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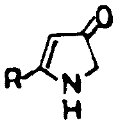
A NEW VERSATILE ROUTE TO 3-HYDROXYPYRROLES(1)

Wilhelm Flitsch*, Klaus Hampel(2a) and Manfred Hohenhorst(2b)
Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität
Orléans-Ring 23, D-4400 Münster

SUMMARY: N-Acylated 3-hydroxypyrroles 5 have been obtained from a reaction of imides 2 with phosphoranes 3.

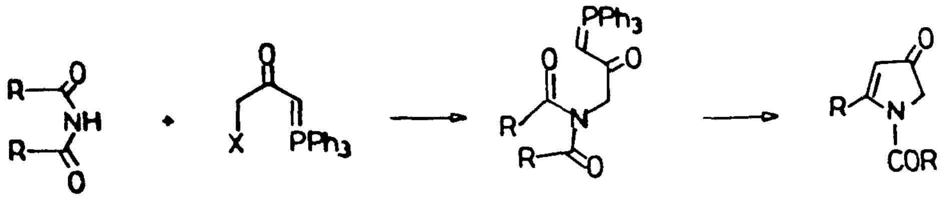
A simple synthesis of N-unsubstituted 1 and N-acylated 3-hydroxypyrroles 5 was imperative for a preparation of 3a-azaazulen-1-ones(3), which should be suited also for a preparation of the hithero unknown parent compound 1a. Derivatives of 1 described so far are usually substituted, at the nitrogen atom and are often difficult to prepare(4). 5-Methyl-3-hydroxypyrrole 1b, moreover, proved to be extremly labile(4b).

Here we present a simple two-step synthesis of N-acylated 3-hydroxypyrroles 5a-c from symmetric imides 2a-c and the phosphoranes 3(5) which is depicted the scheme:



1a R=H
b R=CH$_3$

	a R=H	b R=CH$_3$	c R,R=CH$_2$-CH$_2$
4	49%	58%	78%
5	25%	56%	67%



2 **3 (X=Cl,Br)** **4** **5**

Sodium salts of imides 2 (obtained with sodium hydride at room temperature) were heated with 3 in DMF (4 h, 80°C)(6). Evaporation and chromatography gave derivatives 4[7] which could be cyclized in boiling mesitylene (12 h).

N-Acylated 3-hydroxypyrroles 5[7] are crystalline and fairly stable compounds, which can be obtained even on a large scale.
Deacylation occurred on treatment of 5b with 5N NaOH in oxygen-free methanol[8] in a few minutes at room temperature. Isolation and characterisation of 1b followed a procedure described earlier[4b].

ACKNOWLEDGEMENT
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REFERENCES AND NOTES

1) We use the name 3-hydroxypyrrole for systematic reasons. Δ^2-Pyrrolin-4-ones are generally the more stable tautomer, as reflected in the formulae. (Tautomerism of 3-hydroxypyrroles: H. McNab, presented at the 8th Lakeland Heterocyclic Symposion Grasmere 1987).

2) 2a) K. Hampel, Dissertation, Univ. Münster 1986.
   2b) M. Hohenhorst, Dissertation, Univ. Münster 1986.

3) Following communication: W. Flitsch and M. Hohenhorst, Tetrahedron Lett.

4) a) H. McNab and L.C. Monahan, J. Chem. Soc. Chem. Commun., 1985, 213 and references cited therein.
   b) T. Momose, T. Tanaka, T. Yokota, N. Nagamoto and K. Yamada, Chem. Pharm. Bull., 27, 1448 (1979) and references cited therein.
   c) For o-substituted 3-hydroxypyrroles, see H.W. Pinnick and K.S. Kochhar J. Org. Chem., 49, 3222 (1984) and references cited therein.

5) 3 (X = Cl): R.E. Hudson and P.A. Chopard, J. Org. Chem. 28, 2446 (1963).
   3 (x = Br): K. Isslab and R. Lindner, Liebigs Ann. Chem. 1968, 713.
   Yields of the reactions of both phosphoranes do not differ remarkably.

6) 2a : 1,2-Dimethoxyethane, 80°C, 8 h.

7) The compounds were characterized by elemental analyses as well as by their spectra: selected data: 4a ($CDCl_3$) δ: 3.3 (br, H, CH=PPh), 4.4 (s, 2H, $-CH_2-$), 7.5 (m, 15H, phenyl), 9.05 (s, 2H, CHO). 4b ($CDCl_3$) δ: 2.4 (s, 6H, CH_3), 3.7 (br, 1H, CH = PPh_3), 4.4 (s, 2H, $-CH_2$), 7.5 (m, 15H, Aromatic-H). 4c ($CDCl_3$) δ: 2.6 (s, 4H, CH_2-), 3.7 (br, 1H, CH = PPh_3), 4.25 (s, 2H, $-CH_2$), 7.5 (m, 15H, Aromatic-H). 5a ($CDCl_3$): δ = 4.11, 4.17 (s, 2H, $-CH_2-$), 5.79, 5.86 (d, J_{21} = 3.97 Hz, 1H, =CH-CO), 8.24, 8.66 (d, J_{12} = 3.97 Hz, N-CH=), 8.50, 8.36 (s, 1H, CHO). 5b ($CDCl_3$) δ: 2.21 (s, 3H, $COCH_3$), 2.67 (s, 3H, CH_3), 4.12 (s, 2H, $-CH_2-$), 5.48 (s, 1H, C=CH-). 5c ($CDCl_3$ δ: 2.82 (m, 2H, $-CH_2-$), 3.13 (m, 2H, $-CH_2-$), 3.97 (s, 2H, $-CH_2-$), 5.46 (s, 1H, C=CH-).

8) Solvents were degassed by ultrasonic treatment and subsequently saturated with argon.

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