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Nitroketene acetal chemistry: efficient synthesis of 2-amino-3-nitro-4*H*-chromenes

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ABSTRACT

Base-catalyzed reaction of the nitroketene *N*,*S*-acetals and the ring substituted 2-hydroxybenzaldehydes afforded a combinatorial library of the 2-alkylamino-3-nitro-4-alkylsulfanyl 4*H*-chromenes in excellent yields. Nucleophilic displacement of the C4 alkylsulfanyl group with different thiols afforded 4*H*-chromenes with structural diversity.

The nitroketene *N*,*S*-acetal, *N*-methyl-*N*-[(*E*)-1-(methylsulfanyl)-2-nitro-1-ethenyl]amine (1 *N*-methyl-1*S*-methyl-2-nitroethylene, NMSM) **1a** (Scheme 1) is a versatile molecule.[1] It is embodied with three functional groups on ethylene motif, viz., alkyl amine, methylsulfanyl and nitro, each one of which is amenable for synthetic exploitation and functional group manipulation. With an excellent electron-withdrawing nitro group in place, the nitroethylene substructure in NMSM **1a** is a good Michael acceptor. The methylsulfanyl group is an electron donor and is also a good leaving group. It can be replaced with a variety of nucleophiles following the substitution nucleophilic vinyl (S_NV) mechanism. The ethylene moiety is a polarized push–pull alkene with electron flow emanating from methyl amino/methylsulfanyl to nitro group. Due to polarization, the C1 exhibits electrophilic characteristics and the C2 exhibits nucleophilic characteristics. Molecules of the type NMSM **1a** are synthetic equivalents of nitroacetic acid where the ester is masked as ketene-*N*,*S*-acetal. Also, NMSM **1a** is a synthetic equivalent of the amino acid glycine, which can be realized by reduction of nitro group and unmasking of the acid moiety. Above qualities make NMSM **1a** a multi-faceted building block ready to be exploited to build organic molecules of diverse structures. It is prepared in industrial scale for the manufacture of *anti*-ulcer (histamine H2 receptor antagonists) bulk drugs ranitidine[2] and nizatidine.[3] Surprisingly, however, it has seldom been exploited as a starting material for other heterocycles. We reasoned out that since **1a** has an electrophilic and a nucleophilic carbon at adjacent (C1 and C2) positions it can be condensed with bifunctional molecules having a nucleophilic and an electrophilic centre in 1- and 4-position to generate six-membered rings. Presently, we describe realization of this concept, for a convenient combinatorial synthesis of 2-alkylamino-3-nitro-4*H*-chromenes. Condensation of nitroethylenes with 2-hydroxybenzaldehyde to form 3-nitrocoumarins is known, however, ours is the first report on the formation of 4*H*-chromenes from such molecules.[4] Although chromenes have restricted occurrence among natural product scaffolds they have wide spread industrial and pharmaceutical applications.[5,6] Specifically, 2-amino-4*H*-chromenes are molecules of current interest as they induce apoptosis and thus evaluated as anticancer agents.[7]

In the beginning of the present study, we conducted a reaction of 2-hydroxybenzaldehyde (salicylaldehyde) **2a**—a molecule with nucleophilic phenolic hydroxyl and electrophilic aldehyde located in 1- and 4-position—with NMSM **1a** in THF in presence of piperidine (1.0 equiv; Table 1, entry 1). The reaction provided 4*H*-chromene **3a** in 85% yield. When we employed a catalytic amount (0.1 equiv) of piperidine, the reaction was more clean but it took longer time (72 h; entry 2). The structure of **3a** was assigned on the basis of spectroscopic data and confirmed unambiguously by single crystal X-ray diffraction.[8]

Having discovered a facile synthesis of 4*H*-chromene **3a**, we next focused on improving the reaction conditions to optimize yields by taking the condensation of 2-hydroxybenzaldehyde **2a** and NMSM **1a** as a test case (Table 1). When we tried the condensation with secondary amines like pyrrolidine (Table 1, entry 3) and morpholine (entry 4) in THF or tertiary amine like DBU (entry 5), Et_3N (entry 6) and DABCO (entry 7) in THF the yields were lower

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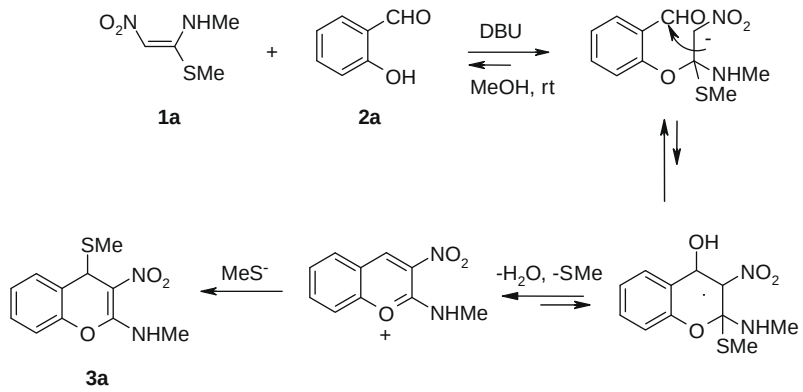


Scheme 1. Mechanism for the formation of 2-alkylamino-3-nitro-4-methylthio-4*H*-chromene **3a**.

and the reaction needed longer time. The reaction with pyridine in THF at rt did not proceed and at reflux provided very low yield of the product (entry 8). With inorganic bases like NaH (1.0 equiv) in THF (entry 9) or NaH (1.0 equiv) in DMF (entry 10), K_2CO_3 in acetone (entry 11) or two-phase reactions with aqueous K_2CO_3, TBAB in DCM (entry 12) or dil. NaOH (aq, 1.1 equiv) and TBAB (0.05 equiv) in DCM (entry 13) the yields were moderate. The reaction was slow or did not take place with basic alumina under neat conditions (entry 14) or KF on neutral alumina under microwave irradiation (entry 15). Since the product has a stereogenic centre (C4), we attempted the condensation with proline (entry 16), proline methyl ester (entry 17) and proline benzyl ester (entry 18) in MeOH. Though product formation took place in all these cases in moderate to good yield and there was no chiral induction into the product. We were happy to find that the CSA reaction worked well with DBU in MeOH (0.1 equiv, entry 19) to provide desired product in 93% yield and reaction was also clean. The condensation was also facile with K_2CO_3 (0.1 equiv) in water to provide the 4*H*-chromene **3a** in 85% yield (entry 20). In summary, the condensation works well with 0.1 equiv of piperidine in THF (entry 2) or DBU in MeOH (entry 19) or K_2CO_3 in water (entry 20) in each case at room temperature. During the reaction the product precipitated. Simple filtration was enough to recover most the product. We employed 10 mol % of DBU in MeOH for generalization of the 4*H*-chromene **3** synthesis.

Table 1
Optimization of reaction conditions

Entry	Base (M equiv)	Solvent	Time (h)	Yield (%)
1	Piperidine (1.0)	THF	8	85
2	Piperidine (0.1)	THF	72	90[a]
3	Pyrrolidine (0.1)	THF	48	54
4	Morpholine (1.0)	THF	192	43
5	DBU (0.1)	THF	15	20[b]
6	Et_3N (1.0)	THF	144	38
7	DABCO (1.0)	THF	96	70
8	Pyridine (1.0)	THF	72	3[c]
9	NaH (1.0)	THF	9	75[c]
10	NaH (1.0)	DMF	5	71
11	K_2CO_3 (1.0)	Acetone	7	45
12	K_2CO_3 (aq, 1.1), TBAB (0.05)	DCM	15	45
13	NaOH (aq, 1.1), TBAB (0.05)	DCM	7	24
14	Basic alumina	Neat[d]	0.1	19
15	KF/neutral alumina	Neat[d]	0.1	—[e]
16	L-Proline	MeOH	48	81[f]
17	L-Proline methyl ester	MeOH	78	68
18	L-Proline benzyl ester	MeOH	72	38
19	DBU (0.1)	MeOH	17	93
20	K_2CO_3 (0.1)	H_2O	15	85[g]

[a] Method B.
[b] Method A.
[c] Reactions were conducted at reflux temperature of the solvent used.
[d] The reaction was conducted under microwave irradiation (2.45 GHz; 400 W, 2 min).
[e] No reaction; extensive decomposition of **1a** took place.
[f] Yield with respect to recovered NMSM.
[g] Method C (see Supplementary data).

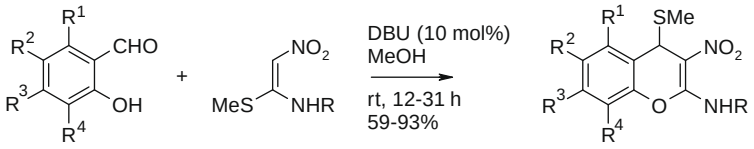
Condensation of various ring-substituted 2-hydroxybenzaldehydes **2b–k** with NMSM **1a** afforded 4*H*-chromenes **3b–k** in 75–93% yield (Table 2). Spectroscopic data of the products matched well with those of the parent 4*H*-chromene **3a**. In addition, the structure of **3d** was confirmed unambiguously by the analysis of single crystal X-ray data.[9] Interestingly, condensation of NMSM **1a** with 2-hydroxy-4-methoxybenzaldehyde **2l** and 2-hydroxy-4-benzoyloxyaldehyde **2m** did not take place. However, the condensation took place with 4-benzyloxy 2-hydroxybenzaldehydes **2j** to afford 4*H*-chromene **3j**. This result indicates that the condensation is subject to subtle changes in the electron density on the carbonyl carbon of the 2-hydroxybenzaldehydes.

We next focused on changing substitution on the amino group in the nitroketene *N,S*-acetal moiety in **1** from methyl to alkyl/aryl groups. The condensation reaction of **1b–g** worked well to provide 4*H*-chromenes **3n–s** in 59–83% yield (Table 2, entries 14–19). By achieving the synthesis of 4*H*-chromenes **3q** and **3r** we have incorporated physiologically relevant arylethylamine unit into 4*H*-chromene (Table 2, entries 17 and 18). Spectroscopic data of 4*H*-chromenes **3n–s** matched well with those of the parent compound **3a**. Additionally, the structure of **3p** was confirmed by single crystal X-ray analysis.[10]

The condensation of 2-hydroxybenzaldehyde **2a** with NMSM **1a** to form 4*H*-chromene **3a** is a highly atom-economic reaction. Possible mechanism for the formation of 4*H*-chromene **3a** is given in Scheme 1. The conversion follows four major steps namely (i) Michael addition, where the anion generated from 2-hydroxybenzaldehyde **2a** adds to NMSM **1a** in conjugate manner; (ii) nitro-aldol condensation to provide the pyran ring; (iii) dehydration and dethiomethylation to generate intermediate benzpyrilium cation and (iv) addition of methylthiolate anion present in the medium to C4 of the benzpyrilium cation forming 3-nitro-4*H*-chromene **3a**. Addition of methylthiolate anion to the benzpyrilium cation was proved to be inter-molecular by conducting an experiment in which in addition to NMSM **1a** and 2-hydroxybenzaldehyde **2a** we employed an equimolar amount of *n*-butanethiol. From this experiment we obtained C4-S^{n}Bu substituted-4*H*-chromene **6d** along with SMe substituted 4*H*-chromene **3a** in almost equal amount.

When we conducted the condensation of 2-hydroxybenzaldehyde **2a** with NMSM **1a** in NaH in THF reflux, along with the major product **3a** (75%), we isolated a minor amount of the adduct **4a** (4%,

Table 2
A combinatorial library of 3-nitro-4*H*-chromenes **3a–s** prepared from substituted 2-hydroxybenzaldehyde **2a–m** and nitroketene *N*,*S*-acetals **1a–g**



2a-m **1a-g** **3a-s**

Entry	2-Hydroxy benzaldehydes **2a–m**	Nitroketene *N*,*S*-acetals **1a–g**	3-Nitro-4*H*-chromenes **3a–s**	Time (h)	Yield (%)
1	**2a**: $R^1 = R^2 = R^3 = R^4 = H$	**1a**: R = Me	**3a**: R = Me, $R^1 = R^2 = R^3 = R^4 = H$	17	93
2	**2b**:R^1 = OMe, $R^2 = R^3 = R^4 = H$	**1b**: R = n-Bu	**3b**: R = Me, R^1 = OMe, $R^2 = R^3 = R^4 = H$	12	89
3	**2c**: $R^1 = R^3 = R^4 = H$, R^2 = OMe	**1c**: R = Ph	**3c**: R = Me, $R^1 = R^3 = R^4 = H$, R^2 = OMe	17	85
4	**2d**: $R^1 = R^3 = R^4 = H$, R^2 = Me	**1d**: R = Bn	**3d**: R = Me, $R^1 = R^3 = R^4 = H$, R^2 = Me;	12	89
5	**2e**: $R^1 = R^3 = R^4 = H$, R^2 = Et	**1e**: R = $(CH_2)_2$Ph	**3e**: R = Me, $R^1 = R^3 = R^4 = H$, R^2 = Et;	17	87
6	**2f**: $R^1 = R^3 = R^4 = H$, R^2 = t-Bu	**1f**: R = $(CH_2)_2C_6H_4OMe$	**3f**: R = Me, $R^1 = R^3 = R^4 = H$, R^2 = t-Bu	17	79
7	**2g**: $R^1 = R^3 = R^4 = H$, R^2 = Br	**1a**: R = Me	**3g**: R = Me, $R^1 = R^3 = R^4 = H$, R^2 = Br	18	76
8	**2h**: $R^1 = R^3 = R^4 = H$, R^2 = Cl	**1a**: R = Me	**3h**: R = Me, $R^1 = R^3 = R^4 = H$, R^2 = Cl;	18	75
9	**2i**: R^1 = Me, R^2 = Cl, $R^3 = R^4 = H$	**1a**: R = Me	**3i**: R = Me, R^1 = Me, R^2 = Cl, $R^3 = R^4 = H$	17	78
10	**2j**: $R^1 = R^2 = R^4 = H$, R^3 = OCH_2Ph	**1a**: R = Me	**3j**: R = Me, $R^1 = R^2 = R^4 = H$, R^3 = OBn	19	82
11	**2k**: $R^1 = R^2 = R^3 = H$, R^4 = OMe	**1a**: R = Me	**3k**: R = Me, $R^1 = R^2 = R^3 = H$, R^4 = OMe	15	85
12	**2l**: $R^1 = R^2 = R^4 = H$, R^3 = OMe	**1a**: R = Me	**3l**: R = Me, $R^1 = R^2 = R^4 = H$, R^3 = OMe	—	—[a]
13	**2m**: $R^1 = R^2 = R^4 = H$, R^3 = OCOPh	**1a**: R = Me	**3m**: R = Me, $R^1 = R^2 = R^4 = H$, R^3 = OCOPh	—	—[a]
14	**2a**: $R^1 = R^2 = R^3 = R^4 = H$	**1b**: R = n-Bu	**3n**: R = n-Bu, $R^1 = R^2 = R^3 = R^4 = H$	18	83
15	**2a**: $R^1 = R^2 = R^3 = R^4 = H$	**1c**: R = Ph	**3o**: R = Ph, $R^1 = R^2 = R^3 = R^4 = H$	31	71
16	**2a**: $R^1 = R^2 = R^3 = R^4 = H$	**1d**: R = Bn	**3p**: R = Bn, $R^1 = R^2 = R^3 = R^4 = H$	21	81
17	**2a**: $R^1 = R^2 = R^3 = R^4 = H$	**1e**: R = $(CH_2)_2$Ph	**3q**: R = $(CH_2)_2$Ph, $R^1 = R^2 = R^3 = R^4 = H$	26	68
18	**2a**: $R^1 = R^2 = R^3 = R^4 = H$	**1f**: R = $(CH_2)_2C_6H_4OMe$	**3r**: R = $(CH_2)_2C_6H_4OMe$, $R^1 = R^2 = R^3 = R^4 = H$	23	73
19	**2a**: $R^1 = R^2 = R^3 = R^4 = H$	**1g**: R = CH(CH_3)Ph	**3s**: R = CH(CH_3)Ph, $R^1 = R^2 = R^3 = R^4 = H$	27	59

[a] No reaction.

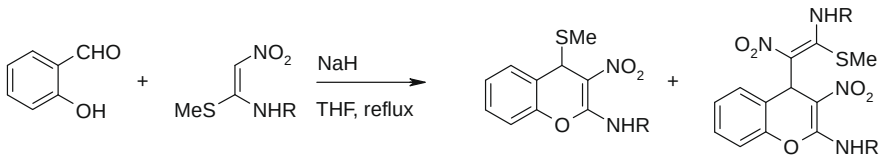
entry 1, Table 3). The ^{1}H NMR spectrum of the minor product indicated it to be formed by the reaction of two molecules of NMSM **1a** and one molecule of 2-hydroxybenzaldehyde **2a**. The product however could not be relieved of contaminants. On the other hand, in the reaction of *N*,*S*-acetal possessing *N*-benzyl group **1d**, the minor product **4d** was formed in 24% yield (entry 4). Formation of the minor 2:1 adduct was proved to be general when the condensation of nitroketene *N*,*S*-acetal **1** with 2-hydroxybenzaldehyde **2a** was conducted with NaH in THF reflux. Thus, four more NMSM derivatives **1b**, **1c**, **1e** and **1f** were reacted with **2a** to realize the 2:1 adducts **4b**, **4c**, **4e** and **4f**, respectively, in 9–24% yield, formed in each case as minor products (Table 3).

Mechanism for the formation of 2:1 adduct **4** also appears to go through benzpyrilium cation (see Scheme 1). This intermediate is quenched by one more unit of *N*,*S*-acetal **1**. This premise was confirmed by treating parent 4*H*-chromene **3a** with NMSM **1a** in presence of NaH in THF and the reaction yielded the 2:1 adduct **4a**.

In the mechanism for the formation of 4*H*-chromene **3a** (Scheme 1) the benzpyrilium cation is the key intermediate. We reasoned out that it should be possible to quench this intermediate with different nucleophiles. As a preliminary work, 3-nitro-4*H*-chromene **3a** was treated with 3-equiv of high boiling aromatic thiols like thiophenol **5a**, 4-methyl thiophenol **5b**, 4-chloro thiophenol **5c** and aliphatic thiols like butane **5d** and octane thiols **5e** in ethanol reflux. These reactions provided C4-substituted 4*H*-chromenes **6a–e** in excellent yields (Table 4).

In conclusion, we have demonstrated a facile and high yielding base-catalyzed condensation of substituted 2-hydroxybenzaldehydes and nitroketene *N*,*S*-acetals to afford 2-alkyamino-3-nitro-4-alkylsulfanyl-4*H*-chromenes in excellent yields. When the conden-

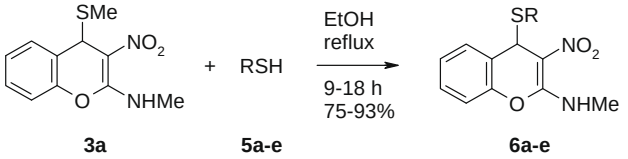
Table 3
Synthesis of 3-nitro-4*H*-chromenes (2:1 adduct) **4a–f** from different substituted nitroketene *N*,*S*-acetals **1a–f**



2a **1a-f** **3a, 3n-r** (1:1 adduct) **4a-f** (2:1 adduct)

Entry	Nitroketene *N*,*S*-acetal	R	Ratio of 1:1 (**3**) and 2:1 (**4**) adducts	Time (h)	Total yield (%)
1	**1a**	Me	**3a**:**4a** (75:4)	7	79
2	**1b**	*n*-Bu	**3n**:**4b** (41:17)	12	58
3	**1c**	Ph	**3o**:**4c** (49:9)	4	58
4	**1d**	Bn	**3p**:**4d** (45:24)	13	69
5	**1e**	$(CH_2)_2$Ph	**3q**:**4e** (38:21)	16	59
6	**1f**	$(CH_2)_2C_6H_4OMe$	**3r**:**4f** (41:17)	13	58

Table 4
Synthesis of 3-nitro-4*H*-chromenes **6a–e** from high boiling thiols **5a–e**



3a **5a-e** **6a-e**

Entry	Thiol (RSH)	Product	Time (h)	Yield (%)
1	**5a**: R = C_6H_5	**6a**: R = C_6H_5	12	90
2	**5b**: R = 4-$CH_3C_6H_5$	**6b**: R = 4-$CH_3C_6H_5$	12	80
3	**5c**: R = 4-ClC_6H_5	**6c**: R = 4-ClC_6H_5	12	75
4	**5d**: R = $CH_3(CH_2)_3$	**6d**: R = $CH_3(CH_2)_3$	18	91
5	**5e**: R = $CH_3(CH_2)_7$	**6e**: R = $CH_3(CH_2)_7$	19	93

sation was conducted in NaH in THF, 4*H*-chromenes, the 2:1 adducts were formed in minor amounts. The C4 methylsulfanyl group in **3a** could be replaced with long chain/aryl thiols.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.04.018.

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