

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

DIAZOACETALDEHYDE

John Hooz^a; Geoffrey F. Morrison^a

^a Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

To cite this Article Hooz, John and Morrison, Geoffrey F.(1971) 'DIAZOACETALDEHYDE', *Organic Preparations and Procedures International*, 3: 5, 227 – 230

To link to this Article: DOI: 10.1080/00304947109356779

URL: <http://dx.doi.org/10.1080/00304947109356779>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

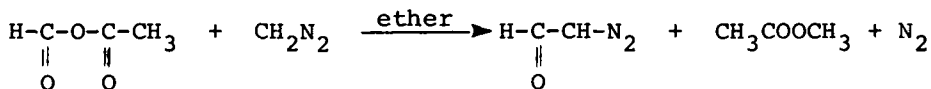
This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

DIAZOACETALDEHYDE

John Hooz and Geoffrey F. Morrison

Department of Chemistry
University of Alberta,
Edmonton, Alberta,
Canada.

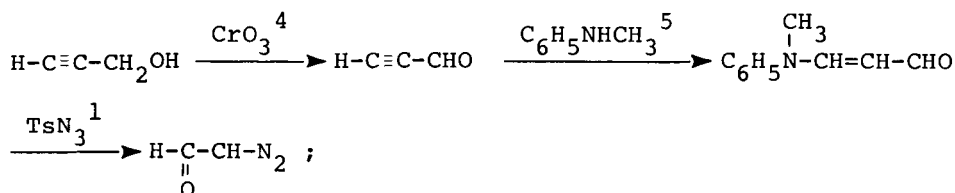


Diazoacetaldehyde serves as a useful precursor for the generation of formylcarbene,¹ and may be employed to functionalize olefins into the corresponding two-carbon-atom chain-extended aldehydes (ethanalation).²

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}

J. HOOZ AND G. F. MORRISON



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 anhydride⁹ (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

DIAZOACETALDEHYDE

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. $34-37^{\circ}/9\text{mm}$. (lit.¹ b.p. ca. $40^{\circ}/10\text{mm}$.), 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

Acknowledgment. We thank the National Research Council of Canada for financial support of this research, and the University of Alberta for a Bursary (G.F.M.).

REFERENCES

1. Z. Arnold, Chem. Commun., 299 (1967).
2. J. Hooz and G.F. Morrison, Can. J. Chem., 48, 868 (1970).
3. F. Kaplan and G.K. Meloy, J. Amer. Chem. Soc., 88, 950 (1966).
4. J.C. Sauer, Org. Syntheses Coll. Vol. 4, 813 (1963).
5. C. Jutz, Chem. Ber., 91, 850 (1958).
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 reports¹ that "diazoacetaldehyde detonates very violently when overheated and great care is required in handling it!"

J. HOOZ AND G. F. MORRISON

7. J.A. Moore and D.E. Reed, *Org. Syntheses*, 41, 16 (1961).
8. F. Arndt, *Org. Syntheses Coll. Vol. 2*, 165 (1943).
9. I. Muramatsu, M. Murakami, T. Yoneda, and A. Hagitani, *Bull. Chem. Soc. Japan*, 38, 244 (1965).

(Received July 16, 1971)