Solid State Ultraviolet Spectra

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The ultraviolet spectra of organic solids can be obtained by studying single crystals,[2] by examining the powder sublimed or otherwise deposited onto quartz plates,[3] or absorbed onto silicic acid,[4] and by measuring the optical properties of a compacted sample in which the absorbing substance has been diluted with another material which is transparent in the spectral region being investigated.[5] This latter technique has been employed extensively in the infrared region but neglected in the ultraviolet, although it was proposed originally for both.

Recently we have found that the potassium bromide disk method is applicable to the study of organic compounds in the 220–400 mμ range. The spectra obtained from three widely divergent samples are shown in Figs. 1, 2, and 3, together with the corresponding solution spectra.

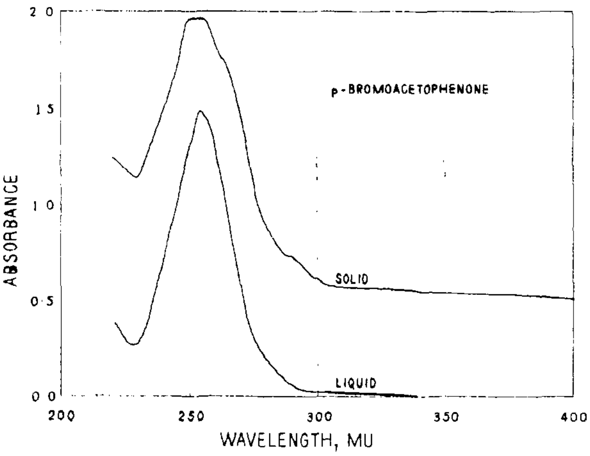

Figure 1

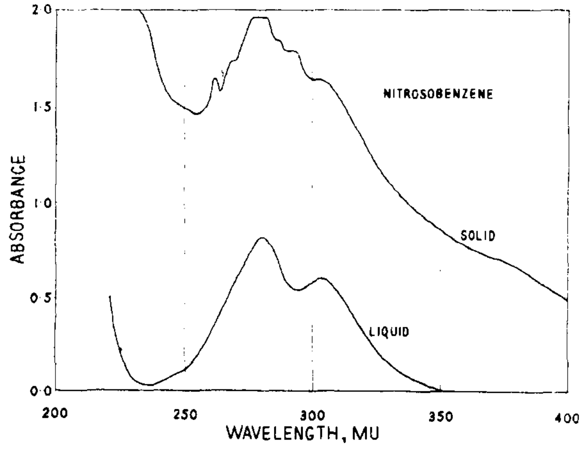

Figure 2

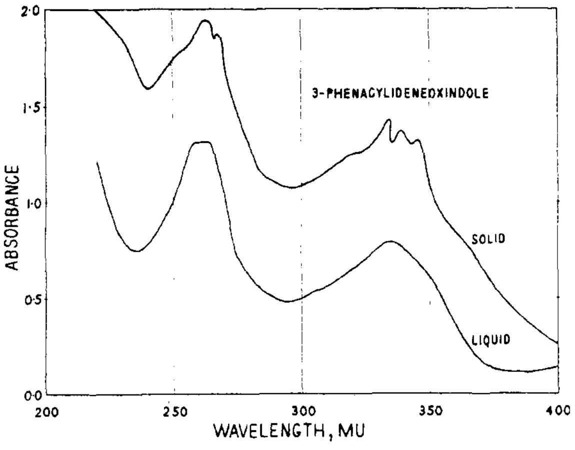

Figure 3

The principal advantages of this method are that (1) only extremely small quantities of sample are required; (2) sample preparation is easy and rapid; (3) sample disks can be filed for future reference; and (4) good quality spectra containing some fine structure are obtained. In addition, the spectra are free of solvent effects and should, therefore, be more amenable to theoretical interpretation.

EXPERIMENTAL

All melting points are uncorrected. Ultraviolet determinations were made with a Beckman DU quartz spectrophotometer.

p-Bromoacetophenone was obtained from Matheson, Coleman, and Bell, and was used without further treatment. It melted at 49–50° (lit.,[6] m.p. 49–50.5°).

Nitrosobenzene was prepared according to the directions of Vogel[7] and recrystallized three times from methanol to give an analytical sample, m.p. 67° (lit.,[8] m.p. 67.5–68°).

3-Phenacylideneoxindole was prepared by the method of Lindwall and Maclennan.[9] After recrystallization twice from ethanol, it melted at 193° (lit.,[9] m.p. 193–194°).

Sample preparation. A. Absolute ethanol solutions. Analytical solutions were prepared by standard volumetric techniques to give a final concentration of 0.02 mg. sample per ml. of absolute ethanol for all compounds examined. Absorption measurements on these solutions were made with 1 cm. silica cells using absolute ethanol as a blank.

B. Potassium bromide disks. Analytical grade potassium bromide and the sample compounds were separately ground in an agate mortar to approximately 200 mesh particle size. The appropriate weight of potassium bromide was taken and the desired weight of sample added directly, its weight being determined by difference from the weight of the mix-

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(2) A. Kronenberger, *Z. Physik*, **63**, 494 (1930).

(3) A. Kronenberger and P. Pringsheim, *Z. Physik*, **40**, 75 (1927).

(4) M. Robin, *J. Chem. Educ.*, **33**, 526 (1956).

(5) M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1805 (1952).

(6) R. Adams and C. R. Noller, *Org. Syntheses*, **Coll. Vol. I**, 110 (1941).

(7) A. I. Vogel, *Practical Organic Chemistry*, 3rd ed., Longmans, Green and Co., New York, 1956, p. 630.

(8) E. Bamberger and L. Storch, *Ber.*, **26**, 473 (1893).

(9) H. G. Lindwall and J. S. Maclennan, *J. Am. Chem. Soc.*, **54**, 4739 (1932).

ture.[10] The mixture was then thoroughly blended by further grinding together, placed in a Perkin-Elmer potassium bromide evacuable die, and pressed under approximately 25,000 p.s.i. (gauge) for 3 min. Spectral measurements were made using the disk holder described by Waggoner[11] with a similarly prepared 400 mg. potassium bromide disk for a blank.

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(10) The final compositions of the disks were: 0.05 mg. of *p*-bromoacetophenone, 0.3 mg. of nitrosobenzene, 0.2 mg. of 3-phenacylideneoxindole, each in 400 mg. of potassium bromide.

(11) W. H. Waggoner, *Chemist-Analyst*, **48**, 80 (1959).

Cyclic Ether Formation by Bis[(1-hydroxyethyl)cyclopentadienyl]iron

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The preparation of divinylferrocene was attempted in this laboratory by the use of diacetylferrocene (I) as a starting material. This was reduced to form bis [(1-hydroxyethyl) cyclopentadienyl]iron (II). This compound was previously reported as melting at 69–71°.[1] Infrared data and other evidence indicate that the compound produced by reduction of diacetylferrocene with sodium borohydride in this laboratory is in fact bis[(1-hydroxyethyl)cyclopentadienyl]iron II and has a melting point of 105–106°.

The attempted dehydration of this dialcohol (II) produced a cyclic ether (III) between the side chains of the two cyclopentadiene rings of ferrocene rather than the desired divinyl ferrocene.

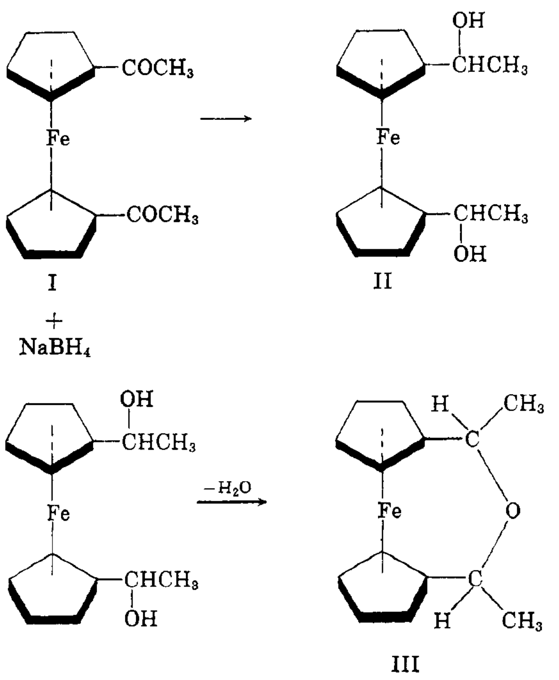
The infrared spectrum of II shows a strong hydroxy bond at 3.10 μ. The carbonyl bond is absent in the spectrum. Additional significant bonds appears at 7.35, 7.60, 9.10, and 12.41 μ. The infrared spectrum of the cyclic ether III shows a disappearance of the hydroxyl bonds. An ether bond at 8.8 μ can be cited as evidence for a cyclic ether. Other bonds appear at 7.68, 9.36, 9.88, 11.95, and 12.35 μ.

EXPERIMENTAL

Diacetylferrocene was prepared by following the procedure of Woodward (2).

Preparation of bis[(1-hydroxyethyl)cyclopentadienyl]iron. In a liter one-neck flask, fitted with a reflux condenser, was placed 27.0 g. (0.0985 mole) of diacetyl ferrocene, 7.56 g. (0.2 mole) of sodium borohydride, and 200 ml. of isopropyl alcohol. The mixture was refluxed for 5 hr. on a steam bath.

The solution was then evaporated to dryness by means of an air stream and water was added to the residue to hydrolyze the salt formed in the reaction. The product was then extracted with ether. The ether was removed and a yellow crystalline solid was obtained, which was recrystallized from methanol The yield was 14.4 g. (53.4%), m.p. 105–106°.



Anal. Calcd. for $C_{14}H_{18}O_2$ Fe: C, 61.31; H, 6.57. Found: C, 61.36; H, 6.72.

Preparation of 1,1′-diethyl-α,α′-epoxybiscyclopentadienyliron (II)(III). In a 1-l. flask, fitted with a reflux condenser, was placed 27.0 g. (0.0985 mole) of diacetylferrocene, 7.56 g. (0.2 mole) of sodium borohydride, and 200 ml. of isopropyl alcohol. The mixture was refluxed for 5 hr. on a steam bath.

The solution was then evaporated to dryness by means of an air stream and 100 ml. of water containing 5 ml. of glacial acetic acid was added to the residue to hydrolyze the salt formed in the reaction. The product was extracted with ether. The ether was evaporated and a yellow crystalline solid was obtained. The product was recrystallized from methanol. The yield was 11.2 g. (44.5%), m.p. 95–96°.

Anal. Calcd. for $C_{14}H_{16}O$ Fe: C, 65.52; H, 6.25. Found: C, 65.53; H, 6.42.

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(1) R. J. Graham *et al.*, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

(2) R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

Preparation of 2,6-Dioxocyclohexanepropionic Acid and δ-Oxoazelaic Acid from Glutaric Anhydride

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The preparation of δ-oxoazelaic acid (5-oxononanedioic acid) from disodioacetone dicarboxylic