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NEW SYNTHETIC REACTION BY ELECTROLYSIS
MALONIC ACID AS A KETONE SYNTHON

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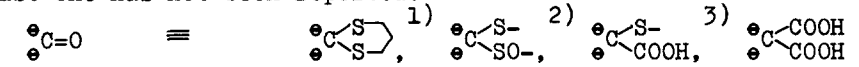
Summary: Malonic acid derivatives(gem-dicarboxylic acids) were converted to the corresponding ketones by the electrolysis. The reaction was employed for the synthesis of jasmones.

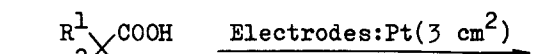
Various ketone synthons which are equivalent to carbonyl dianion have been applied for organic synthesis. However, a useful synthetic reaction associated with the last one has not been reported.[4]



We have resently reported that α-phenylthio(or α-methylthio)carboxylic acid can function as a ketone synthon by anodic oxidation reaction.[5] This finding suggests us that the malonic acid may function as a ketone synthon by electrolysis.

It was found that, in the case of dihexylmalonic acid (1a, $R^1=R^2=C_6H_{13}$) in water, the expected reaction proceeds successfully in two-layer system. The typical results are summarized in Table 1. Also the electrolysis by two-layer system was employed successfully for the synthesis of 2,5-undecadione(2b) from γ-keto malonic acid(1b, $R^1=C_6H_{13}$, $R^2=CH_3CO(CH_2)_2$). However, the electrolysis system similar to above could not convert 1c to 2c. Finally, it was found that 2c can be obtained successfully by the electrolysis of 1c in methanol with acetic acid and sodium acetate.[6]

Table 1 Electrolysis of Dihexylmalonic Acid

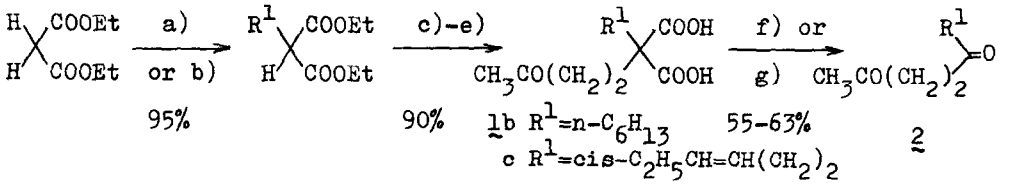


1a 1 mmol in 30 ml of water 2a $R^1=R^2=C_6H_{13}$

NaOH (mmol)	Current (A)	Applied Voltage(V)	Solvent[a]	Yield (%)
2	0.1-0.2	12-22	A	20-23
3	0.12	11	A	41
4	0.04-0.12	5-10	A	37-55[b]
8	0.24	9	A	22
4	0.12	8	B	-[c]
4	0.12	8	-	-[c]

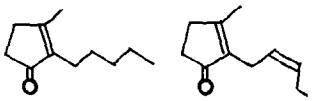
a) Organic solvent was placed on the water layer during the reaction: A=hexane/ether (3/1, 15 ml), B=hexane(15 ml). b) When the yield was 55%, 1a(25%) was recovered. c) 1a was completely recovered.

Thus, the products, 1,4-diketones(2b and 2c) can be converted to jasmones(3) as usual in a good yield.



1b R^1=n-C_6H_{13}
c R^1=cis-C_2H_5CH=$CH(CH_2)_2$

a) n-$C_6H_{13}Br/K_2CO_3$/KI(cat.)/acetone-reflux;
b) cis-C_2H_5CH=$CH(CH_2)_2OSO_2Ph$/EtONa/EtOH-reflux;
c) $CH_3COCHCH_2$/KOH(cat. solved in 50% aq. EtOH)/ether-0°C;
d) KOH/50% aq. EtOH-reflux;
e) H^+
f) electrolysis(22 F/mol)/NaOH(4 equiv.)/water-ether;
g) See Ref. 6).



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References and Notes

1) E. J. Corey and D. Seebach, J. Org. Chem., 31, 4097(1966); D. Seebach, Synthesis, 17(1969).
2) K. Ogura and G. Tsuchihashi, Tetrahedron Lett., 3151(1971); 1383, 2681(1972).
3) B. M. Trost and Y. Tamaru, J. Amer. Chem. Soc., 97, 3528(1975); Tetrahedron Lett., 3797(1975); J. Amer. Chem. Soc., 99, 3101(1977).
4) The oxidative decarboxylation of disubstituted malonic acids using lead tetraacetate has been reported(J. J. Tufariello and W. J. Kissel, Tetrahedron Lett., 6145(1966)). However, the reaction seems to be limited to the cases in which both substituents are very simple. Moreover, since the reaction needs 2 or 3 equivalents of lead tetraacetate, this reaction could not fit to our interest.
5) J. Nokami, N. Matsuura, T. Sueoka, Y. Kusumoto, and M. Kawada, Chem. Lett., 1283(1978).
6) The electrolysis of 1c(1 mmol) in methanol(10 ml) with acetic acid(3 ml) and sodium acetate(20 mg), at a constant current 0.01 A/cm^2 and applied voltage 7-8 V, by using platinum electrodes(2 cm^2), for 50 hours at 15°C gave satisfactorily pure 2c. Further purification was carried out by column chromatography(silica gel, hexane-ether(1/1))(55% yield).

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