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A NOVEL SYNTHESIS OF TERMINAL OLEFINS BY ANODIC OXIDATION OF CARBOXYLIC ACIDS HAVING A TRIMETHYLSILYL GROUP ON THE β-POSITION[1)]

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Anodic oxidation of carboxylic acids having a trimethylsilyl group on the β-position gave exclusively terminal olefins in reasonable yields.

Among a variety of methods in the synthesis of olefins,[2)] the reaction of vinyl anion with alkyl halides is not a versatile method of synthesizing terminal olefins[3)] though this pattern of reaction is often desired in organic synthesis.

We wish to report herein a novel synthesis of terminal olefins using anodic oxidation of carboxylic acids having a trimethylsilyl group on the β-position (trimethylsilylcarboxylic acids) as a key reaction in which oxidative elimination of both trimethylsilyl and carboxylic groups in one step leaves a vinyl group. Thus, the anodic oxidation of sodium salts **1** of trimethylsilylcarboxylic acids **5** yielded terminal olefins exclusively (Table 1).

$$\underset{\text{COONa}}{\overset{\text{RCHCH}_2\text{SiMe}_3}{\mathbf{1}}} \xrightarrow[\text{CH}_3\text{CN - CH}_3\text{OH (5 : 1)}]{\text{- 2e}} \underset{\mathbf{2}}{\text{RCH=CH}_2}$$

Trimethylsilylcarboxylic acids **5** can easily be synthesized from alkyl halides and diethyl trimethylsilylmetylmalonate **3** which is obtainable from trimethylsilylmethylchloride[4)] and diethyl malonate in a yield of 70% (Scheme I).

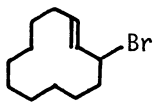
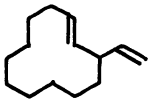
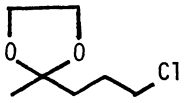
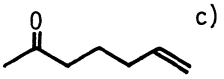
Scheme I

$$\text{Me}_3\text{SiCH}_2\text{Cl} + \text{CH}_2(\text{COOC}_2\text{H}_5)_2 \xrightarrow[70\%]{\text{C}_2\text{H}_5\text{ONa/C}_2\text{H}_5\text{OH}} \underset{\mathbf{3}}{\text{RX + Me}_3\text{SiCH}_2\text{CH}(\text{COOC}_2\text{H}_5)_2} \xrightarrow{\text{C}_2\text{H}_5\text{ONa/C}_2\text{H}_5\text{OH}} \underset{\mathbf{4}}{\text{Me}_3\text{SiCH}_2\overset{\text{R}}{\text{C}}(\text{COOC}_2\text{H}_5)_2} \xrightarrow[2)\ \text{H}^+,\ 3)\ \Delta]{1)\ \text{KOH/C}_2\text{H}_5\text{OH}} \underset{\mathbf{5}}{\text{Me}_3\text{SiCH}_2\overset{\text{R}}{\text{C}}\text{HCOOH}}$$

In this novel method, terminal olefins are derived from alkyl halides in three steps, and the anion generated from **3** may be considered to be a vinyl anion equivalent.

A typical procedure using dodecyl bromide is described below. Compound **4** ($R = C_{12}H_{25}$) was synthesized in a yield of 75% from dodecyl bromide and diester **3** according to the usual malonic acid synthesis. Usual hydrolysis and decarboxylation of diester **4** gave trimethylsilylcarboxylic acid **5**. Anodic oxidation of sodium salt of **5** was carried out using carbon rod electrodes in a mixed solvent of acetonitrile and methanol (5 : 1) under constant current (200 mA/hr, 0.017 A/cm^2) conditions. After 10 *F*/mol of electricity was passed, the reaction mixture was worked up by the usual method, and the product, 1-tetradecene,[5] was isolated by fractional distillation, yield being 83%.

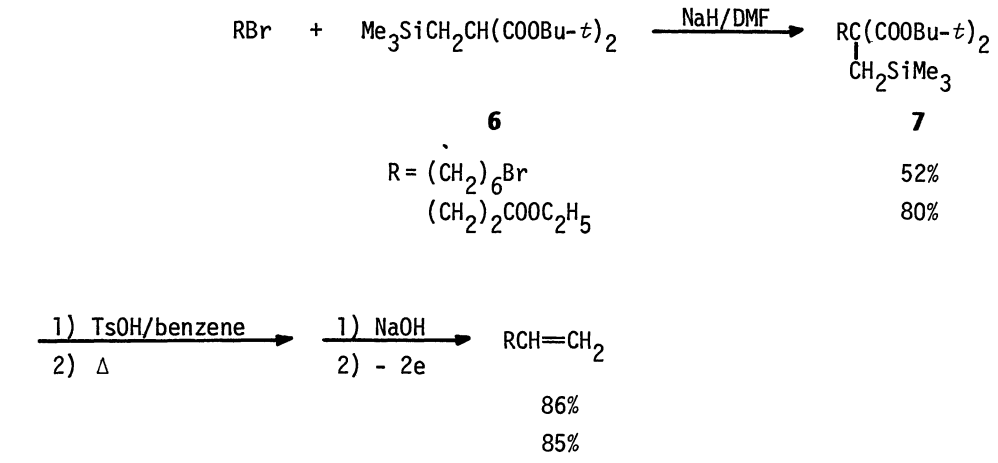
Table 1

Run	RX	Product[a]	Yield, %[b]		Boiling Point (°C/mmHg)
			5 from RX	Electrolysis	
1.	$C_{12}H_{25}Br$	$C_{12}H_{25}CH{=}CH_2$	75	83	125/16
2.	$C_6H_{13}CH(CH_3)Br$	$C_6H_{13}CH(CH_3)CH{=}CH_2$	49	70	72/25
3.	$C_8H_{17}O(CH_2)_4Br$	$C_8H_{17}O(CH_2)_4CH{=}CH_3$	72	87	90—92/2
4.			45	65	101—103/2
5.		 c)	72	78	67—69/50
6.	$Br(CH_2)_6Br$	$C_2H_5O(CH_2)_6CH{=}CH_2$ [d]	43	87	83—84/25

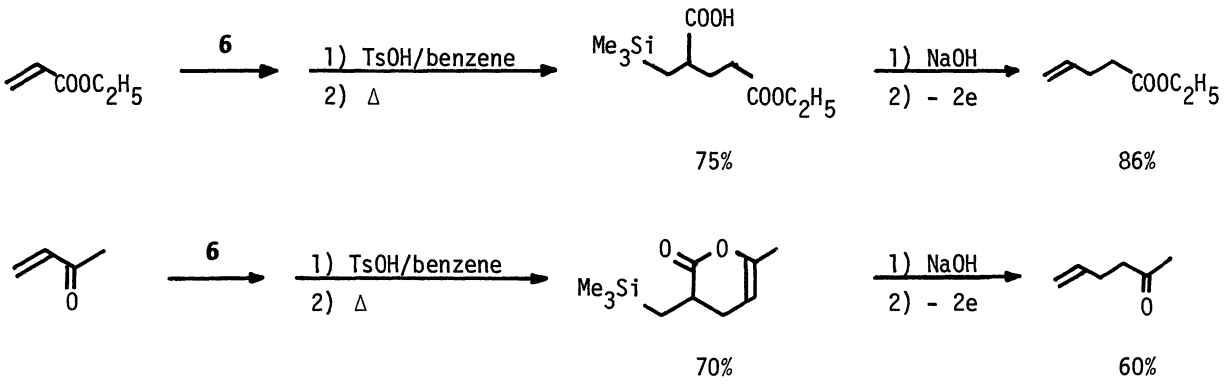
a) Satisfactory spectroscopic and elemental analyses were obtained for all products.
b) Isolated yield.
c) The carbonyl group was deprotected at the stage of **5**.
d) One of the bromine atoms was substituted by an ethoxyl group under hydrolysis conditions.

In case of alkyl halides bearing such functional groups that are unstable under the hydrolysis conditions, di-*tert*-butyl trimethylsilylmethylmalonate **6**[6] is effective as shown in the Scheme II.

Scheme II

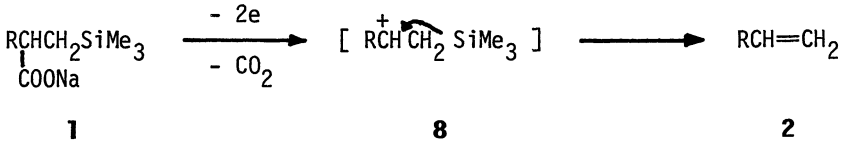


Furthermore, introduction of a vinyl group on the β-carbon atom of α,β-unsaturated compounds is also possible by using diester **6**.

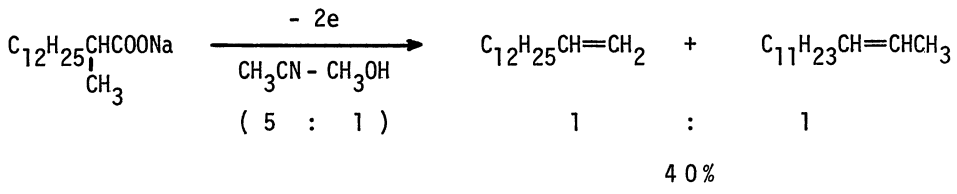


This novel electrooxidative elimination will proceed according to the reaction Scheme III, in which the exclusive elimination of trimethylsilyl cation from the intermediary cation results in the formation of terminal olefins,[7] whereas lack of the trimethylsilyl group in the β-position results in the formation of a mixture (1 : 1) of terminal and inner olefins as depicted in the Scheme IV.[8]

Scheme III



Scheme IV



References and Notes

1) Electroorganic Chemistry. 48.

2) For example; a) J. Reucroft and P. G. Sammes, *Quart. Rev. Chem. Soc.*, **25**, 135 (1971), b) D. J. Faulkner, *Synthesis*, **1971**, 175.

3) J. Millon, R. Lorne, and G. Linstrumelle, *Synthesis*, **1975**, 434.

4) A. F. Reid and C. J. Wilkins, *J. Chem. Soc.*, **1955**, 4029.

5) Bp 125 °C/16 mmHg. Spectroscopic and elemental analyses are as follows: NMR (CCl_4) δ 0.87 (t, 3H, $-CH_3$, J = 7 Hz), 1.10 - 1.55 (m, 20H, $-CH_2-$), 1.83 - 2.65 (m, 1H, -CH=C-), 4.70 - 5.10 (m, 2H, $-C=CH_2$), 5.38 - 6.06 (m, 1H, -CH=C-); IR (neat) 3100, 1645, 910 cm^{-1}. Anal. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37. Found: C, 85.68; H, 14.11.

6) Di-*tert*-butyl malonate was prepared according to the reported method; A. L. McCloskey, G. S. Fonken, R. W. Kluiber, and W. S. Johnson, "Organic Syntheses", Collect. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p. 263.

7) Formation of olefin from β-hydroxyalkylsilane through acid promoted elimination is known to be a versatile method. For example; a) P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, **1972**, 1785; *ibid.*, **1974**, 1133, and b) idem, *J. Am. Chem. Soc.*, **97**, 1464 (1975).

8) Similar results have been reported. W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **86**, 4686 (1964).

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