5-Substituted 3-Nitro-1-trinitromethyl-1,2,4-triazoles


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Abstract—A number of 5-R-substituted 3-nitro-1-trinitromethyl-1H-1,2,4-triazoles (R = Me, Cl, Br, N₃, NH₂, NO₂) were synthesized by nitration of the corresponding ω-(5-R-3-nitro-1H-1,2,4-triazol-1-yl)alkan-2-ones with mixtures of concentrated sulfuric and nitric acids.

Successful nitration of 3-R-substituted 1H-1,2,4-triazol-1-ylalkanones (R = H, Cl, N₃, NO₂) with mixtures of concentrated sulfuric and nitric acids to 1-trinitromethyl-3-R-1H-1,2,4-triazoles and elucidation of some specific features of this reaction [1] prompted us to extend the substrate series and examine nitration under analogous conditions of 5-substituted ω-(3-nitro-1H-1,2,4-triazol-1-yl)alkan-2-ones I–VIII.

3.00 [4] and 3.85 [5], respectively), condensation of these compounds with methyl vinyl ketone in aprotic medium (diethyl ether, acetone) was expected to occur in the absence of a base, as in the synthesis of 4-(3,5-dinitro-1H-1,2,4-triazol-1-yl)butan-2-one [2].

However, under these conditions the yield of compounds V and VII did not exceed 15%; therefore, the presence of a base was necessary, as in the reaction with a weaker NH acid, 5-methyl-3-nitro-1H-1,2,4-triazole (pKₐ > 6).

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Unlike previously studied ω-(3-R-1H-1,2,4-triazol-1-yl)alkan-2-ones [1], the triazole ring in compounds I–VIII contained an additional substituent which was fairly large (in some cases; R = Me, Br, NO₂) and was located in the vicinity of the reaction center. Therefore, some steric hindrances could appear during the multi-step degradative nitration process, and the possibility for synthesizing 3-nitro-1-trinitromethyl-1H-1,2,4-triazoles, as well as stability of the product, casted doubt.

Nevertheless, the nitration of ω-(5-R-3-nitro-1H-1,2,4-triazol-1-yl)alkan-2-ones I–VIII with mixtures of concentrated sulfuric and nitric acids under the conditions described previously for the synthesis of 3-substituted...
1-trinitromethyl-1H-1,2,4-triazoles [1] [weight ratio nitrating mixture–substrate \(M = (20–30):1\), HNO\(_3\)–H\(_2\)SO\(_4\) weight ratio 1:(1–2), reactant mixing at 0–5°C, reaction temperature 20°C, reaction time 12–72 h] in all cases gave the corresponding 5-substituted 3-nitro-1-trinitromethyl-1H-1,2,4-triazoles IX–XV in 40–75% yield (Scheme 2).

Scheme 2.

![Scheme 2](image)

I–III, \(n = 1\); IV–VIII, \(n = 2\); I, VI, XI, R = Br; II, XV, R = H\(_2\)N; III, VIII, XIII, R = O\(_2\)N; IV, IX, R = Me; V, X, R = Cl; VII, XII, R = N\(_2\); XIV, R = O\(_2\)NH.

When the time of nitration of amine III was shorter than 12 h, a mixture of 5-amino- and 5-nitroamino-3-nitro-1-trinitromethyl-1H-1,2,4-triazoles XIV and XV was formed. After 72 h, the only reaction product was 5-amino derivative XV, i.e., the reaction involves initial formation of N-nitroaminotriazole XIV which then undergoes denitration in acid medium (Scheme 3). 5-Amino-3-nitro-1-trinitromethyl-1H-1,2,4-triazole (XV) was also formed when compound XIV was kept in sulfuric acid. N-Nitroamine XIV was isolated as crystal hydrate; its thermogravimetric analysis showed an endothermic peak at about 100°C with a weight loss corresponding to the presence of one molecule of crystallization water.

Scheme 3.

![Scheme 3](image)

The nitration of \(\omega\)-(3-nitro-1H-1,2,4-triazol-1-yl)alkan-2-ones occurred in a way similar to the nitration of their analogs having no substituent in position 5 of the triazole ring. Moreover, \(\omega\)-(3-nitro-1H-1,2,4-triazol-1-yl)alkan-2-ones \((n = 1, 2)\) may be regarded as belonging to both \(\omega\)-(3-R-1H-1,2,4-triazol-1-yl)alkan-2-one and \(\omega\)-(5-R-3-nitro-1H-1,2,4-triazol-1-yl)alkan-2-one \((R = H)\) series. Therefore, we believed that comparison of the data on the nitration of these compounds is relevant. The formation of 5-substituted 3-nitro-1-trinitromethyl-1H-1,2,4-triazoles was monitored by weighing the products isolated under identical conditions by diluting a sample withdrawn from the reaction mixture.

Accumulation of trinitromethyltriazoles in the nitrating mixture follows the same pattern as in the nitration of 3-substituted analogs: the yield initially increases, passes through a maximum, and falls down as a result of decomposition. A typical example is illustrated by the data given in table for the nitration of 4-(5-bromo-3-nitro-1H-1,2,4-triazol-1-yl)butan-2-one (VI). The maximal yield of 5-substituted derivatives is attained in a shorter time and is lower than the yield of 3-substituted trinitromethyltriazoles. In the reactions with 1-(3-nitro-5-R-1H-1,2,4-triazol-1-yl)propan-2-ones, the maximal yield of the nitrilation products is attained in 12–18 h (60–75%), whereas the nitration of 1-(3-nitro-1H-1,2,4-triazol-1-yl)propan-2-one gives 90% of the corresponding 1-trinitromethyl derivative in 36–40 h [1] \((M = 20, \text{HNO}_3-\text{H}_2\text{SO}_4\text{ ratio } 1:1)\). The difference for 4-triazolylbutan-2-ones is somewhat smaller, but the general pattern is the same: under analogous conditions \((M = 30, \text{HNO}_3-\text{H}_2\text{SO}_4\text{ ratio } 1:2)\) the maximal yield of 5-substituted 1-trinitromethyltriazoles (40–60%) is lower than the yield of 3-nitro-1-trinitromethyl-1H-1,2,4-triazole (70% [1]), but it is reached in a shorter time (30–40 h against 96 h [1]). Thus both nitration and decomposition of the nitrilation products in the series of 5-substituted 3-nitrotriazoles occur at a higher rate.

As in the nitration of \(\omega\)-(3-nitro-1H-1,2,4-triazol-1-yl)alkan-2-ones [1], it is advisable to apply more severe conditions for less reactive 4-(3-nitro-5-R-1H-1,2,4-triazol-1-yl)butan-2-ones \((M = 30, \text{HNO}_3-\text{H}_2\text{SO}_4\text{ ratio } 1:2)\). The nitration of triazolylpropanones occurs with a good yield at \(M = 20 (\text{HNO}_3-\text{H}_2\text{SO}_4\text{ ratio } 1:1)\).

The structure of the isolated compounds was confirmed by the analytical and spectral data. It should be noted that all trinitromethyl derivatives of the 3-nitrotriazole series are very sensitive to thermal and mechanical effects; therefore, specific precautions should be taken while handling these compounds, and their synthesis and purification should be performed with