p-Toluenesulfonylhydrazone of Methyl 7-Oxoabietan-18-oate.—A solution of 0.300 g of keto ester, and 0.372 g of p-toluenesulfonylhydrazine in 25 ml of 0.2 M ethanolic hydrochloric acid was heated at reflux for 2 hr and then boiled for 19 min without the condenser. An equal volume of water was added, and the white precipitate was collected and recrystallized from aqueous methanol, affording 0.365 g (90%) of material, mp 81–82°.

Anal. Calcd for $C_{23}H_{42}N_2O_4S$: C, 66.91; H, 8.42; N, 5.57. Found: C, 66.67; H, 8.26; N, 5.31.

Abiet-7-en-18-oic Acid (6). **A.**—To a solution of 0.1 g of sodium in 5 ml of ethylene glycol was added 0.140 g of the p-toluenesulfonylhydrazone. The reaction mixture was poured into water and extracted with ether. The ether solution was extracted with 20% potassium hydroxide solution, acidified, and reextracted with ether. The solvent was removed and the resulting oil was crystallized from acetone to give 0.025 g of product: mp 166–167° (lit.[5b] mp 180–182°); nmr 5.30 (m, H-7), 1.25 (C-4 methyl), 0.87 (d, J = 7 Hz, isopropyl), and 0.82 ppm (C-10 methyl).

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 79.04; H, 10.44.

B.—To a boiling solution of 3.0 g of the mixture of abiet-7- and -13-en-18-oic acids obtained from the reduction of abietic acid in 50 ml of acetone was added 1.4 g of (−)-α-phenethylamine; boiling was continued until the amine salt began to precipitate. The solution was cooled and the precipitate was recrystallized once from acetone, five times from ethyl acetate, and five additional times from aqueous acetone. The acid was regenerated from the salt and recrystallized three times from acetone to give 0.80 g of 6, mp 178–180°. The infrared and nmr spectra were identical with those of abiet-7-en-18-oic acid prepared by the Bamford–Stevens reaction.

Registry No.—**3**, 17611-13-1; **5**, 17611-11-9; **6**, 77611-19-7; **9**, 22565-86-2; **10**, 22565-87-3; **15**, 22565-88-4; **16**, 22565-89-5; **16** 14 acetate, 22565-90-8; **16** 14 tosylate, 22565-91-9; **19**, 22565-92-0; **23**, 22576-93-8; **23** oxime, 22565-93-1; **23** p-toluenesulfonylhydrazone, 22576-94-9.

Acknowledgment.—The spectropolarimeter used in this work was obtained through a National Science Foundation Research Instrument Grant. The mass spectral determination was carried out at the Research Triangle Institute.

Studies on Resin Acids. V. Preparation and Reactions of Ring-A Olefins from Dehydroabietic Acid[1]

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Received June 30, 1969

The lead tetraacetate decarboxylation of dehydroabietic acid has been found to give three olefins (**2**, **5**, and **6**) and the acetate of 18-norabieta-8,11,13-trien-4-ol (**7**). Hydroboration–oxidation of this mixture of olefins gives principally 18-norabieta-8,11,13-trien-19-ol (**12**) and 18-norabieta-8,11,13-trien-3α-ol (**13**), plus small quantities of 19-nor-5β-abieta-8,11,13-trien-7-one (**17**). To elucidate the structure of **17**, it was necessary to prepare 18- and 19-norabieta-8,11,13-trien-7-one by oxidation of the corresponding hydrocarbons. It was found that sodium–ammonia reduction of dehydroabietonitrile gives the 19-nor hydrocarbon (**20**), rather than 18-norabieta-8,11,13-triene as suggested originally. The structure of **17** was confirmed by its synthesis in two steps from methyl 7-oxoabieta-5,8,11,13-tetraen-18-oate (**22**).

The readily available diterpenes, dehydroabietic acid (abieta-8,11,13-trien-18-oic acid[2]) and podocarpic acid (12-hydroxypodocarpa-8,11,13-trien-19-oic acid[2]), have received considerable attention as possible precursors for the synthesis of steroids or steroid analogs.[3] The basic goal of these workers was the conversion of dehydroabietic acid (**1**) into abieta-4(18),8,11,13-tetraene,[4] which was accomplished by various methods and with varying degrees of success. The earliest workers in this area investigated the acid-catalyzed dehydration of abieta-8,11,13-trien-18-ol (**3**) and recognized that this led to mixtures of olefins.[3a,b] Later workers prepared what was described as pure **2** by either Hofmann[3c,d] or Cope[3d] eliminations carried out on 4-dimethylamino-18-norabieta-8,11,13-triene (**4**) or, alternatively, by the lead tetraacetate decarboxylation of **1**.[3e]

The single-step decarboxylation of **1** with lead tetraacetate, carried out in these laboratories some years ago and reported to lead to essentially pure **2**, is by far the most convenient of the methods employed to date for this conversion. However, subsequent reinvestigation of this reaction, making use of techniques which were not available during the course of the earlier work, indicates that the material described as **2** is actually a mixture of three olefins.[5] Repetition of the lead tetraacetate decarboxylation of dehydroabietic acid and careful analysis of the nmr spectrum indicated that the material previously described as pure **2** was in fact a mixture of **2**, abieta-3,8,11,13-tetraene (**5**), and abieta-4,8,11,13-tetraene (**6**) in a ratio of 2:2:1. In addition to a 65% yield of the olefin mixture, there was also obtained an oily acetate in 7% yield. The spectral data for this compound indicated that it was probably the same as the 4-acetoxy-18- or -19-norabieta-8,11,13-triene (**7** or **8**) re-

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(1) Part IV: J. W. Huffman, J. A. Alford, and R. R. Sobti, *J. Org. Chem.*, **34**, 473 (1969). This work was supported in part by Career Development Award GM-5433 from the National Institutes of Health.

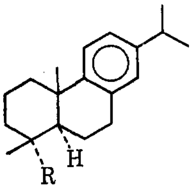
(2) The systematic method of nomenclature employed in this paper is that outlined by J. ApSimon, M. Fetizon, E. Fujita, L. Gough, W. Herz, P. R. Jefries, D. Mangoni, T. Norin, K. Overton, S. W. Pelletier, J. W. Rowe, and E. Wenkert, Abstracts, 6th International Symposium on the Chemistry of Natural Products, Mexico City, April 1969, p 35.

(3) (a) A. Brossi, H. Gutmann, and O. Jeger, *Helv. Chim. Acta*, **33**, 1730 (1950); (b) R. P. Jacobsen, *J. Amer. Chem. Soc.*, **75**, 4709 (1953); (c) H. H. Zeiss and W. B. Martin, *ibid.*, **75**, 5935 (1953); (d) J. W. Huffman and R. F. Stockel, *J. Org. Chem.*, **28**, 506 (1963); (e) J. W. Huffman and P. G. Arapakos, *ibid.*, **30**, 1604 (1965); (f) C. R. Bennet and R. C. Cambie, *Tetrahedron*, **23**, 927 (1967); (g) R. N. Seelye and W. B. Watkins, *Tetrahedron Lett.*, 1271 (1968).

(4) In the case of the workers in ref 3f, the conversion was in the podocarpic acid series.

(5) (a) A. W. Burgstahler, personal communication; A. W. Burgstahler and J. N. Marx, *J. Org. Chem.*, **34**, 1562 (1969). We would like to thank Professor Burgstahler for copies of the nmr spectra of this mixture of olefins, as well as that obtained by the method of Zeiss and Martin.[3c] We would also like to thank Professor Burgstahler for sending us a copy of his manuscript prior to publication. (b) J. F. Biellmann, R. Werrig, P. Daste, and M. Raynaud, *Chem. Commun.*, 168 (1968).

ported by Seelye and Watkins.[3g,6] Hydrolysis of this acetate gave a crystalline alcohol (**9** or **10**), having the same melting point as that reported by Seelye and Watkins.[3g,6] Repetition of the nitrous acid deamination of 4-amino-18-nor-abieta-8,11,13-triene (**11**) gave a mixture of **2**, **5**, and **6** in approximately the same ratio reported earlier,[3g,6,7] plus small amounts of the 4-acetoxy and 4-hydroxy compounds mentioned above. The nmr spectrum of the acetate showed three-proton singlets for the C-4 and C-10 methyl at δ 1.55 and 1.18, while the alcohol had singlets at δ 1.21 and 1.16.[8] By analogy with the chemical-shift differences observed in the steroid series, the conversion of **10** into its acetate should result in the shielding of the angular methyl by *ca.* δ 0.04,[9] with simultaneous strong deshielding of the C-4 methyl owing to the proximity of the acetate group. However, by similar reference to chemical-shift differences in the steroid series, the conversion of **9** into its acetate should somewhat deshield the angular methyl group,[9] with again a rather profound change in the chemical shift of the C-4 methyl. Thus, it is probable that the alcohol is 18-norabieta-8,11,13-trien-4-ol (**9**) and the acetate is **7**.[10] The mechanism of the formation of **7** and **9** during the course of the preparation of the mixture of olefins has been discussed,[3f,6] as has the course of the lead tetraacetate decarboxylation of podocarpic acid.[3f] It is apparent that, since the ratio of olefins obtained by the decarboxylation of **1** is quite different from that observed in the podocarpic acid series,[11] the reaction must not proceed through an "open" carbonium ion, but apparently follows a course similar to that of a nitrous acid deamination.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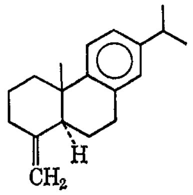
3, R = CH_2OH
4, R = $N(CH_3)_2$
7, R = $OCOCH_3$
9, R = OH
11, R = NH_2
21, R = CN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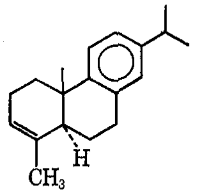
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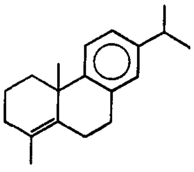
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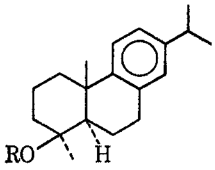
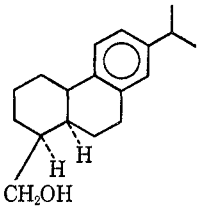

8, R = CH_3CO
10, R = H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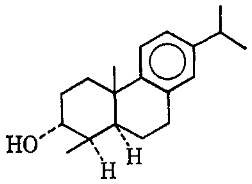
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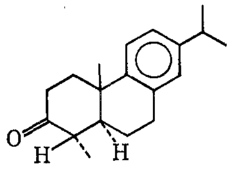
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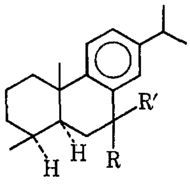
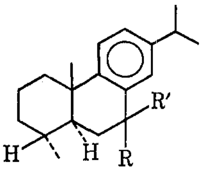
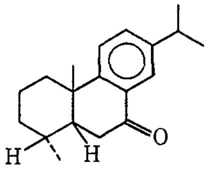

15, R = R′ = O
19, R = R′ = H


16, R = R′ = O
20, R = R′ = H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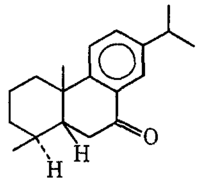
18

In order to compare the various methods of preparation of **2** and its isomers, the Hofmann elimination of **4**[3c,d] was repeated and found to give a mixture containing 80% **2** and 10% each of **5** and **6**.[5a]

Although the various olefins obtained from the lead tetraacetate oxidation could be readily identified by nmr spectroscopy, and the 4(18) olefin has been well characterized by chemical means,[3,5] very little was known concerning the chemical behavior of **5** and **6**. Consequently, the mixture of olefins was subjected to hydroboration–oxidation to give a mixture of hydrocarbons and five alcohols. The hydrocarbons were present in small amount (see Experimental Section) and two of the five alcohols constituted the bulk of the reaction product. From this mixture two pure compounds, the known 18-norabieta-8,11,13-trien-19-ol (**12**)[5] and a crystalline alcohol isomeric with **12**, were obtained. The nmr spectrum of this crystalline alcohol showed a doublet (J = 7 Hz) at δ 0.99 and a C-10 methyl singlet at δ 1.18, with a proton adjacent to a secondary alcohol as a multiplet at δ 3.83. Since $W_{1/2}$ for this signal was 7 Hz, it could be assigned as an equatorial proton, and, assuming the normal *cis* addition of diborane, this alcohol is 18-norabieta-8,11,13-trien-3α-ol (**13**).[12] Oxidation of **13** followed by acid-catalyzed isomerization gave 19-norabieta-8,-

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[6] These authors did not make a stereochemical assignment for the acetoxy function in their original communication. [While this manuscript was in preparation, these authors assigned the 4α configuration to this alcohol: *Tetrahedron*, **25**, 447 (1969)]. It should also be noted that the deamination of a primary amine similar to **11** (probably 4-amino-8α,13β,18-norabietane) to give a mixture of olefins was reported some years ago by V. N. Belov and S. D. Kustova, *Zh. Obshch. Khim.*, **24**, 1087 (1954).

[7] In their work, the authors in ref 3g and 6 assign an nmr chemical shift of δ 1.34 to the C-4 methyl group of **6**. This is almost certainly the C-10 methyl signal from **6**, which is also present in the mixture[3f] (see Experimental Section). The signal for the vinyl methyl at C-4 should be in the range of δ 1.5–1.8, and is buried in the envelope of ring protons.

[8] In these and all the other dehydroabietic acid derivatives discussed, the isopropyl group appears in the nmr as a doublet (J = 6–7 Hz) centered at *ca.* δ 1.2.

[9] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 14–24.

[10] (a) Similar conclusions have been reached by Seelye and Watkins[6] for these compounds and by Bennet and Cambie[3,6] for a similar alcohol in the podocarpic acid series; however, these authors have assigned the nmr peak at δ 1.21 and 1.55 in **9** and **7**, respectively, to the C-10 methyl group, for reasons which are not immediately obvious. (b) J. W. Rowe (personal communication) has isolated **9** as a naturally occuring substance, and his independent nmr assignments agree with ours.

[11] In the podocarpic acid reactions the ratio of **2**/**5**/**6** is *ca.* 3:1:6.[3f]

[12] This compound has apparently been obtained as one component of an unseparated mixture of alcohols from the hydroboration of **5**[5b] (J. F. Biellmann, personal communication).

11,13-trien-3-one (**14**), the spectral properties of which did not agree with those reported by Brannon, *et al.*[13] These authors find the C-10 methyl signal in the nmr at δ 1.26, with the C-4 methyl doublet (J = 7 Hz) at the same position. The nmr spectrum of our sample of **14** clearly shows the C-10 methyl signal at δ 1.37, with the C-4 methyl doublet at δ 1.12.[14] The rotatory dispersion curve of **14** showed a positive Cotton effect (amplitude +16), in agreement with the assigned structure and stereochemistry. It was subsequently found that it was possible to isolate **14** by the direct oxidation of the crude mixture of alcohols. Although tlc indicated that there were three alcohols in addition to **12** and **13** in the hydroboration mixture, they were present in small quantity and could not be isolated in a pure state.

In one hydroboration–oxidation experiment, in which the total crude reaction mixture was oxidized directly with chromic acid, there was obtained in addition to **14** a second, and crystalline, ketone. This ketone showed a carbonyl band in the infrared at 5.97 μ, indicative of a conjugated ketone. The ultraviolet spectrum confirmed this conclusion, and the nmr showed that H-14 was deshielded relative to its normal position. On the basis of these data and microanalysis, it was apparent that this compound is one of the four stereoisomeric 18- or 19-norabieta-8,11,13-trien-7-ones (**15–18**). Although one of these isomers had been prepared previously,[3a] it is of unknown stereochemistry, and, in order to clarify the stereochemistry of the crystalline ketone, the preparation of the two 7 ketones in the natural (5α) series was undertaken. Since it has been shown that catalytic hydrogenation of the mixture of olefins from the decarboxylation of abiet-8(14)-en-18-oic acid proceeds largely by attack from the α face of the molecule to give fichtelite,[15] the similar mixture of olefins from dehydroabietic acid was hydrogenated to give 18-norabieta-8,11,13-triene (**19**). Chromic acid oxidation[16] of **19** gave the desired 7-one (**15**). This compound, although similar to the crystalline ketone mentioned above, was not identical with it.

The preparation of 19-norabieta-8,11,13-triene (**20**) by a multistep sequence from **12** has been described;[5a] however, a much more attractive route appeared to be the direct sodium–ammonia reduction of dehydroabietonitrile (**21**).[17] Although the product of this reduction had tentatively been assigned structure **19**, a comparison of the reported nmr spectrum of the reduction product of **21** with that of **19** indicated that it was probably the 4 epimer **20**. Repetition of the metal–ammonia reduction gave a hydrocarbon which was different from **19** and the spectral properties of which agreed well with those reported for **20**.[5a] However, the melting point of the 12,14-dinitro derivative of this hydrocarbon did not agree with that reported by Burgstahler and Marx,[5a] although the nmr spectrum of the derivative was in accord with theirs.[18] The melting point of our nitro compound agrees well with that reported by Perold and Jeger for the derivative of a hydrocarbon of gross structure **19** or **20**, which was obtained by partial dehydrogenation of fichtelite.[19] The same hydrocarbon could also be obtained by Wolff–Kishner reduction of the aldehyde obtained by oxidation and isomerization of **12**.[20] Chromic acid oxidation of **20** afforded **16**, which again was not identical with the 7 ketone obtained by hydroboration–oxidation.

Although neither **15** nor **16** were identical with the ketone obtained from the hydroboration, a comparison of the nmr chemical shifts of these ketones permitted a tentative assignment of stereochemistry to the original ketone. In the compound with an equatorial methyl groups (**16**), both rings A and B should be in the normal chair and half-chair conformations, respectively; and by comparison with data in the 18,19-bisnorpodocarpa-8,11,13-triene series,[21] this was found to be the case. In compound **16**, the C-10 methyl signal appears at δ 1.16 with a chemical-shift difference of δ 0.07 when compared with the corresponding hydrocarbon (**20**), in excellent accord with those reported by Wenkert, *et al.*[21] In the case of compounds in the 7-ketodehydroabietane series having an axial C-4 methyl, it has been noted that ring B exists in a half-boat conformation, relieving the rather severe 1,3-methyl interaction between the axial C-4 methyl group and the angular methyl.[21] Again, the nmr spectra of **19** and **15** are in agreement with this conclusion, with the C-10 methyl signal in **19** appearing at δ 1.25; however, the difference in chemical shift between **19** and **15** is δ 0.10, somewhat more than that observed by Wenkert, *et al.*[21] The crystalline ketone isolated from the hydroboration must, therefore, be one of the two *cis* isomers (**17** or **18**). If compound **17** were to exist in a steroidlike conformation (**17a**) the C-4 α-methyl group would be axial, while in the nonsteroid conformation (**17b**) it would be equatorial. In the case of **18**, the steroid conformation with C-4 equatorial (**18a**) should be preferred. The angular methyl group in both **17a** and **18a** appears to have the same spatial relationship to the aromatic ring and carbonyl group as it does in **16**, and consequently the chemical shift for these protons should be in the range of δ 1.10–1.25.[21] Since the chemical shift of the C-10 methyl signal in the crystalline ketone appears at δ 1.48, well downfield from that expected for **18a**, it seemed probable that this ketone was 19-norabieta-8,11,13-trien-7-one (**17**).

In an effort to confirm the structure and stereochemistry of the compound assigned structure **17**, methyl

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[13] D. R. Brannon, H. Boaz, B. J. Wiley, J. Mabe, and D. R. Horton, *J. Org. Chem.*, **33**, 4462 (1968). In their original communication [*Chem. Commun.*, 681 (1968)] these authors assign, without explanation, different values to the chemical shift of the C-4 methyl protons than they do in the full paper.

[14] The sample of **14** to which the authors in ref 13 assign the 3-keto structure was obtained in very small quantity, and characterized principally by mass spectrometery. It should be noted that, in two other 3-keto abieta-8,11,13-trienes discussed in ref 13, the C-10 methyl signals appear at δ 1.41 and 1.44. Compound **14** has also been prepared by Biellman,[5b,12] but its properties have not been described in detail.

[15] N. P. Jensen and W. S. Johnson *J. Org. Chem.*, **32**, 2045 (1967); see also ref 5a.

[16] (a) E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 211 (1958); (b) E. Wenkert and J. W. Chamberlin, *ibid.*, **81**, 688 (1959).

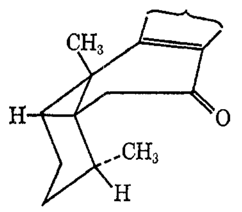
[17] P. G. Arapakos, *ibid.*, **89**, 6794 (1967).

[18] Neither we nor Professor Burgstahler have a satisfactory explanation for this discrepancy in melting points, unless one is dealing with different crystalline modifications of the same compound.

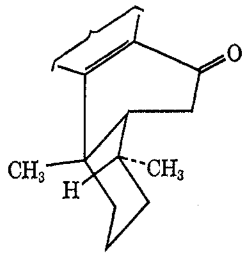
[19] G. W. Perold and O. Jeger, *Helv. Chim. Acta*, **32**, 1085 (1949).

[20] This aldehyde was prepared by Burgstahler and Marx[5a] by chromic acid oxidation of **12**. However, we employed the Moffatt oxidation procedure: K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661, 5670 (1965).

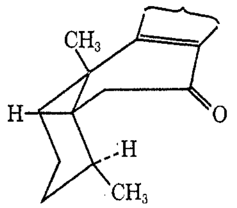
[21] E. Wenkert, A. Alonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30**, 713 (1965).



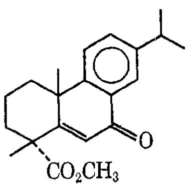
17a



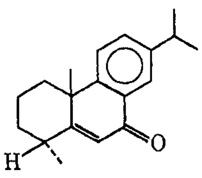
17b



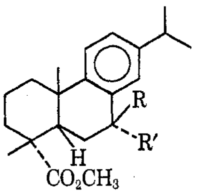
18a



22



23



24, R = H; R′ = OCOCH$_3$
25, R = OCOCH$_3$; R′ = H

7-oxoabieta-5,8,11,13-tetraen-18-oate (**22**)[22] was subjected to vigorous basic hydrolysis with simultaneous decarboxylation to give 19-norabieta-5,8,11,13-tetraen-7-one (**23**). It is assumed that this sequence gives rise to the stable 19-nor isomer, rather than the 18-nor compound. In addition to **23**, a small quantity of **17** was obtained from this reaction, apparently *via* a 1,4-hydride transfer.[23] Catalytic hydrogenation of **23**, employing a rhodium catalyst to minimize hydrogenolysis, gave **17**, identical with the material obtained from the hydroboration–oxidation sequence.

Although the route by which this ketone is formed during the hydroboration sequence is unclear, it must be derived from the Δ^4 olefin (**6**) by β attack of diborane. Since **17** was not obtained in those reactions in which the mixture of alcohols was separated from the other components of the hydroboration mixture, this ketone is probably formed from the corresponding hydrocarbon through benzylic oxidation.

In the lead tetraacetate decarboxylation of podocarpic acid methyl ether, a considerable quantity of C-7 oxidation products was obtained.[3f] Examination of the more polar fractions from the decarboxylation of **1** gave no indication of any appreciable amount of this type of oxidation in the dehydroabietane series under the reaction conditions used. Repetition of the reported lead tetraacetate oxidation of methyl dehydroabietate[24] gave both isomeric 7 acetates (**24** and **25**), rather than just one isomer as reported earlier.[25]

Experimental Section[26]

Decarboxylations of Dehydroabietic Acid. A.—The reaction of dehydroabietic acid with lead tetraacetate was carried out as previously described.[2e] From 27.95 g of acid, there was obtained, after chromatography on alumina, 15.43 g (68%) of a mixture of olefins which consisted of 19-norabieta-3,8,11,13-tetraene (**5**), 19-norabieta-4(18),8,11,13-tetraene (**2**), and 19-norabieta-4,8,-11,13-tetraene (**6**) in a ratio of 2:2:1. The composition of the mixture was determined by the relative areas of vinyl and aromatic peaks in the nmr. The benzene fractions from the chromatography gave 1.95 g (7%) of 4-acetoxy-18-norabieta-8,11,13-triene (**7**) as an oil: nmr 1.96 (s, CH$_3$CO), 1.55 (s, C-4 methyl), and 1.18 ppm (s, C-10 methyl). This ester was hydrolyzed to the 4-ol (**9**) by the method of Cambie. From 1.06 g of acetate, there was obtained, after chromatography on Merck alumina and elution with hexane, 0.048 g of a mixture of the Δ^3, Δ^4, and $\Delta^{4(18)}$ olefins in a ratio of 1:2:1. Elution with benzene gave 0.177 g of recovered acetate, while the methylene chloride fractions afforded 0.415 g (52%) of 18-norabieta-8,11,13-trien-4-ol (**9**) as a white solid. Recrystallization from hexane gave material of mp 90–91° (lit.[3g,10b] mp 91.5–92.5°); nmr 1.21 (s, C-4 methyl) and 1.16 ppm (s, C-10 methyl). The infrared spectrum of this compound was essentially the same as that reported previously for a noncrystalline substance assigned this structure.[3d]

B.—The potassium carbonate elimination reaction of 4-methylamino-18-norabieta-8,11,12-triene was carried out as previously described.[3c,d] From 3.10 g of base hydrochloride there was obtained 0.77 g of a hydrocarbon mixture which, by integration of the nmr spectrum, consisted of 80% 4(18) olefin **2** and *ca.* 10% each of the endocyclic isomers.

C.—4-Amino-18-norabieta-8,11,13-triene (**11**) was prepared essentially according to the method of Seelye and Watkins.[3g,6] The infrared spectrum of this material was identical with that of a sample prepared by the method of Huffman and Stockel.[27] The nmr assignments were in agreement with those of Seelye and Watkins,[3g,6] and the picrate had a melting point of 218–220° (lit. mp 218–220°,[3g] 222–223° [27]). The deamination was carried out according to the procedure of Seelye and Watkins,[3g,6] and, from 10.0 g of amine, chromatography on alumina and elution with hexane gave 1.70 g (18%) of a mixture of hydrocarbons containing 60% **2**, 33% **5**, and 7% **6**. The benzene fractions gave 0.084 g (0.8%) of the 4-acetate (**7**), identical with that prepared above, while benzene–methylene chloride fractions gave 0.120 g (1.2%) of the 4-ol (**9**) as a white solid which was recrystallized from hexane, mp and mmp 89–90°. In contrast to the experience of the earlier workers, no difficulty in crystallizing this material was encountered.

From an analysis of the nmr spectra of the various mixtures of hydrocarbons obtained in these experiments, correlations with the data of Bennett and Cambie, and examination of the spectrum of a pure sample of Δ^4 olefin (*vide infra*), it is possible to assign the following signals in the nmr spectra of the three olefins: 19-norabieta-3,8,11,13-tetraene (**5**), 5.30 (m, H-3) and 1.05 ppm (s, C-10 methyl); 19-norabieta-4(18),8,11,13-tetraene (**2**), 4.70 (d, J = 15 Hz, H-19) and 0.99 ppm (s, C-10 methyl); 19-norabieta-4,8,11,13-tetraene (**6**), 1.66 (s, C-4 methyl) and 1.38 ppm (s, C-10 methyl).

Hydroboration–Oxidation of Abietatetraene Mixture.—To a solution of 4.00 g of the olefin mixture obtained by the lead tetraacetate decarboxylation and 1.40 g of lithium aluminum hydride

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[22] E. Wenkert, R. W. J. Carney, and C. Kaneko, *J. Amer. Chem. Soc.*, **83**, 4440 (1961).

[23] A compound which was assigned structure **23** had been reported earlier;[3d] however, it is not identical with that prepared in this work. It is possible that the earlier compound is actually the C-4 epimer; however, a lack of material precluded a detailed reinvestigation.

[24] G. Dupont, R. Dulou, G. Ourisson, and C. Thibault, *Bull. Soc. Chim. Fr.*, 708 (1955).

[25] The assignments of stereochemistry made in ref 24 are in fact reversed; however, the original stereochemical assignments of P. F. Ritchie, T. F. Sanderson, and L. F. McBurney [*J. Amer. Chem. Soc.*, **75**, 2610 (1953)] are correct. The nmr spectrum of **24** has been noted by W. Herz and H. J. Wahlborg [*J. Org. Chem.*, **30**, 1881 (1965)], while that of **25** is mentioned in ref 13.

[26] Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were taken as films or potassium bromide pellets on a Perkin-Elmer Model 137 spectropolarimeter. Ultraviolet spectra were determined as methanol solutions using a Perkin-Elmer Model 202 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates Model A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Signals are given in parts per million relative to the standard. Optical rotatory dispersion curves were determined in methanol with a Jasco ORD/UV-5 spectropolarimeter. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[27] J. W. Huffman and R. F. Stockel, unpublished work. See also R. F. Stockel, Ph.D. Dissertation, Clemson University, 1962; *Can. J. Chem.*, **41**, 834 (1963).

in 100 ml of dry ether at 0° was added dropwise over a 30-min period 5.0 ml of redistilled boron trifluoride etherate in 80 ml of dry ether. The reaction mixture was allowed to warm to room temperature and stirred for 2.5 hr. Ice and saturated sodium chloride were added and the ether was decanted. The ethereal solution was dried, the solvent was removed *in vacuo* with gentle warming, and the mixture of alkylboranes was taken up in 150 ml of tetrahydrofuran and 80 ml of 10% sodium hydroxide. To this solution was added 60 ml of 30% hydrogen peroxide and the reaction mixture was stirred for 18 hr at room temperature. The aqueous layer was drawn off and extracted three times with ether, and the ethereal extracts were combined with the original organic phase. The combined extracts were washed with water and dried, and the solvents were removed at reduced pressure to give 4.29 g of colorless oil. Tlc [silica gel G, benzene–ethyl acetate (8:1)] showed a six-component mixture, with one component moving near the solvent front. Two of the remaining five components of the mixture appeared to predominate. The mixture was dissolved in hexane and chromatographed on 80 g of Merck acid-washed alumina. Elution with hexane gave 0.555 g of 19-norabieta-4,8,11,12-tetraene (**6**), which was identified by its nmr spectrum (*vide supra*).[28] Elution with benzene-methylene chloride mixtures gave, in order, 0.125 g of a mixture of two alcohols with very similar R_f values on tlc and 0.337 g of 18-norabieta-8,11,13-trien-3α-ol (**13**) as a white solid: nmr 3.83 (m, $W_{1/2}$ = 7 Hz, H-3), 1.18 (s, C-10 methyl), and 0.99 ppm (d, J = 7 Hz, C-4 methyl). The analytical sample, mp 119–120°, was crystallized from hexane.

Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.51; H, 10.50.

Further elution with benzene–methylene chloride mixtures gave 0.203 g of a mixture of the 3α-ol and two other compounds, while the final benzene–methylene chloride fractions gave 0.645 g of 18-norabieta-8,11,13-trien-19-ol (**12**) as a colorless oil. The nmr spectrum agreed well with that reported by Burgstahler and Marx,[5a] with signals at 3.75 (d, J = 6 Hz, H-19) and 1.03 ppm (s, C-10 methyl).

In another run, 1.166 g of the mixture of alcohols, after the separation of the hydrocarbon fraction, was dissolved in 100 ml of acetone and treated with excess Kiliani reagent. After the crude product was isolated in the usual manner, it was separated into 0.094 g of acidic material and 0.987 g of a neutral fraction. Tlc (silica gel G–benzene) indicated that this neutral fraction consisted of two major components, and it was dissolved in hexane and chromatographed on 25 g of acid-washed alumina. Elution with benzene–hexane (3:2) gave 0.167 g of 19-norabieta-8,11,13-trien-3-one (**14**) as a colorless oil:[29] λ_{C-O} 5.86 μ; nmr 1.37 (s, C-10 methyl) and 1.10 (d, J = Hz, C-4 methyl); ORD $[\phi]_{400}$ +324°, $[\phi]_{301}$ +1610°, $[\phi]_{264}$ −810°. For analysis this material was converted into the 2,4-dinitrophenylhydrazone, mp 154–155° from ethanol–ethyl acetate.

Anal. Calcd for $C_{25}H_{30}N_4O_4$: C, 66.65; H, 6.71; N, 12.44. Found: C, 66.42; H, 6.65; N, 12.27.

The acid fraction was dissolved in ether and treated with excess ethereal diazomethane. After removal of the solvents, tlc (silica gel G–benzene) indicated the presence of three compounds and the material was not investigated further.

In one run carried out on 4.0 g of olefins in which the total crude hydroboration mixture was oxidized directly as described above, the first hexane–benzene fractions from the chromatography of the neutral fraction gave 0.045 g of 19-nor-5β-abieta-8,11,13-trien-7-one (**17**): mp 104–105° from hexane; $\lambda_{C=O}$ 5.97 μ; λ_{max} 252 mμ (log ε 4.08) and 303 (3.43); nmr 8.02 (br s, H-14), 1.48 (s, C-10 methyl), and 0.91 ppm (d, J = 7 Hz, C-4 methyl). Owing to the solubility of this material in common solvents, it was converted into the dinitrophenylhydrazone, mp 197–199° from ethanol–ethyl acetate.

Anal. Calcd for $C_{25}H_{30}N_4O_4$: C, 66.65; H, 6.71; N, 12.44. Found: C, 66.51; H, 6.79; N, 12.20.

19-Norabieta-8,11,13-trien-3-one (14).—To a solution of 0.110 g of 18-norabieta-8,11,13-trien-3α-ol (**13**) in 15 ml of acetone was added Kiliani reagent dropwise until a permanent orange color persisted. The reaction mixture was allowed to stand at room temperature for 19 min, 2 drops of water and 3 drops of 10% sodium hydroxide were added, and the precipitated solids were removed. The acetone solution was diluted with water and extracted with three portions of ether, the ethereal extracts were combined, washed with water, and dried, and the solvent was removed *in vacuo* to leave 0.081 g of oil. This oil was taken up in 5 ml of diglyme, 0.5 ml of 2 N hydrochloric acid was added, and the mixture was heated on the steam bath for 30 min. The reaction mixture was diluted with water and extracted with two portions of hexane. The hexane extracts were combined, washed with water, and dried, and the solvent was removed at reduced pressure to give 0.070 g (64%) of ketone, identical with that described above.

18-Norabieta-8,11,13-triene (19).—Catalytic hydrogenation (platinum oxide–ethanol, 30 psi, 25°) of 1.50 g of the mixed olefins from the lead tetraacetate decarboxylation of dehydroabietic acid gave 1.50 g (100%) of hydrocarbon, nmr 1.15 (s, C-10 methyl) and 0.99 ppm (d, J = 7 Hz, C-4 methyl). The 12,14-dinitro derivative had a melting point of 174–176° (lit.[5a] mp 176–177°).

18-Norabieta-8,11,13-trien-7-one (15).—To a solution of 0.70 g of **19** in 25 ml of acetic acid was added a solution of 1.10 g of chromium trioxide in a solution of 2 ml of water and 25 ml of acetic acid. The reaction mixture was stirred at room temperature for 18 hr, the solvent was removed at reduced pressure, and the residue was taken up in ether. The ethereal extracts were washed with water and 10% aqueous sodium hydroxide and dried, and the solvent was removed at reduced pressure to leave 0.28 g of yellow oil. Chromatography on acid-washed alumina and elution with hexane gave 0.056 g of recovered hydrocarbon, while elution with hexane–benzene (3:1) gave 0.092 g (14%) of **15** as a colorless oil: $\lambda_{C=O}$ 5.96 μ; μ_{max} 254 mμ (log ε 3.99) and 303 (3.28); nmr 7.82 (br s, H-14), 1.25 (s, C-10 methyl), and 1.05 ppm (d, J = 7 Hz, C-4 methyl). For analysis this compound was converted into the dinitrophenylhydrazone, mp 180–182° from ethanol.

Anal. Calcd for $C_{25}H_{30}N_4O_4$: C, 66.65; H, 6.71; N, 12.44. Found: C, 66.87; H, 6.55; N, 12.64.

19-Norabieta-8,11,13-trien-18-al.—To a solution of 0.538 g of 18-nor-abieta-8,11,13-trien-19-ol (**12**) in 4 ml of DMSO and 8 ml of benzene was added 1.40 g of dicyclohexylcarbodiimide, 0.20 ml of pyridine, and 0.10 ml of trifluoroacetic acid. The reaction mixture was stirred at room temperature for 21 hr, diluted with ether, and washed thoroughly with water and 10% hydrochloric acid. The ethereal solution was dried and the solvent was removed at reduced pressure to give 0.326 g of brown oil. This oil was taken up in 15 ml of diglyme and treated with 1.5 ml of 2 N hydrochloric acid as described above to give 0.224 g of oil, which was dissolved in hexane–benzene (3:2) and filtered through a short alumina column to give 0.102 g (19%) of aldehyde, the infrared spectrum of which was identical with that reported earlier.[3d] This compound showed nmr signals at 9.53 (d, J = 4 Hz, H-18) and 1.12 ppm (s, C-10 methyl).

19-Norabieta-8,11,13-triene (20). **A.**—To a solution of 3.0 g of sodium in 50 ml of liquid ammonia was added 1.50 g of dehydroabietonitrile. The reaction mixture was stirred at reflux for 2 hr and then the ammonia was allowed to evaporate. The residue was taken up in ether, water was added cautiously, and the aqueous layer was drawn off and washed with ether. The ether layers were combined, washed with water and dilute hydrochloric acid, and dried, and the solvent was removed *in vacuo* to give an off-white oil, the infrared spectrum of which showed the presence of some unreacted nitrile. The oil was taken up in hexane and filtered through alumina to give 0.727 g (53%) of hydrocarbon as a colorless oil with nmr signals at 1.09 (s, C-10 methyl) and 0.93 ppm (d, J = 5 Hz, C-4 methyl). The 12,14-dinitro derivative was prepared and after chromatography and recrystallization from methanol had a melting point of 130–131° (lit. mp 151–153°,[5a] 133–134°[19]).

Anal. Calcd for $C_{19}H_{26}N_2O_4$: C, 65.88; H, 7.56; N, 8.09. Found: C, 65.65; H, 7.39; N, 8.17.

The dinitro derivative had nmr signals at 7.60 (s, H-11), 1.12 (s, C-10 methyl), and 0.95 ppm (d, J = 5 Hz, C-4 methyl).

B.—To a solution of 0.132 g of 19-norabieta-8,11,13-trien-18-al in 15 ml of diethylene glycol was added 1.0 ml of hydrazine and 1.0 g of sodium hydroxide. The reaction mixture was heated at 150° for 2 hr and then at reflux for 4 hr. After cooling, the solution was diluted with water and extracted with two portions of hexane. The hexane extracts were combined, washed with water, and dried, and the solvent was removed. The residue

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(28) In subsequent runs, considerably smaller quantities (0.1–0.2 g) of saturated hydrocarbons (abietatrienes) were obtained in this fraction.

(29) The balance of the material was, from the infrared spectrum of the crude neutral fraction, the 18 and/or 19 aldehyde. Subsequent experience indicated that these aldehydes were somewhat unstable to chromatography on alumina.

was redissolved in hexane and filtered through alumina to give 0.051 g (41%) of **20**, identical with that described in part A.

19-Norabieta-8,11,13-trien-7-one (**16**).—The hydrocarbon was oxidized as described above in the preparation of the 18-norketone. From 0.50 g of starting material there was obtained 0.183 g (33%) of 7-one **16** as a colorless oil: $\lambda_{C=O}$ 5.96 μ; λ_{max} 254 mμ (log ϵ 4.04) and 302 (3.80); nmr 7.90 (br s, H-14), 1.16 (s, C-10 methyl), and 0.90 ppm (d, $J = 5$ Hz, C-4 methyl). For analysis, the dinitrophenylhydrazone, mp 204–295° from ethanol–ethyl acetate, was prepared.

Anal. Calcd for $C_{25}H_{30}N_4O_4$: C, 66.65; H, 5.71; N, 12.44. Found: C, 66.42; H, 6.73; N, 12.29.

19-Norabieta-5,8,11,13-tetraen-7-one (**23**).—To a solution of 1.68 g of methyl 7-oxoabieta-5,8,11,13-tetraen-18-oate (**22**) in 10 ml of diethylene glycol was added 0.60 g of sodium hydroxide and a few drops of water. The reaction mixture was heated at reflux for 18 hr, cooled, diluted with water, and extracted with four portions of hexane. The hexane extracts were washed with water and diluted hydrochloric acid and dried, and the solvent was removed at reduced pressure to give 0.89 g of brown oil. Tlc (silica gel G–benzene) indicated the presence of two compounds, and the mixture was taken up in hexane–benzene (3:1) and chromatographed on alumina. Elution with hexane–benzene (2:1) gave 0.041 g of 19-nor-5β-abieta-8,11,13-trien-7-one (**17**), mp and mmp 100–102°. The more polar hexane–benzene fractions gave 0.173 g of **23** as off-white crystals: mp 65–67°; $\lambda_{C=O}$ 6.03 μ; λ_{max} 256 mμ (log ϵ 4.08), 266 (sh, 4.00), and 304 (3.34); nmr 8.03 (br s, H-14), 6.30 (d, $J = 1.5$ Hz, H-6), 1.48 (s, C-10 methyl), and 1.19 ppm (d, $J = 6$ Hz, C-4 methyl). This compound was too soluble in common solvents to be satisfactorily recrystallized, and was converted into the dinitrophenylhydrazone, mp 222–223° from ethyl acetate, for analysis. A mixture melting point with the derivative, mp 230–231°, of a ketone assigned this structure previously[3d] was 212–220°.

Anal. Calcd for $C_{25}H_{28}N_4O_4$: C, 66.95; H, 6.29; N 12.49. Found: C, 66.68; H, 6.12; N, 12.36.

19-Nor-5β-abieta-8,11,13-trien-7-one (**17**).—Catalytic hydrogenation (5% rhodium on alumina, methanol, 25 psi) of 0.056 g of **23** gave, after filtration and evaporation of solvent, 0.035 g of brown semisolid. The infrared spectrum of this material indicated that it was a mixture of ketone and alcohol, and tlc (silica gel G–benzene) confirmed this observation. The residue was taken np in hexane–benzene (3:1) and chromatographed on Merck acid-washed alumina. Elution with hexane–benzene (1:1) gave 0.009 g of **17** as white crystals, mp 99–101°, mmp 102–104° with the material obtained previously. Elution with benzene–methylene chloride (1:1) gave 0.024 g of a mixture of alcohols, which was not investigated further.

Lead Tetraacetate Oxidation of Methyl Dehydroabietate.—The reaction with lead tetraacetate was carried out as described by DuPont.[24] From 2.00 g of ester there was obtained 0.172 g of methyl 7α-acetoxyabieta-8,11,13-trien-18-oate (**24**): mp 160–161° (lit. mp 167°); $\lambda_{C=O}$ 5.80 μ; nmr 5.89 (q, $W_{1/2} =$ 7 Hz, H-7), 1.27 (s, C-4 methyl), and 1.18 ppm (s, C-10 methyl). Hydrolysis of this ester afforded the 7α-ol, mp 107–108° (lit.[24] mp 111°). The dark brown, gummy residue, 1.94 g, remaining after removing the crystalline α acetate was taken up in 200 ml of methanol to which was added 8.0 g of potassium hydroxide and 10 ml of water. The reaction mixture was heated at reflux for 2 hr, concentrated to a small volume, and diluted with ether, and the ether extracts were washed with water and dried. After removal of the solvent, there was obtained 0.531 g of a dark brown glass which was taken up in benzene and chromatographed on acid-washed alumina. Elution with benzene gave 0.183 g of colorless oil, which appeared to be a mixture of recovered starting material and elimination products. The methylene chloride fractions afforded 0.176 g of a mixture of 7β (**25**) and 7α-ols (**24**), which by integration of the nmr spectrum contained 63% β isomer. A sample of methyl 7β-hydroxyabieta-8,11,13-trien-18-oate (**25**), prepared by borohydride reduction of the 7 ketone, gave nmr signals at 4.82 (t, $J = 8$ Hz, H-7) and 1.28 ppm (s, C-10 methyl and C-4 methyl). The corresponding acetate has a similar spectrum with H-7 shifted to 6.08 ppm.

Registry No.—**1**, 1740-19-8; **2**, 22478-62-2; **5**, 22478-63-3; **6**, 22478-64-4; **7**, 22566-05-8; **13**, 22576-98-3; **14**, 22566-06-9; **14** 2,4-dinitrophenylhydrazone, 22566-07-0; **15**, 22566-08-1; **15** 2,4-dinitrophenylhydrazone, 22593-99-3; **16**, 22566-09-2; **16** 2,4-dinitrophenylhydrazone, 22566-10-5; **17**, 22566-11-6; **17** 2,4-dinitrophenylhydrazone, 22566-12-7; **19**, 19407-17-1; **20**, 19407-18-2; **23**, 22566-15-0; **23** 2,4-dinitrophenylhydrazone, 22566-16-1; **24**, 22565-68-0; **25**, 17901-36-9.

Acknowledgments.—The spectropolarimeter used in this work was obtained through a National Science Foundation Research Instruments Grant. We would like to thank T. F. Sanderson of Hercules, Inc., for a generous gift of dehydroabietonitrile.

The Photochemical Lactolization and Deconjugation of *trans*-Steroidal α,β-Unsaturated Acids

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Received June 30, 1969

The photoisomerization of 2-(*trans*-ylideneacetic acid)-17β-hydroxy-5α-androstan-3-one (**1**) was studied and was shown to give 3ξ,17β-dihydroxy-5′(2′H)-oxo-5α-androstano[3,2-*b*]furan (**2**). Irradiation of the corresponding 17-keto-16-(*trans*-ylideneacetic acid)androst-5(6)-en-3β-ol (**5**) gave only *trans–cis* isomerization of the side chain. A shift of the side-chain double bond in 2-(*trans*-ylideneacetic acid)-3β,17β-dihydroxy-5α-androstane diacetate (**7**) to the C-1(2) position was observed when the irradiation was carried out in acetone. This deconjugated acid **8** was characterized by the facile ketonization of its C-3 hydroxyl function in refluxing alkaline solution. Only *trans–cis* isomerization occurred when 16-(*trans*-ylideneacetic acid)-3β,17β-dihydroxyandrost-5(6)-ene diacetate (**10**) was similarly irradiated. Some aspects of the mechanisms of these transformations are discussed.

In the course of the study of general methods for the synthesis of ring-A fused heterocyclic steroids, we became interested in the chemistry of 2-(*trans*-ylideneacetic acid)-17β-hydroxy-5α-androstan-3-one (**1**).[1] The results of our study of the photochemical behavior of this system are reported here.

Irradiation of **1** using ultraviolet light (3550 Å) for 3–4 hr in methanol gave a product with infrared, ultraviolet, and nmr spectra characteristic of the α,β-unsaturated lactol **2**. This compound was found to be identical with the lactol obtained from the acid-catalyzed cyclodehydration of **3**. The lactol was further characterized by its quantitative conversion into the pyridazone **4** with ethanolic hydrazine.[1]

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[1] M. Debono, R. M. Molloy, and L. Patterson, *J. Org. Chem.*, **34**, 3032 (1969).