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The nitroalkene showing dual behaviors in the same reaction system

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Abstract—The nitroalkene moiety of 1-methyl-3,6,8-trinitro-2-quinolone showed dual behaviors in the same reaction system, namely electron-poor heterodiene and dienophile, and affording polycyclic products.

The cycloaddition is one of the fundamental protocols for the construction of a new ring, which accompanies the formation of two bonds. Highly electron-poor nitroalkenes are excellent dienophiles leading to cycloadducts upon treatment with electron-rich dienes.[1] Nitroalkenes also behave as heterodienes to form a cyclic nitronate (oxazine derivative) in the reaction with electron-rich alkenes, and this chemistry has been significantly developed by Denmark's group.[2] Although nitroalkenes reveal dual behaviors as mentioned above, these reactivities are not observed at the same time, since they require different conditions.[3] Only single example is found in the literature, which yields both products under the same conditions; however, nitro substituted bicyclo[2.2.2]octane is formed from cyclic nitronate via [3,3]-sigmatropic rearrangement.[4] In the present letter, we would like to give a nitroalkene showing dual behaviors in the same reaction system.

The 1-methyl-2-quinolone (MeQone) skeleton is often found as the partial structure of quinoline alkaloids that are isolated from the Rutaceae family.[5] Not only naturally occurring MeQones but also unnatural derivatives have attracted recent attention with regard to biological and pharmacological properties.[6] While modification of the MeQone is comparatively difficult because of its aromaticity, functionalization of 1-methyl-3,6,8-trinitro-2-quinolone (**TNQ**) is readily performed to afford various types of MeQones under mild conditions.[7] The steric repulsion between the 1-methyl and the 8-nitro groups distorts the framework of **TNQ**, which diminishes the aromaticity.[8] As a result, the pyridone ring of **TNQ** behaves as the activated nitroalkene showing somewhat aromaticity.

When **TNQ** was treated with ethoxyethene **1** in the presence of triethylamine, pale brown solid was precipitated. The empirical formula $C_{21}H_{11}N_7O_{10}$ and the MS spectrum reveal that two molecules of **TNQ** and **1** are combined accompanied by the elimination of $C_3H_6O_2$ in addition to nitrous acid and water. Although low solubility of the product prevented the measurement of the ^{13}C NMR, satisfactory ^1H NMR data were given, which showed simple spectrum in spite of large molecules. In the aromatic region, a couple of doublet signals appeared at 9.02 and 10.08 ppm ($J = 2.4$ Hz) and a singlet one at 10.39 ppm, and the integral value for the latter singlet was half of those for each doublet. These facts suggest that the product has a symmetrical structure, and a new aromatic ring was formed between two quinolone rings. Hence, the product was assigned to quinolino[3,4-*b*][1,9]diazaphenanthrene derivative **2**[9] (Scheme 1).

Similar reaction using the same combination of reagents in the absence of triethylamine was conducted. In this case, cyclic nitronate **3** was isolated whose structure was determined by spectral and analytical data,[10] and was additionally confirmed by conversion to quinolones **4** having an acetal function (Scheme 2). Furthermore, signals for ethyl formate **5** were observed in the ^1H NMR of the reaction mixture of **TNQ** and **1** in the presence of triethylamine, which indicated that a retro Diels–Alder reaction proceeded. On the basis of these

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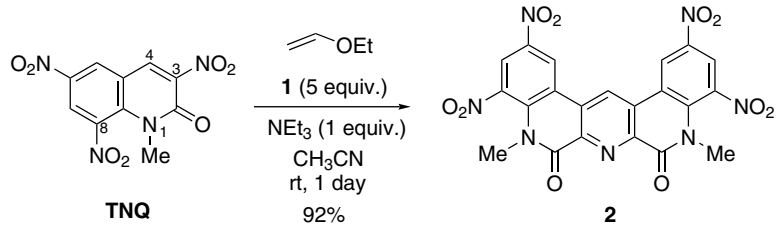
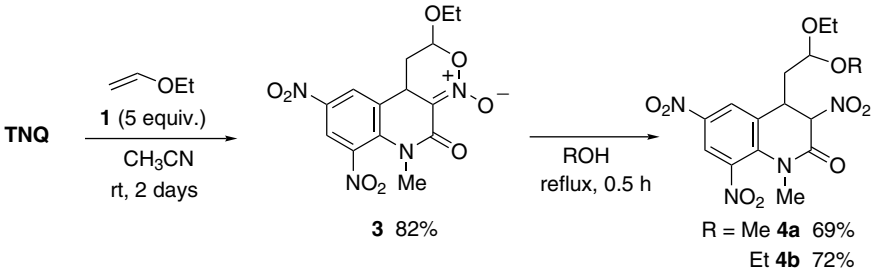
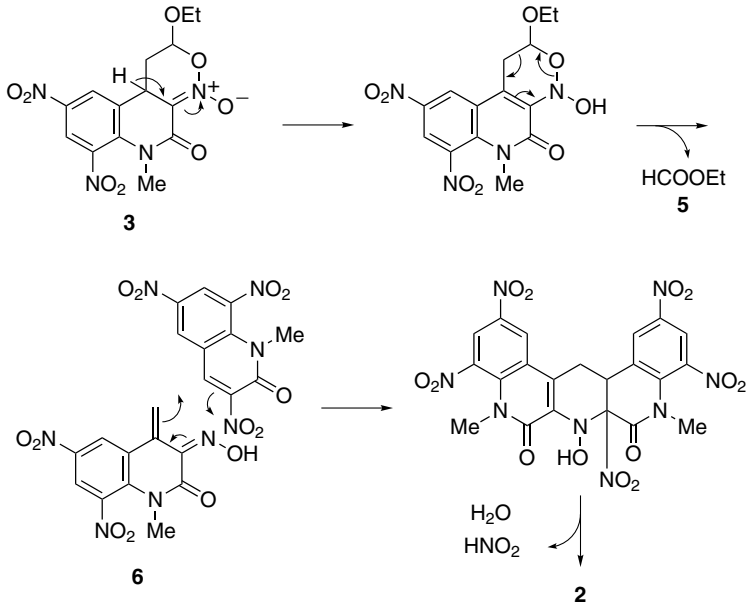


Scheme 1.



Scheme 2.

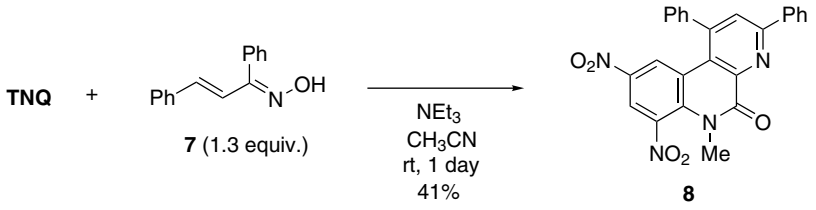


Scheme 3.

experimental facts, a plausible mechanism for the construction of polycyclic product is illustrated in Scheme 3.

The first step for the present reaction is a cycloaddition affording a cyclic nitronate **3**. Triethylamine is considered to accelerate the prototropy from the 4-position to an oxygen atom of the nitronate **3**, and then a retro Diels–Alder reaction occurs to give α,β-unsaturated oxime **6** with loss of ethyl formate **5**.[11] The cycloaddition of the oxime **6** with another molecule of **TNQ** followed by aromatization furnishes quinolinodiazaphenanthrene **2**. In the former cycloaddition, **TNQ** behaves as the electron-poor heterodiene, to the contrary as the electron-poor dienophile in the latter cycloaddition. This consideration was supported by the formation of diazaphenanthrene **8** from the reaction of **TNQ** with α,β-unsaturated oxime **7** in the presence of triethylamine (Scheme 4) though the isolation of intermediate oxime **6** was not successful.

In summary, the nitroalkene moiety of **TNQ** revealed dual behaviors of nitroalkene in the same reaction system at room temperature, which is a first example to the best of our knowledge. The present reaction furnishes useful information for the chemistry of nitroalkene and also of MeQones. Further study using **TNQ** is currently performed to synthesize polycyclic compounds, and results will be shown in due course.



Scheme 4.

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9. 5,9-Dimethyl-6,8-dioxo-2,4,10,12-tetranitroquinolino[3,4-*b*]-[1,9]diazaphenanthrene (**2**): Mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 3.48 (s, 6H), 9.02 (d, $J = 2.4$ Hz, 2H), 10.08 (d, $J = 2.4$ Hz, 2H), 10.39 (s, 1H); IR (KBr/cm^{-1}) 1705, 1695, 1608, 1538, 1463, 1346; MS (FAB): *m*/*z* 522 (M^++1). Anal. Calcd for $C_{21}H_{11}N_7O_{10}$: C, 48.37; H, 2.11; N, 18.81. Found: C, 48.04; H, 2.06; N, 18.52.
10. Cyclic nitronate **3**: Mp 148–155 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11 (dd, $J = 7.1$, 7.1 Hz, 3H), 2.67 (ddd, $J = 14.3$, 5.7, 3.7 Hz, 1H), 2.85 (ddd, $J = 14.3$, 7.9, 3.9 Hz, 1H), 3.27 (s, 3H), 3.67 (dq, 9.7, 7.1 Hz, 1H), 3.95 (dq, 9.7, 7.1 Hz, 1H), 4.1–4.3 (br, 1H), 5.63 (dd, $J = 3.9$, 3.7 Hz, 1H), 8.32 (d, $J = 2.4$, 1H), 8.58 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.5 (q), 29.6 (t), 32.9 (d), 35.0 (q), 66.2 (t), 101.9 (d), 115.6 (s), 120.9 (d), 123.4 (d), 123.8 (s), 131.0 (s), 136.2 (s), 144.5 (s), 157.8 (s); IR (KBr/cm^{-1}) 1703, 1608, 1551, 1481, 1346, 1142; MS (FAB): *m*/*z* 367 (M^++1). Anal. Calcd for $C_{14}H_{14}N_4O_8$: C, 45.90; H, 3.85; N, 15.30. Found: C, 46.16; H, 3.84; N, 15.31.
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