

The Controlled Semi-Hydrogenation of *tert*-Ethynyl Carbinols and Their Acetate Esters¹

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The semi-hydrogenation of *tert*-ethynyl carbinols, $RR'C(OH)C\equiv CH$, and their acetate esters is accomplished readily under low hydrogen pressure with a 5% Pd-BaCO₃ catalyst. Control of temperature within the range 20–40° is critical and is most conveniently managed by adjustment of the amount of catalyst used. Petroleum ether is a preferred solvent. Under optimum conditions the semi-hydrogenation is highly selective, hydrogen uptake ceasing completely after one mole has been absorbed.

DISCUSSION

In connection with other problems under investigation in this laboratory, need arose for assorted dialkylvinylcarbinols and their esters. The semi-hydrogenation of the corresponding ethynyl compounds presents a simple route to these substances, and, indeed, has been used frequently for this purpose.³ The literature on this subject indicates that previous workers have dealt, for the most part, with conditions which result in rapid conversion of the ethynyl group to vinyl accompanied by much slower hydrogenation of vinyl to ethyl. Thus the hydrogenation process usually is interrupted immediately when one mole of hydrogen has been absorbed.

We have found that when the hydrogenation is conducted at an initial pressure of about 50 p.s.i.g. with control of temperature in the range of 20–40°, using 5% Pd-BaCO₃ as a catalyst and preferably in petroleum ether solution, semi-hydrogenation is clean and highly selective. Under optimum conditions 0.2 mole of ethynyl carbinol (or ester) readily absorbs 0.2 mole of hydrogen in 30–60 minutes without further reaction.

It is generally recognized that palladium catalysts manifest a more selective action on triple bond reduction than do platinum or other metal catalysts.^{3e,4} Raphael⁵ has pointed out too that "highly specific acetylene hydrogenations seem to proceed best in light petroleum." The temperature effect appears not to have been studied adequately.

Many experiments now have been carried out, particularly in the case of 3-methyl-1-pentyne-3-ol, using the Parr low pressure machine,⁶ in which an immersed iron-constantan thermocouple was used to observe temperature during reaction. The hydrogenation is exothermic, of course, and reactions of 0.2 mole of carbinol in 50 ml. of petroleum ether, begun at a room temperature of 22 ± 3° and an initial pressure of 50 p.s.i.g., using 0.03–0.04 g. of 5% Pd-BaCO₃, heat spontaneously to near 40° within 20–30 minutes, the temperature then dropping slowly. Under these conditions the semi-hydrogenation is clean and self-terminating. At initial temperatures of, say, 30°, the temperature rises above 40° and over-hydrogenation occurs.⁷

Suitable control of temperature is easily obtained on a laboratory scale by adjusting the amount of catalyst used and hence the rate of reaction. In individual cases, a few preliminary experiments should be carried out to ascertain the amount to be used for consumption of one mole of hydrogen in about 30–60 minutes. Under these conditions heat is dissipated fast enough to avoid extensive over-hydrogenation. Yields of distilled products are very good (80–90%). When the acetylene derivative is not freely soluble in petroleum ether, as in the case of *p*-nitrobenzoate esters, ethyl acetate may be used as a solvent.⁸ Some preliminary work has been done on the controlled hydrogenation of *tert*-acetylenic primary amines⁹ also, and it appears that semi-hydrogenation of these compounds proceeds equally well, except that about twice as much catalyst is needed.

Incidental to this work, the preparation of *tert*-ethynylcarbinyl acetates was studied. Best results were obtained by esterification of the acetylenic carbinols with acetic anhydride containing a small amount of 85% phosphoric acid.

(1) Paper LXIII on substituted acetylenes; previous paper, *J. Org. Chem.*, **21**, 791 (1956).

(2) Abstracted from the M.S. Dissertations of W. A. S., R. P. L., and W. B. S., University of Notre Dame, 1954–1956.

(3) (a) I. N. Nazarov, *et al.*, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 305 (1946); *Chem. Abstr.*, **43**, 6969 (1949). (b) W. G. Young and I. Webb, *J. Am. Chem. Soc.*, **73**, 780 (1951). (c) D. Papa, *et al.*, *J. Am. Chem. Soc.*, **76**, 4441 (1954). (d) E. F. Smith, U. S. Patent 2,516,826 (1950); *Chem. Abstr.*, **45**, 5711 (1951). (e) A. W. Johnson, *Acetylenic Compounds. Vol. I. The Acetylenic Alcohols*, Edw. Arnold Co., London, 1946, p. 90.

(4) R. A. Raphael, *Acetylene Compounds in Organic Synthesis*, Academic Press, Inc., New York, 1955, p. 23.

(5) R. A. Raphael, Ref. 4, p. 26.

(6) Parr Instrument Co., Inc., Moline, Illinois, serial no. 548, max. rating 50 p.s.i.g.

(7) One run started at 40° attained a temperature of 74° within 19 minutes and consumed 125% of the theoretical amount of hydrogen.

(8) It should be noted that the nitro group is not reduced under these conditions. Work by S. Olivia Barrett.

(9) G. F. Hennion and E. G. Teach, *J. Am. Chem. Soc.*, **75**, 1653 (1953). Work by Wm. Teoli.

Products are described in Tables I-III and analytical data for new compounds are given in Table IV.

Studies of reactions of dialkylvinylcarbinols and their esters are now in progress.

EXPERIMENTAL

Diethylvinylcarbinol. Two-tenths mole (22.4 g.) of freshly distilled diethylethynylcarbinol, b.p. 85.8-86.4° at 112-113 mm., n_D^{25} 1.4353, dissolved in 50 ml. of petroleum ether, b.p. 60-71° ("Skellysolve-B"), was treated with 0.0340 g. of 5% Pd-BaCO₃ in a pressure bottle which then was attached to the Parr reactor and purged three times with hydrogen in the usual way. The hydrogen pressure then was adjusted to 40 p.s.i.g. and reaction was begun by mechanical

shaking. The pressure dropped steadily to 22 p.s.i.g. within 60 minutes and remained at this point for an additional 30 minutes, corresponding to the absorption of 0.2 mole of hydrogen. The experiment was repeated to provide more product. The combined material was filtered to remove the catalyst and was distilled through a helix-packed fractionating column, first at atmospheric pressure to remove most of the solvent, then *in vacuo*. Diethylvinylcarbinol was collected in three fractions: (1) b.p. 79.6-80.0° at 112-113 mm., 2.25 g., n_D^{25} 1.4334; (2) b.p. 80.0-80.6° at 112-113 mm., 27.26 g., n_D^{25} 1.4336; (3) b.p. 80.6-81.2° at 112-113 mm., 8.00 g., n_D^{25} 1.4330; total yield, 37.5 g. (82%). Fraction (2) gave a negative acetylene test with ammoniacal silver nitrate and the infrared spectrum had no band near 4.7 μ . The hydroxyl and olefin bands at 2.9 and 6.1 μ , respectively, appeared as expected.

Dialkylethynylcarbinyl acetates. One mole of freshly dis-

TABLE I
VINYL CARBINOLS, RR'C(OH)CH=CH₂

Compound	R	R'	B.p., °C.	Mm.	n_D^{25}	d^{25}
I ^a	CH ₃	C ₂ H ₅	116	739	1.4246	0.8349
II	C ₂ H ₅	C ₂ H ₅	80	112-113	1.4336	.8443
III	CH ₃	<i>iso</i> -C ₄ H ₉	79	61-62	1.4302	.8315
IV	CH ₃	C ₆ H ₅	96	7-8 ^b	1.5298	1.0004
V ^c	(CH ₂) ₅		70	11-12	1.4731	0.9368

^a Ref. (3a). ^b Analytical sample distilled at 51° at *ca.* 0.4 mm. ^c 1-Vinylcyclohexanol; ref. (3a).

TABLE II
ETHYNYL CARBINOL ACETATES, RR'C(OCOCH₃)C≡CH

Compound	R	R'	B.p., °C.	Mm.	n_D^{25}	d^{25}	Yield, %
VI ^a	CH ₃	CH ₃	60	50	1.4159	0.9275	75
VII ^{a, b}	CH ₃	C ₂ H ₅	76	50	1.4234	.9249	73
VIII	C ₂ H ₅	C ₂ H ₅	91	50	1.4293	.9222	60
IX ^a	CH ₃	<i>iso</i> -C ₄ H ₉	82	24	1.4280	.9011	62
X ^c	(CH ₂) ₅		103	24	1.4625	1.0009	80

^a R. Heilmann, *et al.*, *Bull. soc. chim. France*, 284 (1952); *Chem. Abstr.*, 47, 4832 (1953). ^b G. F. Hennion, *et al.*, *J. Am. Chem. Soc.*, 71, 2814 (1949). ^c 1-Ethynylcyclohexyl acetate; ref. (3c).

TABLE III
VINYL CARBINOL ACETATES, RR'C(OCOCH₃)CH=CH₂

Compound	R	R'	B.p., °C.	Mm.	n_D^{25}	d^{25}
XI ^a	CH ₃	CH ₃	49	50	1.4073	0.8895
XII ^a	CH ₃	C ₂ H ₅	70	50	1.4161	.8925
XIII	C ₂ H ₅	C ₂ H ₅	82	49	1.4216	.8916
XIV	CH ₃	<i>iso</i> -C ₄ H ₉	80	26	1.4238	.8802
XV ^b	(CH ₂) ₅		88	16	1.4540	.9662

^a Ref. (3b). ^b 1-Vinylcyclohexyl acetate; ref. (3c).

TABLE IV
ANALYTICAL DATA

Compound	Mol. formula	C		H	
		Calc'd	Obs'd	Calc'd	Obs'd
II	C ₇ H ₁₄ O	73.63	73.67 ^a	12.28	12.50 ^a
III	C ₉ H ₁₈ O	74.94	74.78 ^a	12.58	12.67 ^a
IV	C ₁₀ H ₁₂ O	81.04	81.25	8.16	8.12
VIII	C ₉ H ₁₄ O ₂	70.10	70.58	9.15	9.36
XIII	C ₉ H ₁₆ O ₂	69.19	69.11	10.32	10.52
XIV	C ₁₀ H ₁₈ O ₂	70.55	70.62	10.65	10.89

^a Average of two determinations.

titled *tert*-acetylenic carbinol was treated with 1.2 moles of acetic anhydride containing 10 drops of 85% phosphoric acid. The anhydride was added to the carbinol dropwise with shaking while maintaining the temperature under 40°. The mixture was allowed to stand overnight, washed with two 75-ml. portions of cold water, and the water washings were extracted with ether. The ether extract was added to the main portion of ester and the combined ethereal solution was washed with 10% sodium carbonate solution until the washings remained basic to litmus. The solution then was washed with two 75-ml. portions of ice-water, dried over calcium chloride, and distilled.

Diethylvinylcarbinyl acetate. Two-tenths mole (30.8 g.) of diethylethynylcarbinyl acetate (Table II) in 50 ml. of

petroleum ether was hydrogenated with the aid of 0.0602 g. of 5% Pd-BaCO₃ at an initial pressure of 50 p.s.i.g. as described above. The pressure dropped to 31.5 p.s.i.g. within 30 minutes and remained at the latter reading for an additional 30 minutes, corresponding to absorption of 0.2 mole of hydrogen. Fractional distillation gave three product fractions: (1) b.p. 81.7–82.0° at 49 mm., 13.1 g., n_D^{25} 1.4220; (2) b.p. 82.0–82.2° at 49 mm., 11.2 g., n_D^{25} 1.4219; (3) b.p. 82.2° at 49 mm., 4.3 g., n_D^{25} 1.4215; total yield 28.6 g. (92%). Although the silver nitrate test was negative, the infrared spectrum had a very weak band at 4.7 μ (trace of unreacted material?) and a weak band at 2.9 μ (trace of —OH compound). Bands at 5.8 μ and 6.1 μ (ester carbonyl and olefin) were strong.

Saponification of methylethylvinylcarbinyl acetate. Three-tenths mole (42.6 g.) of methylethylvinylcarbinyl acetate, obtained by semi-hydrogenation of the acetylene compound, was saponified by boiling for four hours with a solution of 28 g. (0.5 mole) of potassium hydroxide and 20 ml.

of water in 100 ml. of methanol. The solution was cooled and 200 ml. of cold water and 100 ml. of ether were added. The aqueous layer was extracted with 50 ml. of ether and the combined ethereal solution was washed with water and dried with magnesium sulfate. Distillation gave 12.9 g., b.p. 114–116°, n_D^{25} 1.4240, d^{25} 0.8321 and 10.5 g., b.p. 116°, n_D^{25} 1.4230, d^{25} 0.8317, in good agreement with the values for methylethylvinylcarbinol listed in Table I.

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