UDC 547.599'314.2.07

62. Michiko Kagawa*1 : Rearrangement of Cyclic Ethynylcarbinols. III.[1] A Few Supplementary Reaction with Monocyclic and Bicyclic Terpenoids.

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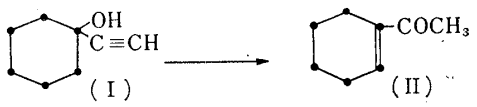
In the preceding paper of this series,[1] it was shown that the Meyer-Schuster rearrangement and Rupe reaction, carried out as the anionotropic rearrangement of ethynylborneol by acid treatment, were attended by the Wagner-Meerwein and Nametkin rearrangements. In the present series of work, the same rearrangement reaction by acid treatment was examined in alicyclic compounds with a more simple structure in order to find the relationship, if any, between the structure and various kinds of rearrangement reactions. Compounds examined were 1-ethynylcyclohexanol,[2] 3-ethynylmenthol,[3] and 4-ethynylcarbomenthol[4] as the monocyclic type, and 1-ethynyl-1,3,3-trimethyl-2-norbornanol,[5] 1-methyl-2-ethynylnorborneol, and 2-ethynylnorborneol as the bicyclic type. The two new compounds, 1-methyl-2-ethynylnorborneol and 2-ethynylnorborneol were prepared respectively from 1-methylnorcamphor[6] and norcamphor[6] by ethynylation in liquid ammonia. Acid treatment was carried out with (a) 90% formic acid, (b) 30% hydrochloric acid, (c) sulfuric acid, and (d) phosphoric acid. Experimental results thereby obtained and those of cyclic ethynylcarbinols found in the literature are summarized in Tables I and II.

Numerous reports have appeared on the rearrangement reaction of 1-ethynylcyclohexanol[2] (I) and it is known that the Rupe reaction chiefly takes place, with formation of an unsaturated ketone. In the present series of work, it was presumed that, under some reaction conditions and according to the kind of acid catalyst used, a Meyer-Schuster rearrangement might take place to form an unsaturated aldehyde but it was found that in all the compounds examined, the Rupe reaction mainly took place.

Reaction of (I) with 30% hydrochloric acid for one hour afforded (II) in 40% yield and a compound coloring Fuchsin was detected in the distillation residue. When reacted with 90% formic acid, (II) was obtained in 45% yield and neither the distillate nor the residue contained a substance coloring Fuchsin. Reaction of (I) with sulfuric acid for 1 hour at 0° to 5° gave (II) in 68% yield and a minute amount of a substance coloring Fuchsin was detected in the latter distillate. (II) was formed in 52% yield when reacted with phosphoric acid at −5° for 30~40 minutes.

Rupe[3] reported that the heating of 3-ethynylmenthol (IV) with formic acid gave Δ^{a3}-*p*-menthaneacetaldehyde, b.p_{12} 107~113°, $[\alpha]_D$ +82.9°(semicarbazone, m.p. 146~149°; oxime,



1-Ethynylcyclohexanol Acetyl 1-Cyclohexenylketone

Chart 1.

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1) Part I. M. Kagawa : This Bulletin, **7**, 306 (1959); Part II : *Ibid.*, **7**, 751 (1959).
2) J. D. Chanley : J. Am. Chem. Soc., **59**, 118 (1937); W. H. Linen : J. Pharm. Pharmacol., **2**, 13 (1950); H. Rupe, E. Kambli : Helv. Chim. Acta, **9**, 672 (1926).
3) H. Rupe : Helv. Chim. Acta, **12**, 204 (1924).
4) *Idem* : *Ibid.*, **14**, 718 (1931).
5) *Idem* : *Ibid.*, **12**, 204 (1929).
6) S. Beckmann, R. Shaber, R. Bamberger : Ber., **87**, 1002 (1956).

TABLE I. Anionotropic Rearrangement of Monocyclo Compounds (1)

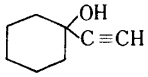
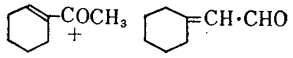
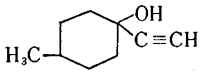
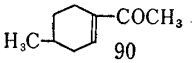
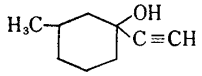
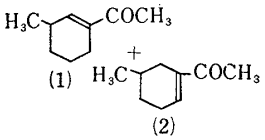
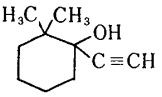
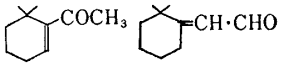
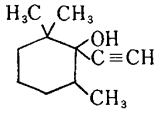
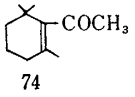
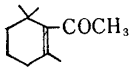
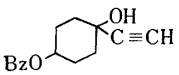
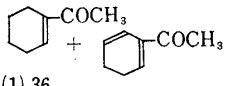
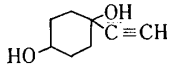
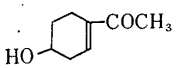
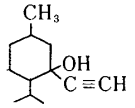
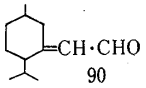
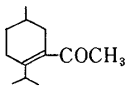
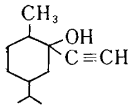
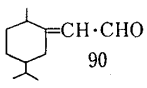
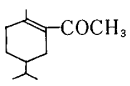
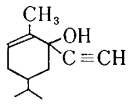
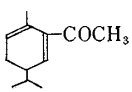
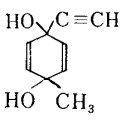
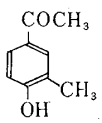
Rupe reaction Ethynylcarbinol	Catalyst	Product, yield (%)	Semicarbazone, m.p. (°C)	Author
	90% HCOOH	 (1) 50 (2) 0.8	(1) 220° (2) 180°	Chanley : J. Am. Chem. Soc., **70**, 244 (1948).
	50% H_2SO_4	(1) 30 (2) trace	(1) 214° (2) 190°	Kagawa
	HCOOH	57 —	220~221°	C. D. Hurd : J. Am. Chem. Soc., **59**, 118 (1937).
	Dawex 50 +HOAc	86 —	219~221°	M. S. Newman : *Ibid.*, **75**, 4740 (1953).
	70% HCOOH	 90	221°	H. Rupe : Helv. Chim. Acta, **14**, 701 (1931).
	80% HCOOH	 (1) (2)	(1) 213° (2) 195°	*Idem* : *Ibid.*, **16**, 685 (1933).
	90% HCOOH	 (1) 50 (2) 0.6	(1) 200° (2) 220°	Chanley : J. Am. Chem. Soc., **70**, 244 (1948).
	Dawex 50 +HOAc	 74		M. S. Newman : *Ibid.*, **75**, 4740 (1953).
	98% HCOOH		2,4-dinitrophenyl-hydrazone 152~154°	P. D. Landor : J. Chem. Soc., **1956** 1015.
	HCOOH	 (1) 36 (2) 25	2,4-dinitrophenyl-hydrazone (1) 211° (2) 194°	Johns : J. Am. Chem. Soc., **71**, 615 (1949).
	HCOOH		2,4-dinitrophenyl-hydrazone 224~227°	
	70% HCOOH	 90	149°	H. Rupe : Helv. Chim. Acta, **12**, 204 (1924).
	80% HCOOH		152°	Kagawa
	70% HCOOH	 90	139~140°	H. Rupe : Helv. Chim. Acta, **14**, 718 (1931).
	80% HCOOH		173°	Kagawa
	HCOOH		193~194°	K. Suga : Nippon Kagaku Zasshi, **79**, 1168 (1958).
	H_2SO_4			E. Zbinal, E. Lahrman : Ber., **92**, 2141 (1959).

Table I. Anionotropic Rearrangement of Monocyclo Compounds (2)

Meyer-Schuster Rearrangement

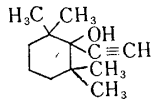
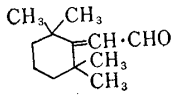
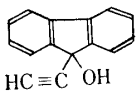
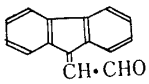
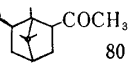
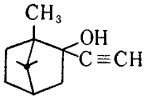
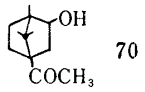
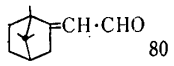
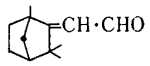
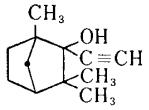
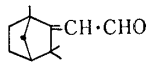
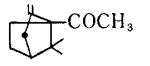
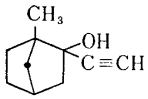
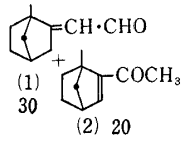
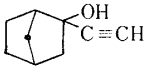
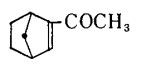
Ethynylcarbinol	Catalyst	Product, yield (%)	Semicarbazone, m.p. (°C)	Author
				P. D. Landor : J. Chem. Soc., **1956** 1015.
	H_2SO_4			G. F. Hennion : J. Am. Chem. Soc., **77**, 3255 (1957).

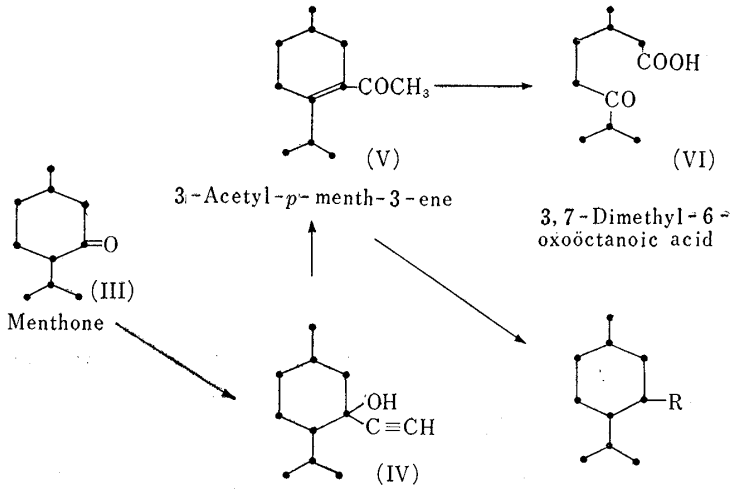
Table II. Anionotropic Rearrangement of Bicyclo Compounds

Ethynylcarbinol	Catalyst	Product, yield (%)	Semicarbazone, m.p. (°C)	Author
	90% HCOOH	 80	202°	C. D. Hurd : J. Am. Chem. Soc., **59**, 118 (1937).
	90% HCOOH (boil)	 70	203°	Kagawa : This Bulletin, **7**, 306 (1959).
	10% HCl 90% HCOOH (cold)	 80	223°	
	86% HCOOH		214°	H. Rupe : Helv. Chim. Acta, **12**, 204 (1929).
	90% HCOOH 10% HCl		224°	Kagawa
	10% H_2SO_4		220°	
	HCl·HCOOH H_2SO_4	 (1) 30 (2) 20	(1) 214° (2) 203°	*Idem*
	HCl HCOOH H_2SO_4 H_3PO_4		214°	*Idem*

m.p. 101°). The structure of this product was proved by its derivation to 3-methyladipic acid, m.p. 91°, and 3,7-dimethyl-6-oxöoctanic acid (semicarbazone, m.p. 152°) by oxidation with alkaline potassium permanganate but this method is rather unambiguous and the aldehyde was not confirmed by the formation of unsaturated acid to be obtained from the aldehyde or of menthone. In order to confirm this point, the following experiments were carried out.

Treatment of (IV) with 90% formic acid or 30% hydrochloric acid afforded (V) and the distillation residue contained a substance which colored Fuchsin. Structure of the unsaturated ketone was determined by its ozonolysis and the Beckmann rearrangement of the oxime of (VII). The melting points of (VIII) and (IX) were the same as that (m.p. 65°) of the

acid derived from 3-bromomenthane by Zelinsky.[7] On the other hand, hydration of (IV) with sulfuric acid, in the presence of mercuric sulfate, and dehydration of its product with phosphorus pentoxide gave (V), which was identical with the product of the Rupe reaction.



3-Acetylmenthane (VII), R=$COCH_3$

p-Menthane-3-carboxamide (VIII), R=$CONH_2$

p-Menthane-3-carboxylic acid (IX), R=COOH

Chart 2.

Rupe[4] reported that the heating of 2-ethynylcarvomenthol (XI) with formic acid afforded $\Delta^{\alpha 2}$-*p*-menthaneacetaldehyde, b.p. 114~116° (semicarbazone, m.p. 139~140°). Its structure was determined by its oxidation with alkaline potassium permanganate to form isopropylsuccinic acid, m.p. 114~118°, and 3-isopropyladipic acid. This still leaves a doubt, as in the case of menthol, since the aldehyde was not derived to the corresponding unsaturated acid by oxidation. In the present series of work, treatment of (XI) 90% formic acid or 30% hydrochloric acid resulted in the formation of (XII) and the presence of a substance coloring Fuchsin was detected in the distillation residue. The structure of this product was established by its ozonolysis to form (XIII), as shown in Chart 3. (XII) was also

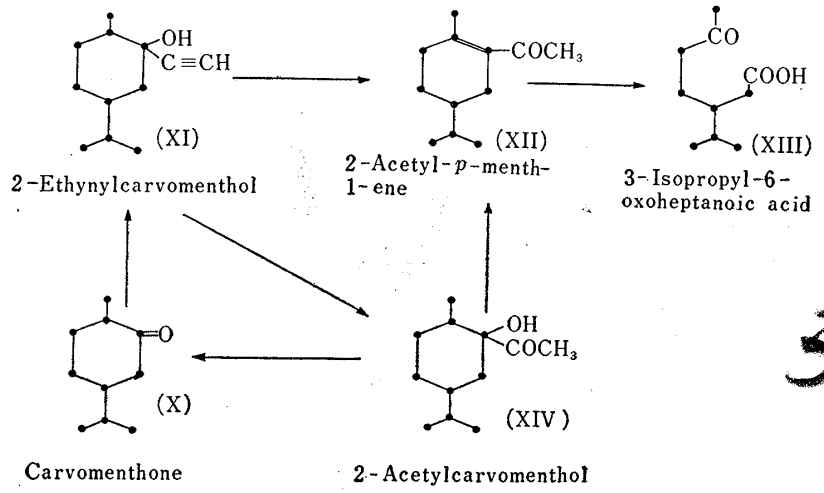


Chart 3.

7) N. D. Zelinsky : Ber., **35**, 4417 (1903).

confirmed by hydration of (XI) with sulfuric acid, in the presence of mercuric sulfate, and dehydration of (XIV) so obtained with potassium hydrogensulfate to (XII), which was identified with the unsaturated ketone obtained by the Rupe reaction of (XI) by mixed fusion, as well as by admixture of their respective semicarbazones.

Rupe[5] reported that 2-ethynyl-1,3,3-trimethyl-2-norborneol forms 1,3,3-trimethyl-$\Delta^{\alpha 2}$-norbornaneacetaldehyde (XVI), b.p_{10} 121~123° (semicarbazone, m.p. 214°) on rearrangement with formic acid. This is assumed to be due to the Meyer-Schuster rearrangement but since the Meyer-Schuster rearrangement and Rupe reaction both progressed separately in the case of 2-ethynylborneol, it was considered that both rearrangement reactions might take place in the case of this compound according to the kind of acid used, and it was also assumed from its structure that although Wagner rearrangement might be accompanied, Nametkin rearrangement would not take place. Following experiment was therefore carried out.

Treatment of (XVI) with 90% formic acid and with 30% hydrochloric acid afforded (XVII), same as by Rupe, as the sodium hydrogensulfite adduct. On the other hand, portion that did not form an addition compound yielded a minute amount of (XIX) as a by-product. Structure of (XVII) was determined by formation of (XVIII) by oxidation with silver oxide, as shown in Chart 4.

Treatment of (XVI) with sulfuric or phosphoric acid, or hydration with sulfuric acid, in the presence of mercuric sulfate, afforded only (XIX). Its structure was determined by its derivation to (XXI) by ozonolysis or by dehydration of (XVI) with phosphorus pentoxide to a hydrocarbon and its hydration to (XIX).

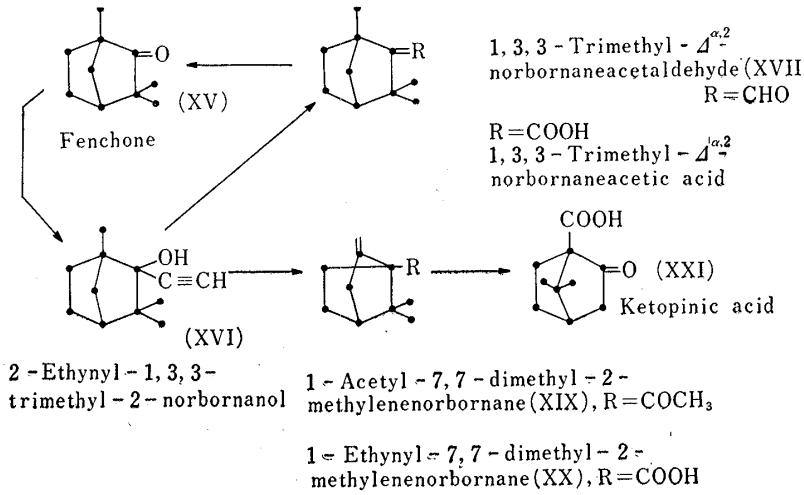


Chart 4.

There is no report on the anionotropic rearrangement of 1-methyl-2-ethynylnorborneol (XXIII). It was anticipated that there would be two possibilities; one would be the formation of an unsaturated ketone by the Rupe reaction accompanying Wagner rearrangement and the other would be the formation of an unsaturated aldehyde by the Meyer-Schuster rearrangement. Treatment of (XXIII) with mineral acid (15% hydrochloric acid, 20% sulfuric acid, or phosphoric acid) or with organic acid (formic acid) afforded (XXIV) and (XXVI) at the same time. The structure of (XXIV) was determined by its oxidation to (XXV) by treatment with silver oxide followed by further oxidation with chromium trioxide to (XXII). The structure of (XXVI) was determined by its oxidation with potassium permanganate to (XXVII), which was identical with the oxidation product of (XXVIII). Hydration of (XXIII) with 20% sulfuric acid, in the presence of mercuric sulfate, afforded (XXIX), whose dehydration with phosphorus pentoxide gave (XXVI), the product of the foregoing Rupe reaction.

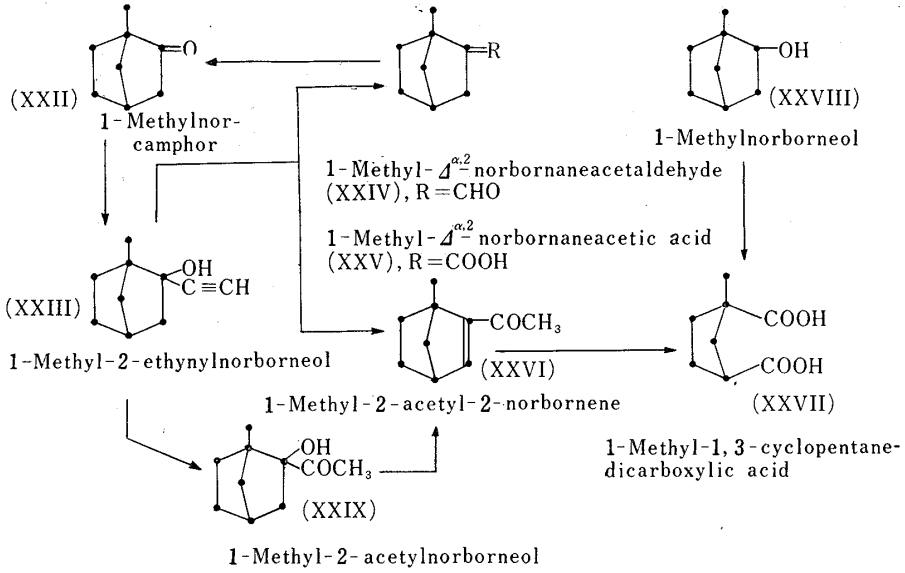


Chart 5.

There is also no published report on the reaction of 2-ethynylnorborneol (XXXI) but it is expected that an α,β-unsaturated aldehyde would be formed by the Meyer-Schuster rearrangement and α,β-unsaturated ketone by the Rupe reaction. It also seemed possible that 1-acetylnorbornene (XLIV) might be obtained by pinacolin rearrangement.

Treatment of (XXXI) with mineral acid, like 30% hydrochloric acid and sulfuric acid, with organic acid like formic acid, or with dehydration agent like phosphorus pentoxide, resulted in the formation of an unsaturated ketone (XXXII) in each case. Its structure was determined by its derivation to (XXXIII) by oxidation with potassium permanganate, as shown in Chart 6. On the other hand, the saturated ketone (XXXIV) obtained by reduction of (XXXII) was oxidized with sodium hypobromite to an acid (XXXV). Its amide (XXXVI) melted at 150°, differing from m.p. 111~112° of (XLIV). Consequently, the acetyl group in the unsaturated ketone (XXXII) was found to be in 2-position and the double bond to be present at 2~3 position in the ring.

Hydration of (XXXI) with sulfuric acid, in the presence of mercuric sulfate gave a hydroxy-ketone (XXXVII) whose dehydration with potassium hydrogensulfate yielded the same substance as the product (XXXII) of the Rupe reaction. Catalytic hydrogenation of (XXXI) gave 2-ethylborneol (XXXVIII) and its treatment with 90% formic acid resulted in extracyclic dehydration to form (XXXIX). Its structure is clear from its infrared spectrum and its oxidation to (XXX) by treatment with chromium trioxide.

Treatment of (XXXIX) with 30% hydrochloric acid effected pinacolin rearrangement to (XL) without dehydration, and oxidation of (XL) to (XLI), with subsequent oxidation afforded (XLII). The structure of (XLII) was determined by its oxidation with potassium permanganate to form a dibasic acid (XLIII). The Grignard reaction of norcamphor (XXX) to (XXXVIII) and its treatment with formic acid afforded (XL) and (XLI), which were derived to (XLII) and its oxidation yielded (XLIII). This fact indicates the same course of reaction took place as in the foregoing example.

The present series of experiments suggest that some part of past literature should be corrected. Rupe[2,3] reported, with regard to monocyclic compounds, that 3-ethynylmenthol and 2-ethynylcarbomenthol undergo the Meyer-Schuster rearrangement but it is clear from the foregoing results that the main reaction is the Rupe reaction and only a slight degree of the Meyer-Schuster rearrangement takes place, as in the case of 1-ethynylcyclohexanol. As for bicyclic compounds, 2-ethynyl-1,3,3-trimethylnorborneol is closely

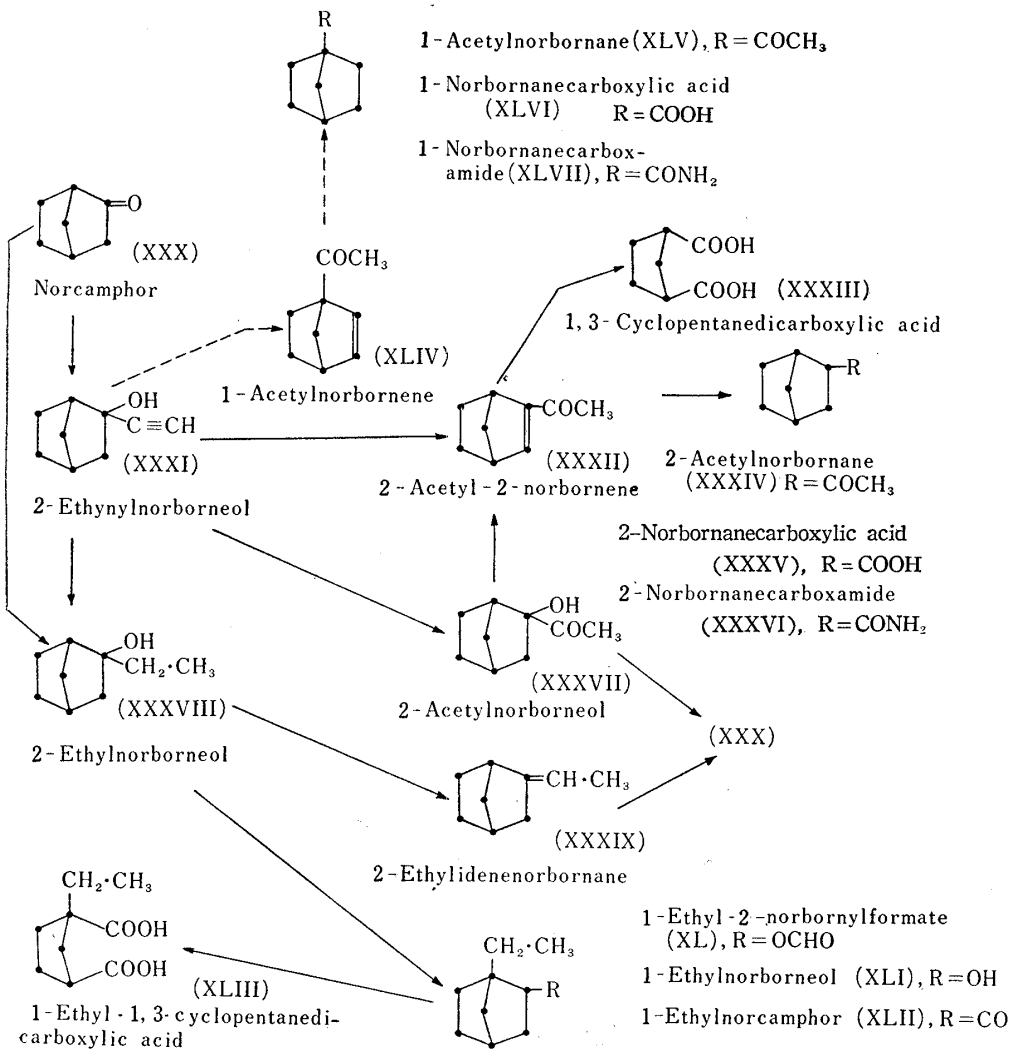


Chart 6.

related to 2-ethynylborneol in structure and should show similar reactivity but the compound underwent the Meyer-Schuster rearrangement by treatment with hydrochloric acid and formic acid, while only the Rupe reaction took place by treatment with sulfuric acid, which are entirely different from the reaction of 2-ethynylborneol.[1] Furthermore, 2-ethynyl-1,3,3-trimethylnorborneol showed specific character in undergoing the Rupe reaction when hydrogenolyzed with sulfuric acid in the presence of mercuric sulfate. Consequently, steric effect of *gem*-dimethyl group appears markedly in anionotropic rearrangement.

In the rearrangement reaction of 1-methyl-2-ethynylnorborneol, Rupe reaction and Meyer-Schuster rearrangement progress at the same time, and unsaturated ketone and aldehyde form at the same time. The compound is sensitive to acid dehydration agent and the Rupe reaction progresses with dehydration. Structurally, this compound is similar to camphors but its Rupe reaction is not accompanied by the Wagner rearrangement and only endocyclic dehydration occurs, which is similar to the case of monocyclic compounds. The foregoing facts have shown that there is no effect of bridged bond and the necessity of the presence of three methyl groups at 1-, 7-, and 7-positions in acetylenic alcohols has become further clear.

Experimental

1-Ethynylcyclohexanol (I)——b.p. 175.5～176°, m.p. 28～32°, n_D^{18} 1.4830. Reported[2] b.p_{14} 74°, n_D 1.4822.

1) Anionotropic Rearrangement of 1-Ethynylcyclohexanol (I)——a) A mixture of 10 g. of (I), 34 cc. of HCl, and 6 cc. of H_2O was stirred at 70° for 1 hr. The reaction mixture was diluted with H_2O and extracted with Et_2O. The extract was washed with dil. Na_2CO_3 solution and H_2O, dried over anhyd. Na_2SO_4, and Et_2O was evaporated. The residue was distilled in vacuum and afforded 4.1 g. of b.$p_{5.5}$ 43～55°(unreacted (I)) and 4.6 g. (yield, 46%) of a fraction of b.$p_{5.5}$ 60～65°, which formed a semicarbazone of m.p. 214°. *Anal.* Calcd. for $C_9H_{16}ON_3$ (II): C, 59.34; H, 8.35; N, 23.02. Found: C, 59.21; H, 8.14; N, 23.14.

b) A mixture of 10 g. of (I) and 90% HCOOH was refluxed for 3 hr., ice water was added to the reaction mixture, and neutralized with Na_2CO_3. This was extracted with Et_2O which was washed with H_2O and dried over anhyd. Na_2SO_4. Evaporation of Et_2O afforded 4.5 g. of (II), b.p_6 61～65°. Yield, 45%.

Semicarbazone: m.p. 214°.

c) A mixture of 10 g. of (I) and 60 cc. of 75% H_2SO_4 was stirred at 0° to 5° for 30 min. and the reaction mixture was treated in a usual manner, from which 6.8 g. (yield, 68%) of (II), b.p_6 64～67°, was obtained.

Semicarbazone: m.p. 214°.

From 1 g. of the distillation residue, 0.08 g. of $\Delta^{\alpha,1}$-cyclohexane acetaldehyde (semicarbazone, m.p. 220°) was obtained.

d) Ten g. of (I) was added gradually into 60 cc. of H_3PO_4 chilled to −5° and the temperature of the reaction mixture was raised gradually to 30～40°. After 40 min. at that temperature, the reaction mixture was poured into ice water, extracted with Et_2O, and the extract was washed consecutively with H_2O, dil. Na_2CO_3 solution, and H_2O. After drying over anhyd. Na_2SO_4, Et_2O was evaporated and 6.7 g. of (II), b.p_6 58～62°, was obtained. Yield, 67%.

Semicarbazone: m.p. 214°.

3-Ethynylmenthol (IV)——b.p. 81～83°, $[\alpha]_D^{20}$ +5.5°.

1) Anionotropic Rearrangement of 3-Ethynylmenthol (IV)——a) A solution of 13 g. of (IV) dissolved in 8 cc. of iso-PrOH was mixed with 50 cc. of 30% HCl and the mixture was heated at 80° for 2 hr. After-treatment as in foregoing cases afforded 7 g. (yield, 53%) of (V), b.p_5 73～80°, $[\alpha]_D^{21}$ +86.6°; IR: ν 1698 cm^{-1} (⁼-CO).

Oxime: m.p. 92°. *Anal.* Calcd. for $C_{12}H_{21}ON$: C, 73.85; H, 10.77; N, 7.18. Found: C, 73.65; H, 9.65; N, 17.80.

b) A mixture of 20 g. of (IV) and 60 cc. of 90% HCOOH was refluxed gently for 2 hr. and treated in a usual manner from which 15 g. (yield, 75%) of (V) was obtained. $[\alpha]_D^{21}$ +86.6°.

Oxime: m.p. 92°.

Semicarbazone: m.p. 152°.

2) Ozonolysis of 3-Acetyl-*p*-menth-3-ene (V)——O_3 was passed through a solution of 3 g. of (V) dissolved in 50 cc. of $CHCl_3$ for 7 hr. with ice cooling, 10% NaOH was added, and warmed on a water bath to effect decomposition. After cool, the reaction mixture was extracted with Et_2O to remove neutral substance, the solution was acidified with HCl, and extracted with Et_2O. The extract solution was washed with H_2O, dried over anhyd. Na_2SO_4, and Et_2O was evaporated to leave an oily acid substance (IV).

Semicarbazone: m.p. 154°. *Anal.* Calcd. for $C_{11}H_{21}O_3N_3$: C, 54.32; H, 8.64; N, 17.28. Found: C, 54.28; H, 8.43; N, 7.26.

Oxidation of 1 g. of *p*-menth-3-ene with 1 g. of CrO_3 and 10 cc. of AcOH gave a lactonic acid (VI) whose semicarbazone, m.p. 154°, showed no depression of melting point on admixture with the above semicarbazone.

3) Formation of 3-Acetylmenthane (VII)——A solution of 20 g. of (V) dissolved in 80 cc. of MeOH and added with 0.5 g. of Raney Ni was catalytically reduced in an autoclave, with initial H_2 pressure of 20 kg./cm^2. The reaction mixture was filtered, the filtrate was concentrated, and the residue was distilled in vacuum, affording 20 g. of (VII), b.p_4 80～85°; $[\alpha]_D^{22}$ −41°.

Oxime: m.p. 76～78°.

Semicarbazone: m.p. 223°. *Anal.* Calcd. for $C_{13}H_{25}ON_3$: C, 65.27; H, 10.54; N, 17.53. Found: C, 64.88; H, 10.29; N, 17.56.

A solution of 6 g. of the above oxime dissolved in 300 g. of AcOH added with 90 g. of conc. H_2SO_4 was refluxed over an open flame for 1 hr., the reaction mixture was poured into ice water, and the solution was neutralized with Na_2CO_3. This was extracted with Et_2O, the extract solution was washed with H_2O, dried over anhyd. Na_2SO_4, and Et_2O was evaporated, affording 4 g. of (VIII), m.p. 159°; $[\alpha]_D^{21}$ +50°(c=8, l=10 cm., EtOH). *Anal.* Calcd. for $C_{11}H_{26}ON$: C, 72.13; H, 11.55; N, 7.63.

Found : C, 72.83; H, 11.62; N, 7.49.

A mixture of 2 g. of (Ⅷ) and 10 cc. of 30% EtOH-KOH was refluxed for 3 hr. and usual after-treatment gave (Ⅸ), m.p. 65° (from MeOH). *Anal.* Calcd. for $C_{11}H_{19}O_2$: C, 71.98; H, 10.38. Found: C, 72.15; H, 10.76.

4) Hydration of 3-Ethynylmenthol (Ⅳ)——A mixture of 5 g. of (Ⅳ), 2.5 g. of $HgSO_4$, and 8% H_2SO_4 was stirred at 80° for 3 hr. and treated in the usual manner from which 3.2 g. (yield, 64%) of 3-acetylmenthol, $b.p_6$ 94~97°, $[\alpha]_D^{20}$ −9.0°, was obtained.

A solution of 3 g. of this substance dissolved in 30 cc. of dehyd. benzene, added with 3 g. of P_2O_5, was refluxed for 7 hr. and the reaction mixture was treated in the usual manner, affording (Ⅴ), $b.p_{3.5}$ 58~60°; $[\alpha]_D^{20}$ +3.8°.

Semicarbazone : m.p. 152°, undepressed on admixture with the semicarbazone of (Ⅴ) described above.

2-Ethynylcarbomenthol[4] (Ⅺ)——$b.p_6$ 98~102°; n_D^{20} 1.4750.

1) Anionotropic Rearrangement of 2-Ethynylcarbomenthol (Ⅺ)——a) A solution of 5 g. of (Ⅺ) dissolved in 2 cc. of iso-PrOH was mixed with 30 cc. of HCl and 3 cc. of H_2O, and the mixture was warmed at 80° for 4 hr. Usual after-treatment afforded 2.3 g. of (Ⅻ), $b.p_5$ 100~105°; n_D^{20} 1.4780.

Semicarbazone : m.p. 173°. *Anal.* Calcd. for $C_{13}H_{23}ON_3$: C, 65.81; H, 8.70; N, 17.72. Found : C, 65.54; H, 9.24; N, 17.68.

b) A mixture of 5 g. of (Ⅺ) and 35 cc. of HCOOH was refluxed gently for 3 hr. and treated in a usual manner, affording (Ⅻ), $b.p_5$ 100~103°; n_D^{20} 1.4776.

Semicarbazone : m.p. 173°.

2) Ozonolysis of (Ⅻ)——O_3 was passed through a solution of 1 g. of (Ⅻ) dissolved in $CHCl_3$ for 3 hr. and the reaction mixture was treated as described above. From acid substance, 0.5 g. of a ketonic acid (ⅩⅢ) was obtained as an oil.

Semicarbazone : m.p. 172°. *Anal.* Calcd. for $C_{11}H_{21}O_3N_3$: C, 54.32; H, 8.64; N, 17.28. Found : C, 54.14; H, 8.65; N, 17.25.

Oxidation of 1 g. of carbomenthone (Ⅹ) with 1 g. of CrO_3 in 10 cc. of AcOH afforded a ketonic acid whose semicarbazone melted at 172°, both alone and in admixture with the foregoing semicarbazone of (ⅩⅢ).

3) Hydration of (Ⅺ)——A solution of 7 g. of (Ⅺ) dissolved in 3 cc. of iso-PrOH was mixed with a solution of 2.5 g. of $HgSO_4$ and 50 cc. of 20% H_2SO_4, and the whole mixture was stirred at 80° for 3 hr. Usual treatment afforded 4.3 g. of (ⅩⅣ), $b.p_4$ 105~110°; n_D^{20} 1.4677.

Semicarbazone : m.p. 225°. *Anal.* Calcd. for $C_{13}H_{25}O_2N_2$: C, 61.17; H, 9.80; N, 16.47. Found : C, 61.26; H, 9.62; N, 16.50.

One g. of this substance was heated with 0.8 g. of $KHSO_4$ at 180°, H_2O formed was allowed to distill out, and the reaction mixture was treated in a usual manner to afford 0.6 g. of (Ⅻ).

Semicarbazone : m.p. 173°.

A solution of 1 g. of the above (ⅩⅣ) dissolved in AcOH and added with 1 g. of CrO_3 was heated at 80° for 3 hr. and usual treatment gave 0.3 g. of (Ⅹ).

Semicarbazone : m.p. 174°.

2-Ethynyl-1,3,3-trimethyl-2-norborneol[4] (ⅩⅥ)——$b.p_5$ 75°; $[\alpha]_D^{16}$ −1.5°.

1) Anionotropic Rearrangement of 2-Ethynyl-1,3,3-trimethyl-2-norborneol (ⅩⅥ)——a) A solution of 35 g. of (ⅩⅥ) dissolved in 125 cc. of iso-PrOH was stirred into a solution of 100 cc. of HCl in 265 cc. of H_2O warmed to 80° and the mixture was maintained at this temperature for 2 hr. The reaction mixture was treated as usual, saturated $NaHSO_3$ solution was added to it, and $NaHSO_3$-adduct afforded 14.5 g. (yield, 41%) of (ⅩⅦ), $b.p_7$ 112°; $[\alpha]_D^{17}$ +19.7°. IR ν cm^{-1} : 1667 (⊢CHO), 829 $\left(\begin{matrix}C\\C\end{matrix}\!\!>\!C=C\!<\!\!\begin{matrix}H\\C\end{matrix}\right)$.

Semicarbazone : m.p. 224°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 66.38; H, 8.93; N, 17.87. Found : C, 65.77; H, 8.58; N, 17.77.

Five g. of the distillation residue and the portion not forming adduct with $NaHSO_3$ gave 7 g. (yield, 20%) of an oily substance, $b.p_5$ 72~92°, which produced a large amount of Ag salt as a precipitate on application of ammoniacal $AgNO_3$, suggesting that majority is (ⅩⅥ). From 7 g. of the oily substance, 0.5 g. of a semicarbazone, m.p. 220°, was obtained and this did not show depression of melting point on admixture with the semicarbazone, m.p. 220°, of the the unsaturated ketone (ⅩⅨ).

b) A mixture of 10 g. of (ⅩⅥ) and 70 cc. of 90% HCOOH was refluxed for 1 hr., treated as above, and $NaHSO_3$-adduct afforded 3 g. (yield, 33%) of (ⅩⅦ), $b.p_7$ 112°; $[\alpha]_D^{16}$ +20°.

Semicarbazone : m.p. 224°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 66.38; H, 8.51; N, 17.87. Found : C, 66.21; H, 8.46; N, 17.75.

From 1.5 g. of the distillation residue, which did not form adduct with $NaHSO_3$, 1.5 g. (yield, 15%) of an oily substance, $b.p_7$ 95~97°, was obtained. Precipitation of Ag salt by application of $AgNO_3$ showed that this substance contains mostly (ⅩⅥ). In a similar manner as above, semicarbazone, m.p. 220°, was obtained.

Oxidation of (XVII)——A mixture of 48 g. of $AgNO_3$ added to 50 cc. of NH_4OH, 4.8 g. of NaOH, and 50 cc. of EtOH was cooled with ice, 2 g. of (XVII) was added to the mixture, and the whole mixture was stirred for 3 hr. The reaction mixture was allowed to stand overnight, filtered, and the filtrate was extracted with Et_2O to remove neutral substance. The aqueous solution was acidified with HCl, extracted with Et_2O, and Et_2O extract was washed with H_2O. After drying over anhyd. Na_2SO_4, Et_2O was evaporated and 1 g. of (XVIII), m.p. 138° (from petr. ether), was obtained. *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 80.89; H, 10.11. Found: C, 79.18; H, 9.71.

A solution of 3 g. of this product dissolved in 7 cc. of AcOH, added with 5 g. of CrO_3, was allowed to stand overnight, warmed on a water bath for 1 hr., and usual treatment of this reaction mixture afforded 1.9 g. of (XV), $b.p_{23}$ 84°.

Semicarbazone: m.p. 180°. *Anal.* Calcd. for $C_{12}H_{19}ON_3$: C, 65.15; H, 8.59; N, 19.0. Found: C, 65.0; H, 8.22; N, 18.13. These data agree with those of (XV).

c) A solution of 10 g. of (XVI) dissolved in iso-PrOH was added into a mixture of 20 g. of H_2SO_4 and 170 cc. of H_2O, the mixture was stirred at 80° for 10 hr., and usual treatment of the reaction mixture afforded 6 g. (yield, 60%) of (XIX), $b.p_2$ 50~52°, m.p. 45°; $[\alpha]_D$ ±0°. IR ν cm^{-1}: 1689 (⌐-CO), 879 $\left(\begin{matrix}H\\H\end{matrix}\!\!>\!C=C\!<\!\!\begin{matrix}C\\C\end{matrix}\right)$.

Semicarbazone: m.p. 220°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 66.38; H, 8.93; N, 17.87. Found: C, 66.10; H, 8.74; N, 17.82.

A solution of 30 g. of (XVI) dissolved in 50 cc. of iso-PrOH was stirred into a mixture of 25 g. of H_2SO_4, 150 cc. of H_2O, and 10 g. of $HgSO_4$, the mixture was stirred at 80° for 3 hr., and usual treatment afforded 15 g. (yield, 50%) of (XIX), $b.p_3$ 72~73°, m.p. 45°; $[\alpha]_D$ ±0°.

Semicarbazone: m.p. 220°.

d) Twenty g. of H_3PO_4 was added to a solution of 30 g. of (XVI) dissolved in 300 cc. of dehyd. benzene, and the whole was refluxed in a water bath for 3 hr. Usual treatment afforded 20 g. (yield, 66%) of (XIX), $b.p_2$ 50~52°, m.p. 45°; $[\alpha]_D$ ±0°.

Semicarbazone: m.p. 220°.

2) Preparation of 1-Ethynyl-7,7-dimethyl-2-methylenenorbornane (XX)——Twenty g. of P_2O_5 was added to the solution of 30 g. of (XVI) dissolved in 500 cc. of dehyd. benzene and the mixture was refluxed for 3 hr. Usual treatment of the reaction mixture afforded 27 g. of (XX), $b.p_3$ 45~48°, $[\alpha]_D^{29}$ +3.2°; n_D^{29} 1.4770.

i) A solution of 10 g. of the above (XX) dissolved in 19 cc. of iso-PrOH was stirred into a mixture of 6 g. of H_2SO_4, 3 g. of $HgSO_4$, and 50 cc. of H_2O and the mixture was heated at 80° for 3 hr. Usual treatment of the reaction mixture afforded 6 g. of (XIX), $b.p_3$ 70~73°, m.p. 45°; $[\alpha]_D$ ±0°. Distillation residue, 3 g.

Semicarbazone: m.p. 220°. *Anal.* Calcd. for $C_{13}H_{21}ON_3$: C, 61.38; H, 8.93; N, 17.7. Found: C, 65.99; H, 9.00; N, 17.72.

ii) A solution of 10 g. of (XX) dissolved in 20 cc. of iso-PrOH was stirred into a solution of 20 g. of H_2SO_4 and 170 cc. of H_2O warmed to 80° and the reaction mixture was maintained at this temperature for 20 hr. Usual treatment afforded 7 g. of (XIX), $b.p_2$ 50~52°; m.p. 45°.

Semicarbazone: m.p. 220°.

3) Ozonolysis of 1-Acetyl-7,7-dimethyl-2-methylenenorbornane——O_3 was passed through an ice-cooled solution of 1 g. of (XIX) dissolved in 100 cc. of petr. ether for 3 hr., the ozonide formed was collected, and saturated $NaHSO_3$ solution was added with ice cooling. This mixture was allowed to stand overnight, warmed to ca. 50° for 0.5 hr., and the cooled mixture was extracted with Et_2O. The extract solution was washed consecutively with H_2O, 15% NaOH solution, and H_2O, and Et_2O was evaporated. The alkaline solution was acidified with HCl and extracted with Et_2O. The Et_2O extract was washed with H_2O, dried over anhyd. Na_2SO_4, and Et_2O was evaporated to give (XXI), m.p. 232° (from Et_2O). *Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 65.93; H, 6.89. Found: C, 65.47; H, 6.53.

Oxime: m.p. 216°.

This product showed no depression of melting point on admixture with the ketopinic acid, m.p. 230° (oxime, m.p. 216°), obtained by oxidation of 10-hydroxycamphor with CrO_3 and AcOH.

1-Methyl-2-ethynylnorborneol (XXIII)——Ethynylation of 59 g. of (XXII) in liquid NH_3 by the usual method afforded 72 g. of (XXIII) as an oil, $b.p_3$ 65~68°; n_D^{20} 1.4953. Yield, 98%. IR ν cm^{-1}: 3511 (OH), 3556 (-C≡CH).

1) Anionotropic Rearrangement of 1-Methyl-2-ethynylnorborneol (XXII)——a) A solution of 10 g. of (XXIII) dissolved in 10 cc. of iso-PrOH was added to a mixture of 50 cc. of HCl and 50 cc. of H_2O, and the solution was stirred at 80° for 1 hr. The reaction mixture was treated by the usual method and $NaHSO_3$-adduct afforded 4 g. (yield, 40%) of (XXIV), $b.p_3$ 90~95°; n_D^{16} 1.5180. IR ν cm^{-1}: 1681, 1642 (⌐-CHO), 840 $\left(\begin{matrix}C\\C\end{matrix}\!\!>\!C=C\!<\!\!\begin{matrix}H\\C\end{matrix}\right)$.

Semicarbazone: m.p. 213°. *Anal.* Calcd. for $C_{11}H_{17}ON_3$: C, 63.76; H, 8.21; N, 20.29. Found: C, 63.62; H, 8.21; N, 20.50.

The portion failing to form $NaHSO_3$-adduct afforded 3.5 g. of oily unsaturated ketone (XXV), $b.p_3$ 67~70°. Yield, 30%. IR ν cm^{-1} : 1652 (⊱-CO), 798 $\left(\begin{matrix}C\\C\end{matrix}\right>C=C\left<\begin{matrix}H\\C\end{matrix}\right)$.

Semicarbazone : m.p. 203°. *Anal.* Calcd. for $C_{10}H_{17}ON_3$: C, 63.76; H, 8.21; N, 20.28. Found : C, 63.70; H, 8.10; N, 20.44.

c) A solution of 5 g. of (XXIII) dissolved in 10 cc. of iso-PrOH was stirred into a mixture of 10 g. of H_2SO_4 and 40 cc. of H_2O and the whole mixture was stirred at 80° for 5 hr. The reaction mixture was treated by the usual method and the aldehyde fraction afforded 1.8 g. (yield, 36%) or (XXIV), $b.p_3$ 90~95°, n_D 1.5182.

Semicarbazone : m.p. 213°.

Ketonic portion afforded 1.0 g. (yield, 20%) or (XXVI), $b.p_3$ 70~75°.

Semicarbazone : m.p. 203°.

2) Oxidation of (XXIV)——Oxidation of 2 g. of (XXIV) with Ag_2O in the usual manner afforded an unsaturated acid (XXV), $b.p_3$ 135°, m.p. 95°; IR ν cm^{-1} : 1667 (⊱-COOH), 840 $\left(\begin{matrix}C\\C\end{matrix}\right>C=C\left<\begin{matrix}H\\C\end{matrix}\right)$. *Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 71.37; H, 8.27. Found : C, 71.39; H, 8.26.

A mixture of 0.5 g. of the foregoing unsaturated acid (XXV) in 0.5 g. of CrO_3 and 10 cc. of AcOH was warmed at 60° for 3 hr. and usual after treatment afforded 0.3 g. of (XXII).

Semicarbazone : m.p. 209°.

3) Oxidation of (XXVI)——A mixture of 2 g. of (XXVI) in a solution of 4.4 g. of $KMnO_4$ and 1.4 g. of KOH dissolved in 100 cc. of H_2O was stirred at 20° for 4 hr. and warmed at 60° for 30 min. to complete the reaction. The reaction mixture was treated in the usual manner to afford a dibasic acid (XXVII), m.p. 96° (from petr. ether). This acid showed no depression of melting point on admixture with the dibasic acid (m.p. 96°; reported[6] m.p. 98°) obtained by similar oxidation of (XXVIII.) *Anal.* Calcd. for $C_8H_{12}O_4$: C, 55.87; H, 6.86. Found : C, 55.79; H, 6.82.

4) Formation of 1-Methyl-2-acetylnorborneol——A solution of 5 g. of (XXIII) dissolved in 10 cc. of iso-PrOH was added with stirring into a mixture of 1 g. of $HgSO_4$, 10 g. of H_2SO_4, and 35 cc. of H_2O, and the mixture was stirred at 80° for 3 hr. Usual after-treatment afforded 2.5 g. of a hydroxy-ketone (XXIX), $b.p_3$ 96~98°, m.p. 20°, leaving 2 g. of a distillation residue. *Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found : C. 71.39; H, 9.46.

A solution of 1 g. of the above (XXIX) dissolved in 10 cc. of dehyd. benzene and added with 0.5 g. of P_2O_5 was refluxed for 3 hr. Usual treatment afforded 0.3 g. of (XXVI).

Semicarbazone : m.p. 203°.

2-Ethynylnorborneol (XXXI)——Ethynylation of 60 g. of (XXX), m.p. 90° (semicarbazone, m.p. 195°) in liquid NH_3 by the usual method gave 74 g. (yield, 82%) of (XXXI), $b.p_4$ 71°, m.p. 40°. IR : ν 3322 cm^{-1} (-OH, -C≡CH).

1) Anionotropic Rearrangement of 2-Ethynylnorborneol (XXXI)——a) A solution of 10 g. of (XXXI) dissolved in 10 cc. of iso-PrOH was added to a mixture of 20 cc. of HCl and 20 cc. of H_2O, and the mixture was heated at 80° for 6 hr. Usual after-treatment afforded 4.0 g. (yield, 40%) of an unsaturated ketone (XXXII), $b.p_2$ 80~85°. IR ν cm^{-1} : 1661 (⊱-CO), 854 $\left(\begin{matrix}C\\C\end{matrix}\right>C=C\left<\begin{matrix}H\\C\end{matrix}\right)$.

Semicarbazone : m.p. 214°. *Anal.* Calcd. for $C_{10}H_{15}ON_3$: C, 62.19; H, 7.77; N, 21.76. Found : C, 62.21; H, 7.58; N, 21.67.

b) A solution of 5 g. of (XXXI) dissolved in 5 cc. of iso-PrOH was stirred into a mixture of 10 g. of H_2SO_4 and 40 cc. of H_2O, and the mixture was stirred at 80° for 3 hr. Usual after-treatment afforded 4.6 g. of an oily product which was distilled in a reduced pressure to give 1.5 g. of (XXXI), $b.p_3$ 70~80°, and 2.0 g. (yield, 40%) of (XXXII), $b.p_2$ 80~85°.

Semicarbazone : m.p. 214°.

c) A mixture of 5 g. of (XXXI) and 35 cc. of 90% HCOOH was refluxed gently for 10 min. and usual after-treatment afforded 4.8 g. of an oily product. Low-pressure distillation gave 1.8 g. of (XXXI), $b.p_3$ 65~80°, and 2.2 g. (yield, 44%) of (XXXII), $b.p_3$ 80~87°.

Semicarbazone : m.p. 214°.

d) Application of P_2O_5 : A solution of 5 g. of (XXXI) dissolved in 50 cc. of dehyd. benzene and added with 3 g. of P_2O_5 was refluxed for 3 hr. and treated by the usual method, affording 4.9 g. of an oily product. Low-pressure distillation of the oil gave 1.2 g. of (XXXI), $b.p_3$ 65~80°, and 2.3 g. (yield, 46%) of (XXXII), $b.p_3$ 80~82°.

Semicarbazone : m.p. 214°.

2) Hydration of 2-Ethynylnorborneol (XXXI)——A solution of 5 g. of (XXXI) dissolved in 5 cc. of iso-PrOH was added to a mixture of 10 g. of H_2SO_4, 1 g. of $HgSO_4$, and 40 cc. of H_2O, and the whole was stirred at 80° for 3 hr. Usual after treatment afforded 5 g. of an oily product which was distilled in low pressure to give 2 g. (yield, 46%) of (XXXVII), $b.p_3$ 70~75°, m.p. 76~77°. IR ν cm^{-1}: 3448 (OH), 1706 (CO). *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found : C, 69.83; H, 9.12.

A mixture of 1.8 g. of the foregoing (XXXVII) and 1.0 g. of $KHSO_4$ was heated at 180° to distill out H_2O and the reaction mixture was treated in the usual manner, affording 0.9 g. of an oily product. Its semicarbazone, m.p. 214°, agreed with that of (XXXII).

3) Oxidation of 2-Acetyl-2-norbornene——A mixture of 2 g. of (XXXII), 4.4 g. of $KMnO_4$, 1.4 g. of KOH, and 100 cc. of H_2O was stirred at 20° for 4 hr. and at 80° for 1 hr., and the reaction mixture was treatment in a usual manner. As an acid substance, a dibasic acid (XXXIII), m.p. 120°(from H_2O), was obtained and it showed no depression of melting point on admixture with the dibasic acid (XXXIII), m.p. 120°, formed by oxidation of (XXX) as above. *Anal.* Calcd. for $C_7H_{10}O_4$: C, 53.16; H, 6.32. Found: C, 52.99; H, 6.26.

4) Catalytic Hydrogenation of 2-Acetyl-2-norbornene (XXXII)——A solution of 4.5 g. of (XXXII) dissolved in 30 cc. of AcOH and added with 0.5 g. of Pd-C was submitted to reduction until absorption of H_2(20°) reached 938 cc. The usual after-treatment afforded 4 g. of an unsaturated ketone (XXXIV), $b.p_2$ 58~58.5°.

Semicarbazone: m.p. 198°. *Anal.* Calcd. for $C_{10}H_{11}ON_3$: C, 61.54; H, 8.70; N, 21.53. Found: C, 61.26; H, 8.74; N, 21.32.

5) Oxidation of 2-Acetyl-2-norbornene——To NaBrO solution prepared from 7 g. of Br_2, 7 g. of NaOH, and 100 cc. of H_2O, chilled to 0°, 3.5 g. of the foregoing (XXXIV) was added and the mixture was maintained at that temperature for 7 hr. Usual after-treatment afforded 2 g. of an oily substance (XXXV).

A mixture of 1 g. of this dicarboxylic acid (XXXV) and 5 cc. of $SOCl_2$ was warmed at 40° and the final heating was made with suction to remove excess $SOCl_2$ and HCl formed. The residual solution was cooled while adding 20 cc. of NH_4OH, the precipitate formed was collected, and dissolved in H_2O. This solution was treated with activated carbon and recrystallization of the residue gave an amide (XXXVI), m.p. 150°. *Anal.* Calcd. for $C_8H_{13}O_2N$: C, 61.93; H, 8.38; N, 9.03. Found: C, 61.54; H, 8.40; N, 9.10.

6) Reduction of 2-Ethynylnorborneol——A solution of 20 g. of (XXXI) dissolved in 50 cc. of MeOH was placed in an autoclave with 1.0 g. of Raney Ni and hydrogenated with initial H_2 pressure of 40 kg./cm^{-2}. Usual after-treatment of the reaction mixture gave (XXXVIII), $b.p_2$ 61°, n_D^{19} 1.4860.

A solution of 7 g. of the foregoing (XXXVIII) dissolved in a mixture of 10 cc. of iso-PrOH, 50 cc. of HCl, and 30 cc. of H_2O was stirred at 80° for 5 hr. and usual after-treatment afforded 5 g. of (XXXIX), $b.p_3$ 45~48°.

A solution of 1 g. of (XXXIX) dissolved in 10 cc. of AcOH was heated with 1 g. of CrO_3 for 3 hr. and (XXX), m.p. 90°(semicarbazone, m.p. 198°), was obtained.

7) Application of Formic Acid to 2-Ethynylnorborneol——A mixture of 3 g. of (XXXVIII) and 21 cc. of 90% HCOOH was refluxed gently for 4 hr. and usual after-treatment afforded 2.5 g. of (XL), $b.p_2$ 50~52°. IR ν cm^{-1}: 1720 (CO), 1185 (formate).

A mixture of (XL) and 20 cc. of EtOH-KOH was refluxed for 1 hr. and 1 g. of (XLI), $b.p_3$ 64~66°, was obtained. IR: ν 3472 cm^{-1}(OH).

A solution of 1 g. of the above (XLI) dissolved in 10 cc. of AcOH and added with 1 g. of CrO_3 was warmed at 60° for 3 hr. and 0.8 g. of an oily product was obtained.

Semicarbazone of (XLII): m.p. 198°. *Anal.* Calcd. for $C_{10}H_{17}ON_3$: C, 61.53; H, 8.70; N, 21.53. Found: C, 61.40; H, 8.68; N, 21.46.

Further, 1 g. of this lactone (XLII) in a solution of 0.7 g. of KOH, 2.2 g. of $KMnO_4$, and 50 cc. of H_2O was stirred at 20° for 4 hr. and at 80° for 1 hr., and usual after-treatment gave 0.6 g. of a viscous oil. Analysis of its K salt agreed with that of (XLIII). *Anal.* Calcd. for $C_9H_{12}O_4K_2$: C, 41.22; H, 4.58; K, 29.77. Found: C, 40.96; H, 4.60; K, 30.05.

Preparation of 2-Ethylborneol(Grignard Method)——A Grignard solution, prepared by the reaction of 4 g. of Mg and 3 g. of EtI in dehyd. Et_2O, was stirred with ice cooling and Et_2O solution of 10 g. of (XXX) was added to it with stirring. The mixture was allowed to stand overnight, poured into ice water, and acidified to weak acidity with dil. H_2SO_4. The Et_2O solution was separated, washed with H_2O, dried over anhyd. Na_2SO_4, and Et_2O was evaporated to leave (XXXVIII), $b.p_3$ 63°, n_D^{21} 1.4864.

Formation of 1-Ethylnorcamphor——A mixture of 5 g. of the foregoing (XXXVIII) and 30 cc. of 90% HCOOH was refluxed gently for 4 hr. and the reaction mixture was treated in the usual manner, affording 4.3 g. of (XL), $b.p_3$ 54°, n_D^{20} 1.465.

A mixture of 2 g. of (XL) and 20 cc. of 10% EtOH-KOH was refluxed on a water bath for 1 hr. and (XLI), $b.p_3$ 65°, n_D^{20} 1.4580, was obtained.

A solution of 1 g. of (XLI) and 1 g. of CrO_3 dissolved in AcOH was warmed to effect oxidation and an oily (XLII) was obtained. Its semicarbazone, m.p. 198°, showed no depression of melting point on admixture with the semicarbazone, m.p. 198°, of (XLII).

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Summary

1) Although 3-ethynylmenthol and 2-ethynylcarbomenthol, among monocyclic compounds of camphor system, have been reported as undergoing Meyer-Schuster rearrangement in the main, the present series of experiments have clarified that the Rupe reaction also progresses in these compounds, same as in 1-ethynylcyclohexanol.

2) 2-Ethynyl-1,3,3-trimethyl-2-norborneol undergoes Meyer-Schuster rearrangement by treatment with hydrochloric acid and formic acid, but only the Rupe reaction takes place, accompanied by the Wagner rearrangement, by treatment with sulfuric acid.

3) 1-Methyl-2-ethynylnorborneol undergoes both Meyer-Schuster rearrangement and Rupe reaction, irrespective of the catalyst used. This compound is similar to monocyclic compounds in that it undergoes endocyclic dehydration during the Rupe reaction.

4) 2-Ethynylnorborneol dose not undergo the Meyer-Schuster rearrangement and only the Rupe reaction takes place, similar to monocyclic compounds in general.

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