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Original Articles

Synthesis of Nitroarylalkenes via Reaction of Nitrobenzyl Sulfones with Nitronate Anions [1]

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Dedicated to Prof. Dr. Dr. Heinz G. O. Becker on the Occasion of his 70th Birthday

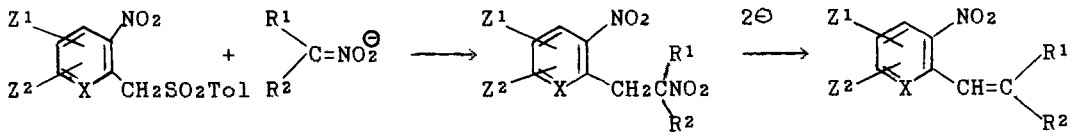
Abstract. o-Nitrobenzyl tolyl sulfones (**1a – e**) react with nitronate anions (**2a, b**) giving nitroaryl derivatives of nitroalkanes (**3**) which eliminate nitrous acid giving nitroarylalkenes (**4a – f**) as final products.

Substituted ortho- and para- nitrobenzyl aryl sulfones which are readily available via Vicarious Nucleophilic Substitution of hydrogen (VNS) in reactions of nitroarenes with carbanions of chloromethyl aryl sulfones [2, 3] are versatile starting materials in organic synthesis. We have already described the conversion of such sulfones into indoles [4], substituted styrenes [5] as well as other transformations [6]. In all these cases the active methylene groups of the benzylic sulfones were engaged in the reactions. It is also known that arylsulfonyl groups located in a nitrobenzylic position can be replaced with some nucleophiles via Single Electron Transfer (SET) initiated process $S_{RN}1$, although reported examples of such reactions are not numerous and limited to tertiary nitrocumyl sulfones [7].

It was therefore of interest to introduce the nitrobenzylsulfones produced via the VNS reaction into a similar process of nucleophilic substitution of the arylsulfonyl group. Because of the high acidity of the methylene group of the sulfones, nucleophilic agents should exhibit low basicity, otherwise deprotonation of the sulfones would inhibite the reaction.

Nitronate anions seemed to be a proper choice because they are active electron donors and enter readily $S_{RN}1$ reactions in spite of being rather weak bases [7]. Moderate basicity of the nitronate anions allow to select such conditions that there is no significant deprotonation of the benzylic sulfones.

We have found that indeed some o-nitrobenzyl tolyl sulfones reacted with sodium salts of secondary nitroalkanes in a boiling mixture 1-propanol-water according to the substitution pattern. The initial products of the substitution – β-nitroarylnitroethane derivatives (**3**) under the reaction conditions eliminated readily nitrous acid giving the corresponding styrene derivatives (**4**) in good yields.

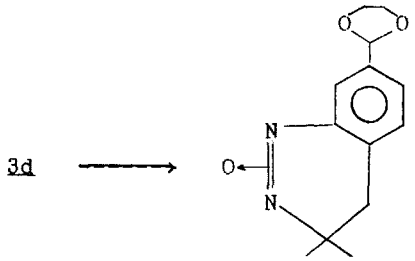


1a-e 2a,b 3 4a-f

$R^1=R^2=CH_3$, 2a

$R^1=R^2=(CH_2)_5$, 2b

X	CH	CH	CH	CH	N
Z^1	H	4-CH_3	H	H	H
Z^2	5-CH_3O	5-CH_3O	4-Bu-t	CH_2O, CH-, CH_2O	6-CH_3O
No	**1a**	**1b**	**1c**	**1d**	**1e**



3d 5d

Both of these reactions are slow, in order to have more or less complete conversion to the final products 48 – 200 hrs are necessary under the specified conditions. When methanol was used instead of 1-propanol, so temperature of the refluxing mixture was substantially lower, there was negligible conversion even after 48 hrs. On the other hand in aprotic solvents e.g. DMF, the mixture become highly coloured, perhaps because of formation of the nitrobenzylic anions, and decomposition was a dominating process. The acidity of the methylenic group seems to limit the scope of the reaction to such **1** in which Z is not an electronwithdrawing substituent. It proceeds satisfactorily with o-nitrobenzyl sulfones, p-isomers gave much worse results.

The substitution and elimination proceed apparently with a similar rate: when the reaction was arrested on an early stage the substituion product was also isolated, although the alkene accounted for the major part of the converted **1**.

In one case the initial substitution product, the dinitro compound **3d** underwent a reductive transformation into **5** instead of the elimination, the expected alkene was formed in minute amounts.

It is reasonable to suppose that the substitution occurs via $S_{RN}1$ mechanism analogous to that reported by Kornblum [7], although attempts to accelerate the reaction by illumination with ultraviolet lamp had no effect on the rate of conversion, relative rates of substitution and elimination.

Experimental

Melting points are uncorrected. The infrared spectra were taken on Acculab 1 (Beckman). The ^{1}H-n.m.r. spectra were measured on Varian EM-360 (60 MHz) or Varian Gemini (200 MHz) using CCl_4 or $CDCl_3$ as solvents and TMS as the internal standard. Chemical shifts are expressed as δ ppm.

Table 1 Nitroarylalkenes (**4a – f**)

Entry	Sub-strates	Products (**3, 4, 5**) Ar	R^1	R^2	No	Yield [%][a]
1	**1a + 2a**	2-O_2N-5-$CH_3OC_6H_3$	CH_3	CH_3	**4a**	75
2	**1a + 2a**[b]	2-O_2N-5-$CH_3OC_6H_3$	CH_3	CH_3	**4a**	32[c]
		2-O_2N-5-$CH_3OC_6H_3$	CH_3	CH_3	**3a**	9
3	**1b + 2a**	2-O_2N-4-CH_3-5-$CH_3OC_6H_2$	CH_3	CH_3	**4b**	50
4	**1c + 2a**	2-O_2N-4-Bu-tC_6H_3	CH_3	CH_3	**4c**	72
5	**1d + 2a**	2-O_2N-4-X-C_6H_3[d]	CH_3	CH_3	**4d**	17
		2-O_2N-4-X-C_6H_3[d]	CH_3	CH_3	**3d**	12
		–	–	–	**5**	40
6	**1e + 2a**	2[3-O_2N-6-$CH_3OC_5H_2N$]	CH_3	CH_3	**4e**	46
7	**1a + 2b**	2-O_2N-5-$CH_3OC_6H_3$	$-(CH_2)_5-$		**4f**	50

[a] isolated yields
[b] reaction quenched before completion
[c] 47 % of **1a** recoverd
[d] X = CH_2O, CH-, CH_2O

Coupling constants are given in hertz (Hz). The mass spectrum was obtained on AMD-604 (AMD Intectra GmbH Germany). Silica gel (230–400 mesh, Merck) was used for column chromatography with hexane-ethyl acetate mixtures as eluents.

4-Methyl-5-methoxy-2-nitrobenzyl 4-tolyl sulfone (**1b**), 4-t-Butyl-2-nitrobenzyl 4-tolyl sulfone (**1c**) and 4-[2-(1,3-Dioxolanyl)]-2-nitrobenzyl 4-tolyl sulfone (**1d**) were prepared according to [8]. 4-Methoxy-2-nitrobenzyl 4-tolyl sulfone (**1a**) and 2-(6-Methoxy-3-nitropyridyl)methyl 4-tolyl sulfone (**1e**) were prepared similiarly to procedure [2]:

1a: m.p.139–141.5°C; IR (nujol): 1525, 1325 (NO_2); ^{1}H-n.m.r. (200 MHz, $CDCl_3$): 2.43 (s, 3H; CH_3); 3.89 (s, 3H; OCH_3); 4.97 (s, 2H; CH_2); 6.94–6.97 (m, 2H; H-3 + H-5); 7.28 (dd, $J_{2'-3'}=8.5$, $J_{3'-5'}=0.7$, 2H; H-3'); 7.58 (d, $J_{2'-3'}=8.5$, 2H; H-2'); 8.01 (d, $J_{3-4}=9.5$, 1H; H-2).
$C_{15}H_{15}NO_5S$ Calcd.: C: 56.07 H: 4.71 N: 4.36 S: 9.98
(321.35) Found: C: 56.10 H: 4.60 N: 4.28 S: 9.77

1e: m.p.168.5–170°C; IR (nujol): 1520, 1340 (NO_2); ^{1}H-n.m.r. (200 MHz, $CDCl_3$): 2.44 (s, 3H; CH_3); 3.75 (s, 3H; OCH_3); 5.16 (s, 2H; CH_2); 6.79 (d, $J_{4-5}=9.1$, 1H; H-5); 7.29 (dd, $J_{2'-3'}=8.5$, $J_{3'-5'}=1.5$, 1H; H-3'); 7.61 (d, $J_{2'-3'}=8.5$, 1H; H-2'); 8.29 (d, $J_{4-5}=9.1$, 1H; H-4)
$C_{14}H_{14}N_2O_5S$ Calcd.: C: 52.16 H: 4.38 N: 8.96 S: 9.95
(322.34) Found: C: 52.04 H: 4.44 N: 9.06 S: 10.26

Reactions of nitrobenzyl sulfones with nitronate anions. (General procedure) Nitrobenzyl tolyl sulfone (1 mmol), nitroalkane (10 mmols), sodium hydroxide (0.4 g, 10 mmols), water (2 ml; in the case of **1e** – 5 ml) and 1-propanol (5 ml) were refluxed for 48–200 hrs (tlc control). When all the sulfone was consumed, the reaction mixture was poured into 150 ml of 5% HCl and extracted with CH_2Cl_2 (3×20 ml). After drying ($MgSO_4$) and evaporating the solvent, the residue was purified by column chromatography followed by recrystallization in cases of solid products.

1-(5-Methoxy-2-nitrophenyl)-2-methylpropene (**4a**)

oil; IR (neat): 1520, 1345 (NO_2); ^{1}H-n.m.r. (60 MHz, CCl_4): 1.70 (s, 3H; CH_3); 1.93 (s, 3H; CH_3); 3.83 (s, 3H; OCH_3); 6.40 (s, 1H; CH-vinyl); 6.58 (s, 1H; H-6); 6.56–6.73 (dd, $J_{4-6}=3.0$, 1H; H-4); 7.83 (d, $J_{3-4}=9.0$, 1H; H-3)
$C_{11}H_{13}NO_3$ Calcd.: C: 63.76 H: 6.32 N: 6.76
(207.21) Found: C: 63.73 H: 6.32 N: 6.64

1-(4-Methyl-5-methoxy-2-nitrophenyl)-2-methylpropene (**4b**)

m.p. 30–31°C (hexane); IR (KBr): 1520, 1330 (NO_2); ^{1}H-n.m.r. (60 MHz, CCl_4): 1.70 (s, 3H; CH_3); 1.90 (s, 3H; CH_3); 2.20 (s, 3H; CH_3-benzyl); 3.87 (s, 3H; OCH_3); 6.43 (s, 1H; CH-vinyl); 6.53 (s, 1H; H-6); 7.70 (s, 1H; H-3)
$C_{12}H_{15}NO_3$ Calcd.: C: 65.14 H: 6.83 N: 6.33
(221.24) Found: C: 65.01 H: 6.82 N: 6.47

1-(4-t-Butyl-2-nitrophenyl)-2-methylpropene (**4c**)

oli; IR (neat): 1540, 1360 (NO_2); ^{1}H-n.m.r. (60 MHz, CCl_4): 1.38 (s, 9H; t-Bu); 1.70 (s, 3H; CH_3); 1.90 (s, 3H; CH_3); 6.38 (s, 1H; CH-vinyl); 7.17 (d, $J_{5-6}=8.0$, 1H; H-6); 7.50 (d, $J_{5-5}=8.0$, 1H; H-5); 7.87 (s, 1H; H-3)
$C_{14}H_{19}NO_2$ Calcd.: C: 72.07 H: 8.21 N: 6.01
(233.30) Found: C: 71.45 H: 8.32 N: 5.90

1-/4-(1,3-Dioxolanyl)-2-nitrophenyl/-2-methylpropene (**4d**)

oil; IR (neat): 1540, 1360 (NO_2); ^{1}H-n.m.r. (60 MHz, CCl_4): 1.70 (s, 3H; CH_3); 1.90 (s, 3H; CH_3); 4.00 (s, 4H; OCH_2CH_2O); 5.70 (s, 1H; OCHO); 6.53 (s, 1H; CH-vinyl); 7.10 (d, $J_{5-6}=8.0$, 1H; H-5); 7.43 (d, $J_{5-6}=8.0$, 1H; H-6); 7.83 (s, 1H; H-3)
$C_{13}H_{15}NO_4$ Calcd.: C: 62.64 H: 6.07 N: 5.62
(249.26) Found: C: 62.59 H: 6.05 N: 5.96

1-/-2-(6-Methoxy-3-nitropyridyl)methyl/-2-methylpropene (**4e**)

m.p. 37–38°C (hexane); IR (KBr): 1585, 1340 (NO_2); ^{1}H-n.m.r. (60 MHz, CCl_4); 1.97 (s, 3H; CH_3); 2.10 (s, 3H; CH_3); 3.70 (s, 3H; OCH_3); 6.43 (d, $J_{4-5}=9.0$, 1H; H-5); 6.60 (s, 1H; CH-vinyl); 7.80 (d, $J_{4-5}=9.0$, 1H; H-4)
$C_{10}H_{12}N_2O_3$ Calcd.: C: 57.68 H: 5.81 N: 13.46
(208.22) Found: C: 57.77 H: 6.00 N: 13.47

(5-Methoxy-2-nitrophenyl)-cyclohexylidenemethane (**4f**)

oil; IR (neat): 1515, 1340 (NO_2); ^{1}H-n.m.r. (60 MHz, CCl_4): 1.46–2.57(m, 10H; CH_2-cyclohexyl); 3.80 (s, 3H; OCH_3); 6.33 (s, 1H; CH-vinyl); 6.55 (s, 1H; H-6); 6.52–6.67 (dd, $J_{4-6}=3.0$, 1H; H-4); 7.83 (d, $J_{3-4}=8.0$, 1H; H-3)
$C_{14}H_{17}NO_3$ Calcd.: C: 67.99 H: 6.93 N: 5.67
(247.29) Found: C: 67.77 H: 6.95 N: 5.98

2-(5-Methoxy-2-nitrobenzyl)-2-nitropropane (**3a**)

^{1}H-n.m.r. (200 MHz, $CDCl_3$); 1.58 (s, 3H; CH_3); 1.74 (s, 3H; CH_3); 3.81 (s, 2H; CH_2); 3.82 (s, 3H; OCH_3); 6.61 (d, $J_{4-6}=2.8$, 1H; H-6); 6.68 (dd, $J_{3-4}=9.1$, $J_{4-6}=2.8$, 1H; H-4); 8.05 (d, $J_{3-4}=9.1$, 1H; H-3);
MS (m/z-HR of H^+): Calcd. for $C_{11}H_{14}N_2O_5$: 254.09027
Found: 254.09014

1-[4-(1,3-Dioxolanyl)-2-nitrobenzyl]-2-nitropropane (**3d**)

oil; IR (neat): 1550, 1540, 1380, 1355 (NO_2); ^{1}H-n.m.r. (60 MHz, CCl_4); 1.53 (s, 6H; CH_3, CH_3); 3.60 (s, 2H; CH_2-benzyl); 3.93 (s, 4H; OCH_2CH_2O); 5.67 (s, 1H, OCH_2O); 6.97 (d, $J_{5-6}=8.0$, 1H; H-5); 7.43 (d, $J_{5-6}=8.0$, 1H; H-6); 7.77 (s, 1H; H-3)
$C_{13}H_{16}N_2O_6$ Calcd.: C: 54.53 H: 5.63 N: 9.79
(286.28) Found: C: 54.45 H: 5.81 N: 8.96

3,4-Dihydro-3,3-dimethyl-7(1,3-dioxolanyl)-1,2-diazanaphthalene (1 or 2)oxide (**5**)

m.p. 129–130°C (EtOH-hexane); IR (KBr): 1475 (N=N-O); ^{1}H-n.m.r. (60 MHz, $CDCl_3$): 1.50 (s, 6H; CH_3, CH_3); 3.03 (s, 2H; CH_2-benzyl); 4.07 (s, 4H; OCH_2CH_2O); 5.73 (s, 1H; OCHO); 7.10–7.26 (m, 2H; H-4 + H-5); 7.40 (s, 1H; H-2)
$C_{13}H_{16}N_2O_3$ Calcd.: C: 62.88 H: 6.50 N: 11.28
(248.28) Found: C: 62.67 H: 6.45 N: 10.84

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