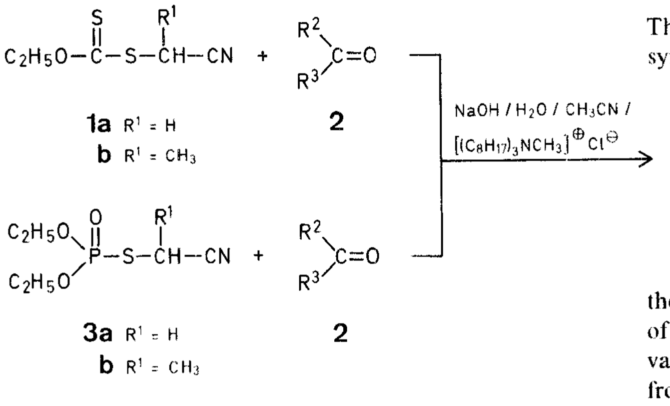
A New and Facile Synthesis of 2-Alkenenitriles from Carbonyl Compounds

Kazuhiko TANAKA*, Noboru ONO, Yoshihiro KUBO, Aritsune KAJI

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo, Kyoto 606, Japan

The direct conversion of carbonyl compounds to 2-alkenenitriles is of great interest since the latter compounds serve as versatile intermediates in organic synthesis[1,2]. Several methods for these transformations have been developed which give good to excellent yields of nitriles in the case of aromatic carbonyl compounds[3-6]. However, few methods are available for the efficient synthesis of 2-alkenenitriles from aliphatic aldehydes or ketones[5-9].



We now wish to report a new, convenient synthesis of 2-alkenenitriles using *O*-ethyl *S*-cyanomethyl dithiocarbonate[10] (**1a**) or *S*-cyanomethyl diethyl phosphorothioate[11] (**3a**). The reactions were easily carried out by stirring a mixture of reagent **1a** or **3a** and carbonyl compounds **2** in a two-phase system in the presence of a catalytic amount of methyltrioctylammonium chloride at room temperature.

Yields and physical constants for 2-alkenenitriles **5** are summarized in the Table. The reaction presumably involves the intramolecular cyclization to thiirane **4** as an intermediate, followed by spontaneous extrusion of sulfur to give the 2-alkenenitrile[12,13].

The utility of this method is further demonstrated by the synthesis of 2-methyl-substituted 2-alkenenitriles utilizing the reagent **1b** or **3b**. Experimental simplicity and absence of isomerized nitriles make the present method highly advantageous for the direct synthesis of 2-alkenenitriles **5** from carbonyl compounds **2**.

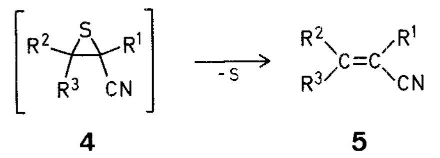


Table. Alkenenitriles **5**

Product No.	R¹	R²	R³	Reagent used[a]	Yield [%]	b.p./torr	Molecular formula[b] or Lit. b.p./torr	I.R. (film) [cm⁻¹] ν_{CN}	$\nu_{C=C}$
5a	H	—(CH₂)₄—		**1a**	46	81°/13	97–98°/24[14]	2225	1640
5b	H	—(CH₂)₅—		**1a, 3a**	56, 36	100°/18	107–108°/22[14]	2220	1630
5c	H	—(CH₂)₆—		**1a**	38	110°/12	123–124°/20[7]	2225	1620
5d	H	—(CH₂)₂—CH(CH₃)—(CH₂)₂		**1a**	45	105°/17	$C_9H_{13}N$ (135.2)	2220	1630
5e	H	CH₃	*n*-C₇H₁₅	**1a**	52	125–132°/20	$C_{11}H_{19}N$ (165.3)	2225	1630
5f	H	CH₃	*n*-C₉H₁₉	**1a**	62[d]	150–153°/19	$C_{13}H_{23}N$ (193.3)	2225	1630
5g	CH₃	H	*n*-C₆H₁₃	**1b, 3b**	74, 58	115°/20	$C_{10}H_{17}N$ (151.3)	2225	1640
5h	CH₃	H	*n*-C₅H₁₁	**1b, 3b**	79, 66	101°/21	$C_9H_{15}N$ (137.2)	2220	1640
5i	CH₃	H	3-heptyl	**1b**	68	110°/20	$C_{11}H_{19}N$ (165.3)	2220	1640
5j	CH₃	H	2-pentyl	**1b**	65	86°/19	$C_9H_{15}N$ (137.2)	2225	1640
5k	CH₃	H	*c*-C₆H₁₁	**1b**	56	110°/15	$C_{10}H_{15}N$ (149.2)	2225	1640
5l	CH₃	H	*s*-C₄H₉	**1b**	54	71°/17	$C_8H_{13}N$ (132.2)	2225	1640
5m	CH₃	H	*n*-C₈H₁₇	**1b**	56	127°/16	$C_{12}H_{21}N$ (179.3)	2225	1640
5n	CH₃	—(CH₂)₅—		**1b**	56	101°/11	102–103°/13[14]	2210	1635
5o	H	CH₃	C₆H₅	**3a**	46	137°/13	$C_{10}H_9N$ (143.2)	2210	1604

[a] All reactions performed using 20 mmol of reagent.

[b] The microanalyses for all products were in satisfactory agreement with the calculated values (C ±0.27, H ±0.35, N ±0.40).

[c] Determined by ¹H-N.M.R. and G.L.C. (conditions: 20% Silicone DC 550 on Celite 545; 0.15 cm × 120 cm, 170°).

[d] Benzyltriethylammonium chloride (100 mg) used instead of methyltrioctylammonium chloride.

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2-Alkenenitriles 5; General Procedure:

To a magnetically stirred mixture of *O*-ethyl *S*-cyanomethyl dithiocarbonate (**1a**; 3.22 g, 20 mmol), carbonyl compound **2** (22 mmol), and methyltrioctylammonium chloride (0.5 mmol) in acetonitrile (3 ml) at 0° under nitrogen is added 50% aqueous sodium hydroxide (13 ml) in one portion. The mixture is stirred at 0° for 5 min and at room temperature for 2 h. The resultant brown mixture is diluted with cold water (300 ml) and extracted with ether (4 × 50 ml). The combined ether extracts are washed with brine and dried (anhydrous sodium sulfate). The crude product is purified either by fractional distillation or subjected to column chromatography (silica gel/benzene) and then distilled under reduced pressure to give the yield shown in the Table.

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^{1}H-N.M.R. (CCl_4) δ [ppm]	*E/Z* ratio[c]
5.20 (m, 1H); 2.5 (m, 4H); 1.76 (m, 4H)	
5.02 (s, 1H); 2.48 (m, 2H); 2.28 (m, 2H); 1.64 (m, 6H)	—
5.06 (s, 1H); 2.60 (m, 2H); 2.41 (m, 2H); 1.60 (m, 8H)	—
5.00 (s, 1H); 2.87 (m, 1H); 2.6–0.8 (m, 11H)	
5.05 (m, 1H); 2.44 (m, 2H); 2.00 (m, 3H); 1.36 (m, 10H); 0.92 (m, 3H)	27/33
4.98 (m, 1H); 2.34 (m, 2H); 1.92 (m, 3H); 1.25 (m, 14H); 0.86 (m, 3H)	68/32
6.00 (m, 1H); 2.28 (m, 2H); 1.88 (m, 3H); 1.37 (m, 8H); 0.92 (m, 3H)	41/59, 44/56
6.08 (m, 1H); 2.20 (m, 2H); 1.85 (d, 3H); 1.32 (m, 6H); 0.88 (m, 3H)	47/53, 47/53
5.85 (m, 1H); 2.35 (m, 1H); 1.85 (m, 3H); 1.24 (m, 8H); 0.85 (m, 6H)	54/46
5.90 (m, 1H); 2.50 (m, 1H); 1.84 (d, 3H); 1.28 (m, 4H); 0.90 (m, 6H)	49/51
5.75 (m, 1H); 2.44 (m, 1H); 1.94 (m, 3H); 1.94–0.8 (m, 10H)	46/54
5.80 (m, 1H); 2.38 (m, 1H); 1.94 (m, 3H); 1.35 (m, 2H); 0.90 (m, 6H)	58/42
5.95 (m, 1H); 2.30 (m, 2H); 1.98 (m, 3H); 1.25 (m, 12H); 0.86 (m, 3H)	42/58
2.46 (m, 2H); 2.26 (m, 2H); 1.84 (s, 2H); 1.60 (m, 6H)	—
7.38 (m, 5H); 5.52–5.32 (m, 1H); 2.40–2.24 (m, 3H)	80/20

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