A New Synthesis of 3,4,5-Triaryl-4,5-dihydro-1,2-oxazole *N*-Oxides

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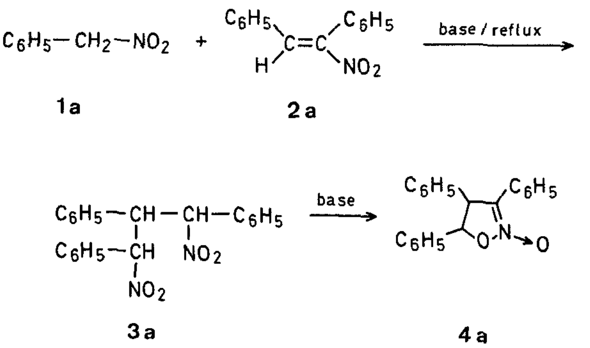
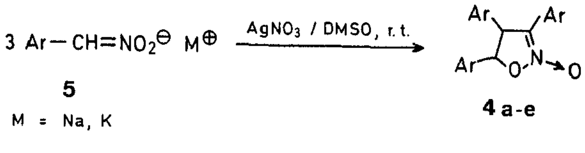
The base-catalysed formation of 3,4,5-triphenyl-4,5-dihydro-1,2-oxazole *N*-oxide (**4a**) from phenylnitromethane (**1a**) and *cis*-α-nitrostilbene (**2a**) is an important method for preparation of cyclic nitronic esters. The methods were discovered and developed by Kohler and coworkers[1]. This reaction may involve the initial formation of the Michael adduct, 1,3-dinitro-1,2,3-triphenylpropane (**3a**), followed by an *O*-alkylation-cyclisation reaction to give **4a**[2].



Scheme A

However, at the moment *cis*-α-nitrostilbenes (**2**) are difficulty accessible and a only a few examples have been synthesised[1]. The author has now observed that appreciable yields of 3,4,5-triaryl-4,5-dihydro-1,2-oxazole *N*-oxides **4** are generally obtained from reactions of arylmethanenitronates **5**. The reactions were easily carried out by stirring a mixture of sodium or potassium salt **5** of **1** and silver nitrate in dimethyl sulfoxide at room temperature for 2 h. The yield of **4** was in the range 38–52%.

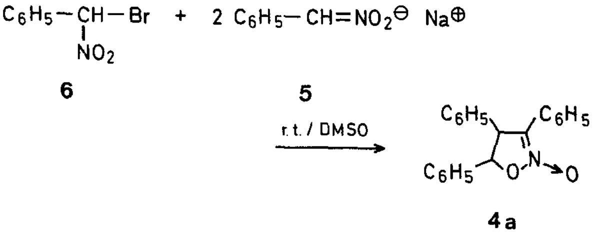


Scheme **B**

This method requires mild temperatures (ambient) and not necessarily strictly anhydrous conditions. Also, since **1** (**5**) is the precursor to **2**, the starting compound is now more easily accessible.

All the compounds **4** obtained are listed in the Table, along with yields, physical data, and spectral data. The structure of **4** was established by I.R., U.V., ^{1}H-N.M.R., mass spectral data, microanalyses, and by an alternate synthesis of one of these compounds, **4a**.

In the course of this study, it was found that bromonitrophenylmethane (**6**) reacted at room temperature with the sodium salt of **1a** in dimethyl sulfoxide to give **4a** in a yield of about 60%.



Scheme **C**

The formation of vicinal dinitroalkanes in the reactions of α-bromonitroalkanes with nitroalkanes in dimethyl sulfoxide, and dimerisation to vicinal dinitro-compounds in the reactions of α-arylalkanenitronates with silver nitrate in dimethyl sulfoxide have been demonstrated[3,4]. Thus, it is remarkable that the present reactions afforded **4** as the main product. To explain these results, it has supposed that, by elimination of nitrous acid, the intermediate compound **7** is converted into **2**, which under the action of **1** gave the cyclic nitronic ester **4** as outlined in the Scheme **D**.

Only two somewhat related examples of this type of cyclisation have been reported. Shechter and Kaplan have reported that the reaction of 1-nitroethane with persulfates in alkaline medium gave 3,4,5-trimethyl-1,2-oxazole in 25% yield[5]. Nenitzescu has reported that anodic oxidation of an aqueous solution of the sodium salt of **1a** gave 3,4,5-triphenyl-1,2-oxazole[6]. The mechanism of their reactions is obscure but clearly involves the intermediate dihydro-1,2-oxazole *N*-oxide ring formation. The mechanism of the formation of **4** in the present reactions is currently under investigation.

Table. Preparation of 3,4,5-Triaryl-4,5-dihydro-1,2-oxazole *N*-Oxides **4**

Product 4	Ar	Yield [%][a] Method A	Yield [%][a] Method B	m.p. (solvent)	Molecula formula[b]	Mass spectrum m/e	^{1}H-N.M.R. (DMSO-d_6) δ [ppm] 4-H	5-H	H_{arom}	I.R. (KBr) [cm^{-1}] ν_{-O-}	$\nu_{C=N}$
4a	C_6H_5	48	53	160–161° (acetic acid)	$C_{21}H_{17}NO_2$ (315.37)	315 ($M^{\oplus}$)	5.41 (d)	5.59 (d)	7.41–8.20 (m)	1220	1613
4b	2-H_3C—C_6H_4	44	42	168–169° (acetic acid)	$C_{24}H_{23}NO_2$ (357.45)	357 ($M^{\oplus}$)	5.42 (d)	5.94 (d)	6.88–7.91 (m)	1200	1620
4c	4-H_3C—C_6H_4	42	46	173–174° (ethanol)	$C_{24}H_{23}NO_2$ (357.45)	357 ($M^{\oplus}$)	5.17 (d)	5.47 (d)	7.09–7.91 (m)	1220	1620
4d	2-Cl—C_6H_4	47	44	140–141° (ethanol)	$C_{21}H_{14}Cl_3NO_2$ (418.71)	418 ($M^{\oplus}$)	5.62 (d)	6.10 (d)	7.40–8.00 (m)	1200	1615
4e	3-O_2N—C_6H_4	—	40[c]	198–199° (acetic acid)	$C_{21}H_{14}N_4O_8$ (450.36)	450 ($M^{\oplus}$)	5.85 (d)	7.03 (d)	7.45–8.82 (m)	1220	1615

[a] Yields of the pure isolated products based on **1**.

[b] All compounds gave satisfactory microanalyses (C ± 0.30%, H ± 0.30%, N ± 0.30%).

[c] Yield after chromatography on neutral alumina.

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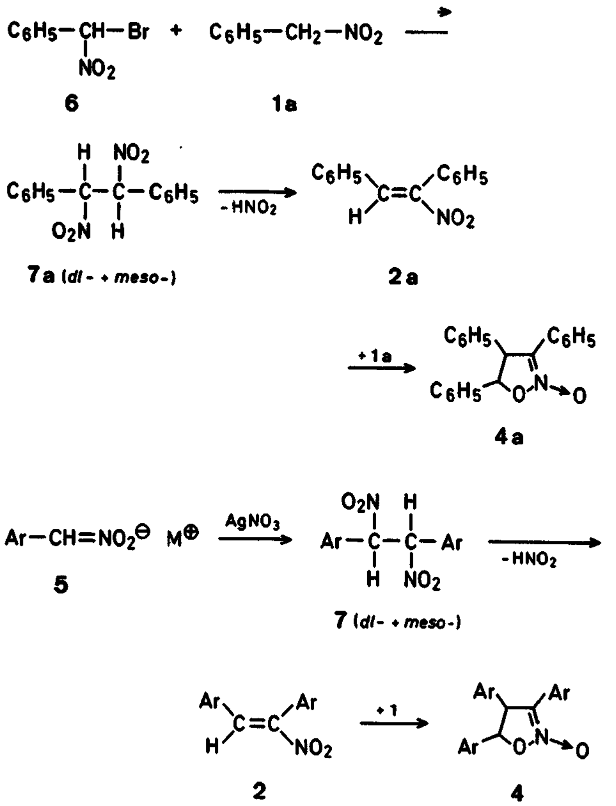

Scheme D

Preparation of 3,4,5-Triaryl-4,5-dihydro-1,2-oxazole *N*-Oxides **4**; General Procedure:

Method A: A sodium salt **5** of **1** (0.05 mol) is added rapidly to a solution of silver nitrate (0.06 mol) in dimethyl sulfoxide (150 ml) with stirring. The reaction is exothermic and starts immediately. The mixture is stirred at room temperature. After 2 h the silver is filtered off and washed with dimethyl sulfoxide; a large amount of water is added to the filtrate and washings. The pale yellow solid which precipitates is collected by filtration, washed with water, and dried. Crystallisation from ethanol or acetic acid gives **4** as colorless needles.

Method B: A mixture of **1** (0.05 mol), water (20 ml), and potassium hydroxide (0.05 mol) is added rapidly to a solution of silver nitrate (0.06 mol) in dimethyl sulfoxide (150 ml). The mixture is stirred at room temperature for 2 h and work-up is carried out as described under Method A.

Preparation of 3,4,5-Triphenyl-4,5-dihydro-1,2-oxazole *N*-Oxide (**4a**):

To a stirred suspension of sodium salt of **1a** (0.05 mol) in dimethyl sulfoxide (70 ml) a solution of **6** (0.05 mol) in dimethyl sulfoxide (15 ml) is added at room temperature. The mixture turns red after 2 h and is then poured into cold water. The precipitates are collected by filtration, dried, and recrystallised from acetic acid; yield: 4.8 g (61%); m.p. 160–161°.

Product **4a** was identified by direct comparison with samples synthesised from **1a** and **2a** according to Lit.[1].

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[1a] E. P. Kohler, *J. Am. Chem. Soc.* **46**, 1733 (1924).

[1b] E. P. Kohler, G. R. Barrett, *J. Am. Chem. Soc.* **46**, 2105 (1924).

[2] A. T. Nielsen, T. G. Archibald, *Tetrahedron Lett.* **1968**, 3375.

[3] N. Kornblum, S. D. Boyd, H. W. Pinnick, R. G. Smith, *J. Am. Chem. Soc.* **93**, 4316 (1971).

[4] R. B. Kaplan, H. Shechter, *J. Am. Chem. Soc.* **83**, 3535 (1961).

[5] H. Shechter, R. B. Kaplan, *J. Am. Chem. Soc.* **75**, 3980 (1953).

[6] C. D. Nenitzescu, *Ber. Dtsch. Chem. Ges.* **62**, 2669 (1929).

0039-7881/78/0132-0056 $ 03.00