was collected by filtration; it was purified by sublimation and identified by melting point, 121–122°, and by a mixed melting point with an authentic sample.

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Some Factors Influencing the Activity of Raney Nickel Catalyst. I. Preparation of Raney Nickel from Nickel–Magnesium Alloy[1]

BY JOHN N. PATTISON AND ED. F. DEGERING[2]

The preparation of Raney nickel from nickel–magnesium alloys has been the subject of three patents.[3,4,5] None of these give details of the preparation or the activity of the catalysts thus prepared. Organic acids, such as acetic, in concentrations of 20% or less were recommended by Zeltner.[4]

We have studied the preparation of Raney nickel from nickel–magnesium alloys and found that a catalyst comparable in activity to that of Pavlic and Adkin W-4[6] can be produced. The activity comparisons were based on the rate of reduction of styrene at ambient temperature in an Adams reductor. In order to eliminate induction effects, only the time for the middle 64% of the reduction was used. Thus we found W-4 to be 2.12 times as active as W-2[7] and the catalyst described in detail below to be 2.02 times as active as W-2.

Experimental

To a 2-liter erlenmeyer flask, equipped with a Hershberg stirrer, add 230 ml. of glacial acetic acid and 500 ml. of water. The temperature of this solution is brought to 50 ± 2° and 100 g. of finely powdered NiMg alloy (50% Ni by weight) is added in small portions over a period of 20 to 30 minutes. Cooling is provided by an external ice-bath in order to maintain the temperature between 48 and 52° during the addition. After all of the alloy has been added, the mixture is digested for 50 minutes at 50° with continued stirring. The catalyst is allowed to settle and the solution decanted. Approximately 500 ml. of 1% acetic acid is added, the mixture is swirled and allowed to settle before decanting again. The mixture is rinsed twice more in this fashion and then transferred to a 75 × 500 mm. Pyrex tube equipped with a side arm 1 inch below the top and a coarse porosity sintered disc at the bottom for the admission of the wash solution. A stainless steel stirrer is placed just above the disc and a baffle is provided near the top to aid in settling. About 10 liters of 1% acetic acid is passed upward through the catalyst which is suspended to a height of about 250 mm. by regulation of the stirring speed. Following this, the catalyst is similarly washed with about 15 liters of distilled water. The rate of flow of the wash solutions is 150 ml. per minute. After the washing is complete, the water is drawn off through the sintered disc and replaced by a suitable solvent such as absolute alcohol or dioxane for future storage. Fresh portions of the solvent are stirred up with the catalyst and withdrawn through the sintered disc four to six times to remove the water. The catalyst should be stored in a tightly closed bottle completely filled with liquid in order to exclude contact with oxygen.

Discussion.—Variation of the mesh size of the alloy and amount of acid used in the activation step had very little effect on the activity of the catalyst produced. However, the amount of nickel in the alloy and the method of washing are very important. A catalyst prepared from a 30% nickel (by weight) alloy was only one-half as active as one prepared from a 50 weight per cent. alloy of nickel. If the acetic acid wash is omitted, the resulting preparation will not reduce styrene at all under these conditions.

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[1] From the Ph.D. Thesis of John N. Pattison, Purdue University, June, 1948; Battelle Memorial Institute, Columbus, Ohio.

[2] Miner Laboratories, Chicago, Illinois.

[3] French Patent 844,783, May 1, 1939.

[4] J. Zeltner, U. S. Patent 2,326,275, August 10, 1943.

[5] J. H. Hahn, U. S. Patent 2,328,140, August 31, 1943.

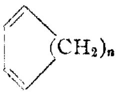
[6] Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

[7] Mozingo, *Organic Syntheses*, **21**, 15 (1941).

Ultraviolet Absorption Spectrum of 1,3-Cycloheptadiene

BY E. PESCH AND S. L. FRIESS

In connection with a study of conjugated unsaturation in cyclic systems, it was of interest to prepare a sample of 1,3-cycloheptadiene (I) to be used for determination of its ultraviolet absorption spectrum. Although the compound has been prepared previously by several workers,[1,2] no mention was made of its absorption characteristics. Further, since the ultraviolet spectra of cyclopentadiene,[3] 1,3-cyclohexadiene[4a,b] and 1,3-cycloöctadiene[5] in suitable solvents are available in the literature, the evaluation of the wave length of maximum absorption for I in the present study fills the blank for the seven-membered diene, and makes possible a correlation of $\lambda_{max.}$ values with ring size in the series of conjugated cyclic dienes



$n = 1, 2, 3, 4$

Experimental[6]

The cyclic diene I was prepared by experimental procedures exactly paralleling those used by Cope[5] for the synthesis of 1,3-cycloöctadiene. The synthetic sequence is outlined below. With the exception of II, all members of the sequence were previously known and characterized.

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[1] Willstätter, *Ann.*, **317**, 204 (1901).

[2] Kohler, Tishler, Potter and Thompson, THIS JOURNAL, **61**, 1057 (1939).

[3] Scheibe, *Ber.*, **59**, 1333 (1926).

[4] (a) Allsopp, *Proc. Roy. Soc.* (*London*), **143A**, 618 (1934); (b) Henri and Pickett, *J. Chem. Phys.*, **7**, 439 (1939).

[5] Cope and Estes, THIS JOURNAL, **72**, 1128 (1950).

[6] Melting points are corrected. Analyses by Mrs. G. L. Sauvage.