The Formic Acid Rearrangement of 3,4-Dimethyl-1-pentyn-3-ol and 3-Isopropyl-4-methyl-1-pentyn-3-ol

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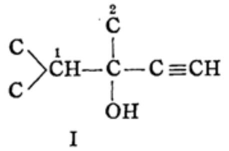
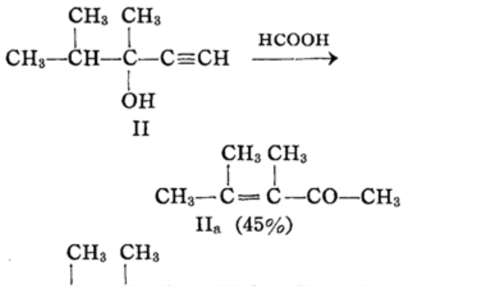
Continuing the study of Rupe reaction of ethynylcarbinols of type I[1], we now show that 3,4-dimethyl-1-pentyn-3-ol (II) and 3-isopropyl-4-methyl-1-pentyn-3-ol (III) on treatment with formic acid afford, in addition to ketone which forms the main product in each case, each corresponding aldehyde (II_b and III_b) in 5* and 6% yield respectively.



I

C^1: Tertiary carbon atom.
C^2: Other than secondary carbon atom.

The reaction product from II was separated into three fractions. The main bulk of the low-boiling fraction (fraction 1; 45% yield) consisted of 3,4-dimethyl-3-penten-2-one (II_a)[2]. The high-boiling fraction (faction 3; 5% yield) reacted with carbonyl reagents (consult Table I) and had an unsaturated aldehydic nature. On treatment with phenylhydrazine it gave a product which had a pyrazoline reaction of a coloration different from that in the case of II_a. The hydrogenation product of this fraction also was positive toward Schiff test, the coloration being different from that of the original substance. Thus, together with analyses, 3,4-dimethyl-2-pentenal (II_b) was assigned to the compound. The facts that it is impossible for the geometrical isomer to exist for II_a and also the trend of Rupe reaction are corroborative of the structure.



$$CH_3-\underset{\displaystyle |}{\overset{\displaystyle CH_3}{CH}}-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}-C\equiv CH \xrightarrow{HCOOH}$$

II

$$CH_3-\overset{\displaystyle CH_3}{C}=\overset{\displaystyle CH_3}{C}-CO-CH_3$$

II_a (45%)

$$CH_3-\overset{\displaystyle CH_3}{CH}-\overset{\displaystyle CH_3}{C}=CH-CHO,\quad CH_3-CH_2-CO-CH_3$$

II_b (5%)*

The intermediate fraction (fraction 2) consisted of a mixture of II_a and II_b; the quantity of the aldehyde contained diminished on standing. The forerun in the case of the distillation contained a considerable amount of methyl ethyl ketone, which owes its origin possibly to the hydrolytic fission of II_a.

The reaction product of III was distilled and three fractions were collected. The greater part of the low-boiling fraction

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[1] T. Takeshima, K. Wakamatsu and A. Furuhashi, This Bulletin, **31**, 640 (1958).

* The actual yield of the aldehyde seemed to be much more, considering its considerable amount contained in fraction 2.

[2] H. Favre and H. Schinz, *Helv. Chim. Acta*, **35**, 2388 (1952); F. C. Whitmore et al., *J. Am. Chem. Soc.*, **63**, 643 (1941).

TABLE I. REACTION PRODUCTS FROM II

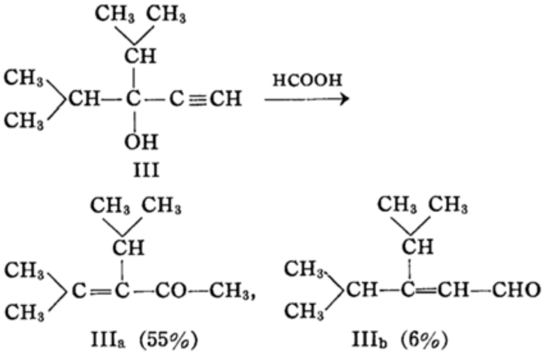
Fraction	B. p., °C	Yield, g. from 20 g. of II	Constituent
Forerun	∼133	A small amount	Considerable amt. of methyl ethyl ketone
1	143∼151	9	II_a
2	152∼159	1.2	II_a, II_b
3	160∼164	1.0	II_b

DERIVATIVES OF THE CARBONYL COMPOUNDS

Original Compd.	2, 4-Dinitrophenylhydrazone		Semicarbazone	
	M. p., °C	Appearance	M. p., °C	Appearance
II_a	132∼133[3]	Lustrous orange plates or long plates	185∼187[4] (slow heating) 198∼199[4] (rapid heating)	Colorless plates
II_b	205∼206	Red plates	163∼164 (slow heating) 173∼174 (rapid heating)	Colorless plates

(fraction 1; 55% yield) was considered to be 3-isopropyl-4-methyl-3-penten-2-one (III_a) reported by Hickinbottom et al.[5]; it gave no crystalline derivative with common carbonyl reagents**.

The high-boiling fraction (fraction 3; 6% yield) had an unsaturated aldehydic nature, which gave characteristic derivatives with carbonyl reagents (consult Table II). On treatment with phenylhydrazine, it yielded an oily product which had a pyrazoline reaction of a coloration different from that in the case of III_a. Viewed from these facts together with analyses and also with the course of the reaction, the compound was assigned 3-isopropyl-4-methyl-2-pentenal (III_b). Here also, the absence of geometrical isomer substantiates the structure. Young and Roberts[6] reported the 2, 4-dinitrophenylhydrazone of m. p. 151.5∼153°C (from ethanol) as the one of III_b without rigid isolation of the original aldehyde which was formed by ozonolysis of crotyldiisopropylcarbinol. However the 2, 4-dinitrophenylhydrazone obtained in the present experiment had m. p. 173.5∼174°C; its appearance (light red plates) resembled that reported[7] (bright red). Further, III_b was hydrogenated to give a saturated aldehyde which afforded a characteristic 2, 4-dinitrophenylhydrazone (consult Table II) and was considered to be 3-isopropyl-4-methylpentanal (IV_b).



The intermediate fraction (fraction 2) which was of a relatively small quantity also contained some III_b.

Experimental

3, 4-Dimethyl-1-pentyn-3-ol (II).—The carbinol was prepared from methyl isopropyl ketone according to the usual manner[8]. B. p. 132∼133°C.

The Formic Acid Rearrangement of II.—Twenty grams of II was gently refluxed for ca. 1 hr. with 160 g. of ca. 80% formic acid. The reaction mixture was allowed to cool and was worked up in the usual manner[1]. Fractions collected were: forerun up to 133°C, a small amount; (1) b. p. 143∼151°C, 9 g., yield 45%; (2) b. p. 152∼159°C, 1.2 g.; (3) b. p. 160∼164°C, 1 g., yield 5%. All these fractions were colorless when freshly

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3) Reported, 132∼133°C. See Ref. 2.

4) Reported, 185.5∼187.5°C and 194∼196°C. See Ref. 2.

5) W. J. Hickinbottom, A. A. Hyatt and M. B. Sparke, *J. Chem. Soc.*, **1954**, 2529.

**Hydrogenation product of III_a which was considered to be 3-isopropyl-4-methyl-2-pentanone (IV_a), on treatment with 2,4-dinitrophenylhydrazine, gave only an oily yellow derivative, the color being apparently different from that in the case of the original ketone.

6) Wm. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **67**, 319 (1945).

7) See Ref. 6.

8) Y. R. Naves and P. Ardizio, *Helv. Chim. Acta*, **31**, 2252 (1948).

TABLE II. REACTION PRODUCTS FROM III

Fraction	b. p., °C	Yield, g. from 20 g. of III	Constituent
1	67∼71 (19 mm.)	11	III$_a$
2	72∼80 (19 mm.)	1	III$_a$, III$_b$
3	85∼91 (19 mm.)	1.2	III$_b$

DERIVATIVES OF THE CARBONYL COMPOUNDS

Original Compd.	2,4-Dinitrophenylhydrazone		Semicarbazone	
	M. p., °C	Appearance	M. p., °C	Appearance
III$_a$	—	Red oil	Could not be obtained	
IV$_a$	—	Yellow oil	—	—
III$_b$	173.5∼174[6]	Light red plates	208∼210	Colorless micro-needles
IV$_b$	86∼88	Yellow plates	—	—

distilled, hardly soluble in water, had camphor-like odor, instantly decolorized bromine water, and reacted with carbonyl reagents. Fraction 1 especially turned yellowish on standing. Fraction 3 had a less camphoraceous odor and, at the same time, a somewhat stimulative smell.

The lower-boiling fractions seemed, from ammoniacal silver nitrate test, still to contain a small amount of the unreacted original carbinol.

Fraction 1 (*3,4-dimethyl-3-penten-2-one, II*$_a$) was treated with phenylhydrazine hydrochloride in ethanolic acetic acid in the usual manner of preparation of pyrazoline. A trace of the reaction mixture thus formed gave a pyrazoline reaction of brownish purple color with sulfuric acid and sodium nitrite; the color was apparently different from that in the case of fraction 3; in the latter case a deep pink-purple color was produced.

Fraction 3 (*3,4-dimethyl-2-pentenal, II*$_b$) gave positive test with Schiff reagent (pink-purple color) and reduced ammoniacal silver nitrate. On heating it turned Fehling solution into turbid bluish green[1]. That the greater part of the fraction consisted of II$_b$ was ascertained from the quantity obtained of its 2,4-dinitrophenylhydrazone mentioned below. A considerable amount of the same derivative was also obtained from fraction 2 when the fraction was treated immediately after the distillation; the aldehyde diminished on standing, owing possibly to autoxidation and polymerization.

Fraction 3 was hydrogenated with palladium. The crude oily product was positive toward Schiff test (pink color). The amount was insufficient for rigid purification.

The forerun up to 133°C, which was of a small amount, contained a respectable quantity of methyl ethyl ketone which was obtained in the form of its 2,4-dinitrophenylhydrazone; the derivative had m. p. 116∼117°C which was undepressed on admixture with an authentic specimen.

2,4-Dinitrophenylhydrazone of II$_a$ was recrystallized from pyridine-ethanol in lustrous orange plates or long plates, m. p. 132∼133°C.

Anal. Found: N, 19.26. Calcd. for $C_{13}H_{16}O_4N_4$: N, 19.17%.

Semicarbazone of II$_a$ was recrystallized from methanol, colorless plates, m. p. 185∼187°C (slow heating), 198∼199°C (rapid heating).

Anal. Found: N, 24.93. Calcd. for $C_8H_{15}ON_3$: N, 24.83%.

2,4-Dinitrophenylhydrazone of II$_b$ was recrystallized from pyridine-methanol, red plates, m. p. 205∼206°C, easily soluble in hot pyridine.

Anal. Found: C, 53.27; H, 5.61; N, 19.17. Calcd. for $C_{13}H_{16}O_4N_4$: C, 53.42; H, 5.52; N, 19.17%.

Semicarbazone of II$_b$ was recrystallized from ethanol, colorless plates, m. p. 163∼164°C (slow heating), 173∼174°C (rapid heating).

Anal. Found: N, 25.33. Calcd. for $C_8H_{15}ON_3$: N, 24.83%.

3-Isopropyl-4-methyl-1-pentyn-3-ol (III).—Prepared from diisopropyl ketone according to the method used in the preparation of II. B. p. 161∼164°C (reported 162∼164°C; prepared by the liquid ammonia method)[9]. Yield, ca. 50%.

Diisopropyl Ketone.—A mixture of 80 g. of isobutyric acid and 110 g. of lead monoxide was refluxed for ca. 3 hr. The whole was heated under diminished pressure to remove water produced and the unreacted acid. The porous solid material obtained was then dry-distilled and finally under a diminished pressure. The crude ketone was washed with a concentrated solution of potassium carbonate, dried over calcium chloride, and distilled. B. p. 122∼128°;C the greater part distilled out at ca. 125°C. Yield, 35%.

The Formic Acid Rearrangement of III.—Twenty grams of III was refluxed with 160 g. of ca. 80% formic acid for ca. 80 min. and worked up as usual. The product was separated into three fractions: (1) b. p. 67∼71°C (19 mm.), 11 g., yield 55%; (2) b. p. 72∼80°C (19 mm.), 1g.; (3) b. p. 85∼91C° (19 mm.), 1.2 g., yield 6%; residue, a small amount of red oil. All these fractions were colorless, hardly soluble in water, had a camphoraceous odor (fraction 3 was accompanied by a somewhat stimulative smell), and instantly decolorized bromine water. The forerun, b. p. ca. 50∼67°C (19 mm.) (ca. 2.7 g.) was somewhat yellowish and seemed still to contain a small quantity of the unreacted carbinol, a few white precipitates being produced with ammoniacal silver nitrate.

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[9] A. F. Thompson, Jr. et al., *J. Am. Chem. Soc.*, **63**, 186 (1941).

Fraction 1 was believed to be *3-isopropyl-4-methyl-3-penten-2-one* (*III*$_a$)[5]; its nature coincided with that reported by Hickinbottom et al. They obtained the compound also from III with the aid of Rupe reaction.

Anal. Found: C, 75.87; H, 11.32. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50%.

Somewhat greater deviation in the carbon content was due possibly to contamination with a compound enriched in oxygen, perhaps the acid formed on autoxidation of III_b.

This fraction, on treatment with 2, 4-dinitrophenylhydrazine, only gave *an oily red derivative; the semicarbazone* could not be obtained. The fraction was refluxed with phenylhydrazine hydrochloride in ethanolic acetic acid, then water was added, and the brown oil separated out gave a pyrazoline reaction of deep bluish violet coloration with sodium nitrite and sulfuric acid.

The same fraction was hydrogenated with palladium to yield an oil of strongly camphoraceous odor, which afforded an oily yellow 2, 4-dinitrophenylhydrazone.

Fraction 3 (*3-isopropyl-4-methyl-2-pentenal, III*$_b$) was positive toward Schiff test (violet color was gradually produced and turned deep pink-purple on standing), and reduced ammoniacal silver nitrate. That the greater part of this fraction consisted of the single compound was ascertained from the quantity obtained of its 2, 4-dinitrophenylhydrazone.

The same fraction on being treated with phenylhydrazine in the manner indicated above, gave a brown oil which had a pyrazoline reaction of deep violet coloration.

2, 4-Dinitrophenylhydrazone of III$_b$ was recrystallized from pyridine containing a little ethanol, light red plates, m. p. 173.5~174°C (reported m.p. 151.5~153°C)[6]. The derivative became thick deep red prisms or needles when allowed to stand overnight in the acidic reagent (the 2, 4-dinitrophenylhydrazine reagent was applied as a methanolic sulfuric acid solution). The melting point of the thick crystals was identical with that of the light red plates, the mixed melting point was undepressed. The light red plates also were converted into the thick crystals on several hours' standing in methanol containing a little sulfuric acid.

Anal. Found: N, 17.52. Calcd. for $C_{15}H_{20}O_4N_4$: N, 17.49%.

Semicarbazone of III$_b$ was recrystallized from methanol, colorless micro-needles, m. p. 208~210°C.

Anal. Found: N, 21.56. Calcd. for $C_{10}H_{19}ON_3$: N, 21.30%.

Hydrogenation Product of III_b (IV).—Half a gram of fraction 3 was hydrogenated in ether with palladium. The reaction product, freed from the ether, was positive toward Schiff test, deep pink color (tinged with purple) being gradually produced. IV was considered to be *3-isopropyl-4-methylpentanal (IV)*.

2, 4-Dinitrophenylhydrazone of IV was recrystallized from pyridine-methanol, yellow plates, m. p. 86~88°C.

Anal. Found: C, 55.67; H, 6.62; N, 17.67. Calcd. for $C_{15}H_{22}O_4N_4$: C, 55.88; H, 6.88; N, 17.38%.

Fraction 2. — The intermediate fraction contained a considerable quantity of III_b as the 2, 4-dinitrophenylhydrazone.

The initial distillate of the forerun in the case of fractionation of the rearrangement product, which was collected at ca. 51°C (19 mm.) and weighed 0.2 g., afforded a small amount of 2,4-dinitrophenylhydrazone of yellow plates, m. p. ca. 124°C (from pyridine-methanol). It seemed to be possibly the derivative of acetone produced by hydrolytic fission of III_a; the amount was insufficient for rigid identification.

Summary

The behavior of 3, 4-dimethyl-1-pentyn-3-ol (II) and 3-isopropyl-4-methyl-1-pentyn-3-ol (III) toward formic acid was investigated. The carbinols, as in the previous report[1], were chosen as model ones in which the tertiary carbon atom is adjacent to the carbon atom carrying the hydroxyl group. Both carbinols gave a significant quantity of the respective aldehydes. These aldehydes were easily isolated on simple distillation.

II gave 3, 4-dimethyl-3-penten-2-one (II_a) in 45% yield and 3, 4-dimethyl-2-pentenal (II_b), a new aldehyde, in 5% yield. III gave 3-isopropyl-4-methyl-3-penten-2-one (III_a) in 55% yield and 3-isopropyl-4-methyl-2-pentenal (III_b) in 6% yield. These carbonyl compounds were characterized. III_b was hydrogenated to give 3-isopropyl-4-methylpentanal (IV) as the 2, 4-dinitrophenylhydrazone.

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