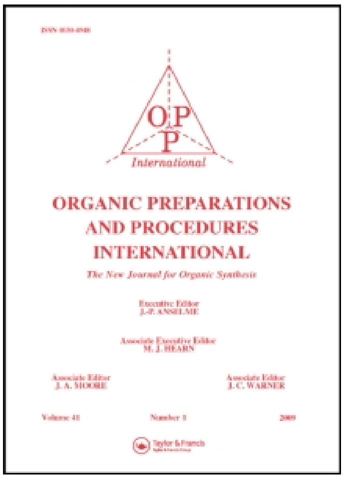


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

2-CYCLOHEXYLIDENECYCLOPENTANONE

Richard D. Sands[a]
[a] Department of Chemistry, Alfred University, Alfred, New York

To cite this Article Sands, Richard D.(1974) '2-CYCLOHEXYLIDENECYCLOPENTANONE', Organic Preparations and Procedures International, 6: 3, 153 — 156

To link to this Article: DOI: 10.1080/00304947409355091

URL: http://dx.doi.org/10.1080/00304947409355091

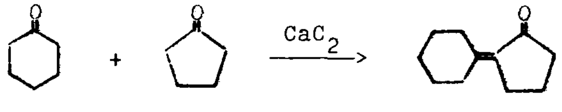
REFERENCES

1. C. Beyer, J. Prakt. Chem., 33, 393 (1886).
2. B. A. Tertov and B. I. Ardashev, J. Gen. Chem. USSR, 27, 3056 (1957).
3. B. I. Ardashev and B. A. Tertov, J. Gen. Chem. USSR, 26, 233 (1956).
4. "Heterocyclic Compounds," R. C. Elderfield, Ed., Vol. 4, p. 15, John Wiley & Sons, Inc., New York, N. Y., 1953.
5. J. E. Gowan and T. S. Wheeler, "Name Index of Organic Reactions," Longmans, Green & Co. Ltd., London, 1960, p. 72.
6. E. Wohnlich, Arch. Pharm., 251, 526 (1913).
7. D. J. Cook and W. E. Schelwalt, Proc. Indiana Acad. Sci., 74, 183 (1964).
8. W. H. Mills, J. E. G. Harris and H. Lambourne, J. Chem. Soc., 119, 1294 (1921).
9. T. Schaefer, Can. J. Chem., 39, 1864 (1961).
10. P. A. Claret and A. G. Osborne, Org. Prep. Proced. Ind., 4, 225 (1972).

2-CYCLOHEXYLIDENECYCLOPENTANONE

Submitted by (6/28/73)
Richard D. Sands
Department of Chemistry
Alfred University
Alfred, New York 14802

Calcium carbide catalyses the self-condensation of cyclopentanone[1] but not that of cyclohexanone[2] while the reverse is true with sulfuric acid;[2,3] sodium hydroxide catalyses the self-condensation of both ketones.[4] Crossed condensations are brought about by all three catalysts,[2] but the calcium carbide method takes less time. Condensation of a mixture of



II

Table I. Condensation of Cyclopentanone and Cyclohexanone

Catalyst	Isomer Distribution (%) of Distilled Product		
	I	II	III
CaC_2	33	64	3
H_2SO_4	0	51	49
NaOH	34	66	0

cyclopentanone and cyclohexanone gives only three dimeric products: 2-cyclopentylidenecyclopentanone (I), 2-cyclohexlidenecyclopentanone (II), and 2-cyclohexylidenecyclohexanone (III). 2-Cyclohexylidenecyclopentanone is the major dimeric product and no 2-cyclopentylidenecyclohexanone is formed.

This crossed condensation reaction provides a more direct route to 2-cyclohexylidenecyclopentanone from readily available materials than the Schmidt reaction of spiro[5.5]-undecan-1-one.[5]

EXPERIMENTAL

A 500-ml. flask was fitted with a Soxhlet extractor large enough to hold a 43 x 123 mm extraction thimble. A mixture of 1 mole each of cyclopentanone and cyclohexanone was placed in the flask and 32 g (0.5 mole) of calcium carbide was put into the extraction thimble. The mixture was heated to boiling and cycled through the extraction for 4 hrs. The reaction mixture was then cooled, washed three times with 100 ml. portions of saturated sodium bisulfite solution and extracted with three 50 ml. portions of ether. The combined ethereal extracts were dried over anhydrous sodium sulfate. Removal of the ether and distillation gave 36 g. of liquid boiling at 120-160° (9 mm.) and left 31 g. of polymeric residue.

The distillate (see Table I) was separated by preparative gas chromatography. A 10 ft. x 3/8 in. column of 20% Dow-710 on 60/80 mesh acid washed Chromosorb W in an Aerograph A-700 Autoprep gave a satisfactory separation under the following conditions: column temperature, 225°; injector temperature, 225°; carrier gas, hydrogen at 100 ml./min.; sample size, 50 ul; attenuator, x 16. Under these conditions 2-cyclopentylidenecyclopentanone had a retention time of 5 1/2 minutes and 2-cyclohexylidenecyclopentanone had a retention time of 6 1/2 minutes.

2-Cyclohexylidenecyclopentanone, 23 g. (14%), exhibited the following properties: bp. 80°/2mm., n_D^{22} 1.5192, ir (neat) 1690 cm^{-1} (C=O), and 2,4-dinitrophenylhydrazone, mp. 213°, lit.[5], mp. 213°.

REFERENCES

1. M. B. Turova-Pollak, I. E. Sosnina and E. G. Treshchova, J. Gen. Chem. USSR, 23, 1111 (1953); Chem. Abs., 47, 12207f (1953).
2. Present work.
3. H. Gault, L. Daltroff and J. Ecktridon, Bull. Soc. Chim. France, 12, 952 (1945).
4. W. Huckel, M. Maier, E. Jordan and W. Seegar, Ann., 616, 46 (1958).

5. R. T. Conley and B. E. Nowak, J. Org. Chem., 26, 692 (1961).

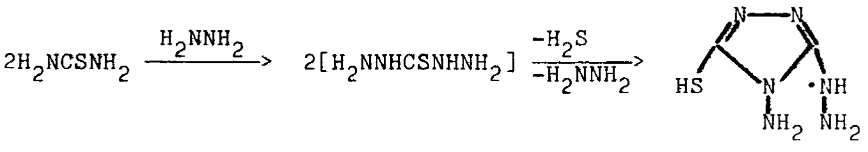
4-AMINO-3-HYDRAZINO-5-MERCAPTO-1,2,4-TRIAZOLE

Submitted by (5/15/73)

R. G. Dickinson and N. W. Jacobsen

Department of Chemistry
University of Queensland
St. Lucia 4067, Queensland, AUSTRALIA

4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole (I) can be prepared from a great variety of acyclic and cyclic compounds containing the thioureido grouping by reaction with hydrazine.[1] The title compound is of special interest because it has



$$2H_2NCSNH_2 \xrightarrow{H_2NNH_2} 2[H_2NNHCSNHNH_2] \xrightarrow[-H_2NNH_2]{-H_2S}$$

I

recently been shown to be a specific, yet highly sensitive reagent for the detection of aliphatic and aromatic aldehydes.[2] The qualitative test depends upon the rapid formation of purple or magenta colored 6-mercapto-3-substituted-s-triazolo-(4,3-b)-s-tetrazine derivatives when one drop of an aldehyde is added to a freshly prepared solution of 0.1 g of the reagent in 2 ml of N-sodium hydroxide and the mixture is aerated using a micro-bubbler. The intense color of the triazolo-tetrazine dye develops rapidly within 1 minute.