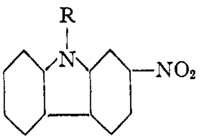
TABLE I



R	M.p.,[a] °C.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found
Methyl	166–166.5	98	12.4[b]	12.4
Ethyl	148.5–149	85	11.7[c]	11.6
Acetyl	229–230	85	11.0	10.8
Methanesulfonyl	202–204	80	9.66	9.97
C_2H_5OCO[d]	153–154.5	90	9.86	9.73
FC_2H_4OCO[e]	167–168	90	9.27	9.10
p-Methylbenzenesulfonyl	272	70	7.65	7.65
Propargyl[f]	188–189	95	11.2	10.9

[a] All melting points are uncorrected. [b] Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.03; H, 4.42. Found: C, 68.90; H, 4.65. [c] Calcd. for $C_{14}H_{12}N_2O_2$: C, 70.00; H, 5.00. Found: C, 70.01; H, 4.81. [d] Prepared using ethyl chlorocarbonate. [e] Prepared using β-fluoroethyl chlorocarbonate. [f] Propargyl bromide was generously supplied by General Aniline & Film Corporation.

denoted completion of the reaction. In some cases it was necessary to charge the mixture with a fresh batch of RX and alkali to complete the reaction. On completion of the reaction the yellow alkaline mixture was poured into excess water. Crystallization from heptane gave yellow needles and plates for the methyl and ethyl compounds, respectively. The remainder of the compounds were crystallized from heptane or benzene–heptane to give light yellow needles. Alcohol can also be used as a crystallizing solvent.

Acknowledgment.—The author is indebted to Dr. Francis E. Ray for his encouragement and interest in this work.

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On the Formic Acid Rearrangement of 2-Phenyl-3-butyn-2-ol

BY TATSUO TAKESHIMA

RECEIVED MARCH 14, 1953

Introduction and Discussion

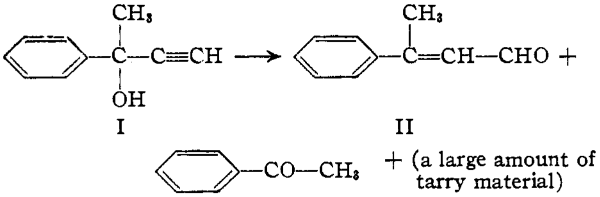
It was reported by Rupe and Giesler[1] that 2-phenyl-3-butyn-2-ol (I) rearranged to β-methylcinnamaldehyde (II) in small yields. The semicarbazone obtained by them is described to give a melting point of 201° after the several crystallizations. However, the melting point of authentic semicarbazone of II has been reported as 205.5–206.5°,[2] 206°.[3]

Hurd and Christ[4] later tried the same reaction, but found no evidence to support Rupe and Giesler's statement. They obtained simply acetophenone (semicarbazone, m.p. 201°) in addition to tarry material.

Our work was undertaken to determine the exact nature of this reaction.

The reaction product obtained by treatment of I with formic acid was fractionated to yield principally two small fractions (b.p. 80–85° (12 mm.), *ca.* 109° (4 mm.)), the residue being a relatively large amount of tarry material. The lower-boiling fraction proved to be acetophenone. The higher-boiling fraction was reactive toward aldehyde reagents and was unsaturated. It gave a semicarbazone, the melting point of which was in good agreement with that of the semicarbazone of II, a 2,4-dinitrophenylhydrazone different from that of acetophenone, and on standing in air gave β-methylcinnamic acid. In addition a small amount of another semicarbazone corresponding to a $C_{10}H_{10}O$ carbonyl compound was obtained from the same fraction and converted to the corresponding 2,4-dinitrophenylhydrazone which was different from that of II. These compounds were not investigated further owing to lack of material.

Thus, II and not the isomeric 3-phenyl-3-buten-2-one was isolated as the rearrangement product. Acetophenone formation may result from cleavage of II[5] or I; its formation is consistent with the observation made by Hurd and Christ.[4]



Acknowledgment.—I wish to express my heartfelt thanks to Messrs. K. Furuhashi and K. Muto for the elementary analyses.

Experimental

2-Phenyl-3-butyn-2-ol (I).—The carbinol was prepared essentially according to the directions of Rupe and Giesler,[1] b.p. 101–104° (12 mm.).

Formic Acid Rearrangement of I.—13.5 g. of I was refluxed with 140 g. of *ca.* 80% formic acid for *ca.* 1.5 hr. and left overnight. The reaction product was then poured onto ice and potassium carbonate, extracted with ether, the ether extracts dried with calcium chloride, concentrated, and the residue was distilled under diminished pressure to yield the following fractions: (1) b.p. 80–85° (12 mm.), *ca.* 2 g., yield *ca.* 18%; (2) b.p. *ca.* 120° (12 mm.) or *ca.* 109° (4 mm.), 1.1 g., yield *ca.* 8%. In addition, a small amount of intermediate fraction boiling at 85–*ca.* 120° (12 mm.), and, as the residue, *ca.* 8 g. of brown-red tarry material were obtained.

Fraction (1) was only weakly reactive toward Schiff reagent.

Anal. Calcd. for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.71; H, 6.58.

Its semicarbazone was prepared in aqueous methanol and recrystallized from methanol to yield colorless needles, m.p. 198–200° (reported 201°,[6] 198–200°,[7] 207°,[8] 206°[8] for acetophenone semicarbazone[8]). (*Anal.* C, 61.29; H, 6.45; N, 23.26.) Its 2,4-dinitrophenylhydrazone was prepared from this semicarbazone in alcoholic sulfuric acid, and washed with ethanol to give orange crystals, m.p. 238–239.5°, which did not depress the melting point (240°) of authentic acetophenone 2,4-dinitrophenylhydrazone (reported 238–240°[9]).

Fraction (2) was a yellowish oil having a greater density than water. It was reactive toward Schiff reagent (light

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(1) H. Rupe and L. Giesler, *Helv. Chim. Acta*, **11**, 656 (1928).

(2) J. F. Arens, D. A. van Dorp, G. van Dijk, B. J. Brandt, P. J. Hubers and H. Pieters, *Rec. trav. chim.*, **67**, 973 (1948).

(3) D. A. van Dorp and J. F. Arens, *ibid.*, **67**, 459 (1948).

(4) C. D. Hurd and R. E. Christ, THIS JOURNAL, **59**, 118 (1937).

(5) *Cf.* O. Wallach, *Ann.*, **289**, 338, 340 (1896); *Ber.*, **32**, 3338 (1899); L. Claisen, *Ann.*, **180**, 19 (1876).

(6) A. Klages, *Ber.*, **37**, 2306 (1904); F. Schlotterbeck, *ibid.*, **40**, 482 (1907).

(7) W. Borsche, *ibid.*, **34**, 4301 (1901).

(8) Beilstein, "Organische Chemie," Zweites Ergänzungs-Werk, Band 7, p. 217. The melting is described to range from 199° to 210° according to the rate of heating.

(9) W. Dirscherl and H. Nahm, *Ber.*, **73B**, 448 (1940).

greenish-yellow color was first produced, being accompanied by the formation of some dregs, then turning pink-purple), gently reduced ammoniacal silver nitrate on heating and decolorized bromine water.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.57; H, 6.83.

Its semicarbazone was prepared in aqueous methanol and recrystallized from methanol to yield long faintly greenish-yellow plates, m.p. 206–206.5° (dec.) (reported 205.5–206.5°,[2] 206°[3] for semicarbazone of II).

Its 2,4-dinitrophenylhydrazone was prepared in alcoholic sulfuric acid, and recrystallized from pyridine containing some alcohol as dark red crystals, slightly soluble in alcohol, easily soluble in pyridine, m.p. 209–210°.

Anal. Calcd. for $C_{16}H_{14}O_4N_4$: C, 58.89; H, 4.32; N, 17.17. Found: C, 59.07; H, 4.26; N, 17.04.

The same 2,4-dinitrophenylhydrazone also was obtained directly from the above semicarbazone. A small amount of another semicarbazone, apparently isomeric, was obtained from the original mother liquor of the above semicarbazone and was recrystallized from methanol containing some water as colorless crystals, easily soluble in methanol, m.p. *ca.* 174°.

Anal. Calcd. for $C_{11}H_{13}ON_3$: N, 20.68. Found: N, 20.01.

This semicarbazone was converted to the corresponding 2,4-dinitrophenylhydrazone as mentioned above, and was washed with ethanol to give orange-red crystals, m.p. *ca.* 173° (*Anal.* C, 58.45; H, 4.10).

Autoxidation of Fraction (2).—The fraction was allowed to stand for a few days in the air, whereupon the greater part crystallized as colorless plates which were washed with ethanol and then had m.p. 98–99.5° (reported 98–99°, 97–98°, 97–98.5° for lower-melting β-methylcinnamic acid[10]).

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(10) Beilstein, "Organische Chemie," Band 9, p. 614; Erstes Erganzungswerk, Band 9, p. 254.

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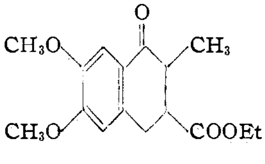
Methoxy 3-Carbethoxy-1-tetralones

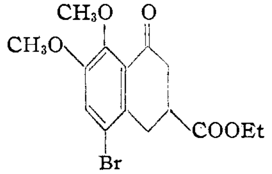
BY GORDON N. WALKER

RECEIVED APRIL 30, 1953

The carbethoxytetralones, I and II, are examples of a class of compounds which are difficult to synthesize by methods involving conventional cyclizations. These two compounds have now been prepared by polyphosphoric acid cyclization of the required acid esters, a method which has been applied successfully to other ketoesters of this type.[1,2]



I



II

The precursor of I was obtained by Stobbe condensation of veratraldehyde with ethyl α-methylsuccinate, hydrolysis *in situ*, partial esterification, and hydrogenation of the resulting acid ester. Cyclization with polyphosphoric acid gave a mixture of I and the corresponding keto acid. Ketoester I was identified by the 2,4-dinitrophenylhydrazone. The synthesis of II involved Stobbe condensation of veratraldehyde with ethyl succinate, hydrogenation of the acid ester, and bromination. The latter reaction led primarily to nuclear monosubstitution under the conditions described in the Experimental section. When the bromo acid ester so obtained was cyclized with polyphosphoric acid, II was formed in moderately good yield. The over-all yield of II from veratraldehyde was 14%. Although II could not be analyzed successfully, it was identified as the 2,4-dinitrophenylhydrazone.

It is possible that II will be of interest in connection with morphine synthetic studies. However, II appeared to be unstable, and attempts to alkylate it with halo-esters did not meet with success.

Experimental[3,4,5]

α-Methyl-3,4-dimethoxyphenylitaconic Acid.—Veratraldehyde (87 g., 0.524 mole) and α-methylsuccinic ester (111 g., 0.591 mole) were added to a solution of 26.5 g. (1.15 g. atoms) of sodium in 500 ml. of absolute ethanol. The mixture was stirred and refluxed for three hours, and excess ethanol (270 ml.) was distilled. The residue was treated with 475 ml. of water. The solution was distilled until 430 ml. of solvents had been collected, and was refluxed for two hours. It was diluted with 1000 ml. of cold water and acidified with 75 ml. of concentrated hydrochloric acid. The solution at this point was decanted from the tar which separated, and was washed with ethyl acetate. Further acidification, refrigeration, and trituration of the crystals with ether afforded 11.2 g. (8%) of di-acid, m.p. 172–176° (dec.). Recrystallization from methanol gave colorless crystals, m.p. 178–180.5° (dec.).

Anal. Calcd. for $C_{14}H_{16}O_6$: C, 59.99; H, 5.76. Found: C, 59.99; H, 5.79.

Monoethyl Ester of α-Methyl-3,4-dimethoxyphenylitaconic Acid.—A solution of 9.4 g. (0.034 mole) of the itaconic acid in 115 ml. of absolute ethanol containing 6 ml. of concentrated sulfuric acid was refluxed for four hours. The neutral product, after isolation in the usual way, consisted of 5.4 g. of oil. This material, apparently the diester, gave the original acid upon hydrolysis with 20% sodium hydroxide solution for three hours. The acidic fraction of the product, isolated by acidification of a dilute alkaline solution, was 4.0 g. of yellow crystals and gum. Recrystallization of this material from aqueous methanol gave 2.8 g. of pale yellow crystals, m.p. 133–135°. Further recrystallization did not raise this melting point.

Anal. Calcd. for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.46; H, 6.98.

2-Methyl-3-carbethoxy-6,7-dimethoxy-1-tetralone and 2-Methyl-3-carboxy-6,7-dimethoxy-1-tetralone. (A) Hydrogenation.—A solution of 2.5 g. of the acid-ester from the preceding experiment in 100 ml. of glacial acetic acid containing 2.0 g. of 5% palladium–charcoal catalyst was shaken under hydrogen (40 lb.) at 75° for 1.5 hours. Filtration of the catalyst and evaporation of the solvent gave 2.5 g. of an oil.

(B) **Cyclization.**—The hydrogenated material was stirred with 14 g. of polyphosphoric acid, and the mixture was heated at 100° for 15 minutes. Hydrolysis of the cooled solution with cold water led to a gum, which was extracted with ethyl acetate. The organic solution was washed with dilute sodium hydroxide solution, dilute acetic acid, sodium bicarbonate solution and water, and was dried over magnesium sulfate. Evaporation of the solvent gave 1.7 g. of neutral product. Trituration with ether afforded 0.9 g. of crystals, m.p. 97–109°. Recrystallization from methanol gave pale yellow crystals, m.p. 120.5–121.5°.

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.70; H, 6.64.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; red crystals, m.p. 241.5–243°.

Anal. Calcd. for $C_{22}H_{24}O_8N_4$: C, 55.93; H, 5.12. Found: C, 56.08; H, 5.22.

The basic solution, upon acidification with hydrochloric acid, deposited 0.4 g. of crystalline material, m.p. 194–201°,

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(1) E. C. Horning and G. N. Walker, THIS JOURNAL, **74**, 5147 (1952).

(2) G. N. Walker, *ibid.*, **75**, 3387 (1953).

(3) Melting points are corrected.

(4) Analyses were carried out by Dr. William C. Alford and his staff.

(5) Infrared spectral measurements were carried out by Mrs. Iris Siewers and Miss Alice Bernardi of the Instrument Laboratory.