

# Indirect Electrochemical Reduction of Unsaturated Alcohols

TORBEN LUND and HENNING LUND

Department of Organic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

Allyl alcohol and some of its derivatives have been reduced electrochemically by a mercury electrode to unsaturated hydrocarbons in a strongly acidic medium containing iodide. During the reaction a shift of the double bond generally occurs. The reaction involves a transformation of the alcohol to an iodide, reaction of the iodide with mercury, protonation of the organomercury compound, and reduction of the mercuric salt to mercury. Benzyl alcohols are similarly reduced to hydrocarbons.

During an investigation on the electrochemical transformation of biomass to other chemicals it became of interest to study the reductive removal of allylic hydroxyl groups. Such a reaction has been accomplished by electrocatalytic reduction of allyl alcohols by a platinized platinum electrode in acidic solutions.<sup>1–4</sup> Under such conditions the saturated hydrocarbon was the main product, but the presence of some alkene and the non-reducibility of the saturated alcohol argued for the first step being the reductive removal of the hydroxyl group.

A reductive cleavage of the carbon-oxygen bond in a derivative of allyl alcohol is found in the reduction of some cephalosporanic acid derivatives to the corresponding 3-methylenecephane derivatives, in which the double bond was not reduced, but moved out of conjugation with the ester group.<sup>5–7</sup>

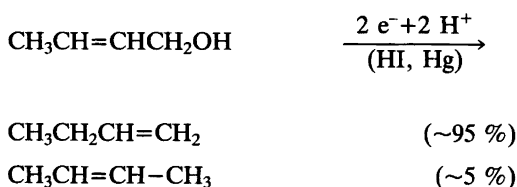
This work reports on the electrochemical reduction of allyl and benzyl alcohols in acid solution containing iodide. The following compounds have been investigated: Allyl alcohol (1), crotyl alcohol (2), 3-butenol-2 (3), 2-butene-1,4-diol (4), propargyl alcohol (5), benzyl alcohol (6), and cinnamyl alcohol (7).

## RESULTS

The alcohols 1–5 were electrolyzed in 6 M hydrochloric acid containing 1 M sodium iodide ("standard medium"); the aromatic alcohols 6 and 7 were reduced in the standard medium to which acetic acid was added to increase the solubility of the substrates. The temperature was held between 40 and 60 °C in most cases, but for some compounds (e.g. 5) the transformation of the alcohol to the iodide required a higher temperature (up to 90 °C). The cathode potential was kept at –0.2 V (SCE).

*Allyl alcohol.* Electrolysis of a solution of 1 (0.5 M) under standard conditions at a mercury cathode resulted in a high current density (0.1–0.2 A cm<sup>–2</sup>) and a copious evolution of propene. After electrolysis a small amount of a 20:1 mixture of allyl iodide and 2-iodopropane could be extracted from the catholyte.

*Crotyl alcohol.* 2 was electrolyzed under similar conditions at a mercury cathode; the evolved gas consisted of ~95 % 1-butene (8) and ~5 % 2-butene (9). After electrolysis unreacted 2 was the only compound detected in the catholyte.

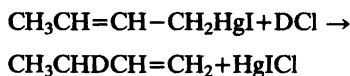


A double bond shift occurs in one of the steps during the reaction. It was attempted to identify the reaction responsible for the shift by doing the reaction stepwise.

Heating crotyl alcohol to 50 °C in the standard medium for 2–4 min resulted in the formation of a mixture of iodobutenes, (*E*)-1-iodo-2-butene (*10*) (85–90 %) and (*Z*)-1-iodo-2-butene (*11*) (15–10 %). The ratio of the two isomers did not change noticeably if the reaction was run at 65 °C. The main product was thus formed without allylic rearrangement.

Electrolysis of the mixture of *10* and *11* under standard conditions at a mercury electrode resulted in a similar mixture (~20:1) of *8* and *9* as obtained at the electrolysis of *2*.

Addition of *10* to boiling diethyl ether in contact with mercury gave after reflux for 3 h crotylmercuric iodide,  $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2-\text{HgI}$  (*12*); the compound can be stored at –20 °C, but decomposes slowly to dicrotylmercury and mercuric iodide at room temperature. Reaction between *12* and 6 M hydrogen chloride resulted in the formation of 1-butene and mercuric salts. A shift in the double bond thus occurs in this step. If *12* reacts with deuterium chloride, 3-deutero-1-butene is formed.



Treatment of *2* with the standard medium and mercury using efficient stirring produced mercuric iodide and a gas consisting of a 20:1 mixture of *8* and *9*. When the chemical reaction had finished, the mercuric iodide was reduced to mercury electrochemically; the electricity consumption was close to that observed in the electrolytic reduction of *2* under standard conditions.

Polarographic data for *12*, *10*, and mercuric iodide in M hydrochloric acid show that they all give a wave at  $-0.24 \pm 0.02$  V (SCE); in aqueous, unbuffered potassium chloride, *10* and *12* give waves at –0.2 and –1.1 V (SCE).

3-Butenol-2 (*3*) gives mainly 1-butene (+~5 % 2-butene) on electrolytic reduction in the standard medium; the mixture is similar to that obtained from *2*. This is apparently a reduction without a shift of the double bond. However, treatment of *3* with the standard medium produced mainly *10* with allylic rearrangement. *10* reacts with mercury to *12*, which with acid forms *10*; in the latter reaction the double bond shifts again, so the position is then the same as in *3*.

2-Butene-1,4-diol (*4*) produces on electrolytic reduction in the standard medium a mixture of 1,3-butadiene (*13*) and *8*. The ratio of *13* to *8* depended on the temperature; it was 3:1 at 45 °C and 1:1 at 35 °C; the dehydration of the intermediate, an unsaturated alcohol, is favoured by the higher temperature. If the temperature was raised to 55–60 °C, the solution turned dark due to polymerization of some of the reaction products.

Attempts to reduce *13* to *8* electrolytically by bubbling *13* slowly through the standard catholyte solution at 40 °C was not met with success; *13* was recovered unchanged. *13* seems thus not to be an intermediate in the formation of *8* from *4* under these conditions.

Propargyl alcohol (*5*) requires a higher temperature (70–90 °C) for its transformation to the iodide than *1–4*; the gaseous mixture obtained from the electrolytic reduction consisted of propyne (50 %), propene (30 %), 1,2-propadiene (15 %), and 5 % unidentified products. The rather drastic conditions may isomerize the initially formed products. Reduction of 3-bromopropyne in the standard solution at 40 °C gave 1,2-propadiene and propyne in the ratio 2:3.

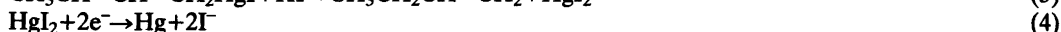
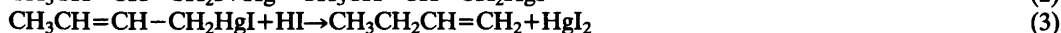
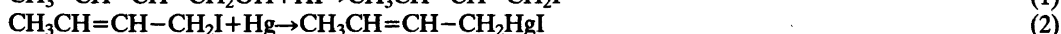
Benzyl alcohol (*6*) was reduced in a 1:1 mixture of acetic acid and the standard medium; the acetic acid was added to increase the solubility of *6*. The reduction produced mainly toluene; benzyl iodide (5 %) was found as side product.

Cinnamic alcohol (*7*) was reduced electrolytically at 50–60 °C in a 1:3 mixture of 6 M hydrochloric acid and acetic acid containing 1 M sodium iodide. The main product (70 %) was 3-phenyl-1-propene (*14*); 3,4-diphenyl-1,5-hexadiene (*15*) was isolated in 10 % yield; the remaining 20 % consisted of isomers and further reduced derivatives of *14* and *15* and traces of a phenylchloropropane.

## DISCUSSION

Crotyl alcohol will be discussed as a model for the reduction of  $\alpha,\beta$ -unsaturated carbinols in the standard medium at a mercury electrode. The sequence given in Scheme 1 is suggested.

Reaction (1) goes relatively fast and proceeds for primary alcohols essentially without allylic rearrangement; *3* reacts with allylic rearrangement, and results from *2* and *3* suggest that the



### Scheme 1.

same equilibrium mixture is obtained from 2 and 3 under the conditions employed here. This is consistent with earlier reported data.<sup>8</sup>

Reaction (2) has been observed for benzyl and allyl iodides and bromides both in alcoholic media<sup>8</sup> and in acetonitrile.<sup>10,11</sup> According to Hush and Oldham<sup>9</sup> dilute solutions of these halides do not react with unpolarized mercury, but under our standard conditions even unpolarized mercury reacted readily with crotyl iodide with formation of crotylmercuric iodide. This is consistent with the finding that alkyl bromides can be reduced by finely divided mercury.<sup>12</sup>

At the low pH of the standard solution the alkylmercuric iodide reacts with protons (3) yielding an alkene; a shift of the double bond occurs. A similar shift has previously been observed in the reaction of crotylmercuric iodide with perchloric acid from which 1-butene (95 %) and *cis*-2-butene (5 %) were formed,<sup>13</sup> and crotylmercuric bromide with acid under different conditions.<sup>14</sup>

The product, 3-deutero-1-butene, from the reaction between deuterium chloride and crotylmercuric iodide shows that the shift in the double bond thus occurs in the protonation step. The protonation at the double bond is thus faster than the electrophilic attack on the carbon-mercury bond. It is noticeable that the shift of the double bond occurs even if it results in a breaking of the conjugation between the double bond and the phenyl ring. A similar double bond shift has been observed<sup>5-7</sup> in the reduction of cephalosporanic acid derivatives.

The mechanism of the formation of 3,4-diphenyl-1,5-hexadien and other dimeric derivatives from 7 is not clear. Dicinnamylmercury could be involved; possibly it could form the products by catalysis by protons.

A competition between a dehydration and another reaction occurs during the reduction of 2-butene-1,4-diol (4). The product mixture of

1,3-butadiene (13) and 1-butene (8) could be explained by assuming that the first reduction produced 3-buten-1-ol (16) in a reaction analogous to that of 2. 16 could then be protonated at C-4 with formation of 2 or it could be protonated at oxygen with loss of water to 13.

### EXPERIMENTAL

**Materials.** The alcohols 1, 2, 3, 4, 6, and 7 were commercial products used without further purification.

**Crotyl iodide.** Crotyl alcohol (containing 6 % *cis*-crotyl alcohol) (17 g) was stirred for 2–4 min in 6 M hydrochloric acid (200 ml) containing M sodium iodide ("standard solution") at 40 °C. The lower phase of iodides was separated, diethyl ether added, and the organic phase washed with an aqueous solution of sodium carbonate and sodium sulfite. After drying (magnesium sulfate) of the organic phase the solvent was removed leaving 26 g of a 10:1 *trans*:*cis* mixture of 1-iodo-2-butenes, the ratio determined from <sup>13</sup>C NMR; in the <sup>1</sup>H NMR of the crude product no signals could be assigned to 3-iodo-1-butene. <sup>13</sup>C NMR (CDCl<sub>3</sub>): *E*-isomer, δ 6.31, 17.1, 128.4, 128.9; *Z*-isomer, 14.6, 26.8, 126.9, 128.1. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.67 (3H, m), 3.8 (2H, m), 5.7 (2H, m).

**Crotylmercuric iodide.** 1-Iodo-2-butene (*E*:*Z*, 10:1; 10.5 g) was added to diethyl ether (150 ml) and mercury (50 ml) and refluxed with stirring overnight. The warm diethyl ether phase was decanted from the mercury, filtered and cooled to –20 °C. Crotylmercuric iodide crystallized (8.0 g, 36 %) as white needles, m.p. 102–105 °C (103–104 °C).<sup>14</sup> IR (KBr): 2950 (w), 955 (s); MS: Mercury isotope pattern around *m/e* 384; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.75 (3H, m), 2.75 (2H, m), 5.6 (2H, m), the spectrum similar to that of crotylmercuric bromide.<sup>15</sup>

**3-Deutero-1-butene.** Crotylmercuric iodide (6.0 g) was added to 6 M deuterium chloride (5 g PCl<sub>5</sub> slowly added to 20 ml D<sub>2</sub>O) and the mixture stirred at ambient temperature for 1 h. The

evolved gas was condensed (acetone-CO<sub>2</sub>) and transferred to an NMR-tube. The product was identified as 3-deutero-1-butene from <sup>1</sup>H NMR. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.0 (3H, two triplets, <sup>3</sup>J<sub>CH<sub>3</sub>CH</sub> 7.3 Hz, <sup>3</sup>J<sub>CH<sub>3</sub>CD</sub> 1.14 Hz), 1.8–2.3 (1H, m), 4.8–5.1 (2H, m), 5.6–6.1 (1H, m, <sup>3</sup>J<sub>CH=,D</sub> 0.95 Hz).

**General procedure for reductions.** The substrate (5 ml) was dissolved in the standard medium (6 M HCl containing 1 M NaI) (250 ml) and reduced at a stirred mercury pool electrode (25 cm<sup>2</sup>) at –0.2 V (Ag/AgI comparison electrode) at 40–60 °C (70–90 °C for 5); initial current density 0.1–0.2 A cm<sup>–2</sup>; anolyte 6 M HCl, anode carbon. The evolved gas was condensed in a cooling trap (–50– –80 °C), 70–80 %. An appropriate sample of the condensed gas was transferred to an NMR-tube containing CDCl<sub>3</sub>, cooled in liquid nitrogen, degassed and sealed. The <sup>1</sup>H NMR spectra were compared with published spectra of propene,<sup>16</sup> 1-butene,<sup>16</sup> 2-butene,<sup>16</sup> 1,3-butadiene,<sup>17</sup> allene,<sup>18</sup> and propyne.<sup>19</sup>

**Reduction of benzyl alcohol (6).** Benzyl alcohol was reduced in a 1:1 mixture of acetic acid and the standard medium as described above. After completion of the reduction the products were extracted twice with diethyl ether; the ether phase was washed twice with water and once with an aqueous solution of potassium carbonate and sodium sulfite. After drying (MgSO<sub>4</sub>) the diethyl ether was distilled off leaving the crude product, toluene (95 %) and small amounts of unidentified compounds.

**Reduction of cinnamyl alcohol (7).** 7 was reduced as above in a 3:1 mixture of acetic acid and the standard medium; the isolation of the crude product was done as described for 6. The product mixture was separated on a column (silica) with light petroleum containing acetonitrile (2 %) as eluent. The main fraction (70 %) was 14, 3-phenyl-1-propene, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.31 (2H, d), 5.0 (2H, m), 5.6–6.3 (1H, m), 7.2 (5H, s); MS (*m/e* (%)): 118 (75), 117 (100), 115 (37), 105 (17), 91 (52), 77 (24). A minor product (10 %) was a mixture of mainly meso and some *d,l*-3,4-diphenylhexa-1,5-diene, m.p. 68–72 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.6 (2H, q), 4.8 (4H, m), 5.6–6.1 (2H, m), 7.2 (10H, m); MS (*m/e* (%)): 234 (0.2), 118 (10), 117 (100), 116 (8), 115 (25), 91 (27), 77 (5). Minor amounts of other dimeric compounds were isolated as mixtures and not identified.

**Acknowledgements.** The investigation was supported by a grant (EFP-82) from *Energiministeriet*.

## REFERENCES

1. Manzhelei, M. E. and Sholin, A. F. *Dokl. Acad. Nauk SSSR* 141 (1961) 897.
2. Manzhelei, M. E. and Sholin, A. F. *Zh. Fiz. Khim.* 37 (1963) 1825.
3. Bobanova, Zh. I., Bogdanovskii, G. A. and Vovchenko, G. D. *Elektrokhimiya* 6 (1970) 909.
4. Horanyi, G., Inzelt, G. and Torkos, K. J. *Electroanal. Chem.* 101 (1979) 101.
5. Ochiai, M., Aki, O., Morimoto, A., Okada, T., Shinozaki, K. and Asahi, Y. *Tetrahedron Lett.* (1972) 2341.
6. Ochiai, M., Aki, O., Morimoto, A., Okada, T., Shinozaki, K. and Asahi, Y. *J. Chem. Soc. Perkin Trans. 1* (1974) 258.
7. Hall, D. A., Berry, D. M. and Schneider, C. J. *J. Electroanal. Chem.* 80 (1977) 155.
8. Winstein, S. and Young, W. G. *J. Am. Chem. Soc.* 58 (1936) 104.
9. Hush, N. S. and Oldham, K. B. *J. Electroanal. Chem.* 6 (1963) 34.
10. Brown, O. R., Thirsk, H. R. and Thornton, B. *Electrochim. Acta* 16 (1971) 495.
11. Bard, A. J. and Merz, A. J. *J. Am. Chem. Soc.* 101 (1974) 2959.
12. Fry, A. J. and Herr, D. *Tetrahedron Lett.* (1978) 1721.
13. Kreevoy, M. M., Steinwand, P. J. and Kayser, W. V. *J. Am. Chem. Soc.* 88 (1966) 124.
14. Sleezer, P. D., Winstein, S. and Young, W. G. *J. Am. Chem. Soc.* 85 (1963) 1890.
15. Kitching, W., Bullpitt, M. L., Sleezer, P. D., Winstein, S. and Young, W. G. *J. Organometal. Chem.* 34 (1972) 233.
16. Ewing, D. F. and Parry, K. A. W. *J. Chem. Soc. B* (1970) 970.
17. Segre, A. L., Zetta, L. and Corato, A. D. *J. Mol. Spectrosc.* 32 (1969) 296.
18. Fantazier, R. M. and Poutsma, M. L. *J. Am. Chem. Soc.* 90 (1968) 5490.
19. Shoolery, J. N., Johnson, L. F. and Anderson, W. A. *J. Mol. Spectrosc.* 5 (1960) 110.

Received July 20, 1983.