−70° and treated with 1 mmole of ozone. The reaction mixture was analyzed by glpc on an EGS column at 125° using methyl myristate as an internal standard. The chromatogram showed two products, A and B, present in amounts, respectively, of 8.2 and 3.9%. The two products were separated by tlc on silica gel GF_{254} with 15% (v/v) diethyl ether in chloroform. Component A (R_f 0.65) was identified as methyl levulinate by its glpc retention time, and infrared spectrum which were identical with those of an authentic sample. The glpc indicated yield was 23% of theory. Component B (R_f 0.76) was shown to be 2-isopropyl-5-oxohexanal by oxidation to the corresponding acid and subsequent esterification with ethereal diazomethane. The infrared spectrum and glpc retention time of the ester thus obtained were identical with those of an authentic sample of methyl 2-isopropyl-5-oxohexanoate. The glpc indicated yield of this keto aldehyde was 9% of theory. Similarly, ozonolysis of IIb (164 mg) and isolation of products gave methyl levulinate (34% yield) and 2-isopropyl-5-oxohexanal (16% yield).

Oxidation of IIa and b with Chromic Oxide in Pyridine[12] to Form Va and b.—A slurry of 120 mg of CrO_3 in 3 ml of pyridine was added to a solution of 121 mg of IIa in 3 ml of pyridine. Tlc examination of the reaction mixture showed that oxidation of IIa was virtually complete after 24 hr at room temperature. After removing the pyridine under vacuum, the residue was extracted twice with diethyl ether to give 85 mg of crude product. Preparative tlc of the product on silica gel G with diethyl ether (R_f 0.70) gave 41 mg of methyl 8-hydroxy-11-isopropyl-4,8-dimethyl-6,14-dioxo-4,9-pentadecadienoate (Va). The purified product was an oil: λ_{max}^{EtCH} 239 mμ (ε 12,600); infrared spectrum (film), 3470, 1738, 1711, 1673, 1610, 977 cm^{-1}; nmr spectrum, $(CH_3)_2\overset{|}{C}–$, δ 0.82; $CH_3–\overset{|}{\underset{|}{C}}–O$, δ 1.26; $CH_3–\overset{|}{C}{=}O$, δ 2.07; $CH_3–\overset{|}{C}{=}\overset{|}{C}–$, δ 2.11; $=C–CH_2–CH_2–(O{=})C–O–$, δ 2.46; $–O–C–CH_2–\overset{|}{C}{=}O$, δ 2.65; $CH_3O–\overset{|}{C}{=}O$, δ 3.66; –OH, δ 4.32; $–CH{=}CH–$, δ 5.4; $–\overset{|}{C}{=}CH–$, δ 6.0.

Similarly, oxidation of 126 mg of IIb and isolation of product gave 45 mg of Vb. This product had λ_{max}^{EtOH} 239 mμ (ε 12,890). The R_f values and infrared spectra of Va and b were identical. The only difference in the nmr spectra was that the $CH_3\overset{|}{C}{=}\overset{|}{C}–$ resonance occurred at about 0.02 ppm farther upfield in Vb than in Va.

Reverse Aldolization of Va and b.—A solution of 41 mg of Va in 5 ml of ethanol was stirred overnight with 5 ml of 5% Na_2CO_3. Extraction of the reaction mixture with diethyl ether and subsequent fractionation of the extract by tlc on silica gel G using diethyl ether as solvent gave 12 mg of norsolanadione (VI, R_f 0.76) which was identified by comparison of its nmr and infrared spectra with those of an authentic sample.[2]

The aqueous phase was acidified with dilute H_2SO_4 to pH 2 and extracted with diethyl ether. The extracted material (12 mg) was treated with ethereal diazomethane and the methyl esters formed were fractionated by tlc on silica gel G using diethyl ether as solvent. The infrared, nmr, and mass spectra of the major product (7 mg, R_f 0.88) allow only methyl 4-methyl-6-oxo-4-heptenoate (VII) as a possible structure. Doublets at δ 1.89 and 2.13 indicated that the VII obtained was probably a mixture of the two geometrical isomers of this structure.

Reverse aldolization of 140 mg of Vb with 5% Na_2CO_3 and the same isolation of products gave 34 mg of VI and 17 mg of VII. Preparative glpc of VII on an Apiezon L column at 100° allowed collection of two components, VII-A and VII-B, in their order of elution. Both components had the same mass, 170, and the same mass fragmentation pattern as the product from Va.

VII-A.—Infrared spectrum (film), 1739, 1689, and 1816 cm^{-1}; nmr spectrum, $CH_3–\overset{|}{C}{=}\overset{|}{C}–$, δ 1.85; $CH_3–(O{=})C–$, δ 2.14; $=C–CH_2–CH_2–(O{=})C–O–$ (multiplet), *ca.* δ 2.61; $CH_3–O–(O{=})C–$, δ 3.63; $–\overset{|}{C}{=}\overset{|}{C}H$, δ 6.09; λ_{max}^{EtOH} 237 mμ (ε *ca.* 9300).

Anal. Calcd for $C_9H_{14}O_3$: mol wt, 170. Found: mol wt, 170.

VII-B.—The infrared spectrum (film) was similar to that of VII-A except that weak absorption occurred at 965 cm^{-1}. The nmr spectrum was similar to that of VII-A except that the doublet at δ 1.85 was shifted downfield to δ 2.13 and the complex A_2B_2 multiplet at δ 2.61 was collapsed to an apparent singlet at δ 2.45. The ultraviolet spectrum showed λ_{max}^{EtOH} 235 mμ (ε *ca.* 11,600).

Component VII-A is assigned the configuration in which the 4-methyl group, δ 1.85, is *trans* to the acetyl group and VII-B, δ 2.13, the configuration in which it is *cis*. These chemical shifts are in good agreement with those for the 3-methyl group in the geometrically isomeric phytenoates[13,14] which are reported to be δ 1.80 when the methyl group is *trans* to the ester carbonyl and δ 2.15 when *cis*.

Acknowledgment.—The authors are indebted to E. Jack Kahler and R. H. Poirier (Battelle Memorial Institute) for their many helpful suggestions.

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[12] G. L. Poos, G. E. Arth, R. E. Bezler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[13] L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp 119–125.

[14] J. W. K. Burrell, L. M. Jackman, and B. C. L. Weedon, *Proc. Chem. Soc.*, 263 (1959).

Resin Acids. VIII. Reaction of Levopimaric Acid with Acetylenic Dienophiles[1,2]

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The diene synthesis of levopimaric acid (1) with acetylenic dienophiles has been investigated. Condensation of 1 with diethyl acetylenedicarboxylate and benzyne at moderate temperatures results in the expected adducts which undergo thermal rearrangement at 200°. At the temperatures necessary to effect condensation of 1 with ethyl propiolate and ethyl phenylpropiolate, thermal isomerization proceeds spontaneously. Structures of the products have been established.

In the course of a program aimed at the utilization of Diels–Alder adducts of levopimaric acid (**1**) for complex syntheses we had occasion to study the reaction of **1** with acetylenic dienophiles and hereby report our results.

The only previous reference to this matter is that of Sandermann[4] who claimed the successful condensation of pine gum or abietic acid with acetylenedicarboxylic ester. The product, presumed to be **2a**, was not isolated, but crude material obtained by condensation of the reactants at 190° was converted, by hydrolysis, to a substance, mp 169–170°, which was assigned formula **2b**. Application of the Alder and Rickert

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[1] Previous paper: W. Herz and R. N. Mirrington, *J. Org. Chem.*, **30**, 4338 (1965).

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[3] U. S. Public Health Service Fellow, 1962–1964; Ethyl Corporation Fellow, 1964–1965.

[4] W. Sandermann, *Ber.*, **74**, 155 (1941); W. Sandermann and R. Höhn, *ibid.*, **76**, 1257 (1943).

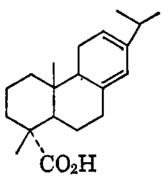
method[5] to the latter and dehydrogenation of the presumed intermediate **3a** failed to furnish retene, thus providing proof for the postulated orientation of the double bonds in ring C of **1**.

Repetition of this condensation with pure levopimaric acid at reflux temperature and isolation of the product subsequent to saponification resulted in a crystalline tricarboxylic acid, mp 191–192° (crude mp 172–173°, hence presumably identical with the material isolated by Sandermann and Höhn[4]), whose infrared spectrum indicated the presence of an aromatic moiety. That the condition selected by Sandermann had resulted in thermal arrangement of the proximate adduct **2a** was established by the nmr spectrum of the product which exhibited the typical ABC pattern of the group $R_3CCH{=}C{<}^{H_a}_{H_b}$ (see Experimental Section)[6] and two signals characteristic of *meta*-oriented aromatic protons (doublets at 8.1 and 7.5, J = 2.5 cps) in addition to two methyl singlets at 1.36 and 1.13 and the double-intensity methyl doublet of the isopropyl group at 1.32 ppm. These observations are only compatible with **3b**, the result of a reversal of the Diels–Alder reaction in the Alder–Rickert sense, a conclusion which was supported by ozonolysis which liberated formaldehyde.[7]

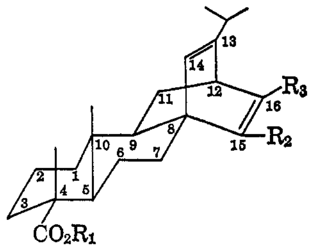
However, reaction of dimethyl acetylenedicarboxylate with **1** or its methyl ester in ether at room temperature permitted the isolation of the "normal" adducts **2a** and **2d** in good yields. The nature of the products was apparent from the nmr spectra which exhibited the broadened singlet of H_{14} near 5.5 ppm and the characteristically shielded[9,10] signal of the C-10 methyl group at 0.65–0.70 ppm, as well as the resonance of a doubly allylic bridgehead proton near 4 ppm.

Thermal isomerization of **2a** resulted in formation of a viscous but homogeneous product **3a** characterized as the crystalline cyclohexylamine salt, whose nmr spectrum exhibited the typical features of **3b** in the aromatic and vinyl proton region. Saponification of **3a** produced **3b**, thus establishing the sequence of reactions leading to this substance.

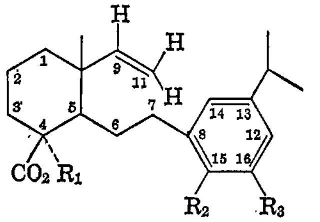
Reaction of **1** with less reactive acetylenic dienophiles at room temperature did not lead to the formation of adducts. With ethyl propiolate, hydrogen transfer or disproportionation of **1** resulted in the formation of dehydroabietic acid, while in the case of ethyl phenylpropiolate, dimerization of the dienophile to 1-phenyl-2,3-dicarbethoxynaphthalene,[11,12] identified by conversion to the corresponding anhydride,[13] took precedence.[14]



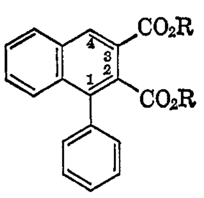
1



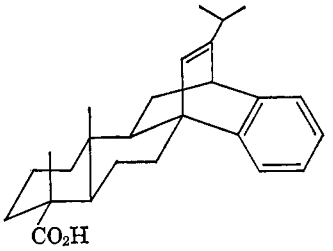
2a, R_1 = H; R_2, R_3 = CO_2Me
b, R_1 = H; R_2, R_3 = CO_2H
c, R_1, R_3 = H; R_2 = CO_2Et
d, R_1 = CH_3; R_2, R_3 = CO_2Me
e, R_1, R_2 = H; R_3 = CO_2Et
f, R_1 = H; R_2 = CO_2Et; R_3 = C_6H_5
g, R_1 = H; R_2 = C_6H_5; R_3 = CO_2Et
h, R_1 = CH_3; R_2, R_3 = H



3a, R_1 = H; R_2, R_3 = CO_2Me
b, R_1 = H; R_2, R_3 = CO_2H
c, R_1, R_3 = H; R_2 = CO_2Et
d, R_1, R_3 = H; R_2 = CO_2H
e, R_1, R_2 = H; R_3 = CO_2Et
f, R_1 = H; R_2 = CO_2Et; R_3 = C_6H_5
g, R_1 = H; R_2 = C_6H_5; R_3 = CO_2Et
h, R_1 = H; R_2 = CO_2H; R_3 = C_6H_5
i, R_1, R_2 = H; R_3 = C_6H_5
j, R_1 = CH_3; R_2 = H; R_3 = C_6H_5
k, R_1, R_3 = H; R_2 = C_6H_5



4a, R = Et
b, R = H



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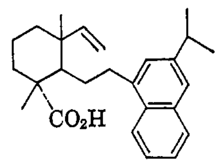

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At the elevated temperatures required to effect condensation between these esters and **1**, the Diels–Alder adducts **2c** (or **2e**) and **2f** (or **2g**) were unstable and underwent isomerization to compounds of type **3**.

Although the formation of two isomers is theoretically possible in the reaction of **1** with unsymmetrical acetylenic dienophiles, only one isomer was detected in each instance. Structures could be assigned on the basis of the nmr spectra. The product resulting from the reaction with ethyl propiolate exhibited three resonances characteristic of aromatic protons. One of these, a widely spaced doublet at 7.97 ppm (J = 7 cps, *ortho* coupling) could be attributed to H_{16} whose appearance at lowest field is due to deshielding by the adjacent carbethoxy group. The other signals were partially superimposed, with H_{14} clearly visible as a doublet of doublets (J = 8 and 2 cps, *ortho* and *meta* coupling). The presence of *ortho* coupling clearly eliminates **3e** and establishes **3c** as the structure of the thermal isomerization product.

The nmr spectrum of the substance resulting from reaction of **1** with ethyl phenylpropiolate exhibited no signals below 7.5 ppm which might have been attributed to protons *ortho* to a carbethoxy group. This suggested structure **3f** rather than **3g**. Confirmation was provided by hydrolysis and decarboxylation to

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[5] K. Alder and H. F. Rickert, *Ann.*, **524**, 180 (1936).

[6] Of the 12 peaks required by theory, only 8 are visible, owing to merging of some of the H_a and H_b frequencies.

[7] Such a reversal has recently been invoked, without proof, to explain the thermal instability of **2d**.[8]

[8] W. A. Ayer and C. E. McDonald, *Can. J. Chem.*, **43**, 1429 (1965).

[9] W. A. Ayer, C. E. McDonald, and J. B. Stothers, *ibid.*, **41**, 1113 (1963).

[10] W. L. Meyer and R. W. Hoffman, *Tetrahedron Letters*, **No. 16**, 691 (1962).

[11] T. Lanser, *Ber.*, **32**, 2481 (1899).

[12] P. Pfeiffer and W. Möller, *ibid.*, **40**, 3841 (1907).

[13] A. Michael and J. E. Bucher, *ibid.*, **28**, 2511 (1895); H. Stobbe, *ibid.*, **40**, 3372 (1907).

[14] For recent references to this reaction, see D. Brown and R. Stevenson, *J. Org. Chem.*, **30**, 1759 (1965).

3i whose nmr spectrum in the aromatic region consisted of a sharp five-proton singlet generated by R_3 and a three-proton singlet broadened somewhat by *meta* coupling, rather than the more complex set of signals to be expected of **3k**. These observations are in harmony with conclusions derived from examination of Dreiding models of **2c**, **2e**, **2f**, and **2g**. Attachment of the carbethoxy group to C-16 rather than C-13 appears to result in greater steric repulsion.

Benzyne, generated by the method of Friedman and Logullo,[15] reacted readily with **1**. The product was difficult to purify owing to contamination with dehydroabietic acid. Extensive chromatography resulted in 17–23% yields of **6** which could be isomerized to **7** by heating at 200°. Condensation between phenylacetylene and **1** could not be effected.

Experimental Section[16]

Condensation of Levopimaric Acid with Dimethyl Acetylenedicarboxylate. A. At Room Temperature.—To a solution of 50 g of **1** ($[\alpha]_D$ −273°)[17] in 200 ml of ether was added with stirring 25 ml of dimethyl acetylenedicarboxylate. The solution warmed gradually and began to reflux after 15–20 min. After this subsided, the solution was allowed to stand for 2 days. Filtration removed 40 g (59%) of colorless crystals, mp 88–92°. Recrystallization from carbon tetrachloride furnished the analytical sample of **2a**: mp 95–99°; $[\alpha]_D$ +76.8° (*c* 1.0, ethanol); infrared bands at 3200–2500 (OH), 1720 (double strength, esters), 1700 sh (acid), 1640 and 1601 cm^{-1} (double bonds); nmr signals at 5.50 br (H_{14}), 4.00 br (H_{12}), 3.85 and 3.75 (methoxyls), 1.18 (C-4 methyl), 1.05 d (J = 7 cps, isopropyl), and 0.69 ppm (C-10 methyl).

Anal. Calcd for $C_{26}H_{36}O_6$: C, 70.24; H, 8.16; O, 21.59. Found: C, 70.36; H, 8.35; O, 21.01.

The cyclohexylamine salt was recrystallized from acetone and melted at 183–187° dec.

Anal. Calcd for $C_{32}H_{49}NO_6$: C, 70.69; H, 9.08; N, 2.58. Found: C, 70.80; H 8.92; N, 2.07.

A solution of 5 g of **2a** in 100 ml of ether was mixed with diazomethane in ether until the yellow color of diazomethane persisted, extracted with dilute base, washed, dried, and evaporated. When crystals began to form, the slurry was triturated with *n*-hexane and filtered to yield **2d**, 4.5 g, mp 95–99°. The analytical sample was recrystallized from ether: mp 117–119°; $[\alpha]_D$ +76.25°; λ_{max} 238 mμ (ϵ 4450); infrared bands at 1740 and 1720 (double strength), 1640 and 1605 cm^{-1}; nmr signals at 5.45 br (H_{14}), 3.93 br (H_{12}), 3.76, 3.68, and 3.62 (methoxyls), 1.15 (C-4 methyl), 1.03 d (J = 7 cps, isopropyl), and 0.65 ppm (C-10 methyl).

Anal. Calcd for $C_{27}H_{38}O_6$: C, 70.71; H, 8.35; O, 20.93. Found: C, 70.61; H, 8.10; O, 21.35.

This substance was also prepared by condensation of 50 g of methyl levopimarate and 25 g of dimethyl acetylenedicarboxylate in 200 ml of ether and allowing to stand overnight. Chilling and filtration yielded 31 g of **2d**, mp 93–98°; concentration of the mother liquors gave additional crops of lower purity. The combined crops were recrystallized twice from ether, yield 45 g (62%), mp 116–118°.

B. By the Method of Sandermann and Höhn.[4]—A mixture of 50 g of **1** and 25 g of dimethyl acetylenedicarboxylate was refluxed at 190–200° for 2 hr in a nitrogen atmosphere. The resin which formed on cooling was dissolved in 300 ml of ethanol, mixed with potassium hydroxide, and heated on the steam bath for 8 hr, cooled, and filtered. The solid salt was taken up in ethanol and the solution was acidified with ethanolic hydrogen chloride. Evaporation at reduced pressure gave a glassy residue which could not be induced to crystallize. However, seed crystals were obtained in the following manner. A 5-g portion of the glassy residue was extracted into ethyl acetate. The organic layer was washed, dried, and concentrated to 15 ml. On cooling and adding 3 ml of *n*-hexane, crystalline **3b** separated, mp 172–173°. Recrystallization from ethyl acetate raised the melting point to 191–192°; $[\alpha]^{25}_D$ −17.1° (*c* 4.05, methanol); infrared bands at 3200–2500 (OH), 1701 sh and 1692 cm^{-1} (double strength, carboxyls); nmr signals (in CF_3CO_2H) at 8.1 d and 7.5 d (J = 2 cps, two aromatic protons), 6.24, 6.10, 5.90, and 5.76 (H_9), 5.27 br, 5.10, 5.02 (H_{11a} and H_{11b}), 1.36 (C-4 methyl), 1.32 d (J = 7 cps, isopropyl), and 1.13 ppm (C-10 methyl).

With the use of seed crystals, the glassy residue could be recrystallized directly from ethyl acetate; mp 190–191°.

Anal. Calcd for $C_{24}H_{32}O_6$: C, 69.21; H, 7.74. Found: C, 68.84; H, 7.70.

The cyclohexylamine salt was recrystallized from acetone; mp 209–211°.

Anal. Calcd for $C_{42}H_{72}N_3O_6 \cdot H_2O$: C, 68.70; H, 10.20; O, 15.30. Found: C, 68.42; H, 10.29; O, 15.75.

Thermal Rearrangement of 2a.—In an atmosphere of nitrogen, 0.5 g of **2a** was heated at 140–150° for 4 hr. The glassy residue obtained on cooling could not be induced to crystallize, but the nmr spectrum indicated that complete conversion to **3a** had taken place: signals at 7.9 d and 7.2 d (J = 2.5 cps, H_{12} and H_{14}), 6.08, 5.87, 5.77, 5.62 (H_9), 5.1 c, 4.9 d, 4.75 d (H_{11a} and H_{11b}), 3.90 and 3.84 (methoxyls), 1.25 (C-4 methyl), 1.15 d (J = 7 cps, isopropyl), and 0.84 ppm (C-10 methyl). The material was homogeneous on tlc. Ozonolysis of 0.1 g of **3a** in 10 ml of methanol at −70 and steam distillation into a saturated solution of dimedone resulted in the formation of a derivative, mp 190°, which did not depress the melting point of authentic material prepared from formaldehyde and dimedone.

For characterization, **3a** was converted to the cyclohexylamine salt which was recrystallized from acetone–*n*-hexane; mp 124–125°.

Anal. Calcd for $C_{32}H_{40}NO_6$: C, 70.68; H, 9.08; N, 2.58. Found: C, 70.80; H, 9.15; N, 2.53.

Hydrolysis of 5 g of **3a** in 15 ml of methanol and 150 ml of 15% potassium hydroxide solution for 18 hr gave, after the usual work-up and recrystallization from ethyl acetate (seeding necessary), 4.1 g of **3e**, mp 191–192°.

Condensation of Levopimaric Acid with Ethyl Propiolate.—A mixture of 7.5 g of **1** and 4 g of ethyl propiolate was refluxed in a nitrogen atmosphere for 4 hr and cooled. The resinous gum was taken up in ether and extracted thoroughly with 1 *N* potassium hydroxide solution. Acidification of the basic solution and re-extraction into ether furnished 3.5 g of **3c** (35%) as a viscous oil which could not be induced to crystallize: single spot on tlc; nmr signals at 7.97 d (J = 8 cps, H_{16}), 7.25 dd (J = 2 cps, H_{12}), 7.18 br (H_{14}), 6.08, 5.87, 5.77, and 5.62 (H_9), 5.1 c, 4.9 d, 4.75 d (two H_{11}), 4.05 (6, ethoxyl), 1.30 (C-4 methyl), 1.22 d (J = 7 cps, isopropyl), and 1.00 ppm (C-10 methyl).

A solution of 0.5 g of **3c** in 5 ml of acetone was mixed with 0.5 ml of cyclohexylamine, warmed for 5 min on the steam bath and chilled. The solid cyclohexylamine salt was washed with acetone and recrystallized from ethyl acetate; mp 145–146°.

Anal. Calcd for $C_{31}H_{40}NO_4$: C, 74.51; H, 9.88; N, 2.80. Found: C, 74.70; H, 9.84; N, 2.85.

A mixture of 3 g of **3c** and 50 ml of 10% sodium hydroxide solution was warmed for 24 hr on the steam bath, cooled, and acidified. Recrystallization of the crude fluffy product from methanol ether furnished 0.5 g of **3d**: mp 125–126°; infrared bands at 1710 (carboxyl), 1645, 1410, and 910 (terminal vinyl), and 1600, 870, and 810 cm^{-1} (1,2,4-trisubstituted benzene); nmr signals were superimposable on those of **3c** (ethoxyl absent).

Anal. Calcd for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66; O, 17.18. neut equiv, 186. Found: C, 74.86; H, 8.45; O, 17.61, neut equiv, 192.

Ozonolysis of **3d** in methanol at −70° furnished formaldehyde, identified as the dimedone derivative. A solution of 2.5 g of levopimaric acid and 3 g of ethyl propiolate in 15 ml of absolute ether was allowed to stand at 25° for 11 days and concentrated *in vacuo*, and the residual gum was chromatographed over 20 g of silicic acid. Benzene eluted 1.2 g of dehydroabietic acid identified by infrared and nmr spectrum, by preparation of the cyclohexylamine salt, mp 119–120°, and by comparison with an authentic sample.

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[15] L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

[16] Melting points and boiling points are uncorrected. Analyses were by D. F. Pascher, Bonn, Germany. Infrared spectra were run in chloroform solution, rotations in chloroform, nmr spectra in deuteriochloroform, unless otherwise specified, on an A-60 spectrometer with tetramethylsilane serving as internal standard. Signals are characterized in the usual way: d, doublet; t, triplet; br, broad singlet or unresolved doublet; c, complex band whose center is given.

[17] We are grateful to Dr. G. W. Hedrick for generous supplies of longleaf yellow pine oleoresin for the preparation of starting material.

Condensation of Levopimaric Acid with Ethyl Phenylpropiolate.—A mixture of 9 g of **1** and 5.3 g of ethyl phenylpropiolate was heated at 210–220° for 4 hr in a nitrogen atmosphere, allowed to cool, dissolved in ether, and extracted with 1 *N* potassium hydroxide solution. Acidification of the basic extract, re-extraction into ether, washing, and drying of the organic extract furnished 5 g of resinous **3f**: homogeneous on tlc; nmr signals at 7.55–7.15 c (seven aromatic protons), 6.09, 5.88, 5.78, 5.62 (H_9), 5.15 c, 4.95 d, 4.80 d (H_{11a} and H_{11b}), 3.95 q (J = 6 cps, ethoxyl), 1.35 (C-4 methyl), 1.28 d (isopropyl), and 0.85 ppm (C-10 methyl).

The neutral fraction was washed, evaporated to dryness, and triturated with 5 ml of methanol. After 2 weeks the material (**4a**) had solidified and was recrystallized from methanol: yield 1.4 g; mp 138°; lit. mp 127–128°,[12] 129–130°;[11] nmr signals at 8.0 c (H_4), 7.9–7.7 c (9 aromatic protons), 4.5 q, 4.0 q (J = 7 cps) 1.4 t, and 1.0 t ppm (7, ethoxyls).

Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.84; H, 5.87.

Hydrolysis of **4a** with aqueous sodium hydroxide and acidification yielded a dibasic acid, mp 151–152°, which was refluxed with acetic anhydride. On cooling, needles separated which melted at 256–257° and were identical with authentic **5**:[13] nmr signals at 8 m (H_4) and 7.7–7.4 c ppm (9 aromatic protons).

An attempted condensation of 9 g of **1** with 5.3 g of ethyl phenylpropiolate in 100 ml of ether at room temperature for 56 days resulted in acid fraction whose nmr spectrum was similar to that of **1**. No product of type **2** could be detected. The neutral fraction contained 4 g of **4a**, mp 138°.

Hydrolysis of 5.0 g of **3f** with 75 ml of 10% sodium hydroxide solution on the steam bath followed by acidification resulted in precipitation of fluffy material (**3h**) which was filtered, washed, dried, and recrystallized from the minimum of benzene–hexane benzene: yield 2.75 g; mp 274–275°; $[\alpha]^{25}\mathrm{D}$ +20 (*c* 0.75, methanol); infrared bands at 1715 (carboxyls), 1645, 1410, 910 (vinyl), 1600, 850, 810 (1,2,3,4-tetrasubstituted aromatic ring), and 770, 710 cm^{-1} (monosubstituted aromatic ring); nmr signals practically superimposable on that of **3f** (ethoxyl absent).

Anal. Calcd for $C_{29}H_{36}O_4$: C, 77.64; H, 8.09; O, 14.27. Found: C, 77.51; H, 8.06; O, 14.66.

Decarboxylation was effected by heating 0.5 g of **3g** with 4 ml of triply distilled quinoline and 1 g of copper powder at 210° until CO_2 evolution ceased. The mixture was cooled and concentrated *in vacuo*, and the residue was taken up in chloroform, filtered, washed thoroughly with dilute acid and water, dried, and evaporated. The crude product was chromatographed over 7 g of silicic acid. The benzene eluate (**3i**), 0.3 g, could not be induced to crystallize, but was homogeneous on tlc and gave a clean nmr spectrum indicating the presence of eight aromatic protons, a vinyl group, two methyl singlets, and an isopropyl group. Half of **3i** was converted to the methyl ester **3j** which was purified by chromatography over silica gel: one spot on tlc; nmr signals at 7.5 (sharp singlet, five aromatic protons of monosubstituted ring), 7.18 br (slightly broadened singlet, $W_{1/2}$ 2.5, no *ortho* coupling, three aromatic protons of 1,3,5-trisubstituted ring), 3.45 (methoxyl), 1.30 (C-4 methyl), 1.18 d (isopropyl), and 0.85 ppm (C-10 methyl). Resonances of the three vinyl protons exhibited the usual patterns. The remaining half of **3i** was converted to the cyclohexylamine salt: yield 0.12 g, after recrystallization from acetone; mp 160°.

Anal. Calcd for $C_{34}H_{49}NO_2$: C, 81.06; H, 9.80; N, 2.78. Found: C, 81.17; H, 9.60; N, 2.68.

Condensation of Levopimaric Acid with Benzyne.—The reaction was accomplished by simultaneous addition through two dropping funnels of 12 g of *o*-aminobenzoic acid in 120 ml of dimethoxyethane and 16 ml of freshly prepared isoamyl nitrite in 120 ml of the same solvent to a refluxing solution of 2 4 g of **1** in 240 ml of dimethoxyethane (nitrogen atmosphere). Addition was complete after 1.5 hr. The mixture was refluxed for an additional 15 min and evaporated at reduced pressure, and the residual dark gum, 30 g, was dissolved in benzene and chromatographed over silicic acid. The yellow benzene eluate, 7 g, showed a single spot on tlc, but was clearly not homogeneous. The impurity appeared to be dehydroabietic acid (nmr, tlc). It was rechromatographed over 2.5 kg of acid-washed alumina. Benzene and benzene–chloroform mixtures eluted gums which were not investigated further. Chloroform eluted 5.1 g (17%) of **6**, mp 132°, which was the chloroform solvate (nmr spectrum). A subsequent run using 70 g of levopimaric acid gave a 23% yield of **6**. It was recrystallized from hexane: mp 132°; $[\alpha]^{25}\mathrm{D}$ +67.4 (*c* 2.45); nmr signals at 7.4 ($CHCl_3$), 7.3 (four aromatic protons), 5.7 br (H_{14}), 3.75 br (H_{12}), 1.25 (C-4 methyl), 1.10 d and 0.97 d (J = 7 cps, isopropyl), and 0.80 ppm (C-10 methyl). On drying at 110° *in vacuo*, the solvate decomposed, but could be reconstituted by refluxing the gum with chloroform and allowing the solution to evaporate at ambient temperature. The analysis indicated the presence of one-half of one molecule of solvent of crystallization.

Anal. Calcd for $C_{26}H_{34}O_2 \cdot 0.5CHCl_3$: C, 72.60; H, 8.39; Cl, 12.11. Found: C, 73.18; H, 7.83; Cl, 12.29.

On drying at 100° *in vacuo* for 3 days and recrystallizing from petroleum ether (bp 60–90°) the melting point rose to 142°.

Anal. Calcd for $C_{26}H_{34}O_2$: C, 82.49; H, 9.05; O, 8.45. Found: C, 81.99; H, 8.99; O, 8.75.

The cyclohexylamine salt was recrystallized from acetone; mp 161°. The material was difficult to prepare for analysis because it decomposed at elevated temperatures.

Anal. Calcd for $C_{32}H_{47}NO_2$: C, 80.45; H, 9.92; N, 2.93. Found: C, 79.80; H, 10.09; N, 2.93.

Solvent-free **6**, 0.5 g, was heated at 210–220° for 4 hr in a nitrogen atmosphere. The resulting gum (**7**) could not be induced to crystallize, but was homogeneous (tlc and nmr spectrum): infrared bands at 1705 (carboxyl), 1630, 1420, 1910 (vinyl group), and 1600, 1580, 795, 755 cm^{-1} (aromatic frequencies); nmr signals at 8–7 c (6 aromatic protons), 6.19, 5.98, 5.88 and 5.72 (H_9), 5.25 br, 5.05 d, 4.90 d (H_{11a} and H_{11b}), 1.30 (C-4 methyl), 0.98 d (J = 7 isopropyl), and 0.83 ppm (C-10 methyl). The substance was characterized as its cyclohexylamine salt, mp 172°, from acetone, which could not be analyzed satisfactorily owing to its ease of decomposition.

Anal. Calcd for $C_{32}H_{47}NO_2$: C, 80.45; H, 9.92; N, 2.93. Found: C, 79.38; H, 9.93; N, 3.27.

Attempted Condensation of Levopimaric Acid with Phenylacetylene.—A solution of 10 g of **1** in 7.4 g of phenylacetylene was refluxed for 17 hr, cooled, dissolved in ether, and extracted with 1 *N* potassium hydroxide solution. Acidification of the basic extract, re-extraction with ether, washing, and drying gave 1.5 g of gum which was chromatographed over acid-washed alumina. The semicrystalline benzene eluate was identified as impure dehydroabietic acid by comparison of the infrared and nmr spectra with a spectrum of an authentic sample and conversion to the cyclohexylamine salt, mp 119–120°. The neutral fraction could not be induced to crystallize.