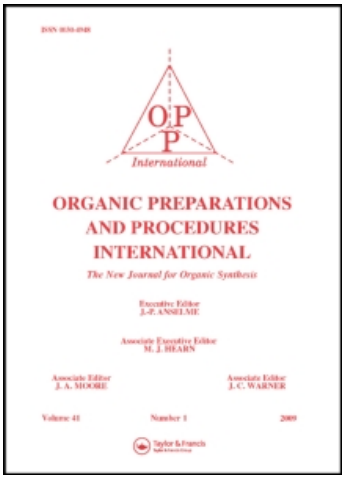

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

VINYLDIAZOMETHANE

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To cite this Article Hooz, John and Kono, Hiromichi(1971) 'VINYLDIAZOMETHANE', Organic Preparations and Procedures International, 3: 1, 47 — 50
To link to this Article: DOI: 10.1080/00304947109356032
URL: http://dx.doi.org/10.1080/00304947109356032

ORGANIC PREPARATIONS AND PROCEDURES INT. 3(1), 47-50 (1971

VINYLDIAZOMETHANE

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$$CH_2{=}CHCH_2NHCONH_2 + HNO_2 \longrightarrow CH_2{=}CHCH_2\underset{\underset{NO}{|}}{N}CONH_2 + H_2O$$

$$CH_2{=}CHCH_2\underset{\underset{NO}{|}}{N}CONH_2 \xrightarrow{KOH} CH_2{=}CH\text{-}CHN_2$$

Vinyldiazomethane has previously been prepared by two methods: (i) treatment of allyl (acetyl t-butyl)-nitrosamine (obtained by reacting nitrous acid with the β-amino ketone made from mesityl oxide and allylamine) with sodium isopropoxide (25% overall yield)[2], and, more commonly[3,4,5], (ii) by the sequence: allylamine→allylurethane→N-nitrosoallylurethane→vinyldiazomethane (17-19% overall yield from allylamine). The latter method suffers the disadvantage, however, that N-nitrosoallylurethane is reported to be unstable toward distillation or any other common purification procedure.[5]

The procedure described below is a convenient two-step synthesis of vinyldiazomethane starting with readily available material. Allylurea is converted to N-nitrosoallyl-

urea, a crystalline and easily purified material. The latter, on treatment with potassium hydroxide in methanol-tetrahydrofuran, affords vinyldiazomethane. The overall yield is ca. 55-60%.

EXPERIMENTAL

N-Allylnitrosourea[6]

To a 500 ml. three-neck flask equipped with a dropping funnel, mechanical stirrer and reflux condenser, and containing a mixture of ice (120 g.) and concentrated sulfuric acid (40 g.) was added dropwise a mixture of allylurea[7] (20 g., 0.2 moles) and sodium nitrite (40 g.) in 150 ml. water while the temperature of the reaction mixture was maintained below 0° (brine ice bath). After completion of the addition, the mixture was vigorously stirred for 4 hrs. below 0°. The N-allylnitrosourea which rose to the surface as a foamy solid was filtered under vacuum and washed with water (four 50 ml. portions). The crude, dried product, mp. 75-77° (22 g., 85%) is sufficiently pure for direct use in the next step.

Further purification may be achieved (with ca. 20-25% loss of material) by dissolving the crude product in ether, washing with saturated brine (three 50 ml. portions), and drying over Na_2SO_4. Evaporation of solvent affords pale-yellow crystals, mp. 82-83°; nmr. ($CDCl_3$, τ) 4.0 - 5.2 (3H multiplet, vinyl protons), 5.56 (2H, doublet, methylene

protons), 3.17 (2H, broad, NH_2); ir. ($CHCl_3$) 3350, 3435, 3423, 1765 cm^{-1}. An analytical specimen, mp. 82-83°, was obtained by washing the crystals with n-pentane.

Anal. Calc'd for $C_4H_7N_3O_2$; C, 37.21; H, 5.42; N, 32.55
Found: C, 37.30; H, 5.33; N, 32.51

Vinyldiazomethane[8]

A solution of N-allylnitrosourea (2.58 g.) in tetrahydrofuran (40 ml.) was added over 30 min. to a stirred, cooled (brine ice bath), solution of potassium hydroxide (1.12 g.) in 10 ml. methanol. After stirring for an additional 1 hr. below 0°, cold brine (25 ml.) was added. The organic layer was separated and the alkaline aqueous layer extracted with 15 ml. tetrahydrofuran. The combined wine-colored organic extracts were washed with cold brine (three 10 ml. portions) and dried (Na_2SO_4). To estimate the yield, an aliquot of the tetrahydrofuran solution of vinyl of vinyldiazomethane was treated with a solution of 2,4,6-trinitrobenzoic acid[4] in tetrahydrofuran. The yield of nitrogen gas, in three independent experiments, was 65-70% of the theoretical amount.

Acknowledgement. We wish to thank the National Research Council of Canada for financial support, and the University of Alberta for the award of a Postdoctoral Fellowship (H.K.).

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6. This preparation is an adaptation of the method described for converting methylurea to N-nitrosomethylurea, F. Arndt, Org. Syn. Coll. Vol. II, 461 (1959).
7. Obtained from Eastman Organic Chemicals, m.p. 85-87°, and used without purification.
8. N-nitrosoallylurea appears to be stable toward storage (dark bottle) at ambient temperatures for ca. two weeks, then gradually decomposes to a yellow oil with liberation of gas. At refrigerator temperatures (ca. 10°), N-nitrosoallylurea appears to be stable for several months.
9. CAUTION! Although we have never experienced any untoward incidents in handling this material, it is advisable to observe adequate safety precautions (hood) in this preparation.

(Received September 28, 1970)