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PREPARATION OF PYRYLIUM SALTS BY OLEFIN DIACYLATION. THE TWO PYRYLIUM SALTS FORMED IN AMYLENE DIACETYLATION WITH VARIOUS CATALYSTS

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THE recent publication of two preliminary notes by Praill,[1] describing the formation of pyrylium salts from olefins, acid anhydrides and perchloric acid, prompts us to report the following results.

As was shown previously[2] pyrylium salts, and hence pyridines, may be prepared by Friedel - Crafts diacylation of olefins. The scope and limitations of this method were studied by variation of the acyl radical and of the olefin, using aluminium chloride, and in some cases stannic chloride, as catalyst, and isolating the pyrylium salts as perchlorates. The diacetylation of trimethylethylene (or t-amyl chloride) in the presence of $AlCl_3$ leads to 2,6-dimethyl-4-ethyl-pyrylium perchlorate, but in the presence of $SnCl_4$ no pyrylium perchlorate could be isolated.

In order to explain this difference, we studied the acetylation of amylene in various conditions, and found that in some cases the pyrylium

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[1] P. F. G. Praill and A. L. Whitear, Proc. Chem. Soc. 312 (1959); P. F. G. Praill, Chem. & Ind. 1123 (1959).

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

salt formed had structure 2,6-dimethyl-4-ethyl (A) while in other cases it had structure 2,3,4,6-tetramethyl (B). These structures were assigned on the basis of the reaction with hot aqueous hydroxide (leading in case A to 3-methyl-5-ethyl-phenol,[2] and in case B to a mixture of 2,3,5- and 3,4,5-trimethylphenol) and with aqueous ammonia (pyridine A: picrate[2] m.p. 120°, chloroplatinate[2] m.p. 213°, methiodide m.p. 205°, picrolonate m.p. 215°; pyridine B: picrate m.p. 107° and 123°,[3] chloroplatinate m.p. 228°, methiodide m.p. 188°, picrolonate m.p. 225°).

The nature of the product formed in the reaction was established by isolation of the pyrylium salt (perchlorates: A m.p. 189°, B 95°; reineckeates: A m.p. 155°, B 187°; chloroantimonates: A m.p. dec. 141°, B 191°) and by treatment of the reaction mixture with aqueous ammonia to give the corresponding pyridine (characterized by its derivatives and I.R. spectrum).

It was thus found that trimethylethylene or t-amyl chloride and acetyl chloride yield only A in the presence of $SbCl_5$, $AlCl_3$, $AlCl_3$ in carbon

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[3] The literature reports for the m.p. of 2,3,4,6-tetramethylpyridine two values: 107° [4,5] and 123°.[6,7] We established that this is a case of dimorphism, the two forms being interconvertible by seeding the melt on the Kofler hot stage, or the saturated alcoholic solution of one form, with crystals of the other.

[4] T. Eguchi, *Bull. Chem. Soc. Japan* **2**, 176 (1927); *Ibid.* **3**, 227 (1928).

[5] R. A. Van Meter et al., *Analyt. Chem.* **24**, 1758 (1952).

[6] H.B. Nisbet and A.M. Pryde, *J.Inst.Fuel* **27**, 58 (1954); *Nature, Lond.* **168**, 832 (1951) R.J. Benzie, J.N. Milne and H.B. Nisbet, *Oil Shale and Cannel Coal* Vol.2, p. 784. The Institute of Petroleum, London (1951).

[7] K. Tsuda, N. Ikekawa, H. Mishima, A. Iino and T. Morishige, *Pharm. Bull.* **1**, 122 (1953); *Chem. Abstr.* **49**, 171j (1955).

disulphide or in nitromethane, while trimethylethylene or t-amyl alcohol and acetic anhydride yield only or mainly B in the presence of boron fluoride etherate, perchloric acid or sulphoacetic acid. Trimethylethylene and acetic anhydride with sodium perchlorate and acetyl chloride alone or in acetic acid[8] also yield only B. The use of $ZnCl_2$ leads to B with t-amyl chloride and acetyl chloride, and to a mixture of A and B with t-amyl alcohol and acetic anhydride. Mixtures are also produced from t-amyl chloride, acetyl chloride and $TiCl_4$ or $FeCl_3$. If the reaction mixture prepared from t-amyl chloride, acetyl chloride and stannic chloride is converted directly to the pyridine, the resultant compound is found to be mainly A, but if the mixture is hydrolysed and left in conc. aqueous-ethanolic solution, the pyrylium chlorostannate B (m.p. 281°) is slowly deposited. However, unsuccessful attempts were made to effect the reaction between trimethylethylene or t-amyl chloride or alcohol and an acetylating mixture prepared from conc. aqueous hydrochloric acid, stannic chloride and acetic anhydride.[9]

These same catalysts were also applied to the diacetylation of isobutylene (introduced as t-butanol or t-butyl chloride). The following new 2,4,6-trimethylpyrylium salts were thus prepared: chloroantimonate m.p. dec. 174°, and reineckeate m.p. 165°. The preparation of 2,4,6-trimethylpyrylium perchlorate from t-butanol, acetic anhydride and perchloric acid was developed into a synthetic method[10] with average yield 55% relative to

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[8] K. B. L. Mathur, J. N. Sharma, K. Venkataraman and H. G. Krishnamurty, J. Amer. Chem. Soc. **79**, 3582 (1957).

[9] R. Jenny, C. R. Acad. Sci., Paris **248**, 355 (1959).

[10] Submitted for publication to Organic Syntheses (1959).

perchloric acid. It was found that if the last reagent added to the mixture of the other two is the alcohol or the anhydride, large amounts of triisobutylene separating as a colourless upper layer are formed.

Experimental details and theoretical implications of this reaction will be discussed in a later paper.

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