[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PORTLAND]

The Acid-Catalyzed Rearrangement of Substituted Phenylethynylcarbinols and Styrylethynylcarbinol

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Phenylethynylcarbinol was reported[2] to rearrange to cinnamaldehyde in 35% yield when the carbinol was steam distilled through hot 28% sulfuric acid. The rearrangement, representing a special case of the Meyer–Schuster rearrangement,[3] was considered to proceed *via* the carbonium ion and was successful because the alternate dehydration to an olefin, which usually predominates,[4] was not possible. The work has now been extended to observe whether the rearrangement could be effected when the ring contained certain activating groups and to ascertain the path of rearrangement when styrylethynylcarbinol was subjected to acidic conditions severe enough to cause rearrangement.

3,4-Methylenedioxyphenylethynylcarbinol rearranged to 3,4-methylenedioxycinnamaldehyde in 45% yield when steam distilled through hot 1% sulfuric acid or 10% potassium bisulfate. Since phenylethynylcarbinol was largely unaltered by these reaction conditions, recovered in 80% yield as the mercury derivative, it is presumed the 3,4-methylenedioxy group increased the ease with which the hydroxyl group was removed thus allowing the reaction to proceed under milder conditions.

Similar treatment of 4-ethoxy-3-methoxyphenylethynylcarbinol gave the corresponding cinnamaldehyde in 27% yield despite the low vapor pressure of the carbinol. All attempts, however, to rearrange 3,4-dimethoxyphenylethynylcarbinol and 4-hydroxy-3-methoxyphenylethynylcarbinol by the steam distillation technic were unsuccessful. The 3,4-dimethoxy compound was polymerized by 1% sulfuric acid or by the vapors from 2% formic acid. It steam distilled unchanged through 10% sodium dihydrogen phosphate and was decomposed in part into veratraldehyde by 10% potassium bisulfate. The 4-hydroxy-3-methoxy compound was converted to a tar even by boiling water.

No evidence has been obtained concerning the nature of the tar-forming reaction, which in fact predominated in all cases. Both the condensation and rearrangement reactions occurred more readily when the ring contained activating groups and the condensation reaction occurred to the exclusion of observable rearrangement when the compounds contained 4-hydroxyl or 4-methoxyl groups. The different behaviors of the 3,4-dimethoxy and 4-ethoxy-3-methoxy carbinols was unexpected in view of the generally similar influence of methoxyl and ethoxyl groups.

The rearrangement of styrylethynylcarbinol was of particular interest because its isomerization could conceivably follow one or both of two paths. Jones and McCombie[5] found that several aliphatic compounds of the type $RR'C{=}CHCH(OH)C{\equiv}CH$ upon treatment with dilute acids at room temperature underwent allylic rearrangements involving the double bond to form compounds of the type $RR'C(OH)CH{=}CHC{\equiv}CH$. They observed however, that styrylethynylcarbinol, which would yield 1-phenyl-2-penten-4-yn-1-ol by a Jones–McCombie rearrangement was unaltered by shaking its ethereal solution forty-eight hours with 10% sulfuric acid. If the styryl portion of the molecule remained intact, rearrangement would be expected to involve the triple bond and yield 5-phenyl-2,4-pentadienal.

Styrylethynylcarbinol was found to rearrange upon steam distillation through 20 or 28% sulfuric acid forming 5-phenyl-2,4-pentadienal in 32% yield. The product was identified in separate experiments as its phenylhydrazone, semicarbazone and by silver oxide oxidation to 5-phenyl-2,4-pentadienoic acid.

Experimental

Ethynylcarbinol Rearrangements.—The rearrangements were conducted by steam distilling the carbinols from one flask through 15 cc. of heated aqueous acidic solution in a second flask in the manner previously described.[2] In the cases of phenylethynylcarbinol and the 3,4-methylenedioxy- derivative, 1 to 3 g. samples were used and 0.5-g. samples reacted in the other rearrangements. The use of larger samples in the present apparatus resulted in lower yields because of increased tar formation. The amount of water required for the distillation ranged from 300 cc. in the case of phenylethynylcarbinol to 1600 cc. in the rearrangements of the 3,4-dimethoxy- and 4-ethoxy-3-methoxy- compounds. From one-fifth to one-half of the latter two carbinols remained in the first flask and crystallized as fairly pure needles upon cooling. Allowance was made for the undistilled material when calculating yields.

The organic product in the distillate was separated from the water with ether and the oil remaining after evaporating the ether was converted to the derivative recorded in Table I. The semicarbazones and phenylhydrazones were prepared by usual procedures.[6] Oxidation to the unsaturated acids was effected by adding to the oil a freshly precipitated silver oxide suspension prepared by adding 17 ml. of *N* sodium hydroxide to a solution of 1.9 g. of silver nitrate in 5 ml. of water. The oxidation reaction mixture was vigorously shaken one hour and filtered to remove the silver and excess silver oxide. Acidification of the filtrate precipitated the acid as fine, white, fairly pure crystals. The acids were purified by recrystallizing from aqueous ethanol.

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[2] MacGregor, THIS JOURNAL, **70**, 3953 (1948).

[3] Meyer and Schuster, *Ber.*, **55**, 819 (1922).

[4] Hennion, Davis and Maloney, THIS JOURNAL, **71**, 2813 (1949).

[5] Jones and McCombie, *J. Chem. Soc.*, 261 (1943).

[6] McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947.

TABLE I

REARRANGEMENT OF ACETYLENIC CARBINOLS

Compound	Reagent	Product	Yield, %	Derivative
3,4-CH_2O_2-phenylethynylcarbinol	20% H_2SO_4	3,4-CH_2O_2-cinnamaldehyde	5.3	Semicarbazone[a]
3,4-CH_2O_2-phenylethynylcarbinol	10% H_2SO_4	3,4-CH_2O_2-cinnamaldehyde	19.6	Semicarbazone
3,4-CH_2O_2-phenylethynylcarbinol	1% H_2SO_4	3,4-CH_2O_2-cinnamaldehyde[b]	46.8[b]	3,4-Methylenedioxycinnamic acid[b]
3,4-CH_2O_2-phenylethynylcarbinol	10% $KHSO_4$	3,4-CH_2O_2-cinnamaldehyde	42.8	Semicarbazone
3,4-Dimethoxyphenylethynylcarbinol[c]	10% $KHSO_4$	Veratraldehyde	11.1	Semicarbazone[d]
3,4-Dimethoxyphenylethynylcarbinol[c]	10% NaH_2PO_4	Unchanged carbinol	28.0	....
4-EtO-3-MeO-phenylethynylcarbinol	1% H_2SO_4	4-EtO-3-MeO-cinnamaldehyde	10.5	Semicarbazone[e]
4-EtO-3-MeO-phenylethynylcarbinol	1% H_2SO_4	4-EtO-3-MeO-cinnamaldehyde	27.0	4-Ethoxy-3-methoxycinnamic acid[f]
Styrylethynylcarbinol	28% H_2SO_4	5-Phenyl-2,4-pentadienal	32.0	Phenylhydrazone[g]
Styrylethynylcarbinol	20% H_2SO_4	5-Phenyl-2,4-pentadienal	32.7	Semicarbazone[h]
Styrylethynylcarbinol	20% H_2SO_4	5-Phenyl-2,4-pentadienal	22.0	5-Phenyl-2,4-pentadienoic acid[i]

[a] M. p. 233–234°; lit. value, 234°, Winzheimer [*Ber.*, **41**, 2380 (1908)]. The m. p. was depressed by admixture with piperonal semicarbazone, m. p. 228–229°. [b] 9.0% yield of 3,4-methylenedioxycinnamaldehyde (m. p. 84.5–85°) crystallized from the aqueous distillate. The remaining aldehyde (37.8%) was removed with ether and oxidized to the cinnamic acid (m. p. 234–235°); lit. value, 238°, Roth and Stoermer [*Ber.*, **46**, 269 (1913)]. [c] 10% or 1% sulfuric acid or the vapors from 2% formic acid caused polymerization and no volatile product was isolated. [d] M. p. 177–177.5°; lit. value, 177°, Briner, Tscharner and Paillard [*Helv. Chim. Acta*, **8**, 406 (1925)]. [e] M. p. 185–187°. The m. p. of 4-ethoxy-3-methoxybenzaldehyde semicarbazone is 199.5–200°. [f] M. p. 190–192°; m. p. lowered by mxing with 4-ethoxy-3-methoxybenzoic acid (m. p. 195°). [g] M. p. 169–170.5°; lit. values, 170–172°, Vorländer, Fischer and Kunze [*Ber.*, **58B**, 1284 (1925)]; 173.5–174°, Wittig, Kethur, Klein and Wietbrock [*Ber.*, **69B**, 2078 (1936)]; 178°, Vorländer and Daehn [*Ber.*, **62B**, 541 (1929)]. M. p. lowered by mixing with cinnamalphenylhydrazone. [h] M. p. 218–219°; lit. values, 218–218.5°, Barraclough, Batty, Heilbron and Jones [*J. Chem. Soc.*, 1549 (1939)]; 219–221°, Vorländer, Fischer and Kunze, *loc. cit.* [i] M. p. 164–164.5°; lit. value, 164°, Vorländer, Fischer and Kunze, *loc. cit.*

Styrylethynylcarbinol.—The carbinol was prepared in liquid ammonia from 0.5 mole of cinnamaldehyde and 0.5 mole of sodium acetylide in the usual manner.[7] The dried ethereal solution of the crude reaction product was added dropwise to petroleum ether (b. p. 40–70°) to precipitate 18.4 g. of a tan amorphous polymer. Evaporation of the petroleum ether mother liquor yielded 28.0 g. (35.6%) of crude crystalline 1-phenyl-1-penten-4-yn-3-ol, m. p. 57–62°. After three recrystallizations from petroleum ether, 12.1 g. (15.3%) of the pure compound, m. p. 65–66.5°, was obtained.[8] The mercury derivative melted at 155–156°.

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Summary

The acid-catalyzed rearrangement of phenylethynylcarbinols having substituents on the 3- and 4-positions was investigated. The 3,4-methylenedioxy- and 4-ethoxy-3-methoxy- derivatives, like the unsubstituted compound, rearranged to the corresponding cinnamaldehydes. The 3,4-dimethoxy- and 4-hydroxy-3-methoxy-compounds could not be successfully rearranged by the techniques used.

Rearrangement of styrylethynylcarbinol involved the triple bond rather than the double bond yielding 5-phenyl-2,4-pentadienal.

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[7] Clapperton and MacGregor, THIS JOURNAL, **71**, 3234 (1949).

[8] The compound was first obtained in 2% yield, m. p. 65–66°, by Jones and McCombie, *J. Chem. Soc.*, 733 (1942).