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Abstract: Several ketone allylhydrazones were electrochemically oxidized in methanol in the presence of sodium methoxide and potassium iodide to afford the corresponding azines. The electro-oxidation involves formation of a new carbon–nitrogen double bond between an allylic carbon atom and the nitrogen atom of a hydrazone to afford a conjugated system. Optimal yields were obtained when 0.5 equivalents of sodium methoxide and a catalytic amount of potassium iodide were used as the supporting electrolyte at room temperature. Presumably, the electro-oxidation involves a two-electron oxidation process where the iodide ion functions as electron carrier.

Keywords: Allylhydrazones, azines, conjugated system, dehydrogenation, electro-oxidation, ketone hydrazones

Hydrazones are often employed as mediators in organic synthesis, in which Ag_2O[1,2] and HgO[3,4] are frequently used as the oxidant in the oxidations of hydrazones. Unfortunately, such metal-based reagents are expensive and/or produce environmentally harmful wastes. In contrast, we have demonstrated that electrochemical methods for organic synthesis, especially those involving nitrogenous compounds such as amines,[5,6] enamines,[7–9] and hydrazones[10,11] as substrates, offer inexpensive, environmentally-friendly alternatives. In particular, we have

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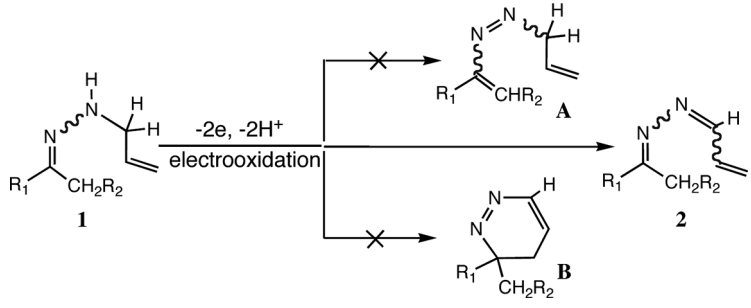
reported the highly effective electrochemical technique for the oxidative conversion of hydrazones to several useful organic compounds.[12–14] In this study, we have successfully carried out the electro-oxidation of ketone allylhydrazones **1** to afford the corresponding dehydrogenation products **2** (azines), as illustrated in Scheme 1. Although a variety of methods are found in the literature for the formation of azines via hydrazones,[10,15–18] to the best of our knowledge, only a few reports have described the chemical behavior of aldehyde or ketone allylhydrazones; moreover, studies that describe the oxidation of ketone allylhydrazones, including those that employ typical chemical oxidizing reagents, have yet to be reported.[19–22] Consequently, we believe that our approach in oxidizing ketone allylhydrazones into the corresponding azines using electrochemical methods is novel.

To begin our study, three probable outcomes for the electro-oxidation of ketone allylhydrazones **1**, as shown in Scheme 1, were proposed. Subsequent experimental results revealed that the ketone allylhydrazones were oxidized by forming an unsaturated bond to yield the corresponding azine **2**, with an extended conjugated system within the entire molecule. Contrary to our expectations, the formation of alkadiene **A** and cyclic **B**, both possessing an azo group, was not observed.[12] According to our results, the electro-oxidation products generally possess one carbon–carbon and two carbon–nitrogen double bonds that are conjugated to each other. Accordingly, the electro-oxidation, under similar reaction conditions, of acetophenone ethylhydrazone, which has a structure analogous to acetophenone allylhydrazone (**1a**), hardly gave the corresponding dehydrogenation product.

To optimize the reaction conditions for the electro-oxidation of the allylhydrazones, we investigated the reaction of **1a** (as a model substrate) to yield the corresponding azine, acetophenone allylidenehydrazone (**2a**). First, the electro-oxidations were examined in the presence of various



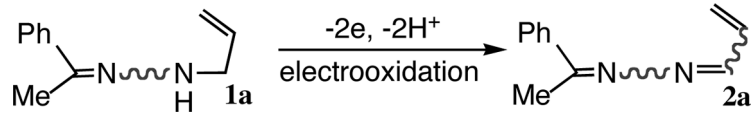
Scheme 1. Probable outcomes for the anodic oxidation of ketone allylhydrazones.

supporting electrolytes, as listed in Table 1. When using neutral salts (runs 1–3), the yields of **2a** were less than 10%— in such cases, considerable amounts of tar-like material remained after removal of the reaction solvent, along with acetophenone (as detected by gas chromatography [GC] analysis). The yield improved markedly by employing basic electrolytes such as NaCN (run 4), NaOH (run 5), and NaOMe (run 6). Furthermore, the addition of a catalytic amount of KI in the presence of NaOMe resulted in the highest yield (88%, run 7). Other halide ion sources such as KBr (run 8) and KCl (run 9), which can often act as electron carriers, did not exhibit any advantageous effects on the yields.[23] Our studies also showed that the amount of the added KI, from 2 mmol (88%) to 10 mmol (75%), had a small effect on the yields.

Preliminary electro-oxidations revealed that the amount of the charge passed (0.5, 1.0, and 1.5 F mol^{-1}) increased the formation of **2a** proportionally (24%, 44%, and 60%, respectively). The maximum yield of 88% was obtained after passage of 2.2 F mol^{-1} (ca. 118 min). Furthermore, excessive passage (3.0 F mol^{-1}) caused a decrease in the yield (73%).

Using the optimal reaction conditions corresponding to the best yields listed in Table 1, the electro-oxidation of ketone allylhydrazones **1b–h** were carried out, and the results are shown in Table 2. During the course of the electrooxidations, the composition of the reaction mixture was monitored using GC analysis to determine the end point of the

Table 1. Electro-oxidation of acetophenone allylhydrazone **1a**[a]

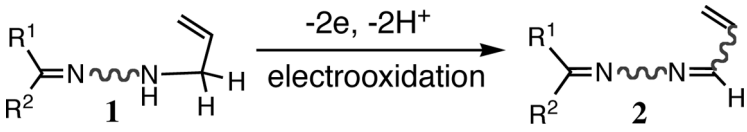


Runs	Supporting electolyte	Quantity (mmol)	Yields of **2a** (%)[b]
1	*p*-TsON(Et)$_4$	5	9
2	$NaClO_4$	5	4
3	KI	5	4
4	NaCN	5	48
5	NaOH	5	63
6	NaOMe	5	69
7	NaOMe + KI	5 + 2	88
8	NaOMe + KBr	5 + 2	31
9	NaOMe + KCl	5 + 2	49

[a]Substrate **1a**: 10 mmol, MeOH: 40 mL, constant current: 0.3 A, current passed: 2.2 F mol^1, rt: ca. 15 °C.

[b]Determined by GC analysis.

Table 2. Electro-oxidation of several ketone allylhydrazones **1**[a]

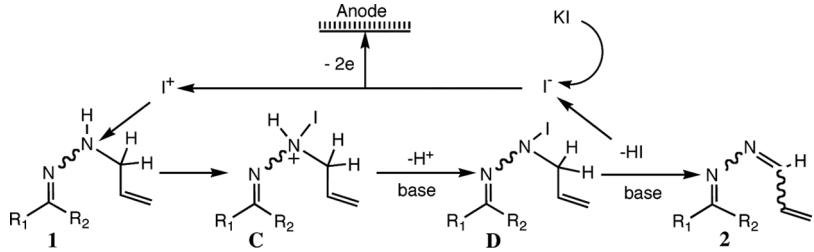


Runs		Substrate R^1	Substrate R^2	Current passed (F mol^{-1})	Yield of **2** (%)[b]
1	**1a**	Ph	Me	2.2	78
2	**1b**	4-Me–C_6H_4–	Me	2.5	78
3	**1c**	4-MeO–C_6H_4–	Me	2.4	83
4	**1d**	4-Cl–C_6H_4–	Me	2.4	77
5	**1e**	Ph	Et	2.4	72
6	**1f**	–$(CH_2)_4$–		2.2	56
7	**1g**	–$(CH_2)_5$–		2.3	61
8	**1h**	*n*-C_3H_7	*n*-C_3H_7	2.5	60

[a]Substrate **1**: 10 mmol, KI: 2 mmol, NaOMe: 5 mmol, MeOH: 40 mL, constant current: 0.3 A, rt: ca. 15 °C.
[b]Isolated yield.

reaction. Although the electrolytic currents that were necessary to consume the allylhydrazones (2.2–2.5 F mol^{-1}) were not significantly different, higher yields of the corresponding azines were observed for the aromatic (**1a–e**) than for the aliphatic substrates (**1f–h**). For these electro-oxidations, the products were obtained as a yellow viscous oily liquid that gradually changed into a brownish liquid with increased viscosity upon standing at room temperature within several days. Especially products obtained from aliphatic substrates were considerably more unstable than those that possessed an aromatic moiety. It is reasonable to assume that the newly formed conjugated systems can extend to include the aromatic moiety and stabilize the structure against decomposition and/or polymerization. Interestingly, the reaction is analogous to our previously reported dehydrogenation of benzyl-type amines,[6] where a hydrogen leaves anodically from a benzylic carbon, whereas a hydrogen leaves from an allylic carbon in this current study.

Although details of the electro-oxidation process remain unclear, a reasonable reaction pathway for the formation of the conjugated system in the presence of iodide ion is shown in Scheme 2. Initially, the iodide ion (I^-, derived from KI) is oxidized on the anode to form an iodonium ion (I^+). The nitrogen atom of substrate **1** would be attacked by the iodonium ion to form ammonium ion **C**, followed by deprotonation to form



Scheme 2. Proposed reaction pathway for the formation of the conjugated system.

N-iodide **D**. Immediate elimination of HI from the *N*-iodide **D** would give desired azine **2**. The iodonium ion would continue to be reproduced on the anode. Presumably, the reaction proceeds only via indirect electrooxidation, in which the iodide ion plays an important role as an electron carrier.[6,24,25] In such a case, NaOMe may serve as a suitable base to facilitate both the deprotonation of ammonium ion **C** and elimination of HI from *N*-iodide **D**. Essentially, substrate **1** loses two protons and two electrons (two-electron oxidation) during the course of the reaction.

In conclusion, we have demonstrated that the electrochemical technique can be effectively utilized to oxidize ketone allylhydrazones **1** to afford the novel conjugated compounds **2**. The benefits of this electrochemical methodology include (1) absence of any oxidants and/or special reagents, (2) mild reaction conditions (room temperature), (3) readily available substrates, and (4) a simple, one-pot procedure.

EXPERIMENTAL

Ketone allylhydrazones were prepared via typical condensation reaction by refluxing the ketone with slightly excess molar amounts (1.1–1.3 molar equivalent to ketone used) of allylhydrazine in ethanol. Azines obtained (**2a–h**) were characterized by IR, mass, and NMR spectroscopy, as listed here. Preparative-scale electro-oxidations were carried out in a tall 50-mL beaker equipped with a fine frit cup (as the cathode compartment), a nickel coil (as the cathode), and a cylindrical platinum net (55 mesh) (as the anode). Electro-oxidations of the substrates were carried out as follows: a solution of the substrate (**1a–h**, 10 mmol) and KI (0.33 g, 2 mmol) in absolute MeOH (40 mL) containing NaOMe (5 mmol) was electro-oxidized under a constant current (0.3 A). During the course of the electro-oxidation, the anolyte was magnetically stirred while the temperature of the cell was maintained at ca. 15 °C. Composition of the anolyte was frequently monitored using GC analysis (SE-30: 2.0 m).

Upon near-complete consumption of the substrate, the DC power supply was switched off, and the reaction mixture was concentrated in vacuo to about 15 mL at approximately 40 °C. The residue was subsequently extracted with *n*-hexane (6 × 30 mL). The hexane extracts were combined and dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was purified by silica-gel column chromatography using a mixture of ether and hexane (1:2) as the elution solvent. The products obtained were stored in a refrigerator.

Data

Acetophenone Allylidenehydrazone **2a**

Bp 97–99 °C/2 mmHg. IR (neat): 2964, 1631, 1598, 1576, 1445, 1364, 1287, 998, 762, 692 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.42$ (s, 3H, CH_3), 5.7–5.8 (m, 2H,=CH_2), 6.6–6.8 (m, 1H, =CH−), 7.3–7.5 (m, 3H, Arom), 7.8–7.9 (m, 2H, Arom), 8.04 (d, $J = 10$ Hz, 1H, −N=CH−). ^{13}C NMR ($CDCl_3$): $\delta = 15.12$, 126.84, 127.08, 128.38, 130.10, 134.74, 138.17, 159.83, 164.15. MS m/z (%): 172 (50) [M^+], 145 (44) [M^+-vinyl], 144 (22), 130 (100), 104 (57), 103 (28), 77 (76), 51 (34). HRMS: m/z calcd. for $C_{11}H_{12}N_2$: 172.1000; found: 172.0997 [M^+].

4-Methylacetophenone Allylidenehydrazone **2b**

Bp 104–106 °C/3 mmHg. IR (neat): 2962, 2921, 1630, 1597, 1362, 1291, 1184, 1116, 997, 927 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.39$ (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 5.7–5.8 (m, 2H, $=CH_2$), 6.6–6.8 (m, 1H, =CH−), 7.21 (d, $J = 8$ Hz, 2H, Arom), 7.77 (d, $J = 8$ Hz, 2H, Arom), 8.05 (d, $J = 10$ Hz, 1H, −N=CH−). ^{13}C NMR ($CDCl_3$): $\delta = 15.04$, 21.37, 126.80, 126.90, 129.10, 134.79, 135.38, 140.34, 159.72, 164.20. MS m/z (%): 186 (49) [M^+], 159 (24) [M^+-vinyl], 144 (100), 132 (12), 118 (41), 117 (28), 91 (43), 65 (24). HRMS: m/z calcd. for $C_{12}H_{14}N_2$: 186.1157; found: 186.1132 [M^+].

4-Methoxyacetophenone Allylidenehydrazone **2c**

Bp 125–127 °C/2 mmHg. IR (neat): 2960, 1628, 1606, 1511, 1363, 1307, 1252, 1175, 1030, 833 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.41$ (s, 3H, CH_3), 3.85 (s, 3H, CH_3O), 5.7–5.8 (m, 2H, =CH_2), 6.6–6.8 (m, 1H, =CH−), 6.93 (d, $J = 9$ Hz, 2H, Arom), 7.85 (d, $J = 9$ Hz, 2H, Arom), 8.06 (d, $J = 10$ Hz, 1H, −N=CH−). ^{13}C NMR ($CDCl_3$): $\delta = 14.88$, 55.35, 113.71, 126.76, 128.43, 130.73, 134.85, 159.76, 161.30, 163.93. MS m/z

(%): 202 (70) [M^+], 175 (22) [M^+-vinyl], 160 (100), 148 (27), 134 (42), 133 (34), 119 (11), 92 (18). HRMS: m/z calcd. for $C_{12}H_{14}ON_2$: 202.1106; found: 202.1117 [M^+].

4-Chloroacetophenone Allylidenehydrazone **2d**

Bp 110–112 °C/2 mmHg. IR (neat): 2926, 1630, 1596, 1489, 1398, 1363, 1289, 1094, 1012, 831 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.41$ (s, 3H, CH_3), 5.7–5.8 (m, 2H, $=CH_2$), 6.6–6.8 (m, 1H, =CH−), 7.38 (d, $J = 9$ Hz, 2H, Arom), 7.81 (d, $J = 9$ Hz, 2H, Arom), 8.03 (d, $J = 10$ Hz, 1;H, −N=CH−). ^{13}C NMR ($CDCl_3$): $\delta = 14.19$, 127.39, 128.16, 128.42, 134.67, 136.17, 136.57, 160.13, 163.04. MS m/z (%): 206 (45) [M^+], 179 (42) [M^+-vinyl], 166 (31), 164 (100), 144 (43), 138 (49), 111 (40), 75 (34). HRMS: m/z calcd. for $C_{11}H_{11}N_2Cl$: 206.0611; found: 206.0600 [M^+].

Propiophenone Allylidenehydrazone **2e**

Bp 95–97 °C/2 mmHg. IR (neat): 2973, 2936, 1629, 1595, 1576, 1446, 999, 924, 772, 693 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta =$ 1.13 (t, $J = 8$ Hz, 3H, CH_3), 2.97 (q, $J = 8$ Hz, 2H, CH_2), 5.7–5.8 (m, 2H, $=CH_2$), 6.6–6.8 (m, 1H, =CH−), 7.4–7.5 (m, 3H, Arom), 7.8–7.9 (m, 2H, Arom), 8.06 (d, $J = 10$Hz, 1H, −N=CH−). ^{13}C NMR ($CDCl_3$): $\delta =$ 12.09, 21.99, 126.94, 127.09, 128.48, 130.01, 134.81, 136.98, 159.94, 169.22. MS m/z (%): 186 (51) [M^+], 159 (28) [M^+-vinyl], 130 (100), 117 (19), 104 (66), 103 (19), 77 (51), 51 (21). HRMS: m/z calcd. for $C_{12}H_{14}N_2$: 186.1157; found: 186.1131 [M^+].

Cyclopentanone Allylidenehydrazone **2f**

Bp 98–101 °C/17 mmHg. IR (neat): 2960, 2871, 2827, 1652, 1618, 1418, 1201, 1117, 1000, 930 cm^{-1}. ^1H NMR (CD_3OD): $\delta = 1.7$–1.9 (m, 4H, $2CH_2$), 2.4–2.6 (m, 4H, $2CH_2$), 5.8–5.9 (m, 2H, $=CH_2$), 6.5–6.6 (m, 1H, =CH−), 7.90 (d, $J = 10$ Hz, 1H, −N=CH−). ^{13}C NMR (CD_3OD): $\delta =$ 30.25, 30.85, 34.01, 34.38, 128.85, 135.34, 161.50, 183.57. MS m/z (%): 136 (59) [M^+], 135 (34), 109 (54) [M^+-vinyl], 80 (100), 54 (51), 39 (37), 28 (36), 27 (35). HRMS: m/z calcd. for $C_8H_{12}N_2$: 136.1000; found: 136.0994 [M^+].

Cyclohexanone Allylidenehydrazone **2g**

Bp 105–107 °C/15 mmHg. IR (neat): 2933, 2858, 1641, 1610, 1448, 1312, 1102, 1059, 1000, 928 cm^{-1}. ^1H NMR (CD_3OD): $\delta = 1.6$–1.8 (m, 6H,

$3CH_2$), 2.3–2.4 (m, 2H, CH_2), 2.6–2.7 (m, 2H, CH_2), 5.8–5.9 (m, 2H, $=CH_2$), 6.5–6.6 (m, 1H, =CH−), 7.89 (d, $J = 10$Hz, 1H, −N=CH−). ^{13}C NMR (CD_3OD): $\delta =$ 26.79, 27.76, 28.81, 29.57, 36.49, 128.55, 135.47, 161.47, 175.52. MS m/z (%): 150 (100) [M^+], 148 (87), 123 (58) [M^+-vinyl], 80 (69), 54 (42), 41 (53), 39 (40), 27 (32). HRMS: m/z calcd. for $C_9H_{14}N_2$: 150.1157; found: 150.1147 [M^+].

4-Heptanone Allylidenehydrazone **2h**

Bp 86–88 °C/17 mmHg. IR (neat): 2961, 2933, 2872, 1637, 1610, 1463, 1378, 1118, 998, 925 cm^{-1}. ^{1}H NMR (CD_3OD): $\delta =$ 0.92 (t, $J = 7$ Hz, 3H, CH_3), 0.97 (t, $J = 7$ Hz, 3H, CH_3), 1.51 (six, $J = 8$ Hz, 2H, CH_2), 1.63 (six, $J = 8$ Hz, 2H, CH_2), 2.3–2.4 (m, 2H, CH_2), 2.4–2.5 (m, 2H, CH_2), 5.8–5.9 (m, 2H, $=CH_2$), 6.5–6.7 (m, 1H, =CH−), 7.86 (d, $J = 10$ Hz, 1H, −N=CH−). ^{13}C NMR (CD_3OD): $\delta =$ 14.26, 14.62, 21.06, 33.80, 39.64, 128.23, 135.56, 160.80, 175.51. MS m/z (%): 166 (11) [M^+], 139 (7) [M^+-vinyl], 123 (39), 97 (48), 82 (100), 68 (51), 54 (63), 41 (77). HRMS: m/z calcd. for $C_{10}H_{18}N_2$: 166.1470; found: 166.1457 [M^+].

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