[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

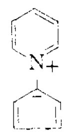
The Effect of Solvent on Spectra. IV. Pyridinium Cyclopentadienylide

BY EDWARD M. KOSOWER AND BRIAN G. RAMSEY

RECEIVED AUGUST 11, 1958

The preparation of the ylide, pyridinium cyclopentadienylide, according to the synthesis of Lloyd and Sneezum, is reported. The behavior of the visible absorption band in solvents of different **Z**-value (empirical polarity measure) corresponds to that of an *intramolecular charge-transfer transition* and this conclusion is supported by comparison with the spectra of 4-carbamidopyridinium cyclopentadienylide. Photolysis of pyridinium cyclopentadienylide in *n*-heptane produces *pyridine* and a very unstable species, possibly the unknown hydrocarbon, *fulvalene*.

Several years ago, Lloyd and Sneezum reported the preparation of an interesting new ylide, pyridinium cyclopentadienylide (I).[1-3] Our interest was aroused by their statement that solutions of I varied in color from yellow in water to bluish-purple in heptane, with intermediate shades between those extremes appearing in solvents of intermediate polarity. Had a single electronic transition been responsible for the color, its sensitivity to the medium would have approached the level which we have recently reported for 1-ethyl-4-carbomethoxypyridinium iodide complex.[4] The intention of our work was to examine the manner in which the spectrum of the ylide I varied with solvent.



I

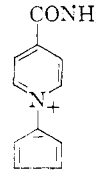
A detailed procedure for the preparation of I has not yet been reported[5] and it was necessary to develop a satisfactory experimental procedure for its synthesis, based on the route used by Lloyd and Sneezum.[3] The compound is rather sensitive to a number of reagents, and, for this reason, we have also confirmed the structure in the manner previously mentioned[3] by quantitative hydrogenation to 1-cyclopentylpiperidine.

Pyridinium cyclopentadienylide can be precipitated by cautious addition of base to an acidic aqueous solution of 1-cyclopentadienylpyridinium ion. When first separated, the crystals form bright red-gold leaflets which become the color of burnished copper upon isolation. *The ylide is extremely sensitive to oxygen, especially in solution, and all operations must be carried out in an inert atmosphere.* The melting point, as might be expected for a zwitterion, is extremely high (>350°), and the solubility is quite low in all neutral solvents. A sufficient concentration can be obtained in most solvents for spectroscopic work, but the solutions are unstable, slowly depositing an insoluble brown precipitate at a rate which is accelerated by oxygen, and apparently unaffected by light. In contrast, a carefully prepared red-purple solution of the ylide in *n*-heptane loses its color only very slowly in the dark, but much more rapidly in the light. The photolysis will be discussed below.

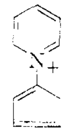
In order to establish the nature of the various transitions which were observed, an increased electron affinity in the pyridinium portion of the ylide was established by the introduction of a carbamido group into the 4-position of the pyridinium ring. The ylide, 4-carbamidopyridinium cyclopentadienylide (II), was prepared by a procedure like that used for the unsubstituted ylide I, and was a lavender-purple powder which appeared to polymerize even when stored dry under nitrogen.

Spectra of the Ylides I and II.—Both ylides absorb in three distinct regions of the spectrum, which may, for convenience, be referred to as the 5000, 3300 and 2400 Å. regions. The unsubstituted ylide I has in addition, in most solvents, a fourth band at *ca.* 2250 Å.

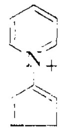
In methanol, I possesses maxima at 4858, 3365, 2450 and 2250 Å.; the band at 4858 Å. disappears upon the addition of acid to the solution, and an increase in the 3365 Å. peak occurs simultaneously. The opposite behavior obtains when base is added. The longest wave length absorption band is therefore assigned as characteristic of the ylide itself, while the 3365 Å. absorption must be due largely to the pyridinium ion of structure III, with the isomeric pyridinium ion IV as another less likely possibility. The absorption maxima for the ylide I in ten solvents are recorded in Table I, while data for the substituted ylide II are listed in Table II.



II

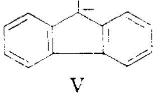


III

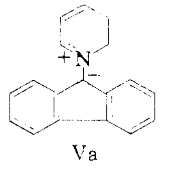


IV

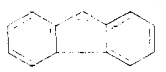
Discussion.—Ingold and Jessop[6] attributed the strong purple color of a solution of 9-fluorenyltrimethylammonium hydroxide to the ylide V and



V



Va



VI

---

(1) Based on a thesis submitted by B. G. Ramsey in partial fulfillment of the requirements for the M.S. degree.

(2) Supported in part by Grant E-1608 of the National Institutes of Allergy and Infectious Diseases of the National Institutes of Health, Public Health Service, and by funds granted by the Wisconsin Alumni Research Foundation through the Research Committee of the Graduate School.

(3) D. Lloyd and N. S. Sneezum, *Chemistry & Industry*, 1221 (1955).

(4) E. M. Kosower, THIS JOURNAL, **80**, 3253 (1958).

(5) After this article was submitted for publication, a complete report appeared in print; D. Lloyd and N. S. Sneezum, *Tetrahedron*, **3**, 334 (1958).

(6) C. K. Ingold and J. E. Jessop, *J. Chem. Soc.*, 2357 (1929).

TABLE I

ABSORPTION MAXIMA OF PYRIDINIUM CYCLOPENTADIENYLIDE

Solvent	λ_{max} (10^{-3} ε)[a], Å.	λ_{max} (10^{-3} ε),[b] Å.	λ_{max} (10^{-3} ε), Å.	λ_{max} (10^{-3} ε), Å.
Water	4534 (4.6)[c]	3333 (6.9)	2450 (11)[d]	2240 (12)
	(20)[c,e]	(8.6)[f]		2290 (14)[g]
1,2-Ethanediol	4882 (1.0)	3370 (10)	....	....
Methanol	4858 (10)	3365 (2.6)	2450 (7.7)[h]	2250 (9.0)
	(18)[c,e]	(5.7)[f]		2300 (9.0)[g]
Ethanol	4958 (15)	3435 ± 40 (2.7)	2459 (8.0)	2250 (9.3)
	(16)[e]	(6.3)[f]		2319 (8.2)[g]
2-Propanol	4977 (14)	3419 (2.0)	2460 (6.4)	2240 (8.0)
t-Butyl alcohol	5012 (13)	3450 (1.1)	2465 (5.6)	2240 (6.0)
Acetonitrile	4953 (19)	..[i]	2455 (8.0)	2250 (9.1)
Acetone	5088 (16)[c]	..[j]		
Chloroform[k]	5112 (22)[c]	..[l]	2464 (11.2)	
n-Heptane	5570[m] ..[n]	..[o]	2456 ..[n]	
	5165[m]			

[a] Accurate to at least ±8 Å. [b] ±10 Å., *except where noted.* [c] Absorption intensities obtained with material of analytical purity. Other ε-values were multiplied by an appropriate factor to correct for the presence of inert, non-absorbing impurity. [d] In solvent containing sodium hydroxide. [e] Maximum ε in the presence of base. [f] Maximum ε in the presence of acid. [g] In solvent plus sulfuric acid. [h] Shoulder. [i] A low intensity maximum is observed at 3371 Å. (ε 1500); its presence in a non-hydroxylic solvent and its general appearance suggest that it is a higher energy intramolecular c–t. transition, but it may be an electronic transition of the conjugated pyridinium ion. [j] Low intensity band at 3850 Å. (ε 2000), probably an i.c.t. transition (see footnote *i*). [k] 0.13 *M* ethanol (C.P. solvent). [l] Low intensity maxima at 3790 Å. (ε 1800) and 3440 Å. (ε 1600), probably i.c.t. (see footnote *i*). [m] Resolved maxima from a broad double maximum with peaks at 5460 and 5240 Å. [n] Solubility in *n*-heptane is so low that an accurate ε could not be determined; the longest wave length band probably has ε above 10,000. [o] Low intensity maxima at 4200 and 3790 Å., probably i.c.t. (see footnote *i*).

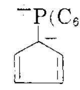
TABLE II

ABSORPTION MAXIMA OF 4-CARBAMIDOPYRIDINIUM CYCLOPENTADIENYLIDE

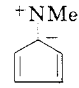
Solvent	λ_{max}, Å[a,b]	λ_{max}, Å.[a,b]	λ_{max}, Å.[a,b]
Water	5178	3610	2362
Methanol	5444	3492	2478
2-Propanol	5500	3600	2540
			2480[c]
Acetonitrile	5450	3390[d]	2480
Chloroform[e]	5578	..[f]	2555
Pyridine	5606		

[a] ±10 Å. [b] ε's were not obtained due to *insoluble* decomposition products in solid samples (see Experimental). [c] After addition of H_2SO_4. [d] Shoulder at 3800 Å.; identification of maximum and shoulder uncertain. [e] 0.13 *M* ethanol (C.P. solvent). [f] Maximum at 3450 Å., similar to that of acetonitrile (see footnote *d*).

Pinck and Hilbert isolated the ylide Va as an unstable purple-blue precipitate which gave indigo colored solutions in most organic solvents.[7] Kröhnke has confirmed these results.[8] The related triphenylphosphonium fluorenylide (VI) forms yellow plates,[9] while the more recently prepared triphenylphosphonium cyclopentadienylide (VII) is pale yellow and apparently quite stable.[10] Although the spectrum of VII was reported in two neutral solvents, 95% ethanol and acetonitrile, inspection of the data in Table I will reveal that the apparent lack of solvent sensitivity may be fortuitous, and that further investigation in water and hydrocarbon solvents would be worthwhile. Dauben[11] has found that trimethylammonium cyclopentadienylide (VIII) is pink, *i.e.*, it lacks the long wave length transition characteristic of V. The purple color of V (and probably Va) may be assigned to transitions within the fluorenylide portion of the molecule. The color of the phosphonium ylides seems to be associated with considerable stabilization of the ground state achieved through expansion of the octet around phosphorus, a view which is confirmed by the low dipole moment found for VIII.[10]



VII



VIII

The color of the ylides I and II must be due to the presence of an ion with a relatively low ionization potential *and* an electron acceptor which cannot expand its valence shell, in this case, the π-bonds of the pyridinium ring. The solvent sensitivity of the longest wave length absorption band (due to the ylide, *vide supra*) and the relationship of the transitions observed in the visible for the unsubstituted pyridinium cyclopentadienylide I and the 4-carbamidopyridinium derivative II are in agreement with the identification of the band in the 5000 Å. region as an *intramolecular charge–transfer transition.*

The transition energies for the i.c.t. band of I and II are plotted against **Z**, a recently developed standard of solvent polarity,[4] in Figs. 1 and 2. The close relationship between the visible absorption bands of I and II is illustrated by a plot of the transition energies of I against those for II (Fig. 3). The whole spectrum of pyridinium cyclopentadienylide (I) under various conditions in ethanol is shown in Fig. 4, and the spectrum in chloroform and *n*-heptane is given in Fig. 5.

Studies of the variation of spectrum with solvent have been reported for pyridine-1-oxide[4] and the

---

[7] L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 2011 (1946).

[8] F. Kröhnke, *Chem. Ber.*, **83**, 253 (1950); *Angew. Chem.*, **65**, 605 (1953).

[9] L. A. Pinck and G. Hilbert, THIS JOURNAL, **69**, 723 (1947).

[10] F. Ramirez and S. Levy, *ibid.*, **79**, 67 (1957); *J. Org. Chem.*, **21**, 448 (1956).

[11] H. J. Dauben, Chemistry Department, University of Washington, personal communication.

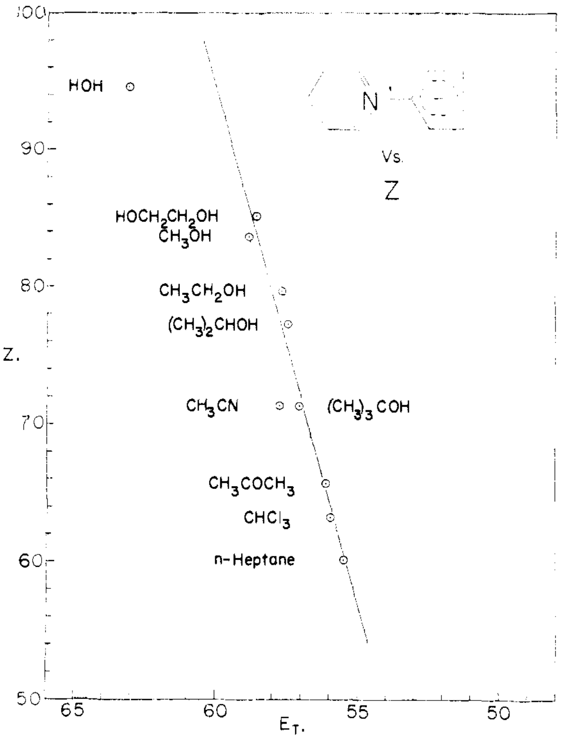


Fig. 1.—A plot of the transition energies (i.c.t. band) of pyridinium cyclopentadienylide (I) against **Z** (empirical solvent polarity); E_T = 0.1332**Z** + 47.41 (water and acetonitrile neglected).

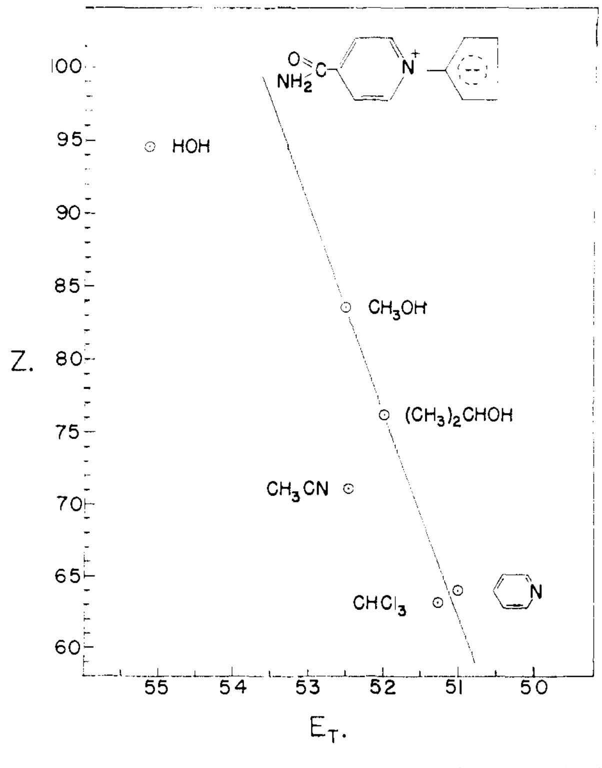


Fig. 2.—A plot of the transition energies (i.c.t. band) of 4-carbamidopyridinium cyclopentadienylide (II) against **Z** (empirical solvent polarity); E_T = 0.06969**Z** + 46.67 (water and acetonitrile neglected).

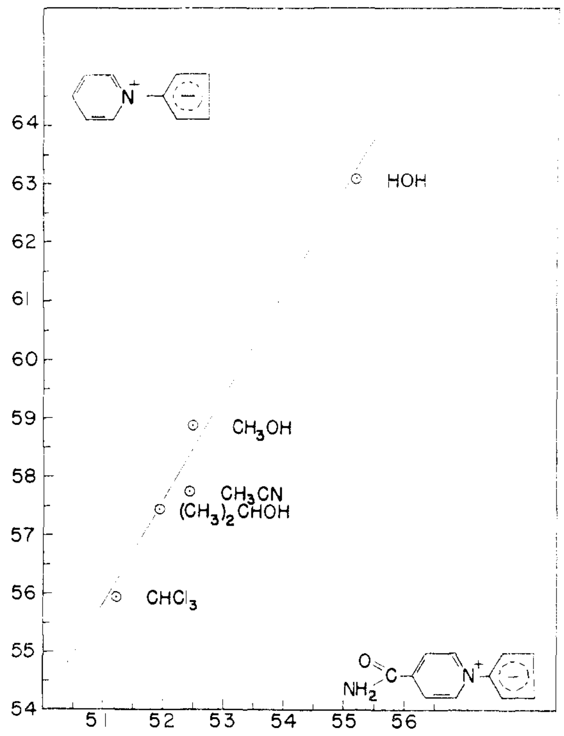
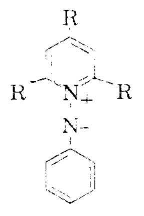


Fig. 3.—Transition energies of I *versus* transition energies of II; E_T(I) = 1.7705E_T(II) = 34.56 (acetonitrile neglected).

betaines (IX) derived from 1-phenylaminopyridinium ions.[12] The former transitions correlate moderately well with **Z**[4] but the data available for the latter[12] are not sufficient to suggest more than that there is some correlation with **Z**, especially in hydroxylic solvents.



IX

As we have already shown,[4] the presence of an electron-withdrawing group on the 4-position of the pyridinium ring in 1-alkylpyridinium iodide complexes moves the charge–transfer band to longer wave lengths. Qualitatively, the shift of the i.c.t. band in water from 4534 to 5178 Å. on the substitution of a 4-carbamido group in I is in accord with its expected behavior. Semi-quantitatively, the ΔE_T value of *ca.* 5 kcal./mole in chloroform is not too far away from that roughly analogous ΔE_T value of *ca.* 6.5 kcal./mole estimated for the same solvent for 1-ethyl-pyridinium iodide[13] and 1-ethyl-4-carbamidopyridinium iodide c.-t. bands.[14] The basis for the utilization of ΔE_T values has been found elsewhere.[14] We may therefore express the i.c.t.

---

[12] K. Dimroth, G. Arnoldy, S. von Eicken and G. Schiffler, *Ann.*, **604**, 221 (1957).

[13] J. A. Skorcz, unpublished results.

[14] E. M. Kosower and S. W. Bauer, unpublished results.

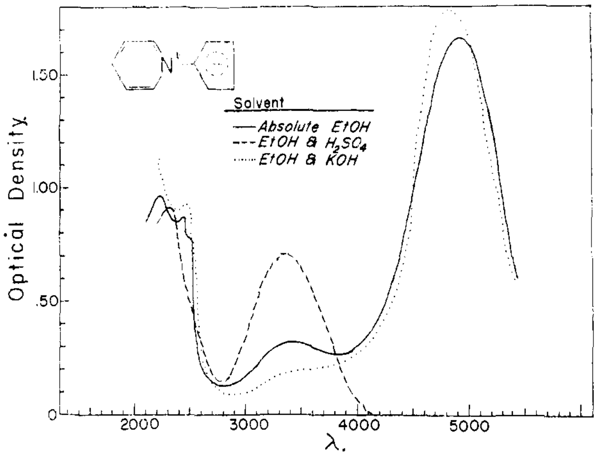


Fig. 4.—Absorption spectra of pyridinium cyclopentadienylide (I) in pure ethanol, ethanol and base, and ethanol and acid (concn. = 0.0160 g./l., 1-cm. cells).

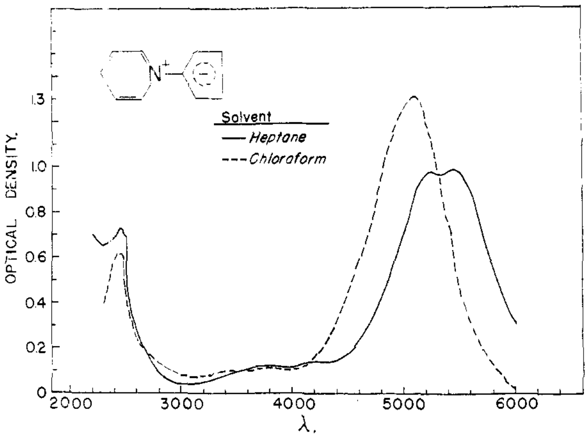


Fig. 5.—Absorption spectra in chloroform and heptane. The concentration in heptane is not known because of low solubility (concn. of chloroform solution = 0.0085 g./l., chloroform, 1-cm. cells; heptane, 5-cm. cells).

transition for I as the transformation X → XI, with the probable dipole directions indicated below the formulas.

X XI

Photolysis.—It was noted that solutions of pyridinium cyclopentadienylide (I) exposed to the light gradually faded and became completely *colorless.* While solutions kept in the dark retained color for two to three weeks, unfiltered light from a mercury vapor lamp (*i.e.*, ultraviolet with a visible component) caused decolorization in four to six hours, and *direct sunlight*[15] resulted in colorless solutions in *two* to *three* hours. A spectrum of the solution (transferred under nitrogen) immediately after loss of color was complete showed four maxima, at 3100, 2635, 2520 and 2456 Å. The broad 3100 Å. band disappears slowly on standing at room temperature or more rapidly on brief heating to *ca.* 60°. The spectrum of the solution is then rather similar to that of pyridine. Fractional distillation of the photolysate gave a fraction with an ultraviolet spectrum (Fig. 6) which matched that of pyridine (in *n*-heptane) in every respect, and differed from spectra of 2-, 3- and 4-methylpyridines in the same solvent. Extraction of the photolysate, before or after distillation, with a solution of picric acid in ethanol yielded pyridine picrate, identical to an authentic sample. Loss of ylide I thus depends upon (1) light absorption in the charge–transfer band (or equivalent thermal excitation) and (2) dissociation of the diradical excited state XI as pyridine and diradical XII from cyclopentadiene. The diradical probably possesses moderate stability, in view of the ease of its formation (the c.–t. bands in *n*-heptane correspond to photons of 50–55 kcal./mole energy), and might be thought of as a singlet molecule, with two electrons in a p-orbital of carbon-1 perpendicular to the plane of the ring, and an empty sp^2 orbital belonging to the same carbon in the plane.

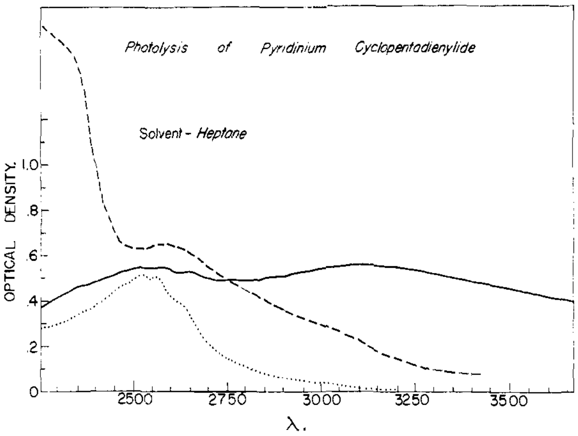
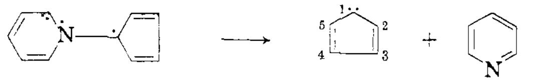
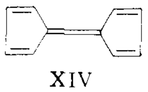


Fig. 6.—Spectra of photolyzed solutions of pyridinium cyclopentadienylide in *n*-heptane: ——, photolyzed solution (sample of 100 ml.); ....., distillate of photolyzed solution (first 10 ml.); – – –, residual solution after distillation of *ca.* 25 ml.

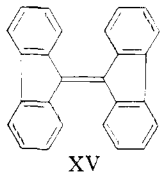


XIa (resonance form of XI) XII XIII

Although it is conceivable that the unstable substance with ultraviolet absorption at 3100 Å. is the diradical XII itself, it is more likely that the diradical has dimerized, and that the previously unreported hydrocarbon, **fulvalene (XIV)**, is present in solution. Attempts to trap the diradical or to prepare a derivative of fulvalene[16] are now in progress. It is worth noting that ylide V decomposes in part to yield 9,9′-bis-fluorenylidene (XV).[6]



XIV



XV

---

[15] Wisconsin spring and summer sunlight, when available.

[16] Perchlorofulvalene has been reported by E. T. McBee, C. W. Roberts and J. W. Idol, Jr., THIS JOURNAL, **77**, 4942 (1955).

Experimental

Preparation of Pyridinium cyclopentadienylide (I).—Bromine (80 g., 0.5 mole) is added dropwise to cyclopentadiene (40 ml., 32 g., 0.48 mole) in chloroform (150 ml.) with stirring and cooling (temperature between −5 and 0°). Pyridine (80 ml., 78 g., 1.0 mole) is then added in the same manner, and the reaction mixture is stored under nitrogen in the dark for 24 hours at room temperature. Lower temperatures and longer reaction times usually give poorer results. After standing, a dark brown viscous oil forms a lower layer in the reaction mixture. The oil is separated, extracted with 5% hydrochloric acid which has been purged with nitrogen, and the dark brown aqueous solution filtered through Norite which has previously been acid washed to remove metal oxides. The Norite treatment is repeated until the solution is colorless to pale yellow. The acid solution is cautiously made slightly basic with potassium hydroxide, maintaining the temperature at 25° or below. The product pyridinium cyclopentadienylide precipitates in bright red-gold leaflets which have the appearance of burnished copper on isolation. *All subsequent operations must be carried out under nitrogen.* The ylide is filtered, washed several times with deoxygenated distilled water, and dried over phosphorus pentoxide under nitrogen pressure of 0.1 mm. The solid is placed in evacuated sealed ampules and stored in the dark; yield 7 g. (*ca.* 10%). *Anal.* Calcd.: C, 83.9; H, 6.3. Found: C, 83.4, H, 6.6.

Attempts to recrystallize the ylide from water, ethanol, ether or benzene were unsuccessful because of low solubility and decomposition of the solutions.

Proof of Structure.—The ylide (0.4327 g.) in acetic acid containing hydrochloric acid absorbed 383 ml. of hydrogen (101% theoretical at S.T.P.) in one hour. The solution was made basic and extraction yielded after distillation some N-cyclopentylpiperidine, with an infrared spectrum identical with that of a sample prepared from cyclopentanone and piperidine by the method of Jones.[17] The picrate had m.p. 173–173.5°, alone and upon admixture with salt prepared from authentic 1-cyclopentylpiperidine, and the melting point was close to that previously reported, 174°.[17]

Acidity of Pyridinium Cyclopentadienylide (I).—The pK_a of the ylide was determined in two ways, the first by direct spectrophotometric measurement of the ratio of acidic and basic forms in a buffer solution, and second by potentiometric titration in acetonitrile solution.[18] The two methods agreed well, and the pK_a was found to be 10.0 ± 0.2, in good accord with the pK_a reported by Dauben[11] for the trimethylammonium cyclopentadienylide.

4-Carbamidopyridinium Cyclopentadienylide (II).—A solution of dibromocyclopentene in chloroform was prepared from 2.7 ml. of cyclopentadiene and 5.2 g. of bromine, and to this solution was added a suspension of isonicotinamide (pyridine-4-carboxamide, 4.5 g., 0.028 moles) in 50 ml. chloroform with stirring and cooling. Sodium acetate (5.0 g.) was added to the reaction mixture, the air replaced with nitrogen, and the whole stored in the dark at room temperature for 8 days. At the end of this period, the brown solid which had separated was filtered off and dissolved in 100 ml. of 1 *N* hydrochloric acid. The acidic solution was filtered through charcoal and the ylide precipitated by careful neutralization of the acid with sodium hydroxide. The product (approximate yield, 1.0 g., 20%) is a lavender-purple solid slightly soluble in hydroxylic solvents and insoluble (no solvent coloration) in *n*-heptane. Although stored in the dry state under nitrogen, after three days extensive polymerization had occurred as evidenced by only partial solubility in aqueous acid.

Spectra.—The solvents were Spectro grade or purified as previously described,[4] except for *n*-heptane. The latter was shaken with concentrated sulfuric acid until the acid layer was colorless, washed with water and distilled from Drierite. Solvents were purged with nitrogen before use, all solutions were prepared in a dry-box in a nitrogen atmosphere and all solution transfers were made in a manner to ensure minimum contamination with oxygen. The spectra were measured with a Cary recording spectrophotometer, model 11. A check in several solvents showed that pyridinium cyclopentadienylide (I) obeys Beer's law, *especially in heptane.* The low solubility of the yields in low polarity solvents necessitated the use of long path length cells (5.00, 10.0 cm.) and the difficulties associated with the oxygen sensitivity of the ylides caused somewhat larger uncertainties in the absorption intensities than might be desirable due to weighing errors. The absorption data are listed in Tables I and II.

Photolysis.—Saturated solutions of pyridinium cyclopentadienylide were prepared in nitrogen-purged *n*-heptane and sealed into 100-ml. volumetric flasks with paraffin. Solutions left in the dark required two to three weeks to decolorize while those exposed to a high-intensity mercury vapor lamp or direct sunlight[15] lost color in 4 to 6 hours and 2 to 3 hours, respectively. An ultraviolet spectrum of the solution, taken immediately after complete loss of color had occurred, showed four maxima, at 3100, 2635, 2520 and 2456 Å. The broad band at 3100 Å. slowly disappears, and is largely gone after 24 hours at room temperature or after brief heating to 60°. The colorless solution after a typical photolysis was fractionated through a jacketed column packed with helices, and the spectrum of the first 10 ml. compared to a series of pyridines, as shown in Table III.

TABLE III

ABSORPTION MAXIMA FOR PYRIDINES IN *n*-HEPTANE[a]

Sample, pyridine	λ_{max}, Å.	λ_{max}, Å.	λ_{max}, Å.
Distillate	2556	2513	
2-Methyl-	2680	2613	2559
3-Methyl-	2685	2627	2574
4-Methyl-	2553		
4-Ethyl-	2540		
Pyridine	2556	2513	

[a] The maxima for pyridine and the picolines are in substantial agreement with the values reported in the literature of H. P. Stephenson, *J. Chem. Phys.* **22**, 1077 (1954).

A suspension of pyridinium cyclopentadienylide (I) (50 mg.) in 500 ml. of *n*-heptane was stirred under the light of a mercury vapor lamp for 8 days. The solution was colorless, but a brown residue, presumably polymeric material, had settled to the bottom of the flask. The spectrum of the clear solution derived from the suspension was essentially the same as that from photolysis of a saturated solution of ylide I. The 500 ml. of solution was divided into two portions. The first was extracted with two 10-ml. portions of ethanol containing 5 drops of saturated picric acid solution in ethanol, and then with 10 ml. of water. The three extracts were combined, evaporated under an air stream to 3 ml. and the solid filtered off and recrystallized. The yellow crystals obtained in this way had a m.p. 166.5–167°, and showed no depression in m.p. upon admixture with authentic pyridine picrate, m.p. 166.5–167°. The second portion of the photolysate was refluxed for 45 minutes, and then worked up in the same way as the first portion, yielding pyridine picrate.

Temperature Effect upon I.c.t. Band.—The maximum for I in acetonitrile is found at 4960 Å. at 25°. The band shifts to 4996 Å. at 59.5°, as measured with the Cary using a thermostated cell compartment.

MADISON 6, WIS.

---

[17] J. E. Jones, *J. Chem. Soc.*, 1392 (1950).

[18] H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).