Tetrahedron, 1967, Vol. 23, pp. 2941 to 2957. Pergamon Press Ltd. Printed in Northern Ireland

THE 4-AZAPENTALENYL ANION

W. H. Okamura[1a] and T. J. Katz[1b]
The Department of Chemistry, Columbia University, New York, N.Y. 10027

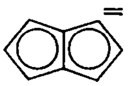
(*Received in USA* 17 *October* 1966; *accepted for publication* 22 *November* 1966)

Abstract—The simplest nitrogen heterocycle isoelectronic with the pentalenyl dianion is the 4-azapentalenyl anion ("azapentalenyl anion," VI). The preparation and properties of this anion are described. It was prepared by reacting 3H-pyrrolizine (IX) in tetrahydrofuran (THF) with n-butyllithium, with potassium, and with sodium. That lithium, sodium, and potassium azapentalenide are ionic is indicated by the similarity of their PMR spectra in THF. The NMR and UV spectra of potassium azapentalenide are recorded in Figs 1 and 4. Lithium azapentalenide in THF reacts with benzophenone and with benzil to give fulvenes, X or XI.

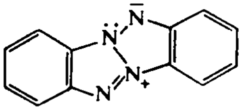
The anion is easily made and useful in preparing these derivatives, but the pK_a of its conjugate acid, 3H-pyrrolizine, estimated to be 29 from the rate of exchange of its protons with deuterium oxide and triethylamine, is greater than anticipated on the basis of the Hückel MO theory.

INTRODUCTION

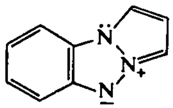
A NUMBER of nitrogen heterocycles containing a conjugated π-electron system isoelectronic with that in the pentalenyl dianion,[2] I, have recently been synthesized. These include compounds II,[3] III,[4] IV[5] and V,[6] but not the simplest such substance, the anion VI, in which only one carbon atom of I is replaced by the isoelectronic ion N^+. The preparation of the benzologue VII from VIII by reaction with phenyllithium in ether has been described briefly.[7] The preparation of the parent anion, VI, from the



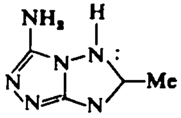
I



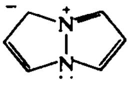
II



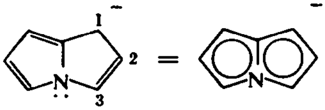
III



IV



V



VI

[1a] National Science Foundation Cooperative Fellow, 1964–1966; [b] To whom inquires should be sent.

[2] T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.* **84**, 865 (1962); T. J. Katz, M. Rosenberger and R. K. O'Hara, *Ibid.* **86**, 249 (1964).

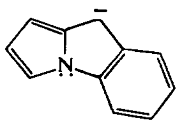
[3] R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.* **84**, 2453 (1962).

[4] B. M. Lynch and Y. Hung, *J. Heterocyclic Chem.* **2**, 218 (1965).

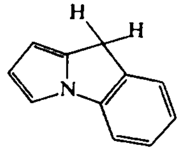
[5] R. G. Child and A. S. Tomcufcik, *J. Heterocyclic Chem.* **2**, 302 (1965).

[6a] S. Trofimenko, *J. Am. Chem. Soc.* **87**, 4393 (1965); [b] T. W. G. Solomons and C. F. Voigt, *Ibid.* **87**, 5256 (1965); [c] *Ibid.* **88**, 1992 (1966).

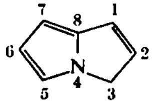
[7] E. Laschtuvka and R. Huisgen, *Chem. Ber.* **93**, 81 (1960).



VII



VIII



IX

known compound[8] 3H-pyrrolizine (IX), recently synthesized in a remarkable way from pyrrole 2-carboxaldehyde and triphenylvinylphosphoniumbromide,[8b] and some aspects of its chemistry are described below.

RESULTS

The azapentalenyl anion (VI). Lithium azapentalenide (VI) was prepared by treating 3H-pyrrolizine (IX) in THF at −78° with n-butyllithium in n-hexane in the same way that lithium pentalenide (I)[2] and other related substances[9–12] had been made from their conjugate acids. The lithium salt precipitates from this cold reaction mixture, but dissolves readily (in concentrations of about 2 molar) at room temperature.

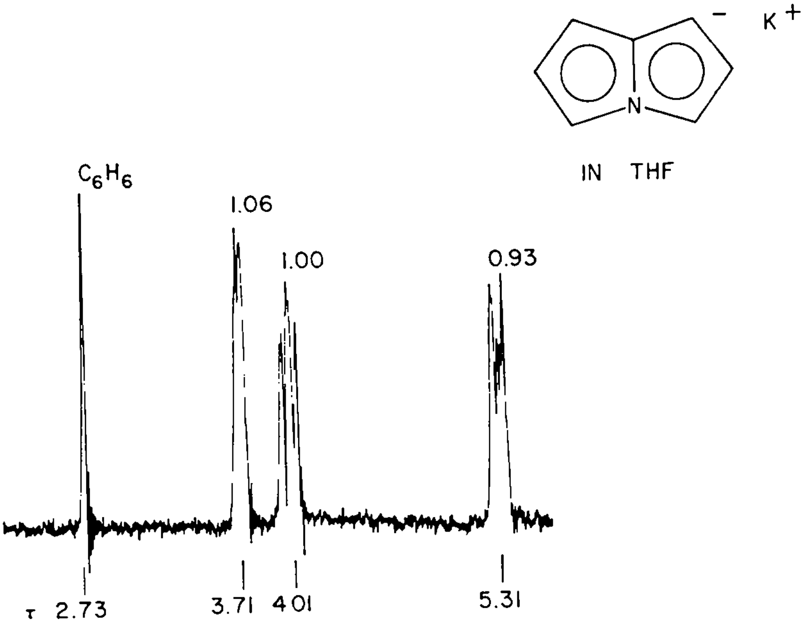


FIG. 1. Proton NMR spectrum (60 c/s) of potassium azapentalenide (2M) in THF with benzene as internal standard. Intensities are shown above the peaks.

[8a] V. Carelli, M. Cardellini and F. Morlacchi, *Ann. Chim. Rome* **53**, 309 (1963); *Chem. Abstr.* **59**, 7463e (1963); [b] E. E. Schweizer and K. K. Light, *J. Am. Chem. Soc.* **86**, 2963 (1964); *J. Org. Chem.* **31**, 870 (1966).

[9] The *as*-indacenyl dianion: T. J. Katz and J. Schulman, *J. Am. Chem. Soc.* **86**, 3169 (1964). The preparation was effected in dimethoxyethane.

[10] Dipentalenyliron dianion: T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.* **85**, 2030 (1963).

[11] Pentalenylcycloocta-1,5-dienerhodium anion: J. J. Mrowca, Dissertation, Columbia University, 1966.

[12] Dibenzopentalene dianion: A. J. Silvestri, *Tetrahedron* **19**, 855 (1963). The solvent was ether.

It can also be prepared in ether, in which it is less soluble. Solutions in THF are slightly yellow, and stable for months in the absence of air. On exposure to air they turn orange-red.

The potassium and sodium salts of the azapentalenyl anion, VI, were also prepared, but in a different way, by treating the 3H-pyrrolizine (IX) in THF with the alkali metals,[13] a preparation that proved particularly effective because it yielded an uncontaminated product: the solutions were only slightly yellow and the NMR spectrum of the potassium salt in perdeuterated THF exhibited no extraneous resonances. However, attempts to prepare the lithium salt in this way, using lithium metal, usually gave the product contaminated with the starting material.

The NMR spectra of the lithium, sodium, and potassium salts were determined in THF containing benzene as an internal standard. Except for small variations in the chemical shifts, the spectra of the three salts appeared identical. They all showed three multiplets of equal intensity, attributable to the three different kinds of protons in the azapentalenyl anion. The spectrum of potassium azapentalenide is shown in Fig. 1. The chemical shifts are summarized in Table 1.

TABLE 1. CHEMICAL SHIFTS OF POTASSIUM, SODIUM AND LITHIUM AZAPENTALENIDE IN THF AT AMBIENT TEMPERATURE

Cation	Chemical Shift (τ)[a]		
	H_A	H_B	H_C
K^+	3·71	4·01	5·31
Na^+	3·52	3·91	5·20
Li^+	3·57	3·97	5·25

[a] The position of the benzene resonance is taken to be τ 2·73.

The NMR spectrum of lithium azapentalenide was simplified by successively decoupling the nuclear spin-spin splitting of one of the protons. The spectra (Fig. 2) show that if the least shielded proton is labelled H_A and the most shielded H_C, then $|J_{AB}| = 2{\cdot}1$ c/s, $|J_{BC}| = 3{\cdot}2$ c/s, and $|J_{AC}| < 1$ c/s. No change in the normal spectrum was observed when the sample was irradiated at frequencies expected to induce nuclear magnetic transitions in ^{14}N.[14]

Quenching an ether suspension of the lithium salt with deuterium oxide gave 3-deuterio-3H-pyrrolizine, of which ca. 75% of the expected amount could be isolated. The deuterated sample could not be purified completely because passage through a vapor fractometer resulted in intermolecular exchange of deuterium atoms. However, a sample containing (by VPC analysis) 89% deuterated 3H-pyrrolizine and 11% solvent was shown by mass spectral analysis[15] to be mainly monodeuterated. (The analysis showed 4·65% C_7H_7N, 83·2% C_7H_6DN, 10·8% $C_7H_5D_2N$, and 1·52% $C_7H_4D_3N$.) That the deuterium atom was in the allylic position and that the atoms and bonds were in the same positions as in the starting material (presumably as in

---

[13] Cf. potassium fluorenide: G. W. H. Scherf and R. K. Brown, *Canad. J. Chem.* **38**, 2450 (1960); or benzylcesium: J. de Postis, *C.R. Acad. Sci. Paris*, **222**, 398 (1946).

[14] Experiment performed by NMR Specialties, New Kensington, Pa.

[15] K. Biemann, *Mass Spectrometry, Organic Chemical Applications* Chap. 5. McGraw-Hill, New York (1962).

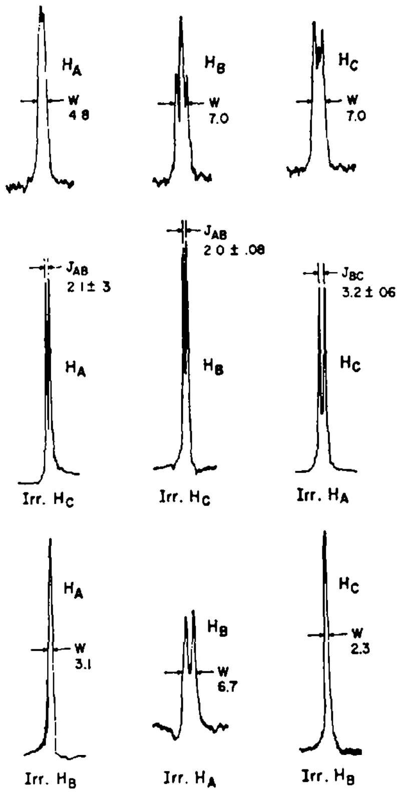


FIG. 2. NMR spectrum (60 c/s) of lithium azapentalenide in THF. The top row is the normal appearance of the resonances, while the others appeared when the sample was irradiated at the resonance frequency of one of the protons. The scale is c/s.

IX—the possibility that the materials are 1H-pyrrolizine and 1-deuterio-1H-pyrrolizine is considered below) was shown by the IR and NMR spectra. The IR spectra of the deuterated and undeuterated materials are most identical. Significantly absent in the deuterated sample is an absorption peak found in the undeuterated one at 1428 cm^{-1}, presumably[16] due to the symmetric bending vibration of the allylic methylene protons.

The NMR spectrum of the deuterated pyrrolizine was similar to that of the undeuterated material, but differed in a way expected if one of the allylic protons were replaced by deuterium. (There were also some small peaks due to unidentified impurities.) The NMR spectrum of 3H-pyrrolizine (IX) in benzene and in methanol is shown in Fig. 3: peaks that are overlapped in the former solvent at τ 3·7 are seen separately in the latter, and peaks that are overlapped at τ 4·1 in the latter are seen separately in the former.[17] A summary of the chemical shifts in these solvents and an

---

[16a] K. Nakanishi, *Infrared Absorption Spectroscopy*, Holden-Day, San Francisco, (1962); [b] A similar change is observed in the IR spectrum of the conjugate acid of pentalenylcycloocta-1,5-dienerhodium anion when the anion is quenched with D_2O.[11]

[17] Solvent effects are discussed in N. S. Bhacca and D. H. Williams, *Applications of NMR Spectroscopy in Organic Chemistry* Chap. 7. Holden-Day, San Francisco, (1964),

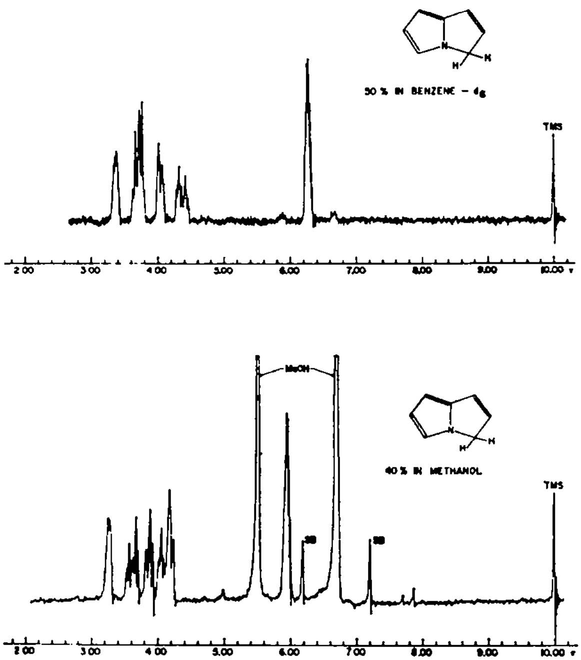


FIG. 3. Proton NMR spectra (60 c/s) of 3H-pyrrolizine with TMS as internal standard. The peaks labeled SB are spinning side-bands.

assignment of their origin is in Table 2. The changes that occur on deuteration provide a basis for the assignment of the resonances of protons 1 and 2. Of these, the less shielded is believed to be 1.[18] Of the remaining protons, 5 is believed to be the least shielded on the basis of precedents that the α protons in pyrroles are usually at lower fields than the β protons.[19] Protons 6 and 7 are assigned according to the appearance of the splitting patterns.[20] The protons 1, 2 and 3 appear to give an AMX_2 pattern further split by cross-ring coupling.[22] From the splittings observed in the olefin proton resonances $|J_{12}| = 6{\cdot}2$, $|J_{13}| = 2{\cdot}2$, and $|J_{23}| = 2{\cdot}0$ c/s. The magnitudes

TABLE 2. CHEMICAL SHIFTS OF PROTONS IN 3H-PYRROLIZINE (τ)

Proton	Solvent	
	Benzene	Methanol
5	3·43	3·20
1	3·8	3·63
6	3·8	3·88
7	4·10	4·1
2	4·42	4·1
3	6·30	5·95

---

[18] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.* **36**, 2346 (1962).

[19] R. L. Hinman and S. Theodoropulos, *J. Org. Chem.* **28**, 3056 (1963).

[20] A first-order analysis of the spectra in Fig. 3 suggests that $|J_{56}| = 2{\cdot}5$ and $|J_{67}| = 3{\cdot}3$ c/s, in accord with analogous couplings in other pyrroles.[21]

[21] S. Gronowitz, A.-B. Hornfeldt, B. Gestblom and R. A. Hoffman, *Arkiv Kemi* **18**, 133 (1961).

[22] Cross-ring couplings are observed in indene[18] and in polycyclic aromatic compounds [S. Sternhell, *Rev. Pure and Appl. Chem.* **14**, 15 (1964)].

of these coupling constants are similar to those in indene.[18] The resonances assigned to protons 1 and 2 are further split into doublets, separated in 1 by 0·7 c/s and in 2 by 0·9 c/s. Proton 3 appears to give a symmetrical septet (ca. 1 c/s between peaks); it appears to be coupled not only to protons 1 and 2, but also (or virtually coupled)[23] to two others ($|J| \sim 1$ c/s).[24] The deuterated 3H-pyrrolizine showed the same NMR spectra (neat[25] and in methanol) as the undeuterated material, except that the presumed AMX_2 pattern was replaced by what appeared to be an AMX pattern with the same coupling constants. Protons 1 and 2 appeared as a doublet of doublets ($|J_{12}| = 5·9$, $|J_{13}| = 2·2$ and $|J_{23}| = 2·2$ c/s) split further by cross-ring couplings.[26,27]

The UV spectrum of potassium azapentalenide, formed by reacting 3H-pyrrolizine in THF with potassium metal, was determined and is recorded together with that of 3H-pyrrolizine in Fig. 4. The anion exhibits a maximum at 295 mμ (ε 9,600) and a shoulder at approximately 210 mμ (ε 20,000). Upon quenching the solution used to determine the UV spectrum with a drop of oxygen-free water, the spectrum of 3H-pyrrolizine was reproduced.

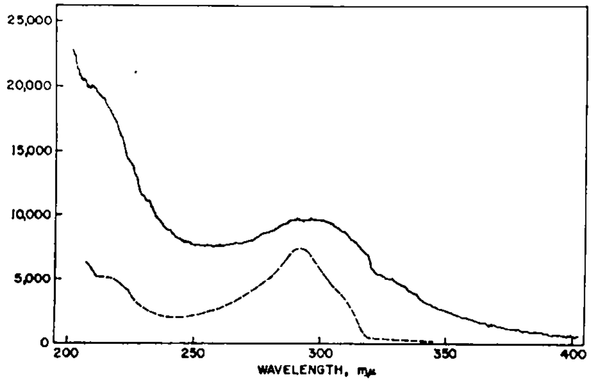
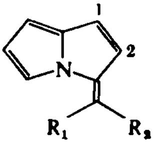
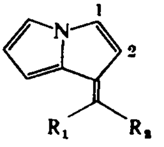


FIG. 4. UV spectra of potassium azapentalenide (———) and 3H-pyrrolizine (- - -) in THF.

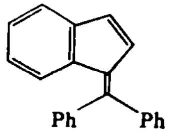
Fulvene derivatives. Lithium azapentalenide in THF reacts with benzophenone to give in 51 % yield an orange-red crystalline fulvene, either Xa or XIa, identified by its analysis and the mass of the parent ion in its mass spectrogram. Its NMR spectrum,



X



XI



XII

a: $R_1 = R_2 = C_6H_5$
b: $R_1, R_2 = C_6H_5, C_6H_5CO$

---

[23] J. I. Musher and E. J. Corey, *Tetrahedron* **18**, 791 (1962).

[24] The methylene protons of indene give rise to a triplet broadened by cross-ring coupling.[18]

[25] The spectrum neat is similar to the spectrum in benzene (Experimental and Ref 8*b*).

[26] Similar changes are observed in the NMR spectra of the conjugate acid of a related anion, pentalenylcycloocta-1,5-dienerhodium anion, when the anion is quenched with D_2O.[11]

[27] Lithium indenide on quenching with D_2O gives 1-deuterioindene [W. R. Roth, *Tetrahedron Letters* No. 17, 1009 (1964)].

shown in Fig. 5, consists of two singlets at τ 2·72 and 2·92 (the phenyl protons), an AB quartet at 3·64 and 3·89 (|J| = 5·9 c/s,[28] presumably H_1 and H_2), and multiplets at 4·22 and 4·39 (the pyrrole protons). Its UV spectrum (Table 3) is remarkably similar to that of the analogous indene derivative, XII.[29]

Similarly benzil condenses with lithium azapentalenide to give in low yield (9%) a fulvene, either Xb or XIb. Its mass spectrum shows, besides the parent ion (base peak at *m/e* 297), prominent peaks at 105 (phenacylium ion, $C_7H_5O^+$) and 192 (the remainder of the molecule). Its IR spectrum shows a CO stretching vibration at 1655 cm^{-1}. Its NMR spectrum (Fig. 5), like the benzhydrylidene derivative, shows an AB quartet (|J| = 5·9 c/s[28]). Of the remaining protons, the resonance of one overlaps this pattern.

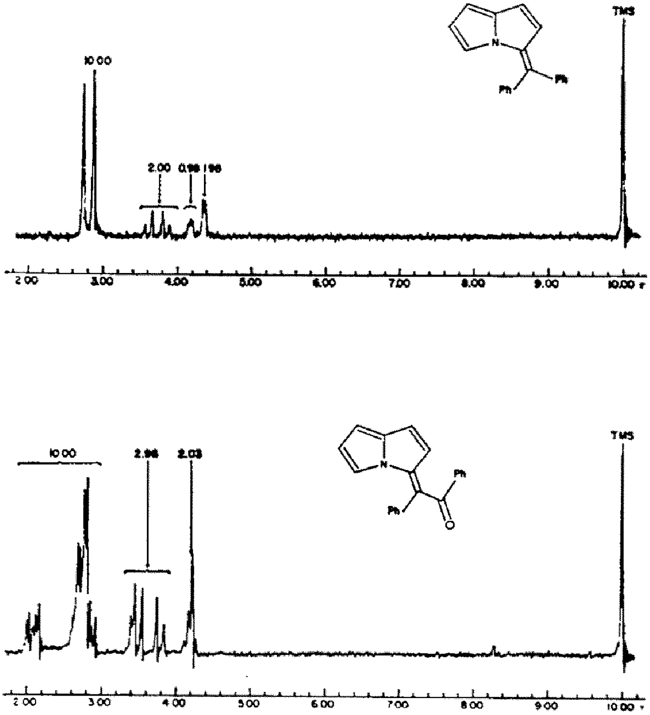


FIG. 5. NMR spectra (60 c/s) of the fulvene derivatives. Intensities are shown above the peaks. TMS is the internal standard. The spectra are labeled with one of the possible structures. Solvents are CCl_4 for the top spectrum and $CDCl_3$ for the bottom.

Acidity of 3H-*pyrrolizine*. The acidity[30] of 3H-pyrrolizine was estimated from the rate of exchange of its protons with 5M D_2O in DMF containing 1M triethylamine, a procedure developed by Dessy *et al.*[31] The logarithms of the relative rates of exchange of various hydrocarbons and the pK_a values suggested[30a] are given in Table 4 and

---

[28] This is the magnitude of the coupling constant of vicinal protons in a number of cyclopentenes. O. L. Chapman, *J. Am. Chem. Soc.* **85**, 2014 (1963); G. V. Smith and H. Kriloff, *Ibid.* **85**, 2016 (1963).

[29] E. Bergmann and A. F. von Christiani, *Chem. Ber.* **63**, 2559 (1930).

[30a] D. J. Cram, *Fundamentals of Carbanion Chemistry* Chap. 1. Academic Press, New York (1965); [b] A. Streitwieser, Jr. and J. H. Hammons, *Progress in Physical Organic Chemistry* Vol. 3; pp. 41 ff. Interscience, New York, (1965).

[31] R. E. Dessy, Y. Y. Okuzumi and A. Chen, *J. Am. Chem. Soc.* **84**, 2899 (1962).

TABLE 3. UV SPECTRA OF THE FULVENE DERIVATIVES IN 95% ETHANOL AND IN CYCLOHEXANE

	$\lambda_{\max}^{m\mu}$ (ε)	
Compound	95% EtOH	Cyclohexane
Xa or XIa	242 (13,000)	247 (15,000)
	342 (17,000)	346 (17,000)
	407 (sh, [a]4100)	413 (sh, 4100)
XII	242 (20,400)	244 (21,000)
	284 (12,900)	286 (13,000)
	339 (15,100)	342 (15,100)
Xb or XIb	222 (sh, 15,000)	228 (sh, 17,000)
	253 (14,000)	248 (16,000)
	332 (16,000)	333 (18,000)
	and tail into the visible	

[a] sh = shoulder

plotted in Fig. 6. The rates were measured at 40·3° at substrate concentrations that were usually 1M. However, because of fluorene's low solubility it had to be studied at 0·5M, and for comparison a few of the other compounds were re-examined at this lower concentration. The least squares straight line that relates the observed logarithms of the relative rates of exchange (log R.A.) to the pK_a's is

$$\mathrm{p}K_a = 19{\cdot}09 - 2{\cdot}139 \log \mathrm{R.A.} \qquad (1)$$

The pK_a's calculated from the observed rates are shown in Table 4. The standard error of estimate of pK_a is 0·4.

TABLE 4. LOGARITHMS OF RELATIVE EXCHANGE RATES (LOG R.A.) AND pK_a'S

	Log R.A.			
Compound	Dessy *et al*[a]	This work[b]	pK_a[c]	pK_a calc.[f]
Cyclopentadiene	2·230		15	
Acetophenone	0·519	0·114	19	18·8
Indene	—	0·439	18·5	18·2
Phenylacetylene	0·000[d]	0·000[d]	18·5	19·1
Fluorene	−1·481	−1·735	22·9	22·8
3H-Pyrrolizine		−4·491[e]		29

[a] Ref. 31.

[b] Rates were measured at 40·3° and are corrected for statistical effects by dividing by the number of exchangeable hydrogens.

[c] Cram's "MSAD" values (Ref. 30*a*).

[d] Rates are given relative to phenylacetylene (cf. Ref. 31).

[e] Extrapolated from rates at 85·0° and 100·6°.

[f] Calculated using Eq. 1.

The rate of exchange of 3H-pyrrolizine was too slow to measure at 40·3° and was extrapolated (using the Arrhenius relationship from rates measured at 85·0° and 100·6° [1]. This rate (Table 4) and Eq. 1 imply that the pK_a of 3H-pyrrolizine is 29.

DISCUSSION

NMR spectra of the azapentalenyl anion

Coupling constants. The NMR spectra of the azapentalenyl anion (Figs. 1 and 2) show three magnetically-distinct kinds of protons, A, B, and C (cf. Table 1) with coupling constants $|J_{AB}| = 2{\cdot}1$, $|J_{BC}| = 3{\cdot}2$, and $|J_{AC}| < 1$ c/s. Because B is coupled to both A and C, it is presumably the proton on carbon 2 (cf. VI). Of the remaining protons, the less shielded one (A) is assigned[32] to the carbon (3) adjacent to the nitrogen. The magnitudes of the observed spin-spin coupling constants are similar to related couplings in the pentalenyl dianion (3·0 c/s)[2], the indenyl anion (3·4 c/s),[33] and 4,8-diazapentalene (2·5 c/s).[6] They are remarkably like those in pyrroles[34] (see the valence bond structure VI).

Chemical shifts. The similarity of the proton chemical shifts of potassium, sodium, and lithium azapentalenide (Table 1) suggest that they are salts of a common anion. The charge densities derived[35] from the observed chemical shifts using the procedure of Schaefer and Schneider[35b] (slightly modified as previously)[9] are compared in Table 5 with simple HMO charge densities[36] assuming $\alpha_N = \alpha_C + \beta_{CC}$ and $\beta_{CN} = \beta_{CC}$.[37]

Agreement at the two carbons not adjacent to the nitrogen appears adequate, and is hardly altered by the choice[36,35] of the presumed proportionality constant relating charge densities and chemical shifts because this constant multiplies a small correction term. The chemical shifts of the pentalenyl dianion I, the azapentalenyl anion VI,

TABLE 5. CHARGE DENSITIES IN VI DERIVED FROM CHEMICAL SHIFTS AND FROM HMO THEORY

Proton	Chemical shift (τ)	Correction for adjacent ring[a]	Charge density[b]	HMO charge density
3	3·57	0·55	−0·17	−0·26
2	3·97	0·29	−0·18	−0·14
1	5·25	0·55	−0·32	−0·30

[a] Ref 35b.

[b] $-0{\cdot}2 - \frac{1}{10{\cdot}7}$ (chemical shift + correction for adjacent ring −4·47). (Cf. Ref. 9.)

---

[32] Of the 5 equivalent protons in cyclopentadienide, the least shielded after a CH has been replaced by NH to give pyrrole, is the one on the α carbon.[10] A similar formal change in the pentalenyl dianion might be expected to split the chemical shifts of the equivalent protons 2 and 4 in the same way.

[33] H. P. Fritz and C. G. Kreiter, *J. Organometallic Chem.* 4, 198 (1965).

[34] $J_{34} = 3{\cdot}40$–$3{\cdot}80$ and $J_{23} = 2{\cdot}40$–$3{\cdot}10$ c/s.[21]

[35a] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.* 82, 5846 (1960); [b] T. Schaefer and W. G. Schneider, *Canad. J. Chem.* 41, 966 (1963).

[36] The charge densities of aromatic ions derived from chemical shifts (after attempting to account for variations in the ring current effect) have been linearly correlated with charge densities calculated using the MO theory;[35] attempts to include nitrogen heterocycles with this correlation have met with mixed results: [a] A. H. Gawer and B. P. Dailey, *J. Chem. Phys.* 42, 2658 (1965); [b] B. M. Lynch and H. J. M. Dou, *Tetrahedron Letters* No. 23, 2627 (1966).

[37] These parameters are between the values $h = 0{\cdot}5$, $k = 1$, $\delta = 0{\cdot}17$ used by some[38] and the values $h = 1{\cdot}5$, $k = 0{\cdot}8$, $\delta = 0$–$0{\cdot}1$ suggested in the extensive compilation of Streitwieser.[39] They have been used in correlating charge densities.[36] The agreement sought in Table 5 is not greatly affected by choosing widely differing parameters.

[38a] R. J. Windgassen, Jr., W. H. Saunders, Jr. and V. Boekelheide, *J. Am. Chem. Soc.* 81, 1459 (1959): [b] W. A. Remers, *Ibid.* 86, 4610 (1964).

[39] A. Streitwieser, Jr., *Molecular Orbital Theory*. Wiley, New York (1961).

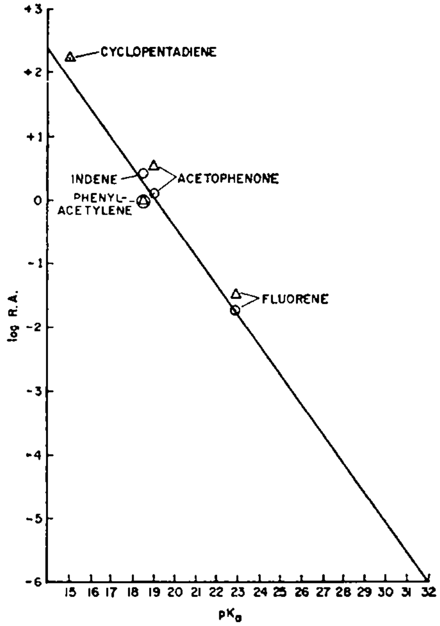


FIG. 6. Logarithms of relative exchange rates (log R.A.) as a function of pK_a. See Table 4. Circles are from this work, triangles from Ref. 31. The line is a graph of Eq. 1.

TABLE 6. CHEMICAL SHIFTS (τ) IN THE PENTALENYL DIANION (I) and ITS NITROGEN DERIVATIVES (VI AND V)

Proton	I[a]	VI	V
3	5·02	3·57	2·95[b], 2·99[c]
2	4·27	3·97	3·52, 3·35
1	5·02	5·25	2·95, 2·99

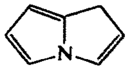
[a] Ref 2.
[b] Ref 6*c*.
[c] Ref 6*a*.

and diazapentalene V are compared in Table 6. Among regularities expected on the basis of simple HMO theory, that the position of proton 2 in VI be intermediate to I and V, that proton 3 be more shielded in VI than in V, and that proton 1 be more shielded in I than in VI, only the first two expectations are confirmed by the data in the Table. The reason for the greater shielding of proton 1 in VI than in I may be a high electron density on the adjacent carbon due to electron repulsion by a pair of electrons localized mainly on the nitrogen.

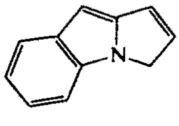
UV spectrum of the azapentalenyl anion. The spectrum of the azapentalenyl anion VI should resemble those of the pentalenyl dianion I and diazapentalene V, for all three are isoelectronic. The positions of the long wavelength maxima of VI and I are the same: λ_{max} 296 mμ (log ε 3·7), shoulder at 210 mμ for dilithium pentalenide in THF;[2] λ_{max} 295 mμ (log ε 3·96), shoulder at 210 mμ for potassium azapentalenide in THF. For V, a max is at 284 mμ.[6c]

Reactions of the azapentalenyl anion with electrophiles

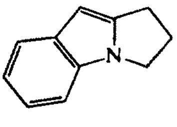
(a) *Water.* The azapentalenyl anion is deuterated by deuterium oxide to give a pyrrolizine that, but for a deuterium atom in the allylic position, is identical with that from which the anion was prepared. The deuteration thus occurs at the 3-position (cf. VI) of the anion if the pyrrolizine's structure is correctly assigned, but at the 1-position (cf. VI) if the substance presumed to be 3H-pyrrolizine (IX) is actually 1H-pyrrolizine (XIII). This possibility appears credible from the observation that a substance reported to be XIV,[8b] the benz derivative of 3H-pyrrolizine, and prepared from indole-2-carboxaldehyde in the same way that 3H-pyrrolizine was prepared from pyrrole-2-carboxaldehyde, has spectroscopic properties not easily reconciled[40] with the structure XIV, and physical and spectroscopic properties similar[41,42] to those reported for the double bond isomer VIII,[7] with which it is presumably identical. The facility of double bond migration in closely related substances has been reported.[38b] That the pyrrolizine is the 3H isomer IX is suggested by the similarity of its UV and NMR spectra with those of 1-methyl-3H-pyrrolizine,[8b,43] and by the chemical shift of its methylene proton resonance, which appears to be at too low fields[44] if the alternative structure XIII were correct. The proximity of the methylenic proton (on C-3) to the protons on C-2 and C-5 is also indicated by the similar, large displacement of the resonances of these protons, compared to the small displacement of protons 1, 6 and 7, when the solvent is changed from methanol to benzene (Table 2).[17,47]



XIII



XIV



XV

[40a] The max in the UV spectrum (λ_{max} 265 mμ (ε17,770))[8b] is at much lower wavelengths than in the indole XV that is the dihydro derivative[8b,7] (cf. Ref 38*b*); [b] The very low chemical shift of the peak at τ 3·04, presumably due to the indole proton, is not easily accounted for. In the dihydroderivative, XV, this proton resonates at τ 3·90.

[41a] Mp. 92–93°[8b] and 89–90;[7] [b] UV spectra: compare footnote 40 and λ_{max} 265 mμ (ε 14,000):[7] [c] The structure assignment has recently been revised: E. E. Schweizer and K.K. Light, *J. Org. Chem.* **31**, 2912 (1966), footnote 2.

[42] The proton chemical shifts reported[8b] for XIV are similar to those reported[38b] for derivatives of VIII.

[43] If this had been 1-methyl-1H-pyrrolizine, its NMR spectrum would have shown besides the resonance of the Me protons only one other non-olefinic proton, not two as reported.[8b] Moreover, the methyl resonance is reported to be a quartet, as expected;[22] had this been 1-methyl-1H-pyrrolizine, the resonance would probably have been a doublet. The compound might, however, be 7-methyl-1-H- or 7-methyl-3-H-pyrrolizine.

[44] The chemical shifts of these protons in cyclopentadiene (τ 7·10),[45] indene (τ 6·67),[46] and fluorene (τ6·19)[45] are displaced to low fields in increments of about 0·45 ppm per benzene ring. The methylene proton in XIII should therefore resonate near τ 6·7 since that of VIII resonates at τ 6·25;[8b] The resonance observed is at much lower field (Table 2).

[45] G. V. D. Tiers, *Characteristic Nuclear Magnetic Resonance (NMR) 'Shielding Values' (Spectral Positions) for Hydrogen in Organic Molecules.* Central Research Lab., Minnesota Mining and Manufacturing Co., St. Paul, Minnesota (1958).

[46] N. S. Bhacca, L. F. Johnson and J. N. Shoolery, *NMR Spectra Catalog,* Varian Associates, Palo Alto, California (1962).

[47] cf. solvent effects on azenes [J. N. Murrell and V. M. S. Gil, *Trans. Faraday Soc.* **61**, 402 (1965)] and 11-ketosteroids [D. H. Williams and D. A. Wilson, *J. Chem. Soc.* **B**, 144 (1966)].

If a solution of potassium azapentalenide in THF is quenched with water, the UV spectrum immediately recorded is identical with that of the 3H-pyrrolizine from which the anion was formed. No double bond isomers of the starting pyrrolizine could be detected in this way. Thus there is no evidence that protonation of the anion occurs at any position other than C-3.

(b) *Ketones*. Reactions of the azapentalenyl anion with benzophenone and with benzil give fulvene derivatives,[48,49] X or XI. Analogy with the reaction of the anion with water suggests that these have the former structures. The NMR spectrum (Fig. 5) of the benzhydrylidene derivative also suggests that in this case the former structure is correct. Thus, the AB quartet at τ 3·69 and 3·89 is probably due to protons 1 and 2, (those not in the pyrrole ring) because the anticipated[21] coupling of all pyrrole protons with each other should not lead to such a simple pattern. The resonances at τ 4·22 and 4·39 are than due to the pyrrole protons. Since the α-protons in the pyrroles generally appear near τ 3·7,[19] this proton's resonance has in the fulvene been shifted to high field, attributable perhaps to the proximity of the benzene ring.[50]

In the case of the fulvene derived from benzil (Xb or XIb), however, the resonance of one of its pyrrole protons does appear (Fig. 5) near τ 3·4, suggesting possibly that its structure is XIb, not Xb. However, this assignment is tentative because the possibility of *cis-trans* isomerism about the exocyclic double bond makes difficult a definitive structural assignment based on what is presently known about the compound.

Acidity of 3H-*pyrrolizine and the relative stabilities of* 1H- *and* 3H-*pyrrolizine*. The pK_a of 3H-pyrrolizine, estimated[30,31,51] from the rate of exchange of its hydrogens with a protonic solvent, should provide a test of theories of bonding in heterocyclic molecules. To make such a test, the pK_a's of six skeletally rigid hydrocarbons were linearly correlated[52] with the ΔM, the difference in HMO binding energy of the π-electrons in the anion and the hydrocarbon.[53] From the least squares correlation[56] (Eq. 2), and

$$pK_a = 46{\cdot}2 - 15{\cdot}6\,\Delta M \tag{2}$$

the estimated pK^a of 3H-pyrrolizine, 29, ΔM was evaluated at 1·1, which was compared with values calculated using the Hückel theory and various values of the parameters[39]

[48a] E. D. Bergmann, *Progress in Org. Chem.* 3, 81 (1955); [b] J. H. Day, *Chem. Rev.* **53**, 167 (1953).

[49] These substances are closely related to a lactam in which the R_1R_2C= fragment of X is replaced by O=. Derivatives of this lactam are known: W. C. Agosta, *J. Am. Chem. Soc.* **82**, 2258 (1960); V. Carelli, M. Cardellini and F. Morlacchi, *Ann. Chim. Rome* **51**, 595 (1961).

[50] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* pp. 125 ff. Pergamon Press, New York (1959).

[51] A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons and A. H. Pudjaatmaka, *J. Am. Chem. Soc.* **87**, 384 (1965).

[52] A. Streitwieser, Jr., *Tetrahedron Letters* No. 6, 23 (1960).

[53] The pK_a's are those given in the recent compilation by Cram,[30a] but are not well established. The hydrocarbons, pK_a's[30a] and ΔM's[52,54] are: fluoradene, 13·6,[55] 2·115; cyclopentadiene, 15, 2·000; indene, 18·5, 1·747; 4,5-methylenephenanthrene, 22·6, 1·514; fluorene, 22·9, 1·523; toluene, 35, 0·721.

[54a] C. A. Coulson and A. Streitwieser, Jr., *Dictionary of π-Electron Calculations*, Freeman, San Francisco (1965).

[55] Cram[30a] gives the pK_a as 11, but this point greatly diverges from the line. The value 13·6 may not be inconsistent with the original data [H. Rapoport and G. Smolinsky, *J. Am. Chem. Soc.* **82**, 934 (1960)] and may be appropriate[30b] for a comparison of acidities in only weakly polar media.

[56] The standard error of estimate in pK_a is 0·2.

h, k, and δ for nitrogen:[57] $0 < h < 2$; $0{\cdot}7 < k < 1{\cdot}0$; $0 < \delta < 0{\cdot}2$. None of these parameters imply that $\Delta M = 1{\cdot}1$—they all give slightly larger values—but with large h, small k, and small δ this value is most nearly approached. Thus $h = 1{\cdot}5$, $k = 0{\cdot}7$, $\delta = 0$ implies $\Delta M = 1{\cdot}29$, while changing one of these parameters has the following effect: $h = 0{\cdot}5$, $\Delta M = 1{\cdot}34$;[58] $k = 1{\cdot}0$, $\Delta M = 1{\cdot}48$; $k = 0{\cdot}1$, $\Delta M = 1{\cdot}52$.

With small h ($\sim 0{\cdot}5$), large k ($1{\cdot}0$), and large δ ($0{\cdot}17$),[38] ΔM is sufficiently large that the pyrrolizine would be expected to approach acetophenone (pK_a 19)[30a] in acidity, which appears false. Moreover, these parameters would imply that 1H-pyrrolizine be more stable than 3H-pyrrolizine, which also appears false.[59] The simple MO theory is such that if $h = 0$, $k = 1$, $\delta = 0$, the 3H and 1H isomers would have the same total π-energy, for they would both be theoretically equivalent to the vinylcyclopentadienyl system. If both h and δ are greater than zero, the isomer (1H) with π electrons on the heteroatom and on the adjacent atom will be favored, while decreasing k should lower the energy more of the isomer (3H) that has the highest free-valence at the heteroatom site. If h is increased there should be little effect on the relative stabilities of the two isomers because the π-electron densities at the two bridgehead atoms of the vinylcyclopentadienyl system are almost the same; but the 3H isomer should be favored if h increases. The actual HMO calculations indicate that if $h = 1{\cdot}5$, $k = 0{\cdot}8$, and $\delta = 0{\cdot}1$, the values recommended by Streitwieser,[39] the 3H isomer is correctly, but scarcely, favored by $0{\cdot}07\beta$. The general conclusion that can be drawn is that if the HMO theory has validity, the stabilities of the pyrrolizine isomers are not correctly ordered unless $k < 1$, and if $h > 0$, the large the δ, the smaller the k.

The failure of the HMO theory to account for the acidity of 3H-pyrrolizine should be compounded if account could be taken of the inductive effect of the nitrogen atom. While it is possible that the pK_a of 3H-pyrrolizine has been estimated incorrectly from the rate of exchange of its allylic protons in basic solution, the much slower rate compared to fluorene should imply a disparity in their pK_a's: that of 3H-pyrrolizine should be considerably greater than that of fluorene (p$K_a = 22{\cdot}9$).[30] Thus although inductive effects are believed to greatly influence hydrocarbon acidities,[30b] 3H-pyrrolizine appears less acidic than anticipated even if these are neglected.

EXPERIMENTAL

3H-*Pyrrolizine* (IX)

The compound was prepared from pyrrole-2-carboxaldehyde and vinyltriphenylphosphonium bromide.[60,8b]

Lithium azapentalenide (VI)

A dry 2-necked round-bottomed flask equipped with a stopper, argon-vacuum inlet, and magnetic stirring bar was flushed free of O_2 by successively evacuating and refilling with argon 3 times. The stopper was replaced by a serum cap and THF and IX introduced by syringe.[61] The soln was cooled with dry ice-acetone and $\sim$1·1 mole equivs of n-Buli[62] were added in drops. (At −78° a ppt forms

---

[57] $\alpha_N = \alpha_C + h\beta$; $\beta_{CN} = k\beta$; $\alpha_{\text{adjacent}}\,C = \alpha + h\beta$.

[58] The effect of this change on ΔM is small because the charge densities at the heteroatom site in vinylcyclopentadienyl (1·188) and in pentalenyl dianion (1·198) are almost the same.

[59] Apparently only one pyrrolizine is known so the point is not definitive.

[60] E. E. Schweizer and R. D. Bach, *J. Org. Chem.* **29**, 1746 (1964).

[61] Concentrations were usually 2 molar or less; a maximum of 5 mmoles of 3HP was used for any one reaction.

[62] The n-butyllithium in n-hexane (Foote Mineral Co.) was titrated [H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.* **66**, 1515 (1944)] and found to be 1·5N in RLi and 1·6N in total base.

if the concentration is greater than 0·1M.) After 10 min the cooling bath was removed, and the stirring was continued for 15 min at ambient temp. The salt dissolves readily at room temp in concentrations of about 2M. The soln is pale yellow, but even traces of O_2 turn it deep red.

A sample for NMR analysis was prepared in an apparatus in which 2 vessels were separated by a sintered glass disc, and the lithium azapentalenide was precipitated from soln with pentane. Filtration gave a blue-gray solid that was freed of solvent at reduced press and dissolved in THF (to which small amounts of benzene were added as an internal standard). The soln was transferred by syringe to an NMR tube attached to glassware allowing continuous flushing with argon. The tube was then evacuated and sealed. The spectrum is shown in Fig. 2.

Sodium and potassium and lithium azapentalenide prepared using alkali metals

NMR samples were prepared using the apparatus in Fig. 7. The alkali metal in 2 to 7 fold excess was cut into pieces under mineral oil, washed with pentane, weighed under N_2, and placed on the sintered disc *d*. Solvent was removed by evacuation at *a* to 10^{-4} mm. A quantity of THF that had been stored over potassium anthracenide was measured (0·7 to 0·8 ml) by distillation into a calibrated vessel and distilled into the side-arm *c*. After the 3-pyrrolizine (1·5 mmole) and the benzene internal standard were degassed and distilled into the same side-arm, the apparatus was sealed at *b*. Upon inverting the apparatus an exothermic reaction occurred, which was moderated by intermittent cooling. After one day the apparatus was evacuated at *i* and, after the breakseal *f* was opened, re-evacuated to 10^{-4} mm. After sealing at *e* the reaction was completed by intermittently shaking the contents for another 3-4 days. The solution was filtered through *d* into the NMR tube *h* and the tube was sealed at *g*. The spectrum of the K-salt in $THF\text{-}d_8$ is shown in Fig. 1. The sodium salt in THF has a similar spectrum. Attempts to prepare samples of the Li-salt in this way for NMR analysis gave solns contaminated with small amounts of starting material.

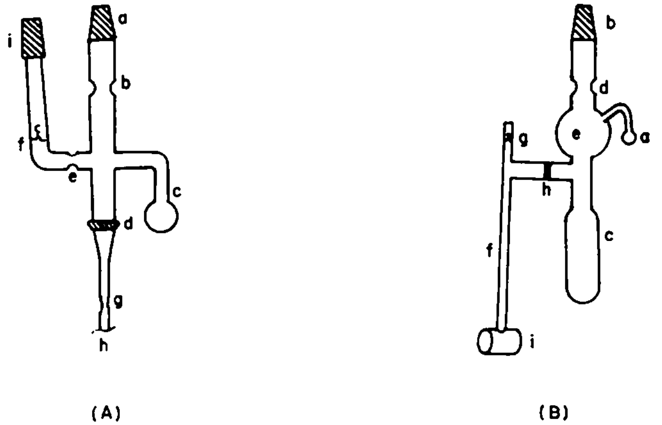


FIG. 7. (A) Apparatus for preparing nmr samples of alkali azapentalenides. (B) Apparatus for determining the UV spectrum of potassium azapentalenide.

Deuteration of lithium azapentalenide

Dry *ether* (5 ml) and IX (0·30 ml, 3·0 mmole) were injected into a 2-necked round-bottomed flask that was flushed with argon, and n-BuLi (2·2 ml, 3·3 mmoles) was added while stirring and cooling to −78°. The suspension was stirred further for 40 min at room temp, re-cooled to −78°, and 5 ml D_2O (99·5% D) was injected. The cooling bath was removed and the ether phase allowed to separate. Pentane (15 ml) was added, the organic phase was removed, and the ice slush was washed with an additional 5 ml portion of pentane. After purging with N_2, the combined yellow pentane soln was dried over anhyd Na_2SO_4, and the solvent was removed at reduced press under N_2. The residual oil was evaporatively distilled on a high vacuum manifold and left only small amounts of an orange, apparently polymeric, material.

The distillate (total wt, 251 mg) was found to consist of 89% deuterated IX and 11% solvent by

VPC (didecylphthalate, 3ft, 103°), or approximately 220 mg (~75% yield) of deuterated IX. The material was analyzed directly since attempts to purify (VPC) the product scrambled the deuterium (see below).

Mass spectral analysis showed that the material contained 4·65% C_7H_7N, 83·2% C_7H_6DN, 10·8% $C_7H_5D_2N$, and 1·52% $C_7H_4D_3N$.[16] The pre-heater was at room temp and the ionization chamber at 250°. The IR spectrum showed a weak C-D stretch at 2145 cm^{-1} and no absorption in the 1400 to 1462 cm^{-1} region, where IX exhibits a band at 1428 cm^{-1}. The NMR spectrum (neat, TMS) of the deuterated material exhibited 5 resonances attributable to the pyrrolizine: multiplets at τ 3·42, 3·83, 4·17 and 6·20 and a double-doublet (further split into doublets) centered at τ 4·33. The splittings in this last multiplet, which is assigned to H_2, are 5·9, 2·2 and 0·9 c/s. There was also some small peaks due to unidentified impurities.

After purification by VPC (didecylphthalate, 3 ft, 103°) the material exhibited a broadened NMR spectrum similar to that of authentic IX. Mass spectral analysis showed that the material contained 32·3% C_7H_7N, 43·4% C_7H_6DN, 19·3% $C_7H_5D_2N$, 4·28% $C_7H_4D_3N$, and 0·71% $C_7H_3D_4N$.[16] The IR spectrum exhibited bands at 2143 and 2183 cm^{-1} (C-D stretch), but also at 1426 and 1438 cm^{-1}.

In another experiment lithium azapentalenide was prepared in THF, its NMR spectrum was determined, and the sample was then quenched with D_2O. The NMR spectrum of the deuterated 3H-pyrrolizine made in this way was similar to that of the sample made in ether, but the yield was low (0·1 g, <33%).

Benzhydrylidene azapentalene Xa *or* XIa

To a cold (−78°), stirred soln of lithium azapentalenide, prepared from IX (0·20 ml, 2·0 mmoles), THF (10 ml), and n-Buli (1·4 ml (2·1 meq.), a soln of benzophenone (374·0 mg, 206 mmoles) in THF (10 ml) was added in drops during a 15 min period. After stirring further at −78° for 30 min, at 0° for 1 hr, and at room temp for 19 hr, the deep brown reaction mixture was ice-cooled and 25 ml of 10% NH_4Claq was added. Ether (50 ml) was added and the colorless aqueous layer separated. After washing with water (4 × 50 ml), the ether layer was dried over $MgSO_4$. The solvent was removed at reduced press leaving an orange-brown residual oil, which could not be induced to crystallize. Chromatography (silica gel, Merck, 25 gm, 2 cm diam column, benzene) gave a red syrup, which easily crystallized to a red-orange solid (276·2 mg, 51% yield based on IX), m.p. 97–101°. Sublimation (80–90°/0·1–0·15 mm) gave greater than 88% recovery of material, m.p. 99·5–102·0°. Recrystallization (pentane) followed by sublimation gave material with m.p. 102·0–102·5°. (Found: C, 88·91; H, 5·68; N, 4·96; mol. wt., 269 (mass spectrometry) *Anal.* Calc. for $C_{20}H_{15}N$: C, 89·19; H, 5·61; N, 5·20%; mol. wt., 269.)

The benzil adduct (Xb *or* XIb). To a cold (−78°), stirred soln of lithium azapentalenide prepared from IX (0·30 ml, 3·0 mmoles), THF (15 ml), and n-Buli (2·1 ml, 3·1 meq), a soln of benzil (674·5 mg, 3·2 mmoles) in THF (25 ml) was added in drops during a 45 min period. The deep purple soln was stirred at −78° for 2 hr, then quenched with 40 ml of 20% NH_4Claq. Ether (30 ml) was added and the colorless aqueous layer separated. The deep orange ether soln was washed with water (4 × 50 ml), dried over $MgSO_4$, and concentrated at reduced press. The IR spectrum of the orange residue showed absorption characteristic of both OH and CO groups. The residue was taken up in a small volume of benzene and chromatographed on silica gel (Merck, 50 g, 2 cm diamr column, benzene). The bulk of the red eluate was collected and the solvent removed at reduced press. The residue was again taken up in benzene and re-chromatographed as above. The deep red eluate on concentration afforded a deep red oil, which crystallized to a red solid (240 mg) on trituration with pentane. Sublimation (70°/0·15 mm) gave a yellow-orange solid identified as benzil by comparison (IR) with an authentic sample. A red-orange solid (117 mg) sublimed at 100–110°/0·05 mm and a considerable amount of a black tar remained. The red-orange solid was taken up in a minimum amount of benzene and pentane (50 ml) was added. Concentration to 25 ml and cooling to −78° afforded 81·8 mg (9·2% yield based on IX) of a red-orange solid, m.p. 119·5–120·5°. Small amounts of product could also be recovered from the mother liquor together with an impure red oil. An analytical sample (sublimation) melted at 121·5–122·0°. Found: C, 85·09; H, 5·30; N, 4·45; mol. wt., 297 (mass spectrometry). Calc. for $C_{21}H_{15}NO$: C, 84·82; H, 5·08; N, 4·71%; mol.wt., 297.)

Acidity of 3H-*pyrrolizine*

The procedure was similar to one used previously.[31] A soln of 1·0M triethylamine and 5·0M D_2O was prepared in dry DMF. Known amounts of H_2O were added and the intensity of absorption at

3450 cm^{-1} measured. The instrument was a double beam grating spectrometer (Perkin–Elmer 421), the sample cell was of 0·2 mm path length with CaF windows, and the reference beam passed through air. (Beer's law applies if [DOH] $<$ 0·4M.)

The weak acid was weighed in an inert atmosphere into a vessel sealed with a serum cap. A calculated quantity of Et$_3$N–DMF was added and the soln was equilibrated at 40·3°. A calculated quantity of D$_2$O–DMF, equilibrated at the same temp, was syringed into the vessel, the contents were mixed by shaking for 20 sec, and the soln was returned to the thermostated bath. Aliquots were removed by syringe, and the DOH absorbance was measured with time when between 10 and 40 mole % of the hydrogens had exchanged. Rate constants calculated from plots of log $[c_0/(c_0 - x)]$ against t, where c_0 is the initial acid substrate concentration, x is the DOH concentration, and t is the time, are in Table 7.

For the slow exchange reactions of IX, an extrapolation to 40·3° was made from kinetic measurements conducted at 85·0 and 100·6°. For these measurements aliquots of the solns for the rate study were prepared at room temp and syringed into ampoules, which were then evacuated and sealed.[aa] The ampoules were placed in the thermostated bath, removed at various intervals, and stored at 0°. The rate data for IX is presented in Table 8. The rate constants in Tables 7 and 8 were divided by the number of exchangeable protons. These corrected rate constants were divided by the rate constant for phenylacetylene, and the logarithms of these ratios are recorded in Table 4.

TABLE 7. THE OBSERVED PSEUDO-FIRST ORDER RATE CONSTANTS AT 40·3 ± 0·1°.

Compound	Run No.	c_0, *M*	k × 10^6 (sec.$^{-1}$)	k × 10^6 (mean)[a]
Indene	1	0·985	725	742 ± 16
	2	1·000	758	
Acetophenone	1	0·997	521	529 ± 8
	2	1·000	537	
Phenylacetylene	1	0·938	129	
	2	0·997	151	135 ± 11
	3	0·954	126	
	1′	0·504	157	
	2′	0·500	170	163 ± 6
Fluorene	1	0·522	5·68	
	2	0·467	6·30	5·99 ± 0·31

[a] The uncertainties are average deviations.

The UV spectrum of potassium azapentalenide in THF (see Fig. 4)

The sample was prepared using the apparatus in Fig. 7B. The apparatus containing freshly cut K in side-arm *a* was attached (*b*) to the high vacuum manifold and evacuated to $<10^{-4}$ mm. 3H-Pyrrolizine (15·0 μl, 14·4 mg, 0·137 mmole) contained in another vessel attached to the manifold was

TABLE 8. KINETIC DATA AND EXTRAPOLATED DATA FOR 3H-PYRROLIZINE

Run No.	c_0, *M*	T°C.[a]	k × 10^7 (sec.$^{-1}$)	k × 10^8 at 40·3°C
1	0·508	85·0 ± 0·1	6·65	1·10
2	0·488	100·6 ± 0·1	22·0	
3	0·980	85·0 ± 0·1	5·37	
4	0·993	100·6 ± 0·1	18·1	0·831

[a] The uncertainties are approximate.

[aa] A blank (5·0M D$_2$O and 1·0M Et$_3$N in DMF) run at 100·6° for 11 days showed $< \sim$1·5 % increase in the DOH concentration.

degassed and distilled into the vessel *c* of calibrated volume. After THF (10 ml, stored over potassium anthracenide) was distilled into *c*, the apparatus ($<10^{-6}$ mm) was sealed at *d*. The soln was allowed to warm to room temp and poured through the sintered glass filter (coarse frit, *h*) into the quartz UV cell *i* of 0·1 mm/path length. The spectrum of 3H-pyrrolizine was recorded before reaction with K was allowed to occur (Fig. 4). Its concentration could be calculated from the max at 289 mμ (optical density, 1·03)[64] as 0·014M, in close agreement with the concentration calculated (0·0137M) from the quantities of 3H-pyrrolizine and THF used.

The soln was returned to vessel *c* and frozen. The side-arm *a* was heated to coat a K-mirror on bulb *e*, and after the bulb had cooled, the soln was allowed to come into contact with the mirror. The soln rapidly turned yellow; its spectrum, after 6 hr and for 4 days thereafter, remained unchanged ($< \pm 1\%$ change in optical density): end absorption below 220 mμ, λ_{min} 258 mμ (ε 7100), and λ_{max} 295 (ε 9600).[65] Dilution of the sample revealed a shoulder near 210 mμ (ε ~20,000).[66] No absorption in the visible region was observed.

After 4 days the soln was quenched in an argon atmosphere by adding a drop of O_2-free water (purged with N_2) through the break-seal *g*. The spectrum of the starting pyrrolizine was reproduced almost exactly: (λ_{max} 288, optical density 1·06).[67] Exposure of the soln to air produced a characteristic red color.

Acknowledgements—We are grateful to the National Institutes of Health (MH-08912) and the Alfred P. Sloan Foundation for their support.

[64] The UV spectrum of 3H-pyrrolizine in THF shows λ_{sh} 215 mμ (ε 5400), λ_{min} 243 mμ (ε 2000), $\lambda\lambda_{max}$ 289; 294 (ε 7600; 7600). (Fig. 4.)

[65] The extinction coefficient was calculated by assuming the yield of the anion to be 100%. The increased extinction at 295 mμ, compared to the starting material leaves little doubt about the wavelength of the max.

[66] This was achieved by running most of the sample back into the vessel *c* and distilling solvent from *c* to *f* by cooling vessel *f*. The concentration was estimated from the known extinction[65] coefficient of the max at 295 mμ.

[67] The pyrrolizine within experimental error, was re-formed quantitatively. The spectrum shows λ_{sh} 213 mμ (ε 5400), λ_{min} 241 mμ (ε 2100), and λ_{max} 287, 293 mμ (ε 7600; 7600).[64]