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PYRYLIUM SALTS FORMED BY DIACYLATION OF ALKENES. PART XII.[1] DIACYLATION OF 2-METHYLPROPENYLBENZENE.

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THE formation of pyrylium salts by olefin diacylation[2] was described for the unsubstituted propene,[3] for all four possible monosubstituted propenes where the substituent is an alkyl or a phenyl group (isobutene,[4] 1-pentene,[5] α-methylstyrene[4,5] and allylbenzene[6]), for three from the seven possible disubstituted propenes (2-pentene,[5] 2-methyl-2-butene[7] and 1,2-diphenylpropene[4]), and for two from the six possible trisubstituted propenes.[4,6]

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[1] Part XI, A. T. Balaban, M. Mărculescu-Frangopol and P. T. Frangopol, Isotopentechnik 2, 235 (1962).

[2] A. T. Balaban and C. D. Nenitzescu, Studii şi Cercetări Chim. Acad. R.P.R. 9, 251 (1961) ; Revue de Chimie Acad. R.P.R. 6, 269 (1961).

[3] A. T. Balaban, D. Fărcaşiu and C. D. Nenitzescu, Tetrahedron 18 1075

[4] A. T. Balaban and C. D. Nenitzescu, Annalen 625, 74 (1959).

[5] P. F. G. Praill and A. L. Whitear, J. Chem. Soc. 3573 (1961).

[6] A. T. Balaban, C, D. Nenitzescu, M. Gavăt and G. Mateescu, J. Chem. Soc. 3564 (1961).

[7] A. T. Balaban and C. D. Nenitzescu, Tetrahedron Letters No. 2, 7 (1960) ; J. Chem. Soc. 3553 (1961).

A program was initiated for filling in the gaps in order to find out whether there exist other olefins, besides 2-methyl-2-butene, which may yield two different pyrylium salts according to the acylating agent employed.[7] The present note reports that the disubstituted propene 2-methylpropenylbenzene (β,β-dimethylstyrene) is such an olefin.

Introduction of 70 % - perchloric acid (25 ml) into a mixture of dimethylbenzylcarbinol (25 g) and acetic anhydride (100 ml) at reflux temperature gave after cooling and dilution with ether a dark lower layer containing 2,4,6-trimethyl-3-phenylpyrylium perchlorate. This was converted by ammonia into 2,4,6-trimethyl-3-phenylpyridine, b. p. 119°/3 mm (9.5 g, 24 % yield) ; the chloroplatinate with m. p. 250° (dec.) and the picrate with m. p. 141° do not depress the m. ps. of the corresponding derivatives obtained previously.[8] The picrolonate has m. p. 232° (from ethanol) and the methiodide m. p. 210° (from ethanol-ether). The same product was obtained on replacing the carbinol by 2-methylpropenylbenzene.

However, when 2-methylpropenylbenzene (16 g) was introduced into a cooled solution of aluminium chloride (45 g) in acetyl chloride (100 ml) and the resulted mixture was left for 48 hr at room temp, a different base was obtained in 18 % yield by hydrolysis of the reaction mixture and treatment with aqueous ammonia. The structure of this base b. p. 134°/3 mm is

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[8] A. T. Balaban, G. Mateescu and C. D. Nenitzescu, Studii şi Cercetări Chim. Acad. R.P.R. 9, 211 (1961) ; Revue de Chimie Acad. R.P.R. 6, 295 (1961).

2,6-dimethyl-4-benzylpyridine since its picrate with m. p. 143° does not depress the m. p. of an authentic sample, kindly supplied by professor Kato.[9] The picrolonate has m. p. 195°, the chloroplatinate m. p. 95° and the methiodide m. p. 163° (lit.[10] m. p. 152°).

Introduction of 2-methylpropenylbenzene (20 g) into a mixture of aluminium chloride (55 g) and benzoyl chloride (110 g) afforded after 48 hrs' standing at room temp and hydrolysis with ice and 150 ml ether an ethereal layer which on strong dilution with ether deposited a dark oily product that was repeatedly extracted with hot 0.5n hydrochloric acid. Treatment of the aqueous extracts with perchloric acid afforded the dibenzoylation product as a yellow pyrylium perchlorate, m. p. 256° (from acetic acid) in 5 % yield. Its U.V. spectrum in acetic acid presents two bands at 392 mμ (ε 25,000) and 283 mμ (ε 19,600). The close similarity with the spectrum of 2,4-diphenyl-4-methylpyrylium perchlorate[11] is in agreement with both structures 2,6-diphenyl-4-benzylpyrylium and 2,3,6-triphenyl-4-methylpyrylium. However, the presence of methyl bending bands at 1448vs and 1379s cm^{-1} indicates the latter structure ; the I.R. spectrum presents in addition characteristic[12] pyrylium bands at 1621vs and 1474vs and phenyl bands at 1583m and 1503s.

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[9] T. Kato, J. Pharm. Soc. Japan 75, 1228, 1231 (1955).

[10] E. H. Huntress and E. N. Shaw, J. Org. Chem. 13, 674 (1958).

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

[12] A. T. Balaban, G. D. Mateescu and M. Elian, Tetrahedron 18 1083

This perchlorate was converted by alcoholic ammonia into 2,3,6-triphenyl-4-picoline, picrate m. p. 157°, picrolonate m. p. 145°.

Thus 2-methylpropenylbenzene behaves in the diacylation reaction substantially like 2-methyl-2-butene, which with acylating agents like acetyl chloride and aluminium chloride or antimony pentachloride yields the pyrylium salt formed exclusively by Hofmann eliminations, while with other acylating agents like propionyl or benzoyl chloride and aluminium chloride, or acetyl chloride and zinc or stannic chloride, or acetic anhydride and perchloric acid, yields the pyrylium salt formed by Saytzeff (and Hofmann) eliminations.[7,13] These results may be rationalized on the basis of currently accepted views on the mechanism of olefin-forming eliminations[14] and of the results of recent I.R. spectroscopic evidence[15] that the Friedel-Crafts acylating complex of acetyl chloride and antimony pentachloride has an ionic structure, while the antimony pentachloride complexes of propionyl and benzoyl chloride are polarized donor-acceptor complexes.

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[13] G. Baddeley and M. A. R. Khayat, Proc. Chem. Soc. 382 (1961).

[14] Cf. C. K. Ingold, Proc. Chem. Soc. 265 (1962).

[15] G. A. Olah, S. J. Kuhn, W. S. Tolgyesi and E. B. Baker, J. Amer. Chem. Soc. **84**, 2733 (1962).