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THE IMINO-WITTIG REARRANGEMENT

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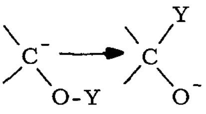
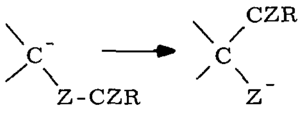
Summary: Iminoethers 15 are rearranged by LDA into α-aminoketones 18.

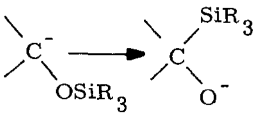
The rearrangement of the O-linked substituent in an α-oxycarbanion 1 to carbon giving 2 is generally known as the Wittig rearrangement.[1,2] In the classical Wittig, the substituent Y in 1 → 2 is an alkyl group, but recently examples of the migration of other substituent types have been reported. Thus 3 → 5 has been denoted[3] the oxo-Wittig, 4 → 6[4] is the dithio-Wittig, and 7 → 8[5] the sila-Wittig. We now report the first examples of the imino-Wittig rearrangement of type 9 → 10; we believe that this is a novel type although examples of the aza-Wittig 11 → 12 have been reported,[6] albeit solely for the allylic systems shown.



1 2



3 Z = O
4 Z = S
5 Z = O
6 Z = S



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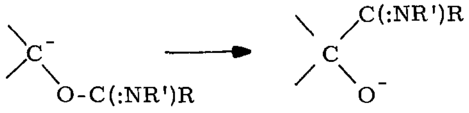
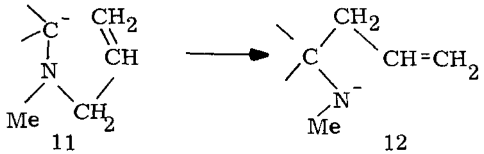


9 10



11 12

Benzoyl-p-toluidide 13[7] was converted via the iminochloride 14[8] into iminoethers 15 (Table 1) by standard methods. Treatment of the imino-ethers 15a-c with lithium diisopropylamide (LDA) in THF converted them via the α-oxycarbanions 16 and the α-hydroxyimines 17 into α-amino ketones 18a-c (Table 2). The products were characterised by IR (νNH at 3310-3400 cm^{-1} and νC=O at 1675-1690 cm^{-1}) and NMR spectra. Attempted rearrangement of 15d and 15e failed: here the R group is electron donor in character and this reduces the acidity of the CH$_2$-protons.

The metallations were conducted in THF solution at -5 – -0°C: the rearrangement 16 → 17 appears to be fast.

Table 1. Preparation of iminoethers 15

15	R	Yield %	Mp°C	Crystal form[a]	Molecular formula	Found C	Found H	Found N	Required C	Required H	Required N
a	C_6H_5	74	65-66	Plates	$C_{21}H_{19}NO$	83.4	6.2	4.7	83.7	6.4	4.6
b	2-Pyridyl	62	74-76	Needles	$C_{20}H_{18}N_2O$	79.5	6.3	9.0	79.4	6.0	9.3
c	p-ClC_6H_4	84	102-105	Prisms	$C_{21}H_{18}ClNO$[b]	75.0	5.4	4.1	75.1	5.4	4.2
d	Furfuryl	77	78-80	Needles	$C_{19}H_{17}NO_2$	78.1	5.9	4.8	78.3	5.9	4.8
e	p-$H_3COC_6H_4$	67	73-75	Prisms	$C_{22}H_{21}NO_2$	79.8	6.4	4.2	79.7	6.4	4.2

[a] All crystallised from 95% EtOH, except 15e crystallised from EtOAc - petroleum ether (40-60°). [b] Found: Cl, 10.5. Required: Cl, 10.6%.

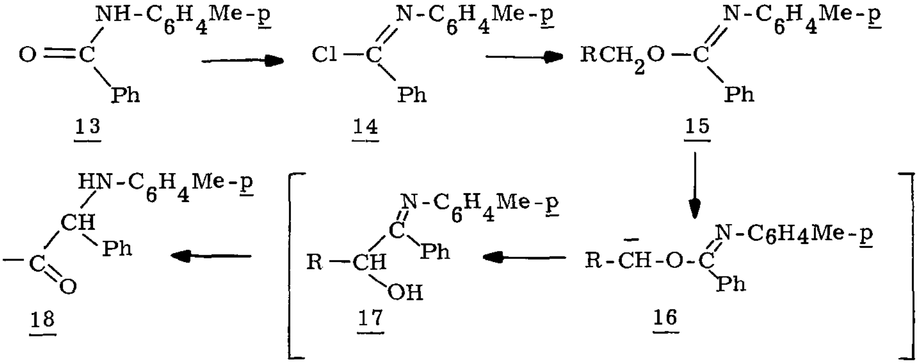


Table 2. Preparation of α-aminoketones 18

18	R	Yield %	Mp°C	Crystal form	Molecular formula	Found C	Found H	Found N	Required C	Required H	Required N
a	C_6H_5	46	143-145	Needles[a, b]	$C_{21}H_{19}NO$	83.3	6.4	4.6	83.7	6.4	4.6
b	2-Pyridyl	42	125-127	Plates[c]	$C_{20}H_{18}N_2O$	79.7	5.6	9.4	79.4	6.0	9.3
c	p-ClC_6H_4	43	145-147	Needles[a]	$C_{21}H_{18}ClNO$[d]	75.0	5.3	4.2	75.1	5.4	4.2

[a] From 95% EtOH. [b] Lit. m.p. 145-146° [C.L. Stevens and R.J. Gasser, *J. Am. Chem. Soc.* **79**, 6057 (1957)]. [c] From EtOAc - petroleum ether (40-60°). [d] Found: Cl, 10.6. Required: Cl, 10.6%.

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