TABLE X

GAS–LIQUID CHROMATOGRAPHIC ANALYSIS[a] OF THE OZONOLYSIS METHYL ESTERS DERIVED FROM OCTADECADIENOIC ACIDS

Octadecadienoic acid IX			Retention time, min. Column temperature, 100°			Column temperature, 190°			
Isomer	m	n	Reference methyl ester		Cleavage ester	Reference methyl ester		Cleavage ester	Impurity, %
$\Delta^{8,11}$	5	6	Heptanoate	4.28	4.32	Octanedioate	7.50	7.25	2.9
$\Delta^{9,12}$[b]	4	7	Hexanoate	2.60	2.55	Nonanedioate	9.4	8.5[c]	9.7
$\Delta^{10,13}$	3	8	Pentanoate	1.6	1.6	Decanedioate	13.2	11.8[c]	5.7
$\Delta^{11,14}$	2	9	Butanoate	0.91	0.92	Undecanedioate	17.7	17.4	3.8
						Malonate	1.4		

[a] An "Aerograph" unit with a catherometer detector was used. Samples (2–3 μl.) were injected into a 5-ft. packed helical column containing a polyester stationary phase ("LAC-446"). Helium was used at a constant flow rate (rotameter reading, 85.0 mm.). [b] Methyl ester of Hormel "high purity" linoleic acid. [c] Column temperature: 195°.

due to deterioration on storage, or to partial isomerization of the acids[35] during the 2-hr. period on the column is not known.

Cleavage Analysis of Skipped Unsaturated Acids IX.—The procedure given below for the ozonolysis and analysis of methyl *cis*-10,*cis*-13-octadecadienoate was followed for all the methyl esters.

Ozonized oxygen was passed through a solution of 0.2 g. of the methyl ester of 10,13-octadecadienoic acid (IX, $m = 3$, $n = 8$) in 10 ml. of pure chloroform in a bath at −18°. The gas flow was interrupted when the emergent gases developed a brown color in an aqueous potassium iodide solution, and the reaction mixture was then allowed to stand at room temperature for 0.5 hr.

Solvent was removed at 30° by distillation *in vacuo*, and the residual oil was treated with a slurry of freshly prepared silver oxide (0.9 g.), 10 ml. of water, and 1.6 ml. of 10% aqueous sodium hydroxide in several portions. The mixture was stirred vigorously and heated at 90–95° during and for 1 hr. after the addition.[17] Hydrochloric acid (20%) was added to pH 2. The mixture was extracted several times with ether, and the combined extracts, after one rinsing with water, were dried with magnesium sulfate. Treatment of the solution with diazomethane, as described above for the preparation of the methyl octadecadienoates, esterified all free carboxylic acid groups. When volatile material was removed at steam temperatures under a moderately reduced pressure, 0.2 g. of residue consisting largely of methyl valerate and dimethyl sebacate remained. Yields ranging from 80–95% were obtained at this point. No dimethyl malonate was recovered.

Table X summarizes the results of gas–liquid chromatographic analysis of the mixture. One or more minor peaks revealed the presence of lower, homologous diesters. The diester tracings were used to obtain the percentage impurities listed in Table X. Whether the values obtained in this way in fact reflect the degree of inhomogeneity in the 18-carbon acids, or whether the values are artifacts or the consequence of the degradation of initially homogeneous cleavage products[25] was not determined.

Acknowledgment.—We wish to thank Abbott Laboratories, North Chicago, Ill., for a grant which supported this work in part. We also appreciate the cooperation of Drs. S. R. Lipsky, R. A. Landowne, and R. K. Beerthuis in carrying out gas–liquid chromatographic analyses of our final products, and of Mr. James Pavlin in coaching us on the handling of isobutylaluminum compounds. Hercules Powder Company very kindly provided a generous sample of triisobutylaluminum.

(35) The methyl esters of polyunsaturated acids suffer no significant change during gas–liquid chromatography at 197° with Apiezon M as the stationary phase [W. Stoffel, W. Insul, Jr., and E. H. Ahrens, Jr., *Chem. Abstr.*, **53**, 3973 (1959); *Proc. Soc. Exptl. Biol. Med.*, **99**, 238 (1958)].

Yerba Buena. II. The Identification of Micromerol as Ursolic Acid[1]

GEORGE H. STOUT AND KENNETH L. STEVENS

Chemistry Department, University of Washington, Seattle 5, Washington

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It has been shown that micromerol is mainly ursolic acid, mixed, in some cases, with smaller amounts of oleanolic acid. The three-dimensional crystal structure of methylmicromerol bromoacetate (methyl ursolate bromoacetate) has been determined in the course of this study, providing an independent confirmation of the stereochemistry of the α-amyrin system.

Among the numerous products isolated by Power and Salway[2] from *yerba buena* (*Satureia douglassii*) were two colorless alcohols to which were assigned the formulas $C_{33}H_{52}O_3 \cdot 2H_2O$ and $C_{30}H_{46}O_4 \cdot 2H_2O$ and the names micromerol and micromeritol. Of these, micromerol was present in significantly greater quantities. Although the proposed formulas were not in agreement, the properties described for these compounds suggested strongly that they were triterpene carboxylic acids.

In the course of our isolation of xanthomicrol[1] we obtained by cooling the crude, concentrated ethereal extract of *yerba buena* a copious greenish white precipitate. This showed on thin-layer chromatography (t.l.c.)[3] two major components having the color reactions of triterpenes.[4] The less polar material was present in considerably larger amounts and proved to be a colorless hydroxy acid, whose properties were in agreement with those reported for micromerol. Our sample and its derivatives, however, gave analyses compatible with the formula $C_{30}H_{48}O_3$, *i.e.*, a mono hydroxylated triterpene acid.

Methylation of micromerol with diazomethane gave a methyl ester which showed the same melting points for the hydrated and dried forms as reported by Powers. Since the ester appeared to be rather more easily crystallized and purified than micromerol itself, most of our material was isolated in this form by chromatography

(1) Previous paper, G. H. Stout and V. F. Stout, *Tetrahedron*, **14**, 296 (1961).

(2) F. B. Power and A. H. Salway, *J. Am. Chem. Soc.*, **30**, 251 (1908).

(3) We wish to thank Mr. Erich Gauglitz, U. S. Bureau of Commercial Fisheries, Seattle, for first pointing out to us the striking advantages of this technique.

(4) C. R. Noller, R. A. Smith, G. H. Harris, and J. W. Walker, *J. Am. Chem. Soc.*, **64**, 3047 (1942).

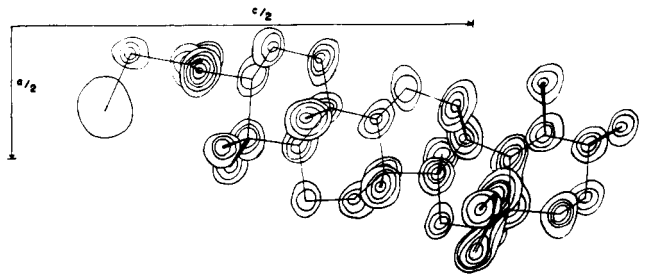


Fig. 1.—Electron density projection on (010) of methylmicromerol bromoacetate. Contours at 1e/Å.^{3} starting at 2e/Å.^{3} except for bromine.

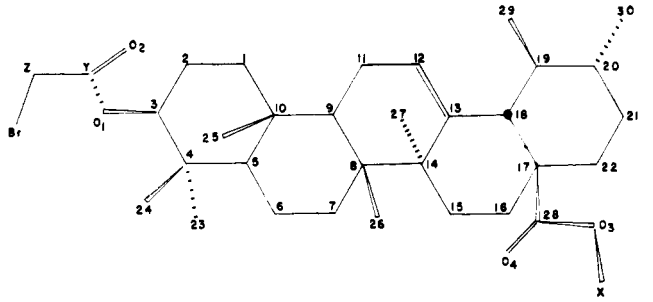
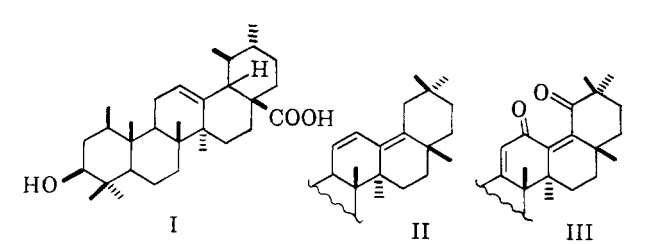


Fig. 2.—Numbering system and observed stereochemistry of methylmicromerol bromoacetate.

following methylation of the whole crude terpene fraction.

Consideration of the literature constants for micromerol[2,5a] had suggested that it was probably identical with ursolic acid[5b,6] (I), and a direct comparison between micromerol and ursolic acid appeared to substantiate this view. Further investigation, however, produced two striking anomalies. Acetylation of methylmicromerol gave a monoacetyl derivative (A) whose melting point of 203–206° was in marked disagreement with that reported for acetyl methyl ursolate[5b] (243–244°). Treatment of this acetate



I II III

with selenium dioxide in refluxing acetic acid gave products whose ultraviolet spectra showed the chromophores II and III. The formation of a diene and a dienedione under these conditions is commonly used as proof that the compound oxidized belongs to the β-amyrin group of the triterpenes.[7] The problem was compounded when it was found that if micromerol was first acetylated and then methylated, a methyl acetate (B) melting 245–250° was obtained. Although the infrared and n.m.r. spectra of the two methyl acetates were nearly superimposable, and although both were homogeneous by t.l.c., all attempts to show them to be dimorphic crystalline forms were fruitless. Mixed samples melted at intermediate temperatures, and seeding solutions of the low-melting form did not produce high-melting material.

In order to clarify the problem of the nature of the ring system involved, and to locate the substituents if we were dealing with a new β-amyrin derivative, methylmicromerol bromoacetate was prepared and subjected to three-dimensional X-ray analysis. This compound crystallizes in the space group $P2_12_12_1$ with four molecules to the unit cell and with dimensions, a = 7.83 Å., b = 14.19 Å., and c = 27.11 Å. The molecular weight found was 581 (calculated 592). Since the fine details of molecular structure were not in question, limited data were collected, consisting of 1113 reflections, of which 839 were observed and 274 unobserved. Almost all the reflections had $(\sin\theta)/\lambda$ less than 0.43 Å.$^{-1}$, so that the resolution was approximately 0.7 Å., ample to show discrete atoms but insufficient to provide good values for bond lengths.

The bromine atom was readily located from an unsharpened three-dimensional Patterson calculation, and starting with phases based on the bromine alone five cycles of Fourier and structure factor calculations revealed all of the atoms in the molecule. The Fourier calculations used for locating atoms included both F_o syntheses and difference syntheses in which each difference $(|F_o| - |F_c|)$ was weighted by the factor $|F_c|/|F_o|$ if $|F_c| < |F_o|$, corresponding approximately to the uncertaintiy in the phase information supplied by each calculated structure factor.[8] The resulting electron difference maps proved extremely useful in locating missing and badly misplaced atoms.

After all of the atoms had been found and the oxygen atoms assigned on chemical grounds and on their appearance on difference maps, refinement by block diagonal[9] and full matrix[10] least squares using an overall temperature factor gave a final residual index[11] value of R = 16.1%. Fig. 1 shows a Fourier synthesis based on the final parameters, and Fig. 2 gives the numbering system of the heavy atoms, for which parameters are given in the Experimental section.

The structure indicated for micromerol by the X-ray analysis is that of an α-amyrin with a C-28 carboxyl group and a 3β hydroxyl, corresponding to the structure of ursolic acid. Although the standard deviation in bond lengths is 0.12 Å., C_{12}–C_{13} is shorter than the remainder of the ring system bonds by an amount which is probably significant[12] and corresponds to the expected location of the double bond. Thus the original view that micromerol is ursolic acid is substantiated.

It should be noted that this determination represents the first published X-ray study of an α-amyrin and as such is an independent conformation of the structure proposed previously on the basis of degradation[13]

(5) (a) J. Simonsen and W. C. J. Ross, "The Terpenes," Vol. 4, Cambridge University Press, 1957, p. 437; (b) *ibid.*, Vol. 5, p. 116ff.

(6) The existence of the solvated form, m.p. 115°, of methyl ursolate produced by crystallization from 95% ethanol is often ignored, but has been reported by F. B. Power and C. W. Moore, *J. Chem. Soc.*, **97**, 1099 (1910).

(7) C. Djerassi, C. H. Robinson, and D. B. Thomas, *J. Am. Chem. Soc.*, **78**, 5685 (1956).

(8) F_o and F_1 are the observed and calculated structure factors, respectively.

(9) A modified version of UCLALS1, by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, University of California at Los Angeles, 1961.

(10) W. R. Busing and H. A. Levy, "A Crystallographic Least Squares Refinement Program for the IBM 704," Oak Ridge National Laboratories, 1959.

(11) $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$.

(12) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

(13) E. J. Corey and J. J. Ursprung, *Chem. Ind.* (London), 1387 (1954), *J. Am. Chem. Soc.*, **78**, 183 (1956); A. Melera, D. Arigoni, A. Eschenmoser, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **39**, 441 (1956).

and partial synthesis.[14] Although the ring system appears to be somewhat bowed, presumably from repulsion between the axial methyl groups, the stereochemistry found is in complete agreement with that shown in I.

In view of this conclusive evidence that micromerol is an α-amyrin, the selenium dioxide oxidation was studied further. It was found that when the low-melting methyl micromerol acetate was partially oxidized, the recovered material was high-melting and gave no melting point depression with authentic methyl acetylursolate. Furthermore, the dienedione produced was found to be identical with the dienedione from oleanolic acid. If crystallized micromerol was used as the starting material, the same, high-melting, methyl acetate was formed regardless of the order of methylation and acetylation.

Consequently, it may now be said that although micromerol is identical with ursolic acid, it may occur together with smaller amounts of a β-amyrin[15] which may be very difficult to remove and which may affect its properties to a striking degree. Pure methyl-micromerol or methyl ursolate is very difficult to crystallize, but the impure form crystallizes readily. Apparently the β-amyrin component is concentrated during the isolation of the methyl esters from the crude methylated mixture and further during the purification of the acetylmethyl compound (A), as the melting point depression found corresponds to that produced by not less than 50% added oleanolic acid. T.l.c. is powerless to resolve the problem, as corresponding derivatives of the α- and β-amyrin series are not separated on the plates.

All of the material used for the studies described above was obtained from *yerba buena* gathered from one vacant lot near Seattle and probably representing a botanically homogeneous sample. A more recent collection made at a similar season but covering a considerably wider area around Deception Pass, Washington, has yielded only ursolic acid and not more than a trace of oleanolic acid; so the proportions of these two triterpenes are apparently rather variable within the species.

Experimental[16]

Isolation of Micromerol.—Crude triterpene material was obtained by chilling the concentrated ethereal extract of defatted *yerba buena*.[1] The crude material (9.15 g., representing about 1850 g. of dry plant) was digested with a large amount of ethanol and filtered hot. On cooling, the filtrate deposited a fine precipitate which was recrystallized twice more from ethanol (charcoal) to give 1.49 g. of micromerol, m.p. 281–286° (cap., cor.) lit.,[2] 277°, $[\alpha]^{24}D$ +40.5° (*c*, 0.347; abs. ethanol). A mixture melting point with authentic ursolic acid, m.p. 280–287° (cap., cor.), from bearberry (*Arctostaphylos uva-ursi*)[17] gave m.p. 281–285°, (cap., cor.).

Anal. Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.59. Found: C, 78.95; H, 10.61.

Methylmicromerol (Impure).—Crude terpene mixture (2.0 g.) was dissolved in ethanol (100 ml.) and treated at ice-bath temperature with an excess of diazomethane in ether. After 20 min. formic acid and water were added, and the solution was extracted with ether. The ethereal extract was washed with water, 5% sodium hydroxide, and water, dried, and evaporated to give a partially crystalline, greenish-white solid. This was chromatographed on Merck acid-washed alumina (80 g.), and crystalline methylmicromerol (1.26 g.) was obtained from the fractions eluted with benzene. Recrystallization from ethanol gave material, m.p. 110–115°, which after being dried in vacuum at 85° had m.p. 166–168°, lit.,[2] m.p. 167°. T.l.c. showed only one spot. $[\alpha]^{22}D$ +67° (*c*, 0.400; $CHCl_3$).

Anal. Calcd. for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71; $-OCH_3$, 6.58. Found: C, 78.95; H, 10.55; $-OCH_3$, 7.37.

Acetylmethylmicromerol. (A-Impure).—Methylmicromerol (0.843 g.) prepared as above was treated with acetic anhydride (5 ml.) and pyridine (5 ml.) at room temperature for 18 hr. Water and ether were added, and the ethereal solution was washed with dil. hydrochloric acid, 10% sodium hydroxide, and water. Evaporation of the ether gave a white solid which was crystallized from methanol to give the low-melting form of acetylmethyl-micromerol (0.536 g.), m.p. 203–206°, unchanged by recrystallization. $[\alpha]^{24}D$ +74.3° (*c*, 0.635; $CHCl_3$).

Anal. Calcd. for $C_{33}H_{52}O_4$: C, 77.30; H, 10.22; $-OCH_3$, 5.66. Found: C, 76.97; H, 10.63; $-OCH_3$, 6.46.

Acetylmicromerol.—Crystallized micromerol (0.500 g.) was treated for 48 hr. at room temperature with pyridine (5 ml.) and acetic anhydride (5 ml.) The reaction was worked up as usual to give a white solid which crystallized from ethanol to give a monoacetate (0.379 g.), m.p. 290–293°, (cap., cor.).

Anal. Calcd. for $C_{32}H_{50}O_4$: C, 77.06; H, 10.11. Found: C, 76.85; H, 9.92.

Power and Salway[2] report an unstable acetate m.p. 188°. This is undoubtedly the mixed anhydride of acetylmicromerol and acetic acid.

Methylacetylmicromerol (B-Pure).—Acetylmicromerol (0.100 g.), was methylated in ethanol solution with an excess of diazomethane. Work-up in the usual manner and crystallization from ethanol gave product m.p. 245–250°. The melting point was not depressed by authentic acetylmethylursolate.

Anal. Calcd. for $C_{33}H_{52}O_4$: C, 77.30; H, 10.22. Found: C, 77.49; H, 10.19.

Selenium Dioxide Oxidation of Acetylmethylmicromerol.—Low melting acetylmethylmicromerol (A) (0.225 g.) in acetic acid (12.75 ml.) was refluxed with freshly sublimed selenium dioxide (0.128 g.), for 24 hr. The precipitated selenium was filtered off and the mixture of products was chromatographed on Davidson silica gel using 4:1 petroleum ether–ether containing 1% acetic acid as the eluent. The first crystalline fractions, m.p. 230–250°, were a mixture of two compounds partially separable by fractional crystallization. Two crystallizations from ethanol gave high-melting acetylmethylmicromerol (0.036 mg.) m.p. 245–250°, undepressed by admixture with form B above. The mother liquors showed an ultraviolet spectrum with λ_{max}^{EtOH} 243, 252, 260 mμ, corresponding to the $\Delta^{11,13(18)}$-diene of oleanolic acid, but a pure sample was not obtained.

Continued elution of the column gave another crystalline compound (0.016 g.), m.p. 244–246°, $[\alpha]^{25}D$ −152° (*c*, 0.36; $CHCl_3$), whose ultraviolet spectrum, λ_{max}^{EtOH} 278 (ϵ 14,600), was that of a $\Delta^{9(11),13(18)}$-diene-12,19-dione. A mixture melting point with the dienedione prepared by selenium dioxide oxidation

TABLE I

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Br	0.3197	0.6960	0.1034	C15	0.7636	0.5841	0.4899
O1	.1771	.6684	.2090	C16	.7899	.5950	.5497
O2	.1539	.8267	.2103	C17	.6970	.5111	.5684
O3	.6580	.3408	.5502	C18	.5092	.5097	.5637
O4	.8736	.4027	.5350	C19	.4171	.6016	.5933
C1	.1482	.5740	.3418	C20	.4552	.5761	.6499
C2	.0906	.5918	.2815	C21	.6704	.5771	.6559
C3	.1995	.6599	.2654	C22	.7327	.4908	.6265
C4	.4336	.6402	.2627	C23	.5233	.7214	.2461
C5	.4565	.6167	.3218	C24	.4661	.5486	.2343
C6	.6602	.5986	.3327	C25	.3566	.4389	.3299
C7	.6780	.6148	.3894	C26	.6212	.4463	.4171
C8	.5685	.5465	.4190	C27	.4985	.6963	.4806
C9	.3683	.5689	.4052	C28	.7245	.4139	.5540
C10	.3189	.5442	.3444	C29	.2141	.5934	.5900
C11	.2317	.4990	.4342	C30	.3947	.6607	.6826
C12	.3044	.4853	.4918	Cx	.7153	.2516	.5328
C13	.4325	.5275	.5020	Cy	.1535	.7480	.1944
C14	.5788	.5992	.4759	Cz	.1162	.7505	.1338

(14) E. J. Corey and E. W. Cantrall, *J. Am. Chem. Soc.*, **81**, 1745 (1959).

(15) This compound very probably is oleanolic acid, but since two asymmetric centers are lost in the formation of the oleanolic acid dienedione, it is conceivably a skeletal stereoisomer.

(16) Unless otherwise specified, melting points were taken on a Kofler hot stage and are uncorrected.

(17) C. E. Sando, *J. Biol. Chem.*, **90**, 477 (1931).

of methyl acetyloleanolate showed no depression, and the infrared spectra were identical.

Anal. Calcd. for $C_{33}H_{46}O_6$: C, 73.57; H, 8.61. Found: C, 73.79; H, 8.63.

Methylmicromerol Bromoacetate.—Methylmicromerol (0.048 g.) in benzene (2.8 ml.) was treated with bromoacetyl bromide (0.1 ml.) and diethylaniline (0.2 ml.) at room temperature for 20 hr. Water and ether were added, and the ethereal solution was washed with water, dilute hydrochloric acid, and water. Evaporation of the ether left a reddish-brown oil which was chromatographed on Davidson silica gel to give a colorless oil which crystallized from pentane. Repeated crystallizations from pentane gave crystals suitable for X-ray studies, m.p. 146–150°.

Anal. Calcd. for $C_{33}H_{51}O_4Br$: C, 66.98; H, 8.68; Br, 13.50. Found: C, 67.10; H, 8.63; Br, 13.30.

X-Ray data were collected photometrically from Weissenberg photographs taken on a Nonius camera which was set to integrate in two directions.[18] Levels $h = 0$ to $h = 5$ were taken on a crystal rotating about the a axis. The final parameters relative to the conventional origin[19] are given in Table I. The final over-all temperature factor was B = 3.29 Å.^{2}

Acknowledgment.—This work was supported in part by the National Institutes of Health, grant CY-4082.

(18) E. H. Wiebenga and D. W. Smits, *Acta Cryst.*, **3**, 265 (1950).

(19) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p. 105.

Organic Sulfur Compounds. IX.[1] Addition of Diethyldithiophosphoric Acid to Dienes

A. A. OSWALD,[2] K. GRIESBAUM,[2] AND B. E. HUDSON, JR.[3]

Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey

Received October 26, 1962

O,O′-Diethyldithiophosphoric acid (phosphorodithioic acid O,O′-diethyl ester) was added by a radical mechanism to a variety of diolefins to study the factors determining the formation of the various isomeric monoadducts. Selective monoadditions of diethyldithiophosphoric acid to the unsubstituted olefinic bond in the bicycloheptene part of polycyclic diolefins (*endo*-dicyclopentadiene, Aldrin, 2,5-norbornadiene) could be readily carried out, probably in a *cis–exo* manner. On radical addition of diethyldithiophosphoric acid to 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, and 2,5-dimethyl-2,4-hexadiene, the thiophosphoryl-thiyl radical preferentially attacked the first carbon atom of the basic 1,3-butadiene skeleton in the first propagation step so as to give the more stable intermediate allylic radical. The latter in turn abstracted a hydrogen from the dithiophosphoric acid at the less highly substituted allylic carbon atom to yield the corresponding 1,4- and 1,2-monoadducts. Addition to piperylene, which proceeds *via* a radical intermediate having two secondary allylic carbon atoms, resulted in almost equal quantities of 1,2- and 1,4-adducts.

I. Introduction

The addition of crude O,O′-dialkyldithiophosphoric acids (phosphorodithioic acid O,O′-dialkyl esters) to olefins is a much explored reaction[4] since many of the adducts are important oil additives[4–7] and insecticides.[7–11] Additions of crude dialkyldithiophosphoric acids, which are synthesized from alcohols and phosphorus pentasulfide,[12,13] to unsymmetrical olefins yield the normal addition products according to Markownikoff's rule.[4] This is probably the result of the presence of P_4S_3 in the crude acid. P_4S_3 could reduce the peroxide type catalysts of radical addition.[13]

Bacon and LeSuer[13] added purified O,O′-diethyldithiophosphoric acid (phosphorodithioic acid O,O′-diethyl ester, O,O′-diethylphosphorodithioate) to the monoölefins in an anti-Markownikoff manner. Radical type additions of dialkyldithiophosphoric acids to diolefins, however, remained unexamined. We became interested in the latter reaction in connection with our studies of thiol–diolefin addition reactions.[14–16] At first the reactivity, towards the addition of diethyldithiophosphoric acid, of different types of double bonds in various diolefins containing isolated double bonds was determined and compared to the corresponding thiol additions.[14] Then a study of dialkyldithiophosphoric acid-conjugated diene additions was undertaken to determine whether the "1,2-" or "1,4-mechanism" of these reactions is affected by the same factors as it was in the case of thiol–diene systems.[15,16]

Diethyldithiophosphoric acid was chosen as a reagent because it is readily available and easy to purify.[13] Some polycyclic diolefins—*endo*-dicyclopentadiene, Aldrin, and 2,5-norbornadiene—were selected for the study as diolefins containing isolated double bonds. Simple diolefins—1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, piperylene, and 2,5-dimethyl-2,4-hexadiene—were used as conjugated diolefins.

II. Results

It was found that purified diethyldithiophosphoric acid and other dialkyldithiophosphoric acids readily add at room temperature to most of the diolefins examined (Table I). The addition can be catalyzed by

(1) Presented at the 143rd National Meeting of the American Chemical Society, Los Angeles Calif., April, 1963.

(2) Esso Research and Engineering Co., Central Basic Research Laboratory, P. O. Box 45, Linden, N. J.

(3) Esso Research and Engineering Co., Analytical Research Division, Bayway Refinery, P. O. Box 121, Linden, N. J.

(4) G. R. Norman, W. M. LeSuer, and T. W. Mastin, *J. Am. Chem. Soc.*, **74**, 161 (1952); U. S. Patent 2,802,856 (1957).

(5) F. B. Augustine, U. S. Patent 2,561,773 (1951); 2,665,295 (1954); 2,528,732 (1950).

(6) C. W. Georgi, "Motor Oils and Engine Lubrication," Reinhold Publishing Corp., New York, N. Y., 1950, p. 167.

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(9) G. Matolcsy and A. Oswald, *Magy. Kém. Folyoirat*, **60**, 348 (1954); *Novénytermelés*, **4**, 351 (1955).

(10) J. T. Cassaday, U. S. Patent 2,578,652 (1951).

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