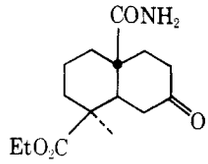
treatment of decalone **15** with $H_2SO_4$. Reaction of this amide with NaOEt produces the imide. The water content of commercial "concentrated" $H_2SO_4$ was not routinely examined in these reactions, and it is quite possible that such a result was due to a variation in the water concentration.



i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# Diterpenoid Total Synthesis, an A → B → C Approach. 11. C-Ring Deoxy Aromatic Systems. Total Synthesis of Methyl (±)-Dehydroabietate[1]


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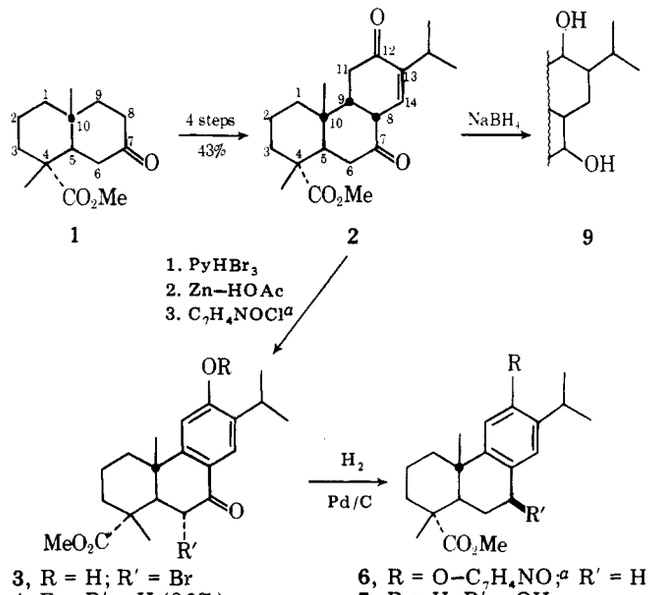
Condensation of 4α-carbomethoxy-4β,10-dimethyl-*trans*-7-decalone (1)[2] with ethyl formate followed by DDQ dehydrogenation produces the corresponding 8-formyl-$\Delta^8$-7-octalone, which is converted to trans-syn-cis tricyclic enedione **2** by sequential Michael addition of *tert*-butyl isovalerylacetate and treatment of the adduct with acid. Reaction of **2** with pyridine hydrobromide perbromide affords 7-keto-12-phenol **4** and its 6α-bromo derivative, and the latter is transformed to **4** by zinc–acetic acid. Hydrogenolysis of the 12-(2′-benzoxazolyloxy) derivative of **4** leads to methyl (±)-dehydroabietate.


Total syntheses which have been fully described in previous parts of this series have all involved target diterpenoids which bear one or more hydroxyl groups on ring C. However, the general synthetic plan can also be adapted for preparation of C-aromatic terpenoids devoid of C-ring oxygen functions, as illustrated here in a total synthesis of methyl dehydroabietate (**8**, Scheme I).

Conversion of the carbomethoxydimethyldecalone **1**[1a] to enedione **2** is completely analogous to the annulation sequence which was used in synthesis of ferruginol[3] and carnosic acid[4] (see Scheme I of accompanying part 9[5]), although in this system the yield was not quite as high (43% overall) and the intermediates and enedione were all noncrystalline. Surprisingly, enedione **2** is much less stable than most of the corresponding compounds we have examined, and it must be used within a few hours of its preparation. As initially isolated, however, it appears spectrally ($^1H$ NMR, IR) to be free of contaminants and to correspond to the $\Delta^{13,14}$ trans-syn-cis structure shown.[5]

The initial plan for aromatization of ring C with ejection of the C-7 and C-12 oxygens envisioned reduction of enedione **2** to a 13-ene-7,12-diol followed by bisdehydration and rearrangement of the 7,8 unsaturation. However, sodium borohydride reduction produces saturated diol **9** (probably as a mixture of diastereomers) rather than the enediol, a reaction which has subsequently been found typical of such enediones.[5] Alternate reductants were not investigated as a route to the enediol. Instead, attention was turned to reversal of the deoxygenation–aromatization sequence.

Scheme I

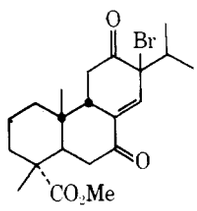



**3**, R = H; R′ = Br
**4**, R = R′ = H (82%)
**5**, R = $C_7H_4NO$;[a] R′ = H (88%)
**6**, R = O–$C_7H_4NO$;[a] R′ = H
**7**, R = H; R′ = OH
**8**, R = R′ = H (80%)

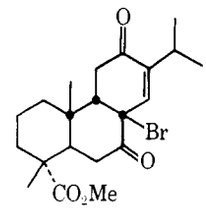
[a] $C_7H_4NO$ = 2-benzoxazolyl.

Aromatization of enedione **6** by pyridine hydrobromide perbromide is more complex than the corresponding reaction in the ferruginol or carnosol series.[3,4] In those instances, where

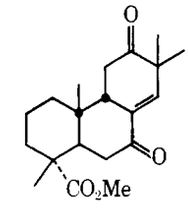
the C-4 substituents are both methyl, reaction of equimolar amounts of enedione and oxidant leads to nearly quantitative yields of keto phenols analogous to **4**. Identical treatment of enedione **2** produces a mixture of **4** and its 6α-bromo derivative **3**,[6] and leaves a significant amount of the enedione unaltered. An excess of pyridine hydrobromide perbromide must be used to consume all of this enedione, which is thereby converted to a mixture of the two phenols **3** and **4**. Exposure of this mixture to zinc–acetic acid affords pure keto phenol **4** in 82% yield from the enedione. Our data do not indicate whether bromo ketone **3** is formed by bromination of keto phenol **4** or by 6-bromination of an intermediate bromo enedione such as **10** or **11** prior to dehydrohalogenation in ring C.




**10**




**11**




**12**

Thus it is not clear whether the effect of the 4α carbomethoxy group has been to retard the rate of bromination of **2** or of dehydrohalogenation of **10** and/or **11** or to enhance the rate of 6-bromination of **10**, **11**, or **4** in comparison with the earlier examples.[7] Nonetheless, it is pertinent that bromination of enedione **12**, a structural analogue of **10** which also contains a 4α ester, indeed leads to a 6α-bromo derivative.[8]

Removal of the phenolic and ketonic oxygens from keto phenol **4** was accomplished hydrogenolytically through the 2-benzoxazolyl ether **5**.[9] Several reductive processes are occurring competitively under these conditions, and in early experiments we encountered products which differed from run to run and appeared variously to contain the 7-deoxy ether **6** and the 12-deoxy 7 alcohol **7** in addition to or to the exclusion of methyl dehydroabietate (**8**). It seems probable that initial hydrogenolysis liberates 2-hydroxybenzoxazole which poisons the catalyst toward some of the hydrogenolysis reactions,[9] because by interrupting the reaction after initial hydrogen absorption, washing an ether solution of the mixture with alkali to remove the heterocycle, and then repeating the hydrogenolysis over fresh catalyst, methyl (±)-dehydroabietate (**8**) is obtained in 80% yield from the keto ether. IR and $^1$H NMR spectra of this sample are identical with those of the authentic (+) enantiomer.

## Experimental Section

General procedures and techniques were the same as described earlier.[3,4] KOH and $NaHCO_3$ solutions were aqueous; HOAc was glacial. Brine refers to saturated aqueous NaCl. General procedures for isolation of reaction products are abbreviated as follows: (A) the specified organic solution was washed with the indicated sequence of aqueous solutions followed by water or brine and dried ($MgSO_4$ or $Na_2SO_4$ unless otherwise specified), and solvent was removed either in vacuo or by evaporation on the steam bath under a stream of dry $N_2$; (B) the indicated aqueous mixture was thoroughly extracted with the specified organic solvent followed by the steps in procedure A; (C) the reaction mixture was added to water or brine followed sequentially by the steps in procedures B and A. When no temperature is specified, operations were conducted at room temperature, ca. 23 °C. $^1$H NMR spectra are reported for $CDCl_3$ solutions and IR spectra for $CHCl_3$ solutions unless otherwise indicated.

**4α-Carbomethoxy-4β,10-dimethyl-8-hydroxymethylene-5α-decalone-7.** Reaction of 960 mg (4.03 mmol) of **1**,[1a] mp 80–84 °C, with the KO*t*-Bu from 950 mg (24.4 mg-atoms) of K and 50 mL of *t*-BuOH followed by 1.7 mL (21 mmol) of $HCO_2Et$ in 10 mL of *t*-BuOH was conducted as described for the analogous reaction of 10-carbethoxy-4,4-dimethyl-5α-decalone-7[4] to afford 1.020 g (95%) of the crude 8-hydroxymethylene derivative as a viscous yellow oil: UV max (95% EtOH) 282 nm (ε 5800); (base) 315 nm (ε 6100); IR 1718, 1638, 1580 cm$^{-1}$; $^1$H NMR τ 1.55 (s, 1 H), 6.35 (s, 3 H), 8.78 (s, 3 H), 9.07 (s, 3 H). Purification was not attempted.

**4α-Carbomethoxy-4β,10-dimethyl-8-formyl-5α-Δ$^8$-octalone-7.** The procedure is a modification of that used for the 10-carbethoxy-4,4-dimethyl analogue.[4,10] A solution of 543 mg (2.04 mmol) of crude hydroxymethylene ketone and 5 drops of HOAc in 11 mL of dry dioxane was rapidly treated with 486 mg (2.14 mmol) of commercial (Aldrich) 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), mp 213–216 °C, stirred for 5 min ($N_2$ atmosphere), and filtered. The residue was washed with 10 mL of dioxane which was added to the filtrate, 241 mg (1.06 mmol) of DDQ was added, and the mixture was stirred for 5 min ($N_2$) and filtered. The residue was washed with 5 mL of $CHCl_3$ which was combined with the filtrate and evaporated in vacuo (ca. 23 °C), this residue was taken up in 40 mL of $CHCl_3$ and filtered, and 80 mL of hexanes was added. Isolation A (4 × 50 mL of 5% $NaHCO_3$ wash) left 411 mg (76%) of the formyl enone as a pale yellow oil: UV max (95% EtOH) 235 nm (ε 5100); (base) 303 nm (ε 13 300); IR 1725, 1705, 1685, 1610 cm$^{-1}$; $^1$H NMR τ −0.02 (s, 1 H), 2.56 (s, 1 H), 6.33 (s, 3 H), 8.72 (s, 3 H), 8.80 (s, 3 H).

**Methyl 7,12-Dioxo-5α,8β,9β-abiet-13-en-15-oate (2).** A mixture of 96 mg of NaH (3.99 mmol, as 165 mg of a 58% dispersion in mineral oil) and 800 mg (4.00 mmol) of *tert*-butyl isovalerylacetate[3] in 20 mL of dry PhH was stirred under $N_2$ for 15 min, 700 mg (2.65 mmol) of crude formyl enone in 60 mL of PhH was added, and after 2 h HOAc was added to produce pH 6.[4] Isolation C ($CHCl_3$; 5% $NaHCO_3$ wash) afforded 1.40 g of a mixture of the Michael adduct and *tert*-butyl isovalerylacetate as a yellowish oil: $^1$H NMR τ 1.54 (s, 1 H), 6.23 (d, *J* = 8 Hz, 1 H), 6.28 (s, 3 H), 6.93 (d, *J* = 8 Hz, 1 H), 8.57 (s, 9 H), 8.73 (s, 3 H), 8.99 (s, 3 H), 9.07 (d, *J* = 7 Hz, 6 H), plus resonances of *tert*-butyl isovalerylacetate.[3] This mixture was used without purification in the next reaction.

A mixture of 1.40 g of crude adduct (contaminated with excess *tert*-butyl isovalerylacetate from its preparation) and 150 mg of TsOH in 60 mL of HOAc was heated under reflux for 2 h ($N_2$ atmosphere), cooled, and treated with 0.5 g of NaOAc.[4] Solvent was removed in vacuo, the residue was partitioned between $CHCl_3$ and water, and isolation B ($CHCl_3$; 5% $NaHCO_3$ wash) afforded 700 mg of yellowish oil. Chromatography on 9 g of Florisil (1 × 14 cm; hexane, hexane–PhH, PhH, and PhH–$Et_2O$ elution) provided 608 mg (66% based on formyl enone) of **2** as a viscous, yellow oil: UV max (95% EtOH) 230 nm (ε 4500); (base) 237 nm (ε 4250), 260 (4400); IR 1713, 1675 cm$^{-1}$; $^1$H NMR τ 3.27 (dd, *J* = 6 and 1 Hz, 1 H), 6.35 (s, 3 H), 8.65 (s, 3 H), 8.75 (s, 3 H), 8.93 (d, *J* = 7 Hz, 3 H), 8.97 (d, *J* = 7 Hz, 3 H). Either in solution or neat, **2** decomposed within a few hours, so it was used immediately in the next reaction.

**Methyl 12-Hydroxy-7-oxo-5α-abieta-8,11,13-trien-15-oate (4).** A mixture of 550 mg (1.60 mmol) of chromatographed **2** and 610 mg (1.91 mmol) of pyridine hydrobromide perbromide, mp 132–135 °C, in 50 mL of HOAc was stirred for 35 min ($N_2$ atmosphere) and subjected to isolation C ($CHCl_3$; 5% $NaHCO_3$ wash) to afford a mixture of **3** and **4** as a tan solid: $^1$H NMR τ 2.12 (s, 1 H), 3.23 (s, 1 H), 5.02 (d, *J* = 12.5 Hz, 1 H), 8.51 (s, 3 H), plus resonances of **4** (below). A solution of this mixture in 100 mL of HOAc containing 2 g of Zn dust was stirred at 45 °C for 4 h,[11] filtered, and subjected to isolation C ($CHCl_3$; 5% $NaHCO_3$ wash) to provide 450 mg (82%) of **4** as a colorless solid, mp 220–230 °C. Several recrystallizations from EtOAc gave pure **4** as colorless needles: mp 238–240 °C; UV max (95% EtOH) 232 nm (ε 14 100), 289 (12 400); IR (KBr) 3250 (br), 1725, 1645 cm$^{-1}$; $^1$H NMR τ 2.08 (s, 1 H), 3.23 (s, 1 H), 3.35 (s, 1 H), 6.35 (s, 3 H), 8.67 (s, 3 H), 8.75 (d, *J* = 7 Hz, 6 H), 8.77 (s, 3 H).

Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19. Found: C, 72.92; H, 8.10.

**Methyl 12-(2′-Benzoxazolyloxy)-7-oxo-5α-abieta-8,11,13-trien-15-oate (5).** According to a general procedure of Musliner and Gates[9] a mixture of 139 mg (0.400 mmol) of **4**, mp 234–236 °C, 68 mg (0.44 mmol) of 2-chlorobenzoxazole, and 250 mg of anhydrous $K_2CO_3$ in 20 mL of dry $Me_2CO$ was stirred under reflux for 18 h (dry atmosphere), solvent was removed in vacuo, and the residue was partitioned between $CHCl_3$ and water. Isolation B ($CHCl_3$) gave 210 mg of oil which was chromatographed on 8 g of Florisil [1 × 16 cm, elution with petroleum ether (bp 40–45 °C), PhH, $Et_2O$, and mixtures thereof]. 2-Chlorobenzoxazole was eluted in 50:50 petroleum ether–PhH fractions, and 90:10 PhH–$Et_2O$ fractions afforded 162 mg (88%) of **5** as a colorless, amorphous solid which was used directly in the next reaction: mp 62–78 °C; UV max (95% EtOH) 250 nm (ε 13 500), 261 (14 500), 270 (14 000), 275 (13 300); IR 1718, 1675 cm$^{-1}$; $^1$H NMR τ 1.85 (s, 1 H), 2.65 (s, 1 H), 2.35–2.82 (m, 4 H), 6.32 (s, 3 H), 8.65 (s, 3 H), 8.68 (s, 3 H), 8.71 (d, *J* = 7 Hz, 3 H), 8.73 (d, *J* = 7 Hz, 3 H).

**Methyl (±)-Dehydroabietate (8).** According to the general procedure of Musliner and Gates[9] 157 mg (0.340 mmol) of chromato-

graphed **5**, mp 62–78 °C, in 20 mL of 95% EtOH was hydrogenated for 20 h at 1 atm over 75 mg of 30% Pd/C. Filtration, distillation of solvent in vacuo, dissolution of the residue in $Et_2O$, and isolation A (5 N KOH wash) left 110 mg (98%) of **7**: IR 3580, 1715 $cm^{-1}$; $^1H$ NMR $\tau$ 2.60 (broad s, 1 H), 2.87 (broad s, 2 H), 5.14 (t, $J$ = 8.5 Hz, 1 H), 6.35 (s, 3 H), 8.73 (s, 3 H), 8.73 (s, 3 H), 8.78 (d, $J$ = 7 Hz, 6 H). This crude **7** in 10 mL of 95% EtOH was hydrogenated for 12 h at 1 atm over 50 mg of 30% Pd/C. Filtration, distillation of solvent in vacuo, dissolution of the residue in $Et_2O$, and isolation A afforded 96 mg (90% based on **5**) of **8** as a colorless oil which was crystallized from EtOH–$H_2O$ to give 85 mg (80%) of pure **8** as colorless needles: mp 70–72 °C (lit. 71.5–73 °C[12]); UV max 268 nm ($\epsilon$ 700), 276 (700); IR 1715 $cm^{-1}$; $^1H$ NMR $\tau$ 2.70–3.15 (m, 3 H), 6.36 (s, 3 H), 8.74 (s, 3 H), 8.79 (d, $J$ = 7 Hz, 6 H), 8.80 (s, 3 H). IR and $^1H$ NMR spectra were identical with those of the authentic (+) enantiomer prepared by $CH_2N_2$ esterification of (+)-dehydroabietic acid.

Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.45; H, 9.65.

**Registry No.**—**1**, 16981-49-0; **2**, 62475-60-9; **3**, 62448-50-4; **4**, 62475-61-0; **5**, 62448-51-5; **7**, 62475-62-1; **8**, 10178-27-5; 4$\alpha$-carbomethoxy-4$\beta$,10-dimethyl-8-hydroxymethylene-5$\alpha$-decalone-7, 62448-52-6; 4$\alpha$-carbomethoxy-4$\beta$,10-dimethyl-8-formyl-5$\alpha$-$\Delta^8$-octalone-7, 16981-50-3; *tert*-butyl isovalerylacetate, 39140-54-0; 4$\alpha$-carbomethoxy-4$\beta$,10-dimethyl-8-formyl-9-(5-methyl-3-oxohexanoic acid-2-yl)-*tert*-butyl ester, 62448-53-7; 2-chlorobenzoxazole, 615-18-9.

## References and Notes


(1) (a) Part 10: W. L. Meyer, T. E. Goodwin, R. J. Hoff, and C. W. Sigel, *J. Org. Chem.*, preceding paper in this issue. (b) Abstracted from the Ph.D. Dissertation of C.W.S., Indiana University, 1967. (c) Supported by Grant AM-10123 from the National Institute of Arthritis and Metabolic Diseases. (d) Preliminary communication: W. L. Meyer and C. W. Sigel, *Tetrahedron Lett.*, 2485 (1967). (e) National Institutes of Health Predoctoral Fellow, 1965–1967.

(2) For position numbering and nomenclature conventions see structures **1** and **2** and footnote 2 of ref 5.

(3) W. L. Meyer, G. B. Clemans, and R. A. Manning, *J. Org. Chem.*, **40**, 3686 (1975).

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(5) W. L. Meyer, R. A. Manning, P. G. Schroeder, and D. C. Shew, *J. Org. Chem.*, accompanying paper in this issue.

(6) The bromo compound has not been isolated in pure form; its formulation is based on two aromatic proton singlets ($\tau$ 2.12 and 3.23), a 12.5-Hz doublet at $\tau$ 5.02 (–CHBrCO–), and a downfield 16-methyl singlet ($\tau$ 8.51) which accompany resonances of **4** in the $^1H$ NMR spectrum of the mixture; cf. R. C. Cambie, G. R. Clark, D. R. Crump, and T. N. Waters, *Chem. Commun.*, 183 (1968).

(7) Cf. discussion of structures **25–31** in ref 3.

(8) T. E. Goodwin, Ph.D. Dissertation, University of Arkansas, 1974.

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(10) This modification, which improved the yield of the 8-formyloctalone somewhat, is due to Goodwin.[8]

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(12) G. Stork and J. W. Schulenberg, *J. Am. Chem. Soc.*, **84**, 284 (1962).


# Phosphonic Acid Chemistry. 2. Studies on the Arbuzov Reaction of 1-Bromo-4,4-diethoxy-2-butyne and Rabinowitch Method of Dealkylation of Phosphonate Diesters Using Chloro- and Bromotrimethylsilane[1]


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The Arbuzov reaction of the title compound **2** and trimethyl phosphite [$(MeO)_3P$] was shown to yield a mixture of phosphonate and diphosphonate products, the composition of the reaction mixture being a function of reaction conditions. The phosphonates **1**, **3**, and **11** were identified as products of the reaction. The structure of the unexpected allenylphosphonate **11** was established in the usual manner as well as by conversion to the alkenylphosphonate **12**. The Arbuzov reaction of **2** and triisopropyl phosphite [$(i\text{-}PrO)_3P$] was shown under comparable conditions to yield moderate yields of the 1-alkynylphosphonate **14**. Certain interconversions, **1** → **3** by $Al_2O_3$ and **1**, **3**, **11** → diphosphonates, were effected. The Rabinowitch method of dealkylating phosphonate diesters [refluxing chlorotrimethylsilane ($Me_3SiCl$)] was used to convert **3** into **4**. Attempts to convert **1** into **5** were unsuccessful. A side product, the alkadienylphosphonate **17**, was isolated and characterized. The conversion of **1** into **5** and of **3** into **4** using bromotrimethylsilane ($Me_3SiBr$) was tried unsuccessfully. Reaction mixtures were obtained consistent with the alkadienylphosphonate **26** as being the chief product of these reactions, but work-up yielded no characterizable products.


Arbuzov reactions of propargyl halides have been reported[2–4] to give complex reaction mixtures from which 2-alkynylphosphonates are difficultly isolable in pure form and good yield. As part of our program[5] to prepare new and novel analogues of pyridoxal phosphate (PPal), we undertook the synthesis of the phosphonate **1**, using the Arbuzov reaction

$(CH_3O)_2P(O)CH_2C{\equiv}CCH(OC_2H_5)_2$

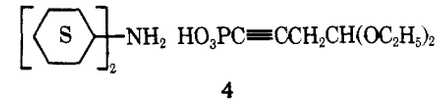
**1**

$BrCH_2C{\equiv}CCH(OC_2H_5)_2$

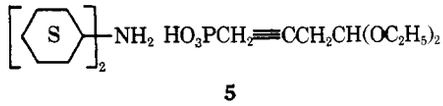
**2**

$(CH_3O)_2P(O)C{\equiv}CCH_2CH(OC_2H_5)_2$

**3**



**4**



**5**

$HC{\equiv}CCH_2Br$ **6**

$C_2H_5OCH_2C{\equiv}CCH(OC_2H_5)_2$ **7**

of **2** and trimethyl phosphite ($(MeO)_3P$). This communication reports the chemistry of this reaction, the synthesis of **1** and **3**, and the synthesis of the dicyclohexylamine (DCH) salt **4** which was of interest to us.[6] The preparation of the desired