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THE PREPARATION OF SOME PYRIDINIUM *CYCLO*PENTADIENYLIDES

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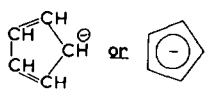
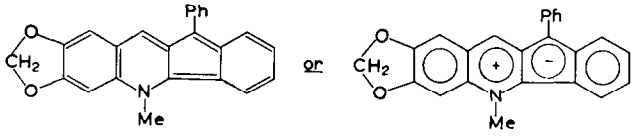
Abstract—The preparation of some pyridinium *cyclo*pentadienylides is described. A brief survey of earlier work in this field is included.

THE formation of the negatively charged *cyclo*pentadienide ring (I) was first recognised by Thiele[1] in 1901, when he prepared potassium *cyclo*pentadienide. Armit and Robinson,[2] in studies on anhydronium bases such as (II), pointed out that the pentagonal carbocyclic ring in these compounds would be stabilised by the sharing of a lone pair of electrons from the pyridine nitrogen atom, as it would thereby achieve an "aromatic sextet" of electrons. Goss and Ingold[3] similarly connected the acidity of *cyclo*pentadiene and its derivatives with the aromatic sextet of electrons realised in its negative ion.

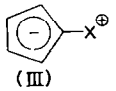


(I)

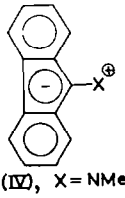


(II)

The negatively charged *cyclo*pentadienide ring could be achieved not only by anion formation, but also in a dipolar molecule such as (III), and Ingold and Jessop[4] ascribed a structure of this type (IV) to the purple-coloured transitory intermediate obtained in the degradation of fluorene-9-trimethylammonium salts with alkali. Later, they isolated and described a more stable sulphonium analogue (V).[5] Investigations[6] of the dipole moment of (IV) and (V) confirmed their highly polar character.



(III)
(VIII), X=N_2

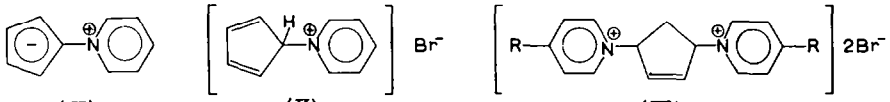


(IV), X=NMe_3
(V), X=SMe_2
(VI), X=N_2
(VII), X=O_2

[1] J. Thiele, *Ber. Dtsch. Chem. Ges.* **34**, 68 (1901).
[2] J. W. Armit and R. Robinson, *J. Chem. Soc.* **127**, 1604 (1925).
[3] F. R. Goss and C. K. Ingold, *J. Chem. Soc.* 1268 (1928).
[4] C. K. Ingold and J. A. Jessop, *J. Chem. Soc.* 2357 (1929).
[5] C. K. Ingold and J. A. Jessop, *J. Chem. Soc.* 713 (1930).
[6] G. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.* 146 (1945); H. Hartmann and H. Grossel, *Z. Elektrochem.* **61**, 337 (1957).

Since Ingold and Jessop's work, the preparation of other fluorenylides has been described by a number of workers.[6–9] Most of these compounds are unstable, but those derived from nitrofluorenes[7] have markedly greater stability. Other compounds, not specified as ylides in the literature, but which have probably at least a measure of ylide structure, include the red crystalline diazofluorene (VI)[10] and fluorenone peroxide (VII).[11]

The first compound to be described with an ylide structure (III) derived from *cyclo*pentadiene itself was diazo*cyclo*pentadiene (VIII),[12] prepared by Doering and DePuy in 1953, although it is possible that other unstable compounds of this type had been prepared.[13] Subsequently the preparation of a number of *cyclo*pentadienylides with *exo*cyclic ammonium[14–16] or phosphonium[17] groups has been reported.



(IX) (X) (XI)

Pyridinium *cyclo*pentadienylide (IX)[14] was prepared by the action of two molecules of pyridine on one molecule of dibromo*cyclo*pentene, followed by treatment with alkali. This ylide separated out as a red-brown crystalline precipitate, which when freshly prepared has a coppery lustre. On exposure to air, and especially in direct light, it tarnishes slowly, apparently owing to oxidation, but samples stored *in vacuo* or under nitrogen appear unchanged after 18 months. If the solution obtained by treatment of the dibromo*cyclo*pentene with pyridine is kept for some time before treatment with alkali, the resultant ylide appears to be rather more stable than when this intermediate is basified at once. The most striking property of this ylide is the intensity and diversity of the colours of its solutions. The shade varies with the polarity of the solvent, ranging from colourless in acidic aqueous solution, through orange in alcohols, red in acetone, chloroform and methylene dichloride to a reddish-purple in ether, benzene, pyridine and ethylaniline, and a blueish-purple in light petroleum. Kosower,[18] discussing charge-transfer spectra, has commented that such a range of

[7] E. D. Hughes and K. I. Kuriyan, *J. Chem. Soc.* 1609 (1935); A. Novelli and A. P. G. de Varela *Ciencia e Invest.* 82 (1948); *Chem. Abstr.* **42**, 5912 (1948).

[8] F. Krollpfeiffer and K. Schneider, *Liebigs Ann.* **530**, 34 (1937); L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.* **60**, 494 (1938); *Ibid.* **68**, 751, 2011 (1946); G. Wittig and G. Felletschin *Liebigs Ann.* **555**, 133 (1944); G. Wittig, M. Heintzeler and M. H. Wetterling, *Liebigs Ann.* **557**, 201 (1947); G. Wittig, R. Mangold and G. Felletschin, *Liebigs Ann.* **560**, 116 (1948); G. Wittig, *Angew. Chem.* **63**, 15 (1951).

[9] F. Kröhnke, *Chem. Ber.* **83**, 253 (1950).

[10] M. Staudinger and O. Kupfer, *Ber. Dtsch. Chem. Ges.* **44**, 2197 (1911); M. Staudinger and A. Gaule, *Ber. Dtsch. Chem. Ges.* **49**, 1951 (1916); L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.* **68**, 867 (1946).

[11] G. Wittig and G. Pieper, *Ber. Dtsch. Chem. Ges.* **73**, 295 (1940).

[12] W. von E. Doering and C. H. DePuy, *J. Amer. Chem. Soc.* **75**, 5955 (1953).

[13] See J. Thiele, *Ber. Dtsch. Chem. Ges.* **33**, 666 (1900); A. Eibner and O. Laue, *Ber. Dtsch. Chem. Ges.* **39**, 2022, (1906); A. Roedig and L. Hörnig, *Chem. Ber.* **88**, 2003 (1955); A. P. Terent'ev and L. L. Gomberg, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 662 (1938); *Chem. Abstr.* **33**, 1285 (1939).

[14] D. Lloyd and J. S. Sneezum, *Chem. & Ind.* 1221 (1955).

[15] W. W. Spooncer, Dissertation, Univ. of Washington (1955); *Chem. Abstr.* **50**, 10664 (1956); and personal communication.

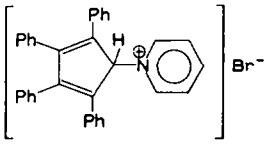
[16] D. N. Kursanov, N. K. Baranetskaia and V. N. Setkina, *Dokl. Akad. Nauk SSSR* **113**, 116 (1957).

[17] F. Ramirez and S. Levy, *J. Org. Chem.* **21**, 488, 1333 (1956); *J. Amer. Chem. Soc.* **79**, 67 (1957).

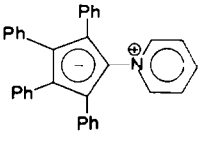
[18] E. M. Kosower and P. E. Klinedinst, *J. Amer. Chem. Soc.* **78**, 3493 (1956).

colours might be expected of a compound with this structure. The compound is only sparingly soluble in the non-polar solvents, but its solubility is rather greater in more polar ones; it dissolves in acid and is reprecipitated by alkali. On slow heating it decomposes before melting.

The structure of (IX) follows from its mode of preparation, its physical properties and its quantitative reduction to N-*cyclo*pentylpiperidine, identified by means of an oxalate and a picrate, which were shown to be identical (mixed m.p.) with authentic specimens.[19] It also appears to couple with benzenediazonium chloride (cf. Ramirez and Levy[17]) to give a product whose solutions are more intensely coloured than those of the original ylide, the chloroform and benzene solutions being red-purple and alcoholic solutions bright red.



(XIII)



(XIV)

Ylides were similarly obtained by the action of α-, β- and γ-picolines, 2:6-lutidine and 2:4:6-collidine on dibromo*cyclo*pentene.

It was thought possible that the intermediates firstly formed by the action of pyridine or its analogues on dibromo*cyclo*pentene, and which are transformed by caustic alkali into ylides, might have structures such as (X) or (XI)*; Ramirez and Levy[17] have already postulated the latter formulation. The former seemed unlikely in view of the stability of this intermediate; further, it gave a picrate (m.p. 192°) that was different from the picrate obtained from the ylide itself (dec. 95°). Elementary analysis of the picrate of the intermediate obtained from γ-picoline (and also from a similar compound obtained from dimethylsulphide and dibromo*cyclo*pentene) confirm this supposition.

Ylides derived from indene (cf. Kröhnke[9]) and from 2:3:4:5-tetraphenyl*cyclo*-pentadiene have also been investigated. A different preparative route was used, the dienes being brominated with N-bromosuccinimide and the resultant bromo derivatives treated with pyridine or other base.

In the case of indene, the 1-bromoindene reacts with pyridine to give a deep-red solution, presumably of indene-1-pyridinium bromide, which, on treatment with caustic alkali, gives a dark-blue material, which can be extracted into chloroform. The blue coloration is very fugitive and the pyridinium indenylide thus resembles the corresponding fluorenylide in its instability. Both of these ylides are therefore less stable than the *cyclo*pentadiene derivatives; this may be due to the annellation of the benzene rings.[22]

When pyridine was added to 1-bromo-2:3:4:5 tetraphenyl*cyclo*pentadiene, after a short time a yellow precipitate began to form, which was filtered off after the mixture had been set aside for 24 hr. This proved to be N-(2:3:4:5-*tetraphenyl*cyclo*pentadienyl*)-*pyridiniumbromide* (XIII). It is insoluble in water, but on shaking it with water to

* Formula (XI) assumes 1:4-addition of bromine to *cyclo*pentadiene.[17,20,21]

[19] J. Loevenich, H. Utsch, P. Moldrickx and E. Schaefer, Jr., *Ber. Dtsch. Chem. Ges.* **62**, 3084 (1929).
[20] J. Thiele, *Liebigs Ann.* **314**, 296 (1900); E. H. Farmer and W. D. Scott, *J. Chem. Soc.* 172 (1929).
[21] W. G. Young, H. K. Hall, and S. Winstein, Jr., *J. Amer. Chem. Soc.* **78**, 4338 (1956).
[22] Cf. B. Pullman and G. Berthier, *Bull. Soc. Chim. Fr.* **15**, 551 (1948).

which a little alcohol has been added a deep blue-purple precipitate appears, whose formation is hastened by the addition of alkali. This precipitate is 1-pyridinium-2:3:4:5-tetraphenyl*cyclo*pentadienylide (XIV). It appears to be completely stable in the solid state, but decomposes in solution when exposed to air. As in the case of the unphenylated ylides the colour of the solutions depends on the solvent, in this case being red with alcohol and blue with benzene or ether.The ylide formed a picrate that was identical with that prepared from the intermediate (XIII). Corresponding ylides could be obtained by using β- or γ-picoline instead of pyridine, but α-picoline and 2:6-lutidine gave only small yields of such ylides, very possibly owing to steric hindrance in these cases. Quinoline and *iso*quinoline also gave ylides only in small yields, and they appeared to be less stable.

EXPERIMENTAL

Bromination of cyclo*pentadiene*.[20] *cyclo*Pentadiene (10 g) dissolved in chloroform (33 ml) was cooled in ice–salt, and bromine (23·5 g, 7·5 ml) in chloroform (30 ml) was added during 1 hr, the mixture being stirred meanwhile.

Pyridinium cyclo*pentadienylide* (IX). The solution of dibromo*cyclo*pentene was added to a solution of pyridine (26·5 g, 27 ml) in chloroform (20 ml) and set aside overnight. Chloroform was then distilled off at room temperature, the residue was extracted with water and the extract was made alkaline by addition of sodium hydroxide solution. A lustrous red-brown precipitate of *pyridinium* cyclo*pentadienylide* was formed (18·9 g, 87 per cent) (Found: C, 82·5; H, 6·8; N, 8·2. $C_{10}H_9N$ requires C, 83·9; H, 6·3; N, 9·8 per cent). Satisfactory analyses were difficult to obtain throughout this series of compounds, although analyses were conducted with special care. It seems likely that strenuous retention of water or uptake of atmospheric oxygen may be the cause of these errors. (IX) was only very sparingly soluble in non-polar solvents, but rather more soluble in polar solvents such as acetone, chloroform or methylenedichloride.

Hydrogenation of (IX). The ylide (IX) (0·5 g) was dissolved in ethanol and shaken with hydrogen over Adams's platinum oxide catalyst; 420 ml of hydrogen was rapidly taken up (including absorption by catalyst; calc. 390 ml). After filtration from the catalyst and removal of the ethanol, the residue was distilled and gave a main fraction, b.p. 83°/10 mm, of N-*cyclo*pentylpiperidine, which gave a *picrate*, m.p. 167–168°, after crystallisation from ethanol (Found: C, 50·2; H, 5·7; N, 14·3. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·8; N, 14·7 per cent), and an oxalate,[19] m.p. 181°, both of which were shown to be identical (mixed m.p.) with derivatives obtained from a genuine sample of N-*cyclo*pentylpiperidine, prepared as described by Loevenich *et al.*[19]

Reaction of other pyridine analogues with dibromo*cyclo*pentene*. To the base* (1 g) in a little chloroform was added an equivalent amount (0·5 mol. equiv.) of a solution of dibromo*cyclo*pentene in chloroform. The mixture was set aside for 1–2 days with occasional shaking. Chloroform was then distilled off at room temperature, and the residue was extracted with water and made alkaline. Any precipitate was filtered off or, alternatively, the alkaline solution was extracted with chloroform to obtain the ylide.

*Bis-γ-picolinio*cyclo*pentene salts* (XI, R = CH_3; see footnote, p. 336). Two

* α-, β- and γ-picoline, 2:6-lutidine and 2:4:6-collidine.

molecular equivalents of γ-picoline were added to a solution of dibromo*cyclo*pentene in chloroform. The solution was set aside overnight, chloroform was removed at room temperature, and then an ethanolic solution of picric acid was added to the residue in ethanol. The *picrate* of *bis-γ-picolinio*cyclo*pentene* separated and was crystallised from water, m.p. 223–225° (Found: C, 49·4; H, 3·2; N, 15·7. $C_{29}H_{24}O_{14}N_8$ requires C, 49·2; H, 3·4; N, 15·8 per cent). *Bis(dimethylsulphono)*cyclo*pentene dipicrate* m.p. 162–164° (XII) is similarly obtained from dibromo*cyclo*pentene and dimethyl sulphide (Found: C, 39·1; H, 3·0; N, 13·1; S, 9·9. $C_{21}H_{22}O_{14}N_6S_2$ requires C, 39·0; H, 3·4; N, 13·0; S, 9·9 per cent).

Pyridinium Indenylide. 1-Bromoindene, prepared by the action of N-bromosuccinimide on indene,[23] was treated with excess of pyridine. On addition of sodium hydroxide solution to the deep-red solution thus obtained, a dark-coloured deposit was formed, which was extracted into chloroform to give a blue solution. The colour faded in a few minutes.

Pyridinium 2:3:4:5-*tetraphenyl*cyclo*pentadienylide* (XIV) *and related homologues.* 1-Bromo-2:3:4:5-tetraphenyl*cyclo*pentadiene (1·0 g) was prepared by the method of Kainer[24] and set aside overnight with an excess (6 ml) of pyridine. The solution soon turned red and a yellow precipitate formed, which was filtered off, washed with *n*-hexane and recrystallised from ethanol. This proved to be N-(2:3:4:5-*tetraphenyl*-cyclo*pentadienyl*) *pyridinium bromide* (XIII), m.p. 213·5–215·5° (1·09 g, 93 per cent) (Found: N, 2·7; Br, 14·9; $C_{34}H_{26}NBr$ requires N, 2·7; Br, 15·1 per cent). (XIII) is insoluble in water, but, when shaken with water containing a little ethanol or acetone, it gives a dark-blue crystalline precipitate of *pyridinium*-2:3:4:5-*tetraphenyl*-cyclo*pentadienylide* (XIV), m.p. 208–210° (Yields averaged 87 per cent) (Found: C, 90·6; H, 5·6; N, 3·2. $C_{34}H_{25}N$ requires C, 91·3; H, 5·6; N, 3·1 per cent). The formation of (XIV) from (XIII) is hastened by the presence of sodium hydroxide. (XIV) is soluble in ethanol to give a red solution, and in benzene and ether to give blue solutions. It is stable to air as the solid, but not in solution; the colours of the solutions fade after a few hours' exposure. (XIV) forms a *picrate*, m.p. 226–228°, after crystallisation from ethanol (Found: C, 69·7; H, 4·7; N, 7·7. $C_{40}H_{28}N_4O_7 \cdot C_2H_5OH$ requires C, 69·8; H, 4·7; N, 7·8 per cent); an identical picrate (mixed m.p.) may be obtained from (XIII). γ-Picoline reacts similarly with 1-bromo-2:3:4:5-tetraphenyl*cyclo*pentadiene to give N-(2:3:4:5-*tetraphenyl*cyclo*pentadienyl*)-*γ-picolinium bromide* (XV), m.p. 218–220° (Yields average 76 per cent) (Found C, 77·2; H, 5·2; N, 2·3; Br, 14·8. $C_{35}H_{28}NBr$ requires C, 77·5; H, 5·2; N, 2·6; Br, 14·8 per cent), and *γ-picolinium*-2:3:4:5-*tetraphenyl*cyclo*pentadienylide*, m.p. 208–210° (89 per cent yield from (XV)) (Found: C, 90·2; H, 5·5; N, 3·0. $C_{35}H_{27}N$ requires C, 91·1; H, 5·9; N, 3·0 per cent). β- and α-Picoline, 2:6-lutidine, quinoline and *iso*quinoline were allowed to react similarly with the bromodiene, but β-picoline alone of these gave a worthwhile yield of the hydrobromide intermediate.

Acknowledgements—We thank Mr. P. R. W. Baker of the Wellcome Research Laboratories for his help in carrying out elementary analyses.

We are also indebted to the University of St. Andrews and the Department of Scientific and Industrial Research for research awards (to J. S. S.).

[23] Ng. Ph. Buu-Hoi, *Liebigs Ann.* **556**, 1 (1944).
[24] H. Kainer, *Liebigs Ann.* **578**, 232 (1952).