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PYRYLIUM SALTS FORMED BY DIACYLATION OF OLEFINS—XVI*

A LOW-MELTING HYDRATE OF 2,6-DI-n-PROPYL-4-METHYLPYRYLIUM PERCHLORATE

A. T. Balaban, E. Romaş and C. Renţia
Institute of Atomic Physics, P.O. Box 35, Bucharest, Roumania

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Abstract—From t-butyl chloride and n-butyryl chloride in the presence of aluminium chloride, 2,6-di-n-propyl-4-methylpyrylium perchlorate (I) was obtained by diacylation of intermediately formed isobutene. The crystalline perchlorate, m.p. 85°, is converted by water into a dihydrate m.p. 11° which is immiscible with cold water or aprotic organic solvents, but dissolves in alcohols. Similar low-melting liquids are formed by 2,4,6-trimethylpyrylium chloroferrate and chloride with aprotic organic solvents. The UV, IR and NMR spectra of the hydrate and deuterohydrate of I and its deuterated derivative (IV) indicate weak bonding of the water.

In a previous communication[1] the formation of a liquid 2,6-di-n-propyl-4-methylpyrylium perchlorate was mentioned. By conversion into a pyridine with ammonia and by analysis of its picrate and chloroplatinate the structure of this compound was established. All attempts to obtain a crystalline perchlorate (I) from the aqueous mixture failed.

By removing the water from this liquid perchlorate it is now found that pure 2,6-di-n-propyl-4-methylpyrylium perchlorate (I) is a crystalline colourless solid with m.p. 85° giving the correct analytical results and the expected UV, IR and NMR spectra. However, at 20° water immediately converts it into a liquid. Dehydration of this liquid regenerates the original crystalline perchlorate. This reversibly formed liquid hydrate had been obtained in the reference cited above.[1] The analysis of the liquid corresponds to a dihydrate $C_{12}H_{19}ClO_5 \cdot 2H_2O$ (II).

This liquid hydrate (II) melts at 11°, is immiscible with water at room temperature or with aprotic organic solvents such as ether or benzene, but dissolves readily in alcohols (EtOH, MeOH) or carboxylic acids (acetic acid).

In $5 \cdot 10^{-5}$ molar solution, compound I presents in water two UV absorption bands at 229 mμ (lg $\epsilon = 3 \cdot 67$) and at 288 mμ (lg $\epsilon = 4 \cdot 10$). This spectrum is almost identical with that of 2,6-di-isopropyl-4-methylpyrylium perchlorate.[2] In methylene dichloride the latter band appears at 291 mμ (lg $\epsilon = 4 \cdot 10$). The negative solvatochromy is characteristic of the longest wavelength band of pyrylium salts.[3]

Table 1 lists the IR absorption bands of the crystalline compound (I), its liquid hydrate (II) formed with water, the related liquid deuterohydrate (III) formed with deuterium oxide, the deuterohydrate IV and the deuterated compound (VI) obtained

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* Part XV, M. Frangopol, A. Genunche, P. T. Frangopol and A. T. Balaban, *Tetrahedron*, **20**, 1881 (1964).

[1] A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann. Chem.*, **625**, 74 (1959).

[2] A. T. Balaban, V. E. Sahini and E. Keplinger, *Tetrahedron*, **9**, 163 (1960).

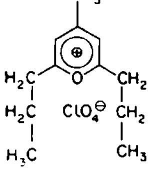
[3] A. T. Balaban, M. Gavăt, P. T. Frangopol, M. Mocanu and C. D. Nenitzescu, *Rev. Roumaine Chim.*, **9**, 79 (1964).

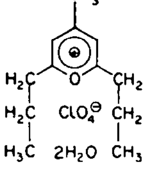
TABLE 1. INFRARED BANDS OF PYRYLIUM PERCHLORATES[a]

I[b]	II[c]	III[c]	IV[c]	VI[b]	Assignment
	3100–3400 vs–3700	3200–3400 m–3700	3200–3440 w–3600		νOH (H_2O)
			3270 vw	3280 vw	
			3170 vw	3279 vw	
			3090 vw	3090 m	
3068 ms	3065 ms	3060 ms	3060 ms	3067 ms	νCH β-position
2970 vs	2970 vs	2970 vs	2970 vs	2970 vs	νCH sat.
2935 s	2938 s	2935 s	2939 s	2939 s	νCH sat.
2878 ms	2878 ms	2878 ms	2878 ms	2880 s	νCH sat.
		2370–2520 s–2700	2370–2530 s–2700		νOD (D_2O)
			2350 vw	2360 vw	CD sat.
			2300 vw	2290 w	νCD sat.
			2100 vw		νCD sat.
1650 vs	1642 vs	1647 vs	1640 vs	1640 vs	ν8a II[5]
1550 vs	1540 vs	1539 vs	1538 vs	1540 vs	ν8b II[5]
1501 s	1501 s	1490 m			δCH_3 (as)
1470 ms	1470 ms	1470 ms	1470 ms	1468 ms	ν19a II[5]
1450 sh	1450 sh	1450 sh		1450 sh	δCH_3 (as)
1420 vw	1420 vw	1420 vw	1420 vw	1420 vw	ν19b II[5]
1390 m	1390 ms	1390 m	1390 mw	1394 m	δCH_3(s)
1344 mw	1342 mw	1343 mw	1330 mw	1334 m	
1310 vw	1308 vw	1300 w	1275 sh	1275 sh	
1254 m	1258 m	1250 w	1257 m	1257 ms	
1220 m	1215 m	1215 sh			
				1190 m	
		1000–1200	900–1270		D_2O
1040 w	1040 w				
				1000 mw	
980 m	979 m	974 m	975 ms	980 m	
870 mw, br	870 mw	870 m		942 m	
			840 w	840 w	
			819 mw	821 w	
800 w	799 w	799 w			
			785 vw	785 vw	
752 w	754 w	755 m		755 vw	
525 vw	525 vw				
510 vw	510 vw	510 vw			
			490 vw	490 vw	
	400–550–700	350–450–600			H_2O
465 vw		470 vw		460 vw	
	420 vw			423 w	

[a] Values in cm^{-1}; bands due to the anion (1100, 945, 625 cm^{-1}) are not included; [b] Potassium bromide pellet; [c] Liquid film.

by heating I under reflux in deuterium oxide. The deuteration affects only benzylic hydrogens.[4] The assignments from Table 1 are in agreement with previous data.[5] The previously[4] unassigned band at 1490–1501 cm^{-1} which disappears on deuteration has now been assigned to the γ-methyl asymmetrical deformation mode. In 2,4,6-trimethylpyrylium perchlorate two bands disappear on deuteration: a medium-intensity band at 1502 cm^{-1} and a strong band at 1521 cm^{-1}. The former can now be


I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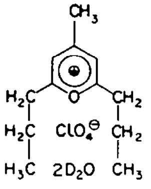
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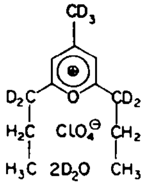
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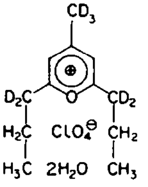
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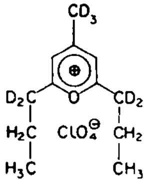
VI

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[4] A. T. Balaban, E. Gîrd and C. N. Renţea, *Abh. dtsch. Akad. d. Wiss.*, 1964, 659.

[5] A. T. Balaban, G. D. Mateescu and M. Elian, *Tetrahedron* **18**, 1083 (1962).

assigned to the γ-methyl δ_{as} mode, the latter to the δ_{as} mode of the α-methyl groups. These high frequencies of the methyl and methylene deformation vibrations originate probably in the marked positive charge of the α and γ carbon atoms of the pyrylium ring.

As seen from Table 1, in the hydrates the absorption frequencies of the pyrylium cation I are not markedly affected, and no new bands attributable to rocking, wagging or stretching modes of coordinated water molecules are visible in the 600–1000 cm^{-1} range. Therefore the water is weakly bonded in the hydrate, similarly to lattice water in crystalohydrates.[6]

The NMR spectrum of I in trifluoroacetic acid as solvent is in agreement with the structure and with previous data.[7] The γ-standing methyl gives rise to a peak at τ 7·20, and the β protons to a peak at τ 2·21. The α-standing methylene appears as a triplet centred on τ 6·80, the median methylene group is a sextet (splitting by two methylene and three methyl protons) centred on τ 8·02, and the methyl groups of the propyl residues appear as a deformed triplet centred on τ 8·88; the coupling constants between methylene–methylene and methylene–methyl protons are equal to 7·4 c/s. In liquid sulphur dioxide the NMR spectrum (Fig. 1) is similar, except for a general shift upfield and a splitting of the γ-methyl peak.

The dihydrate II (Fig. 1) presents a spectrum which is identical with that of I in trifluoroacetic acid, with a supplementary peak at τ 6·2 due to the water protons. The integral curve shows that the number of water protons associated with one mole pyrylium salt is 3·5, in satisfactory agreement with the chemical analysis. The upfield shift of 1 ppm of the water protons can be interpreted either as being due to the ring current of the pyrylium ring, the water molecules lying mostly above and below the aromatic ring, or to specific interactions in the dihydrate (e.g. hydrogen bonds with the ClO_4 anion), preventing the formation of intermolecular hydrogen bonds as in free water, or to both effects.

Taking into account the increasing interest in molten salts evidenced by the monographs,[8] and reviews[9] published recently, a study of reactions in these liquid hydrates would be very interesting. One could also employ as solvents the molten anhydrous pyrylium perchlorates with side-chains in positions 2 and 6, longer than n-propyl, whose m.ps are lower than 100°, and whose decomposition begins only above 250°,[1] or the 1-alkyl-2,4,6-trimethylpyridinium perchlorates with the n-alkyl group ethyl, butyl or longer, whose m.ps are also lower than 100°.[10] Unusual reactions have been reported recently in molten tetraalkylammonium nitrates.[11]

While the crystalline perchlorate (I) cannot be obtained from aqueous solution, but only from anhydrous solvents (e.g. EtOH–ether) or by dehydrating *in vacuo* the

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[6] K. Nakamoto, "*Infrared Spectra of Inorganic and Coordination Compounds*", J. Wiley and Sons, New-York, 1963, p. 155.

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

[8] B. R. Sundheim (editor), "*Fused Salts*", McGraw-Hill, New York (1964); M. Blander (editor), "*Molten Salt Chemistry*", Wiley-Interscience, New York, 1964.

[9] W. Sundermeyer, *Angew. Chem.* **77**, 241 (1965); H. Bloom and J. O'M. Bockris, in "*Modern Aspects of Electrochemistry*", No. 2 (J. O'M. Bockris, editor), Butterworths, London, 1959, p. 160; E. A. Ukshe, *Usp. Khim.* **34**, 322 (1965).

[10] C. Toma and A. T. Balaban, *Tetrahedron* (in press).

[11] J. E. Gordon, *J. Amer. Chem. Soc.* **86**, 4492 (1964).

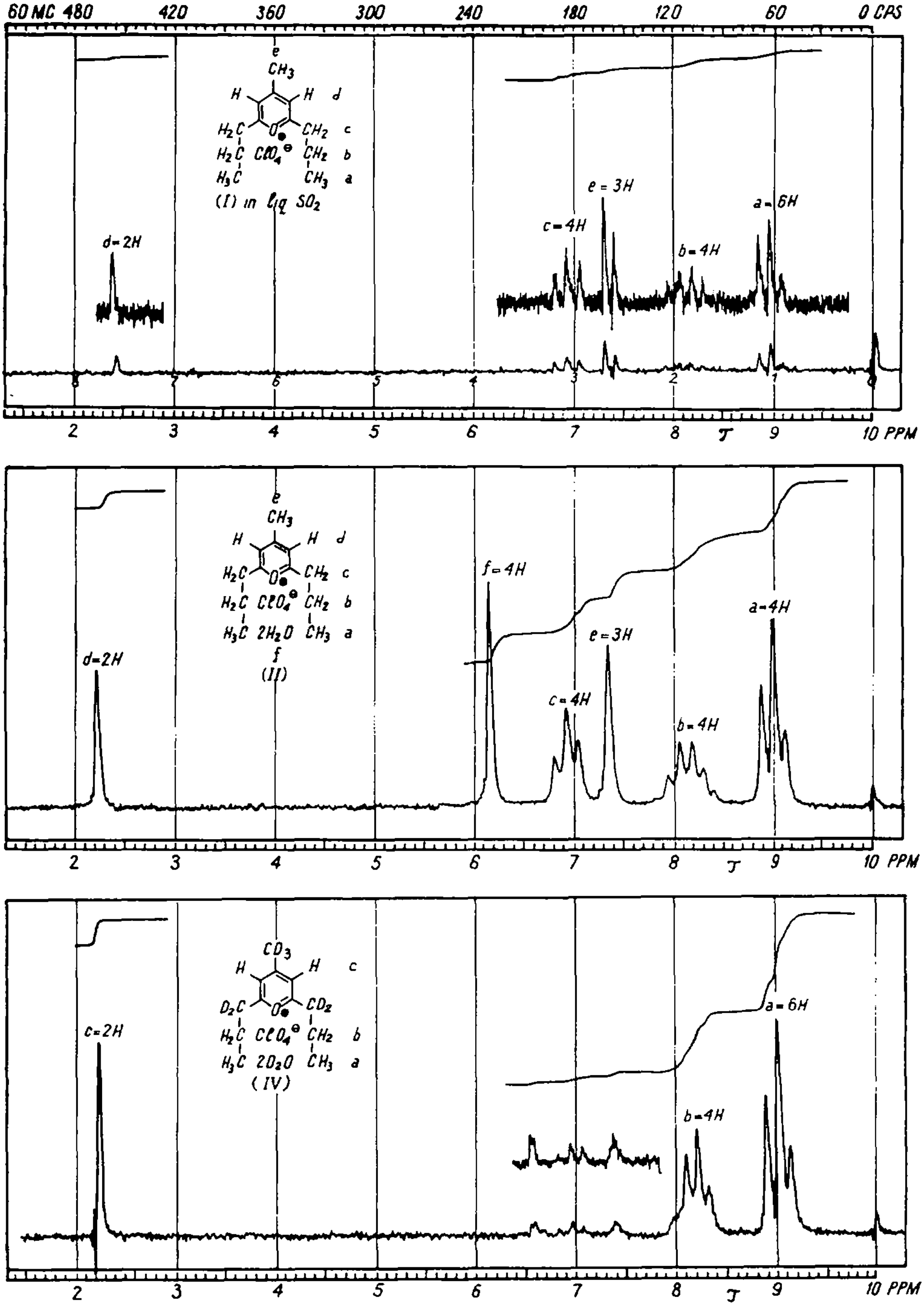
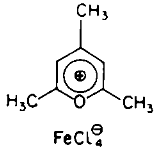
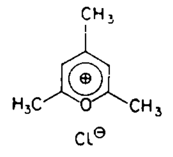


FIG. 1. Nuclear magnetic resonance spectra of 2,6-di-n-propyl-4-methylpyrylium perchlorate (I) in liquid sulphur dioxide, of its dihydrate (II) (pure liquid) and of the dideuterohydrate of the deuterated compound IV (pure liquid). Integral curves are also shown on the spectra.

liquid hydrate, 2,4,6-trimethylpyrylium chloroferrate (VII)[12] can be obtained crystalline from aqueous solutions acidified with hydrochloric acid. Crystals of VII, m.p. 41°, are immediately converted into a liquid by aprotic solvents such as chloroform or benzene; they are however, soluble in and may be recrystallized from, lower alcohols.



VII



VIII

Similarly, 2,4,6-trimethylpyrylium chloride VIII which had been prepared in benzene as a liquid[13] is now found to crystallize when the benzene is removed *in vacuo*, giving very hygroscopic crystals, m.p. 110°, with an IR spectrum similar to that of other 2,4,6-trimethylpyrylium salts.[5]

EXPERIMENTAL

Preparation of I. In a 4-necked flask fitted with stirrer, reflux condenser, immersed thermometer and dropping funnel, 230 g n-butyryl chloride (prepared from butyric acid and benzoyl chloride)[14] and 230 g powdered $AlCl_3$ were introduced with cooling and mechanical stirring. Then from the dropping funnel, 98 g (110 ml) t-butyl chloride[15] was added during 1 hr at 15–20° with external cooling. Hydrogen chloride was evolved during the addition and during subsequent stirring for 4 hr. The mixture was stirred occasionally and after 48 hr was poured onto 2 kg crushed ice and 50 ml HCl. The upper ketonic layer was discarded, the aqueous solution was extracted twice with ether and then heated to boiling to remove all dissolved ether. The clear filtered solution was treated with excess perchloric acid. The upper liquid layer of perchlorate was separated and shaken several times with cold water, causing it to fall to the bottom. The purified liquid melted at 11° (Found: C, 45·93; H, 7·36. $C_{12}H_{19}ClO_5 \cdot 2H_2O$ requires: C, 45·79; H, 7·36%). The compound was dried in a desiccator over H_2SO_4 or P_2O_5 under red. press (not lower than 15 mm because of splashing), giving yellowish crystals, m.p. 80–82°.

An analytical sample was obtained by dissolving the product in anhydrous MeOH, and adding anhydrous ether yielding white crystals, m.p. 85°. (Found: C, 51·97; H, 6·75. $C_{12}H_{19}ClO_5$ requires: C, 51·71; H, 6·87%.)

The hydrate and deuterohydrate were obtained from the crystalline perchlorate by shaking for 5 min with excess cold H_2O and D_2O, respectively. For deuteration of I to IV, compound I was refluxed in D_2O (10-fold amount) for 4 hr, the solution then filtered, cooled and the lower layer of deuterohydrate (IV) separated. It was converted into the hydrate V by shaking for 5 min with water.

IR spectra were recorded with a Jena UR-10 apparatus using KBr pellets (I, VI) or as liquid films between NaCl windows (II–V). UV absorption spectra were registered with an Optica (Milano) CF4 double-beam grating spectrophotometer. NMR spectra were recorded with a 40 Mc Perkin–Elmer apparatus in trifluoroacetic acid, and with a JNH-3H-60 apparatus in SO_2 solution or in pure liquids.

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[12] A. T. Balahan and C. D. Nenitzescu, *J. Chem. Soc.*, 1961, 3553.

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[14] H. C. Brown, *J. Amer. Chem. Soc.*, **60**, 1325 (1938).

[15] J. F. Norris and A. W. Olmsted, *Org. Synth.* Coll. Vol. I, 144 (1941).