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AROYLATION OF N-ALKYLMETHANIMINES. A SYNTHESIS OF NOVEL SUBSTITUTED 2-AZA-BUTA-1,3-DIENES.

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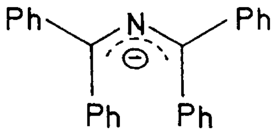
Summary: The aroylation of carbanions derived from N-benzyl-diphenylmethanimine and N-(diphenylmethyl)-arylmethanimines yields highly substituted 2-aza-buta-1,3-dienes in which the imino group is conjugated with an enol ester. A similar reaction with N-(diphenylmethyl)-diphenylmethylmethanimine gives the expected iminoketone.

The acylation of carbanions derived from imines has not been studied as extensively as other acylation reactions[1]. We wish to report the first case of formation of carbanions derived from imines in which the nitrogen atom is flanked by two negatively charged carbon atoms e.g. 1. The reaction is carried out by treating the imine 2 under nitrogen with NaH in HMPA[2]. The formation of the carbanion, presumed to be 1, is evidenced by the development of a deep red colour. The anion 1 is trapped as the acylated product 3 using benzoyl chloride as the trapping agent.



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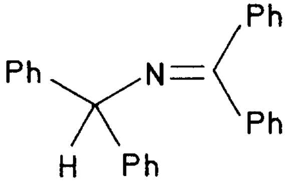

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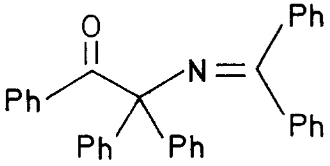

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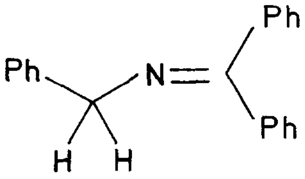
Extension of the above reaction to other imines (4,5) failed to yield monoacylated products and instead gave the dienes 6 which are derived by a second acylation of the putative monoacylated compound 7. The generality of the reaction can be seen from the tabled results. The yields are fair to good, although conditions have not been optimized.

The type of product formed in the diacylation is clearly independent of the starting imine since the same product (6a) is obtained from both (4) and (5a).



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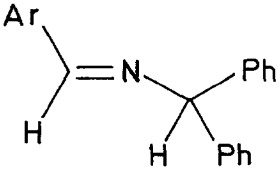
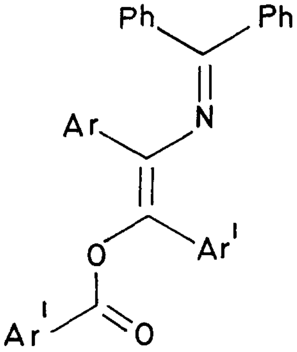


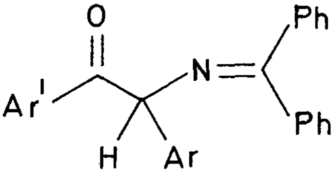
5

5a: Ar = C_6H_5
5b: Ar = 4-CH_3-C_6H_4
5c: Ar = 4-CH_3O-C_6H_4
5d: Ar = 4-NO_2-C_6H_4
5e: Ar = 4-Cl-C_6H_4



6

6a: Ar = Ar'= C_6H_5
6b: Ar = 4-CH_3-C_6H_4 ; Ar'= C_6H_5
6c: Ar = 4-CH_3O-C_6H_4 ; Ar'= C_6H_5
6d: Ar = 4-CH_3O-C_6H_4 ; Ar'= 4-CH_3O-C_6H_4
6e: Ar = 4-NO_2-C_6H_4 ; Ar'= C_6H_5
6f: Ar = 4-NO_2-C_6H_4 ; Ar'= 4-CH_3O-C_6H_4
6g: Ar = 4-NO_2-C_6H_4 ; Ar'= 4-NO_2-C_6H_4
6h: Ar = 4-Cl-C_6H_4 ; Ar'= C_6H_5



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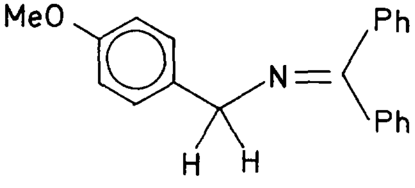

8

The structure of the diene (6) is based mainly on analytical (microanalysis and mass spectrometry) and spectroscopic evidence e.g. the presence of an enol ester CO group around 1730 cm^{-1} in the IR spectrum[3] (tabled results). Further proof of the structural arrangement shown in 6 was obtained by the facile hydrolisis using H_2SO_4/H_2O/THF of the imine group in 6a to yield benzoin benzoate[4]. All the attempts made in order to detect the presence of more than one stereoisomer in the diacylated products 6 have failed except in the case 6g in which two stereoisomers were separated by silica gel column chromatography. Their configurations have not yet been established.

It is worthwile to note that although 1 reacts with benzoyl chloride at a tertiary position yielding 3 the anion from 5 only undergoes acylation at the secondary carbon even in cases where electron density distribution would favour acylation at the more hindered one. We believe that the regioselectivity observed in 6 is due mainly to steric factors, that is a preference for acylation at the secondary site.

Table   Yields (%) and physical constants from aroylation of imines

Imine	Benzoyl Chloride	Product	Yield^a(%)	IR(KBr) (cm^{-1})
2	C_6H_5COCl	3	64	1685 (C=O)
4	C_6H_5COCl	6a	60	1725 (C=O)
5a	C_6H_5COCl	6a	60	1725 (C=O)
5b	C_6H_5COCl	6b	56	1730 (C=O)
5c	C_6H_5COCl	6c	55	1725 (C=O)
	$4\text{-}CH_3O\text{-}C_6H_4COCl$	6d	52	1725 (C=O)
	$4\text{-}NO_2\text{-}C_6H_4COCl$	8	82	1615 (C=N)
5d	C_6H_5COCl	6e	56	1735 (C=O)
	$4\text{-}CH_3O\text{-}C_6H_4COCl$	6f	52	1730 (C=O)
	$4\text{-}NO_2\text{-}C_6H_4COCl$	6g	87^b	1750(1745)^c(C=O)
5e	C_6H_5COCl	6h	72	1730 (C=O)

a) Isolated yields after column chromatography are shown.
b) Overall yield of a mixture of two stereoisomers in 4.4:1 ratio.
c) In brackets IR absortion of the minoritary stereoisomer.

The lack of reaction between 5c and p-nitrobenzoyl chloride remains an enigma at this point. There is little doubt however, that the anion is formed in this case since the HMPA solution of the imine becomes deep red on treatement with NaH. The colour disappears on the addition of the acid chloride but no product other than the isomerised imine 8 is obtained. It is not known at this stage whether a product is formed but is rapidly hydrolized during work up. Further experiments are in hand to resolve this situation.

The diacylated products (6) are of considerable interest since, as far as we are aware, this is the first time such molecules with an enol ester in conjugation with an imine, have been synthesized. Furthermore, the acylation of 4 and 5 is a new and direct route to the poorly known fully open-chain 2-aza-1,3-dienes which have previously been prepared by thermal ring opening of 1-azetines[5].

Studies on the thermal and photochemical reactivity of the dienes (6) and the imino-ketone (3) are under way.

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