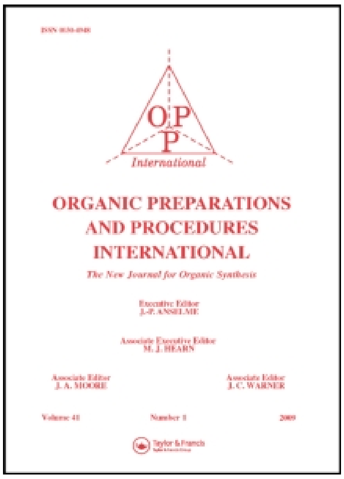

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DIAZOACETALDEHYDE

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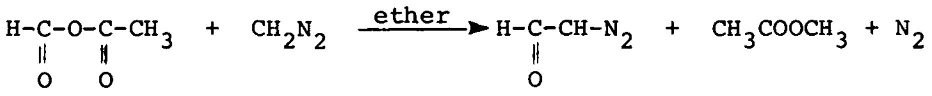
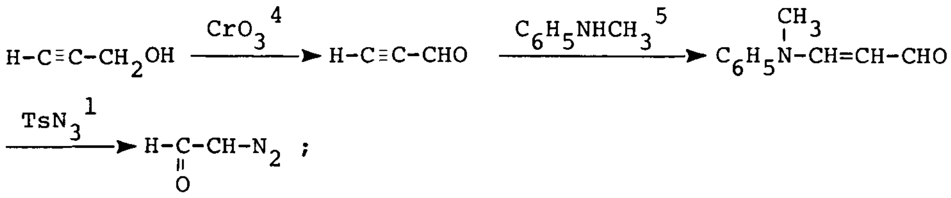


$$H-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 + CH_2N_2 \xrightarrow{ether} H-\underset{\underset{O}{\|}}{C}-CH-N_2 + CH_3COOCH_3 + N_2$$

Diazoacetaldehyde serves as a useful precursor for the generation of formylcarbene,[1] and may be employed to functionalize olefins into the corresponding two-carbon-atom chain-extended aldehydes (ethanalation).[2]

Two procedures have previously been utilized for its preparation: (i) the reaction between formyl fluoride and diazomethane,[3] and (ii) by heating an excess of p-toluenesulfonyl azide with β-N-methylanilinoacrolein and distilling the product as rapidly as it is formed.[1]

The former process gives a crude mixture (in unstated yield) from which it has not been possible to obtain a pure product by chromatography or differential extraction.[3] The latter method gives a pure product, but requires a multi-step approach as shown below[4,5,1]



$$H\text{-}C{\equiv}C\text{-}CH_2OH \xrightarrow{CrO_3{}^{4}} H\text{-}C{\equiv}C\text{-}CHO \xrightarrow{C_6H_5NHCH_3{}^{5}} C_6H_5\overset{CH_3}{\overset{|}{N}}\text{-}CH{=}CH\text{-}CHO \xrightarrow{TsN_3{}^{1}} H\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH\text{-}N_2\ ;$$

for which the overall yield, from commonly available starting materials, is approximately 23%.

The procedure described below is a simple and convenient synthesis of diazoacetaldehyde starting with readily available materials. Formic acetic anhydride is treated with diazomethane in ether solution. Nitrogen is liberated, and the volatile co-product, methyl acetate, is readily removed by rotary evaporation. Diazoacetaldehyde is isolated by distillation in 46% yield.

EXPERIMENTAL

Diazoacetaldehyde.[6] A solution of diazomethane (*ca.* 0.8 mole) in ether was prepared from bis-(N-methyl-N-nitroso)terephthalamide according to the procedure developed by Moore and Reed,[7] and dried over potassium hydroxide pellets.[8]

To the dried, cooled (0°), magnetically-stirred solution of diazomethane was added a solution of formic acetic anhydride[9] (13.2 g., 0.15 mole) in 200 ml. ether over a period of 2 hours. The resultant mixture was stirred at 0° for an additional 2.5 hours. After removal of all volatile material under reduced pressure (water aspirator) by means of a rotary evaporator (water bath temperature *ca.* 45°), the remaining flocculent polymethylene was separated by filtration. The residue was distilled (bath temperature not greater than 50°[1,6]) to provide diazoacetaldehyde as a yellow oil, b.p. 34-37°/9mm. (lit.[1] b.p. ca. 40°/10mm.), ir. ($CHCl_3$) 3110 (CH diazo), 2830 and 2750 (CH aldehyde), 2125 and 2100 (N_2), 1640 cm^{-1} (C=O of α-diazocarbonyl), in 46% yield, identical with an authentic specimen prepared by Arnold's procedure.[1]

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6. CAUTION! Although we experienced no adverse incidents in handling this material, it is strongly advisable to observe adequate safety precautions (efficient fume hood, safety shield) in this preparation. Arnold reports[1] that "diazoacetaldehyde detonates very violently when overheated and great care is required in handling it!"

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