the viscosity of the solutions decreased rapidly with time to a limiting value.

A 50% aqueous solution of lithium chloride was found to be an unreactive solvent for the polymer III. Solutions of the polymer were studied in Fenske viscometers. A plot of the reduced viscosity (η_{sp}/c) against the specific viscosity (η_{sp}) was linear and had negligible slope. Extrapolation to zero specific viscosity gave an intrinsic viscosity, [η], of 0.13 deciliter/g. Solutions of the polymer were also subjected to a light scattering molecular weight determination following the techniques and instrumentation employed by Heilweil and Van Winkle.[16] Calculations were made as outlined by Flory.[17] In this manner the minimum molecular weight for polymer III was found to be 8,500 or about 36 repeating units.

2. **Piperazine.**—Piperazine (300 mmol.), dissolved in 400 ml. of benzene, was added slowly under anhydrous conditions to a stirred suspension of 43.3 g. (105 mmol.) of I in 300 ml. of benzene at 0°. The stirring was continued while the mixture warmed to room temperature. Centrifugation afforded a white solid which was washed with benzene and ethanol. A portion of this polymer was acetylated to yield product IV, as described for the ethylenediamine polymer; yield 81% (basis I).

Anal. Calcd. for $[C_{10}H_{12}N_2O_6(CH_3CO)_4]_n$: C, 50.46; H, 5.61; N, 6.54; CH_3CO, 40.1. Found: C, 50.10; H, 5.67; N, 6.55; CH_3CO, 39.2.

No solvent was available that did not degrade the polymer and no melting point was found; decomposition began on heating above 250°.

Another portion of the polymer, before acetylation, was treated with sodium in methanol as described above. The deacetylated polymer V was again obtained in poor yield.

Anal. Calcd. for $[C_{10}H_{16}N_2O_6]_n$: C, 46.15; H, 6.15; N, 10.77. Found: C, 46.35; H, 6.19; N, 10.81.

The infrared spectra,[2] thermal behavior and solubility properties of V were similar in all respects to the ethylenediamine analog III. From viscosity studies in 50% aqueous lithium chloride an intrinsic viscosity, [η], of 0.11 deciliter/g. was derived.

Attempted Nitration of Polymers.—A variety of nitration techniques[13] were applied to various preparations of the deacetylated polymers. In no case was a satisfactory yield obtained; the products appeared to be mainly water-soluble or were decomposed by water.

Synthesis of Model Compounds. 1. **1,1′-(Tetra-*O*-acetylgalactaroyl)-dipiperidine (VI).**—Piperidine (16.2 ml., 164 mmol.) was added slowly to a stirred suspension of 16.3 g. (39 mmol.) of tetra-*O*-acetylgalactaroyl dichloride (I) in 550 ml. of benzene at 0°. The heterogeneous mixture was stirred at room temperature for 24 hr. The solid recovered by filtration was washed with benzene, ethanol and water. The dried crude product was crystallized from hot chloroform–ethanol; yield 15.4 g. (76%), m.p. 255–256°.

Anal. Calcd. for $C_{24}H_{36}N_2O_{10}$: C, 56.25; H, 7.03; N, 5.47. Found. C, 56.26; H, 7.20; N, 5.37.

2. **1,1′-(Galactaroyl)-dipiperidine (VII).**—Deacetylation of VI by stirring 12.9 g. overnight at room temperature with 200 ml. of 0.6 *N* sodium methoxide in methanol afforded a yellow solid that was recovered by filtration. After washing the solid with methanol, a suspension in methanol was neutralized by the addition of 2 *N* hydrochloric acid. The insoluble material was recovered by filtration and washed with water. Pure 1,1′-(galactaroyl)-dipiperidine was obtained on crystallization from hot N,N-dimethylformamide; yield 2.5 g. (29%), m.p. 238–239° dec.

Anal. Calcd. for $C_{16}H_{28}N_2O_6$: C, 55.81; H, 8.14; N, 8.14. Found: C, 55.66; H, 8.39; N, 8.34.

3. **Tetra-*O*-acetylgalactaric Bis-(phenylhydrazide) (VIII).**—Phenylhydrazine (38.0 ml., 386 mmol. was added slowly to a stirred suspension of 29.0 g. (70 mmol.) of tetra-*O*-galactaroyl dichloride (1) in 550 ml. of benzene at 0°. The mixture was stirred overnight at room temperature and the solid was filtered, washed with benzene, ethanol, dilute aqueous alkali and water. The crude product was extracted with boiling acetone. The insoluble tetra-*O*-acetylgalactaroyl bis-(phenylhydrazide) (VIII) was crystallized twice from N,N-dimethylformamide solution by adding ethanol and cooling; yield 16.6 g. (42%), m.p. 257–258°.

Anal. Calcd. for $C_{26}H_{30}N_4O_{10}$: C, 55.91; H, 5.37; N, 10.03. Found: C, 55.99; H, 5.55; N, 9.88.

4. **Galactaric Bis-(phenylhydrazide) (IX).**—Deacetylation of VIII, 7.1 g., was accomplished by stirring with 140 ml. of 0.6 *N* sodium methoxide in methanol for 24 hr. at room temperature. The heterogeneous reaction mixture was filtered. The solid, suspended in methanol, was treated with 2 *N* hydrochloric acid until neutral, filtered, washed with methanol and water, and twice recrystallized from hot N,N-dimethylformamide–acetone to give pure crystalline galactaric bis-(phenylhydrazide); yield 2.9 g. (73%), m.p. 242–244°.

Anal. Calcd. for $C_{18}H_{22}N_4O_6$: C, 55.38; H, 5.64; N, 14.36. Found: C, 54.90; H, 5.64; N, 13.79.

5. **Bis-(2-hydroxyethyl) Tetra-*O*-acetylgalactarate.**—During the course of an unsuccessful attempt to prepare a polyester by the condensation of tetra-*O*-acetylgalactaroyl dichloride with ethylene glycol a small amount of crystalline material was isolated. Thus, I, 11.9 g., was dissolved in 60 ml. of ethylene glycol with heating. The solution was concentrated at 2 mm. pressure and 145–155°. Methanol was added to the resulting sirup and the white solid which formed was separated and washed with methanol and water. Crystallization from acetone afforded bis-(2-hydroxyethyl) tetra-*O*-acetylgalactarate; yield 80 mg., m.p. 209°.

Anal. Calcd. for $C_{18}H_{26}O_{14}$: C 46.42; H, 5.57; mol. wt., 468. Found: C, 46.47; H, 5.23; mol. wt., 457 (Rast).

Acknowledgment.—We appreciate the coöperation of Dr. Quentin Van Winkle in carrying out the light scattering molecular weight studies.

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[16] I. J. Heilweil and Q. Van Winkle, *J. Phys. Chem.*, **59**, 944 (1955).

[17] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 291–303.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Sabinene Hydrate: a Constituent of American Peppermint Oil[1]

BY JOHN W. DALY, F. CHARLOTTE GREEN AND RICHARD H. EASTMAN

RECEIVED JUNE 23, 1958

The methyl Grignard reaction with sabina ketone forms two isomeric sabinene hydrates, one of which is identical with an alcohol isolated from American peppermint oil. This isomer is assigned the *trans* (methyl/isopropyl) configuration on the basis of the yields of the isomers in the Grignard reaction, on the Von Auwer–Skita rule, and on differences in the chemical properties of the two isomers.

A new terpene alcohol, which melted at 62°, was isolated from American peppermint oil by fractional distillation. The compound was very unstable under acid conditions, which suggested that it was a tertiary alcohol. A Zerewitinoff determination[2] showed one active hydrogen per molec-

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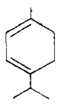
[1] From the Doctoral Dissertations of J. W. Daly and F. C. Green, in the Department of Chemistry at Stanford University, reported in part at the 133rd A.C.S. Meeting, San Francisco, Calif., April 16, 1958.

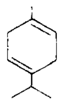
[2] T. Zerewitinoff, *Ber.*, **40**, 2027 (1907).

ular weight of 154 ($C_{10}H_{18}O$). The compound did not react immediately with bromine in carbon tetrachloride or with a dilute solution of potassium permanganate. These properties, in conjunction with the empirical formula, indicated that the alcohol was bicyclic. Elucidation of the structure of the alcohol attended identification of the products formed by various methods of dehydration. The methods chosen were those in which a minimal rearrangement or isomerization of the products would be expected.

The dehydration of alcohols with alumina has been reported to result in little isomerization.[3,4] On dehydration of the alcohol from peppermint oil at 150° over alumina, however, α-terpinene (I), γ-terpinene (II) and *p*-cymene (III) were formed. At 200° these compounds and, in addition, 2,4(8)-*p*-menthadiene (IV) were isolated. Traces of other menthadienes also were present in the product from this reaction. It was apparent that not only was dehydration taking place, but that one of the rings present in the alcohol had opened. In addition, the diene formed underwent isomerization and dehydrogenation.

Since the Tschugaeff reaction[5,6] usually proceeds without rearrangement, the formation of the methyl xanthate of the new terpene alcohol from peppermint oil was attempted. The alcohol proved unusually unreactive in the Tschugaeff reaction. Even when the alcohol was boiled in toluene containing sodium for hours, 75% of the alcohol was recovered after the decomposition of the methyl xanthate. The other products of the Tschugaeff reaction were identified as sabinene (VI) and α-thujene (V).


I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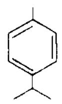
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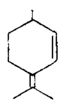
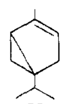
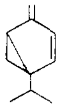
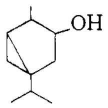

IV


V

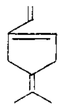
In the course of preparing an authentic sample of α-thujene from thujyl alcohol (VII), two interesting observations were made. One was the extreme stability of the tosylate of thujyl alcohol under conditions which usually cause an E_2 elimination in *p*-toluenesulfonates.[7] Elimination finally occurred after prolonged heating in 2,6-lutidine. The products isolated were α-terpinene and γ-terpinene, which probably were formed by isomerization of α-thujene, the initial product of the reaction.[8]

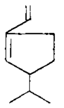
The other anomalous reaction attended the pyrolysis of thujyl acetate. In addition to α-terpinene and *p*-cymene, a mixture of hydrocarbons constituted 35% of the product. It appeared to be made up of three similar compounds in which a double bond of the type $RHC{=}CH_2$ was present as shown by strong peaks in the infrared absorption spectrum at 10.1 and 11.0 μ due to the $RHC{=}CH_2$ structure.[9,10] The ultraviolet absorption spectrum of the mixture had a maximum at 232 mμ which suggests that the major component was a conjugated diene.[11] The low retention time of these compounds on a Carbowax-coated vapor phase chromatography column seemed to preclude the possibility that they were open chain compounds such as myrcene (VIII). It seemed more likely that the compounds were cyclopentene derivatives such as IXa and IXb.


VI

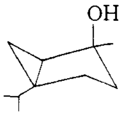

VII

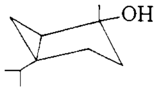

VIII


IXa


IXb

Isolation and identification of sabinene and α-thujene from the terpene alcohol indicated the structure of sabinene hydrate (Xa or Xb) for the new terpene alcohol from peppermint oil. Wallach[12] had reported the isolation of a sabinene hydrate from the reaction of methylmagnesium iodide with sabina ketone (XI), but the properties of his compound were not those of the presumed sabinene hydrate from peppermint oil. Since both isomers Xa and Xb should result, even if not in equivalent amounts from a Grignard reaction with sabina ketone, Wallach's preparation was repeated using methylmagnesium bromide.


Xa (*cis*)


Xb (*trans*)

Sabina ketone, obtained from the permanganate–periodate oxidation[13] of *d*-sabinene, was treated with methylmagnesium bromide. The reaction mixture was decomposed with water and distilled with steam. The products were separated using a Carbowax-coated vapor phase chromatography column. Both isomeric sabinene hydrates thus were obtained. The isomer formed in only 2-5% yield was identical in physical properties to the alcohol isolated from peppermint oil. The other isomer, which melted at 36-37.5°, was probably that sabinene hydrate which had been characterized by Wallach. In one Grignard reaction the product contained 25% of 1-terpinen-4-ol (XII), a compound that Wallach had reported to be formed from sabinene hydrate on treatment with a dilute solution of acid.[14] In the above-mentioned Grignard reaction, the formation of 1-terpinen-4-ol must have been caused by the introduction of traces of acid during the reaction.

Cram's rule[15] predicts that the alkyl group in a

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[3] S. Goldwasser and H. S. Taylor, THIS JOURNAL, **61**, 1751 (1939).

[4] W. G. Appleby, C. J. Dobratz and S. W. Kapranos, *ibid.*, **66**, 1938 (1944).

[5] L. Tschugaeff, *Ber.*, **32**, 3332 (1899).

[6] P. G. Stevens and J. H. Richmond, THIS JOURNAL, **63**, 3132 (1941).

[7] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[8] J. L. Simonsen, "The Terpenes," Vol. II, 2nd ed., Cambridge University Press, 1949, pp. 13–14.

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[10] R. T. O'Conner and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

[11] L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 88 ff.

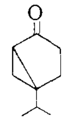
[12] O. Wallach, *Ann.*, **357**, 65 (1907).

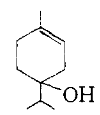
[13] R. V. Lemieux and E. von Rudloff, *Canad. J. Chem.*, **33**, 1701 (1955).

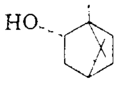
[14] O. Wallach, *Ann.*, **360**, 82 (1908).

[15] D. J. Cram and F. A. Abd Elhafez, THIS JOURNAL, **74**, 5828 (1952).

Grignard reaction will enter preferentially from the least hindered side of the carbonyl function. In the reaction considered, the methyl group should enter equatorially to form *cis*-sabinene hydrate (Xa) as the preponderant product. This assignment would make the naturally-occurring sabinene hydrate the *trans* isomer Xb and the compound reported by Wallach, *cis*-sabinene hydrate.


XI


XII


XIIIa


XIIIb

The von Auwers–Skita rule[16] states that a *cis* isomer has a higher boiling point, refractive index, and often a lower melting point than the *trans* isomer. The assignment of configuration, as derived above on the basis of Cram's generalization, conforms with this rule since the constants for the *cis* isomer are b.p. 195-200°,[12] n^{60}D 1.4489, and m.p. 36.5-37.2°, while the constants for the *trans* isomer are b.p. 193-198°, n^{60}D 1.4430, and m.p. 61-62°.

The retention times of *cis*- and *trans*-sabinene hydrates on a Carbowax-coated vapor phase chromatography column were, respectively, 60 and 39 minutes. Using a silicon-coated vapor phase chromatography column on which the boiling point of a compound appears to be the primary determinant of retention time, the times were 64 minutes for the *cis* isomer and 58 minutes for the *trans* isomer. The large difference between the retention times of the two isomers on the Carbowax column may be due to the differing degrees to which the compounds interact with the immobile phase of the column by means of hydrogen bonds. However, the hydroxyl group of the *cis* isomer, which is in the more hindered axial position, should interact to a lesser extent with the Carbowax than the equatorial hydroxyl of *trans*-sabinene hydrate. According to this interpretation, the relative retention times should be opposite to those observed.

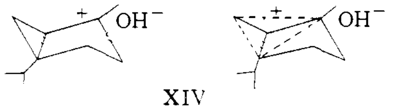
In order to study the importance of steric effects on retention times, borneol (XIIIa) and isoborneol (XIIIb) were chromatogrammed on a Carbowax column. The retention times were 101 minutes for borneol and 90 minutes for isoborneol. Since on the basis of molecular models, steric considerations would appear to be of greater importance in these compounds than in the case of the sabinene hydrates, it seems likely that the great difference in retention times between the sabinene hydrates is due to effects other than steric.

Bellamy[9] states that in the case of intermolecular hydrogen bonds, the absorption maximum will shift to shorter wave lengths on dilution with a non-polar solvent. The maximum for the associated OH stretching frequency shifted toward shorter wave lengths in both cases when the solvent was carbon tetrachloride, but only for *trans*-sabinene hydrate when the dilution was carried out in *n*-hexane, which suggests that the intermolecular hydrogen bonds formed by *cis*-sabinene hydrate are of greater strength than those formed by the *trans* isomer, a situation not at variance with the retention times of the two isomers.

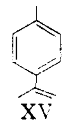
The infrared studies were extended to include the interaction between the sabinene hydrates and a material (1,2-dimethoxyethane) capable of forming hydrogen bonds,[17] but the results failed to provide additional evidence for stronger hydrogen bonding in the case of the *cis* isomer.

Dehydration of *cis*-sabinene hydrate over alumina at 150° led to the same products that were formed from *trans*-sabinene hydrate. In a Tschugaeff, the reaction with sodium occurred much more readily with *cis*-sabinene hydrate. The same end products, sabinene and α-thujene, were, however, obtained on pyrolysis of the methyl xanthate.

Although on purely steric grounds, the isomer with the equatorial hydroxyl (*trans*-sabinene hydrate) would be expected to react more readily with sodium, it apparently does not. The failure of the reactivity to accord with the stereochemistry may be due to the differing strengths of the two alcohols as proton donors. Contributions to the structure of sabinene hydrate, such as XIV, which are most likely in the *trans* isomer, would be expected to lessen its strength as a proton donor. The stability of non-classical carbonium ions of the type XIV has been proposed by Roberts[18] in his investigations on the solvolysis of cyclopropylcarbinyl derivatives. The participation of the cyclopropane ring in forming a stable carbonium ion of this type would also explain the greater sensitivity of *trans*-sabinene hydrate to acidic dehydrating conditions, since in the case of the *cis* compound the cyclopropane ring cannot readily assist in the loss of water and concomitant formation of a carbonium ion.



XIV


XV

The acetylation of *trans*-sabinene hydrate with a mixture of acetic anhydride and potassium acetate led to the isolation of only a small amount (12%) of an ester, which was contaminated with *p*-cymene. Attempted saponification of this ester was unsuccessful, suggesting that the hydroxyl group was tertiary. The main products from the attempted acetylation of *trans*-sabinene hydrate were α-terpinene, γ-terpinene, and a small amount of α-thujene.

Acetylation of *cis*-sabinene hydrate under the same conditions led to the isolation of a saturated ester in 45% yield. This ester proved resistant to saponification and only hydrocarbons were formed on prolonged refluxing in a solution of 20% sodium hydroxide. The other products from the acetylation of the *cis* isomer were, as in the case of the *trans* compound, α-thujene, α-terpinene, γ-terpinene and *p*-cymene. The results of the two acetylation reactions suggest a greater stability for the *cis*-acetate, which agrees with the supposi-

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(16) H. D. Orloff, *Chem. Revs.*, **54**, 358 (1954).

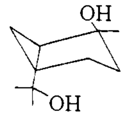
(17) N. B. Coggeshall and E. L. Saier, THIS JOURNAL, **73**, 5414 (1951).

(18) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951).

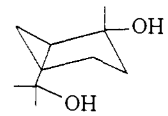
tion that E_1 elimination should occur readily in the *trans*-acetate since the cyclopropane ring can assist in the formation of the carbonium ion XIV.

The acetylation also was carried out with both isomers at 80° using acetic anhydride and pyridine. *cis*-Sabinene hydrate gave the same results, essentially as had been observed with acetic anhydride and potassium acetate. *trans*-Sabinene hydrate, however, formed another acetate, in addition to the products isolated from the acetylation carried out with potassium acetate as the catalyst. This acetate may be that of *trans*-sabinene hydrate since it reacted only slowly with a dilute solution of potassium permanganate.

The rates of the acetylation of the isomers in pyridine were studied. The rate of disappearance of alcohol was measured and found to be the same for both isomers within experimental error, which suggests that steric factors may be of only moderate importance in influencing the properties of the two isomers.



XVIa



XVIb

Both *cis*- and *trans*-sabinene hydrate, on oxidation with potassium permanganate, afforded crystalline diols (XVIa and XVIb). Dehydration of the diol from *trans*-sabinene hydrate over alumina formed *p*-cymene and 1-*p*-tolyl-1-methylethylene (XV), thus indicating the position of the second hydroxyl group. The interesting course of the permanganate oxidation in converting a tertiary hydrogen to hydroxyl has been under investigation in this Laboratory for some time and will be the subject of a future communication.

Acknowledgments.—We wish to express appreciation to Hercules Powder Co. for their support of this work and to the American Chicle Co. for a generous gift of peppermint oil.

Experimental

Isolation of *trans*-Sabinene Hydrate from American Peppermint Oil.—A sample of 1800 ml. of American peppermint oil was fractionated in a 100 × 2.5 centimeter Stedman fractionating column.[19] Intermediate to the cineol-limonene (b.p. 62–4°, 15 mm.) and the menthone (b.p. 89–91°, 15 mm.) flats, fractions were obtained which crystallized on cooling. These fractions were centrifuged at 0° in Skau tubes containing filter paper on top of the perforated plate. The crystals,[20] collected on the filter paper, were sublimed at reduced pressure to yield 7 g. of white crystals of m.p. 60–61°, b.p. 193–198° (cor.), $n^{60}\mathrm{D}$ 1.4430, and $[\alpha]^{25}\mathrm{D}$ +32.2° (c, 4.2% in ethanol). A Zerewitinoff determination showed 1.01 active hydrogens per molecular weight of 154; spectrum[21,22] infrared, KBr pellet, 3.00 μ (OH).

The filtrate from the centrifugation was refractionated in a 60 × 1.2 centimeter glass helices column at 15 mm. and at a reflux ratio of 30:1. The fractions which crystallized on cooling were centrifuged as described above, and the resulting crystals were sublimed to yield 6.5 g. of *trans*-sabinene hydrate of m.p. 60–61°, an over-all yield of 0.8%.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.93; H, 11.70. Found: C, 78.10; H, 11.70.

Dehydration of *trans*-Sabinene Hydrate over Alumina.—A 40 × 2 centimeter quartz combustion tube, packed with 8–14 mesh activated alumina for the final 22 cm. of its length, was used for the dehydration studies. The alumina-containing portion of the tube was heated to the desired temperature with an electric furnace. A sample of alcohol, ranging from 100 to 750 mg., was introduced, volatilized by external heating and swept through the tube by nitrogen, flowing at a rate of 10 cc./min. The recovery of material averaged about 40–50%.

The dehydration was carried out at 200° and the product was fractionated on a 12-foot vapor phase chromatography column[23] containing Carbowax 4000 on brick dust.[24] The column temperature was 175° and the flow rate of helium was approximately 80 cc./min. Three fractions were collected.

Fraction 1 made up 3–5% of the product and had a retention time of 8.5 minutes. The ultraviolet absorption spectrum of this fraction in ethanol showed a broad maximum at 238 mμ. Ten microliters of this fraction was heated with a small amount of 10% palladium-on-carbon at 180° for one hour in a small tube. The infrared spectrum of the product of this reaction was identical with the spectrum of *p*-cymene.[25]

Fraction 2 (retention time 10.2 min.) comprised 40–45% of the product. The infrared absorption spectrum was identical to that of α-terpinene,[26] as was the ultraviolet spectrum ($\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 265 mμ).

Fraction 3 was separated into three components on a 12-foot vapor phase chromatography column which contained silicone oil on Celite 545.[26] The column temperature was 175° and the flow rate of helium was 80 cc./min. The three components of this fraction will be referred to as 3a, 3b and 3c.

Fraction 3a comprised 20–25% of the product from the dehydration of sabinene hydrate. The infrared spectrum was identical with that of *p*-cymene.

Fraction 3b, which accounted for 15–20% of the product, had an infrared spectrum identical with that of γ-terpinene.[25]

Fraction 3c made up 10–15% of the dehydration product of sabinene hydrate. The ultraviolet absorption spectrum had a maximum at 245 mμ. The infrared spectrum of this fraction was identical to that of 2,4(8)-*p*-menthadiene ($\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 244 mμ), prepared by the method of O'Conner and Goldblatt.[10]

The dehydration of sabinene hydrate was also carried at 150° over alumina and the product was analyzed by vapor phase chromatography. Three fractions were collected and were judged to be α-terpinene (38%), γ-terpinene (28%) and *p*-cymene (34%) on the basis of their infrared absorption spectra.

Oxidation of *trans*-Sabinene Hydrate.—The oxidation was carried out as follows: 4 g. of sabinene hydrate was placed in an 8-ounce small-mouth bottle, containing 100 ml. of water and 2 g. of potassium carbonate. Three grams of potassium permanganate was added and bottle was mechanically shaken for 24 hours. An additional 3 g. of potassium permanganate was then added and the agitation was continued until all of the permanganate color had disappeared (48–60 hr.). The mixture was then filtered and the solid material was resuspended in 100 ml. of water which contained 2 g. of potassium carbonate. Two grams of potassium permanganate was added and the mixture was agitated until the permanganate had decolorized, usually 2–3 days. After filtration the two filtrates were combined and extracted continuously with ether. The ether was removed by distillation to afford white crystals of diol (2.2 g., 44%) of m.p. 121–123°. After repeated sublimation, the diol had the properties: m.p. 123.5–124.5°, $[\alpha]^{25}\mathrm{D}$ +33.0° (*c* 5.7% in ethanol). A Zerewitinoff determination showed 1.88 active hydrogens per molecular weight of 170; spectrum: infrared, KBr pellet, 2.97 μ (OH).

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[19] D. F. Stedman, U. S. Patent 2,047,444, July 14, 1936.

[20] It was necessary to wash all glassware with which *trans*-sabinene hydrate was to come in contact with sodium bicarbonate solution. Otherwise dehydrations occurred.

[21] Infrared spectra with the model 21 Perkin–Elmer instrument.

[22] Ultraviolet with the Beckman DU instrument.

[23] C. Phillips, "Gas Chromatography," Butterworths Scientific Publications, London, England, 1956.

[24] The packing for the Carbowax-coated column was prepared by triturating 40 g. of 80 mesh firebrick (acid-washed) with 16 g. of Carbowax 4000 dissolved in 150 ml. of benzene. The benzene was then evaporated before packing the column.

[25] An authentic sample of this material was provided by the Hercules Powder Co.

[26] The packing for the silicone coated column was prepared by the trituration of silicone oil (20 g.) with graded Celite 545 (50 g., acid-washed).

Anal.[27] Calcd. for $C_{10}H_{18}O_2$: C, 70.59; H, 10.56. Found: C, 70.74; H, 10.44.

Dehydration of the Diol from *trans*-Sabinene Hydrate over Alumina.—The diol was dehydrated at 200° over alumina in the same manner by which the alumina dehydration of sabinene hydrate was carried out. The product was fractionated on a 4-foot Carbowax-coated column maintained at 100° and at a helium flow rate of 160 cc./min. Two fractions were collected. The first fraction (retention time 18 min., 80%) had an infrared absorption spectrum identical with that of *p*-cymene.

The second fraction (retention time 40 min.) amounted to 20% of the dehydration product; spectra: infrared, 6.61 μ (benzenoid), 11.32 μ ($R_2C{=}CH_2$); ultraviolet, λ_{max}^{alc} 248 mμ.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.87; H, 9.13. Found: C, 90.89; H, 9.13.

A sample of 42 mg. of this second fraction was dissolved in 5 ml. of ethanol and reduced with hydrogen at atmospheric pressure using 10 mg. of 10% palladium-on-charcoal as a catalyst. A total of 7.85 ml. of hydrogen was taken up which corresponds to 1.1 molecules of hydrogen per formula weight ($C_{10}H_{12}$) of 132. On removal of the ethanol by distillation, an oil remained. The infrared absorption spectrum of this oil was identical with that of *p*-cymene contaminated with a small amount of starting material. On the basis of the above evidence, this fraction is proposed to be 1-*p*-tolyl-1-methylethylene.

Dehydration of *trans*-Sabinene Hydrate by the Method of Tschugaeff.[5]—A 750-mg. sample of sabinene hydrate was solved in 5 ml. of dry toluene. After the addition of 125 mg. of sodium, the solution was refluxed and stirred for 6 hours. Although the sodium did not react completely, 1 ml. of carbon disulfide was added and both heating and stirring were continued for 10 hours at which time 1 ml. of methyl iodide was added. After 4 hours of refluxing, the material was distilled under reduced pressure. The highest boiling fraction contained most of the product and a large amount of toluene. This fraction was separated into its constituents on a silicone-coated vapor phase chromatography column at 180°. Unreacted sabinene hydrate made up 77% of the product, α-thujene 7% and sabinene 16%. α-Thujene and sabinene were identified by comparison of their infrared absorption spectra to those of authentic samples of α-thujene, prepared from thujyl alcohol as described by Tschugaeff,[28] and of sabinene, isolated from oil of savin.[29]

Thujyl Acetate.—A 1.5-ml. sample of thujyl alcohol was heated at 100° with 2 ml. of acetic anhydride and 50 mg. of potassium acetate for 4 hours. The excess acetic anhydride was decomposed with water and potassium carbonate. The oil (1.5 ml.) was separated and used without purification for further experiments; spectrum: infrared, 5.80 μ (ester).

The crude mixture of acetates was pyrolyzed at 400° through a 40 × 2 centimeter quartz tube packed with glass wool. Nitrogen was passed through the tube at a flow rate of 10 cc./min. The contact time per pass was 4–6 minutes. After 6 passes through the column, the low intensity of infrared absorption at 5.80 μ in the carbonyl region of the spectrum indicated that only a small amount of ester remained. The pyrolysis product then was analyzed on a 4-foot Carbowax-coated column at 100°. Three fractions were obtained.

The first fraction (30%, retention time 14 min.) was refractionated on the same Carbowax-coated column at 100°. The chromatogram showed that the first fraction was made up of three components with retention times at a flow rate of 80 cc./min. of 11.7 (16%), 14.0 (72%) and 16.6 minutes (12%). Although the mixture was not resolved completely, a cut was taken at 13–15 minutes; spectra: infrared, 6.13 μ (C=C), 10.0 μ, 11.03 μ ($RHC{=}CH_2$); ultraviolet: λ_{max}^{alc} 232 mμ. The retention time of a sample of the open chain terpene myrcene, prepared as described by Goldblatt,[30] under these conditions was 33 minutes.

The second fraction (35%, retention time 28 min.) had an infrared spectrum identical with that of α-terpinene, while the third fraction (30%, retention time 44 min.) had an infrared spectrum identical with that of *p*-cymene.

Thujyl *p*-Toluenesulfonate.—After recrystallization from benzene, 2.7 g. of *p*-toluenesulfonyl chloride was added to 2 g. of thujyl alcohol and 4 g. of pyridine. The mixture was stirred constantly and the temperature was kept below 20° during the addition of the chloride and for an additional 3 hours. An excess of cold, dilute hydrochloric acid was then added and the oil which separated was extracted with ether. The ether was dried and removed at the steam-bath. The residue (3.0 g.) crystallized, and the crystals were removed by filtration and washed with petroleum ether (b.p. 35–55°). Recrystallization from *n*-hexane afforded 1.55 g. (38%) of white crystals (m.p. 86.5–87.5°).

Anal. Calcd. for $C_{17}H_{24}O_3S$: C, 66.20; H, 8.10. Found: C, 66.07; H, 7.84.

An 800-mg. sample of the crystalline tosylate and 300 mg. of potassium hydroxide were dissolved in 8 ml. of ethanol and the mixture was refluxed for 8 hours. The solution was diluted with water and extracted with ether. The ether solution was dried and the solvent was removed by distillation. Seven hundred milligrams (86%) of the tosylate was recovered and no other products were detected by infrared spectroscopy.

A 900-mg. sample of the crystalline tosylate and 8 ml. of 2,6-lutidine (b.p. 142–5°) were refluxed for 52 hours, during which time the solution darkened. Six milliliters of a 4:1 ether–chloroform mixture was added and the solution was extracted three times with dilute hydrochloric acid. After washing with water twice, the ether–chloroform solution was dried and the ether and chloroform were removed by distillation. An oil (150 mg., 39%) remained. It was fractionated on a 4-foot Carbowax-coated column at 100°. Two components were present and were identified as α-terpinene (58%) and γ-terpinene (42%) by infrared spectroscopy.

Sabina Ketone.—Ten grams of *d*-sabinene, isolated from oil of savin,[29] 70 g. of potassium periodate, 2 g. of potassium permanganate and 5 g. of potassium carbonate were added to 2 liters of water and the mixture was agitated for 48 hours. The manganese dioxide was removed by filtration and the aqueous portion extracted continuously with ether for 10 hours. The ether solution was dried and the solvent was removed by distillation to afford 4.5 g. (47%) of crude sabina ketone.

The crude sabina ketone (32 g.) from a number of periodate oxidations was fractionated in a small glass-helices fractionating column at a pressure of 10 mm. and at a reflux ratio of 15:1. Two fractions were obtained, one of which was sabinene (13 g., b.p. 47–51.5°, 10 mm.) as judged by its infrared absorption spectrum. The other fraction was sabina ketone (12 g., 33%) of b.p. 89–90.5° (10 mm.), $n^{25}D$ 1.4675, and $[\alpha]^{25}D$ −24.9°. The values reported by Short and Read are b.p. 89° (10.5 mm.), $n^{25}D$ 1.4676, and $[\alpha]^{21.6}D$ −24.5°; spectrum: infrared, 5.82 μ ($\triangleright$—C=O).

Synthesis of *cis*- and *trans*-Sabinene Hydrate.—Twenty milliliters of ether and 80 mg. of magnesium were placed in a 50-ml. standard-taper, three-neck flask, equipped with a condenser, a dropping funnel and a standard-taper bend, connecting to a 5-ml. flask. The system was protected from moisture with a calcium chloride tube. The condenser was fitted with hose and an ice–salt mixture (−10°) was circulated through it. Methyl bromide (3.2 g.) was weighed into the 5-ml. flask and distilled from this flask into the reaction vessel. The connecting bend and flask were then replaced by a standard-taper glass stopper. After the reaction had subsided, the mixture was refluxed with occasional shaking for 1 hour. It then was cooled and shaken during the dropwise addition of 3 g. of sabina ketone, dissolved in 4 ml. of ether. The solution next was refluxed for 30 minutes. After cooling, chips of ice were added to decompose the excess Grignard reagent. A stream distillation was carried out, and the distillate was extracted with ether. The ether solution was dried and the ether was removed by distillation. An oil (3.1 g., 92%), which largely crystallized on cooling remained, and oil was analyzed on a 12-foot Carbowax-coated column at 130° and a a flow rate of 120 cc./min. Three fractions were isolated: Fraction 1 was made up of hydrocarbons and comprised 10–15% of the product. Fraction 2, designated *trans*-sabinene hydrate (retention time 39 min., 2–5%), was a crystalline solid of m.p. 59–60° and $[\alpha]^{26}D$ +31° (*c* 1% in alcohol); and a mixture of this material with the alcohol

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(27) Analyses by Microchemical Specialties, Berkeley, Calif.

(28) L. Tschugaeff, *Ber.*, **33**, 3120 (1900).

(29) A. G. Short and J. Read, *J. Chem. Soc.*, 1415 (1939).

(30) L. A. Goldblatt and S. Palkin, THIS JOURNAL, **63**, 3517 (1941).

isolated from peppermint oil (m.p. 60-61°, $[\alpha]^{25}\mathrm{D}$ +32° (*c* 4.2% in alcohol)) had m.p. 59.5-61°. The infrared absorption spectrum of the synthetic material was identical with that of the material from peppermint oil. Fraction 3 (retention time 60 min., 80-85%) was assigned the structure of *cis*-sabinene hydrate. This material melted at 36-37° (reported[12] 38-39°). On sublimation, *cis*-sabinene hydrate was obtained with the constants: m.p. 36.5-37.2°, $n^{60}\mathrm{D}$ 1.4489, and $[\alpha]^{25}\mathrm{D}$ +47.2° (*c* 10% in ethanol); spectrum: infrared, KBr pellet, 3.00 μ (OH).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.93; H, 11.70. Found: C, 77.76; H, 12.08.

Vapor Phase Chromatography Retention Times.—The retention times of *cis*- and *trans*-sabinene hydrate on a 20-foot silicone-coated column at 140° were, respectively, 64 and 58 minutes. The retention times of borneol, prepared as described by Jackson and Menke,[31] and of isoborneol, prepared by the method of Noyce and Denney,[32] on a 12-foot Carbowax-coated column at 130° and at a flow rate of 120 cc./min. were, respectively, 101 and 90 minutes.

Spectral Investigation of *cis*- and *trans*-Sabinene Hydrate.—The position of the OH stretching frequency in the infrared absorption spectra of the sabinene hydrates was investigated under a variety of conditions.

In *n*-hexane a 50% solution of α-terpineol had an OH stretching band ascribed to associated OH groups at 3.01 μ. This peak shifted to 2.97 μ and a less intense peak ascribed to free OH absorption appeared at 2.80 μ on dilution with 4 volumes of *n*-hexane. Under the same conditions *trans*-sabinene hydrate showed initially a maximum at 2.99 μ which shifted on dilution to 2.97 μ while the peak ascribed to free OH absorption appeared at 2.80 μ. With *cis*-sabinene hydrate, the peak at 3.01 μ did not shift to shorter wave lengths on dilution. However, a low intensity peak at 2.80 μ did appear.

In carbon tetrachloride the OH absorption peak for both *cis* and *trans*-sabinene hydrate shifted hypsochromically on dilution. The maxima for *trans*-sabinene hydrate were at 2.97 μ (30% in carbon tetrachloride) and 2.94 μ (4% in carbon tetrachloride). For *cis*-sabinene hydrate the values were, under the same conditions, 2.97 and 2.95 μ. With both sabinene hydrates, a peak ascribed to free OH absorption appeared at 2.78 μ.

On addition of 1,2-dimethoxyethane to dilute solutions of *cis*- and of *trans*-sabinene hydrate in carbon tetrachloride, the peak at 2.78 μ ascribed to free OH groups disappeared and was replaced by a peak at 2.88 μ.

Dehydration of *cis*-Sabinene Hydrate over Alumina.—The dehydration of *cis*-sabinene hydrate was carried out at 150° in the manner that has been described for the dehydration of *trans*-sabinene hydrate over alumina. The product was analyzed on a 4-foot Carbowax-coated column at 100° and a flow rate of 100 cc./min. The fractions were collected. Their infrared absorption spectra identified them as a α-terpinene (36%), γ-terpinene (26%) and *p*-cymene (38%).

Dehydration of *cis*-Sabinene Hydrate by the Tschugaeff Method.—A sample of 50 mg. of *cis*-sabinene hydrate was dissolved in 250 μl. of benzene. Twelve milligrams of sodium was added and the mixture was heated at 80° for 6 hours by which time all of the sodium had reacted. Carbon disulfide (100 μl.) then was added and the solution was maintained at 80° for 3 hours. A yellow, gelatinous precipitate was formed. After the addition of 150 μl. of methyl iodide, the temperature was maintained at 80° for another 4 hours. The low-boiling constituents were distilled off and the residue was heated at 140° for 10 minutes under a reflux condenser. The product was distilled and separated into two fractions on a 4-foot Carbowax-coated column at 100°. The fractions were identified as α-thujene (30%) and sabinene (60%) by infrared spectroscopy.

Oxidation of *cis*-Sabinene Hydrate.—Three hundred milligrams of potassium permanganate was added over a period of 7 days to an agitated mixture of 180 mg. of *cis*-sabinene hydrate and 4 ml. of 2.5% sodium bicarbonate solution. When the final addition of potassium permanganate had been decolorized, the solution was filtered and the filtrate was extracted exhaustively with ether. The ether solution was dried and the ether was removed by distillation to leave 65 mg. (33%) of a white solid of m.p. 98-102°. The solid was sublimed twice at reduced pressures and then recrystallized from ethyl acetate-petroleum ether (b.p. 35-55°). The crystals obtained melted at 104.5-105.2°; spectrum: infrared, KBr pellet, 3.00 μ (OH).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.59; H, 10.56. Found: C, 70.67; H, 10.63.

Acetylation of *trans*-Sabinene Hydrate.—A mixture of 300 μl. of acetic anhydride, 300 mg. of *trans*-sabinene hydrate and 30 mg. of potassium acetate was heated at 100° for 4 hours. The excess acetic anhydride was decomposed by the addition of water and potassium carbonate. The solution was extracted with 200 μl. of *n*-hexane. The hexane extract was analyzed on a 4-foot Carbowax-coated column at 100°. Four fractions were collected and the first three were identified as α-thujene (13%), α-terpinene (26%), and γ-terpinene (51%) by infrared spectroscopy. The infrared absorption spectrum of fraction 4 (12%, retention time 30-31 min.) had a peak at 5.80 μ (ester), and a small peak at 6.62 μ (benzenoid) which in conjunction with a peak at 12.28 μ (*p*-cymene) indicated that *p*-cymene made up part of fraction 4. Twenty microliters of fraction 4 were refluxed with 500 μl. of a 10% solution of sodium hydroxide for two hours. The water layer was then extracted with 100 μl. of *n*-hexane. The hexane solution was dried and the hexane was removed by distillation. The infrared absorption spectrum of fraction 4 was unchanged by this treatment. The maximum at 5.80 μ (ester) was still present.

Acetylation of *cis*-Sabinene Hydrate.—The acetylation of *cis*-sabinene hydrate was carried out as described above for *trans*-sabinene hydrate. The product was analyzed on a 12-foot Carbowax-coated column at 130°. The retention times of the first 4 fractions indicate that they are α-thujene (5%, 6 min.), α-terpinene (16%, 12 min.), γ-terpinene (30%, 16 min.) and *p*-cymene (8%, 18 min.). The fifth fraction, an ester (45%, 76 min.), was collected. This ester was not oxidized by a dilute solution of potassium permanganate; spectrum: infrared, 5.80 μ (ester).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.48; H, 10.21. Found: C, 73.42; H, 10.26.

A sample of 200 mg. of this acetate of *cis*-sabinene hydrate was added to 5 ml. of a 20% solution of sodium hydroxide. The mixture was refluxed for 16 hours, cooled, and extracted with ether. The ether solution was dried and the ether was removed by distillation to leave an oil. This oil was analyzed on a Carbowax-coated column at 130°. The chromatogram indicated that no ester or alcohol was present and that the only products formed were hydrocarbons. The retention times of these hydrocarbons indicated that they were α-thujene (22%, 7 min.), sabinene (13%, 10 min.), α-terpinene (20%, 13 min.), γ-terpinene (36%, 18 min.) and *p*-cymene (9%, 20 min.).

Acetylation of *trans*-Sabinene Hydrate with Acetic Anhydride and Pyridine.—A mixture of 2 ml. of acetic anhydride, 2 ml. of pyridine and 500 mg. of *trans*-sabinene hydrate was maintained at 80° for 4 hours. Water and potassium carbonate then were added to decompose the excess acetic anhydride. The solution was extracted with ether and the ether solution was washed 4 times with equal volumes of water. After drying the solution, the ether was removed by distillation. The infrared absorption spectrum of the residual oil showed peaks at 2.95 μ (OH) and at 5.82 μ (ester). The oil was analyzed on a 12-foot Carbowax-coated column at 130°. The chromatogram showed the presence of hydrocarbons and three slower moving components. These slower components were shown by infrared spectroscopy to be an ester (10%), identical with that ester isolated from the acetylation of *trans*-sabinene hydrate with acetic anhydride and potassium acetate, *trans*-sabinene hydrate (45%), and another ester (30%).

TABLE I

THE RATE OF REACTION OF SABINENE HYDRATE WITH ACETIC ANHYDRIDE AND PYRIDINE

Time, hr.	Concn. of sabinene hydrate, %	
	cis-	*trans*-
0	12.6	11.9
2	10.6	10.4
4	10.0	9.3
8	6.7	6.4
20	2.4	2.7

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[31] C. L. Jackson and A. Menke, *Am. Chem. J.*, **5**, 270 (1884).

[32] D. S. Noyce and D. B. Denney, THIS JOURNAL, **72**, 5743 (1950).

The first ester reacted immediately with a dilute solution of potassium permanganate; spectrum: infrared, 5.80 μ (ester).

The other ester was oxidized slowly by potassium permanganate; spectrum: infrared, 5.82 μ (ester). It was concluded that this ester was the acetate of *trans*-sabinene hydrate.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.48; H, 10.21. Found: C, 73.29; H, 10.49.

Acetylation of *cis*-Sabinene Hydrate with Acetic Anhydride and Pyridine.—The acetylation of *cis*-sabinene hydrate was carried out as described above for *trans*-sabinene hydrate. *cis*-Sabinene hydrate (40%) and its acetate (44%) and a mixture of hydrocarbons (16%) were isolated as the products of this reaction by vapor phase chromatography.

Comparative Reaction Rates of the Sabinene Hydrates with Pyridine and Acetic Anhydride.—A sample of 50 mg. of sabinene hydrate was dissolved in 200 μl. of acetic anhydride and 200 μl. of pyridine. The reaction mixtures of both isomers were maintained at 80°. Aliquots of 10 μl. were removed at 0, 2, 4, 8 and 20 hours. These aliquots were analyzed on a 12-foot Carbowax-coated vapor phase chromatography column maintained at 130°. The area of the peak resulting from the alcohol was divided by the total area of all the chromatogram peaks to give the approximate percentage of the alcohol. The results are given in Table I.

STANFORD, CALIF.

[CONTRIBUTION FROM THE FATTY ACID PRODUCERS' COUNCIL OF THE ASSOCIATION OF AMERICAN SOAP AND GLYCERINE PRODUCERS, INC., AND THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Phosphorus Derivatives of Fatty Acids. V.[2] Vinyl α-Diethylphosphonates

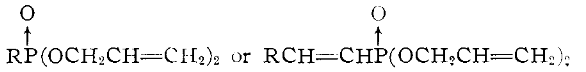
BY RICHARD SASIN,[3] ROSE MARIE NAUMAN[3] AND DANIEL SWERN

RECEIVED JULY 7, 1958

Vinyl α-bromo esters have been prepared in 30–60% yield from vinyl acetate and the appropriate C_2 to C_{18} straight chain α-bromocarboxylic acid (equation 1). By heating the vinyl α-bromo esters with triethyl phosphite, the corresponding vinyl α-diethylphosphonates were prepared in 35–75% yield (equation 2). The vinyl α-phosphonates are colorless, odorless liquids which are insoluble in water and soluble in organic solvents. Under prolonged heating with benzoyl peroxide, they form polymers with a low degree of polymerization.

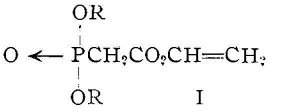
The first three papers in this series,[4-6] described the preparation and properties of dialkyl acylphosphonates, dialkyl acyloxyethyl phosphonates and trialkyl α-phosphonates, respectively. The present investigation deals with the synthesis and properties of some new vinyl esters of α-diethylphosphonocarboxylic acids.

The literature describes numerous examples of unsaturated esters of phosphonic acids.[7-10] These compounds have the general formulas



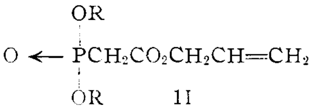
$$R\overset{O}{\overset{\uparrow}{P}}(OCH_2CH{=}CH_2)_2 \text{ or } RCH{=}CH\overset{O}{\overset{\uparrow}{P}}(OCH_2CH{=}CH_2)_2$$

In contrast to alkenyl phosphonates, the literature reports relatively few examples of alkenyl phosphonocarboxylates. The examples appear to be limited to the vinyl (I) and allyl (II) phosphonoacetates.[11-13] In these compounds, the alkenyl group of the ester is attached to carbon and not to phosphorus as in the previous types.



$$O \leftarrow \overset{OR}{\underset{OR}{P}}CH_2CO_2CH{=}CH_2$$

I

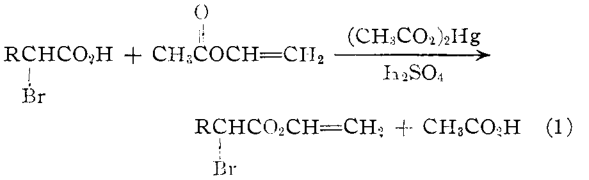


$$O \leftarrow \overset{OR}{\underset{OR}{P}}CH_2CO_2CH_2CH{=}CH_2$$

II

Apparently there are no reports on the systematic preparation and study of the physical and chemical properties of the vinyl (α-diethylphosphono)-carboxylate esters, a previously unreported series of polymerizable esters.

This paper describes the preparation and properties of the vinyl esters of bromoacetic, α-bromocaproic, -pelargonic, -capric, lauric, -myristic, -palmitic and -stearic acids. These compounds, most of which have not been described previously, were prepared from the appropriate α-bromocarboxylic acid and vinyl acetate by acidolysis in the presence of mercuric sulfate.



$$\underset{Br}{RCH}CO_2H + CH_3\overset{O}{\overset{\|}{C}}OCH{=}CH_2 \xrightarrow[H_2SO_4]{(CH_3CO_2)_2Hg} \underset{Br}{RCH}CO_2CH{=}CH_2 + CH_3CO_2H \quad (1)$$

$R = H, C_4H_9, C_7H_{15}, C_8H_{17}, C_{10}H_{21}, C_{12}H_{25}, C_{14}H_{29}, C_{16}H_{33}$

The properties, yields obtained and analyses of the vinyl α-bromo esters are summarized in Table I. These esters are colorless, odorless (except for the acetate which is strongly lachrymatory), high-boiling liquids insoluble in water and soluble in organic solvents.

By heating the vinyl α-bromo esters with triethyl phosphite in a Michaelis–Arbuzov reaction, the corresponding vinyl α-diethylphosphonates were prepared.

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(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented at the Fall Meeting of the American Chemical Society, Chicago, Ill., September 7–12, 1958. Paper IV in this series, *Ind. Eng. Chem.*, data series (1958).

(3) Fellow of the Fatty Acid Producers' Council of the Association of American Soap and Glycerine Producers, Inc.

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