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O-ALKYL-N-ARYLHYDROXYLAMINES N-ALKOXY-2,4,6-TRI- AND -2,6-DINITROANILINES

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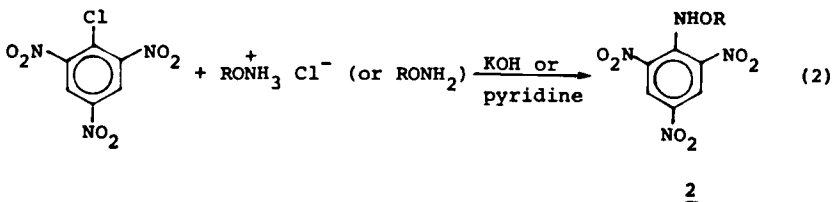
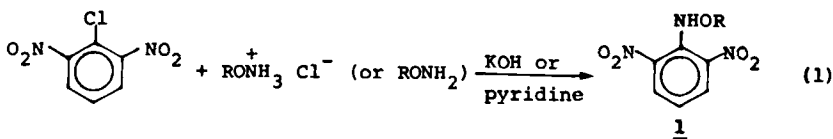
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A previous paper¹ had described the synthesis of N-alkoxy-picramides from alkoxyamine hydrochlorides and picryl chloride in the presence of sodium hydrogen carbonate in refluxing ethanol. The yields were at best 50% and the purification of the products required chromatography and repeated recrystallizations since under these conditions, substantial amounts of side-products were formed. We now describe a more selective and milder one-pot procedure leading to higher yields (60-90%) of products of sufficient purity, even without recrystallization (Eqs. 1 and 2).

a) R = Me b) R = Et c) R = CHMe₂ d) R = CPh₃

For the methoxy, ethoxy and isopropoxy derivatives 1a-c and 2a-c, the method involves reacting the alkoxyamine hydrochloride with 2,6-dinitrochlorobenzene or picryl chloride in aqueous-ethanolic dioxane at room temperature in the presence of potassium hydroxide. After completion

of the reaction, the nearly pure product precipitated on dilution with water. A similar method had been used for the reaction of 2,4-dinitrochlorobenzene with methoxyamine hydrochloride.² For the trityloxy derivatives 1d and 2d, the free base was used in dioxane at 60° in the presence of pyridine, then the products were isolated by evaporation of most of the solvent and by addition of diethyl ether to cause precipitation of the products. In all cases, the only notable difference is that 2,6-dinitrochlorobenzene reacts more sluggishly than picryl chloride with alkoxyamines. The yields of trityloxy derivatives are slightly lower than that of other alkoxy derivatives.

TABLE 1. Physical Data of Ar-NH-OR

Comp.	Ar (poly-nitro)	R	mp. (°C)	(lit. ¹ mp.)	Molecular formula	% N	
						Calcd.	Found
<u>1a</u>	2,6	Me	114	(118)	C ₇ H ₇ N ₃ O ₅	19.71	19.47
<u>1b</u>	2,6	Et	76	(75-76)	C ₈ H ₉ N ₃ O ₅	18.50	18.44
<u>1c</u>	2,6	<u>i</u> -Pr	72		C ₉ H ₁₁ N ₃ O ₅	17.42	17.01
<u>1d</u>	2,6	Ph ₃ C	161		C ₂₅ H ₁₉ N ₃ O ₅	9.52	9.49
<u>2a</u>	2,4,6	Me	146	(168 ^a)	C ₇ H ₆ N ₄ O ₇	21.70	21.32
<u>2b</u>	2,4,6	Et	104	(108)	C ₈ H ₈ N ₄ O ₇	20.58	20.18
<u>2c</u>	2,4,6	<u>i</u> -Pr	110		C ₉ H ₁₀ N ₄ O ₇	19.58	19.50
<u>2d</u>	2,4,6	Ph ₃ C	140		C ₂₅ H ₁₈ N ₄ O ₇	11.52	11.15

a) This high mp. indicates that the sample may have decomposed partly, as it happens during prolonged storage.

It will be observed from Table 2 and from checking the experimental data that the ¹H-NMR peaks of 1b provide evidence of ASIS (aromatic solvent induced shift) in C₆D₆ (shielding of all NMR peaks). The infrared spectra of all the alkoxy derivatives 1 and 2 (KBr pellet) exhibit common bands

around 3300 (NH stretch), 1620 (arom. 1, 2), 1600 (arom. 2), 1540 (NO₂

TABLE 2. ¹H-NMR Spectra (δ values, ppm)

Comp.	Solvent	CH ₃	CH ₁₍₂₎	NH ^a	3,5-H ₂	4-H
<u>1a</u>	CCl ₄	3.71		9.82	7.99 ^b	6.98 ^b
<u>1b</u>	CCl ₄	1.20 ^c	3.94 ^c	9.82	7.98 ^b	6.96 ^b
<u>1c</u>	CCl ₄	1.25 ^c	4.10 ^c	9.85	7.98 ^b	6.98 ^b
<u>1d</u> ^d	(D ₃ C) ₂ SO			9.90	7.90 ^b	7.00 ^b
<u>2a</u>	C ₆ D ₆	3.00		9.50	7.95	
<u>2b</u>	CDCl ₃	1.28 ^c	4.08 ^c	10.50	8.94	
<u>2c</u>	CDCl ₃	1.32 ^c	4.23 ^c	10.50	8.93	
<u>2d</u> ^d	(D ₃ C) ₂ SO			10.60	8.60	

a) Broad band, disappears on shaking with deuterium oxide.

b) $J = 8$ Hz between 3,5-H₂ doublet and 4-H triplet.

c) $J = 7$ Hz for Et triplet/quadruplet and *i*-Pr doublet/septet.

d) Phenyl multiplet centered at 7.3 ppm.

asym. 1, 2), 1370 (NO₂ sym. 1, 2), 1350 (sym. 2), 1430, 1400, 1300, 1280, 1100, 1060, 940, 850, 770, 740 and 730 cm⁻¹; some of the last bands are due to out-of-plane vibrations of phenyl hydrogen atoms.

The alkoxypolynitroanilines reported here are interesting because, as we shall report separately, oxidation converts them into persistent aminyl free radicals. The stability of these free radicals in solution, even in the presence of oxygen, is due to steric factors (shielding of the position with highest spin density from attacking reagents by the bulky *ortho*-nitro groups) and to electronic capto-dative (push-pull) delocalization.³

EXPERIMENTAL SECTION

All melting points are uncorrected. IR spectra were recorded with a Jena UR-20 instrument. ¹H-NMR spectra were obtained at 60 MHz with a Varian EM-

360 L instrument. Commercial dioxane and picryl chloride (Fluka) were used; the dioxane was subjected to further purification according to literature procedure.⁴ Alkoxyamine hydrochlorides were prepared according to the literature procedures: methoxy,^{5,6} ethoxy,⁷ and isopropoxy.^{8,9} Trityloxyamine⁸ was prepared as the free base.

N-Alkoxydicramides (2a-2c, N-methoxy-, N-ethoxy- and N-isopropoxy-2,4,6-trinitroaniline, respectively).- To a stirred suspension of picryl chloride (0.5 mmol) in 2 ml of 96% ethanol, was added a suspension of 3 mmol alkoxyamine hydrochloride and 3 mmol potassium hydroxide in 2.5 ml of a 3:2 (vol.) mixture of dioxane and water, in several portions at room temp. The reddish-brown mixture became clear and was left at room temperature overnight. After dilution with 50 ml water, the yellow crystalline product was collected and washed with 30% ethanol. It may be recrystallized from 96% ethanol, but TLC (silica gel with benzene as eluent) showed no impurities. The products may be stored in the refrigerator for long periods of time, but decompose slowly at room temperature; after three months at 25°, 2a exhibited a higher melting point.

N-Trityloxydicramide (2d, N-triphenylmethoxy-2,4,6-trinitroaniline).- To a stirred solution of picryl chloride (0.5 mmol) in 2 ml dioxane, a solution of 1.0 mmol trityloxyamine and 1.0 mmol dry pyridine in 2 ml dioxane was added with stirring at 60° for 30 minutes. Most of the solvent was evaporated under reduced pressure and the residue was precipitated with diethyl ether. The product was collected and washed with water and diethyl ether. It may be recrystallized from 96% ethanol, but is sufficiently pure by TLC.

N-Alkoxy-2,6-dinitroanilines (1a-1c).- The reaction with 2,6-dinitrochlorobenzene was carried out as with picryl chloride, but the reaction time was ten days at room temperature with occasional shaking. The work-up was as described above.

N-Trityloxy-2,6-dinitroaniline (1d).— A similar procedure as for 2d was followed, but the reaction time was five days at 30°. The reaction mixture was worked up as described for 2d.

Yields ranged from 70–80% for 1a–1c, 80–90% for 2a–2c, 60% for 1d and 2d.

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REFERENCES

1. A. T. Balaban, M. Frangopol, N. Negoita, P. T. Frangopol and M. Paraschiv, *Rev. Roum. Chim.*, 14, 941 (1969).
2. G. Biggi and F. Pietra, *J. Chem. Soc. (B)*, 44 (1971).
3. A. T. Balaban, *Rev. Roum. Chim.*, 16, 725 (1971); *Buletinul Inst. Politehnic Bucuresti, Ser. Chim. Metalurg.*, 43, No. 4, 65 (1981) and further references therein.
4. R. L. Augustine and J. A. Caputo, *Org. Syn. Coll. Vol. 5*, 869.
5. O. Scherer, G. Hoerlein, R. Huebner and G. Schneider, *Germ. Pat.* 112,082; *Chem. Abstr.*, 56, 8561 (1962).
6. B. O. Ioffe and K. N. Zelenin, *Izv. Vyssh. Uchebn. Zaved., Khim. i Khim. Tekhnol.*, 6, 78 (1963); *Chem. Abstr.*, 59, 6244 (1963).
7. R. T. Major and R. J. Hedrick, *J. Org. Chem.*, 30, 1270 (1965).
8. W. B. Lutz, *ibid.*, 36, 3835 (1971).
9. B. J. R. Nicolaus, L. Mariani and F. Testa, *Ann. Chim. (Roma)*, 53, 281 (1963).
10. H. P. Schultz, *Org. Syn. Coll. Vol. 4*, 364; F. D. Gunstone, and H. Tucker, *ibid.*, 160.

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