Tetrahedron Letters,Vol.30,No.39,pp 5309-5312,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

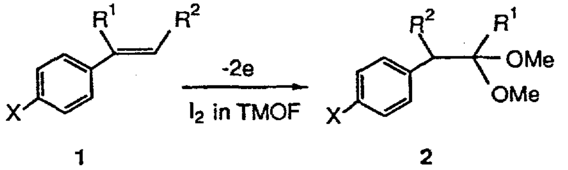
ELECTROOXIDATIVE REARRANGEMENT OF CONJUGATED ARYLOLEFINS TO ARYLACETALDEHYDE DIMETHYL ACETALS [1]

Tatsuya Shono,* Yoshihiro Matsumura, Susumu Katoh, Kaoru Ikeda,
Tetsuhiro Fujita, and Tohru Kamada

Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Sakyo, Kyoto 606, Japan

Summary: Electrochemical oxidation of conjugated arylolefins 1 in trimethyl orthoformate containing iodine gave arylacetaldehyde dimethyl acetals 2 in high yields.

It has been known that anodic oxidation of conjugated arylolefins 1 forms α,β-disubstituted products,[2] coupling products,[3] or α-bromoketals[4] depending on the electrolysis conditions. We report herein a novel pattern of anodic oxidation of 1 which affords arylacetaldehyde dimethyl acetal 2 (eq 1). Since arylolefins 1 are easily available starting compounds, this anodic method is one of the most convenient syntheses of arylacetaldehydes which are versatile intermediates in a variety of organic syntheses.[5]



(1)

TMOF;CH(OMe)$_3$

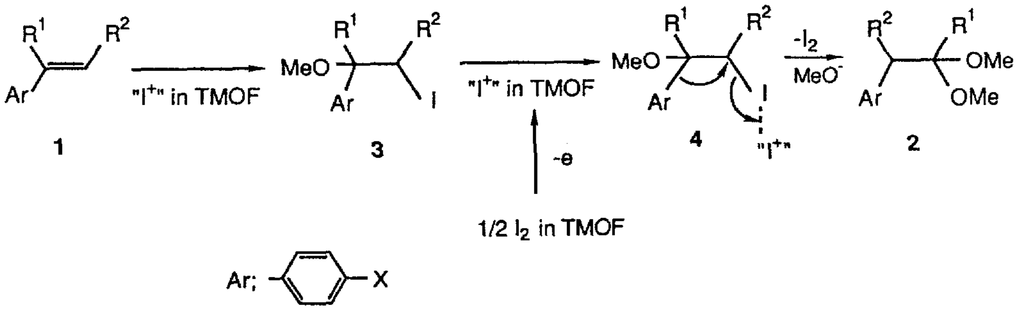
The experimental procedure is simple as shown in the following details. Into an undivided electrolysis cell equipped with two platinum electrodes (2cm x 1cm) and a magnetic bar was placed a solution of trimethyl orthoformate (TMOF, 10mL) containing 1 (4 mmol), iodine (1~4.8 mmol) and lithium perchlorate ($LiClO_4 \cdot 3H_2O$, 0.7g). Oxidation was carried out under a constant current (0.1 A/cm^2) at room or elevated temperature.

Since TMOF has a low electric conductivity,[6] the surface of cathode was gradually covered by nonconducting materials during the electrolysis, the direction of current was alternated with a short interval (for example, 7 seconds) in order to keep the amount of current constant. After the passage of amounts of electricities shown in Table 1, the usual workup gave 2. The yields of 2 obtained under several reaction conditions are summarized in Table 1.

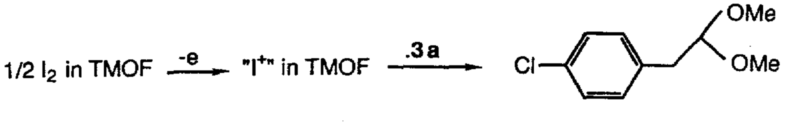
The oxidative rearrangement of 1 to 2 seems to proceed through the intermediate formation of β-iodo-α-methoxy compounds 3 followed by the 1,2-aryl migration of 3 since the intermediary formation of 3 was confirmed in the course of the electrochemical oxidation (Scheme 1). In order to ascertain the proposed mechanism, some of the intermediates 3 independently prepared[7] were treated with iodine or H_2SO_4 in TMOF. However, the 1,2-aryl migration leading to 2 did not take place but the starting materials 3 were recovered. This result suggested that the 1,2-aryl migration required some other promoter than iodine or acid.

On the other hand, we have already reported that the anodic oxidation of iodine in suitable solvents formed iodine active species "I^+". Hence, it was reasonable that this "I^+" behaved as a Lewis acid type promoter to assist the 1,2-aryl migration through the intermediate step like 4 with regenerating I_2.[8]

Scheme 1



This hypothesis was proved by the fact that the addition of a TMOF solution of "I^+", prepared by electrolyzing (2F/mol) a TMOF solution of iodine (1.33 mmol) in a divided cell,[10] into a solution of 3a (3; R^1=R^2=H, X=Cl; 0.2 mmol) in TMOF resulted in the formation of 2a in 98% yield (eq 2).[11]



(2)

2a 98%

The fact that the electrochemical reaction of 1 using 0.25 equivalent of iodine gave the rearranged products 2 in more than 100% yield based on the amount of iodine (runs 1, 5, 8, 11, and 14) also supported the reaction mechanism involving the regeneration of iodine.[13] The yield of 2 based on 1 was, however, not necessarily satisfactory when less than one equivalent of iodine was used, since in this case the direct anodic oxidation of 1 took place competitively to a considerable extent to give α, β-dimethoxylated compound as a byproduct.[14] This side reaction was considerably excluded by increasing the concentration of iodine (runs 4, 7, 13, 15, and 17) and/or by carrying out the electrochemical oxidation at higher temperature (compare run 2 with run 3, and run 9 with run 10).

In contrast with the satisfactory results for the formation of acetals 2a-f, the acetal 2g was not obtained under the same reaction conditions described above, while the

Table 1. Electrochemical Oxidation of 1 in TMOF containing Iodine

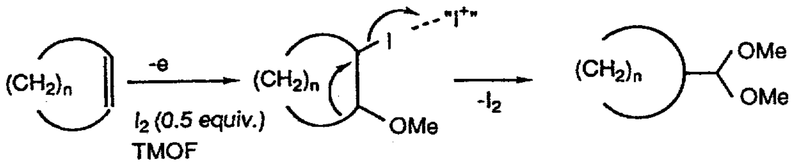
Run	Substrates 1				I_2	Reaction	Electricity	Isolated Yields(%)	
		R^1	R^2	X	(equiv. to 1)	Temp.	(F/mol)	of Products 2 [a]	
1	1a	H	H	Cl	0.25	refl.	6	2a	60 (240)
2	1a				0.5	r.t.	13	2a	58
3	1a				0.5	refl.	5.5	2a	76
4	1a				1.2	r.t.	8	2a	95
5	1b	H	Me	H	0.25	refl.	4	2b	66 (266)
6	1b				0.5	refl.	4	2b	71
7	1b				1.2	r.t.	3	2b	95
8	1c	H	H	Me	0.25	refl.	4	2c	70 (280)
9	1c				0.5	r.t.	4	2c	66
10	1c				0.5	refl.	3.7	2c	73
11	1d	H	H	H	0.25	refl.	6	2d	69 (276)
12	1d				0.5	refl.	4	2d	70
13	1d				1.2	r.t.	5	2d	96
14	1e	H	H	CO_2Me	0.25	refl.	12	2e	35 (140)
15	1e				1.2	r.t.	50	2e	70
16	1f	H	CH_2OMe	H	0.5	refl.	7	2f	36 (72)
17	1f				1.2	r.t.	5	2f	97
18	1g	Me	H	H	1.2	r.t.	6		–[b]
19	1g				1.2[c]	r.t.	17	2g	80[d]

[a] *The figures in parenthesis are the yields based on the amount of iodine.*

[b] Many unidentified products were yielded.

[c] 2,6-Lutidine (0.5 equiv.) was added.

[d] The product was isolated as phenyl-2-propanone after workup the reaction mixture with aqueous hydrochloric acid.



(3)

5a,b

a; n=4

b; n=5

6

7a,b

a; 51%

b; 70%

addition of 2,6-lutidine to the reaction mixture remarkably improved the yield of 2g (run 19).

Some cyclic olefins 5 were also transformed to ring-contracted products 7 by application of this electrooxidation system (eq 3). The reaction seemed to proceed through the intermediate state 6 in which the rearrangement was promoted by "I⁺".

Acknowledgement: One of the authors (Y.M.) thanks to the Ministry of Education, Science and Culture, Japan, for a Grant-in-Aid for Scientific Research on Priority Area (1) (No. 62607001 and 63607001).

References:

1. Electroorganic Chemistry 119.
2.a) Inoue,T.; Tsutsumi,S. Bull. Chem. Soc. Jpn., 1965, 38, 661.
  b) Inoue,T.; Koyama,K.; Matsuoka,T.; Tsutsumi,S. Ibid., 1967, 40, 162.
3.a) Inoue,T.; Koyama,K.; Matsuoka,T.; Matsuoka,K.; Tsutsumi,S. Tetrahedron Lett., 1963, 1409.
  b) Schäfer,H.J.; Steckhan,E. Chem. Ing. Teck., 1972, 44, 186.
  c) Steckhan,E.; Schäfer,H.J. Angew. Chem., 1974, 86, 480.
  d) Engels,R.; Schäfer,H.J.; Steckhan,E. Justus Liebigs Ann. Chem., 1977, 2044.
4. Nikishin,G.I.; Elinson,M.N.; Makhova,I.V. Tetrahedron Lett., 1988, 29, 1603.
5. Paparatto,G.; Gregprio,G. Ibid., 1988, 29, 1471.
6. Foos,J.S.; McVeigh,J. J. Electrochem. Soc., 1983, 130, 628.
7. The intermediates 3 were prepared by treatment of 1 with more than one equivalent of I_2 in TMOF overnight at room temperature in quantitative yields. Although the formation of 3 by using "I⁺" in TMOF was much faster than that by using I_2 in TMOF, the reaction was not able to be terminated at the stage of 3 in the former case.
8. The contribution of direct electrochemical oxidation of 3 to the formation of 2 from 3a to a certain extent may not be ignored since alkyl iodides are directly oxidizable by electrochemical method.[9]
9. Miller,L.L.; Hoffman,A.K. J. Am. Chem. Soc., 1967, 89, 593.
10. The dark brown color of the anolyte gradually faded with passing electricity and finally it turned to clear yellow when 16 F/mol of electricity was passed.
11. The formation of "I⁺" in TMOF was also confirmed by aromatic iodination.[12]
12. Shono,T.; Matsumura,Y.; Katoh,S.; Ikeda,K.; Kamada,T. Tetrahedron Lett., 1989, 30, 1649.
13. Halogen mediator, see a) Shono,T.; Matsumura,Y.; Inoue,K. J. Am. Chem. Soc., 1984, 106, 6075.
  b) Shono,T.; Matsumura,Y.; Inoue,K.; Iwasaki,F. J. Chem. Soc. Perkin Trans.1, 1986,73, and references cited therein.
14. In the absence of iodine, direct anodic oxidation of 1 in TMOF containing $LiClO_4$ gave α, β-dimethoxylated products.

(Received in Japan 17 June 1989)