Catalytic Hydrogenation of Pyrylium Salts: A Convenient Route to Alkyl-Substituted Tetrahydropyrans

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2,4,6-Trialkylpyrylium perchlorates afford in high yields by hydrogenation on palladium catalyst at room temperature the corresponding all-cis-2,4,6-trialkyltetrahydropyrans, whereas other reaction conditions lead to mixtures of tetrahydropyrans and hydrogenolyzed products.

The chemistry of pyrylium salts, which has been recently reviewed [1], offers broad areas of synthetic applicability [2]. In view of the current interest in this field we report here our findings regarding the catalytic hydrogenation of pyrylium perchlorates. This reaction, which has not been previously described, may prove useful in synthesizing variously substituted tetrahydropyrans with a specific configuration.

Pyrylium salts have been reduced with hydride donors [3] to mixtures of α- and γ-pyrans, with zinc dust [4] to 4,4'-bis-4H-pyrans as well as photochemically or electrochemically [4, 5]. We found that 2,4,6-trimethylpyrylium perchlorate (1a) can be reduced also catalytically, either on palladium (5% on charcoal) or on platinum.

In order to investigate the general applicability and the stereochemistry of this reaction we hydrogenated pyrylium perchlorates 1a–1d. Aqueous suspensions of 2,4,6-trisubstituted pyrylium perchlorates 1a–1d and the catalyst, together with ethyl ether, were submitted to hydrogen pressures of 10–20 atm in an autoclave with electromagnetic stirring. When using palladium as catalyst, three moles of hydrogen per mole 1 were absorbed at room temperature by 1a–1c, while 1d reacted only at 100 °C and absorbed more hydrogen. Titration of the aqueous layer after catalyst filtration indicated the presence of one mole HC\textsubscript{2}O\textsubscript{4} per mole of 1. After neutralization with aqueous sodium hydrogen carbonate and distillation of the ethereal layer, pure (96–98% by GLC) 2,4,6-trialkyltetrahydropyranic products 2a–2c were obtained in good yields (78–85%); it is notable that in each case only one stereoisomer was isolated. Unlike these “clean” products, mixtures of several compounds were obtained from 1d, consisting of the corresponding 2,4,6-triphenyltetrahydropyran 2d (22%), 1,3,5-triphenylpentane 3d (62%), and other products in lower (<4%) amounts*.

![Catalytic Hydrogenation of Pyrylium Salts](image)

When using platinum as catalyst, at room temperature, mixtures resulted even from 1a; these mixtures consisted of 2a (63%), the corresponding 1,5-pentandiol 4a (4-methyl-2,6-heptanediol, 28%) and other minor (<3%) products. Another observation deserves mentioning: compounds 2a and 2b, formed on standing crystalline ether peroxides 5.

It is thus apparent that the hydrogenation of pyrylium salts 1 in mild conditions (room temperature,

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* Column chromatography on alumina separates neatly 2d and 3d using petroleum ether and then ethyl ether.
palladium catalyst) leads exclusively to tetrahydropyrans 2, whereas higher temperatures or platinum catalysts lead to mixtures of 2 with the corresponding ring-opened products, the 1,5-pentanediols 4. The latter diols, when benzylic (e.g. 4d) undergo easily dehydrogenation and subsequent hydrogenation affording the parent hydrocarbon 3.

The $^1$H NMR spectra and decoupling experiments indicate that the isolated stereoisomer 2 has the 2,4,6-substituents all-cis. Thus the signal for the $\alpha$-ring protons appears as a sextet (two overlapping quartets) in 2a, a fairly broad doublet in 2b and sharp double doublets in 2c and 2d, all with a large coupling constant (10.5—11.5 Hz) which advocates an axial position for these $\alpha$-hydrogens. Irradiation of 2c at 1.5 ppm revealed the chemical shift of the $\beta$-equatorial protons by cancellation of the small dehydration and subsequent hydrogenation affording the parent hydrocarbon 3.

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Compounds with constitutions 2a and 2d were reported earlier (refs. [11, 12] respectively) but no stereoschemical assignments were made. The slight discrepancies in boiling point and refraction index between the present compound 2a and the 2,4,6-trimethyltetrahydropyran obtained by previous methods, may be due to different stereoisomeric forms.

![Diagram](image)

**Experimental**

Spectroscopic data: for 2a IR (CCl$_4$) $\nu_{\text{max}}$ 2978, 2960, 2913, 2908, 2875, 2845, 1370, 1325, 1183, 1127, 1095, 1035; $^1$H NMR (CDCl$_3$) $\delta$ = 0.8 (m-partially obscured, 2H, $H^e$), 0.91 (d, 3H, $H^a$), 1.18 (d, 6H, $J = 6.5$ Hz, 4-CH$_3$), 1.58 (broad d, 3H, $J_{3a3e} = 10.5$ Hz, $H^e$ and $H^a$); 3.43 (sextet, 2H, $J_{2a3a} = 11$ Hz, $H^2$); for 2b IR (CCl$_4$) $\nu_{\text{max}}$ 2920—2905, 2860—2835, 2228—2215, 1312, 1150, 1105, 1053; $^1$H NMR (CDCl$_3$) approx. 85% $d_6$ $\delta$ = 0.8 (m, $H^e$), 1.6 (broad d, $H^e$ and $H^a$), 3.42 (broad d, $J_{3a3e} = 10.5$ Hz, $H^a$); for 2c IR (CCl$_4$) $\nu_{\text{max}}$ 2970—2945, 2910, 2870, 2825, 1375—1365, 1187, 1105, 1040; $^1$H NMR (CDCl$_3$) $\delta$ = 0.8 (m-partially obscured, 2H, $H^a$), 0.90 (s, 18H, C(CH$_3$)$_3$), 0.93 (d-partially obscured, 3H, 4-CH$_3$), 1.51 (dd and m, 3H, 3H, $J_{3a3e} = 11$ Hz, $H^e$ and $H^a$), 2.84 (dd, 2H, $J_{3a3e} = 11.3$ Hz, $J_{3a3e} = 2$ Hz, $H^e$); for 2d $^1$H NMR (CDCl$_3$) $\delta$ = 1.4—2.4 (m, 5H), 4.75 (dd, 2H, $J_{2a3a} = 10.5$ Hz, $J_{2a3e} = 2.5$ Hz, $H^a$), 7.25—7.65 (m, 15H, C-H$_3$); for 3d $^1$H NMR (CDCl$_3$) $\delta$ = 2.0 (m, 4H, 2-CH$_2$), 2.5 (m, 5H, 1-CH$_2$ and 3-CH$_2$), 7.1—7.3 (m, 15H, C-H$_3$); for 4a IR (CCl$_4$) $\nu_{\text{oH}}$ 3625; for 5a IR (CCl$_4$) $\nu_{\text{max}}$ 2970—2950, 2920, 1368, 1196, 1168, 1097, 1045, 884; $^1$H NMR (CDCl$_3$) $\delta$ = 0.86 (d, 6H, $J = 7$ Hz, 4-CH$_3$), 1.20 (d, 6H, $J = 7$ Hz, 6-CH$_3$), 1.47 (s, 6H, 2-CH$_3$), 1.86 (m, 6H, $H^e$, $H^a$ and $H^e$), 4.04 (broad quartet, 2H, $H^e$).

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