2-*endo*-*p*-anisylepicamphor (XVIII). To 50 ml. of freshly distilled triethylene glycol placed in a 100 ml. three-necked round-bottomed flask fitted with thermometer, nitrogen system, and reflux condenser connected to a still head from a hydrazine distillation apparatus was added 1.0 g. (0.043 g.-atom) of sodium and the temperature raised to 180° for 3 hr. The ketone (2.64 g., 0.01 mole) was added and the temperature maintained at 180° 2 hr. longer, when 8 ml. (8.1 g., 0.25 mole) of anhydrous hydrazine, prepared according to the method of Barton,[37] was distilled over sodium hydroxide into the flask. The temperature was maintained at 180° for 18 hr., then part of the hydrazine (about 4 cc.) distilled until a temperature of 210° was achieved. The temperature was controlled at 210° for 24 hr., the solution cooled, diluted with water, and extracted with ether. The ethereal layer was washed with water dried over magnesium sulfate, and evaporated to yield 1.4 g. (60%) of *p*-bornylphenol (I) as rhombical prisms, m.p. 133–134.5°, after recrystallization from benzene–petroleum ether. The mixture melting point of the above sample, m.p. 133–134.5°, and a sample of the product from pyridine hydrochloride fusion of *p*-bornylanisole, m.p. 135–136°, obtained from reduction of *p*-anisylbornylene (VII) with liquid ammonia, showed no depression, m.p. 133–135°. The infrared and NMR spectra were identical.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 82.86; H, 9.55.

To a solution of 0.35 g. (0.01 mole) of the *p*-bornylphenol above, m.p. 133–134.5°, dissolved in 50 ml. of acetone and placed in a 100 ml. three-necked round-bottomed flask fitted with mechanical stirrer, condenser, and nitrogen system, was added 12.0 g. (0.09 mole) of potassium carbonate and 13.87 g. (0.11 mole) of dimethylsulfate. The mixture was stirred vigorously and heated at reflux for 3 hr. when it was cooled to room temperature, the potassium carbonate removed by filtration through Filter-Cel, and the acetone removed under reduced pressure. The excess dimethyl sulfate was decomposed by the careful addition of concd. ammonium hydroxide, the mixture extracted with ether, the ethereal solution washed with water, 10% hydrochloric acid, 5% sodium bicarbonate, and water, dried, and the ether removed under reduced pressure to afford 0.31 g. (83%) of *p*-bornylanisole as a colorless liquid, b.p. 110°/0.1 mm., $n^{25}D$ 1.5397. The product was shown to be identical with the product from sodium reduction of *p*-anisylbornylene by gas chromatography, by comparison of the infrared and NMR spectra and physical constants.

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Geometrical Isomers of 3-Methyl-5-phenyl-2,4-pentadienoic Acid. The Two 4-*cis* Isomers and Their NMR Characteristics

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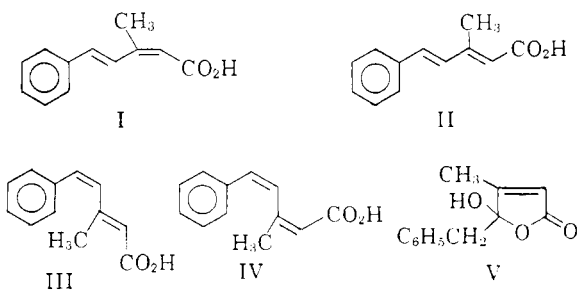
The NMR characteristics of the two unknown geometric isomers (2-*cis*-4-*cis* and 2-*trans*-4-*cis*) of 3-methyl-5-phenylpentadienoic acid and their esters have been obtained from 30% and 95% pure samples of these compounds prepared by partial hydrogenation of the acetylenic esters. The NMR data establish differences in the compounds which have been used to assign the 3-*s*-*trans* structure to the 4-*cis* isomers.

Previous studies[1] of the geometrical isomers of 3-methyl-5-phenyl-2,4-pentadienoic acid have shown that the two known isomers have the 2-*trans*-4-*trans* (II), m.p. 160°, and the 2-*cis*-4-*trans* (I), m.p. 158°, configurations. We have now examined the possibility of preparing the two unknown 4-*cis* isomers (III, IV) by partial hydrogenation of the esters of the corresponding 2-*cis* and 2-*trans* isomers of 3-methyl-5-phenylpent-2-en-4-ynoic acids and have, in the course of these studies, shown that their NMR absorption characteristics provide a conclusive basis for structural assignment in the series and establish that the 4-*cis* isomers exist in a preferred 3-*s*-*trans* conformation.

The two geometrical isomers of 3-methyl-5-phenylpent-2-en-4-ynoic acid are obtained as a mixture of their methyl esters on dehydration of methyl 3-hydroxy-3-methyl-5-phenyl-4-pentynoate over phosphorus oxychloride–pyridine. The ester of the hydroxy acid is formed in 70–80% yield in the Reformatsky reaction between 4-phenyl-3-butyn-2-one and methyl bromoacetate. Saponification of the *cis*-*trans* mixture of the esters gives a solid acid, m.p. 128°. This acid has NMR characteristics (Table I) which indicate that it is the *trans* acid and that it is at least 95% pure stereochemically. Re-esterification of the acid gives the 2-*trans* ester again 95% pure stereochemically. The *cis* acid has not been separated from the mother liquor from which the *trans* acid was crystallized in a solid form. The liquid acid is approximately 60% *cis* stereochemically, based on its NMR ab-



(1) Richard H. Wiley, *J. Chem. Soc.*, 3831 (1958).

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA

Compound	C-2—H	C-3—CH_3	C-4—H	C-5—H	Ar—H	CO_2CH_3	J_{4-5} Coupling
I	4.30	8.00	1.58	3.13	2.90	6.34	16 c.p.s.
II	4.20	7.67	3.32	3.32	2.82	6.45	16 c.p.s.
III[a]	4.23	7.88	3.99	3.57	2.85	6.52	12 c.p.s.
IV[b]	4.30	8.27	3.07	3.57	2.85	6.50	12 c.p.s.
trans-Acetylenic ester	3.95	7.63			2.83	6.43	
cis, trans-Acetylenic ester mixture	3.95	7.63			2.83	6.43	
	4.13	8.00			2.78	6.37	

[a] Data from the 90–95% samples described in the Experimental. [b] Data from the 60% sample described in the Experimental.

sorption, and gives an ester of comparable purity. The position of the methyl proton absorption at τ = 7.63 for the trans (methyl *cis* to methoxycarbonyl) and at τ = 8.00 for the *cis* isomers provide unequivocal structural assignments based on the deshielding characteristics of the methoxycarbonyl *cis* to the methyl protons.[2] The C-1 proton absorption occurs at τ = 3.95 (*trans* isomer) and τ = 4.13 (*cis* isomer), which is consistent with a deshielding effect attributable to the acetylenic bond *cis* to the C-1 proton.

A lactone, to which the α,β-unsaturated γ-lactone structure V has been assigned, is formed during the alkaline saponification and acidification of methyl 5-phenyl-3-methyl-2-penten-4-ynoate. The structure is supported by the ultraviolet (λ_{max} 220, ϵ 5700), infrared (maxima at 1757 cm.$^{-1}$), and NMR absorption characteristics. The last show a tertiary, alcoholic (τ = 5.12), an olefinic (τ = 4.50), three olefinic methyl (τ = 7.97), and two benzylic (τ = 6.85) protons. The alternative δ-lactone structure is not in accord with the infrared carbonyl maximum at 1757 cm.$^{-1}$, which is characteristic of unsaturated γ-, but not δ-, lactones. The formation of a lactone of this type, which requires addition of a molecule of water and subsequent lactone formation, has been observed in our studies with some, but not all, 2-penten-4-ynoate structures. The reaction apparently takes place only with certain substituted types. The data will be presented in a separate report.

Hydrogenation of methyl 3-methyl-5-phenyl-2-*trans*-pent-2-en-4-ynoate over Lindlar catalyst[3] gives a product for which the NMR data (Table I) show the 3-methyl proton absorption at τ = 7.88 deshielded as required for its *cis* to methyl-methoxycarbonyl structure (III) but apparently somewhat less than might have been predicted. The C-2 proton absorption appears at τ = 4.23 and the C-4:C-5 protons as unsymmetrical doublets (J = 12 c.p.s.) at τ = 3.99 and 3.57. The coupling constant is characteristic for the *cis* relation. A trace (5%) of methyl absorption at slightly higher fields is present. Saponification of this ester gave a mixture of isomeric acids which has not been induced to crystallize. Hydrogenation of the ester containing 60% of the 2-*cis* isomer gave a product for which the NMR absorption spectra (Table I) showed the presence of two major absorption peaks with τ values of 7.88 and 8.27 attributable to two sets of olefinic methyl (*i.e.*, C=C—CH_3) protons in the 4-*cis* isomers. These are clearly distinguished from (much smaller) methyl proton peaks at τ = 7.63 and 8.00 attributable to the olefinic methyl proton in traces of unreduced acetylenic ester.

To complete the NMR analysis the data for the methyl ester of the 2-*cis*-4-*trans* (I) and 2-*trans*-4-*trans* (II) acids have been obtained (Table I). The methyl protons for these isomers occur at τ = 7.67 (2-*trans*-4-*trans*) and τ = 8.00 (2-*cis*-4-*trans*). The C-2 proton absorptions occur as quartets centered at τ = 4.20 (*trans-trans*) and τ = 4.30 (*cis*-4-*trans*). The C-4:C-5 proton absorption for the *trans-trans* isomer occurs as a quartet at 3.32. Such protons have been noted previously[4,5] to be nearly equivalent. The C-4:C-5 protons for the 2-*cis*-4-*trans* isomer occur as doublets (J = 16 c.p.s.) centered at τ = 1.58 (C-4) and τ = 3.13 (C-5). The coupling constants are typical for *trans* structures.

An NMR study of the thermal stability of the mixture of the 2-*cis*-4-*cis* (IV) and 2-*trans*-4-*cis* (III) esters has shown that the former is isomerized rather readily under conditions where the latter is unchanged. A mixture of the two isomers (in approximately equivalent amounts) was heated for two hours at 160–185°. Comparison of the NMR spectra before and after heating showed the 8.27-τ peak (olefinic methyl of IV) had diminished considerably in size and that two new peaks at 8.00 τ and 7.67 τ (olefinic methyl of I and II) were present. The 7.88-τ peak (olefinic methyl of III) present in the original solution had not changed appreciably in its size relative to the total for all of the olefinic methyl peaks. The olefinic proton region of the spectrum also underwent changes indicative of isomerization of the 2-*cis*-4-*cis* isomer (IV).

The presence of four different environments for

(2) L. M. Jackman and Richard H. Wiley, *J. Chem. Soc.*, 2881 (1960); 2886 (1960).

(3) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(4) Richard H. Wiley, P. F. G. Nau, and T. H. Crawford, *J. Org. Chem.*, in press.

(5) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 944 (1959).

the methyl groups in these four structures is accounted for as follows. The methyl protons in the 2-*cis*-4-*trans* isomer (II) can be assumed to occur in a normal position, free from the magnetic anisotropic effect of neighboring groups, at τ = 8.00. In the 2-*trans*-4-*trans* isomer (II) the methyl protons are subjected to the deshielding influence of the *cis* (to it) carbonyl group and their absorption occurs at τ = 7.67. This is equivalent to the deshielding ($\Delta\tau$ = −0.33) observed with many other pairs of isomers.[2] In the 2-*trans*-4-*cis* isomer (III), the methyl protons should be deshielded an equivalent amount but are not (τ = 7.88; $\Delta\tau$ = −0.12). Relative to II, these protons are subjected to a shielding influence ($\Delta\tau$ = +0.21) and the obvious structural unit capable of exerting such a shielding effect is the phenyl group, which can do so when the molecule is in the 3-*s*-*trans* conformation shown in III. Models show this conformation to be somewhat more crowded than the alternative 3-*s*-*cis* conformation with the C-2 proton in the shielding zone of the benzene ring. This is, however, definitely precluded by the occurrence of the C-2 proton absorption at τ = 4.23 almost precisely the same position at which it occurs in the *trans*-*trans* isomer. Similarly, the methyl protons of the *cis*-*cis* isomer (τ = 8.27) are susceptible to shielding by the phenyl group in the 3-*s*-*trans* conformation. Here the shielding is equivalent to 0.27-τ units and the agreement between the two values ($\Delta\tau$ = 0.21; 0.27) seems plausible.

The NMR data for the four isomers indicate that the C-2 protons are subject to a deshielding influence in the pair of 2-*trans* isomers (τ = 4.22, 4.23) as compared to their position for the pair of 2-*cis* isomers (τ = 4.30, 4.30). This deshielding is attributed to the olefinic bond in the 4–5-position. In the 2-*trans* isomers this group is *cis* to the C-2 proton and exerts a deshielding influence not observed when it is *trans*. Similar effects have been noted in the muconic acid isomers[6] and are also to be seen in the data for the pent-2-en-4-ynoic acid given above for which the C-2 proton *cis* to the acetylenic group is deshielded by 0.18-τ units, over twice the effect seen for the ethylenic group.

In the NMR studies of the acids in pyridine solution, it has been observed that the deshielding effect of the *cis*-carboxylate ion is considerably greater than the deshielding of the *cis*-methoxycarbonyl group. Thus, the 3-methyl absorption for the 2-*trans*-4-*trans* isomer (II) occurs at τ = 7.67 (methyl ester in carbon tetrachloride) and at τ = 7.42 (acid in pyridine). This shift is of considerable value in establishing the correct assignment of the NMR absorption bands attributable to 3-*cis* methyl groups in geometrical isomers of unsaturated acids.

(6) J. A. Elvidge, *J. Chem. Soc.*, 474 (1959).

Experimental

NMR Measurements.—All measurements were made with a Varian Associates HR-4302 high resolution spectrometer with a 60-megacycle 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 as τ values.[7] Samples were examined in 30–40% concentration with carbon tetrachloride as solvent except as noted.

Methyl 3-Hydroxy-3-methyl-5-phenyl-4-pentynoate.—A solution of 10.0 g. (0.070 mole) of 4-phenyl-3-butyne-2-one[8] and 12.8 g. (0.084 mole) of methyl bromoacetate in 65 ml. of dry benzene was added to 5.60 (0.086 mole) of dry, acid-etched zinc (40-mesh granular) at a rate sufficient to keep the benzene gently refluxing. After the addition was completed, the reaction mixture was refluxed for 10 min., 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. Distillation after drying over anhydrous magnesium sulfate gave the following fractions: 1) 100°/0.25 mm., 0.20 g.; 2) 100–107°/0.25 mm., 3.48 g.; 3) 103–104°/0.15 mm., 8.59 g.; and 4) 104–110°/0.15 mm., 0.10 g. In a number of runs the yield of material boiling between 103–107°/0.15 mm. varied between 70 and 80%. Distillation of the third fraction through a spinning band column gave a colorless analytical sample, b.p. 103°/0.3 mm., n^{27}D 1.5325.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.54; H, 6.39.

Ethyl 3-hydroxy-3-methyl-5-phenyl-4-pentynoate.[9]—The ethyl ester, b.p. 111°/0.25 mm., n^{25}D 1.5258, was prepared similarly using ethyl bromoacetate.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.13; H, 6.91.

Methyl 3-Methyl-5-phenylpent-2-en-4-ynoate.—A cooled mixture of 20.3 ml. (34 g., 0.222 mole) of freshly distilled phosphorus oxychloride in 60 ml. of dry pyridine was added to a cooled solution of 12.1 g. (0.056 mole) of the hydroxyacetylenic ester in 20 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 product was acidified with cold 4 *N* sulfuric acid and extracted with ether until the ether phase was almost colorless. The ether phases were combined and washed successively with water, saturated bicarbonate solution, and water. Distillation after drying over anhydrous magnesium sulfate gave the following fractions: 1) 94°/0.15 mm., n^{25}D 1.5863, 2.46 g.; 2) 86°/0.10 mm., n^{25}D 1.5900, 2.24 g.; 3) 85°/0.08 mm., n^{25}D 1.5910, 1.32 g.; 4) 85–86°/0.08 mm., n^{25}D 1.5920, 2.70 g. Distillation of fraction 2 through a spinning band column gave the colorless analytical sample, b.p. 98°/0.4 mm., n^{25}D 1.5888.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.05; H, 6.33.

Fraction 2 was a 70:30 *cis*/*trans* mixture and fraction 3 was a 65:35 *cis*/*trans* mixture based on relative intensity of NMR absorption at τ = 8.00 and τ = 7.65.

A number of dehydrations of the β-hydroxy ester with phosphorus oxychloride gave yields of 70–78% of the crude product. No appreciable decrease in the yields was noticed when phosphorus oxychloride from a freshly opened ampoule was used or when a 6 *M* excess of phosphorus oxychloride was used instead of the 12 *M* excess used above.

Ethyl 3-Methyl-5-phenylpent-2-en-4-ynoate.—Dehydration of the ethyl hydroxy ester using the same procedure

(7) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(8) D. Nightingale and F. Wadsworth, *J. Am. Chem. Soc.*, **67**, 416 (1945).

(9) K. E. Shulte, J. Reisch, and O. Heine, *Arch. Pharm.*, **294**, 231 (1961).

gave the ethyl pentenynoate, b.p. 97°/0.12 mm., $n^{25}D$ 1.5796.

trans-**3-Methyl-5-phenylpent-2-en-4-ynoic Acid.**—The unsaturated acetylenic ester (26.5 g., 0.133 mole) was refluxed for 3 hr. with 11.1 g. (0.199 mole) of potassium hydroxide in 225 ml. of methanol and 5 ml. of water. After standing 48 hr. at room temperature, the precipitated crystalline potassium salt was collected, washed several times with small volumes of ether, and air-dried to yield 3.47 g. of the crude product. An additional 4.84 g. of crystalline potassium salt was precipitated by concentrating the filtrate to a volume of 25 ml. Acidification of the potassium salt (8.31 g.) precipitated the acid. One recrystallization from cyclohexane gave 5.90 g. (24%) of colorless needles, m.p. 126.5–128°. The analytical sample was recrystallized from cyclohexane and dried at 65°/0.20 mm. for 2.5 hr., m.p. 127–128°.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.40; H, 5.56.

The *p*-bromophenacyl ester was prepared by the usual technique. Several recrystallizations from ethanol gave colorless needles, m.p. 117.5–119°.

Anal. Calcd. for $C_{20}H_{15}O_3Br$: C, 62.88; H, 3.95. Found: C, 62.94; H, 3.92.

Attempted Preparation of *cis*-3-Methyl-5-phenylpent-2-en-4-ynoic Acid.—The mixed acetylenic esters (2.3 g.) in benzene (70 ml.) containing 100 mg. of iodine were irradiated in a quartz vessel with ultraviolet light at a distance of 2 cm. for 20 hr. The NMR spectrum of the crude ester, after removal of solvent, showed an increase in the *cis*/*trans* isomer ratio from 60:40 to 75:25. Saponification of 0.90 g. of the crude irradiated ester with 5% methanolic potassium hydroxide at room temperature for 6 days gave a brown, viscous oil which contained a small amount of crystalline material. After cooling the oil several days at 0° in a small volume of nitromethane, a crystalline material of m.p. 122–128° was obtained, which showed no melting point depression when mixed with the *trans* acetylenic acid, m.p. 128°. The filtrate gave a brown oil from which the *cis* acid could not be induced to crystallize.

4,5-Dihydroxy-3-methyl-5-phenyl-2-pentenoic Acid γ-Lactone (V).—The liquor from the precipitated potassium salt was diluted with water, extracted with ether to remove neutral material, and acidified with cold 4 *N* sulfuric acid. The precipitated oil was extracted with ether and dried, and the solvent was removed under reduced pressure to give 16.8 g. of a crude, viscous, yellow oil. The crude oil was dissolved in ether and washed with a saturated solution of bicarbonate. The ether layer, after drying and removal of the solvent, gave 4.60 g. of an oily, neutral solid. One recrystallization from 2:1 toluene–petroleum ether (b.p. 30–60°) gave 1.62 g. of light yellow plates, m.p. 98–105°. Additional recrystallization gave a colorless product identical by mixed melting point and infrared spectrum to an analytical sample, m.p. 107–108.5°, isolated from the liquors of a methanol–water recrystallization of crude acetylenic acid (the potassium salt of the *trans* acid was not separated). The analytical sample was dried under high vacuum over phosphorus pentoxide for 2.5 hr.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.50; H, 6.02.

This material has the chemical properties of a lactone (insoluble in 5% sodium bicarbonate, soluble in 5% sodium hydroxide at room temperature and recovered unchanged upon acidification). The infrared absorption shows a carbonyl stretching frequency at 1757 cm.$^{-1}$ (0.02 g./ml. in chloroform) characteristic of an α,β-unsaturated γ-lactone and a hydroxyl band at 3344 cm.$^{-1}$ (0.02 g./ml. in chloroform) characteristic of an intermolecularly hydrogen bonded hydroxyl group. The ultraviolet absorption spectrum showed only end absorption at 220 mμ (ε 5700).

Methyl *trans*-3-Methyl-5-phenylpent-2-en-4-ynoate.—The methyl ester of the pure *trans* acetylenic acid m.p. 127–128°, was prepared by adding a slight excess of diazomethane in ether to an ether solution of the acid. The ether solution was washed with dilute aqueous alkali and dried over anhydrous magnesium sulfate. The solvent was removed to give the crude product. Distillation *in vacuo* gave the colorless analytical sample, b.p. 97°/0.10 mm., $n^{25}D$ 1.5978.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.16; H, 6.25.

Methyl 3-Methyl-5-phenyl-2-*trans*-4-*cis*-pentadienoate (III).—The pure *trans* acetylenic ester (615 mg.) in 30 ml. of methanol was shaken with Lindlar's catalyst[3] (400 mg.) and hydrogen until 75.0 ml. at 23°/755 mm. had been absorbed (1.00 mole: absorption about 4.5 ml./min.). The reaction was then interrupted, the catalyst was separated, and the methanol was removed under reduced pressure to yield 0.57 g. (92%) of light yellow oil, $n^{25}D$ 1.5626. A product differing slightly in refractive index ($n^{25}D$ 1.5651) was obtained from a second hydrogenation. Both materials were combined and distilled *in vacuo* to give the following fractions: 1) 87–89°/0.13 mm., $n^{25}D$ 1.5624, 0.16 g.; and 2) 89–91°/0.13 mm., $n^{25}D$ 1.5625, 0.50 g. Fraction 2 ($\lambda_{max}^{CH_3OH}$ = 286/10,100) gave the following analytical data.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.20; H, 7.11.

NMR data (Table I) based on relative intensity of absorption at τ = 7.88, τ = 7.67, and τ = 8.27 showed that the analytical sample was approximately 90% 2-*trans*-4-*cis*, 5% 2-*trans*-4-*trans*, and 3% 2-*cis*-4-*cis* with about 2% of more saturated ester.

When hydrogenation (548-mg. sample) was carried out with 300 mg. of catalyst, the uptake of hydrogen stopped after 5 hr. (64.3 ml., 0.96 mole at 23°/754 mm.) and gave a product of higher refractive index ($n^{25}D$ 1.5698) and higher ultraviolet absorption ($\lambda_{max}^{CH_3OH}$ = 289/11,900). Analysis of the crude material gave the following results.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.05; H, 6.81.

NMR (Table I) showed that this product was approximately 95% 2-*trans*-4-*cis*, 5% 2-*trans*-4-*trans*, and less than 5% 2-*cis*-4-*cis*. A small sample of the 2-*trans*-4-*cis* isomer which was heated at 155° at atmospheric pressure for 1 hr. and 20 min. showed no change in relative amounts of *cis*-*trans* isomers.

Saponification of the 2-*trans*-4-*cis* methyl ester (90% purity) at room temperature for 5 days with a 2.5% methanolic potassium hydroxide solution gave a yellow oil (0.21 g.) which was shown to be a mixture of 65% of the 2-*trans*-4-*cis*, 27% 2-*cis*-4-*cis*, and 8% 2-*trans*-4-*trans* isomers by its NMR spectrum. Efforts to induce the oil to crystallize were unsuccessful.

Methyl 3-Methyl-5-phenyl-2-*cis*-4-*cis*(60%)-pentadienoate (IV).—A *cis*-*trans* mixture of the acetylenic ester (597 mg.) in 30 ml. of methanol was hydrogenated with Lindlar's catalyst in the same manner as for the trans ester. Removal of the catalyst and solvent gave a light yellow oil (0.55 g., 92%) which was combined with the product from two additional hydrogenations and distilled *in vacuo* to give the following fractions: 1) 82–93°/0.10 mm., $n^{25}D$ 1.5576, 0.35 g.; 2) 92–93°/0.10 mm., $n^{25}D$ 1.5594, 0.34 g.; and 3) 92–93°/0.10 mm., $n^{25}D$ 1.5622, 0.54 g. Fraction 3 ($\lambda_{max}^{CH_3OH}$ 285/9600) gave the following analytical data.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.20; H, 7.11.

The NMR spectrum (Table I) of the analytical sample showed it to be approximately 60% 2-*cis*-4-*cis*, 33% 2-*trans*-4-*cis*, and 7% 2-*trans*-4-*trans* in addition to a small amount of more saturated ester.

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The Rearrangement of a Keto Epoxide to a Lactone. A Novel Transformation in the Bicyclo[2.2.1]heptane Series[1]

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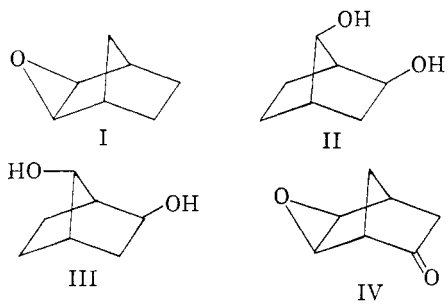
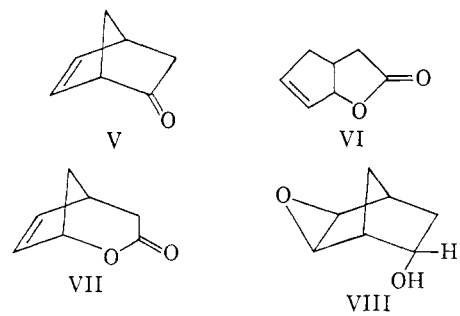
In a study concerned with the ability of a carbonyl function to serve as a participating and migrating group in molecular rearrangements, *exo*-2,3-epoxybicyclo[2.2.1]heptan-5-one (IV) was synthesized and subjected to acid hydrolysis. The resultant product was found to be the lactone VI, previously characterized as the chief peracetic acid oxidation product of dehydronorcamphor (V), rather than either of the expected ketodiols (IX or X). This novel rearrangement may be rationalized in terms of a 1,3-diol cleavage of the hydrate of IV, and finds analogy in the facile cleavage of *exo*-bicyclo[2.2.1]heptan-2-ol-6-one (XIV) to the ketoaldehyde XV. The possibility that the peracetic acid oxidation of V to give VI may have involved IV as an intermediate is considered and rejected, since peracetic acid was found to oxidize IV to the epoxy lactone XVII.

The acid-catalyzed opening of the epoxide ring of *exo*-2,3-epoxybicyclo[2.2.1]heptane (I) has been shown to yield *exo*-2-*syn*-7-bicyclo[2.2.1]heptanediol (II),[3] accompanied by *exo*-2-*anti*-7-bicyclo-[2.2.1]-heptanediol (III).[4] In an attempt to make use of this type of rearrangement to evaluate the possible role of the carbonyl function as a participating and migrating group,[5] we have studied the acid-catalyzed rearrangement of the keto epoxide IV.

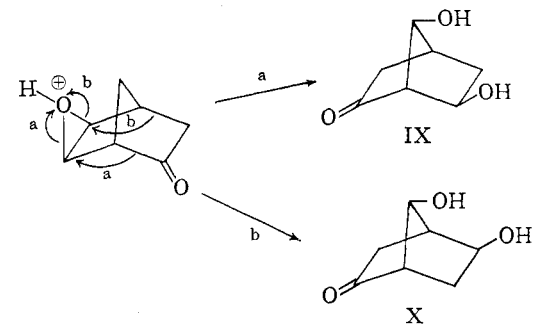


In an initial attempt to prepare IV, the peracetic acid oxidation of dehydronorcamphor (V) was found to yield a lactonic product (VI accompanied by a small amount of VII) rather than the desired epoxide.[6] We have now found that Sarett oxidation of the corresponding epoxy alcohol VIII provides a satisfactory route to IV.[7,8]



It was anticipated that acid hydrolysis of IV would yield IX in the event that the carbonyl function migrated (*a*) or X in the event that the methylene group migrated (*b*) (Chart I).

CHART I



In fact, this hydrolysis yielded neither IX nor X; the product showed no hydroxylic absorption in the

(1) The support of this work by a research grant from the National Science Foundation is gratefully acknowledged.

(2) Fellow of the Alfred P. Sloan Foundation.

(3) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954); H. Kwart and W. G. Vorsburgh, *ibid.*, **76**, 5400 (1954); K. Alder and H. Wirtz, *Ann.*, **601**, 138 (1956).

(4) H. Krieger, *Suomen Kemistilehti*, **B31**, 340 (1958) has shown that this reaction is more complex than was realized.

(5) For some examples of carbonyl migrations, see A. Eschenmoser, H. Schintz, R. Fischer, and J. Colonge, *Helv. Chim. Acta*, **34**, 2329 (1951); H. O. House, *J. Am. Chem. Soc.*, **76**, 1235 (1954); H. O. House and R. L. Wasson, *ibid.*, **79**, 1488 (1955).

(6) J. Meinwald, M. C. Seidel, and B. C. Cadoff, *ibid.*, **80**, 6303 (1958).

(7) Several other approaches to IV are described in the Experimental. We have omitted any discussion of the synthesis or proof of configuration of VIII, since recent work of Henbest and Nicholls,[8] published after our own studies in this area were completed, have already covered these points adequately.

(8) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221 (1959).