August, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 2417—2418 (1985)* 2417

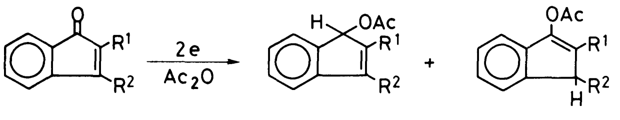
Electrochemical Reductive Acylation of 2,3-Disubstituted 1-Indenones

Nobuhiro TAKANO,* Noboru TAKENO, Mutsuo MORITA, and Yoshio OTSUJI[†]
Department of Industrial Chemistry, Muroran Institute of Technology, Mizumoto-cho, Muroran 050
[†]Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture,
Mozu-Umemachi, Sakai, Osaka 591

(Received February 8, 1985)

Synopsis. The electrochemical reductive acylation of 2,3-disubstituted 1-indenones in the presence of acetic anhydride in aprotic media such as DMF, DMSO, and acetonitrile gave 2,3-disubstituted 1-acetoxy-1*H*-indenes (**2**) and 1,2-disubstituted 3-acetoxy-1*H*-indenes (**3**) in good yields. The ratios of **2** to **3** in the products were affected by the substituents.

The synthesis of organic compounds using electrochemically generated intermediates is a current topic in synthetic organic chemistry.[1)] Previously, we have reported that two reductive acylation products, **2a** and **3a**, are obtained in good yields by the cathodic reduction of 2,3-diphenyl-1-indenone (**1a**) in the presence of acetic anhydride (Scheme 1).[2)] As an extension of this synthetically useful reaction, we have studied the electrochemical behavior of a variety of indenone derivatives. We now wish to report an efficient, one-step synthesis of 2,3-disubstituted 1-acetoxy-1*H*-indenes (**2a—m**) and 1,2-disubstituted 3-acetoxy-1*H*-indenes (**3a—m**) by the cathodic reduction of 1-indenone derivatives (**1a—m**) in the presence of acetic anhydride and discuss the substituent effect on this reaction.



1a-m **2 a-m** **3 a-m**

a: $R^1 = R^2 = Ph$; **b**: $R^1 = Ph$, $R^2 = 4\text{-MeOPh}$;
c: $R^1 = 4\text{-MeOPh}$, $R^2 = Ph$; **d**: $R^1 = Ph$, $R^2 = 4\text{-ClPh}$;
e: $R^1 = Ph$, $R^2 = Me$; **f**: $R^1 = Ph$, $R^2 = Et$; **g**: $R^1 = Ph$, $R^2 = i\text{-Pr}$; **h**: $R^1 = Ph$, $R^2 = \text{Benzyl}$; **i**: $R^1 = Ph$, $R^2 = \text{Cyclohexyl}$; **j**: $R^1 = Ph$, $R^2 = \text{1-Naphthyl}$;
k: $R^1 = Me$, $R^2 = Ph$; **l**: $R^1 = Et$, $R^2 = Ph$;
m: $R^1 = R^2 = Me$

Scheme 1.

Experimental

The electrolyses were performed in a double cylindrical cell which was divided into the cathode and anode compartments with a sintered glass diaphragm. The working electrode (cathode) was a mercury pool and the auxiliary electrode (anode) was a platinum plate. A 0.1 mol dm^{-3} solution of $n\text{-Bu}_4NBF_4$ in DMF was used as both catholyte and anolyte. Acetic anhydride (20 g) and an indenone derivative (0.5 g) were added to the catholyte (100 cm^3). The solution was deoxygenated by bubbling purified N_2 and stirred with a magnetic stirrer. The electrolysis was then carried out at room temperature under controlled potential using a potentiostat and continued until the current dropped to the initial background current. The total electricity passed was measured by use of an integrator. Upon completion of the electrolysis, the catholyte was diluted with water and extracted several times with ether. The combined ether extracts were washed with a saturated $NaHCO_3$ solution and water, dried over Na_2SO_4, and evaporated. The crude products were separated and purified by column chromatography on silica gel using benzene-hexane (1:5) as eluent. The structures of products were confirmed by their IR and NMR spectral data (Table 1).

TABLE 1. NMR AND IR SPECTROSCOPIC DATA FOR ACYLATION PRODUCTS

Product	NMR (CCl_4)δ(ppm, TMS)			IR (Nujol)ν(cm^{-1})	
	-O-Ac	>CH-OAc	>CH-R^2	C=O	C-O
2b	2.00	a)	—	1741	1256
3b	2.33	—	4.90	1774	1174
2c	2.06	a)	—	1736	1250
3c	2.42	—	4.90	1767	1178
2d	1.98	6.92	—	1744	1236
3d	2.33	—	4.86	1762	1200
2e	1.90	6.80	—	1736	1230
3e	2.25	—	3.84$^{b)}$	1763	1196
2f	1.92	6.75	—	1734	1230
3f	2.23	—	3.95$^{c)}$	1761	1193
2g	1.95	6.70	—	1734	1234
3g	2.30	—	3.93$^{d)}$	1761	1200
2h	1.98	a)	—	1735	1227
3h	2.20	—	4.20$^{e)}$	1764	1196
2i	1.89	6.68	—	1735	1225
3i	2.20	—	3.84$^{d)}$	1764	1200
2j	2.10	a)	—	1733	1221
2k	2.12	6.27	—	1735	1227
3k	2.28	—	4.26	1763	1200
2l	2.12	6.40	—	1737	1227
3l	2.30	—	4.40	1763	1200
2m	2.02	6.10	—	1733	1230
3m	2.31	—	3.23$^{b)}$	1761	1200

a) This signal overlaped with that of aromatic ring protons. b) Quartet. c) Triplet. d) Doublet. e) Multiplet.

Results and Discussion

The results of the electrolyses are summarized in Table 2. Only the *O*-acylation products, **2a—m** and **3a—m**, were obtained in good yields under the conditions shown in Table 2. Curphy and co-workers have reported that in the electrochemical reductive acylation of benzophenone under similar conditions, acylation takes place on both carbonyl carbon and carbonyl oxygen atoms.[3)] However, in the case of indenone derivatives, *C*-acylation products were not detected at all.

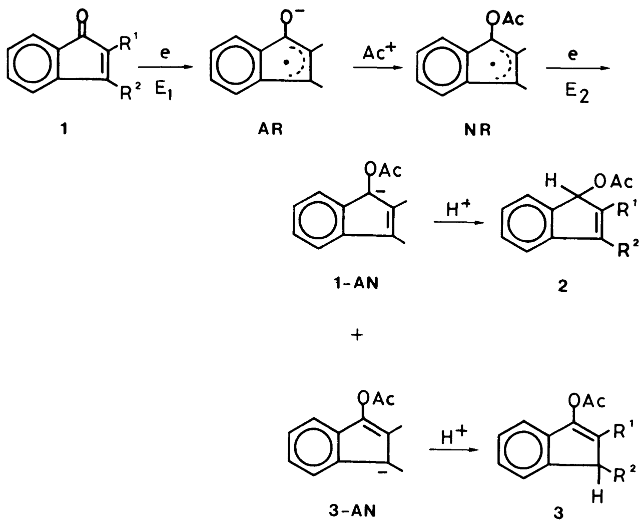
We have shown that the reductive acylation of **1a** to

TABLE 2. CONTROLLED-POTENTIAL ELECTROLYSIS OF 1-INDENONES IN THE PRESENCE OF ACETIC ANHYDRIDE IN DMF

1-Indenone[a]	Electrolysis[b] potential V *vs.* SCE	*n* F/mol	Product[c] Yield %	Product[c] Ratio **2/3**
1a	−1.20	2.02	98	67/33
1a	−1.30	2.10	97	59/41[d]
1a	−1.30	2.13	96	56/44[e]
1a	−1.80	2.23	82	68/32
1b	−1.35	2.00	98	59/41
1c	−1.30	2.03	95	57/43
1d	−1.20	1.98	98	63/37
1e	−1.40	1.83	87	38/62
1f	−1.40	1.81	86	37/63
1g	−1.40	1.97	89	40/60
1h	−1.40	1.96	88	50/50
1i	−1.40	1.88	79	45/55
1j	−1.30	1.74	97	100/0
1k	−1.40	1.97	48	77/23
1l	−1.40	2.00	52	67/33
1m	−1.60	2.01	57	63/37

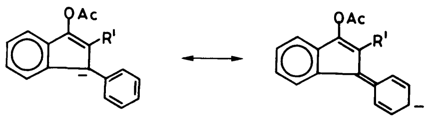
a) 1-Indenones were prepared by the methods described in the literatures.[6,7] b) Elecrolysis potentials based on half-wave potentials. c) Isolated yield based on 1-indenones. d) Electrolysis was carried out in DMSO. e) Electrolysis was carried out in acetonitrile.

2a and **3a** is achieved by way of the reaction of the electrogenerated anion radical (**AR**) with acetyl cation and proceeds *via* the ECE mechanism as shown in Scheme 2.[2] The same mechanism presumably operates for the reductive acylation of the compounds studied in this paper. Support for this mechanism was obtained by observing the voltammetric behavior of the substrates[4] and also by the coulometric analyses of the reactions which showed that the electricity (*n*) passed during each reaction was very close to two electrons for all the compounds studied (Table 2). Furthermore, the product ratio of **2a** to **3a** in the electrolysis of **1a** at −1.80V where the formation of the dianion of **1a** should predominate was virtually the same as that in the electrolysis at −1.20V where the formation of the anion radical of **1a** should predominate. This result suggests that disproportionation occurs rapidly between the substrate indenone and its electrogenerated dianion if formed, to produce two molecules of the anion radical (**AR**) which is converted into the final products by the reaction with acetyl cation *via* the path way shown in Scheme 2.



Scheme 2.

The substituent effect on the product ratios in the electrolyses of indenone derivatives is noteworthy. When 3-substituted 2-aryl-1-indenones were used as substrates, alkyl, benzyl, and cyclohexyl substituents at C-3 lowered the ratios of 2,3-disubstituted 1-acetoxy- (**2**) to 1,2-disubstituted 3-acetoxy-1*H*-indenes (**3**) in the products, compared with aryl substituents at the same position (Table 2). This tendency may be explained on the basis of the mechanism of Scheme 2. In this scheme, the second one-electron reduction stage (**NR**→ **1-AN** and/or **3-AN**) is faster than the first one-electron reduction stage (**1**→**AR**), since **NR** is more readily reducible than the starting substrate; $E_1 < E_2$.[5] As a result, the product distribution is most probably considered to be determined at the final protonation stage which depends on the relative electron densities on the reaction centers of **1-AN** and **3-AN**. The inductively electron-donative alkyl substituents at C-3 favor the formation of **3** particularly by increasing the electron density on the reaction center of **3-AN**. On the other hand, the aryl substituents at C-3 favor the formation of **2** particularly by decreasing the electron density on the reaction center of **3-AN**. This is due to the resonance of the aryl groups (Eq. 1).



(1)

For **1m** whose substituents at C-2 and C-3 are the electron-donative alkyl groups, the formation of **2** is favored by increasing the electron density on the reaction center of **1-AN**.

References

1) H. Lund, *Denki Kagaku*, **45**, 2 (1977) and references cited therein.

2) N. Takano, N. Takeno, and M. Morita, *Nippon Kagaku Kaishi*, **1983**, 1753.

3) T.J. Curphy, L. D. Trivedi, and T. Layloff, *J. Org. Chem.*, **39**, 3831 (1974).

4) The voltammetric behavior of 2,3-disubstituted 1-indenones (**1b**—**m**) in DMF was analogous to that of **1a**. Thus the polarograms of indenones in DMF in the absence of acetic anhydride showed two one-electron reduction waves I and II. When acetic anhydride was added to the solution the wave I grew in height at the expense of the wave II. At sufficiently large acetic anhydride concentration the wave I showed a single two-electron wave.

5) G. J. Hoijtink, J. van Schooten, E. de Boer, and W. Y. Aalbersberg, *Recl. Trav. Chim. Rays-Bas*, **73**, 355 (1954).

6) H. Burton and C. W. Shoppee, *J. Chem. Soc.*, **1935**, 1156.

7) N. Takano, N. Takeno, and M. Morita, *Nippon Kagaku Kaishi*, **1984**, 2003.