Selective Anodic Oxidation of Acetylenic Alcohols

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Acetylenic carboxylate and aldehydes are known as useful intermediates for synthesis of a variety of heterocyclic compounds[1)] and polyacetylene derivatives, obtained by polymerization of these acetylenic derivatives, have been expected to be applied to materials for electrons. Acetylenic carboxylic acids were generally synthesized by CrO_3-oxidation which were suffered from much toxicity. [2)] In this connection, for development for synthetic method possessing high economical efficiency and convenience, acetylenic carboxylic acids from acetylenic alcohols were synthesized by direct anodic oxidation in aqueous sulfuric acid.[3)] However, in this anodic oxidation, the product couldn't be easily isolated by due to much difficulty during workup-treatment in complete removal of sulfuric acid, because of high acidity of acetylenic carboxylic acid (pka=1.85).

In this study, we wish to present facill synthesis of acetylenic carboxylates by anodic oxidation of the corresponding acetylenic alcohols in aqueous sulfuric acid followed by esterification of the resulting carboxlic acids under basic condition. Furthermore, convenient method for synthesis of acetylenic aldehydes including diphenylmethylsilylpropiol aldehyde was also developed from catalytic oxidation using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in a double layer system of KBr aqueous and methylene chloride solution.

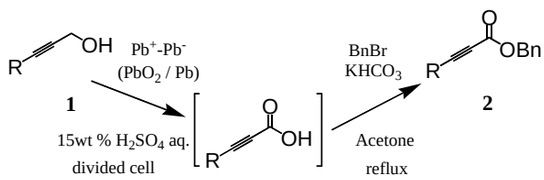
Synthesis of benzylacetylenic carboxylates by anodic oxidation of acetylene alcohols was carried out at 3-5^{o}C using a divided cell in the presence of aqueous 15wt% sulfuric acid as a supporting electrolyte and a solvent under the constant current condition (current density: 10mA/cm^2) until 6F/mol of electricity passed through the system. The product was extracted by diethyl ether or butyl acetate. The crude product obtained was dissolved into acetone, followed by esterification using benzyl bromide and potassium hydrogen-carbonate under reflux for 6hr. As a result, the corresponding acetylenic carboxylates were obtained in satisfactory overall yields esterification (65-80%), as shown in Table 1.

On the other hand, anodic oxidation of acetylenic alcohols was carried out at 3-5^{o}C using an undivided cell in a double layer system consisting of aqueous 25% potassium bromide solution and dichloromethane (volume ratio 1/2) containing TEMPO as a catalyst (10mol%) under the constant current condition (current density: 10mA/cm^2) until 2.5F/mol of electricity passed through the system.

The corresponding acetylenic aldehydes were obtained in moderate yields as the predominate product, as shown in Table 2. Use of a flow cell as a reaction vessel in these reaction were on progress for application to the large-scale production.

As a conclusion, we successfully developed selective synthesis of acetylenic carboxylic ester and aldehydes, which are difficult to prepare by other and methods.

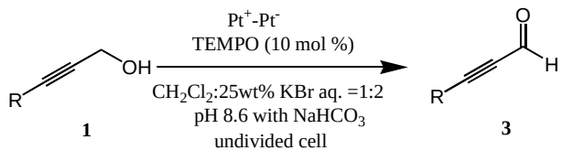
Table 1.Synthesis of Acetylenic Carboxylic Acid Benzyl Esters by Anodic Oxidation from Acetylenic Alcohols



Entry	R	Yield (%)[a)]
1	H	80 [**2a**]
2	Me	74 [**2b**]
3	Et	71 [**2c**]
4	*n*-Pr	65 [**2d**]

Reaction Condition: Substrate (15-40mmol), 15wt% H_2SO_4 aq. (100ml), Current Density (10mA/cm^2), Supplied Electricity (6F/mol), 3-5^{o}C, BnBr (1.5eq.),$KHCO_3$ (5eq.), Acetone (60ml), a) Isolated Yield

Table 2. Synthesis of Acetylenic Aldehydes by Anodic Oxidation from Acetylenic Alcohols



Entry	R	Yield (%)[b)]
1	*n*-Pentyl	60[**3a**]
2	Ph	66[**3b**]
3	$MeSiPh_2$	62[**3c**]

Reaction Condition: Substrate (5-10mmol), CH_2Cl_2:25wt% KBr aq.=1:2 (60ml), Current Density (5mA/cm^2), Supplied Electricity (2.5F/mol), 3-5^{o}C, b) GC Yield

References

1) Penoni, A.; Volkmann, J.; Nicholas,K. M., *Org. Lett.*, **2002**, 4(5), 699

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3) Nishiguchi, I.; Hirashima, T., *Kagaku to Kogyo*, **1988**, 62(9), 372