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OXIDATION OF HEXAHYDROPYRIMIDINES INTO 3,4,5,6-TETRAHYDROPYRIMIDINIUM SALTS IN THE PRESENCE OF PALLADIUM CATALYST

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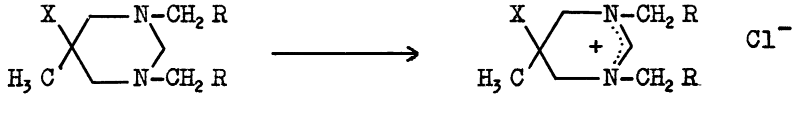
Treatment of 5-amino- and 5-nitro-5-methyl-1,3-disubstituted hexahydropyrimidines with palladium chloride gave the corresponding 3,4,5,6-tetrahydropyrimidinium chlorides, which were also obtained from the air oxidation of hexahydropyrimidine hydrochlorides in the presence of palladium black.

In the course of a continuing study on hexahydropyrimidines,[1)] it was found that the oxidation of hexahydropyrimidines (I) in the presence of palladium or its chloride gave 3,4,5,6-tetrahydropyrimidinium chlorides (II).

General procedure of the reaction is as follows: A half molar amount of fine powdered palladium chloride was added into an aq. solution (or suspension) of I,[2)] and the whole was heated on a water-bath for 20-30 min by passing nitrogen through the solution. After removal of palladium, the filtrate was evaporated to dryness in vacuum and the residue, II, was recrystallized from acetone. The same products were also obtained by heating an aq. solution of monohydrochloride of I (0.002 mole) in the presence of palladium black (100 mg) under stirring on a water-bath for 1-1.5 hr. In the latter procedure, the presence of the air was found to be required. Yields were almost quantitative in both methods. All products possess the characteristic absorption at 1683-1692 cm^{-1} in the IR spectra and the signal (singlet, 1H) at 8.15-8.75 ppm in the NMR spectra indicating the presence of the amidinium moiety. Compounds obtained hereof are listed in Table 1.

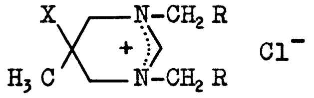


Ia-e

IIa-e

X = NO_2 or NH_2

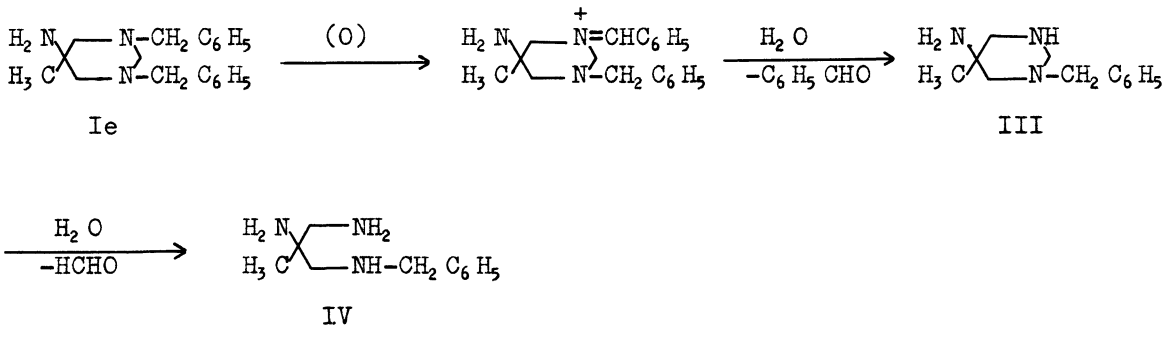
Table 1. 5-Amino- and 5-nitro-5-methyl-1,3-dialkyl-3,4,5,6-tetrahydropyrimidinium chlorides (II)



Compound No.	X	R	mp (°C)	NMR (δ, ppm)[a] 5-CH_3	2-CH	4- and 6-CH_2	R-CH_2-N	IR (KBr, cm^{-1}) $N\overset{+}{=}C(H)=N$
IIa	NO_2	H	98.5	1.80(s,3H)	8.17(s,1H)	4.05(ABq,4H)	3.30(s,6H)	1685
IIb	NO_2	CH_3	82-83	1.78(s,3H)	8.22(s,1H)	4.07(ABq,4H)	3.55(q,4H)	1683
IIc	NO_2	C_6H_5	218-220	1.63(s,3H)	8.75(s,1H)	3.92(ABq,4H)	4.71(s,4H)	1685
IId	NH_2	CH_3	91-93	1.43(s,3H)	8.15(s,1H)	3.45(s,4H)	3.32(q,4H)	1692
IIe	NH_2	C_6H_5	185-187	1.08(s,3H)	8.62(s,1H)	3.15(s,4H)	4.70(s,4H)	1690

a) NMR spectra were taken at 60 MHz in D_2O with DSS as an internal reference. s = singlet, q = quartet.

A preliminary work on the air oxidation of Ie in the absence of the catalyst was attempted. Reflux of a 10 % HCl solution of Ie for 20 hr afforded 5-amino-1-benzyl-5-methylhexahydropyrimidine (III, mp 72-74°C, 1 % yield) and N'-benzyl-2-methyl-1,2,3-propanetriamine3) (IV, 13 % yield) accompanied with a liberation of benzaldehyde.



Work is in progress to find scope and limitation of this oxidation.

References

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