adding Ph_3P (1.9 g, 7.2 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred for 30 min and pentane (50 ml) was added, causing a yellow oil to deposit on the bottom of the flask. The solution was chilled and the organic phase was carefully drawn off. Evaporation of the solvent gave **7**, whose spectral properties are described in the text.

1,1,2-Trimethylpropylphenylphosphinic Acid (6). Compound **5** (200 mg, 0.83 mmol) was suspended in NaOH (10 ml of 5 *N* solution) and refluxed for 2 hr. Upon cooling white crystals of **8** were deposited (140 mg, 75% crude yield) whose ^{1}H NMR was in agreement with the literature.[6] Recrystallization from water gave needles, mp 94–95° (after drying) (lit. mp 91–93°).

Acknowledgment. I acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No.—**4a,** 54193-52-1; **4a**-*d,* 54193-53-2; **4b,** 54293-23-1; **4b**-*d,* 54293-25-3; **5,** 54193-50-9; **6,** 28660-28-8; **7,** 54193-51-0; aluminum chloride, 7446-70-0; phenylphosphonous dichloride, 644-97-3; 2,3-dimethyl-2-butene, 563-79-1.

References and Notes

(1) (a) A. Weissberger and E. C. Taylor, Ed., "The Chemistry of Heterocyclic Compounds: Derivatives of Phosphorus", Wiley, New York, N.Y., 1970; (b) R. Wagner, L. D. Freeman, H. Goldwhite, and D. G. Roswell, *J. Am. Chem. Soc.*, **89,** 1102 (1967); (c) S. Chan, H, Goldwhite, H. Keyzer, D. G. Roswell, and R. Tang, *Tetrahedron,* **25,** 1097 (1969); (d) E. W. Koos, J. P. Vanderkool, E. E. Green, and J. K. Stille, *J. Chem. Soc., Chem. Comun.*, 1085 (1972).

(2) (a) E. Jungermann, J. J. McBride, Jr., R. Clutter, and A. Mais, *J. Org. Chem.*, **27,** 607 (1962); (b) J. J. McBride, Jr., E. Jungermann, J. V. Killheffer, and R. J. Clutter, ibid., **27,** 1833 (1962); (c) S. E. Cremer and R. J. Chorvat, ibid., **32,** 4066 (1967); (d) S. E. Cremer, F. L. Weitl, F. R. Farr, P. W. Kremer, G. A. Gray, and H. Hwang, ibid., **38,** 3199 (1973).

(3) Other olefins, including 2-pentene, 2-methyl-2-butene, and 4-methyl-2-pentene, reportedly gave uncharacterized adducts in low yields.[2a]

(4) P. Crews and J. Engstrom, unpublished results.

(5) No attempt was made to exclude oxygen during the work-up; hence it is not surprising that the phosphine intermediate (i.e., **7**) is oxidized to **5**. Air oxidation of alkyl phosphines has long been recognized to be a facile process. As an example, Buckler [S. A. Buckler, *J. Am. Chem. Soc.*, **84,** 3093 (1962)] has shown that Bu_3P: can be rapidly air oxidized in organic or aqueous solvent to $Bu_3P \rightarrow O$.

(6) J. R. Corfield, M. J. P. Harger, J. R. Shutt, and S. Trippett, *J. Chem. Soc. C*, 1885 (1970).

(7) (a) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, Chapter 12; (b) K. U. Ingold in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 70–83.

(8) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88,** 3832 (1966).

(9) D. B. Denney and L. S. Shih, *J. Am. Chem. Soc.*, **96,** 317 (1974).

(10) R. Vilceanu, Z. Simon, and A. Chirac, *Rev. Roum. Chim.*, **18,** 1353 (1973).

(11) O. Ganson and W. Shittenheim, *J. Am. Chem. Soc.*, **93,** 4294 (1971).

(12) R. P. Bell and D. M. Goodall, *Proc. R. Soc. London, Ser. A*, **294,** 273 (1966).

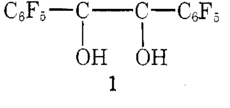
Polyfluorobenzopinacols

Robert Filler* and Hyung H. Kang[1]

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

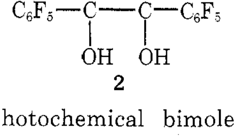
Received June 4, 1974

We report the preparation and chemical behavior of decafluorobenzopinacol (1)[2] and our attempts to prepare perfluorobenzopinacol (2), a compound which is still unknown.



$$C_6F_5-\overset{C_6H_5}{\underset{OH}{C}}-\overset{C_6H_5}{\underset{OH}{C}}-C_6F_5$$

1

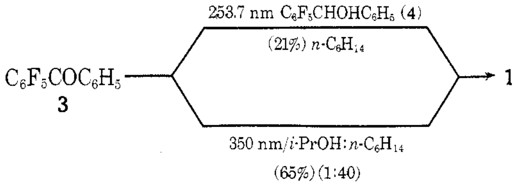


$$C_6F_5-\overset{C_6F_5}{\underset{OH}{C}}-\overset{C_6F_5}{\underset{OH}{C}}-C_6F_5$$

2

Decafluorobenzopinacol. Photochemical bimolecular reduction of pentafluorobenzophenone (3) by irradiation with 253.7-nm light in the presence of 2-propanol gave only an intractable tar. Under these conditions, benzophenone is converted to benzopinacol in high yield.[3] When 2-propanol was replaced by pentafluorobenzhydrol (4), the desired benzopinacol 1 was isolated in 21% yield. This conversion was more readily accomplished (65% yield) by irradiating 3 with 350-nm light in a 2-propanol–*n*-hexane (1:40) system (Scheme I).

Scheme I

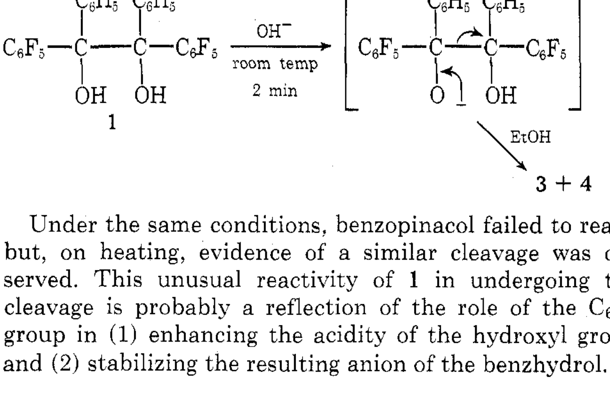


Compound 1 was also prepared by chemical reduction of 3 with zinc and acetic acid.[4] All of the samples of 1 exhibited a melting range of 153–156°. Mixture melting points showed no depression and the infrared spectra were identical. The wide melting range suggested the presence of a mixture of *dl* and meso forms, but attempts to separate components by chromatography on silica gel were unsuccessful.

Decafluorobenzopinacol (1) showed a remarkable reluctance to undergo the pinacol–pinacolone rearrangement under conditions in which most benzopinacols react with ease. No evidence of a rearrangement product could be detected on treatment with a wide range of mineral and organic acids. Frequently, fragmentation into 3 and 4 was observed (vide infra).

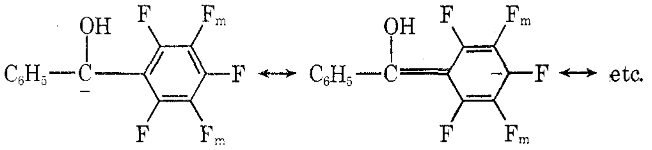
In considering the participation of 1 in this rearrangement, we must consider both the ease of formation of the electron-deficient carbenium ion center and the intrinsic migratory aptitudes of the phenyl and pentafluorophenyl groups in the subsequent 1,2 shift. From previous studies we would anticipate that phenyl would migrate without difficulty and much more readily than pentafluorophenyl.[5] The failure to observe a rearrangement product strongly suggests the dominance of the electron-withdrawing inductive effect of the pentafluorophenyl group (σ_I 0.25[7]) which so destabilizes the carbenium ion[8] as to preclude any migration. Resistance to rearrangement of 1,1,1,4,4,4-hexafluoro-2,3-diphenyl-2,3-butanediol was also attributed to the destabilizing influence of the trifluoromethyl group (σ_I 0.33–0.41[7]) to development of carbenium ion character.[9] Perfluoropinacol[10a] and the diol derived from octafluoroacetophenone[10b] behaved similarly.

In contrast to its behavior in acidic medium, compound 1 reacted with exceptional facility when treated with 0.1 *N* ethanolic sodium hydroxide solution at room temperature to give an equimolar mixture of pentafluorobenzophenone (3) and pentafluorobenzhydrol (4) in nearly quantitative yield (eq 1).



$$C_6F_5-\overset{C_6H_5}{\underset{OH}{C}}-\overset{C_6H_5}{\underset{OH}{C}}-C_6F_5 \xrightarrow[\text{2 min}]{OH^-,\ \text{room temp}} \left[C_6F_5-\overset{C_6H_5}{\underset{O^-}{C}}-\overset{C_6H_5}{\underset{OH}{C}}-C_6F_5\right] \xrightarrow{EtOH} 3 + 4 \quad (1)$$

Under the same conditions, benzopinacol failed to react, but, on heating, evidence of a similar cleavage was observed. This unusual reactivity of 1 in undergoing the cleavage is probably a reflection of the role of the C_6F_5 group in (1) enhancing the acidity of the hydroxyl group and (2) stabilizing the resulting anion of the benzhydrol. In this regard, the meta fluorines (F_m) play a major role, consistent with the known stabilizing effect of fluorine attached to the carbon adjacent to a carbanionic center.[11]



Much more surprising than the *alkaline* cleavage were the observations that this fragmentation also proceeds under *acidic* conditions which normally lead to rearrangement to the pinacolone. Thus, nearly quantitative yields of **3** and **4** were obtained by heating **1** under reflux with iodine in glacial acetic acid, dilute sulfuric acid, and water–methanol. Under these latter conditions, we are likely dealing with thermal cleavage.

Perfluorobenzopinacol. All attempts to prepare perfluorobenzopinacol (**2**) from $(C_6F_5)_2C{=}O$ (**5**) by photochemical means were unsuccessful. Various light sources, solvents, and hydrogen donors (2-propanol, ether, benzene, *n*-hexane, cyclohexane, and tributyltin hydride[12]) were used. In general, polymeric residues were obtained, although some $(C_6F_5)_2CHOH$ (**6**) was isolated using $(n\text{-}C_4H_9)_3SnH$ at 350 nm. Subsequent to these studies, the clean photoreduction in 2-propanol of **5** to **6** was reported.[13] In contrast to these observations, perfluoropinacols are readily obtained by photoinitiated bimolecular reduction of hexafluoroacetone and octafluoroacetophenone.[10]

An attempt to convert **5** to **2** by chemical reduction, using "magnesium subiodide",[14] was unsuccessful. Treatment of **5** with sodium amalgam in tetrahydrofuran gave a deep blue mixture which exhibited ESR signals, suggesting the formation of the ketyl, $(C_6F_5)_2\dot{C}{-}O^-Na^+$, the precursor of the desired dimer **2**, which, however, was not isolated after acidification. Finally, in contrast to the behavior of **3**, compound **5** was reduced almost quantitatively to **6** with zinc and acetic acid.

Dimerization of the intermediate radical $(C_6F_5)_2\dot{C}{-}OH$ or ketyl may be particularly difficult owing to C–F dipole–dipole repulsions of the ortho fluorines as the two pairs of C_6F_5 groups come into close proximity. The shifting of the odd-electron density to ortho or para fluorines has also been suggested to explain the absence of dimerization.[13]

Experimental Section

Melting points are uncorrected and were obtained on an Electrothermal melting point apparatus. Infrared spectra were obtained on a Beckman Ir-8 infrared spectrophotometer or a Perkin-Elmer Model 137 Infracord spectrometer using sodium chloride cells with a path length of 0.1 mm. Ultraviolet spectra were measured on a Cary Model 14 spectrophotometer.

Elemental analyses were carried out by Micro-Tech Laboratories, Skokie, Ill., and M-H-W Laboratories, Garden City, Mich.

Fluorinated starting materials were purchased from Pierce Chemical Co., Rockford, Ill.

2,3,4,5,6-Pentafluorobenzhydrol (4). This compound, mp 46–47°, was obtained in 76% yield from benzaldehyde and pentafluorophenylmagnesium bromide by a previously reported procedure.[15]

Decafluorobenzhydrol (6). This compound, mp 75–77°, was prepared in 83% yield according to a procedure described previously.[15]

2,3,4,5,6-Pentafluorobenzophenone (3). This compound, mp 33–34°, was obtained in 80% yield by oxidation of **4** with chromium trioxide in glacial acetic acid, as described previously.[15]

Decafluorobenzophenone (5). This compound, mp 90–92°, was prepared in 74% yield by chromic acid oxidation of **6** as described previously.[15]

1,2-Diphenyl-1,2-bis(pentafluorophenyl)ethanediol (1). A. By Photolysis of 2,3,4,5,6-Pentafluorobenzophenone (3) with 2,3,4,5,6-Pentafluorobenzhydrol (4) in *n*-Hexane. Pentafluorobenzophenone (1.2 g, 0.0044 mol) and 1.5 g (0.0055 mol) of pentafluorobenzhydrol were dissolved in a minimum amount of *n*-hexane (10 ml) containing a small drop of glacial acetic acid. This solution, contained in a quartz tube, was flushed with nitrogen for 20 min, then irradiated with ultraviolet light (253.7 nm, Srinivasan-Griffin reactor) for 20 hr at room temperature under a nitrogen atmosphere. A white, crystalline material, which deposited at the bottom of the reaction vessel, was filtered off, washed with *n*-hexane, and dried. The product, the decafluorobenzopinacol **1**, weighed 0.5 g (21%), mp 140–143°. It readily dissolved in ether, and was deposited as a fine, white powder upon addition of *n*-hexane to the ethereal solution. Several purifications from ether–hexane raised the melting point to 153–156°: ir ($CHCl_3$) 3620, 1525, 1490 cm^{-1}.

Anal. Calcd for $C_{26}H_{12}O_2F_{10}$: C, 57.15; H, 2.21. Found: C, 57.21; H, 2.41.

B. By Photolysis of 2,3,4,5,6-Pentafluorobenzophenone (1) in Isopropyl Alcohol and *n*-Hexane. A solution containing 1 g (0.00368 mol) of pentafluorobenzophenone, 1 drop of glacial acetic acid, 0.5 ml (0.008 mol) of isopropyl alcohol, and 20 ml of *n*-hexane was irradiated (350 nm), following the general procedure described above. The yield was 0.65 g (65%). The product was identified as **1** by melting point, mixture melting point, and infrared spectrum.

When this reaction was carried out in isopropyl alcohol only, without using *n*-hexane, only polymeric residue was obtained. The nature of this oily residue was not identified.

However, when the photochemical reaction was carried out using only *n*-hexane as solvent, the desired product was obtained in about 20% yield.

C. By Reduction of 2,3,4,5,6-Pentafluorobenzophenone with Zinc. To 18 g (0.0663 mol) of pentafluorobenzophenone, dissolved in 72 ml of glacial acetic acid, was added 36 g of zinc powder in ten portions over a period of 30 min while the reaction mixture was stirred vigorously and kept below 40° by means of a cold-water bath. External cooling was not needed after all of the zinc powder had been added. The thick reaction mixture was stirred for about 24 hr at room temperature. Then 500 ml of cold water was added to the mixture, and the resulting solids were filtered off, air dried, and extracted with acetone (150 ml). The acetone extract was filtered and evaporated to give 16.4 g of crude product. The crude decafluorobenzopinacol so obtained was further purified by dissolving in a minimum amount of ether and reprecipitating by addition of *n*-hexane. The final yield was 11.2 g (62%) of white powder, which had a melting point and infrared spectrum identical with those of the material prepared photochemically. There was no depression in a mixture melting point determination.

Reactions of Decafluorobenzopinacol (1). In 0.1 *N* Sodium Hydroxide. When 0.5 g of **1** was added to 10 ml of 0.1 *N* sodium hydroxide solution in 95% ethanol, the solid dissolved immediately. The solution became moderately warm and gave a transient blue color. Within 2 min, the alkaline solution was neutralized with dilute hydrochloric acid. The material isolated from this reaction gave an infrared spectrum identical with that of an authentic mixture of pentafluorobenzophenone and pentafluorobenzhydrol. The yield was nearly quantitative.

As a control experiment, 1.0 g of benzopinacol was mixed with 20 ml of base for 2 min. No liberation of heat was observed. Benzopinacol (0.96 g) was recovered. However, when the same mixture was heated under reflux for 2 min, the product obtained was shown by infrared analysis to be a mixture of benzophenone and benzhydrol.

In Acetic Acid with Iodine. **1** (3 g, 0.0055 mol) was dissolved in 10 ml of glacial acetic acid and a small amount (0.04 g) of iodine was added. The pink solution was heated under reflux for 5 min. The solvent and most of the iodine were removed under reduced pressure, and the resulting viscous residue was taken up in 30 ml of ether and washed with water containing a pinch of sodium bisulfite. The ethereal layer was washed with water, dried (magnesium sulfate), filtered, and evaporated to give a clear semisolid, which solidified slowly on cooling in the refrigerator. This product (2.7 g) had an infrared spectrum identical with that of an equimolar mixture of pentafluorobenzophenone and pentafluorobenzhydrol.

The mixture of products thus obtained was separated into its components by column chromatography. About 1 g of product was dissolved in a minimum volume of *n*-hexane and added to a 20-cm column of alumina (25 g, acidic, pH 4). The column was then slowly eluted with *n*-hexane (200 ml) and then with benzene (200 ml). Most of the pentafluorobenzophenone was found in the first 100-ml fraction of *n*-hexane. Pentafluorobenzhydrol was readily eluted with benzene. Pentafluorobenzophenone and pentafluorobenzhydrol so separated were positively identified by melting points and infrared spectra. Similar behavior was observed on heating compound 1 for 24 hr with dilute sulfuric acid, trifluoroacetic, trichloroacetic, formic, and oxalic acids, and water–methanol (50:50, v/v).

In Concentrated Sulfuric Acid. When 0.5 g of 1 was mixed with 10 ml of concentrated sulfuric acid, the white powder appeared to be completely insoluble. The heterogeneous mixture became light orange in color after a few days of vigorous mixing at room temperature. The mixture was then slowly added into a large amount of cracked ice. A white solid separated immediately. About 0.4 g of material was isolated and identified as starting material by mixture melting point and comparison of infrared spectra. In fuming sulfuric acid (30%), only a water-soluble white solid was obtained.

Attempted Preparation of Perfluorobenzopinacol (2). Photochemical. Photochemical reactions were carried out in a manner similar to that described previously. Only intractable tar was obtained when decafluorobenzophenone (5) was irradiated in isopropyl alcohol, *n*-hexane, isopropyl alcohol–*n*-hexane, or cyclohexane, with ultraviolet light at 350 nm. Tar formation appeared to be even more extensive when 253.7-nm light was used. A mixture of decafluorobenzophenone and decafluorobenzhydrol in *n*-hexane was also irradiated, but the resulting material neither solidified nor could it be distilled in vacuo. The reaction of decafluorobenzophenone with tributyltin hydride in benzene or acetonitrile was carried out according to the procedure described by Hammond.[12] No solid could be isolated, even after column chromatography.

Reaction with Zinc. To a glacial acetic acid solution (5 ml) containing 1 g of decafluorobenzophenone was added 2 g of zinc powder and the mixture was stirred vigorously for 24 hr at room temperature. The reaction mixture was poured into a large volume of cold water. The resulting solid, together with zinc, was collected by filtration, dried, and extracted with ether. From the ether layer was isolated 0.9 g of white solid. This compound was identified as decafluorobenzhydrol (6) by mixture melting point and by its infrared spectrum.

Reaction with Sodium Amalgam. Decafluorobenzophenone (2.7 g) and sodium amalgam (2%, 54 g) were mixed vigorously in 54 ml of tetrahydrofuran under a nitrogen atmosphere. The reaction mixture turned to a red-wine color in a few minutes, then blue after 2 hr, and was deep red after 24 hr. The blue mixture exhibited ESR signals. Only a dark-brown, oily residue was obtained after the reaction mixture was decomposed with dilute acetic acid.

Reaction with "Magnesium Subiodide". This procedure was based on the method described by Gomberg and Bachmann.[14] Decafluorobenzophenone (3.64 g, 0.01 mol), dissolved in 5 ml of benzene, was added into "magnesium subiodide", prepared from magnesium powder (0.486 g suspended in 12.5 ml of ether or THF) and 1.4 g of iodine. This mixture was gently refluxed for 1 day, but all of the starting ketone was recovered.

Registry No.—**1**, 54293-20-8; **3**, 1536-23-8; **4**, 1944-05-4; **5**, 853-39-4; **6**, 1766-76-3; sodium hydroxide, 1310-73-2; iodine, 7553-56-2; zinc, 7440-66-6.

References and Notes

(1) Abstracted, in part, from the Ph.D. Thesis of H. H. Kang, June 1967.

(2) Abstracts, Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 1966.

(3) A. Schönberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).

(4) A. Zagumenny, *Ber.*, **14**, 1402 (1881).

(5) The conversion of $(C_6F_5)(C_6H_5)CHCHO$ to $C_6F_5CH_2COC_6H_5$ in sulfuric acid illustrates this strong migratory preference of C_6H_5 over C_6F_5 in acidic medium: R. Filler and Y. S. Rao, *J. Org. Chem.*, **39**, 3421 (1974). In marked contrast, an overwhelming preference of C_6F_5 over C_6H_5 is observed in 1,2 shifts in alkaline medium (ref 6).

(6) R. D. Chambers, M. Clark, and D. J. Spring, *J. Chem. Soc., Perkin Trans. 1*, 2464 (1972).

(7) W. A. Sheppard, *J. Am. Chem. Soc.*, **92**, 5419 (1970).

(8) S. V. Kulkarni, R. Schure, and R. Filler, *J. Am. Chem. Soc.*, **95**, 1859 (1973).

(9) W. A. Mosher and N. D. Heindel, *J. Am. Chem. Soc.*, **85**, 1548 (1963).

(10) (a) W. J. Middleton and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964); (b) I. S. Chang, J. T. Price, A. J. Tomlinson, and C. J. Willis, *Can. J. Chem.*, **50**, 512 (1972).

(11) R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse, D. L. H. Williams, J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc., Chem. Commun.*, 239 (1974).

(12) G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

(13) N. Filipescu, J. P. Pinion, and F. L. Minn, *Chem. Commun.*, 1413 (1970).

(14) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **49**, 236 (1927).

(15) A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 808 (1961).

Carbon-13 Nuclear Magnetic Resonance Spectra of 2*H*-1-Benzopyran-2-ones (Coumarins) in Chloroform and Sulfuric Acid

Stanley A. Sojka

Chemistry Division, Naval Research Laboratory,
Washington, D.C. 20375

Received October 15, 1974

Coumarins appear extensively in nature as photosensitizing agents[1] and have recently been employed as blue-green laser dyes.[2] Our interest in the photobleaching of laser dyes has prompted us to examine the carbon-13 NMR spectra of coumarins in neutral and acidic solvents. Ultimately, it is the structure, electronic distribution, and environment of the dye which determine its photostability. The lifetime of laser dyes could be improved if these factors could be understood and controlled. The carbon-13 chemical shift can be a reliable indicator of the ground-state electronic environments of carbon atoms in molecules[3] and should provide valuable insight into the nature of the coumarin structure.

Results

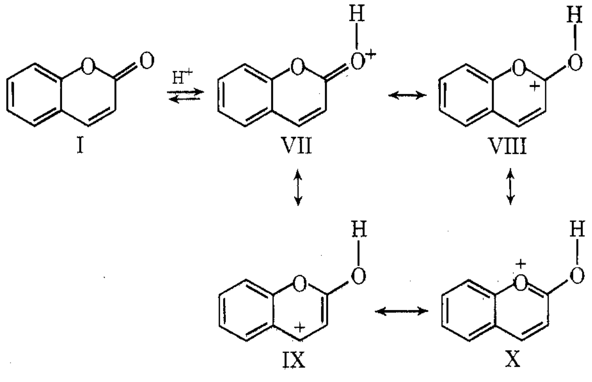
Table I gives the carbon-13 chemical shifts obtained in $CHCl_3$ and 96% H_2SO_4, as well as the chemical shift difference, Δ, between these two solvents. Assignments of resonance positions to individual carbon atoms were based on known substituent effects,[4] splitting patterns in proton-coupled spectra, and internal consistency. A positive Δ indicates that the resonance is deshielded in H_2SO_4 relative to $CHCl_3$.

There is a general deshielding pattern ($+\Delta$) for all carbons except C-3, which is shielded for coumarins I–III and V. With few exceptions, most notably coumarin VI, the aromatic carbon resonances are deshielded 0–9 ppm. Larger deshielding trends of between 10 and 20 ppm are observed for C-2 and C-4 with the shift of C-4 always larger than that of C-2. A shielding of 2–6 ppm for C-3 is observed for I–III and V while C-3 is deshielded in IV and VI.

The one-bond carbon–hydrogen coupling constants, $^1J_{CH}$, are included in parentheses in Table I as well as their difference in neutral and acidic solvent. In general, the value of $^1J_{CH}$ is larger in 96% H_2SO_4 solution. Peak assignments were aided by noting that the $^1J_{CH}$ of C-3 was frequently about 10 Hz larger than the remaining $^1J_{CH}$ values.

Discussion

The observed chemical shift trends are interpreted to result predominantly from protonation of the carbonyl oxygen (VII). A deshielding effect is associated with a loss of charge density for carbons of similar hybridization,[3] Thus,



large contributions from resonance forms VIII and IX, which place positive charge at C-2 and C-4, can be used to