© 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 1791—1794 (1983)

Electrochemical Additions of the Allyl and the Benzyl Groups of Allyl and Benzyl Halides to Acetone

Shohei SATOH,[†] Hiroshi SUGINOME, and Masao TOKUDA*
Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060

(Received October 12, 1982)

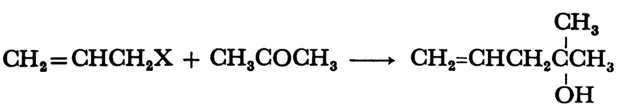
Electrolysis of allyl chloride and five molar excess of acetone in hexamethylphosphoric triamide containing 0.5 M[††] tetrabutylammonium perchlorate gave an addition product, 2-methyl-4-penten-2-ol, in a 53% yield. Allyl groups of 1-chloro-2-methyl-2-propene, 1-chloro-2-butene(**3**), 3-chloro-1-butene(**4**), 1-chloro-3-methyl-2-butene(**5**), and 3-chloro-3-methyl-1-butene(**6**), and benzyl groups of benzyl chloride, benzyl bromide, and 1-chloro-1-phenylethane can similarly be added to acetone by electrolysis to give the corresponding alcohols in fair to good yields. Among these electrochemical reactions, those of **3**, **4**, **5**, and **6** with acetone give respectively two isomeric homoallyl alcohols, one of the isomers is not accessible by the usual chemical reaction between allylic organometallics and acetone.

The electrochemical cleavage of the carbon-halogen bond of organic halides generates radical and/or carbanion as the important intermediates.1) Dimers and hydrocarbons have been the only products isolated in these studies.1) Although radical or carbanion generated by ordinary chemical reaction is being used in a variety of organic syntheses, carbanion or radical, which was electrochemically generated, has rarely been used for C–C bond formation.2) For instance, with regard to a nucleophilic addition of a carbanion generated electrochemically to a carbonyl carbon, only the additions of tetrachloromethane3,4) or ethyl trichloroacetate3) to carbonyl compounds and the additions of allyl or benzyl chloride to carbon dioxide2e) have been reported.5)

In this paper we report successful additions of the carbanions generated electrochemically from substituted allyl and benzyl halides to ketones in hexamethylphosphoric triamide (HMPA) under mild conditions.

Results and Discussions

Electrochemical addition of the allyl group of allyl chloride (**1a**) to acetone was successfully carried out by using HMPA as a solvent. Thus, electrolysis of **1a** in the presence of five molar excess of acetone in HMPA containing 0.5 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte using an undivided cell gave 2-methyl-4-penten-2-ol (**9**) in a 53% yield.



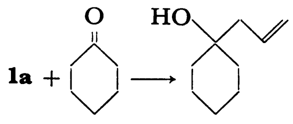
$$CH_2{=}CHCH_2X + CH_3COCH_3 \longrightarrow CH_2{=}CHCH_2\overset{CH_3}{\underset{OH}{C}}CH_3$$

9

1a: X = Cl
b: X = Br
c: X = I

Table 1 summarizes the results of this electrochemical addition carried out under several different electrolytic conditions. The Table indicates that HMPA is the best solvent and gives a yield of **9** much higher than that obtained by using other solvents such as DMF or THF (runs 1—3). The ratio of acetone to **1a** is important (runs 3—6) and increasing the ratio of acetone to **1a** generally gives a higher yield of **9**. The use of ten molar excess of acetone, however, resulted in a lower yield of **9**. This lower yield can probably be attributed to a lack of sufficient HMPA (2 ml). (The total volume of the solution was kept nearly constant in all runs and the volume of HMPA in usual runs was 5.5 ml). With regard to the electrode material, platinum cathode gave the best yield of **9** while mercury and carbon as the cathode gave a yield lower than platinum (runs 7 and 8). A change of the current density from 10 to 50 mA/cm^2 did not show any appreciable change in the yield (runs 11—14). The electrolysis at a cathode using a divided cell under the same conditions as that of run 3 in Table 1 gave only 19% yield of **9**. Thus, the use of an undivided cell rather than a divided cell may be preferable although this electrochemical reaction is a cathodic reaction.

Electrochemical reaction of **1a** with cyclohexanone under the same conditions as that of run 3 in Table 1 gave 1-allylcyclohexanol (**10**) in a 42% yield. Controlled potential electrolysis at −2.2 V *vs* Ag/AgI gave **10** in a 55% yield.



10

Electrochemical additions of the allyl- or the benzyl groups of various allyl halides or benzyl halides to acetone in HMPA containing 0.5 M TBAP gave the corresponding alcohols **9**—**17** and the results are summarized in Table 2. 1,5-Hexadiene from the electrochemical reactions of allyl bromide (**1b**) or allyl iodide (**1c**) with acetone, and bibenzyl from the reaction of benzyl bromide (**7b**) were obtained as by-products. The allyl anion generated by a two electron reduction of **1b** or **1c** underwent a nucleophilic attack on **1b** or **1c** to give 1,5-hexadiene1e,2e) along with a nucleophilic addition reaction giving **9**. The presence of the side reaction pathway in the reactions of **1b** and **1c** would have led to a lower yield of **9**, whereas the electrochemical reaction of **1a** gave only **9** because of its lower reactivity towards allyl anion.

It should be noted that the addition products such

[†] Present address: Nippon Engelhard, Ltd., Ichikawa 272.

[††] 1 M = 1 mol dm^{-3}.

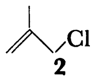
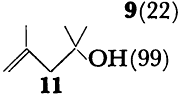
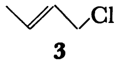
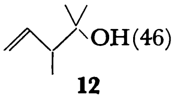
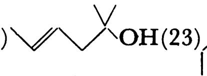
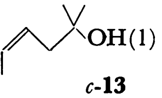
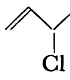
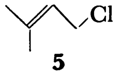
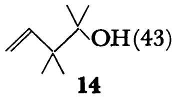
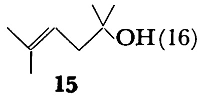
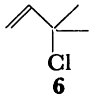
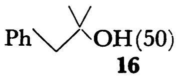
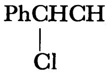
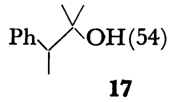
as **13** and **15** obtained in the electrochemical reactions of **3**, **4**, **5**, or **6** with acetone in the present study can not be obtained by the reaction of allylic organometallics derived from these halides with ketone. The organometallic reactions give exclusively the products **12** or **14** having the allyl group attached at the more heavily substituted carbon terminus.[6,7,8] The reactions of a metal with allyl halides **3** and **4** lead to the same organometallic compound which contains mainly the primary type of allylic organometallics, irrespective of the

Table 1. Results of electrohcemical reaction of allyl chloride (**1a**) with acetone[a]

Run	Molar ratio Acetone/**1a**	Solvent	Supporting electrolyte[b]	Curr. dens. / mA cm^{-2}	F/mol	Yield/% of **9**
1	5	THF	0.5 M TBAP	25	2	9
2	5	DMF	0.5 M TBAP	25	2	10
3	5	HMPA	0.5 M TBAP	25	2	53
4	2	HMPA	0.5 M TBAP	25	2	24
5	1	HMPA	0.5 M TBAP	25	2	13
6	10	HMPA	0.5 M TBAP	25	2	17
7[c]	5	HMPA	0.5 M TBAP	25	2	14
8[d]	5	HMPA	0.5 M TBAP	25	2	36
9	5	HMPA	0.2 M TBAP	25	2	43
10	5	HMPA	0.5 M TEAP	25	2	14
11	5	HMPA	0.5 M TBAP	10	1	24
12	5	HMPA	0.5 M TBAP	25	1	29
13	5	HMPA	0.5 M TBAP	50	1	26
14	5	HMPA	0.5 M TBAP	100	1	17

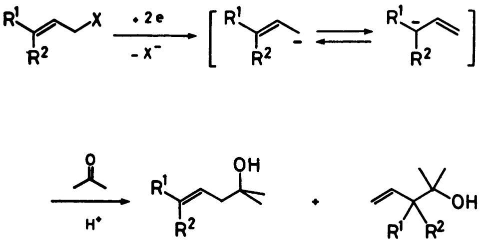
a) Electrolyzed at 0 °C using an undivided cell with a platinum cathode. Amount of **1a** used was 10 mmol. b) TBAP: Tetrabutylammonium perchlorate; TEAP: tetraethylammonium perchlorate. c) Mercury pool was used as a cathode. d) Carbon was used as a cathode.

Table 2. Results of electrochemical reactions of allyl or benzyl halides with acetone[a]

Halides	Products (yield/%)[b]		
1a	**9**(53)		
1b	**9**(30)		
1c	**9**(22)		
 **2**	 (99) **11**		
 **3**	 (46) **12**	 (23) *t*-**13**	 (1) *c*-**13**
 **4**	**12**(44)	*t*-**13**(15)	*c*-**13**(18)
 **5**	 (43) **14**	 (16) **15**	
 **6**	**14**(54)	**15**(18)	
$PhCH_2Cl$ **7a**	 (50) **16**	$PhCH_3$(21)	
$PhCH_2Br$ **7b**	**16**(46)	$PhCH_3$(15)	$PhCH_2CH_2Ph$(16)
 $\mathrm{Ph}\underset{\mathrm{Cl}}{\underset{\vert}{\mathrm{C}}}\mathrm{HCH_3}$ **8**	 (54) **17**	$PhCH_2CH_3$(9)	

a) A mixture of halide (10 mmol) and acetone (50 mmol) in 5.5 ml of HMPA containing 0.5 M Bu_4NClO_4 was electrolyzed at 0 °C using platinum plate electrodes. Current density was 25 mA/cm^2 and electricity passed was 2.0 F per mol of halide. b) Yields are based on halides used. Numbers in parentheses are also a current yield of each product.

structure of the starting halides **3** or **4**.[6] Such organometallics derived from **3** or **4** undergo the addition reaction to acetone to give exclusively **12** with a complete allylic rearrangement.[6] On the other hand, the electrochemical reactions of **3** or **4** with acetone produced different proportions of **12** and **13**. These depended on the properties of the electrode material, the readiness of the reduction of the substrates, or other electrolytic conditions. For instance, the electrochemical addition of **4** to acetone on a platinum cathode gave **12** and **13** in the ratio of 62 : 38 whereas on a carbon cathode the ratio was 29 : 71.[9] An effect of the readiness of the reduction of the substrates on these regiochemistries was observed in the electrochemical conjugate additions of **5** to α,β-unsaturated esters.[20,9] Although the electrochemical conjugate addition of **5** to diethyl fumarate which is more readily reduced than **5** took place at the less heavily substituted carbon terminus of **5**, the addition of **5** to ethyl crotonate which is less readily reduced than **5** occurred at the more heavily substituted carbon of **5**.[20,9] These regiochemistries are of considerable interest from the mechanistic and synthetic points of views, and this will be discussed more fully in later papers.



Scheme 1.

A probable path, which involves nucleophilic addition of allyl or benzyl anion to a carbonyl carbon, is shown in Scheme 1. Cyclic voltammetry shows that the reduction peak of acetone does not appear at a potential less negative than −2.5 V *vs.* Ag/AgI whereas the reduction peaks of **1a**, **1b**, **1c**, **2**, **3**, **4**, **7a**, and **7b** were observed at −2.35, −1.90, −1.43, −2.40, −2.40, −2.20, −2.00 and −1.80 V *vs.* Ag/AgI, respectively. Thus, a two electron reduction of allylic or benzylic halides is involved in this electrolysis to give the corresponding carbanions,[1e] which react with a carbonyl carbon.

One of the roles of HMPA as a solvent would be to stabilize carbanion intermediates leading to an increased yield of **9** as compared to those in other solvents. We found that a controlled potential electrolysis of **1a** and acetone in HMPA at −2.0 V or −1.5 V *vs.* Ag/AgI, which is a reduction potential less cathodic than that of **1a**, gave 30—34% yield of **9**. This may be partly due to a specific property of HMPA which has been suggested to be selectively adsorbed on the metal surface.[10] It may be also due to some difference of the reduction potentials between the microelectrolysis and the macroelectrolysis.[11] It should be noted that the elecrochemical reduction of naphthalene in HMPA took place at a potential less cathodic than the half-wave potential of naphthalene[11] although this electrolytic system was considerably different from that of the present electrochemical reaction with acetone. The exact roles of HMPA during the course of the present electrochemical reaction are now under investigation.

Experimental

All the products were isolated and purified by distillation and by preparative GLPC with a JEOL JGC-20K or a Varian Autoprep 700 instrument. Spectroscopic measurements were carried out as described previously.[20] Quantitative GLPC analyses were carried out with a Hitachi 063 instrument using an internal standard method.

Materials. Hexamethylphosphoric triamide (HMPA) was dried over calcium hydride and distilled before use over lithium aluminium hydride under nitrogen at a reduced pressure. Acetone was treated with potassium permanganate and distilled. Most of the allyl or benzyl halides were commercially available and were distilled before use. 1-Chloro-3-methyl-2-butene (**5**) and 3-chloro-3-methyl-1-butene (**6**) were prepared from isoprene by the described procedure.[12] **5** (43%): bp 107—109 °C.[20] **6** (70%): bp 10—12 °C/20 mmHg (1 mmHg ≈133.322 Pa); ^{1}H NMR, δ 1.66 (6H, s), 5.15—6.1 (3H, m).

General Procedure for Electrolysis. For most of the preparative electrolyses, a normal undivided cell (2.8 cm dia.) equipped with a magnetic stirrer, a reflux condenser, and a serum cap for introduction of nitrogen gas was used. Electrolysis was carried out under a nitrogen atmosphere at a constant current using two platinum plate electrodes (2×2 cm^2). A typical procedure is as follows: A mixture of halide (10 mmol) and acetone (50 mmol) in 5.5 ml of HMPA containing 0.5 M Bu_4NClO_4 was electrolyzed at 0 °C with a current desity of 25 mA/cm^2 until 2.0 F of electricity per mol of halide was passed. After electrolysis, the reaction mixture was dissolved in diethyl ether and the solution was washed with thiosulfate solution and water, and dried over magnesium sulfate. The usual work-up of the solution gave a product mixture which was subjected to distillation and preparative GLPC to give pure products. Some physical properties of the products are recorded below.

*2-Methyl-4-penten-2-ol (**9**)*: n_D^{21} 1.4240; IR (neat) 3370, 3080, 1150, and 915 cm^{-1}; ^{1}H NMR ,δ 1.13 (6H, s), 1.48 (1H, s), 2.15 (2H, d), 5.1 (2H, m), and 5.85 (1H, m); MS *m/z* (rel intensity) 85 (M^+-CH_3, 4), 59 (100), and 43 (51). Calcd for $C_6H_{11}O$ (M^+-1): *m/z* 99.081. Found: *m/z* 99.081

*1-Allycylohexane (**10**)*: n_D^{25} 1.4729; IR (neat) 3380, 980, and 910 cm^{-1}; ^{1}H NMR, δ 1.19 (1H, s), 1.45 (10H, m), 2.17 (2H, d), 5.1 (2H, m), and 5.85 (1H, m); MS *m/z* (rel intensity) 122 (M^+-H_2O, 19), 99 (86), and 81 (100). Calcd for $C_9H_{16}O$: *m/z* 140.118. Found: *m/z* 140.118.

*2,4-Dimethyl-4-pentent-2-ol (**11**)*: n_D^{25} 1.4318; IR (neat) 3380, 3075, and 890 cm^{-1}; ^{1}H NMR, δ 1.18 (6H, s) 1.30 (1H, s), 1.83 (3H, s), 2.15 (2H, s), 4.73 (1H, m), and 4.90 (1H, m); MS *m/z* (rel intensity) 96 (M^+-H_2O, 10), 81 (73), and 59 (100). Calcd for $C_7H_{14}O$: *m/z* 114.104. Found: *m/z* 114.103.

*2,3-Dimethyl-4-penten-2-ol (**12**)*: n_D^{21} 1.4325; IR (neat) 3400, 3080, and 915 cm^{-1}; ^{1}H NMR, δ 0.95 (3H, d), 0.96 (1H, s), 1.07 (6H, s), 2.07 (1H, qi), 5.00 (2H, m), and 5.75 (1H, m); MS *m/z* (rel intensity) 96 (M^+-H_2O, 16), 81 (71), and 59 (100). Calcd for $C_7H_{14}O$: *m/z* 114.104. Found: *m/z* 114.104.

trans-*2-Methyl-4-hexen-2-ol(*t*-**13**)*: n_D^{20} 1.4321; IR (neat) 3370, 3030, and 970 cm^{-1}; ^{1}H NMR, δ 1.01 (1H, s), 1.08 (6H, s), 1.65 (3H, m), 2.02 (2H, m), and 5.42 (2H, m); MS *m/z* (rel intensity) 96 (M^+-H_2O, 16), 81 (100), and 59 (79). Calcd for $C_7H_{14}O$: *m/z* 114.104. Found: *m/z* 114.104.

cis-*2-Methyl-4-hexen-2-ol (*c*-**13**)*: n_D^{20} 1.4370; IR (neat) 3370, 3020, 1655, and 690 cm^{-1}; ^{1}H NMR, δ 1.04 (1H, s), 1.13 (6H, s), 1.59 (3H, d), 2.12 (2H, d), and 5.50 (2H, m); MS *m/z* (rel intensity) 96 (M^+-H_2O, 45), 81 (100), and 59 (78). Calcd for $C_7H_{14}O$: *m/z* 114.104. Found: *m/z* 114.105.

2,3,3-Trimethyl-4-penten-2-ol (14): n_{D}^{20} 1.4453; IR (neat) 3450, 3080, 915 cm^{-1}; ^{1}H NMR, δ 1.03 (6H, s), 1.12 (6H, s), 1.26 (1H, s), 5.05 (2H, m), and 6.05 (1H, m); MS *m/z* (rel intensity) 70 (32), 59 (100), and 43 (57). Calcd for $C_8H_{15}O$: *m/z* 127.112. Found: *m/z* 127.114.

2,5-Dimethyl-4-hexen-2-ol (15): n_{D}^{20} 1.4437; IR (neat) 3370, and 850 cm^{-1}; ^{1}H NMR, δ 1.15 (6H, s). 1.64 (3H, s), 1.75 (3H, s), 2.10 (2H, d), and 5.24 (1H, m); MS *m/z* (rel intensity) 70 (52), 59 (100), and 43 (57). Calcd for $C_8H_{16}O$: *m/z* 128.120. Found: *m/z* 128.120.

2-Methyl-1-phenyl-2-propanol (16): n_{D}^{24} 1.5110; IR (neat) 3350, 720, and 695 cm^{-1}; ^{1}H NMR, δ 1.16 (6H, s), 1.64 (1H, s), 2.69 (2H, s), and 7.21 (5H, s); MS *m/z* (rel intensity) 92 (100) and 59 (95). Calcd for $C_{10}H_{14}O$: *m/z* 150.105. Found: *m/z* 150.105.

2-Methyl-3-phenyl-2-butanol (17): n_{D}^{24} 1.5113; IR (neat) 3370, 765, and 695 cm^{-1}; ^{1}H NMR, δ 1.10 (3H, s), 1.12 (3H, s), 1.32 (3H, d), 1.42 (1H, s), 2.71 (1H, q), and 7.22 (5H, s); MS *m/z* (rel intensity) 106 (100), 91 (97), and 59 (95). Calcd for $C_{11}H_{16}O$: *m/z* 164.120. Found: *m/z* 164.121.

Cyclic Voltammetry. Cyclic voltammetry was carried out with a Yanaco V8 potentiostat at a sweep rate of 0.2 V s^{-1} using a platinum disk electrode (1 mm dia.) in HMPA containing 0.1 M Bu_4ClO_4. A potential was measured in V *vs* Ag/AgI.

References

1) a) A. J. Fry, "Synthetic Organic Electrochemistry," Harper and Row Publishers, New York (1972), p. 170; b) M. R. Rifi, "Organic Electrochemistry," ed by M. M. Baizer, Marcel Dekker, Inc., New York (1973), p. 279; c) M. R. Rifi, F. H. Covitz, "Introduction to Organic Electrochemistry," Marcel Dekker, Inc., New York (1974), p. 194; d) M. R. Rifi, "Technique of Electroorganic Synthesis," ed by N. L. Weinberg, John Wiley and Sons, Inc., New York (1975), Part II, p. 170; e) A. J. Bard and A. Merz., *J. Am. Chem. Soc.*, **101**, 2959 (1979).

2) a) M. R. Rifi, *J. Am. Chem. Soc.*, **89**, 4442 (1967); b) M. R. Rifi, *Collect. Czech. Chem. Commun.*, **36**, 932 (1971); c) R. Gerdil, *Helv. Chim. Acta*, **53**, 2100 (1970); d) A. J. Fry and W. E. Britton, *J. Org. Chem.*, **38**, 4016 (1973); e) M. M. Baizer and J. L. Chruma, *ibid.*, **37**, 1951 (1972); f) W. M. Moore, A. Salajegheh, and D. G. Peters, *J. Am. Chem. Soc.*, **97**, 4954 (1975); g) T. Iwasaki and K. Harada, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1730; h) T. Shono, I. Nishiguchi, and H. Ohmizu, *Chem. Lett.*, **1977**, 1021; i) F. Barba, M. D. Velasco, and A. Guirado, *Synthesis*, **1981**, 625; j) M. Tokuda, T. Taguchi, O. Nishio, and M. Itoh, *J. Chem. Soc., Chem. Commun.*, **1976**, 606; k) M. Tokuda and O. Nishio, *ibid.*, **1980**, 188; l) S. Satoh, T. Taguchi, M. Itoh, and M. Tokuda, *Bull. Chem. Soc. Jpn.*, **52**, 951 (1979); m) S. Satoh, M. Itoh, and M. Tokuda *J. Chem. Soc., Chem. Commun.* **1978**, 481; n) S. Satoh, M. Itoh, H. Suginome, and M. Tokuda, *Bull. Fac. Eng. Hokkaido Univ.*, **102**, 33 (1981); o) S. Satoh, H. Suginome, and M. Tokuda, *Bull. Chem. Soc. Jpn.*, **54**, 3456 (1981).

3) F. Karrenbrock and H. J. Schäfer, *Tetrahedron Lett*, **1978**, 1521.

4) T. Shono, H. Ohmizu, S. Kawakami, S. Nakano, and N. Kise., *Tetrahedron Lett.*, **22**, 871 (1981); T. Shono, N. Kise, A. Yamazaki, and H. Ohmizu, *ibid.*, **23**, 1609 (1982).

5) Although Wawzonek *et al.* and H. Lund *et al.* have obtained addition products by the electrochemical reduction of benzophenone or 9-fluorenone and alkyl halides, the products probably resulted from a trapping reaction of ketone anion radical by alkyl halide. S. Wawzonek and A. Gudersen., *J. Electrochem. Soc.*, **107**, 537 (1960); H. Lund and J. Simonet, *Bull. Soc. Chim. Fr.*, **1973**, 1843.

6) G. Courtois and L. Miginiac, *J. Organomet. Chem.*, **69**, 1 (1974).

7) V. Rautenstrauch, *Helv. Chim. Acta*, **57**, 496 (1974).

8) J. A. Katzenellenbogen and R. S. Lenox., *J. Org. Chem.*, **38**, 326 (1973).

9) S. Satoh, H. Suginome, and M. Tokuda., *Tetrahedron Lett.*, **22**, 1895 (1981).

10) H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Am. Chem. Soc.*, **89**, 186 (1967); **91**, 4191 (1969).

11) T. Asahara, M. Seno, and H. Kaneko, *Bull. Chem. Soc. Jpn.*, **41**, 2985 (1968).

12) W. J. Jones and H. W. T. Chorley, *J. Chem. Soc*, **1946**, 832.