Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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To cite this article: R. Nijs, H. D. Verkruijsse, S. Harder, A. C.H. T. M. van der Kerk & L. Brandsma (1991) A Peculiar Reaction of Aminoallenes with Aromatic and Heteroaromatic Aldehydes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 21:5, 653-656, DOI: 10.1080/00397919108020832

To link to this article: http://dx.doi.org/10.1080/00397919108020832

SYNTHETIC COMMUNICATIONS, 21(5), 653-656 (1991)

A PECULIAR REACTION OF AMINOALLENES WITH AROMATIC AND HETEROAROMATIC ALDEHYDES

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Abstract:

Addition of the allenic amine $H_2C=C=CHNMe_2$ and the corresponding *N*-morpholinoallene to a solution of an aromatic or heteroaromatic aldehyde, RCH=O, and lithium bromide in tetrahydrofuran followed by treatment of the reaction mixture with a small amount of acetic acid at elevated temperatures affords the aldehydes $RCH=C(CH_2NR'_2)CH=O$ (NR'_2 = NMe_2 or morpholino) in reasonable yields.

Whereas the chemistry of enamines ($C=C-NR_2$) has been studied extensively[1], relatively few data on the reactivity of aminoallenes ($C=C=CNR_2$) are known. A possible reason is that their preparation is experimentally not easy because of their extreme air and water sensitivity. Satisfactory and well-described preparative methods for some representatives of this class of compounds have been published about ten years ago[2,3]. We also reported on reactions of $H_2C=C=CHNMe_2$ with some electrondeficient acetylenic[4] and olefinic compounds[5]. The initial steps in these reactions show resemblance with typical enamine reactions.

In the present communication we report a peculiar reaction of aromatic and heteroaromatic aldehydes with dimethylaminoallene and morpholinoallene.In a

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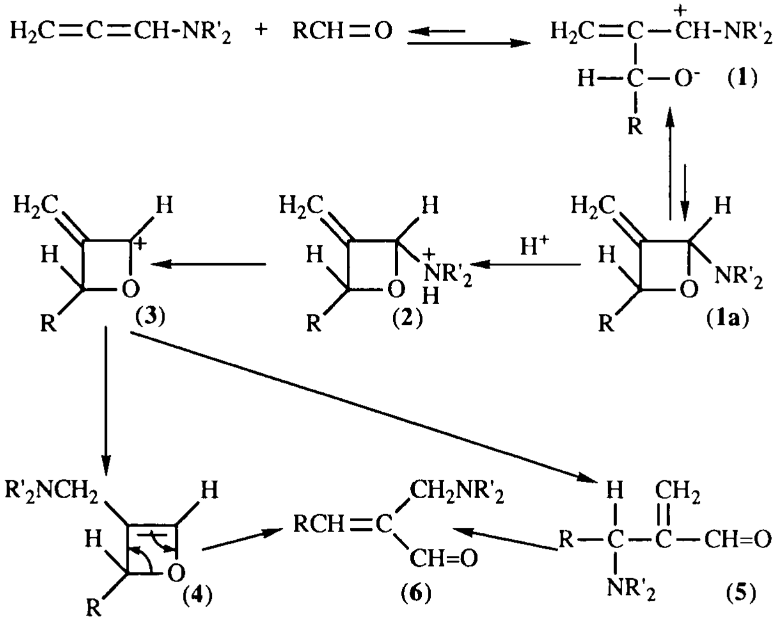
number of preliminary experiments the reaction of *N*,*N*-dimethylaminoallene, $H_2C{=}C{=}CHNMe_2$, with benzaldehyde was investigated. The reaction was carried out at temperatures ranging from -20 to +30°C, using tetrahydrofuran, diethyl ether or acetonitrile as solvent. In all cases a distinct heating effect was observed, but the (viscous) residue remaining after removal of the solvent under reduced pressure showed an NMR spectrum which could not be interpreted. However, heating of the solution, obtained by addition (at -15°C) of the aminoallene to a 50% excess of benzaldehyde in the presence of LiBr, at 60-70°C with a small amount of acetic acid gave a compound whose structure is most probably (**6**). Analogous



products were obtained in good yields in the reactions between dimethylaminoallene or *N*-morpholinoallene and benzaldehyde, 2-thiophenecarboxaldehyde and 2-furancarboxaldehyde. Cyclohexanecarboxaldehyde and dimethylaminoallene gave the expected product in ~20% yield only, while from the reactions with propanal and pivaldehyde completely different products were obtained. When inversed-order addition was applied in the reactions of aminoallenes with (hetero) aromatic aldehydes or when the reactions were carried out in the absence of LiBr, (**6**) was obtained in considerably lower yields. The

Table

Preparation of the aldehydes* $RCH=C(CH_2NR'_2)CH=O$ (**6**) from $RCH=O$ and $H_2C=C=CHNR'_2$

Compound (6) R	NR'$_2$	yield (%)	b.p. (°C/mm Hg)	n^{20}_D	^{1}H NMR chem. shifts** $\delta(H_2C\text{-}C=)$	$\delta(HC=)$	$\delta(HC=O)$
Ph	NMe$_2$	75	150/10	1.5790	3.3	7.6	9.7
2-Thienyl	NMe$_2$	70	~105/0.4	1.6272	3.4	7.6	9.7
2-Furyl	NMe$_2$	66	~100/0.2	1.5850	3.4	7.2	9.6
Ph	Morph	69	~120/0.5	1.5828	3.2	7.3	9.3
2-Thienyl	Morph	65	~120/0.5	1.6096	3.2	7.3	9.3
2-Furyl	Morph	71	~115/0.5	1.5912	3.4	7.1	9.3
Cyclohexyl	NMe$_2$	18	~110/0.5	1.5049	2.9	6.0-6.3(d)	9.1

Purities at least 98% (after dissolution in 2 M HCl and treatment with K_2CO_3, see exp. part).

* The determined (MS) accurate molecular weights corresponded with the calculated ones.

** δ-values in ppm, relative to Me_4Si (0 ppm). The signals tabulated appeared as singlets.

structure of (**6**) is based upon ^{1}H, ^{13}C NMR and mass-spectra (expected parent peaks). In all ^{1}H NMR (200 MHz) spectra the CH_2 and CH= protons appeared as singlets. A NOE experiment with (**6**), R = 2-thienyl suggested the structure in which the vinylic protons and the formyl group are on the same side of the double bond. The coupling constant of 9.5 Hz for the formyl carbon and the vinylic proton led to the same conclusion[6]. The formation of the products may be explained by assuming that in the first reaction a Zwitter-ionic intermediate (**1**) is formed being in equilibrium with a small concentration of the ring-closed isomer (**1a**). Protonation at nitrogen by acetic acid may lead *via* (**2**) to carbenium ion (**3**) which either through the oxete derivative (**4**) or through the aldehyde (**5**) may give the product (**6**). The NMR spectra also did not give any indication for the presence of the isomer (**5**).

Procedure:

All reactions were carried out under nitrogen. THF was distilled from $LiAlH_4$ under nitrogen. The allenes were prepared as described[2,3]. Benzaldehyde was purified by shaking with dilute aqueous potassium carbonate, drying over $MgSO_4$ and distilling *in vacuo*. The heteroaromatic aldehydes were purified by vacuum distillation.

A mixture of 0.20 mol of the aminoallene and 40 ml of THF was added over 30 min to a mixture of 0.30 mol (50 mol % excess) of the aldehyde, 2.5 g of anhydrous lithium bromide and 50 ml of THF. During this addition the temperature was maintained between –15 and –20°C. After an additional 15 min (at –15°C) the cooling bath was removed and the temperature allowed to rise to +10°C. Glacial acetic acid (1.5 ml) was added, after which the turbid solution was heated under gentle reflux for 30 min. The reaction mixture was then poured into 200 ml of ice water and, after vigorous shaking, the layers were separated. The organic layer and two ethereal extracts were dried over $MgSO_4$ and subsequently concentrated *in vacuo*. Careful fractional distillation (at oil-pump pressure, <1 mm Hg) through a 20-cm Vigreux column, gave (after the first fraction of the starting aldehyde) (**6**) as a viscous, yellow liquid. Further purification was achieved by dissolving the products in cold (0°C) 2 M aqueous HCl, extracting the solution with pentane (to remove impurities) and subsequently adding at (0°C) a concentrated aqueous solution of K_2CO_3, until pH 9 was reached: the pure aldehyde was isolated *via* extraction,For further details see the table.

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(Received in The Netherlands 7 January, 1991)