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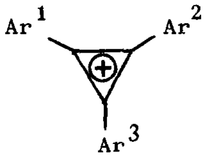
SYNTHESES AND PROPERTIES OF THE 2-THIENYL CYCLOPROPENIUM IONS

G.MARTELLI,[1a] P.SPAGNOLO,[1b] L.TESTAFERRI, and M.TIECCO*

Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, Italy

The recently reported[2] investigation on the tri-2-thienylcyclopropenium ion (I) prompted us to present the results of our researches on the synthesis and properties of the 2-thienyl derivatives (I)-(III) of this cyclic cation which represents the smallest aromatic system.



I : $Ar^1 = Ar^2 = Ar^3 =$ 2-Thienyl
II : $Ar^1 = Ar^2 =$ 2-Thienyl, $Ar^3 =$ Phenyl
III: $Ar^1 =$ 2-Thienyl, $Ar^2 = Ar^3 =$ Phenyl
IV : $Ar^1 = Ar^2 = Ar^3 =$ Phenyl

Our interest in the study of the ability of the thiophen nucleus to delocalize a positive charge or an odd electron induced us to investigate several thienyl substituted triarylmethyl cations[3] by nmr as well as their reduction products, the triarylmethyl radicals,[4] by esr spectroscopy. Both these kinds of researches led to the conclusion that the 2-thienyl is more efficient than the phenyl group in delocalizing the positive charge or the odd electron.

On the basis of these results it was of interest to undertake a study in order to evaluate the stabilizing effect of the 2-thienyl ring on the cyclopropenium ions. For this purpose we have carried out the syntheses of the perchlorates (I)-(III) and compared their properties with those of the triphenylcyclopropenium ion (IV).[5] The perchlorates (I)-(III) were prepared[6] according to the procedure reported for the synthesis of (IV), using $HClO_4$ 70%, and showed the characteristic[7] ir broad absorption (KBr) at 1420 cm^{-1}. The physical and spectral data of compounds (I)-(IV) are collected in the following table.

Comp'd	Mp(°C)	UV	60MHz NMR[9]				pK_{R^+}[10]
		λ_{max} nm(MeCN)	Phenyl		2-Thienyl		
			H_o	H_m,H_p	H_3,H_5	H_4	
I	259-60	271,297sh,345sh,356,378[8]			8.58	7.70	3.80
II	241-42	266,298sh,328sh,345,356	8.44	7.95	8.63	7.75	3.65
III	239-40	262,295sh,315sh,333,343	8.60	8.00	8.75	7.80	3.45
IV	269-70	256,294sh,307,322	8.68	8.03			3.15

It can be observed that the progressive substitution of a phenyl by a 2-thienyl group causes a gradual shift of the absorption bands of the cyclopropenium ions to longer wavelengths indicating that the 2-thienyl is more effective than the phenyl group in delocalizing the positive charge. Similarly, the shifts to lower fields of the thiophen protons and the shifts to higher fields of the benzene protons, which can be revealed from the comparison of the nmr spectra of (II) and (III) with those of (I) and (IV), confirm[3] that the 2-thienyl can acheive a larger amount of positive charge than the phenyl group.

The greater delocalizing capability of the 2-thienyl group should also produce a stabilization of the cyclopropenium ions (I)-(III) in respect to (IV). This is confirmed by the values of the pK_{R^+}; the stability increases regularly with the increase of the number of the heterocyclic nuclei linked to the aromatic three-membered ring, the largest stabilization being observed in the cation (I).

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References and Notes

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6) Satisfactory elemental analyses were obtained.
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8) These data are in good agreement with those reported in the literature.[2,5]
9) δ, ppm from TMS, in liquid SO_2 solution. The three protons of the 2-thienyl group give rise to a deceptive ABX system and the spectrum is reduced to a "doublet" (H_3,H_5) and a "triplet" (H_4). A complete analysis to determine the three coupling constants was not carried out, but from the spacing in the "triplet" the value of $1/2(J_{4,5}+J_{3,4})$ can be obtained; the value of 4.6HZ measured in this way is in good agreement with the reported values[2] determined from the spectrum at 100MHz.
10) Determined by potentiometric titration in MeCN-H_2O (1:1). The values of 4.33 for (I)[2] and of 2.80 for (IV)[5] have been reported, but in that case the pK_{R^+} were measured in 23% EtOH.

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