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NITRATION OF STYRENES USING 2-METHYL-5-TRINITROMETHYLTETRAZOLE

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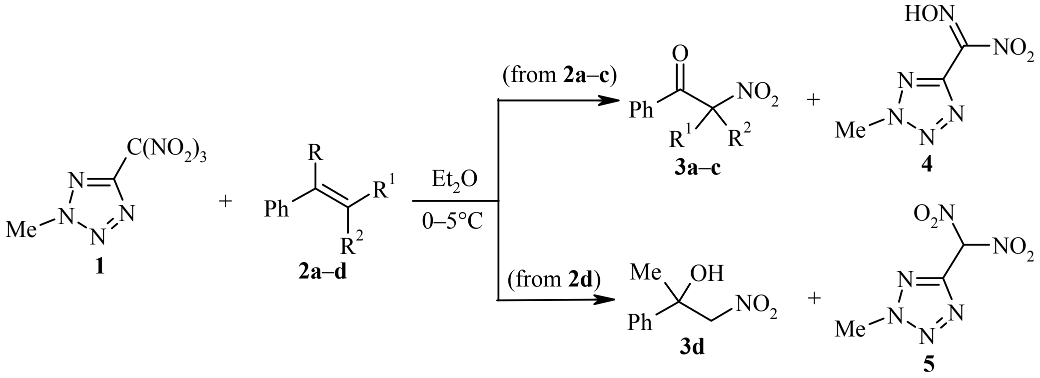
Details of the methods of synthesis, chemical properties, and practical importance of tetrazoles have been reported in the studies [1, 2] and in a series of reviews [3-5]. At the same time, the chemical transformations of 5-trinitromethyltetrazoles have been investigated to a lesser degree. It is only known that 5-trinitromethyl-1*H*-tetrazole is denitrated in the presence of an alkaline solution of hydroxylamine to give the potassium salt of 5-dinitromethyltetrazole, while its reaction with excess diazomethane results in the formation of a mixture of the isomeric 5-(1-methyltetrazolyl)- and 5-(2-methyltetrazolyl)trinitromethanes [6].

We have found that 2-methyl-5-trinitromethyltetrazole (**1**) reacts with the styrenes **2a-d** as a nitrating agent. The reaction of tetrazole **1** with the ethenes **2a-d** in a neutral medium results in the denitration of compound **1** to give the α-nitro ketones **3a-c** (from the alkenes **2a-c**) or the 1-methyl-2-nitro-1-phenyl-1-ethanol **3d** (from alkene **2d**). In addition, the degradation products of compound **1** (the nitromethanone oxime **4** from the reactions with compounds **2a-c** or the 5-dinitromethyltetrazole **5** from the reaction with compound **2d**) are formed in low yields.



a R = R^1 = R^2 = H; **b** R = R^1 = H, R^2 = Me; **c** R = H, R^1 = R^2 = Me; **d** R = Me, R^1 = R^2 = H

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The nature of the reaction products allows us to propose that the reaction of compound **1** with alkenes **2a-d** occurs by a known scheme [7, 8] through a stage of charge-transfer complex formation from nitroalkyl ether of *aci*-dinitrotetrazolylmethane, which dissociates *via* an intramolecular oxidation-reduction to the α-nitro ketones **3a-c** or nitroalcohol **3d**.

IR spectra were recorded on an Infralum FT-02 spectrophotometer in KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II 300 SF spectrometer (300 and 75 MHz, respectively) in DMSO-d$_6$ with HMDS as internal standard. Elemental analysis was carried out on a EuroVector Euro EA 3000 CHNS analyzer. The tetrazole **1** was prepared by the method reported in the study [6]. Compounds **2a-d** were synthesized from the corresponding carbonyl compounds and alkylmagnesium halides to yield alcohols which were then dehydrated [9].

Reaction of 2-Methyl-5-trinitromethyltetrazole (1) with Alkenes 2a-d (General Method). Compound **1** (1.17 g, 5 mmol) in absolute diethyl ether (30 ml) was added to a solution of compound **2a-d** (5 mmol) in the same solvent (20 ml) at 0-5ºC. The reaction mixture was maintained at 25ºC for 140 h, solvent was evaporated under reduced pressure, and the residue was chromatographed on an activated Silicagel 100/400µ grade column (10×250 mm). The eluent for compounds **3a-d** was benzene, while for the compounds **4**, **5** it was diethyl ether.

2-Nitro-1-phenyl-1-ethanone (3a). Yield 0.48 g (58%). Colorless crystals, mp 105-107ºC (mp 105-107ºC [10]). The ^{1}H NMR spectrum agreed with that given in the literature [11]. Found, %: C 58.25; H 4.15; N 8.37. $C_8H_7NO_3$. Calculated, %: C 58.18; H 4.24; N 8.48.

2-Methyl-2-nitro-1-phenyl-1-ethanone (3b). Yield 0.58 g (65%). Oily liquid, η_D^{20} 1.5465 (η_D^{20} 1.5465 [12]). The ^{1}H NMR spectrum agreed with that given in the literature [11]. Found, %: C 60.45; H 4.94; N 7.71. $C_9H_9NO_3$. Calculated, %: C 60.34; H 5.03; N 7.82.

2,2-Dimethyl-2-nitro-1-phenyl-1-ethanone (3c). Yield 0.49 g (55%). Oily liquid, η_D^{20} 1.5280 (η_D^{20} 1.5280 [12]). The ^{1}H NMR spectrum agreed with that given in the literature [11]. Found, %: C 62.27; H 5.58; N 7.13. $C_{10}H_{11}NO_3$. Calculated, %: C 62.18; H 5.70; N 7.25.

1-Methyl-2-nitro-1-phenyl-1-ethanol (3d). Yield 0.47 g (52%). Oily liquid, η_D^{20} 1.5190 (η_D^{20} 1.5190 [10]). The ^{1}H NMR spectrum agreed with that given in the literature [13]. Found, %: C 59.74; H 5.97; N 7.63. $C_9H_{11}NO_3$. Calculated, %: C 59.67; H 6.08; N 7.73.

(2-methyltetrazol-5-yl)nitromethanone Oxime (4). Yield 0.13 g (15%), Colorless crystals, mp 185-187ºC. IR spectrum, ν, cm^{-1}: 1555, 1380 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.53 (3H, s, CH_3); 13.75 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 39.6 (CH_3); 65.2 (C); 146.9 (C-5). Found, %: C 21.02; H 2.26; N 48.91. $C_3H_4N_6O_3$. Calculated, %: C 20.94; H 2.34; N 48.83.

2-Methyl-5-dinitromethyltetrazole (5). Yield 0.09 g (10%). Colorless crystals, mp 37-38ºC (Et_2O–hexane, 1:1) (mp 37-38ºC [6]). The ^{1}H NMR spectrum agreed with that given in the literature [6]. Found, %: C 19.22; H 2.03; N 44.58. $C_3H_4N_6O_4$. Calculated, %: C 19.15; H 2.13; N 44.68.

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