

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>

IMPROVED PREPARATIONS OF CYCLONONEN-3-OL, CYCLONONEN-3-ONE, CYCLONONANONE AND CYCLONONANOL

Goverdhan Mehta^{ab}

^a Department of Chemistry, The Ohio State University, Columbus, Ohio ^b Department of Chemistry, Indian Institute of Technology, KANPUR, India

To cite this Article Mehta, Goverdhan(1970) 'IMPROVED PREPARATIONS OF CYCLONONEN-3-OL, CYCLONONEN-3-ONE, CYCLONONANONE AND CYCLONONANOL', *Organic Preparations and Procedures International*, 2: 4, 245 – 248

To link to this Article: DOI: 10.1080/00304947009458621

URL: <http://dx.doi.org/10.1080/00304947009458621>

PLEASE SCROLL DOWN FOR ARTICLE

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

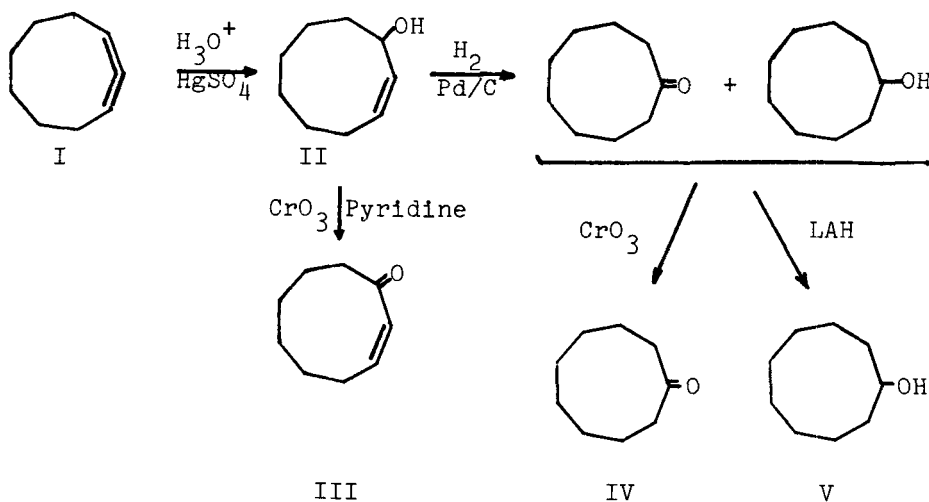
This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

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.

IMPROVED PREPARATIONS OF CYCLONONEN-3-OL,
CYCLONONEN-3-ONE, CYCLONONANONE
AND CYCLONONANOL

Goverdhan Mehta¹
Department of Chemistry
The Ohio State University
Columbus, Ohio 43210

An improved method for the preparation of the title compound is described. 1,2-Cyclononadiene(I) obtained via 9,9-dibromobicyclo (6.1.0) nonane^{2,3} was hydrated by a modification of the procedure of Sharma, Shoulders and Gardner⁴ to give II in 74% yield. Oxidation of II with Sarett's reagent⁵ yielded III. Catalytic reduction of II over 5% palladium on carbon produced a mixture of IV and V,



GOVERDHAN MEHTA

which could be reduced by LAH to give pure V or oxidized by Jones reagent⁶ to yield IV.

EXPERIMENTAL

Cyclonon-2-en-1-ol(II). Cyclonona-1,2-diene (30 g., 0.24 mole) dissolved in tetrahydrofuran (200 ml.) was added to a solution prepared from dilute sulfuric acid (20 g. in 30 ml. of water), mercuric sulfate (3 g.) and tetrahydrofuran (300 ml.). The mixture was refluxed for 4 hr. under nitrogen and filtered to remove the precipitated inorganic salts. The organic phase was separated by dilution with water (200 ml.) and extraction with three 100-ml. portions of ether. The combined ethereal extract was washed with 50-ml. portions of brine, dried and freed of solvent to give 28.3 g. of a pale yellow oil. Distillation yielded 25.1 g. (74%) of a colorless liquid, bp. 88-90°/1 mm., n_D^{26} 1.4961; lit.⁴ reports 17% yield. The vpc analysis of the product indicated < 99% homogeneity. The above liquid on trituration with pentane and chilling readily crystallized to give a white, waxy solid, mp. 31°. Its IR spectrum displayed signals due to two olefinic protons between τ 3.67 and 4.52 (multiplet) and a one proton absorption at τ 5.34 (broad).

Catalytic Reduction of Cyclonon-2-en-1-ol. The unsaturated alcohol (6 g.) in ethyl acetate (40 ml.) was hydrogenated at 25°C and atmospheric pressure over 5% Pd-C catalyst (600 mg.). After an uptake of approx. 0.7 mole further consumption of hydrogen ceased. The catalyst was removed by filtration and the residue was distilled to give 4.8 g. of colorless oil (96%).

IMPROVED PREPARATIONS OF CYCLONONEN-3-OL.

Vpc examination of the above material in conjunction with IR and NMR spectroscopy indicated it to be a 70:30 mixture of cyclononanol and cyclononanone.

Cyclononanol. The above material (2.1 g.) in dry ether was reduced with an excess of lithium aluminum hydride. Usual work-up followed by distillation gave 2.0 g. (94%) of cyclononanol as a viscous colorless liquid, bp. 85-6°/2 mm., n_D^{26} 1.4914.

Cyclononanone. The mixture from hydrogenation of cyclonon-2-en-1-ol (2 g.) in acetone (10 ml.) was oxidized by Jones' reagent (0.7 M) and worked up routinely to furnish on distillation 1.68 g. (84%) of cyclononanone, bp. 78-9°/3 mm., n_D^{26} 1.4773. A semicarbazone was prepared by standard procedure, mp. 177-79°, lit.⁷ mp. 179.5-180.5°.

Cyclonon-2-en-1-one. Cyclonon-2-en-1-ol (1 g., 0.007 mole) in pyridine (3 ml.) was oxidized by Sarett's reagent⁵ (prepared by adding chromium trioxide (430 mg.) to 3 ml. of pyridine) and left aside at room temperature for 24 hrs. under a nitrogen atmosphere. Dilution with 25 ml. of water and extraction with two 25 ml. portions of ether, followed by washing with 10% sodium bicarbonate and two 15 ml. portions of brine and drying, gave a pale yellow oil (690 mg.). Distillation yielded 617 mg. (61%) of colorless liquid, bp. 81-2°/3mm., n_D^{26} 1.5029. Its IR spectrum had bands characteristic of α,β -unsaturated ketones at 1670 cm^{-1} . Its NMR spectrum showed two low field olefinic protons between τ 3.5 and 4.17 (multiplet).

ACKNOWLEDGEMENT

The author wishes to thank Professor Paul G. Gassman for providing the opportunity for the pursuit of this project. The research was supported by Grant GP-11270 from the National Science Foundation.

REFERENCES

1. Present address: Department of Chemistry, Indian Institute of Technology, IIT Post Office, KANPUR, India.
2. W. E. Doering and A. K. Hoffman, J. Am. Chem. Soc., 76, 7162 (1954).
3. L. Skattelbol and S. Solomon, Org. Syn., 49, 35 (1969).
4. R. K. Sharma, B. A. Shoulders and P. D. Gardner, J. Org. Chem., 32, 241 (1967).
5. G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, J. Am. Chem. Soc., 75, 422 (1953).
6. K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, J. Chem. Soc., 39 (1946); L. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, (1968), p. 142.
7. A. T. Blomquist, L. H. Liu and J. C. Bohrer, J. Am. Chem. Soc., 74, 3643 (1952).

(Received January 7, 1970)