003 mol) of the head-to-tail 3-chlorocoumarin dimer. The mixture was then added to a suspension of 0.25 g (0.006 mol) of sodium hydride (54.7%) in 5 ml of tetrahydrofuran. The mixture was stirred for 1 hr and then 1 N hydrochloric acid added to neutralize any unreacted sodium hydride. A yellow oil formed which was extracted with chloroform and the chloroform solution dried over anhydrous sodium sulfate. The chloroform was stripped off and the residue recrystallized from benzene. A white solid precipitate was formed, 250 mg (28%), mp 256–258°. The infrared spectrum showed strong absorption at 1721, 1608, and 1447 cm^{-1}. The nmr spectrum contained one β-coumarin hydrogen at τ 2.08 (singlet) and eight aromatic hydrogens centered at 2.50 (multiplet). The uv spectrum showed uv max (CH_3OH) 284 mμ (ε 20,000) and 315 mμ (ε 15,100). The compound gave a molecular ion at m/e 324 (326).

Anal. Calcd for $C_{18}H_9O_4Cl$: C, 66.6; H, 2.8; Cl, 10.9. Found: C, 66.4; H, 2.9; Cl, 11.4.

α-Chloro-2,3-dihydro-3-*o*-hydroxybenzylidene-2-oxo-4H-2-benzopyran-Δ$^{4,\alpha}$-acetic Acid Lactone (16).—In a Pyrex test tube was placed 1.0 g (0.003 mol) of the heat-to-tail 3-chlorocoumarin dimer. The test tube was then heated at 290° for 20 min in a Wood's metal bath. The evolution of hydrogen chloride was easily detected with litmus paper. After heating, the test tube was cooled and the contents recrystallized from benzene to yield 270 mg (30%) of a light tan solid, mp 279°. The infrared spectrum showed strong absorption at 1724, 1610, 1560, and 1485 cm^{-1}. The nmr spectrum contained one β-coumarin hydrogen at τ 2.12 (singlet) and eight aromatic hydrogens centered at 2.55 (multiplet). The uv spectrum showed uv max (CH_3OH) 291 mμ (ε 16,600) and 327 mμ (ε 18,800). The compound gave a molecular ion at m/e 324 (326).

Anal. Calcd for $C_{18}H_9O_4Cl$: C, 66.6; H, 2.8; Cl, 10.9. Found: C, 66.2; H, 3.3; Cl, 10.7.

Registry No.—**7**, 16666-82-3; **8**, 16666-83-4; **9**, 16666-84-5; **10**, 16666-85-6; **14**, 16666-86-7; **16**, 16666-87-8.

Acknowledgments.—We thank Mr. L. Brancone and staff for the microanalyses, Mr. W. Fulmor and staff for the ultraviolet and nmr spectra, and Dr. J. Karliner for the mass spectra.

Bile Acids. XXIV. Raney Nickel in the Preparation of Allocholanic Acids[1]

M. N. MITRA AND WILLIAM H. ELLIOTT

Department of Biochemistry, St. Louis University School of Medicine, St. Louis, Missouri 63104

Received February 21, 1968

Treatment of methyl polyhydroxy-5β-cholanoates, such as methyl cholate (I) or methyl chenodeoxycholate (XI), with Raney nickel in boiling *p*-cymene provided a mixture of 5α-cholanoates now separated and characterized as the 3,7-diketones (III and XIII), the 7-deoxy derivatives (II and XII), and the methyl 3-ketoallocholanoates (IV and XIV, respectively). Methyl deoxycholate (X) and methyl lithocholate (XVI) afforded the corresponding 3-keto-5α-cholanoates, II and XII, respectively; reduction provided the isomeric hydroxyallocholanoates, VIII and IX and XVII and XVIII. Treatment of methyl 7β-tritiocholate (XX) with Raney nickel gave tritiated IV (XXIII) and II (XXI); the amount of tritium retained in *p*-cymene was equivalent to that lost in the formation of the diketone III.

During a study of the metabolism of cholestanol-4-^{14}C in our laboratory[2-4] a new method of synthesis of allocholic acid[1c] and allochenodeoxycholic acid[5] was developed. The first step in this method provides a mixture of products after treatment of methyl cholate (I) or methyl chenodeoxycholate (XI) with Raney nickel in boiling *p*-cymene. After chromatography on alumina these mixtures yielded three major compounds from distinct fractions (A, B, and C) in each case.

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(1) (a) This investigation was supported in part by the National Institutes of Health (Grant No. HE-07878 and AM-09992). (b) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966. (c) For Paper XXIII in this series, see M. N. Mitra and W. H. Elliott, *J. Org. Chem.*, **33**, 175 (1968). (d) The following abbreviations have been used: tlc, thin layer chromatography; plc, preparative layer chromatography; glpc, gas–liquid partition chromatography; R_t, retention time relative to methyl deoxycholate (methyl 3α,12α-dihydroxy-5β-cholanoate; absolute time = 29 min.).

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