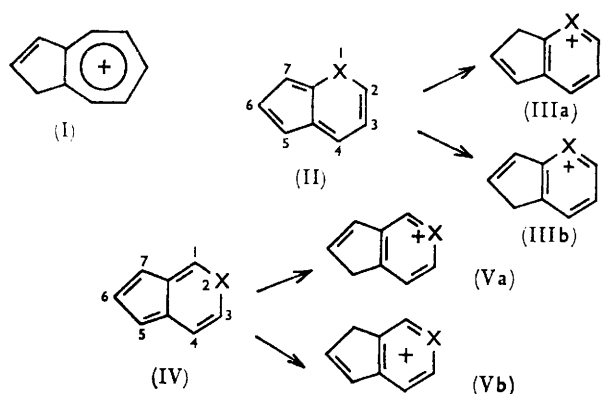


Pseudoazulenes. Part IV.¹ The Site of Protonation in Cyclopenta[*b*]-pyrans

By G. V. Boyd and A. W. Ellis

Chemical shifts and visible absorption maxima indicate that 2-phenylcyclopenta[*b*]-[1]-benzopyran is protonated solely on C-1 (five-membered ring) an analogous cation is probably formed from 2,4,6-triphenylcyclopenta[*b*]pyran. The site of protonation in cyclopenta[*b*]pyran and its derivatives is discussed in terms of molecular orbital theory.

AZULENE is reversibly protonated on the five-membered ring to yield the tropylium ion (I).² The pseudoazulenes

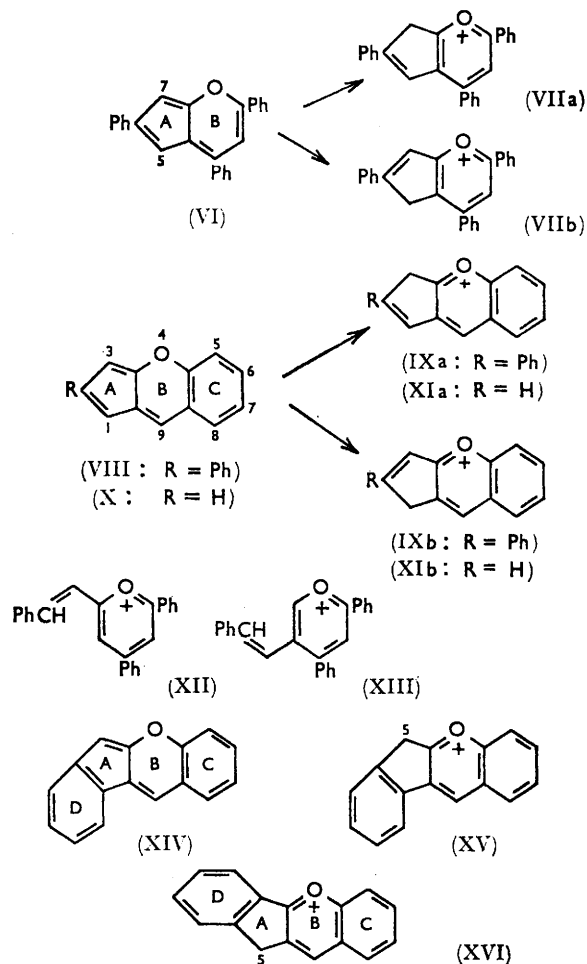


(II) and (IV) ($X = O, S,$ or NR) give rise to analogous cations, but because of their lower symmetry two tautomeric forms (IIIa, IIIb) and (Va, Vb) can now be written. Since these cations are particular cases of Wheland's σ -intermediates³ in electrophilic substitution, their structure is of interest, and we report here on the conjugate acids in the cyclopenta[*b*]pyran series (II; $X = O$). As the parent compound is not known, we investigated the substituted bases (VI),⁴ (VIII),⁴ and (XIV).⁵ The preparation of (XIV) is described in the Experimental section.

Electronic Spectra.—It was tentatively suggested⁴ that the yellow colour of the pyrylium perchlorate (λ_{\max} , 445 $m\mu$) derived from compound (VI) accorded better with structure (VIIa) than structure (VIIb) since the open-chain model for the latter, the styrylpyrylium ion (XII), is red (λ_{\max} , 458 $m\mu$)⁶ (see Table 1). However, since the model (XIII) for the alternative cation (VIIa) is not available, this argument loses much of its force. Similar remarks apply to the yellow benzopyrylium salts formed from the pyran (VIII). In this case, neither of the open-chain models for the tautomeric cations (IXa) and (IXb) is known.

Indeed, the implicit assumption that 2-vinylpyrylium salts should absorb at longer wavelengths in the visible region than the corresponding 3-vinylpyrylium salts does not appear to be justified. Since pairs of such salts are not known, we calculated the positions of the first absorption bands of selected vinylpyrylium ions by a previously described⁷ method. The results (Table 1)

show that the assumed sequence holds for the simple ions (IIIb > IIIa) ($X = O$) but is reversed on annelation (XIb < XIa). Reversal is also predicted for the styrylpyrylium ions (VIIb < VIIa) and (IXb < IXa).



While such calculations usually predict the correct sequence of first-transition energies for closely related molecules, the results for the indenopyrylium salts of unequivocal structure (XV) and (XVI), and for the triphenylpyrylium ions (VIIa) and (VIIb) show that the simple method is too crude to enable us to assign a structure to the latter. In the case of the protonated benzopyran (VIII), the observed absorption maximum,

¹ Part III is considered to be G. V. Boyd, *Tetrahedron Letters*, 1965, 1421.

² A. G. Anderson, jun., and W. F. Harrison, *J. Amer. Chem. Soc.*, 1964, **86**, 708.

³ G. W. Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

⁴ G. V. Boyd, *J. Chem. Soc.*, 1958, 1978.

⁵ G. V. Boyd, *Chem. and Ind.*, 1957, 1244.

⁶ R. Wizinger and H. Sontag, *Helv. Chim. Acta*, 1955, **38**, 363.

⁷ G. V. Boyd and N. Singer, *Tetrahedron*, 1965, **21**, 1263.

which is in fair agreement with that predicted for the 1H-cation (IXb), suggests that protonation occurs on C-1. The presence of minor amounts of the alternative ion would, of course, not be revealed.

Nuclear Magnetic Resonance.—An examination of the proton magnetic resonance spectrum of the conjugate

TABLE 1

Electronic absorption spectra of pyrylium perchlorates, and calculated first transitions (solvent: acetic acid containing *ca.* 1% of 70% perchloric acid)

Compound	$\lambda_{\max.}$ (m μ) (log ϵ in parentheses)		Other bands Obs.
	Obs.	Calc. (± 17 m μ)	
(IIIa; X = O)	—	401	—
(IIIb; X = O)	—	403	—
(XIa)	—	432	—
(XIb)	—	418	—
(VIIa)	445	483	{ 355 (4.14), 294 (4.15),
(VIIb)	(4.52)	476	255 (4.32)
(IXa)	434	462	{ 418 * (4.69), 288 (3.75),
(IXb)	(4.76)	449	264 (3.84), 256 (3.84),
			248 * (3.71)
(XV)	420 (3.67)	401	347 * (3.91), 334 (4.00),
			320 * (3.98), 274 (4.38),
			250 * (4.11)
(XVI)	400 (4.37)	405	287 (3.27), 277 (3.38),
			261 * (3.71), 251 (3.74)

* Inflection.

acid of compound (VIII) also indicates that it probably is protonated at C-1.

Chemical shifts and assignments are listed in Table 2. The perchlorate salts and the parent bases yielded identical spectra in trifluoroacetic acid, hence no chemical change other than protonation had occurred. Solvent effects, apart from protonation, are expected to be similar for all the compounds studied; thus, by maintaining equal concentrations, chemical-shift changes as a result of solvent effects can be ignored. However, to confirm this the solutions were diluted two-fold but no variations of chemical shifts were observed.

TABLE 2

Chemical shifts (τ) for cyclopenta[*b*]pyrylium salts

Compound	Methyl-ene	Ring A	Ring B	Ring c ^{a, b}	Ring D ^a	Phenyl group ^c
(XV)	5.23	—	0.38	2.27	1.54 ^d	—
(IXa) or (IXb)	5.47	2.15	1.12	2.30	—	1.86
(XVI)	5.52	—	0.67	1.93	1.66	—
(VIIa) or (VIIb)	5.52	2.17	—	—	—	1.85

^a Four protons. ^b Principal peak. ^c Five protons. ^d $J_{A_2B^1} \sim 7$ c./sec.

Assignment of the lines at 0.38, 1.12, and 0.67 in the spectra of the first three salts to the protons attached to the pyrylium nucleus is consistent with the deshielding experienced by a proton on a positively charged ring.⁸ The relative values of the chemical shifts of these protons are in qualitative agreement with the deshielding values calculated from a consideration of ring currents, particularly of ring D in (XV) and (XVI), and of the phenyl group in (IX).

⁸ A. T. Balaban, G. R. Bedford, and A. R. Katritzky, *J. Chem. Soc.*, 1964, 1646.

We next consider the methylene resonance of compound (IX). Only one line is observed for these protons; hence, the cyclopentapyran (VIII) is protonated in only one position. This methylene resonance at τ 5.47 is at a higher field than that of the α -methylene-pyrylium ion (XV) (τ 5.23) but close to that of the β -methylene ion (XVI) (τ 5.52). Such a difference in chemical shifts between α - and β -methylene protons is in accord with the findings of Balaban, Bedford, and Katritzky⁸ on numerous monocyclic pyrylium salts. These authors found that α -methyl groups invariably absorb at lower fields than β -methyl groups, and that the resonances occur at nearly the same field in closely related salts. The position of the methylene resonance in α -ethyl groups also remained nearly constant.

The methylene peak of the ion (IX) thus appears to be that of a β -methylene group, and we therefore suggest that the protonated species is probably (IXb).

Support for this assignment was sought in the chemical shift of the α -vinyl proton in the model styrylpyrylium salt (XII) which, on the basis of the foregoing argument, should absorb near τ 2.15. We examined the perchlorate of this salt and found that the resonances of the two olefinic protons and the two pyrylium protons lay within a broad multiplet extending from τ 1.70 to 3.00, which also contained the peaks due to the fifteen phenyl protons, and it was not possible to assign the vinyl resonance.

The proton magnetic resonance spectrum of the pyran (VI) in trifluoroacetic acid exhibits a single methylene peak at τ 5.52 which, from the previous discussion, suggests that this compound is protonated solely at C-5. The resonance line for the vinyl proton is obscured by the phenyl protons; however, a prominent line appears at τ 2.17, which, in relation to (IX), might be ascribable to this proton.

DISCUSSION

Electrophilic aromatic substitution has been discussed^{9a} mainly in terms of two extreme models: the "isolated molecule" in which the position of entry is determined by the electron distribution in the substrate, and the increasingly favoured Wheland model,³ where the thermodynamic stability of the intermediate cation is the orientational criterion. The appropriate molecular orbital (MO) indices for these models are, respectively, highest electron density, q_i , and lowest localisation energy, L_i^+ . The two models usually predict the same position of attack in non-alternant hydrocarbons and heterocyclic molecules, but exceptions are known, *e.g.*, fluoranthene.^{9a} Cyclopenta[*b*]pyran is such a case, in which, as Borsdorf¹⁰ showed, the electron densities decrease in the order $q_7 > q_5 > \dots$, while the opposite sequence is found for the localisation energies: $L_5^+ < L_7^+ < \dots$. The same holds¹⁰ for the cyclopentabenzopyran (X): $q_3 > q_1 \dots$; $L_1^+ < L_3^+ < \dots$.

⁹ A. Streitwieser, jun., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961, (a) ch. 11; (b) p. 135.

¹⁰ R. Borsdorf, *Z. Chem.*, 1964, 4, 422; 1965, 5, 187.

The calculations have been extended* to 2-phenylcyclopenta[*b*]-[1]-benzopyran (VIII) and the triphenylcyclopentapyran (VI), and it is found that introduction of the phenyl substituents does not alter the general picture.

$$\text{For (VIII): } q_3 (1.193) > q_1 (1.177) > \dots ; \\ L_1^+ (0.598) < L_3^+ (0.699) < \dots$$

$$\text{For (VI): } q_7 (1.212) > q_5 (1.194) > \dots ; \\ L_5^+ (0.610) < L_7^+ (0.666) < \dots$$

Hence, different sites for electrophilic attack are predicted by the two theoretical models for all four molecules. For the indenopyran (XIV), however, both indices point to C-5 as the most reactive position.¹⁰

Protonation of unsaturated compounds provides the simplest case of electrophilic attack, uncomplicated by steric factors. Since we studied the phenomenon in solution we were dealing with an equilibrium in which the structure of the product is determined by its thermodynamic stability. The pyrylium ions are, in fact, Wheland's σ -intermediates, and the site of protonation of the benzopyran (VIII) at C-1, and of the triphenylpyran (VI) at C-5 is correctly predicted by Wheland's L_i^+ index.

We believe that our findings for the substituted cyclopentapyrans can be extended to the parent molecules, as it seems unlikely that a phenyl group placed centrally on the five-membered ring, or phenyl groups on the pyran ring, could affect the relative stabilities of the conjugate acids. We suggest therefore that cyclopenta[*b*]pyran (II; X = O) and its benzo-derivative (X) would be protonated preferentially on C-5 and C-1, respectively, as required by simple MO theory.

* Like Borsdorf,¹⁰ we used simple Hückel orbitals with the hetero-atom parameters recommended by Streitwieser.^{9b}

Calculations on the nitrogen and sulphur analogues of cyclopenta[*b*]pyran give the same position of protonation for these systems, while C-7 is predicted (unpublished work) to be the preferred site in the [*c*]-series (IV; X = O, S,² or NR²).

EXPERIMENTAL

Proton magnetic resonance spectra were determined in trifluoroacetic acid at 60 Mc./sec. on a Perkin-Elmer R.10 spectrometer, and are referred to sodium 3-trimethylsilylpropanesulphonate as internal standard. Molecular orbital calculations were carried out on the London University "Atlas" computer.

Benzo[*b*]indeno[1,2-*e*]pyran (XIV).⁵—A solution of indan-2-one (2.55 g.), salicylaldehyde (2.12 g., 0.9 mol.), piperidine (5 drops), and acetic acid (2 drops) in ethanol (12 ml.) was refluxed for 6 hr.; crystallisation of the product commenced after 30 min. The pyran (3.3 g., 87%) crystallised from toluene as dark red flat prisms, m. p. 182–184° (Found: C, 87.9; H, 4.5. Calc. for C₁₆H₁₀O: C, 88.0; H, 4.6%).

5H-*Benzo*[*b*]indeno[2,1-*e*]pyrylium Perchlorate (XVI).—This compound, m. p. 238° (decomp.) (Found: C, 60.4; H, 3.4. C₁₆H₁₁ClO₅ requires C, 60.3; H, 3.5%), was prepared by (a) adding 70% perchloric acid to an acetone solution of the corresponding tetrachloroferrate¹¹ (70%), or (b) saturating a solution of indan-1-one (2.0 g.) and salicylaldehyde (1.85 g.) in ether (60 ml.), containing 70% perchloric acid (5 ml.), with hydrogen chloride and leaving the mixture overnight (3.1 g., 65%).

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¹¹ W. H. Perkin, R. Robinson, and M. R. Turner, *J. Chem. Soc.*, 1908, **93**, 1085.