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Diacylation of Activated Olefins Promoted by Electrochemically Generated $NO_3\bullet$[1]

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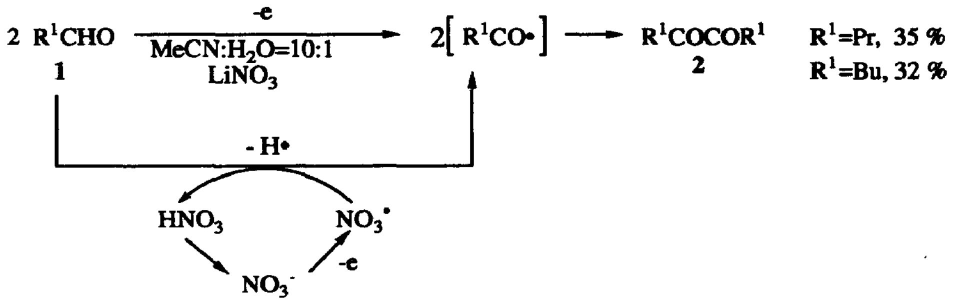
Abstract: It has been found in this study that an acyl radical is formed by the reaction of an aldehyde with a radical $NO_3\bullet$ generated by the anodic oxidation of NO_3^- and the reaction of this acyl radical with activated olefins lead to the formation of a diacylated compound.

The reactivity of an electrochemically generated radical species has attracted much attention in recent years since this type of radical species brings about some kinds of unique reaction which have never been actualized by the hitherto known conventional nonelectrochemical methods. The trifluorometylation of activated olefins by the electrochemically generated trifluoromethyl radical, for instance, has been reported recently.[5,6]

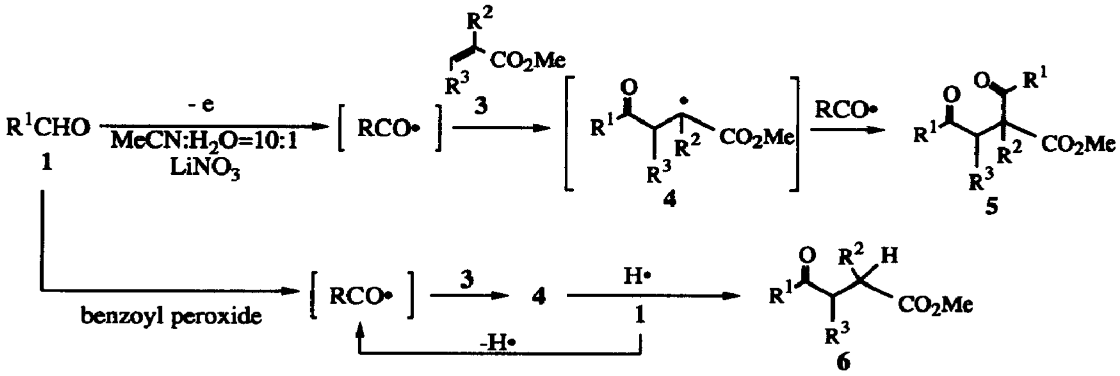
It has been found in this study that an acyl radical is formed by the reaction of an aldehyde (**1**) with a radical $NO_3\bullet$[7-9] generated by the anodic oxidation of NO_3^- and the formation of the acyl radical under the electrochemical reaction conditions brings about some types of unique reaction which are remarkably different from the reactions promoted by the acyl radical generated under nonelectrochemical reaction conditions. Namely, the reactions shown in the following Schemes 1 and 2 have been found to be promoted by the electrochemically generated acyl radical:

As shown in Scheme 1, the anodic oxidation of a solution of **1** and a catalytic amount of $LiNO_3$ (0.1 equiv. based on **1**) has been found to yield 1,2-diketone (**2**). The initiation of this reaction is the anodic oxidation of NO_3^- to form a radical $NO_3\bullet$ and in the second step, the hydrogen atom of the formyl group is abstracted by the radical $NO_3\bullet$ to give the corresponding acyl radical which dimerizes subsequently. Since NO_3^- is regenerated in this second step, it acts as a type of the mediator in the formation of **2**.



Scheme 1

It has also been found that the anodic oxidation of a solution of **1** and an activated olefin (**3**) under similar reaction conditions lead to the diacylation of **3** (Scheme 2), whereas it has well been known that the acyl radical generated by the reaction of **1** with benzoyl peroxide gives the corresponding monoacylated product (**6**) by its reaction with **3**.[10,11] Although the radical intermediate (**4**) formed by the addition of the acyl radical to **3** seems to be the common intermediate for the formation of **5** and **6**, the difference between electrochemical and nonelectrochemical methods may be explainable by the unique reaction atmosphere of the electrochemical reaction. Namely, in the electrochemical reaction, all the key reactions, that is, the formation of the radical NO_3• and the acyl radical from **1**, and its addition to **3** take place at the vicinity of the surface of anode. Consequently, the local concentration of the radical species including the intermediate **4** is very much higher than in the reaction carried out under the nonelectrochemical conditions mentioned above. Hence, the dimerization of the acyl radical or the reaction of the acyl radical with **4** much favorably takes place than the nonelectrochemical reaction in which the hydrogen abstraction by the radical species is the most probable reaction pattern.

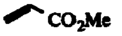
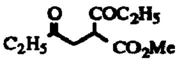
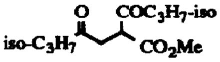
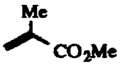
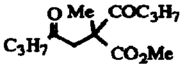
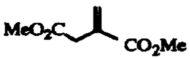
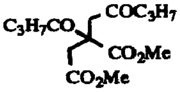
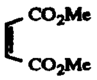
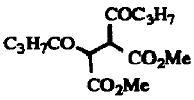
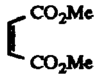


Scheme 2

As shown in Table 1, the use of $LiNO_3$ has been found to be essential for the formation of **5** since the anodic oxidation of a solution of **1a** (R^1=Pr) and **3a** (R^2=R^3=H) in the presence of the other types of electrolyte such as H_2SO_4 (run 1), $LiClO_4$ (run 2), LiCl (run 3), or LiBr (run 4) did not give **5a** (R^1=Pr, R^2=R^3=H). On the other hand, in the presence of a catalytic amount of $LiNO_3$ (0.1 equiv. based on **3a**), the anodic oxidation of a solution of **1a** and **3a** gave the corresponding **5a** with a reasonable yield (run 5).

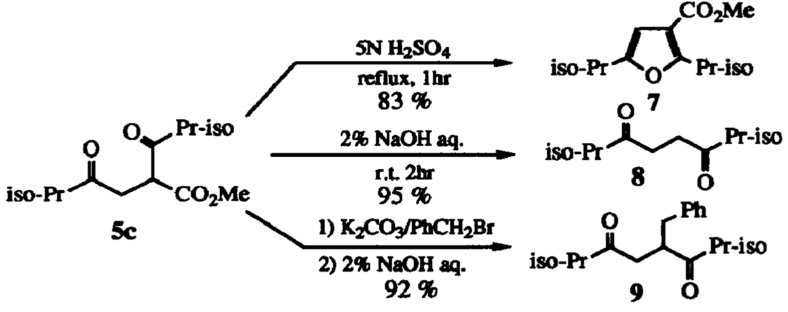
A typical experimental procedure is as follows: A solution of **1** (50 mmol) and **3** (5 mmol) in a mixed solvent (MeCN:H_2O=10:1, 20 mL) containing $LiNO_3$ (5 mmol) was put into an undivided electrolysis cell (50 mL) equipped with two platinum electrodes (2x2 cm) and a magnetic bar. The anodic oxidation was carried out under conditions of constant current (200 mA). After 10 F/mol of electricity based on **3** was passed, the reaction mixture was poured into a saturated solution of NaCl (100 mL). The organic solution was extracted with ether (4x20 mL), and the combined organic solution was dried over $MgSO_4$. In the reaction of **1a** with dimethyl maleate (run 9, Table 1), the use of a divided cell was found to be necessary (run 10) for the formation of the product **1f**, otherwise the electrochemical reduction of dimethyl maleate to dimethyl succinate took place predominantly. The products (**5a**-**5f**) obtained by evaporation of the solvent were purified by a silica gel column (hexane:AcOEt=5:1). These products gave satisfactory spectroscopic values for the assigned structures.[12]

Table 1. Reaction of Aldehyde with Activated Olefin.[a,b]

run	Aldehyde (1)	Supporting Electrolyte	Activated Olefin	product (5)	Yield[c] (%)
1	C_3H_7CHO (1a)	H_2SO_4	 (3a)	(5a)	0
2	(1a)	$LiClO_4$	(3a)	(5a)	0
3	(1a)	LiCl	(3a)	(5a)	0
4	(1a)	LiBr	(3a)	(5a)	0
5	(1a)	$LiNO_3$	(3a)	(5a)	58
6	C_2H_5CHO (1b)	$LiNO_3$	(3a)	 (5b)	58
7	iso-C_3H_7CHO (1c)	$LiNO_3$	(3a)	 (5c)	34
8	(1a)	$LiNO_3$	 (3b)	 (5d)	40
9	(1a)	$LiNO_3$	 (3c)	 (5e)	34
10	(1a)	$LiNO_3$		 (5f)	0
11	(1a)	$LiNO_3$		(5f)	47[d]

a) The reaction was carried out in a mixed solvent (MeCN : H_2O=10 : 1) using 0.1 eq. of a supporting electrolyte based on 3.
b) Unless otherwise stated, an undivided cell was used. c) Isolated yields. d) The reaction was carried out in a divided cell.

The products (5a-5f) shown in the Table 1 have been found to be convenient key compounds for organic synthesis since the compound 5c, for example, was transformed to a derivative of furan (7), 1,4-diketone (8), or regioselectively alkylated 1,4-diketone (9)[13] with high yields (Scheme 3).



Scheme 3

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2) Research Institute for Science and Technology.
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4) Department of Metallurgy.
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11) Patrick,T.M. *J. Org. Chem.* **1952**, *17*, 1009.
12) **5a**: IR(neat) 1720, 1750$\mathrm{cm^{-1}}$; NMR ($CDCl_3$) δ 092 (t, 6H, J=7.5Hz), 1.63 (m ,4H), 2.46 (t, 2H, J=7.5Hz), 2.68 (t, 2H, J=7.2Hz), 3.00 (d,1H,J=6.9Hz), 3.08 (d,1H,J=6.9Hz), 3.75 (s, 3H), 4.07 (t, 1H, J=6.9Hz); Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H,8.83. Found:C, 63.22; H,8,77.

    5b: IR(neat) 1715, 1745$\mathrm{cm^{-1}}$; NMR ($CDCl_3$) δ 1.05 (t ,3H, J=7.2Hz), 1.08 (t, 3H, J=7.2Hz), 2.46 (t, 2H, J=7.2Hz), 2.72 (t,2H, J=7.2Hz), 3.00 (d, 1H,J=6.9Hz), 3.07 (d, 1H, J=6.9Hz), 3.74 (s,3H), 4.06 (t, 1H, J=6.9Hz); Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98;H, 8.05. Found: C,60.11; H, 7.92.

    5c: IR (neat) 1715, 1745$\mathrm{cm^{-1}}$; NMR ($CDCl_3$) δ 1.07 (d, 6H, J=6.0Hz), 1.17 (d, 6H, J=6.0Hz), 2.63 (m, 1H), 2.80(m, 1H), 2.99 (d,1H,J=6.6Hz), 3.04 (d,1H,J=7.2Hz), 3.68 (s, 3H), 4.07 (d,d, 1H, J=6.6 and 7.2Hz); Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H,8.83. Found:C, 63.02;H, 8,55.

    5d: IR (neat) 1715, 1745$\mathrm{cm^{-1}}$; NMR ($CDCl_3$) δ 0.93 (t, 6H, J=7.5Hz), 1.41 (s, 3H), 1.60 (m ,4H), 2.40 (t, 2H, J=7.5Hz), 2.64 (t, 2H, J=7.2Hz), 3.04 (s,2H), 3.83 (s, 3H),; Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H,9.15. Found: C,64.19; H,8.89.

    5e: IR (neat) 1715, 1740$\mathrm{cm^{-1}}$; NMR ($CDCl_3$) δ 0.89 (t, 6H, J=6.9Hz), 1.60 (m ,4H), 2.40 (t, 2H, J=6.8Hz), 2.55 (t, 2H, J=6.8Hz), 3.14 (s, 2H), 3.29 (s, 2H), 3.66 (s, 3H), 3.73 (s, 3H); Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H,805. Found:C,60.11; H,8,22.

    5f: IR (neat) 1720, 1740$\mathrm{cm^{-1}}$; NMR ($CDCl_3$) δ 0.91 (t, 6H, J=7.5Hz), 1.64 (m ,4H), 2.76 (t, 4H, J=7.5Hz), 3.71 (s, 3H), 4.50 (s, 2H); Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.73; H,7.75. Found: C,58.90; H,7.77.
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