[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Conversion of Acetone to Isoprene

BY HUGH S. TAYLOR AND WILBUR J. SHENK

The work here reported concerns a three-stage conversion of acetone to isoprene. It was suggested by references to the work of Favorskii[1] who obtained isoprene by condensing acetone with acetylene over powdered anhydrous potassium hydroxide, reducing the 3-methylbutyn-1-ol-3 electrolytically to the butenol and dehydrating the butenol. Because of insufficient details of the Favorskii procedure, we have been unable to follow his methods but have examined a method of synthesis using a recent method for the preparation of the butynol[2] from sodium acetylide and acetone, employing reduction by copper–zinc couples and catalytic hydrogenation with palladium–synthetic polyvinyl alcohol catalyts[3] for the preparation of the butenol, followed by catalytic dehydration of the alcohol to isoprene with the aid of activated alumina.[4] The 3-stage process thus developed appears to be an excellent one for the preparation of isoprene in the laboratory. In the first stage the range of the yields is from 80 to 90%, in the second 75 to 90% and in the final stage 80 to 95%. On this basis, from 100 g. of acetone and a consumption of 40 g. of sodium the minimum and maximum yields of pure isoprene are 56 and 89 g., respectively. In the whole program recorded in the experimental part our average yield was 77 g. of isoprene from 100 g. of acetone used, or 65% of the theoretical yield.

Experimental

3-Methylbutyn-1-ol-3.—The procedure of Hennion and Froning[2] was followed closely, with yields as high as 85% compared with their report of 88%. A side-reaction with the formation of 2,5-dimethylhexyn-3-diol-2,5 occurs, as was observed by Hennion and Froning, if an excess of acetylene is not kept present while acetone is added. From our observations, slow evaporation of the liquid ammonia and aging of the reaction mixture before hydrolysis favor diol formation.

3-Methylbuten-1-ol-3.—(a) Reduction of the butyn-1-ol-3 with coppered zinc dust gave a 50% yield of the butenol admixed with lower boiling side-products. A solution of 10 g. butynol in 100 g. water was added to 20 g. of coppered zinc dust prepared by the method of Strauss.[5] The reaction, after slight initial heating, proceeded spontaneously and was complete in twenty hours. The product was steam distilled, salted out with potassium carbonate, separated from the aqueous layer, dried over potassium carbonate and fractionated. A 50–55% yield, b. p. 92–98°, was obtained, with 40% of low boiling products, b. p. 60–90°. The purity of the product was low, judged by the impure isoprene obtained from it.

(b) Following the method of Nord and Rampino,[3] 13 cc. of the butynol was added to a solution containing 38 cc. of 2% polyvinyl alcohol solution (R. H. 351, high viscosity, 55, polymer), 3 cc. of palladium chloride (0.95% solution) and 140 cc. of water to which was added 1.2 cc. of 4% sodium carbonate solution for neutralization of the acid formed in the reduction process, the whole operation being conducted in an atmosphere of hydrogen. Semi-hydrogenation was complete in twenty-five minutes, 6.8 liters of hydrogen having been added. Hydrogenation slowed down markedly when shaking ceased. Thus, the process can be stopped readily when 52% of the hydrogen necessary to reduce completely the triple bond has been added. At this point test showed that the amount of triple bond material present was less than 1.7%.

The colloid was next coagulated with sodium chloride and the methylbutenol extracted from the salt solution by steam distillation. The product was salted out with potassium carbonate, separated, dried with anhydrous sodium carbonate and rectified. This yielded an azeotrope, b. p. 86–87°, sp. gr. 0.872 (23°), containing 76.8% butenol and the methylbutenol, b. p. 96.5–97.5° at 757 mm., sp. gr. 0.827 (23°). The azeotrope was dehydrated with anhydrous copper sulfate, giving methylbutenol on redistillation; total yield 84% of the theoretical. The purity of the product was confirmed by the high yields of pure isoprene obtained from it.

Isoprene.—Dehydration of 3-methylbuten-1-ol-3 over activated alumina (Alorco, 8–14 mesh) was effected at 290–300° using the technique of Goldwasser.[4] The butenol was fed at 5 cc. of liquid per hour to 20 g. of the catalyst; yields (88% theoretical) of isoprene, b. p. 34–34.5, sp. gr. 0.68 at 23°, were obtained in several different runs. The activity of the catalyst remains unimpaired if, after each 100 cc. alcohol is dehydrated, air is blown through the catalyst chamber for a brief interval. With the butenol prepared by copper–zinc reduction the yields of pure isoprene never exceeded 70%.

Summary

A three-stage conversion of acetone to isoprene has been studied, the reactions involving the production of 3-methylbutyn-1-ol-3 from acetone and sodium acetylide, formation of 3-methylbuten-1-ol-3 by catalytic hydrogenation, with palladium-

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(1) A. E. Favorskii, *Bull. Soc. Chim.*, [5] **6**, 1347 (1939).

(2) G. F. Hennion, *Proc. Indiana Acad. Sci.*, **47**, 117 (1938); J. F. Froning and G. F. Hennion, THIS JOURNAL, **62**, 653 (1940).

(3) F. F. Nord and L. Rampino, St. Louis Meeting, Am. Chem. Soc., April, 1941.

(4) S. Goldwasser and H. S. Taylor, THIS JOURNAL, **61**, 1751 (1939).

(5) Strauss, *Ann.*, **342**, 238 (1905).

synthetic polyvinyl alcohol catalyst, and catalytic dehydration of the butenol to isoprene on activated alumina. An over-all yield of 77 g. (65%) of isoprene per 100 g. of acetone has been obtained and yields up to 90 g. should be practicable.

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Some Kinetic Considerations of the Thermal Decomposition of Benzenediazonium Chloride in Various Solvents*

BY CHAS. E. WARING AND JOHN R. ABRAMS

The thermal decomposition of benzenediazonium chloride in a number of different alcohols and acids has been studied by Pray,[1] who found a substantially constant rate in all the alcohols and a slightly different but also substantially constant rate in acids, the rate in water being closely the same as that for acids. The purpose of the present investigation has been to extend the work of Pray and others to cover several amyl alcohols in order to ascertain whether the rate is affected by branched chains or by the increased viscosity of the solvent. It has also been our purpose to analyze these reactions in terms of the more recent theories of the kinetics of reactions in solution.

Experimental

(a) **Material.**—Since traces of water would influence the rate of decomposition of benzenediazonium chloride, precaution was taken to ensure the dryness of all materials employed. All solvents were tested for moisture just before using. All starting materials were of the highest purity obtainable commercially.

(1) Isoamyl, active amyl, *t*-amyl, pentanol-2 and ethyl alcohols were dried by refluxing for four to five hours over fresh lime and then distilled. Purity was established by boiling point determinations.

(2) Benzenediazonium chloride was prepared by the method of Hantzsch and Jochem.[2] Only that material which was white and in a fine crystalline condition (not in clumps) was used to make a run. It was found that the salt could be stored under anhydrous ether in an ice-box for several weeks without deterioration.

(b) **Apparatus.**—The reaction vessel, partially submerged in a thermostat regulated to within 0.01°, was a large Pyrex test-tube with a capillary side arm connected to a 100-ml. water-jacketed nitrometer graduated in tenths of a ml. This was provided with a glass stirrer rotating in a mercury seal in a rubber stopper. All glass to rubber joints were sealed with Picein cement.

(c) **Procedure.**—In making a run, essentially the same procedure as that of Pray was followed. Throughout each run the temperature of the nitrometer and the barometric pressure were recorded regularly. Volume readings, which were accurate to ±0.02 ml. below 50° and to about 0.05 ml. at 50°, were corrected to S. T. P.

TABLE I

DECOMPOSITION OF BENZENEDIAZONIUM CHLORIDE IN ISOAMYL ALCOHOL, t = 20.0°

Time, min.	Vol., ml.	log $(V_\infty - V_t)$	$k \times 10^3$, min.$^{-1}$
0	0	1.8441	
10	1.66	1.8337	2.40
20	3.27	1.8233	2.39
30	4.94	1.8122	2.54
40	6.59	1.8011	2.58
50	8.21	1.7898	2.59
60	9.79	1.7785	2.60
70	11.37	1.7670	2.65
80	12.87	1.7557	2.62
90	14.33	1.7444	2.60
100	15.76	1.7326	2.72
120	18.49	1.7105	2.53
140	21.08	1.6881	2.59
160	23.57	1.6653	2.62
180	25.88	1.6431	2.56
200	28.17	1.6198	2.67
220	30.32	1.5968	2.65
240	32.32	1.5743	2.60
260	34.24	1.5515	2.63
280	36.10	1.5282	2.68
300	37.76	1.5062	2.56
320	39.41	1.4833	2.64
340	40.94	1.4609	2.58
360	42.44	1.4378	2.66
380	43.74	1.4148	2.64
410	45.88	1.3795	2.71
∞	69.84		
			Av. = 2.60 ± 0.05

ISOAMYL ALCOHOL

Temp., °C.	$k_{av.} \times 10^3$, min.$^{-1}$	No. runs	$r \times 10^3$
20.0	2.61	3	±0.0144
30.0	11.6	4	.143
40.0	47.5	6	.342
50.0	192	5	2.33

ACTIVE AMYL ALCOHOL

Temp., °C.	$k_{av.} \times 10^3$, min.$^{-1}$	Duplicate
30.0	11.9	11.9
35.0	24.8	24.5
40.0	50.4	51.4

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* Presented at the Detroit Meeting of the American Chemical Society.

(1) Pray, *J. Phys. Chem.*, **30**, 1417 and 1477 (1926).

(2) Hantzsch and Jochem, *Ber.*, **34**, 337 (1901).