

A CONVENIENT PREPARATION OF CONJUGATED NITRO OLEFINS BY ELECTROCHEMICAL METHOD

Atsutaka Kunai,* Yasuo Yanagi, and Kazuo Sasaki

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Shitami, Saijo-cho, Higashi-Hiroshima 724, Japan

Abstract. A convenient transformation of aliphatic olefins into conjugated nitro olefins was attained by electrolytic oxidation. When cyclohexene, cyclooctene, and 1-hexene were electrolyzed in aq. NaNO_2 - NaNO_3 solution, corresponding nitro olefins were formed in good yields.

Aliphatic nitro compounds have been recognized as useful intermediates in organic syntheses.¹⁾ Of these, increasing attention has been paid to conjugated nitro olefins.^{1c,d) 2)} Many works dealing with the transformation of cyclic or acyclic olefinic units into unsaturated nitro units have been reported, e.g., addition of dinitrogen tetroxide followed by base catalyzed elimination,³⁾ nitration in conc. nitric acid,⁴⁾ or nitro-mercuration²⁾ or nitro-selenylation⁵⁾ followed by elimination of the metallic moiety.

These methods, however, seem to require special cares, in practice, for maintenance of the particular reaction conditions or for handling the highly toxic reagents, which make them disadvantageous and less convenient. We should like to report a much more convenient synthesis of nitro olefins which is achieved by means of anodic oxidation of cyclic and acyclic olefins in aqueous NaNO_2 solution, under non-specialized and mild conditions.

A typical procedure is as follows. Electrolysis: Cyclohexene (6.1 mmol) and NaNO_2 (50 mmol) were added to a heterogeneous mixture of CH_2Cl_2 (5 cm³) and an aq. base solution containing appropriate supporting electrolyte (25 cm³), placed in an anode compartment of a divided cell. This anolyte was stirred vigorously at 10-15°C and polarized using a Pt plate (6 cm²) at a current of 300 mA. After the electrolysis, products were extracted with ether. The extract was swirled with triethylamine (6 mmol) for 20 min, acidified with 30% acetic acid, washed with 5% NaHCO_3 and water, and dried. The concentrated extract was subjected to glc analysis (PEG 20M and SE 30). Results are shown in Tables 1 and 2. Isolation of Nitro Olefin⁶⁾: Cyclohexene (6.25 mmol) was electrolyzed in 2M NaNO_2 -2M NaNO_3 solution (5 F mol⁻¹). After the same treatment as above, products were distilled in vacuo to afford 571 mg of crude 1-nitrocyclohexene containing small amounts of 2-nitro-1-cyclohexyl nitrate and low boiling point materials. Pure 1-nitrocyclohexene was isolated by liquid chromatography (Merck, Lobar column B) using hexane- CHCl_3 (2:1) as an eluent; 294 mg, 37% based on cyclohexene used; ν_{max} (neat) 1515 and 1335 cm⁻¹ (C=C- NO_2); δ (CDCl_3) 7.25 (t, 1H, olefinic), 2.1-2.9 (m, 4H, allylic), and 1.5-2.1 ppm (m, 4H, others); m/e 127 (M^+) and 81 (M^+-NO_2).

As indicated in Table 1, nitration of cyclohexene was effected in moderate yields with use of NaNO_2 as a nitrating agent and by passing ca. 6 F mol⁻¹ of the electricity whenever the base solution was water containing various neutral supporting electrolytes, such as NaClO_4 , NaCl , or KH_2PO_4 - K_2HPO_4 . The yield

was almost independent of current density.

In these cases, the anolyte mixture turned weakly acidic in the course of the electrolysis (initially 7 and finally 3-4). When the pH of the solution was adjusted at values higher than 6 by addition of NaHCO_3 , only a small amount of 1-nitrocyclohexene was formed. Moreover, when the anolyte containing both cyclohexene and NaNO_2 was treated without passing the current at pH 3-4 for several hr, nitrocyclohexene was formed only in few percents. These facts clearly indicate that the nitration in the nitrite solution occurs under weakly acidic conditions and the electrolysis of the mixture is essential.

Interestingly, when 70% acetonitrile was used as a solvent, where homogeneous solution was resulted, yields of nitrocyclohexene were miserably poor. This situation was the same when 50% dioxane was used.

Among experiments, improved results were obtained when the base solution was water containing 2M NaNO_3 (Table 2). By passing 4 F mol^{-1} of electricity into this solution containing cyclohexene and NaNO_2 , 1-nitrocyclohexene was produced in 41% yield (57% selectivity). Similarly, good selectivities were realized for cyclooctene (66%) and 1-hexene (84%). Detailed examination of optimum reaction conditions and mechanistic studies are in progress.

Table 1. Anodic Nitration of Olefins (6.1 mmol) in Aqueous NaNO_2 Solution (2M, 25 cm^3) at a Current Density of 50 mA cm^{-1}

Run,	Olefin,	Base Solution,	Q/ F mol^{-1}	Yield ^{a)} of Nitro Olefin/ %
1	Cyclohexene	1M NaClO_4	4.0	1-Nitrocyclohexene, 29
2	Cyclohexene	1M NaClO_4	6.0	1-Nitrocyclohexene, 34
3	Cyclohexene	1M NaCl	4.1	1-Nitrocyclohexene, 25
4	Cyclohexene	1M NaNO_3	4.1	1-Nitrocyclohexene, 29
5	Cyclohexene	0.5M KH_2PO_4 -0.5M K_2HPO_4	6.0	1-Nitrocyclohexene, 25
6	Cyclooctene	1M NaClO_4	4.3	1-Nitrocyclooctene, 36

a) Yields were determined by glc and based on olefin used.

Table 2. Anodic Nitration of Olefins (6.25 mmol) in Aqueous Solution Containing 2M NaNO_2 and 2M NaNO_3 (25 cm^3).

Run,	Olefin,	Q/ F mol^{-1}	Conversion/ %	Yield of Nitro Olefin/ %	Selectivity/ %
1	Cyclohexene	4.0	72	1-Nitrocyclohexene, 41	57
2	Cyclooctene	4.0	86	1-Nitrocyclooctene, 57	66
3	1-Hexene	4.5	75	1-Nitro-1-hexene, 63	84

REFERENCES AND NOTES

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