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A SIMPLE CONVERSION OF N,N-DIMETHYL-2-ALKENYLAMINE TO 2-ALKENAL

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Treatment of N,N-dimethyl-2-alkenylamine with 30% H_2O_2 followed by acetic anhydride affords 2-alkenal (α,β-unsaturated aldehyde) in good isolated yield.

N,N-Dialkyl-2-alkenylamines (1), which are easily prepared by the alkali-metal catalyzed telomerization of 1,3-diene with dialkylamine[1)], are useful intermediates in organic synthesis. Recently a variety of methods are available for the transformation of (1) into 2-alkenol,[2)] 2-chloroalkene,[3)] 2-alkenyl phenyl selenide[4)] and optically active enamine.[5)]

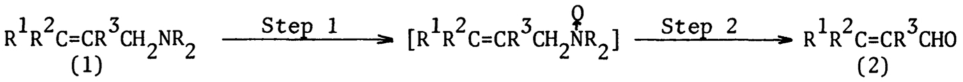
A simple, selective procedure for the conversion of (1) to 2-alkenal (α,β-unsaturated aldehyde) (2) via the Polonovsky reaction[6)] is presented here.

$$\underset{(1)}{R^1R^2C{=}CR^3CH_2NR_2} \xrightarrow[\text{2) } (CH_3CO)_2O]{\text{1) } H_2O_2} \underset{(2)}{R^1R^2C{=}CR^3CHO}$$

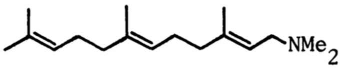
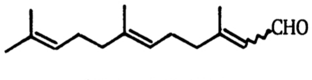
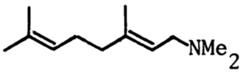
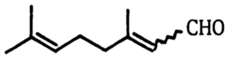
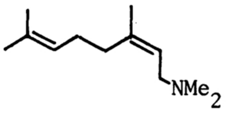
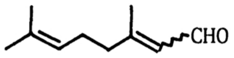
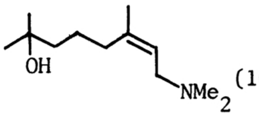
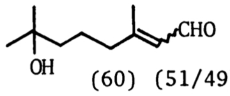
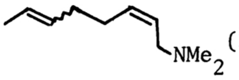
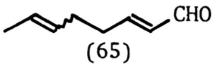
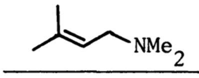
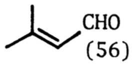
N,N-Dimethyl-2-alkenylamine (1) reacts with excess 30% H_2O_2 in methanol. Degradation of excess of H_2O_2 with PtO_2, and evaporation of the reaction mixture under reduced pressure (to remove H_2O and methanol) provides the corresponding amine oxide in quantitative yield. Conversion of the amine oxide to 2-alkenal (2) is conveniently achieved by adding acetic anhydride. Accordingly, the crude amine oxide is diluted with the solvent, and reacts with 1 - 3 mol. equiv. of acetic anhydride at room temperature. The reaction is clean and complete in less than 1 hr, providing 2-alkenal (2) in good isolated yield (56 - 76% yield based on the starting amine). The ratio of 2-(E)/2-(Z) of 2-alkenal obtained by this method depend extremely on the structure of the starting amines (1).

The results are summarized in Table.[7]

Table Conversion of N,N-dimethyl-2-alkenylamine (1) to 2-alkenal (2)



$$\underset{(1)}{R^1R^2C{=}CR^3CH_2NR_2} \xrightarrow{\text{Step 1}} [R^1R^2C{=}CR^3CH_2\overset{O}{N}R_2] \xrightarrow{\text{Step 2}} \underset{(2)}{R^1R^2C{=}CR^3CHO}$$

Step 1[a]			Step 2[b]			
(1) (mmol)	30% H_2O_2 (ml)	CH_3OH (ml)	$(CH_3CO)_2O$ (mmol)	Solvent (ml)	(2) Yield(%)[c]	(2E/2Z)
 (8)	8	15	25	Benzene 10	 (70)	(71/29)
 (30)	5	15	90	Et_2O 20	 (76)	(81/19)
 (15)	5	15	45	Benzene 10	 (67)	(40/60)
 (10)	5	10	50	Benzene 5	 (60)	(51/49)
 (23)	17	40	70	Benzene 10	 (65)	
 (30)	17	80	90	Et_2O 20	 (56)	

a) 24 h at room temp. b) 1 h at room temp. c) isolated yield

References

1) K. Takabe, T. Katagiri, and J. Tanaka, Tetrahedron Lett., 1972, 4009, idem., Bull. Chem. Soc. Jpn., 46, 222 (1973).

2) V. Rautenstrauch, Helv. Chim. Acta, 56, 2492 (1973), K. Takabe, T. Katagiri, and J. Tanaka, Tetrahedron Lett., 1975, 3005.

3) K. Takabe, T. Katagiri, and J. Tanaka, Chem. Lett., 1977, 1025.

4) S. Murahashi and T. Yana, J. Am. Chem. Soc., 102, 2456 (1981).

5) K. Tani, T. Yamagata, S. Otsuka, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita, and R. Noyori, J. Chem. Soc., Chem. Commun., 1982, 600.

6) For a recent review; M. Ikeda and Y. Tamura, Yuki Gosei Kagaku Kyokai Shi, 38, 10 (1980) and references cited therein.

7) The structures of all compounds were verified by compatible spectral data.

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