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The Interaction of Salts of Nitro Compounds with Nitroso Compounds

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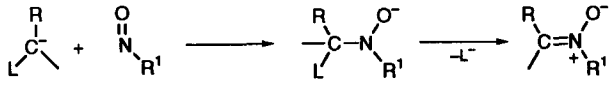
The salts of nitro compounds react readily with nitroso compounds under normal conditions to give the corresponding nitrones.

The general reaction type below for the preparation of nitrones is well known, where L is a leaving group which also stabilizes an α-negative charge, such as sulfonate,[1] nitrogen[2] or pyridinium.[3,4]



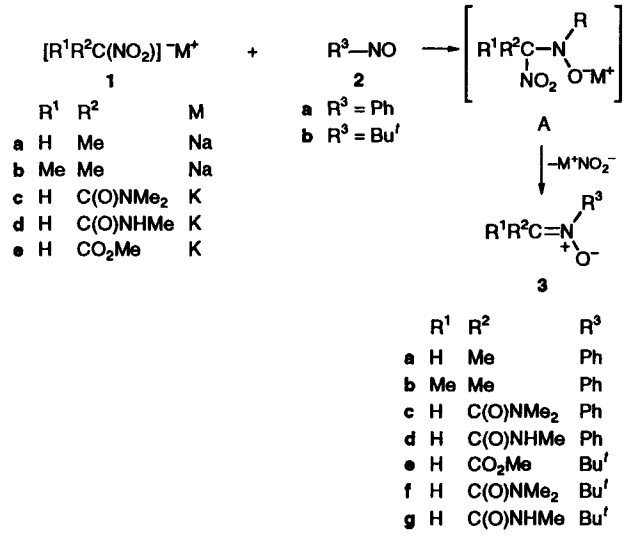
A nitro group also appears to be a good leaving group in this reaction. However, the interaction of derivatives of nitro compounds with nitroso compounds has not been studied previously.

We have found that nitro compound salts react readily with nitroso compounds, resulting in the corresponding nitrones (Scheme 1).

The rate of the reaction depends strongly on the substituents in both reagents (Table 1).

Use of the protonic solvent (here MeOH) is possible only for reactions proceeding quickly at a temperature lower than room temperature.

In the case of slower processes it is necessary to use dipolar



	R^1	R^2	M
a	H	Me	Na
b	Me	Me	Na
c	H	$C(O)NMe_2$	K
d	H	C(O)NHMe	K
e	H	CO_2Me	K

	R^1	R^2	R^3
a	H	Me	Ph
b	Me	Me	Ph
c	H	$C(O)NMe_2$	Ph
d	H	C(O)NHMe	Ph
e	H	CO_2Me	But
f	H	$C(O)NMe_2$	But
g	H	C(O)NHMe	But

Scheme 1

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Table 1 Synthesis of nitrones 3 from nitro compound salts 1[a] (Scheme 1).

Reagents	Solvent	Reaction conditions	Product 3 yield (%)	Physical constants
1a + **2a**[b]	MeOH	1.5 h (–10 °C)	**a** (90)	oil (ref. 5)
1b + **2a**[b]	MeOH	1 h (0 °C)	**b** (90)	oil (ref. 5)
1c[b] + **2a**	DMF	0.5 h (–7 °C)	**c** (94)	m.p. 91–92 °C
1d[b] + **2a**	MeCN	1 h (5 °C)	**d** (97)	m.p. 145–146 °C
1e[b] + **2b**	DMF	2 h (20 °C) 12 h (50° C)	**e** (90)	b.p. 84–87 °C/0.35 mm Hg (110–120 °C/0.55 mmHg[6]) n_D^{20} 1.4875
1c[b] + **2b**	DMF	8 h (20 °C) 4 h (45° C)	**f** (65)	m.p. 83–86 °C
1d[b] + **2b**	DMF	2 h (20 °C) 20 h (50° C)	**g** (40)	m.p. 59–62 °C

[a] **1** and **2** were taken in an equimolar ratio, the concentrations usually being 0.4–0.8 mol dm^{-3}. The original nitro- and nitroso compounds are described in the literature. The amides $R^2R^1NC(O)CH_2NO_2$ ($R^2=R^1=Me$ and $R^1=H$, $R^2=Me$) were obtained by refluxing 2-nitromethyl acetate with saturated aqueous solutions of the corresponding amines.[7] Salts **1** were obtained by reaction of nitro compounds with MeONa or KOH in MeOH. [b] In suspension.

aprotonic solvents, such as MeCN or DMF, in which the resulting nitrones are more stable.

The data obtained make it possible for us to suggest the addition of a nitro compound anion to a nitroso group exclusively as C-nucleophiles, giving intermediate **A**, with subsequent elimination of nitrous acid salt as the most appropriate route. The structure of the nitrones obtained was confirmed by NMR spectroscopy (Table 2). All previously described nitrones were characterized by their physical constants, which are in good agreement with the literature values. The structure of the newly synthesized nitrones was confirmed by elemental analysis data.

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References

1 A. W. Johnson, *Chem. Ind.*, 1963, 1119.
2 J. F. Baldwin, A. K. Qureshi and B. Sklarz, *J. Chem. Soc.*, 1969, 1073.
3 H. R. Nace and D. H. Nelander, *J. Org. Chem.*, 1964, **29**, 1677.
4 F. Krohnke, *Angew. Chem., Int. Ed. Engl.*, 1963, **2**, 380.
5 Y. Inouye, K. Takaya and H. Kakisawa, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3541.
6 K. N. Zelenin, I. P. Bezhan and A. Yu Yershov, *Khim. Geterotsikl. Soedin.*, 1988, 838 [*Chem. Heterocycl. Compd. (Engl. Transl.)*, 1988, 688].
7 B. Ciommer, G. Frenking and H. Schwarz, *Chem. Ber.*, 1981, **114**, 1503.

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Table 2 NMR data for the nitrones 3 [$(CD_3)_2SO$, 20 °C].

Compound	^{1}H NMR δ/ppm, *J*/Hz				^{13}C NMR δ/ppm				^{14}N NMR δ/ppm ($MeNO_2$)
3	CH=N	Me	R^3	NHC(O)	C=N	Me	R^3	C=O	($\Delta\nu_{0.5}$/Hz) ($=\overset{+}{N}-\bar{O}$)
a[a]	7.36 (1H,m)	2.22 (3H,d; $^3J_{H,H}$ 5,8)	7.41–7.43 (3H,m) 7.63–7.64 (2H,m)	—	136.3	13.5	121.5 (C_o) 129.1 (C_m) 130.0 (C_p) 147.3 (C–N)	—	−94±1 (300)
b[b]	—	1.97 (3H,s) 2.35 (3H,s)	7.30–7.48 (5H,m)	—	148.6	19.3 21.9	123.4 (C_o) 129.5 (C_m) 129.2 (C_p) 145.3 (C–N)	—	−106±2 (450)
c	8.20 (1H,s)	2.96 (3H,s) 3.04 (3H,s)	7.55–7.57 (3H,m) 7.87–7.90 (2H,m)	—	129.0	33.8 35.6	121.3 (C_o) 129.2 (C_m) 130.7 (C_p) 146.4 (C–N)	161.3	−91±1 (350)
d	7.95 (1H,s)	2.85 (3H,d; $^3J_{H,H}$ 4,5)	7.56–7.59 (3H,m) 7.87–7.89 (2H,m)	9.93 (s, widened)	129.9	25.3	121.6 (C_o) 129.2 (C_m) 131.3 (C_p) 146.8 (C–N)	160.8	−83±1 (300)
e	7.54 (1H,s)	3.69 (3H,s)	1.46 (9H,s)	—	121.0	51.2	27.5 (Me) 74.1 (C–N)	160.9	−48±2 (400)
f	7.44 (1H,s)	2.86 (6H,s)	1.42 (9H,s)	—	125.5	33.6 35.3	27.2 (Me) 70.1 (C–N)	162.2	−70±1 (300)
g	7.31 (1H,s)	2.77 (3H,d; $^3J_{H,H}$ 4,8)	1.46 (9H,s)	9.94 (s, widened)	126.7	25.1	27.2 (Me) 72.6 (C–N)	161.3	−61±1 (300) −275±2 (400)[c]

[a] In $CDCl_3$ at 0 °C. [b] In $CDCl_3$ at 20 °C. [c] ^{14}N δ/ppm ($MeNO_2$), ($\Delta\nu_{0.5}$/Hz) in MeNHC(O) group.