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An Investigation of the Reaction of 2-Aminobenzaldehyde Derivatives with Conjugated Nitro-olefins: An Easy and Efficient Synthesis of 3-Nitro-1,2-dihydroquinolines and 3-Nitroquinolines

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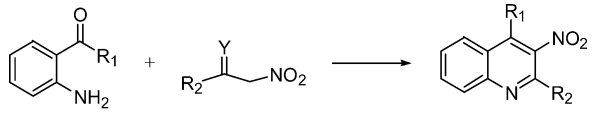
2-Aryl-3-nitro-1,2-dihydroquinolines **3** were prepared from the reaction of β-nitrostyrenes **2** and 2-aminobenzaldehyde **1** in the presence of DABCO. Not only β-nitrostyrenes but other alkyl nitro olefins also can be used in this reaction as well. When DDQ or silica gel was added to a solution of 3-nitro-1,2-dihydroquinolines **3**, 3-nitro-2-substituted-quinolines **4** were obtained. When 2-aminobenzaldehyde derivatives **7** and **12** were reacted with β-nitrostyrenes **2**, unique rearrangement products were produced.

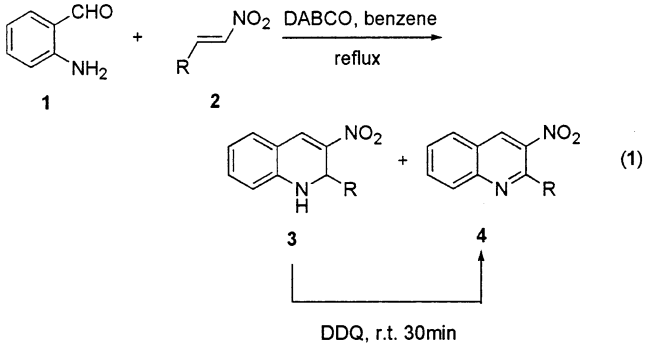
Introduction

Quinolines[1−5] are important and widely used heterocyclic compounds in organic chemistry, and a variety of methods for the preparation of nitroquinolines have been reported.[2] Three general methods are typically used to prepare nitroquinolines. First, nitroquinolines can be prepared by the nitration of quinolines.[2a,g,h,j] However, several regioisomers occur during the nitration. Second, 3-nitro-2-substituted quinolines can also be prepared via the reaction of 3-nitroquinoline *N*-oxide with limited reactants.[2i,f] Third, a method involving a modified Friedlander synthesis[1e] involves the condensation of certain nitro compounds with 2-amino carbonyl compounds (Scheme 1).[2b−e] The preparation of 2-aryl-3-nitroquinolines from the condensation of 2-aminobenzaldehyde and ω-nitroacetophenones has been reported by Baumgarten and Saylor.[2e] We herein describe an easy and convenient method for the selective preparation of 1,2-dihydro-2-substituted 3-nitroquinolines and 2-aryl-3-nitroquinolines (eq 1). 1,2-Dihydroquinolines are usually prepared by the reduction[3] of quinolines or by the nucleophilic attack[4] of quinolines and are useful in preparing some biologically active quinoline derivatives.[5] Our work expands the scope of this reaction to include 1,2-dihydroquinolines.

SCHEME 1. Condensation of Nitro Compounds with 2-Amino Carbonyl Compounds



R_1 = H, alkyl, aryl, OH, CO_2H; R_2 = H, alkyl, aryl; Y = O, N-OH



2, **3**, **4** **a**: R = Ph, **b**: R = *p*-$MeOC_6H_4$, **c**: R = *p*-ClC_6H_4, **d**: R = 2-thiophenyl, **e**: R = 1-naphthalenyl, **f**: R = 3-indolyl, **h**: R = methyl, **i**: R = ethyl, **j**: R = butyl, **k**: R = H

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TABLE 1. Condensation of 2-Aminobenzaldehyde with Aryl Nitro Olefins (2a−f)

entry	2	reflux time (h)	before addition of DDQ: 3[a] (%)	before addition of DDQ: 4[a] (%)	after addition of DDQ: 4[b] (%)
1	**2a**	15.5	**3a** (86)	**4a** (tr)	**4a** (67)
2	**2a**	48	**3a** (36)	**4a** (15)	
3	**2b**	18.5	**3b** (99)	**4b** (tr)	**4b** (91)
4	**2c**	15	**3c** (85)	**4c** (9)	**4c** (95)
5	**2d**	12	**3d** (19)	**4d** (8)	**4d** (25)
6	**2e**	45.5	**3e** (90)	**4e** (9)	**4e** (96)
7	**2f**	16	**3f** (47)[c]	**4f** (8)	**4f** (31)

[a] All yields were obtained from ^{1}H NMR spectral data with a known amount of toluene as an internal standard. [b] All yields were obtained from ^{1}H NMR spectral data with a known amount of DMF as an internal standard. [c] In entry 7, **3f** underwent disproportionation easily to form 3-nitroquinoline and indole, and the yield of 3-nitroquinoline before addition of DDQ was 18%.

TABLE 2. Condensation of 2-Aminobenzaldehyde with Alkyl Nitro Olefins (2h−k)

entry	2	reacton time (h)	before addition of DDQ: 3[a] (%)	before addition of DDQ: 4[a] (%)	after addition of DDQ: 4[b] (%)
1	**2h**	1.5[c]	**3h** (7)	**4h** (tr)	
2	**2h**	8[c]	**3h** (tr)	**4h** (tr)	
3	**2h**	9, 3.5[d]	**3h** (69)	**4h** (tr)	**4h** (63)
4	**2i**	12, 4[d]	**3i** (94)	**4i** (tr)	**4i** (85)
5	**2i**	15, 4[d]	**3j** (99)	**4j** (tr)	**4j** (97)
6	**2k**	5, 2[d]	**3k** (78)	**4k** (8)	**4k** (82)

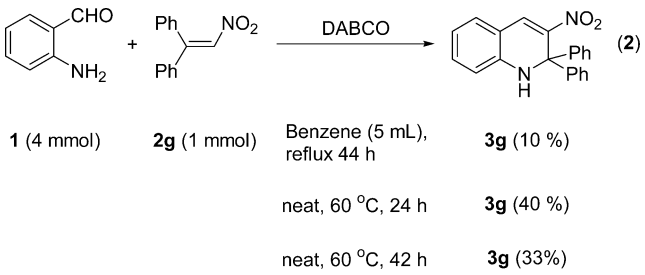
[a] All yields were obtained from ^{1}H NMR spectral data with a known amount of toluene as an internal standard. [b] All yields were obtained from ^{1}H NMR spectral data with a known amount of DMF as an internal standard. [c] 60 °C. [d] The reaction solution was heated at 45 °C for few hours before DABCO was added. After the addition of DABCO, the solution was further heated at 45 °C for another few hours.

Results and Discussion

Part a. Condensation of 2-Aminobenzaldehyde with Aryl Nitro Olefins. *β*-Nitrostyrenes **2** (1 equiv) were reacted with 2-aminobenzaldehyde[6] **1** (1.5 equiv) and DABCO (0.5 equiv) in refluxing benzene to generate 2-substituted 3-nitro-1,2-dihydroquinolines **3** in yields of 19−99% and traces (<10%) of 2-aryl-3-nitroquinolines **4** (eq 1 and Table 1). The reaction solution always turned dark red due to the color of compound **3**. When the crude mixture was analyzed by ^{1}H NMR, the reaction appeared to be very clean and only DABCO, **3**, and **4** were observed in the solution, along with a trace of **1**. An increased reaction time led to an increased yield of compound **4** (entry 2,f Table 1). It is therefore necessary to control the reaction time so as to generate only product **3**.

1,2-Dihydroquinolines can be oxidized to quinolines by using several oxidants.[7] However, DDQ has not been reported as one of these. It has been reported that DDQ is a widely used dehydrogenation reagent, e.g., in aromatization reactions.[8] 1,2-Dihydro-2-substituted 3-nitroquinolines **3** can be further oxidized by DDQ to generate 3-nitroquinolines **4**. Based on this result, we attempted to prepare **4** in a one-pot reaction of **1** and **2** in the presence of DABCO under refluxing conditions followed by oxidation by DDQ at room temperature for 30 min. As expected, the oxidation reaction was complete within a few minutes, and the yields of **4** were also very high. The experimental results are shown in Table 1. When the reaction shown in eq 1 was conducted without DABCO, neither product **3** nor 2-aryl-4-hydroxy-3-nitro-1,2,3,4-tetrahydroquinoline was observed.

It is interesting to note that the bulky nitro olefin **2g** is able to react with 2-aminobenzaldehyde to form **3g**, although a long reaction time in benzene is needed (reflux 44 h, eq 2) and the yield of **3g** is low (10%). When the reaction proceeded without solvent at 60 °C for 24 h, a better yield (40%) of **3g** was obtained, and the yields (33%) of **3g** decreased when a 42 h reaction was carried out at 60 °C under similar conditions.



Part b. Condensation of 2-Aminobenzaldehyde with Alkyl Nitro Olefins. After our study of the condensation of 2-aminobenzaldehyde with aryl nitro olefins, we examined the condensation of 2-aminobenzaldehyde with alkyl nitro olefins under similar conditions. When 1-nitropropene **2h**, compound **1**, and DABCO were mixed in benzene at 60 °C, only 7% of compound **3** was obtained (entry 1, Table 2). It is likely that 1-nitropropene **2h** has isomerized to the allylic nitro compound or polymerization may have occurred in the presence of DABCO[9] under these conditions, and as a result, only a low yield of compound **3** was observed. To avoid this isomerization or polymerization, 1-nitropropene **2h** must react with compound **1** before DABCO is added. When 1-nitropropene **2h** and compound **1** were heated at 45 °C for 9 h, followed by the addition of DABCO and heating the solution for another 3.5 h, 69% of compound **3** was obtained as expected (entry 3, Table 2). When other nitroalkenes that are able to isomerize to allylic nitro compounds or polymerize were used, procedures similar to those described above were used (entries 4−6 of Table 2). After treatment with DDQ, high yields of 2-alkyl-3-nitroquinoline were obtained (Table 2).

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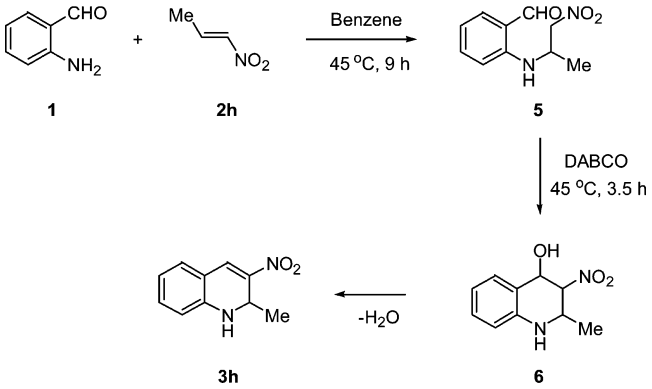
SCHEME 2. Intermediate 5 Generated from the 1,4-addition of 1-nitropropene (2h) with 2-Aminobenzaldehyde (1) Proceeds Smoothly to Intermediate 6 in the Presence of DABCO Followed by Dehydration To Give Product 3h

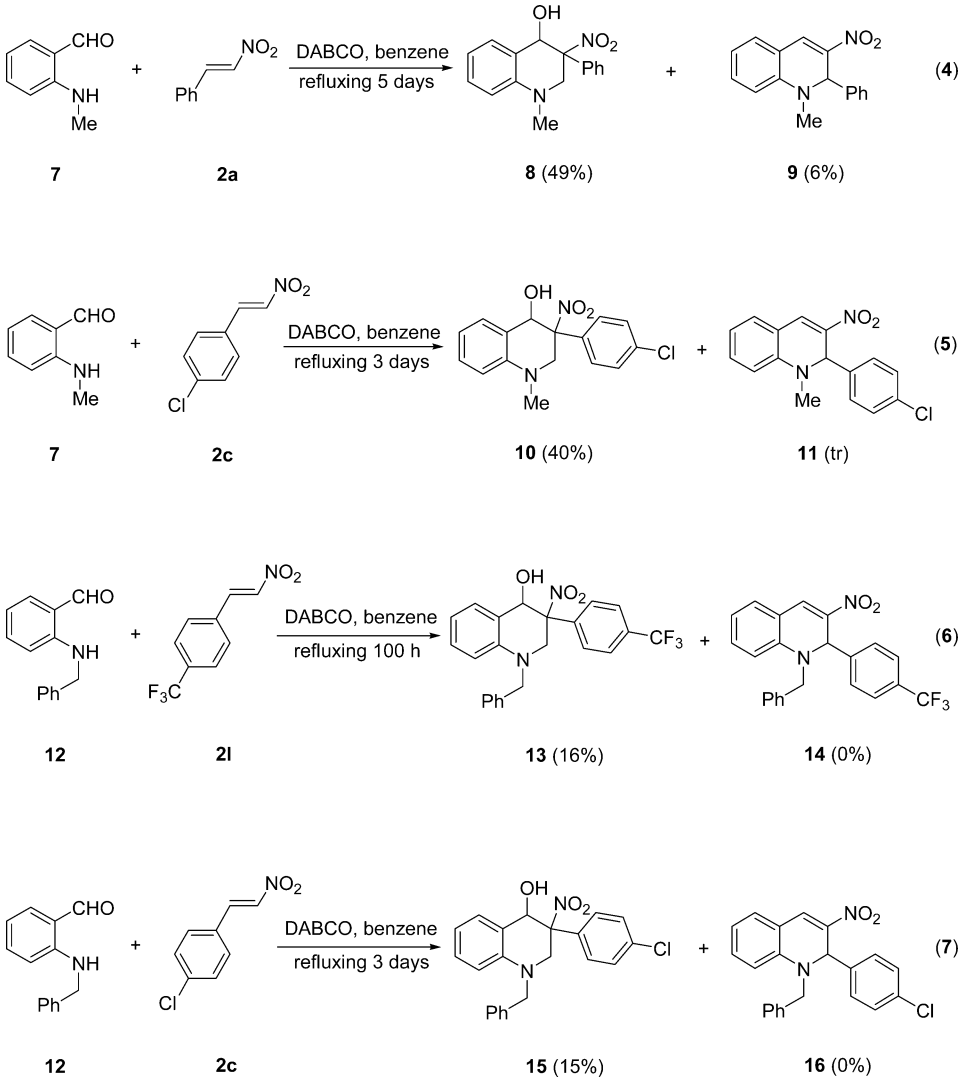


1 2h 5 6 3h

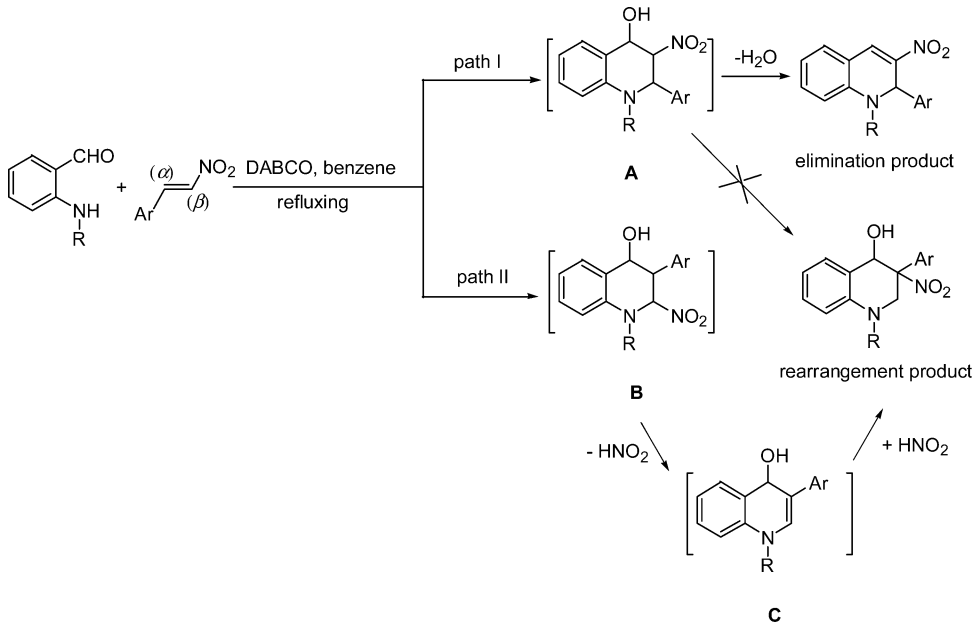
Based on ^{1}H NMR analyses of the mixture at different stages (entry 3, Table 2), we found that **2h** can be first attacked by the amino group of **1** to gain a 1,4-addition intermediate **5**, and **5** can then be deprotoned by DABCO to form the anion, which undergoes intramolecular nucleophilic addition to generate intermediate **6** and finally **6** undergoes dehydration to give product **3h** (Scheme 2). This assumption was verified by the isolation of two isomers of **6** whose spectral data were all consistent with the proposed structures when compound **5** was purified by flash column chromatography. According to the description above, there is no doubt that the condensation of 2-aminobenzaldehyde with alkyl nitro olefins were ascribed to stepwise rather than concerted reaction.

Part c. Use of Silica Gel as a Replacement of DDQ. Although the use of DDQ for the aromatization of a variety of compounds is widely utilized, it is expensive and the final crude is difficult to purify due to the increased viscosity.[8] Herein, an alternative method for the aromatization of 1,2-dihydroquinolines by using silica gel becomes significant. Silica gel is used to support reactants and catalyze various reactions.[10] During the purification of product **3** by flash column chromatography, it was found that small amounts of product **3** were converted to product **4** in the presence of silica gel. On the basis of this fact and the oxidation of 1,2-dihydroquinolines by oxygen,[7d,e] silica gel was added to the reaction solution after the complete formation of **3**, and the solution was then heated at 110 °C for 1 h. When

SCHEME 3

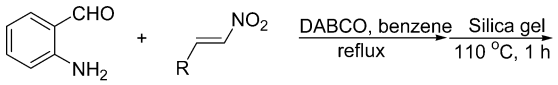


SCHEME 4. Two Possible Routes To Give the Rearrangement Products[a]

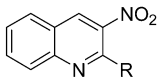


[a] The first possibility is related to the aryl rearrangement of 2-aryl-4-hydroxy-3-nitro-1,2,3,4-tetrahydroquinoline (intermediate **A**), which is produced via the Michael addition of the *β*-nitrostyrene (path I). The other possibility is to proceed through the rearrangement of the nitro group of intermediate B obtained from path II.

TABLE 3. Use of Silica Gel as a Replacement for DDQ To Generate Compound 4



1 **2**



4 (**3**)

entry	2	reflux time (h)	4[a] (%)
1	**2a**	15.5	**4a** (85)
2	**2b**	18.5	**4b** (75)
3	**2c**	15	**4c** (99)
4	**2e**	45.5	**4e** (94)
5	**2h**	9, 3.5[b]	**4h** (63)
6	**2i**	12, 4[b]	**4i** (80)
7	**2j**	15, 4[b]	**4j** (85)

[a] All yields were obtained from ^{1}H NMR spectral data with a known amount of toluene as an internal standard. [b] The reaction solution was heated at 45 °C for a few hours before DABCO was added. After the addition of DABCO, the solution was further heated at 45 °C for another few hours.

the solution was heated at 110 °C, the benzene evaporated. The silica gel was then washed with CH_2Cl_2, and upon evaporation of the solvent, product **4** was obtained (eq 3 and Table 3). It is obvious that the treatment with silica gel is a better method than the use of DDQ in the purification and the yields of 3-nitroquinolines **4** in both treatments were only slightly different.

Part d. Condensation of 2-Aminobenzaldehyde Derivatives with Nitro Olefins. Steric effects frequently play an important role in reactions. When *N*-methyl-2-aminobenzaldehyde[11] **7** was used, the results were different from eq 1 and Table 1. For example, only 49% of **8** and 6% of **9** were observed when **7** was reacted with **2a** under reflux for 5 days (Scheme 3, eq 4). Similarly, only 40% of **10** and traces of **11** were observed when **2c** was used (Scheme 3, eq 5). We also got the similar results when compound **12**[11] was used (Scheme 3, eqs 6 and 7). Although the more reactive *β*-nitrostyrene **2l** was used, the reaction time was still lengthy and the yield of **13** was low (Scheme 3, eq 6). In eqs 5 and 6, an increase in refluxing time failed to improve the product yield.

The elimination products **9** and **11** were produced from intermediate **A** in Scheme 4, which was obtained by a Michael addition of nitrostyrene. There are two possible ways (Scheme 4) to produce the rearrangement products **8**, **10**, **13**, and **15**. The first possibility is related to the aryl rearrangement of 2-aryl-4-hydroxy-3-nitro-1,2,3,4-tetrahydroquinoline (intermediate **A** in Scheme 4) which is produced via the Michael addition (path I of Scheme 4) of *β*-nitrostyrene. The second possibility is to proceed through the rearrangement of the nitro group of intermediate **B** in Scheme 4 which is produced from path II. To determine the mechanism of the formation of the rearrangement product, ^{13}C-labeled and deuterium-labeled nitrostyrenes **2m**, **2n**, and **2o** were reacted with

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(11) Methyl iodide and potassium carbonate were added to the methyl anthranilate THF solution. After 3 days at room temperature, the solution was quenched and *N*-methyl methylanthranilate was isolated by flash chromatography. The procedures of ref 6a to give *N*-methyl-2-aminobenzaldehyde were then followed. A similar procedure was used to obtain *N*-benzyl-2-aminobenzaldehyde, where benzyl bromide replaced methyl iodide.

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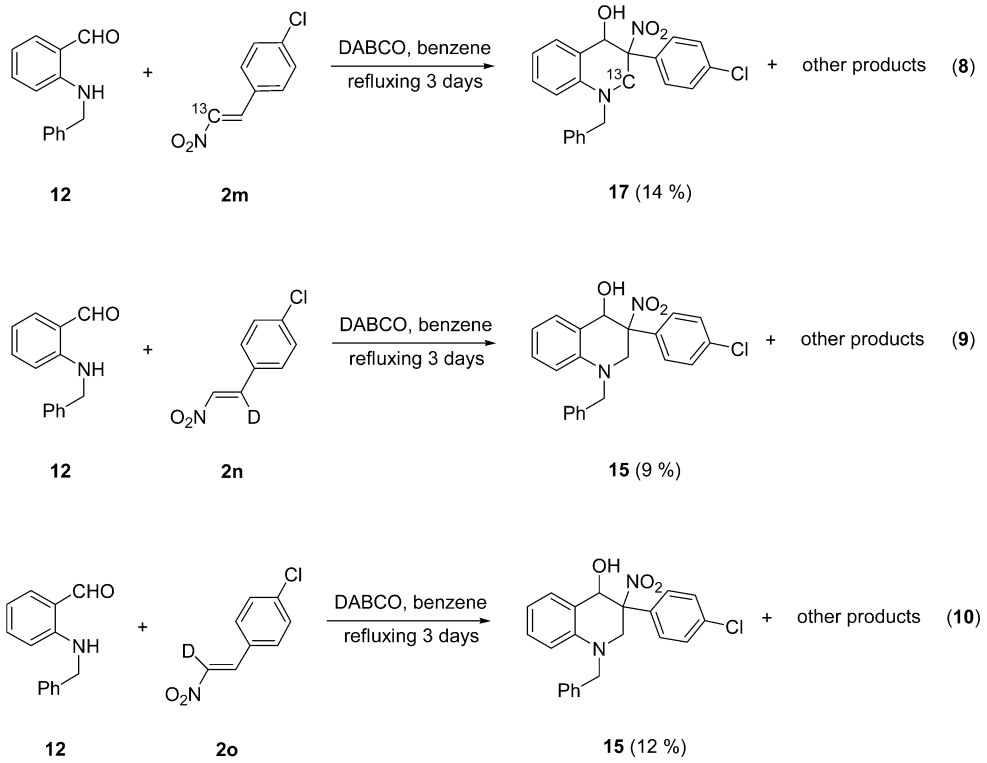
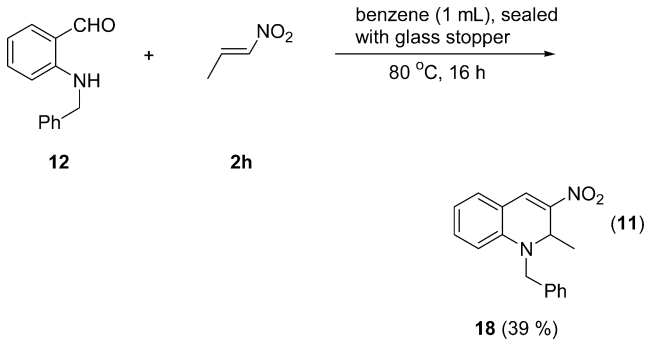
SCHEME 5



12, respectively (Scheme 5, eqs 8−10). From eq 8 using **2m**, product **17** was produced in a reaction where the amino group of **12** attacked the β carbon (path II in Scheme 4) but not the α carbon (path I of Scheme 4) of β-nitrostyrene **2m** to form intermediate **B** (Scheme 44). In eqs 9 and 10, product **15** was also obtained. The reason **15** in eq 9 is obtained is due to the loss of deuterium on intermediate **B** (Scheme 4) during the rearrangement, and this suggests that the rearrangement from intermediate **B** to the rearrangement product, as in **15**, occurred via intermediate **C**. Intermediate **B** lost HNO_2 to form intermediate **C**, and NO_2^- was then added to the 3-position of intermediate **C** to form the rearrangement product (Scheme 5). In eq 10, the loss of deuterium may be due to the basic environment which permits the exchange of the acidic deuterium on intermediate **B**.

It is not surprising that when the less sterically bulky nitro olefin **2h** was used instead of **2l** or **2c** in a reaction with **12** (eq 11), only the Michael addition product **18** (39%) was obtained. In conclusion, the reactions in eq 6 and 7 only proceeded through path II but not path I (Scheme 4), and products **9** and **11** prove that 1, 4-addition (path I in Scheme 4) occurred in eqs 4 and 5. A different steric bulky group on the amino group of 2-aminobenzaldehyde derivatives, **1**, **7**, and **12**, and different steric bulky groups R on nitro olefins **2** caused the reaction to proceed by a different mechanism. When 2-aminobenzaldehyde **1** was used (eq 1), only Michael addition occurred. However, when the steric hindrance increased, the reactions through path II occurred. The reactions (eqs 4 and 5) proceeded through both paths I and II (Scheme 4) when **7** containing a methyl group attached on amino group was reacted with β-nitrostyrenes **2a** and **2c**. When **12**, which contains a benzyl group attached to the amino group, was reacted with β-nitrostyrenes **2c** and **2l** (eqs 6 and 7), only the products through path II (Scheme 4) were obtained. However, when a less bulky nitro olefin **2h** reacted with **12**, only a Michael addition product was observed (eq 11).



After purification of **8** and **10**, the ^{1}H NMR and ^{13}C NMR spectra were obtained using $CDCl_3$ as the solvent. When the NMR tubes containing compound **8** and **10** were kept at room temperature for 1 week, crystals appeared. When the crystals were analyzed by the X-ray crystallography, surprisingly, their structures were found to be **19** and **20** (Figure 1). A possible mechanism is

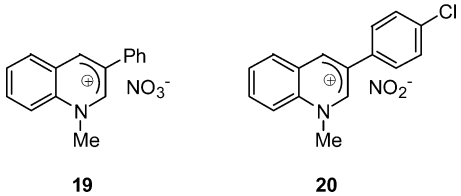
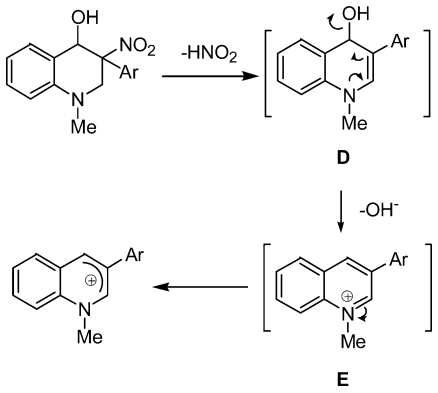


FIGURE 1. Two surprising crystal structures **19** and **20** were obtained, respectively, in mild acidic condition when pure **8** and **10** were kept in NMR tubes at room temperature for 1 week.

SCHEME 6. Possible Mechanism To Form Products 19 or 20[a]



[a] The key step is the transformation of intermediate D to intermediate E under mild acidic conditions.

proposed for this in Scheme 6 to proceed through intermediate **D** and **E**. Intermediate **D** in Scheme 6 and intermediate **C** in Scheme 4 are the same. However, **19** and **20** were not found in eq 3 and 4, respectively, possibly due to the basic reaction conditions employed and the transformation from intermediate **D** to intermediate **E** (Scheme 6) would be improved in the mild acidic condition. Intermediate **D** can proceed smoothly to intermediate **E** (Scheme 6) in $CDCl_3$ because it is mildly acidic.

Conclusion

In terms of scientific relevance, examples of addition/condensation reactions involving nitro olefins can be found in the literature, although not with 2-aminobenzaldehydes. This study of such reactions involving nitro olefins with 2-aminobenzaldehydes represents an interesting variation in the Friedlander-type-quinoline synthesis. The two-step/one-pot variant is an improvement in that 3-nitro-1,2-dihydro quinolines can be obtained from the first step and 3-nitroquinolines can be produced from the second step and all the yields are reasonable to good. In the second step (oxidation), two choices including the use of DDQ or silica gel can be selected and silica gel seems to be preferred to DDQ due to the ease of purification. When *N*-substituted 2-aminobenzaldehydes were used in the reactions, unique rearrangement products **8**, **10**, **13**, and **15** were obtained. The rearrangement leading to **8**, **10**, **13**, **15**, and their salts **19** and **20** are unusual. In fact, **19** and **20** represent interesting electrophiles and their preparation and use would be as interest in future studies. Finally, this method can be recommended for its ease of handling, the control of the desired products, and the high yields of the products.

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Supporting Information Available: Experimental procedures for all compounds not described in the text. LRMS, HRMS, and NMR spectra of representative compounds. X-ray data for **3g**, **4a**,**c**,**i**, **13 (isomer B)**, **15 (isomer A)**, **17**, **19**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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