3-Methyl-5-arylpent-2-en-4-ynoic Acids

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Received May 20, 1963

N.m.r. data for a series of 2-(H, CH_3, C_6H_5) and 3-(H, CH_3, C_6H_5) substituted 5-phenylpent-2-en-4-ynoic acids and their esters (III) have established the presence of significant amounts (up to 90%) of the *cis* structures in unseparated mixtures. The pure acids obtained by saponification of these isomeric mixtures of esters have 2-*trans* structures with the exception of the 3-phenyl-2-methyl acid (IIIE) which was isolated pure in the 2-*cis* form. Cyclization to the lactone structure (II) was observed only with the 3-methyl types and apparently is not directly related to the proportion of 2-*cis* isomer present.

We have described previously[1] the preparation of 3-methyl-5-phenyl-2-*trans*-penten-4-ynoic acid, the formation of a γ-lactone during the saponification of its ester, and an unsuccessful attempt to isolate the 2-*cis* acid pure. A study of the effect of structural variations on the preparation and properties of a series of similar acids is described in this paper.

These acids have been obtained by the Reformatskiĭ reaction of methyl bromoacetate, ethyl α-bromopropionate, and methyl α-bromophenylacetate with 4-phenyl-3-butyn-2-one, 1,3-diphenyl-2-propynone, and phenylpropargyl aldehyde. Although these reactions usually proceeded smoothly, difficulties were encountered in initiating the reactions of phenylpropargyl aldehyde with methyl α-bromoacetate and ethyl α-bromopropionate, and 4-phenyl-3-butyn-2-one with methyl α-bromophenylacetate.

The intermediate hydroxy esters (I) from the Reformatskiĭ reaction were easily dehydrated with phosphorus oxychloride–pyridine or *p*-toluenesulfonic acid to give 59–86% yields of a mixture of isomeric (*cis–trans*) unsaturated esters. N.m.r. spectral data showed two maxima for the C-3 olefinic methyl protons in the analytical samples of ester IIIC ($R'' = C_2H_5$) corresponding to 45% of the 2-*cis* and 55% of the 2-*trans* isomers. Similar n.m.r. spectral data for the crude ester IIIE ($R'' = C_2H_5$) showed that it contained approximately 90% of the 2-*cis* and 10% of the 2-*trans* isomers and data for crude ester IIIF ($R'' = C_2H_5$) showed the presence of 30% of the 2-*cis* and 70% of the 2-*trans* isomers.

With one exception (IIIE, $R'' = C_2H_5$, 2-*cis* configuration) saponification of the mixed unsaturated esters gave only the 2-*trans* acetylenic acids in 8–77% yield. Although n.m.r. spectral data showed that the 2-*cis* isomer was present in approximately 45% concentration in the 2,3-dimethyl acetylenic ester (IIIC, $R'' = C_2H_5$), and 30% in the 3-methyl-2-phenyl acetylenic ester (IIIF, $R'' = C_2H_5$), the 2-*cis* isomer was not isolatable by techniques previously successful with other 2-*cis* acids.[2,3] The one 2-*cis* acid (IIIE, $R'' = H$) which was isolated was obtained in 34% yield (based on starting ketone) from an ester which contained approximately 90% of the 2-*cis* isomer. The 2-*trans* isomer of this acid was not isolated.

In two instances (IIIC, $R'' = C_2H_5$, and IIIF, $R'' = CH_3$) saponification of the acetylenic esters gave lactones as minor by-products. The lactone (IIA) from the 2,3-dimethyl ester (IIIC) was characterized as an α,β-unsaturated γ-lactone by n.m.r., ultraviolet, and infrared spectral data. Analytical data corresponded to an empirical formula $C_{13}H_{14}O_3$ (IIIC + H_2O). N.m.r. absorption showed the presence of phenyl (2.89 τ), two benzylic (6.75 and 7.05 τ, coupling constant = 13.6 c.p.s.), and six olefinic methyl protons (8.38 and 8.05 τ). The benzylic proton absorption occurred as two unsymmetrical doublets, centered at 6.75 and 7.05 τ, and indicates that the structure of the lactone isolated corresponds to formula II in which methyl–phenyl interaction, as seen in Dreiding models, imposes restricted rotation on the benzyl group. Carbonyl absorption at 1755 cm.$^{-1}$ (2% solution in chloroform) is characteristic of an α,β-unsaturated γ-lactone.[4] End absorption at 220 mμ (ε 7700) is also consistent with this structure. The second lactone (IIB), from 2,5-diphenyl-3-methyl-2-penten-4-ynoate, was isolated pure in trace amounts and no spectral data were obtained. The empirical formula determined by analysis ($C_{18}H_{16}O_3$) corresponded to the addition of one mole of water to the acetylenic acid IIIF. These data are consistent with those reported previously[1] for the lactone isolated from the saponification and acidification of methyl 3-methyl-5-phenyl-2-penten-4-ynoate. The fact that the two lactones discussed here were obtained in small quantities in relation to the amount of 2-*cis* ester present in the ester mixture indicates that the 2-*cis* acetylenic acid does not necessarily cyclize directly to the lactone. Since the two lactones discussed here and one isolated and discussed previously[1] have a 3-methyl group, it appears that lactone formation is associated with structures having a 3-methyl (or perhaps alkyl) group.

Configurations have been assigned to the α,β-unsaturated acetylenic acids (III) on the basis of the n.m.r. absorption characteristics of their methyl esters (Table I). There are three principal structure features which introduce variations in long range shielding and deshielding effects in these structures.[1-3] These are (1) the *cis* and *trans* carboxy-3-methyl units, (2) the *cis* and *trans* correlations in the 2-ene-4-yne structures, and (3) planer–nonplaner benzenoid structures. Each of these structural relations places various protons within shielding or deshielding zones of the magnetically anisotropic units—carbonyl, acetylenic or olefinic, or aromatic ring—and provides criteria for assignment of *cis–trans* structures. The more important factors among these which can be applied to the en-ynoic acids will be discussed in the following paragraphs.

The unsubstituted methyl 5-phenyl-2-penten-4-yno-

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[1] Richard H. Wiley, T. H. Crawford, and C. E. Staples, *J. Org. Chem.*, **27**, 1535 (1962).

[2] Richard H. Wiley, P. F. G. Nau, and T. H. Crawford, *ibid.*, **26** 4285 (1961).

[3] Richard H. Wiley, P. F. G. Nau, H. C. van der Plas, and T. H Crawford, *ibid.*, **27**, 1991 (1962).

[4] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA FOR METHYL- AND PHENYL-SUBSTITUTED 5-PHENYLPENT-2-EN-4-YNOIC ACIDS AND ESTERS[a]

$C_6H_5-C\equiv C-C(R)=C(R')-CO_2H(CH_3)$

		R′			R			
		H	CH_3	C_6H_5	H	CH_3	C_6H_5	5-C_6H_5
5-C_6H_5	E (*trans*)	3.80 (J = 16)			3.07 (J = 16)			2.73
(IIIA)	A (*trans*)	3.81 (J = 16)			3.01 (J = 16)			2.72
5-C_6H_5-3-CH_3[b]	E (*trans*)	3.95				7.63		2.83
	A (*trans*)	3.91				7.63		2.74
	E (*cis*)	4.13				8.00		2.78
5-C_6H_5-2-CH_3 (IIIB)	A (*trans*)		7.88		3.13			2.73
5-C_6H_5-2,3-di-CH_3	E (*trans*)		7.83			7.76		2.79
(IIIC)	A (*trans*)		7.78			7.67		2.73
	E (*cis*)[c]		8.02			8.07		
3,5-Di-C_6H_5	E (*trans*)	3.64					2.53	2.83
(IIID)	A (*trans*)	3.47					2.3	2.73
3,5-Di-C_6H_5-2-CH_3	E (*cis*)		7.71				2.85	2.85
(IIIE)	A (*cis*)		7.51				2.75	2.75
	E (*trans*)[d]		8.07				2.27	2.82
2,5-Di-C_6H_5-3-CH_3	E (*trans*)			2.91		7.71		2.73
(IIIF)	A (*trans*)			2.91		7.58		2.68
	E (*cis*)[d]					8.10		

[a] τ-values, see ref. 8. E, methyl ester; A, acid. [b] See ref. 1. [c] From mixture of ethyl esters, from acids, 8.17 τ for C-2 methyl protons. [d] From mixture of esters.

ate (IIIA) shows a coupling constant of 16 c.p.s. for the C-2–C-3 protons which is typical of a *trans* configuration.[5] Infrared absorption at 958 cm.$^{-1}$ is also consistent with a 2-*trans* configuration for this ester.[6] A 2-*trans* configuration for 2-methyl-5-phenyl-2-penten-4-ynoic acid (IIIB) is established by comparison of C-3 proton absorption (3.13 τ) with that of the unsubstituted 5-phenyl-2-*trans*-penten-4-ynoic acid (3.01 τ), IIIA, for which the *trans* configuration has been established by the C-2–C-3 proton coupling constant of 16 c.p.s. Although there is a difference of 0.12 τ units in these two C-3 proton values, it is to be noted that the difference between *cis* and *trans* C-3 protons is usually greater than this, *i.e.*, 0.39 to 0.55 τ units, in carboxyl types.[7] In the acetylenic compounds the C-3 proton is deshielded by the triple bond since the absorption occurs below that (3.95 τ) for the ethylenic analog.[1]

The 2-*trans* configuration is established for the methyl ester of acid IIIC (2,3-dimethyl) by C-3 methyl proton absorption at 7.76 τ (*cis* to carbomethoxy) and C-2 methyl proton absorption at 7.83 τ. In pyridine solution the C-3 methyl protons of the acid IIIC show enhanced deshielding similar to that observed previously[1-3] for other acids of this type, thus confirming the 2-*trans* configuration.

A 2-*trans* configuration is established for acid IIID (3-phenyl) on the basis of C-3 phenyl proton absorption of the methyl ester at 2.53 τ (phenyl protons *cis* to carbomethoxy, see Fig. 1). Proton absorption for the C-5 phenyl group occurs at 2.83 τ, a position identical with that observed for methyl 3-methyl-5-phenyl-2-trans-penten-4-ynoate.[1] The low field aromatic proton maximum shows more structure than does the high field maximum, and this is attributable to different deshielding of the *ortho*, *meta*, and *para* ring proton by the *cis* carboxyl. Absorption for the C-2 proton at 3.64 τ is considerably lower than that observed for methyl 3-methyl-5-phenyl-2-*trans*-penten-4-ynoate[1] (3.95 τ) apparently as a result of deshielding by the acetylenic linkage.

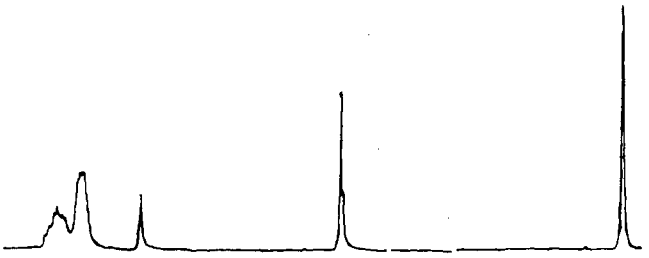

Fig. 1.—N.m.r. spectrum of methyl 3,5-diphenyl-2-penten-4-ynoate (IIID, R = CH_3). The maxima are, from left to right, at 2.53 (Ar-H), 2.83 (Ar-H), 3.64 (C-2 H), 6.31 τ (CH_3O), and tetramethylsilane.

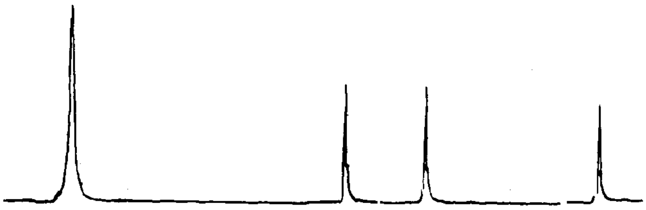

Fig. 2.—N.m.r. spectrum for methyl 3,5-diphenyl-2-methyl-2-penten-4-ynoate (IIIE, R = CH_3). The maxima are, from left to right, at 2.85 (both Ar-H), 6.64 (OCH_3), 7.71 τ (C-2 CH_3), and tetramethylsilane.

A 2-*cis* configuration is assigned to acid IIIE on the basis of a single absorption maximum at 2.85 τ for the C-3 and C-5 phenyl protons of the methyl ester (see Fig. 2). The fact that the C-3 phenyl protons do absorb at the same field strength as the C-5 phenyl protons indicates that the C-3 phenyl group is *trans* to the carbomethoxy group (*cis* configuration). Phenyl protons (C-3) *cis* to carbomethoxy (2-*trans* configuration) would be expected to be deshielded and absorb at a lower field strength (*ca.* 2.5 τ) than do the C-5 phenyl protons. The effect should be similar to that observed for the C-3 phenyl group of IIID (R″ = CH_3) discussed

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(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 85.

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 45-47.

(7) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960).

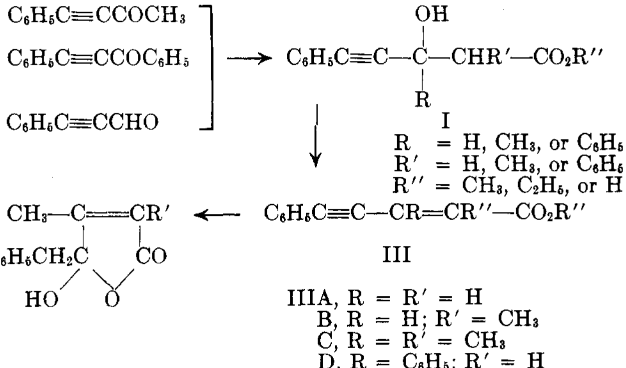
Fig. 3.—N.m.r. spectrum for mixture of *cis*- and *trans*-3,5-diphenyl-2-methyl-2-penten-4-ynoic acids (IIIE, R = H). The maxima are, from left to right, at 2.27 (low), 2.75 (Ar-H), three unassigned minor peaks, 7.51 (C-2 CH_3, *cis*), 8.17 τ (C-2 CH_3, *trans*), a broad unassigned minor peak, and tetramethylsilane.

Fig. 4.—N.m.r. spectrum for methyl 2,5-diphenyl-3-methyl-2-penten-4-ynoate (IIIF, R = CH_3). The maxima are, from left to right, at 2.73 (Ar-H), 2.91 (Ar-H), 6.36 (OCH_3), 7.71 τ (C-3 CH_3), and tetramethylsilane.

previously. Although there is no trace of absorption at this value for the pure IIIE, there is a weak band centered at *ca.* 2.3 τ in mixtures of the crude esters and acids from which IIIE is prepared (see Fig. 3). The relative intensity of absorption at 7.71 and 8.07 τ (C-2 methyl protons) in the crude, unsaturated ethyl ester from which acid IIIE was obtained indicate the presence of approximately 90% of the 2-*cis* isomer. Samples of the crude acid, m.p. 163–166°, also show *ca.* 10% of the 2-*cis* isomer (C-2 methyl proton, 8.17 τ).

Methyl proton absorption (C-3) at 7.71 τ for methyl 2,5-diphenyl-3-methyl-2-penten-4-ynoate (IIIF) is in the range for olefinic methyl protons *cis* to a carbomethoxy group,[1-3] and establishes a 2-*trans* configuration for this ester and acid (see Fig. 4). Absorption for the C-5 phenyl protons occurs at a slightly higher field strength (2.91 τ) than does that for the C-2 phenyl protons (2.73 τ) and presumably is caused by a shielding effect of the C-2 phenyl group *cis* to the C-5 phenyl group. Stuart models indicate a restricted rotation of the C-2 phenyl group which holds the C-5 phenyl in its shielding zone. This shielding effect is also consistent with a 2-*trans* configuration for this ester.

The formation of 90% of the 2-*cis* isomer (IIIE) from the 2-methyl-3-phenylhydroxy ester and 70% of the *trans* isomer from the 2-phenyl-3-methylhydroxy ester requires explanation. Although we have not made an exhaustive study of the crude (presumably unisomerized) products of such dehydrations, in several others in addition to those reported herein which we have studied, the ratio of *cis–trans* isomers is much more nearly one to one. It seldom exceeds three to two. Assuming that isomerization or fractionation of the product is not distorting the stereochemical picture, there are two principal factors which govern the steric course of elimination reactions in systems of this type. If the reaction is E2 in character, the configurations of the pair of hydroxy esters (VI and its enantiomer) determine the course of the elimination. The configurations of the hydroxy esters are in turn determined by the nature of the transition state of the Reformatskiĭ reaction. The *trans* isomer is, therefore, produced preferentially if VI is formed preferentially. If the reaction is E1, the asymmetry about C-3 is lost and the configuration is determined by considerations of strain in the transition state for the elimination of the proton from the benzyl carbonium ion (IV). The *cis* isomer is, therefore, produced preferentially if IV is favored. In the 3-phenyl structure leading to IIIE (*cis*) a benzyl carbonium ion intermediate (IV) is involved in the E1 mechanism and apparently its formation and collapse to the less hindered structure (*cis* methyl-phenyl less hindered than *cis* carboxy-phenyl) governs the course of the reaction. In the isomeric 2-phenyl-3-methyl structure, in which there is no benzyl carbonium ion possibility, the alternative E2 mechanism requires the conformation in the activated complex (V) which has the methyl and phenyl *trans* and leads to the pair of diastereomers (VI) which on *trans* elimination gives the *trans* IIIF isomer. It is thus possible that in these two contrasting structural situations the E1 and E2 mechanisms have been clearly distinguished. In other structural situations (2,3-dimethyl, IIIC) less pronounced alternative E1 and E2 processes may occur together leading to mixtures of products. Thus, assuming that the results are not artifacts, produced by uncontrolled isomerization or fractionation, it appears that one has in this approach a useful method of analysis of reaction mechanism type in elimination reactions.



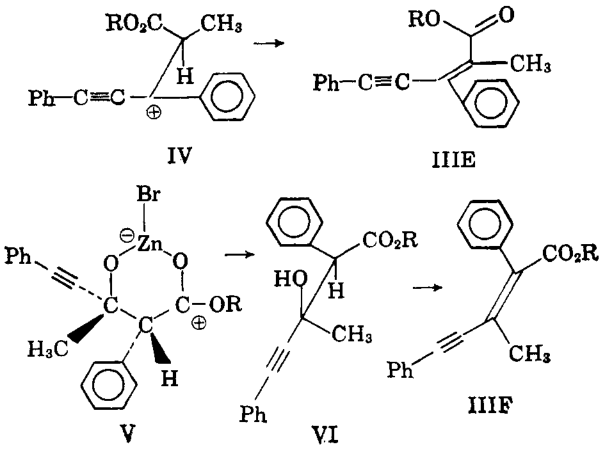
I

R = H, CH_3, or C_6H_5
R′ = H, CH_3, or C_6H_5
R″ = CH_3, C_2H_5, or H

III

IIIA, R = R′ = H
B, R = H; R′ = CH_3
C, R = R′ = CH_3
D, R = C_6H_5; R′ = H
E, R = C_6H_5; R′ = CH_3
F, R = CH_3; R′ = C_6H_5

II



IV IIIE

V VI IIIF

Experimental

All n.m.r. measurements were made with a Varian Associates HR-4302 high resolution spectrometer with a 60-Mc. oscillator with super stabilizer and field homogeneity control. The calibrations were made by the side-band technique at several frequencies. Tetramethylsilane was used as an internal reference standard and the chemical shifts are reported in τ values.[8] Samples were examined in 10–15% concentration with carbon tetrachloride or deuteriochloroform as solvent. Ultraviolet absorption measurements were made with a Beckman DK-2 recording spectrometer in the solvents (Spectro Grade) stated. Infrared absorption measurements were made with a Baird double beam recording spectrometer with sodium chloride optics in chloroform (5% solutions) or as potassium bromide pellets. Melting points are uncorrected.

Methyl 3-Hydroxy-5-phenyl-4-pentynoate (I, R = R′ = H; R″ = CH_3).—A solution of 9.25 g. (0.071 mole) of freshly distilled phenylpropargyl aldehyde (Aldrich) and 13.2 g. (0.086 mole) of methyl bromoacetate in 60 ml. of dry benzene was added to 5.85 g. (0.089 mole) of dry, acid-etched zinc at a rate sufficient to keep the benzene refluxing gently. Several crystals of iodine were added to initiate the reaction. When the addition was completed the reaction mixture was refluxed for 1 hr., cooled, decomposed with 6 ml. of glacial acetic acid in 100 ml. of water, diluted with 50 ml. of ether, and washed successively with water, saturated bicarbonate solution, and water. The washed organic phase was dried over anhydrous magnesium sulfate and the reaction product was distilled *in vacuo* to yield 8.01 g. (55%) of crude hydroxy ester, b.p. 127–128° (0.35 mm.). Redistillation of a portion of this material gave a colorless analytical sample of b.p. 127° (0.35 mm.), $n^{25}D$ 1.5505. An infrared spectrum (in $CHCl_3$) showed bands at 2240 (C≡C), 1721 (C=O), 1600 and 1493 (phenyl group), and 1170 cm.$^{-1}$ (C–O–).

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.57; H, 5.85.

3-Hydroxy-5-phenyl-4-pentynoic Acid (I, R = R′ = R″ = H).—The aforementioned hydroxy ester (0.50 g.) was refluxed for 1 hr. with a solution of 0.25 g. of potassium hydroxide in 14 ml. of methanol and 1 ml. of water. Most of the methanol was removed under reduced pressure and the residue was diluted with 25 ml. of water, washed with ether, and acidified. The precipitated oily acid was extracted with ether and dried. Removal of solvent left the crude hydroxy acid, m.p. 120–122°. Additional recrystallization from benzene–petroleum ether (b.p. 30–60°) gave 0.20 g. (43%) of colorless crystals, m.p. 124–125°.

Methyl 5-Phenyl-2-penten-4-ynoate (IIIA, R″ = CH_3).—A cooled solution of 7.4 ml. (12.4 g., 0.081 mole) of freshly distilled phosphorus oxychloride in 50 ml. of dry pyridine was added to a cooled solution of 8.25 g. (0.040 mole) of the hydroxy ester in 15 ml. of dry pyridine. The reaction mixture was heated at 95–100° for 3.5 hr., cooled to 5, and decomposed by pouring cautiously into an ice–water mixture. The dark reaction mixture was acidified with cold 4 *N* sulfuric acid and extracted with ether until the ether phase was almost colorless. The combined ether phases were washed successively with water, saturated bicarbonate solution, and water, and dried over anhydrous magnesium sulfate. Removal of solvent left 4.45 g. (59%) of semisolid, oily, unsaturated ester. Several recrystallizations from petroleum ether (b.p. 30–60°) at −20° gave an analytical sample as colorless needles, m.p. 48–49°. Two recrystallizations gave a 50% yield of the ester, m.p. 48–49°. An infrared spectrum (in $CHCl_3$) showed characteristic bands at 2210 (C≡C), 1707 (C=O), 1619 and 1490 (phenyl group), 1170 (C–O–), and 958 cm.$^{-1}$ (–CH=CH–, *trans*); ultraviolet absorption, $\lambda_{max}^{CH_3OH}$ 298 (ϵ 24,000), 248 (ϵ 8700 sh), 236 (ϵ 7500 sh), and 226 mμ (ϵ 9800 sh); n.m.r. absorption (in CCl_4), 2.73 (C-5 Ar-H), 3.07 (J = 16 c.p.s.) (C-3 H), 3.80 (J = 16 c.p.s.)(C-2 H), and 6.35 τ (OCH_3).

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.68; H, 5.57.

5-Phenyl-2-penten-4-ynoic Acid (IIIA, R″ = H).—Saponification of the 2-*trans* ester (1.27 g., 0.007 mole, m.p. 45–49°) with 5% methanolic potassium hydroxide gave 0.90 g. (77%) of the crude acid. Several recrystallizations from hexane gave an analytical sample, m.p. 148.5–149.5° (lit.[9] m.p. 147–148.6°); n.m.r. absorption (in $CDCl_3$), 2.72 (C-5 ArH), 3.01 (J = 16 c.p.s.) (C-3 H), and 3.81τ (J = 16 c.p.s.) (C-2 H).

Anal. Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.99; H, 4.88.

2-Methyl-5-phenyl-2-penten-4-ynoic Acid (IIIB, R″ = H).—A Reformatskiĭ reaction of phenylpropargyl aldehyde (7.08 g., 0.054 mole), ethyl α-bromopropionate (11.8 g., 0.65 mole), and zinc (4.40 g., 0.067 mole) gave 1.35 g. (10.7%, 24% allowing for recovered unchanged aldehyde) of crude product (presumably the hydroxy ester) of b.p. 130–138° (0.45 mm.), $n^{23}D$ 1.5375–1.5506. This ester (1.8 g.) was dehydrated with phosphorus oxychloride–pyridine as described previously to give 1.0 g. (60%) of crude, dark oil. Saponification of this oil with methanolic potassium hydroxide gave a crystalline potassium salt (0.50 g.) which was acidified to precipitate the substantially pure acetylenic acid (0.29 g., 33% from crude hydroxy ester). Several recrystallizations from hexane gave the analytical sample as colorless blades, m.p. 136.5–137.5°. This acid yellows upon exposure to light. An infrared spectrum (KBr pellet) showed bands at 1661 (C=O), 1613 (benzene ring), 1289 and 1253 (C–O–), and 759 and 685 cm.$^{-1}$ (monosubstituted phenyl group); ultraviolet absorption, $\lambda_{max}^{CH_3OH}$ 307 (ϵ 21,600), 292 (ϵ 24,300), 247 (ϵ 15,000 sh), 237 (ϵ 13,600 sh), 226 mμ (ϵ 20,900 sh); n.m.r. absorption (in $CDCl_3$), 2.73 (Ar-H), 3.13 (C-3 H), and 7.88 τ (C-2 CH_3).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 77.40; H, 5.41. Found: C, 77.61; H, 5.65.

Ethyl 2,3-Dimethyl-3-hydroxy-5-phenyl-4-pentynoate (I, R = R′ = CH_3; R″ = C_2H_5).—A Reformatskiĭ reaction of 4-phenyl-3-butyn-2-one[10] and ethyl α-bromopropionate gave an 83% yield of crude hydroxy ester, b.p. 111–117° (0.10 mm.), $n^{23}D$ 1.5220–1.5239. Redistillation of a portion of this material gave a nearly colorless analytical sample of b.p. 111–112° (0.10 mm.), $n^{23}D$ 1.5242. An infrared spectrum (in $CHCl_3$) showed bands at 3620 (OH), 2255 (C≡C), 1715 (C–O), 1495 (phenyl group), and 1192 cm.$^{-1}$ (C–O–).

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.02; H, 7.40.

Ethyl 2,3-Dimethyl-5-phenyl-2-penten-4-ynoate (IIIC, R″ = C_2H_5).—Dehydration of the preceding hydroxy ester with phosphorus oxychloride–pyridine according to the procedure described previously gave a 65% yield of the crude unsaturated ester, b.p. 97–105° (0.07 mm.), $n^{22}D$ 1.5613–1.5710. Redistillation of a portion of this material gave a nearly colorless analytical sample of b.p. 108° (0.05 mm.), $n^{23}D$ 1.5681. An infrared spectrum (in $CHCl_3$) showed bands at 2212 (C≡C), 1707 (C=O), 1274 and 1186 (C–O–), and 1100 cm.$^{-1}$. N.m.r. absorption at 8.02 and 8.07 (C-2 methyl and C-3 methyl protons *trans* to carbethoxy) and 7.78 and 7.84 τ (C-2 methyl and C-3 methyl protons *cis* to carbethoxy) showed that the analytical fraction of the unsaturated ester contained approximately 45% of the 2-*cis* and 55% of the 2-*trans* isomers.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.74; H, 7.29.

2,3-Dimethyl-5-phenyl-2-penten-4-ynoic Acid (IIIC, R″ = H).—Saponification of the unsaturated ester (12.1 g., 0.053 mole) with methanolic potassium hydroxide according to the procedure described previously gave 3.09 g. (29%) of pale yellow needles, m.p. 133–141°. Repeated recrystallization, in hexane (EK-P1135), raised the melting point to 144.5–146° (2.0 g.) and to 143–145°. An infrared spectrum showed bands at 3200–2500 (acid OH), 1662 (C=O), 1590 (phenyl group), 1300 and 1202 (C–O–), and 756 and 686 cm.$^{-1}$ (monosubstituted phenyl group); ultraviolet absorption, $\lambda_{max}^{0.003\ N\ H+ in\ CH_3OH}$ 309 (ϵ 15,300), 292 (ϵ 23,000), 247 mμ (ϵ 6500); n.m.r. absorption, 2.73 (Ar-H), 7.67 (C-3 CH_3), and 7.78 τ (C-2 CH_3).

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.95; H, 6.08.

Lactone (IIA).—Slow evaporation at room temperature of the liquors from recrystallization of the crude acid above gave 1.2 g. of an oily, semisolid material, from which 0.3 g. of oily, crystalline plates were recovered. Several recrystallizations of this crystalline product from hexane gave colorless crystals, m.p. 87.5–89°. The pure material was insoluble in sodium bicarbonate solution. An infrared spectrum (2% in $CHCl_3$) showed bands at 1755 (α,β-unsaturated carbonyl), 1689 (C=C), 1603 and 1497 (phenyl group), 1383 (CH_3 symmetrical deformation), and 977 cm.$^{-1}$ (unassigned); ultraviolet absorption, $\lambda_{max}^{CH_3OH}$ 220 mμ (ϵ 7000, end absorption); n.m.r. absorption (in $CDCl_3$), 2.88 (Ar-H), 5.60 (OH), 6.75 and 7.05 (J = 13.6 c.p.s., benzylic protons), 8.05 (C-3 methyl protons), and 8.38 τ (C-2 methyl protons).

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[8] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[9] T. L. Jacobs, D. Dankner, and A. R. Dankner, *J. Am. Chem. Soc.*, **80**, 864 (1958).

[10] D. Nightingale and F. T. Wadsworth, *ibid.*, **67**, 416 (1945).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.66; H, 6.65.

Methyl *trans*-2,3-Dimethyl-5-phenyl-2-penten-4-ynoate (IIIC, R″ = CH_3).—The methyl ester was prepared by diazomethane esterification of the pure, m.p. 144.5–146°, 2-*trans* acid, b.p. 98° (0.08 mm.), $n^{22}D$ 1.5912. An infrared spectrum showed bands at 2203 ($C\equiv C$), 1705 ($C=O$), 1608 and 1495 (phenyl group), 1276, 1192, and 1171 (C–O–), and 1104 cm.$^{-1}$; ultraviolet absorption, $\lambda_{\max}^{CH_3OH}$ 293 (ϵ 23,000), 275 (ϵ 18,000 sh), 247 (ϵ 7700 sh), and 226–227 mμ (ϵ 9800 sh); n.m.r. data, 2.79 (Ar-H), 7.76 (C-3 CH_3), 7.83 (C-2 CH_3), and 6.41 τ (OCH_3).

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.32; H, 6.67.

Benzoylphenylacetylene.—This ketone, prepared according to the directions described previously[11] was found to be contaminated with a material which showed carbonyl absorptions in the infrared at 1790 and 1729 cm.$^{-1}$. This contaminant (presumably benzoic anhydride) was removed in part by refluxing the ketone with a 15% aqueous sodium carbonate solution, followed by distillation and recrystallization. The ketone partially purified in this manner (m.p. 45–48°) was used in the Reformatskiĭ reaction.

Methyl 3,5-Diphenyl-3-hydroxy-4-pentynoate (I, R = C_6H_5; R′ = H; R″ = CH_3).—A Reformatskiĭ reaction with benzoylphenylacetylene and methyl bromoacetate according to the procedure described previously gave an 80% yield of crystalline hydroxy ester of m.p. 80.5–81.5° (from hexane).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.76. Found: C, 77.00; H, 5.76.

3,5-Diphenyl-3-hydroxy-4-pentynoic Acid (I, R = C_6H_5; R′ = R″ = H).—Saponification of the preceding hydroxy ester with 5% methanolic potassium hydroxide gave the hydroxy acid, m.p. 137–139° dec. (from benzene–cyclohexane).

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.85; H, 5.26.

Methyl 3,5-Diphenyl-2-penten-4-ynoate (IIID, R″ = CH_3).—A solution of the preceding hydroxy ester (13.9 g., 0.050 mole) in 200 ml. of benzene was refluxed for 1 hr. with 0.70 g. of *p*-toluenesulfonic acid. The theoretical volume of water (0.90 ml.) was collected in a Dean–Stark water trap. The reaction mixture was washed with bicarbonate solution and water and was dried over anhydrous magnesium sulfate. After removing the solvent, the residual oil was diluted with 50 ml. of methanol and cooled in an ice bath to precipitate 8.50 g. of crystalline unsaturated ester, m.p. 72–74°. An additional 2.70 g. of ester, m.p. 72–74°, was recovered from the methanolic liquors. The yield of unsaturated ester varied from 83–86% for several dehydrations. The analytical sample was recrystallized from methanol, m.p. 73–74°. An infrared spectrum (in $CHCl_3$) showed bands at 2212 ($C\equiv C$), 1706 ($C=O$), 1603, 1594, and 1492 (phenyl group), and 1277 and 1168 cm.$^{-1}$ (C–O–); ultraviolet absorption, $\lambda_{\max}^{CH_3OH}$ 302 (ϵ 19,600), 261 (ϵ 14,000 sh), 247 (ϵ 15,500), and 233 mμ (ϵ 17,300); n.m.r. absorption (in CCl_4), 2.83 (C-5 Ar-H), 2.53 (C-3 Ar-H), 3.64 (C-2 H), and 6.31 τ (OCH_3).

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.50; H, 5.37.

3,5-Diphenyl-2-penten-4-ynoic Acid (IIID, R″ = H).—The preceding unsaturated ester (4.50 g., 0.017 mole) was mixed with an excess of 5% methanolic potassium hydroxide and was allowed to stand 5 days at room temperature. Acidification of the ether-washed saponification mixture precipitated a crude, yellow solid, m.p. 112–122°. Recrystallization from 3:1 petroleum ether–ethyl acetate gave 2.50 g. (59%) of pale yellow needles, m.p. 129–133°. The analytical sample had a melting point of 132.5–134°. The acid yellowed on exposure to light. An infrared spectrum (in KBr) showed bands at 3200–2500 (acid OH), 1661 ($C=O$), 1603 and 1572 (phenyl group), 1282 and 1205 (C–O–), and 756 and 685 cm.$^{-1}$ (monosubstituted phenyl group); ultraviolet absorption, $\lambda_{\max}^{CH_3OH}$ 297 (ϵ 18,700), 260–261 (ϵ 17,200 sh), 251 (ϵ 18,300), and 229 mμ (ϵ 17,700); n.m.r. absorption (in $CDCl_3$), 2.73 (C-5 Ar-H), 2.33 (C-3 Ar-H), and 3.47 τ (C-2 H).

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.18; H, 5.00.

3,5-Diphenyl-2-methyl-2-penten-4-ynoic Acid (IIIE, R″ = H).—A Reformatskiĭ reaction of benzoylphenylacetylene and ethyl α-bromopropionate according to the procedure described previously gave the crude hydroxy ester which was dehydrated directly with *p*-toluenesulfonic acid. Saponification of the crude unsaturated ester with 5% methanolic potassium hydroxide and recrystallization of the crude acid (m.p. 163–166°) from nitromethane gave a 34% yield of colorless needles, m.p. 165–167°. An infrared spectrum (KBr) showed bands at 3200–2500 (acid OH), 1658 ($C=O$), 1605 (phenyl group), 1287 and 1259 (C–O–), and 756 and 690 cm.$^{-1}$ (monosubstituted phenyl group); ultraviolet absorption, $\lambda_{\max}^{0.003\,N\,H^+ \text{ in } CH_3OH}$ 295 (ϵ 21,500), 286 (ϵ 20,800 sh), 250 mμ (ϵ 15,700); n.m.r. absorption (in $CDCl_3$), 2.75 (C-5 and C-3 Ar-H), and 7.51 τ (C-2 CH_3).

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.07; H, 5.31.

Methyl 3,5-Diphenyl-2-methyl-2-penten-4-ynoate (IIIE, R″ = CH_3).—Diazomethane esterification of the preceding acid gave the crude methyl ester. Several recrystallizations from petroleum ether (b.p. 30–60°) at −20° gave colorless crystals, m.p. 51.5–52.5°. An infrared spectrum showed bands at 2198 ($C\equiv C$), 1706 ($C=O$), 1603 and 1493 (phenyl group), and 1277 and 1145 cm.$^{-1}$ (C–O–); ultraviolet absorption, $\lambda_{\max}^{CH_3OH}$ 295–296 (ϵ 20,800), 280 (ϵ 18,900 sh), and 247 mμ (ϵ 14,400); n.m.r. absorption (in CCl_4), 2.85 (C-5 and C-3 Ar-H), 7.71 (C-2 CH_3), and 6.64 τ (OCH_3).

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.37; H, 5.88.

2,5-Diphenyl-3-methyl-2-penten-4-ynoic Acid (IIIF, R″ = H).—A Reformatskiĭ reaction of 5.30 g. (0.037 mole) of 4-phenyl-3-butyn-2-one, 10.1 g. (0.044 mole) of methyl α-bromophenylacetate,[12] and 2.97 g. (0.045 mole) of zinc gave 6.15 (57%) of a viscous yellow oil, b.p. 145–157° (0.20 mm.), presumably the hydroxy ester. Trituration of this oil with petroleum ether (b.p. 30–60°) gave 0.40 g. of a white powder (m.p. 162–195°) which was probably a *dl–meso* mixture of dimethyl α,α'-diphenylsuccinate. Dehydration of the petroleum ether-washed hydroxy ester (5.57g., 52 %) with phosphorus oxychloride–pyridine and saponification of the crude dark unsaturated ester gave the crude acetylenic acid as a brown gum. By warming this gum with 30 ml. of cyclohexane 0.41 g. (8.3% based on hydroxy ester) of crystalline acid, m.p. 160–167°, was obtained. Additional recrystallization of this material from cyclohexane gave the analytical sample as colorless needles, m.p. 168.5–170°. An infrared spectrum (in KBr) showed important bands at 1658 ($C=O$), 1597 and 1570 (phenyl group), 1277 and 1235 (C–O–), and 761 and 687 cm.$^{-1}$ (monosubstituted phenyl group); ultraviolet absorption, $\lambda_{\max}^{CH_3OH}$ 302 (ϵ 18,900) and 243–244 mμ (ϵ 13,800); n.m.r. absorption (in $CDCl_3$), 2.68 (C-5 Ar-H), 7.58 (C-3 CH_3), and 2.91 τ (C-2 Ar-H).

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.33; H, 5.62.

The unsaturated ester prepared in 32% yield from 4-phenyl-3-butyn-2-one and ethyl α-bromophenylacetate was shown to be a 70:30 *cis–trans* mixture by C-3 methyl proton absorption at 7.72 (135.5 c.p.s., 2-*trans* isomer) and 8.10 τ (114.1 c.p.s., 2-*cis* isomer). An indeterminable amount of diethyl α,α'-diphenylsuccinate was also present.

Lactone.—The cyclohexane liquors from recrystallization of the preceding acid gave 30 mg. of fine, colorless needles, m.p. 145.5–146.5°. The needles were insoluble in sodium bicarbonate solution.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.30; H, 5.60.

Methyl 2,5-Diphenyl-3-methyl-2-penten-4-ynoate (IIIF, R″ = CH_3).—Diazomethane esterification of the preceding acetylenic acid and recrystallization of the crude product from petroleum ether at −20° gave the colorless analytical sample, m.p. 68–69°. An infrared spectrum (in $CHCl_3$) showed characteristic bands at 2185 ($C\equiv C$), 1704 ($C=O$), 1602 and 1493 (phenyl group), and 1286 and 1272 cm.$^{-1}$ (C–O–); ultraviolet absorption, $\lambda_{\max}^{CH_3OH}$ 304 (ϵ 20,000) and 242 mμ (ϵ 12,300); n.m.r. absorption (in CCl_4), 2.73 (C-5 Ar-H), 7.71 (C-3 CH_3), 2.91 (C-2 Ar-H), and 6.36 τ (OCH_3).

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.59; H, 6.00.

Acknowledgment.—C. E. S. is grateful for a National Science Foundation Cooperative Graduate Fellowship held during 1960–1961 and 1961–1962. Partial support under National Science Foundation Grant G-11108 is acknowledged. The authors are indebted to Dr. T. H. Crawford and Dr. N. F. Bray for assistance with determination and analysis of the n.m.r. spectra.

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(11) J. V. Nef, *Ann.*, **308**, 275 (1899).

(12) J. H. Boyer and D. Straw, *J. Am. Chem. Soc.*, **75**, 1642 (1953).