vacuo to remove traces of solvent before acceptable analytical data could be obtained.

3-Vinylpyridine (IX).—IX was prepared by the method of Doering and Weil[4] with constructive modifications. α-(3-Pyridyl)-ethyl chloride hydrochloride (XI) which is strongly deliquescent, was purified by sublimation at 0.5–0.7 mm. and 70–80° rapidly, and without decomposition, to give long, colorless, prismatic needles, m.p. 111–112° (reported[4] m.p. 109–110°) in a yield of 53.0% from β-pyridylmethylcarbinol.

Three reactions of sublimed XI (15.0 g., 0.084 mole), 23 cc. of trimethylamine[15] and 40 cc. of absolute methanol were placed in a sealed tube for 48 hr. at room temperature, for 10 hr. at 80° and for 10 hr. at 125°, respectively. The reaction mixtures were worked as previously described.[4] From the first run, 65% of the starting material was recovered. From the second and third, 4 and 54% of the theoretical amount of α-(3-pyridyl)-ethyldimethylamine was obtained by ether extraction of the solvent-free residue in 8% aqueous sodium hydroxide. In the usual way, solid potassium hydroxide was added to raise the concentration to 40–50%, and the solution of residual quaternary hydroxide was boiled vigorously to give 3-vinylpyridine in 28, 65 and 38% yields, respectively.

4-(β-Pyridyl)-cyclohexene-1 (X).—From experiments 7 and 8 (Table I), X was isolated by distillation, b.p. 98–100° at 3 mm., and was converted to the **picrate**, m.p. 117–118.5° after one recrystallization from absolute ethanol.

Anal. Calcd. for $C_{17}H_{16}N_4O_7$: C, 52.6; H, 4.2; N, 14.4. Found: C, 52.8; H, 4.1; N, 14.9.

3-Phenylpyridine.—X was dehydrogenated by boiling a solution of 0.50 g. (0.003 mole) and 0.70 g. (0.007 mole) of maleic acid in 10 cc. of water for 8 hr., in the presence of 0.5 g. of palladium-black. The reaction product was converted directly to the crude picrate: 0.70 g., 61%, m.p. 157–159° with softening from 145°. One recrystallization from ethanol afforded long, fine, yellow needles, m.p. 161–163° with softening beginning *ca.* 150°. Repeated recrystallization from acetone was required to eliminate this softening behavior; reported values of m.p.: 161–163.5°,[16] 162–164°,[17] 159–160°,[14] 162–163°.[18]

3-Cyclohexylpiperidine Hydrochloride.—The catalytic reduction of 0.32 g. (0.002 mole) of X, dissolved in 40 cc. of 1.5 *N* hydrochloric acid in the presence of 0.1 g. of platinum oxide, was complete in 3.5 hr., a total of four equivalents of hydrogen being absorbed. The filtered solution was evaporated to dryness under reduced pressure, the crude hydrochloride being crystallized several times from dry acetone, m.p. 161.5–162.5°. The free amine gave a positive Hinsberg test for secondary amines.

Anal. Calcd. for $C_{11}H_{22}ClN$: C, 64.8; H, 10.9. Found: C, 64.9; H, 11.0.

4-Phenylcyclohexene-1.—This compound was prepared by the method of Alder and Rickert[11] (expt. 9, Table I). A mixture of 20.8 g. (0.20 mole) of styrene (freshly distilled, b.p. 64° at 45 mm.), 28 cc. (0.34 mole) of butadiene and 0.2 g. of hydroquinone was heated in a sealed tube at 125° for 40 hr. Distillation of the product gave 14.65 g. (70.4%) of unchanged styrene, b.p. 45–50° at 27 mm., and 3.50 g. (11.1%) of 4-phenylcyclohexene-1; b.p. 103–110° at 11 mm., reported b.p. 98–115° at 11 mm.[11]

Dehydrogenation of 1.0 g. with selenium according to Alder and Rickert[11] afforded 0.6 g. (61%) of pure biphenyl, m.p. 70–71°, undepressed on admixture with an authentic sample.

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[15] Purified using the phosphorus pentoxide method of Ingram, M.S. Dissertation, University of Chicago, 1940.

[16] Z. H. Skraup and A. Cobenzyl, *Monatsh.*, 456 (1883).

[17] R. Forsyth and F. L. Pyman, *J. Chem. Soc.*, 2912 (1926).

[18] G. Ciamician and P. Silber, *Ber.*, **20**, 191 (1887).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Reactions of Acetylenic Compounds Catalyzed by Sulfonated Polystyrene Resins

BY MELVIN S. NEWMAN

RECEIVED MAY 8, 1953

The rearrangement of 1-ethynylcyclohexanol to 1-acetylcyclohexene is brought about in excellent yield by heating in aqueous acetic acid with Dowex-50, a sulfonated polystyrene resin. It is shown that neither 1-ethynylcyclohexene nor 1-acetylcyclohexanol is an intermediate in this rearrangement. If Dowex-50 is treated with small amounts of mercuric ion a resin (Hg–resin) is obtained which is remarkably effective in promoting hydration of the acetylenic linkage. Several examples are given, including the hydration of acetylene to acetaldehyde.

It is well known that ethynylcarbinols are converted into α,β-unsaturated ketones on heating with formic acid.[1] Several different reagents have been used to effect this change. In the case of 1-ethynylcyclohexanol (I) the yield of 1-acetylcyclohexene (II) is about 60–70%.[2] In this work, it is shown that 84–87% yields of II may be obtained from I by heating with a stirred suspension of Dowex-50[3] in about 90% acetic acid for a short time. Similarly, diethylethynylcarbinol and 1-ethynyl-2,2,6-trimethylcyclohexanol[4] were converted into 3-ethyl-3-penten-2-one[5] (84%) and 2,6,6-trimethyl-1-acetylcyclohexene[6] (75%), respectively. On similar treatment of 3-hydroxy-3-phenyl-1-butyne a reaction leading, presumably, to 3-phenyl-3-buten-2-one occurred, but only polymer was obtained.[7] Further work is required to establish the generality of this method.

In homogeneous solution it is believed that the eneyne, formed by dehydration of the ethynylcarbinol, is the first intermediate and that this is then hydrated to the α,β-unsaturated ketone.[8] In the study of the rearrangement of I into II by means of

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[1] See (a) J. D. Chanley, THIS JOURNAL, **70**, 244 (1948), and (b) A. W. Johnson, "The Chemistry of the Acetylenic Compounds, Vol. I, The Acetylenic Carbinols," Edward Arnold and Co., London, 1946, p. 124 ff. This reaction is usually called the Rupe reaction, although Rupe believed the rearranged products were unsaturated aldehydes.

[2] See J. H. Saunders, *Org. Syntheses*, **29**, 1 (1949).

[3] A sulfonated polystyrene polymer with about 12% cross linking obtained from the Dow Chemical Co. The sample used was 200–400 mesh.

[4] The author is indebted to Professor E. R. H. Jones for a generous gift of 2,2,6-trimethylcyclohexanone.

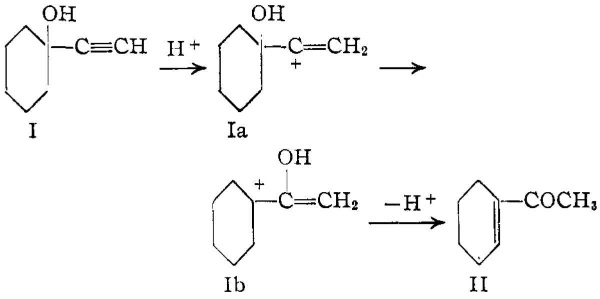
[5] R. Locquin and R. Heilman, *Bull. soc. chim.*, **45**, 1112 (1929); R. Heilmann, *Compt. rend.*, **215**, 112 (1942).

[6] H. B. Henbest and G. Woods, *J. Chem. Soc.*, 1150 (1952), showed that the crude ketone obtained by treating the ethynylcarbinol with formic acid consisted of 2,6,6-trimethyl-1-acetylcyclohexene, (b.p. 88–90° at 20 mm., $n^{20}\text{D}$ 1.4775, when pure) which did not form a 2,4-dinitrophenylhydrazone, and a small amount of a compound, presumably 2,2,6-trimethylcyclohexylideneacetaldehyde, which formed a red 2,4-dinitrophenylhydrazone, m.p. 214–215°.

[7] C. D. Hurd and R. E. Christ, THIS JOURNAL, **59**, 118 (1937), reported a similar experience.

[8] (a) G. F. Hennion, R. B. Davis and D. E. Maloney, *ibid.*, **71**, 2813 (1949). See also (b) J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 2652 (1951). It should be pointed out that the qualitative evidence presented should be supported by kinetic measurements. We are presently engaged in such a study.

the heterogeneous catalyst herein described, it is clear that the dehydration–hydration mechanism[8] (I → III → II) does not obtain since 1-ethynylcyclohexene (III) is only slowly converted into II. Furthermore, since 1-acetylcyclohexanol (IV), is unchanged under the reaction conditions, the mechanism cannot involve a hydration–dehydration mechanism (I → IV → II). In further work, the following mechanism will be used as a working hypothesis, where H+ initially represents the acidic surface.



In suitably selected cases, molecular rearrangements rather than hydroxyl migration might occur through the intermediates Ia. Other fates for Ib are also possible. Although Dowex-50 resin is an excellent catalyst in the rearrangements described above it did not prove a very efficient catalyst for the hydration of the triple bond in hydrocarbons. Accordingly it was attempted to promote the activity by the inclusion of mercuric ions, since mercuric ion is a well known catalyst in homogeneous acid-catalyzed hydration of acetylenes. When Dowex-50 resin was stirred into a solution containing mercuric sulfate in dilute sulfuric acid, a resin, hereinafter termed Hg–resin, was obtained which had remarkable efficiency in promoting the hydration of the acetylenic linkage. Acetylene, propargyl alcohol, 4-octyne, 1-ethynylcyclohexene (III) 1-ethynylcyclohexanol (I) and 2-methyl-3-butyne-2-ol were all smoothly hydrated to the corresponding (and expected) carbonyl compounds as described in the Experimental. While ion exchange type resins have been used to effect a number of acid- and base-catalyzed reactions[9] this appears to be the first case where such resins have been modified by the inclusion of other catalytic ions on the surface. How effective and general this principle will prove remains to be seen.

Experimental

The Dowex-50 resin (200–400 mesh) was prepared for use by suspending in dilute sulfuric acid, followed by washing many times by decantation and air-drying for several days. It was finally dried in a vacuum desiccator over calcium chloride for two days (but not to constant weight). The mercury-treated resin (Hg–resin) was prepared by adding 100 g. of the above prepared resin to about 2 l. of a solution containing 1 g. of mercuric oxide in dilute sulfuric acid. The resin was then washed and dried as above.

1-Acetylcyclohexene (II). (a) **From 1-Ethynylcyclohexanol.**—In the best of several similar experiments a stirred mixture of 39.0 g. of 1-ethynylcyclohexanol,[10] 100 cc. of acetic acid, 10 cc. of water and 20 g. of resin was heated at reflux for 45 min. As soon as reflux temperature had been reached the resin began to darken and in a few minutes had changed from the original brown to almost black. After cooling the resin was filtered off and washed with ether. The filtrate and washings were diluted with water and made slightly alkaline by cautious addition of 40% sodium hydroxide solution. The organic product was taken into ether and the ether solution was washed with saturated sodium chloride solution and filtered through anhydrous magnesium sulfate. The ether was removed through a short packed column and the residue on distillation yielded 33.8 g. (86.7%) of II, b.p. 96–98° at 22 mm., n^{26}_{D} 1.4872. This liquid gave a negative test for acetylenic hydrogen (aqueous alcoholic silver nitrate containing a bit of universal indicator test paper) and the infrared spectrum showed no hydroxyl absorption. The semicarbazone, m.p. 219–221.5° dec., $\epsilon_{\max}$ 24,150 at 260 mμ[1a] and red 2,4-dinitrophenylhydrazone, m.p 199–201° dec., $\epsilon_{\max}$ 16,500 at 255 mμ,[6] were prepared and the melting points were not depressed on mixing with authentic samples. No careful search for traces of cyclohexylideneacetaldehyde was made.[1a]

In two similar runs except that in the second the catalyst recovered from the first was reused the yields were 84.0 and 83.8%, respectively.

(b) **From 1-Ethynylcyclohexene (III).**—After heating a stirred mixture of 14.6 g. of III,[8b,10] b.p. 74.5° at 66 mm., n^{17}_{D} 1.4970, 60 cc. of acetic acid, 6 cc. of water and 15 g. of Hg–resin at reflux for 70 min., there was obtained 10.8 g. (63%) of II, b.p. 75–78° at 8 mm. The recovered resin contained many small globules of mercury. In an exactly similar experiment except that 15 g. of ordinary resin was used in place of the Hg–resin, there was obtained only 5.8 g. of a fraction which was mainly, but not entirely, II. There was considerable unchanged III in the forerun.

1-Acetylcyclohexanol (IV).—A stirred mixture of 67.3 g. of I, 250 cc. of methanol, 50 cc. of water and 20 g. of Hg–resin was held at reflux for four hours. At the end of this period only a faint positive test for acetylenic hydrogen was obtained. There was separated 65.0 g. (84%) of IV, b.p. 78–82° at 7–8 mm., n^{26}_{D} 1.4725. After fractionation through a two-foot packed column, the main fraction boiled at 88.0–88.6° at 12 mm. and had n^{28}_{D} 1.4712. The oxime melted at 106–107° after sintering at about 90°. If the m.p. tube were placed in a bath preheated to 100°, the crystals melted immediately and then rapidly resolidified. This behavior suggests a polymorphic form[11] with a m.p. above 90°. The semicarbazone melted with decomposition at temperatures between 210 and 215°, depending on rate of heating.[12]

When a stirred mixture of 24.0 g. of IV, 60 cc. of acetic acid, 6 cc. of water and 14 g. of resin was refluxed for 40 min. and worked up as usual there was recovered 19.2 g. (80%) of IV, b.p. 80–84° at 7 mm., $n^{24.5}_{\mathrm{D}}$ 1.4725. This experiment rules out IV as a possible intermediate in the conversion of I to II.

1-Acetyl-2,6,6-trimethylcyclohexene.—A stirred mixture of 20.0 g. of 1-ethynyl-2,2,6-trimethylcyclohexanol,[12,13] 80 cc. of acetic acid, 8 cc. of water and 12 g. of resin was held at reflux for 90 min. After the usual procedure there was obtained 14.8 g. (74%) of crude 1-acetyl-2,6,6-trimethylcyclohexene,[6] in two fractions, b.p. 102–110° at 21 mm., n^{27}_{D} 1.4800, and b.p. 110–111° at 21 mm., n^{27}_{D} 1.4806, neither of which gave a red precipitate with 2,4-dinitrophenylhydrazine reagent.[6]

3-Ethyl-3-pentene-2-one.—A stirred mixture of 24.0 g. of 3-ethyl-1-pentyne-3-ol,[14] 50 cc. of acetic acid, 5 cc. of water and 15 g. of resin was held at reflux for 30 min. After the usual work-up 20.2 g. (84%) of the unsaturated ketone, b.p. 147–153°, was obtained.[5] We obtained only one semicarbazone, m.p. 198–200°, and found no evidence of the lower melting isomer reported previously.[5]

4-Octanone.—A stirred mixture of 24.4 g. of 4-octyne,[15] 80 cc. of acetic acid, 8 cc. of water and 20 g. of Hg–resin

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(9) R. Kunin, *Ind. Eng. Chem.*, **44**, 79 (1952).

(10) The author acknowledges with gratitude a special grant from the Graduate School in support of this work and the help of Mr. Frank Avonda for the preparation of a quantity of this and other intermediates.

(11) R. Locquin and S. Wouseng, *Compt. rend.*, **176**, 516 (1923), reported the oxime as melting at 94–95°.

(12) Compare G. W. Stacy and C. A. Hainley, THIS JOURNAL, **73**, 5911 (1951).

(13) H. Sobotka and J. D. Chanley, *ibid.*, **71**, 4136 (1949).

(14) Obtained as a gift from the Air Reduction Co., Murray Hill, N. J.

(15) We wish to thank Professor C. E. Boord and Dr. K. Greenlee for this sample.

was held at reflux for 200 min. At the start the condensate was not homogeneous but near the end it was clear. By fractionation of the products there was obtained 2.7 g. (12%) of 4-octyne and 25.2 g. (89% if allowance is made for recovered octyne) of 4-octanone, b.p. 126–127°, n^{24}_{D} 1.4173. The semicarbazone[16] melted at 95–96°.

In a similar experiment in which untreated resin was used, after refluxing for 260 min. only a small amount of ketone (less than 25%) was formed. After 16 hr. of reflux, about 69% of 4-octanone was obtained.

3-Hydroxy-3-methyl-2-butanone.—When 20 g. of Hg-resin was added to a stirred solution of 37.3 g. of 2-methyl-3-butyne-2-ol[14] in 100 cc. of ethanol and 15 cc. of water there was spontaneous evolution of heat and darkening of the resin. After a short time the mixture was refluxed for 20 min. The resin was removed and the filtrate vacuum distilled. This distillate, b.p. 36–43° at 10 mm., was rectified in a small column to yield 18.8 g. (42%) of 3-hydroxy-3-methyl-2-butanone,[17] b.p. 137–137.4°, n^{26}_{D} 1.4176. This ketone yielded an oxime,[17] m.p. 86.2–87.8° from water, and a semicarbazone,[17] m.p. 164.0–166.6° dec. The lower boiling fractions undoubtedly contained some unchanged ethynylcarbinol and unsaturated ketone. There was also some higher boiling residue (*ca.* 6 g.). In another experiment in which 39.7 g. of ethynylcarbinol, 150 cc. of water and 15 g. of Hg-resin were held near 80° for 5 hr. there was obtained 33.0 g. (68.5%) of 3-hydroxy-3-methyl-2-butanone b.p. 137–138°, n^{23}_{D} 1.4145.

Hydroxyacetone.—When a stirred solution of 10.4 g. (0.2 mole) of propargyl alcohol[18] in 100 cc. of water at 23° was treated with 2 g. of Hg-resin the temperature rose spontaneously to 55° in 13 min. The temperature was held at 50° for 25 min. by intermittent cooling and then it dropped to 40°. After a total time of 100 min. the resin was filtered and the filtrate made up to 120 cc. with water washings. A 12-cc. aliquot (0.02 mole in theory) was treated with phenylhydrazine hydrochloride and sodium acetate to yield an immediate yellow precipitate which weighed 2.85 g. (87%) and melted alone and mixed with an authentic sample of the phenylhydrazone of hydroxyacetone[19] at 99.0–101.4° dec. The semicarbazone[20] melted at 193–196° dec.

Acetaldehyde.—A slow stream of purified acetylene was passed through a stirred suspension of 2 g. of Hg-resin in 100 cc. of water at room temperature for 20 minutes. The resin was filtered. The filtrate smelled strongly of acetaldehyde which was identified as its 2,4-dinitrophenylhydrazone,[21] m.p. 146–147°.

No attempt was made to determine the efficiency of conversion of acetylene to acetaldehyde, but since it is possible to remove all of the catalyst both acidic and mercurial by filtration of the resin, there may be commercial possibilities in this process.

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[16] E. E. Blaise, *Compt. rend.*, **176**, 1150 (1923).

[17] J. Kapron and J. Wiemann, *Bull. soc. chim.*, **12**, 945 (1945); J. Schmidt and P. Austin, *Ber.*, **35**, 3725 (1902).

[18] We wish to thank the General Aniline and Film Corp., Easton, Penna., for a generous sample of propargyl alcohol.

[19] G. Pinkus, *Ber.*, **31**, 32 (1898).

[20] J. U. Nef, *Ann.*, **335**, 250 (1904).

[21] The 2,4-dinitrophenylhydrazone of acetaldehyde has been shown to exist in two modifications (see W. M. D. Bryant, THIS JOURNAL, **60**, 2814 (1938)). The form isolated in this work melted near 147° and was orange. The infrared absorption spectrum in a Nujol mull was almost identical to that obtained with the yellow, m.p. 168°, form. The main feature of the orange form, m.p. 147°, was a strong absorption at 11.75 μ which was not present in the spectrum of the yellow form. I am indebted to Dr. E. Malmberg and Miss F. Zamnik for this measurement.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

1-Cyano-1,3-butadienes. VI. Copolymerization of the *cis*- and *trans*-1-Cyano-1,3-butadienes with Butadiene[1]

BY H. R. SNYDER, K. CHADWICK MURDOCK AND C. S. MARVEL

RECEIVED APRIL 15, 1953

A technique for the separation of substantial quantities of the labile *trans*-1-cyano-1,3-butadiene from its *cis* isomer is described. Melting point data and infrared spectra determinations have confirmed the assignments of configuration previously given to these isomers. The *cis* compound copolymerized with butadiene about 2.5 times more rapidly than the *trans* isomer. When various mixtures of the isomeric cyanodienes were copolymerized with butadiene, however, it was found that at any given percentage conversion the composition of the copolymer was independent of the *cis–trans* ratio in the monomer charge. Moreover, the geometrical configurations and elastomeric properties of copolymers from the two isomers were practically identical. It was concluded that in their copolymerizations with butadiene both isomers have identical monomer reactivity ratios, but that inhibitors of copolymerization were engendered during copolymerizations involving the *trans* isomer. The Diels–Alder adducts of the *trans* isomer with itself and with butadiene were shown to be powerful polymerization inhibitors.

In previous studies[2–5] the separation of the isomeric forms of 1-cyano-1,3-butadiene and certain of their reactions have been reported. It has been of interest to extend the study of the copolymerization[2] of the pure isomers with butadiene in order to learn whether there are any correlations of the geometrical configuration of the cyanodienes with their reactivities in copolymerization or with the structure and properties of the resulting copolymers. Differences in the physical properties of the copolymers could be due to at least three factors: (1) differences in their structural homogeneity, caused by differences in the monomer reactivity ratios[6,7] of the isomeric monomers, (2) variations in the geometrical configuration about copolymer double bonds, and (3) differences in the ratios of 1,2- to 1,4-addition of the monomer units.

No comparative polymerization studies seem to have been made with geometrically isomeric butadiene derivatives. At least ten terminally substituted butadienes have been allowed to copolymerize with butadiene,[8] but apparently none of these had been separated into its *cis* and *trans* isomers.

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[1] The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] H. R. Snyder, J. M. Stewart and R. L. Myers, THIS JOURNAL, **71**, 1055 (1949).

[3] H. R. Snyder and G. I. Poos, *ibid.*, **71**, 1057 (1949).

[4] H. R. Snyder and G. I. Poos, *ibid.*, **71**, 1395 (1949).

[5] H. R. Snyder and G. I. Poos, *ibid.*, **72**, 4096, 4104 (1950).

[6] T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952.

[7] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[8] H. W. Starkweather, P. O. Bare, *et al.*, *Ind. Eng. Chem.*, **39**, 210 (1947).