ammonium salt (109 g.) recrystallized from ethanol–tetrahydrofuran as yellow crystals, m.p. 180° dec.

Anal. Calcd. for $C_{20}H_{40}N_4S_2$: C, 59.94; H, 10.06; N, 13.98; S, 16.01. Found: C, 60.47; H, 10.14; N, 14.12; S, 16.26.

The ultraviolet spectrum in ethanol had absorption at 340 mμ (ε 21,300) and 272 (14,500). The infrared spectrum had absorption at 2160, 2140, 2050, and 1440 cm.$^{-1}$.

Tetraethylammonium 2,2-Dicyano-1-ethylthioethylene-1-thiolate.—Bis(tetraethylammonium) 2,2-dicyanoethylene-1,1-dithiolate (20.0 g., 0.05 mole) was heated to 180° (20 mm.) in a flask connected to a trap cooled to −80°. The triethylamine evolved was collected and converted to its hydrochloride, m.p. 254–256°, in 95% yield (6.5 g.). The pyrolysis residue crystallized on cooling and was recrystallized from methanol as yellow crystals, m.p. 52–54°, in 85% yield (13.55 g.). The ultraviolet spectrum had absorption at 342 mμ (ε 21,800) and 285 (10,000).

Anal. Calcd. for $C_{14}H_{25}N_2S_2$: N, 15.38. Found: N, 15.43.

The salt was readily converted to known 1,1-dicyano-2,2-bis(ethylthio)ethylene,[2] with ethyl bromide in ethyl acetate.

Dicyanomethylene-1,3-dithietane.—Dipotassio-1,1-dimercapto-2,2-dicyanoethylene (109 g., 0.5 mole) was suspended in 1 l. of acetonitrile (Union Carbide commercial grade, not dried). Diiodomethane (267 g., 1.0 mole) was added, and the reaction mixture was stirred vigorously with a mechanical stirrer and was refluxed for 23 hr. A gray solid (136 g.), presumably potassium iodide, was separated by filtration from the dark brown solution. The acetonitrile filtrate was evaporated on a rotary evaporator. Then the residue was extracted with 500 ml. of water to remove any potassium iodide and was dissolved in about 1 l. of hot benzene. The brown benzene solution was partly decolorized with charcoal and a filter aid (Celite). Yellow-brown crystals, m.p. 145–149° (49.9 g., 65%), were obtained when the benzene solution was concentrated and cooled. Additional crystals, m.p. 146–150° (8.5 g.), were obtained by concentration of the mother liquors. The product can be purified further by sublimation, which is tedious, or by recrystallization from benzene or benzene–hexane. The infrared spectrum had absorptions at 3058, 2976, 1493, and 1425 cm.$^{-1}$, and the ultraviolet spectrum exhibited maxima at 303 mμ (ε 15,500) and 253 (5100).

Bis(tetraethylammonium) 2,2-dicyanoethylene-1,1-dithiolate could be used instead of the dipotassium salt, but the yields were not improved.

The dithietane is soluble at room temperature in glacial acetic acid, chloroform, dichloromethane, dimethyl sulfoxide, acetonitrile, dioxane, dimethylformamide, and acetone. It is somewhat less soluble in benzene, ethanol, methanol, water, and ethyl acetate and is insoluble in carbon tetrachloride, hexane, ether, and carbon disulfide.

Anal. Calcd. for $C_5H_2N_2S_2$: C, 38.93; H, 1.31; S, 41.58; mol. wt., 154. Found: C, 38.83; H, 1.55; S, 41.18; mol. wt., 166.

1,1-Dicyano-2-(S,N-methylpyridinium)mercaptoethylene-2-thiolate.—Pyridine (12 g., 0.15 mole) was added to a solution of dicyanomethylene-1,3-dithietane (7.7 g., 0.5 mole) in 150 ml. of hot benzene. The clear solution became turbid within 5 min. and was refluxed for 22 hr. At the end of this time there was considerable solid in the flask, and the solution was dark brown. The solid was removed by filtration and washed with benzene. The yield was 9.4 g. (81%). The tan solid was recrystallized three times from water–acetonitrile to give white to pale yellow crystals, m.p. 193–194° dec.

Anal. Calcd. for $C_{10}H_7N_3S_2$: C, 51.48; H, 3.03; N, 18.04; S, 27.49; mol. wt., 233. Found: C, 51.79; H, 3.06; N, 18.02; S, 27.86; mol. wt. (boiling point elevation of acetone), 235 and 250.

The infrared spectrum had absorption at 2260, 2240, 1650, and 1500 cm.$^{-1}$. The ultraviolet spectrum in acetonitrile showed absorption at 338 mμ (ε 19,300) and 263 (9860). The proton magnetic resonance spectrum in dimethyl sulfoxide (60 Mc., tetramethylsilane as internal reference) showed absorption at 455, 420, 395, and 294 c.p.s. The ratio of the total area of absorption at 455, 420, and 395 c.p.s. to the area of the absorption at 294 c.p.s. was 5:2.

The pyridinium zwitterion was soluble in dimethyl sulfoxide, acetonitrile, dimethylformamide, hot acetic acid, and hot methanol. It had low solubility in ethanol, benzene, chloroform, dioxane, tetrahydrofuran and carbon tetrachloride. A deep wine red color develops when the zwitterion in dimethyl sulfoxide is treated with basic reagents such as sodium carbonate, sodium methoxide, or sodium azide. It is not clear whether this color is due to the anion formed by removing a methylene proton or to a thiophene derivative formed by cyclization.[8]

1,1-Dicyano-2(S,N-methylpyridinium)mercapto-2-methylmercaptoethylene *p*-Toluenesulfonate.—The pyridinium zwitterion (6.9 g., 0.03 mole) was heated with 25 ml. of methyl *p*-toluenesulfonate. After about 12 hr. a buff solid (9.8 g.) was removed by filtration and washed with benzene. It was recrystallized three times from acetonitrile to yield white crystals, m.p. 175.6–176.0°.

Anal. Calcd. for $C_{18}H_{17}N_3O_3S_3$: C, 51.53; H, 4.09; N, 10.02; S, 22.93. Found: C, 51.79; H, 4.19; N, 10.18; S, 22.94.

The infrared spectrum had absorption at 2200, 1650, 1500 cm.$^{-1}$. The ultraviolet spectrum in acetonitrile had absorption at 332 mμ (ε 11,500), 263 (5770), and 219 (9860). The ultraviolet spectrum of 1,1-dicyano-2,2-bis(methylthio)ethylene had maxima at 330 mμ (ε 13,300), 290 (6850), and 220 (2995).

The proton magnetic resonance spectrum in deuterium oxide (60 Mc., tetramethylsilane as internal reference) showed a complex multiplet, poorly resolved, centered at 495, a singlet at 386, and two singlets at 183 and 172 c.p.s. The relative areas were, respectively, 9:2:3:3.

The compound was soluble in water and partially soluble in acetonitrile, ethanol, and chloroform. It was insoluble in methylene chloride and dioxane.

1,1-Dicyano-2-(S-methyltriphenylphosphonium)mercaptoethylene-2-thiolate.—Dicyanomethylene-1,3-dithietane (15.4 g., 0.10 mole) was dissolved in 350 ml. of hot benzene, and triphenylphosphine (34.3 g., 0.15 mole) in 150 ml. of benzene was added in one portion. Within 2 min. the clear solution became turbid and was refluxed for 20 min. The tan solid (27.4 g., 66%) was removed by filtration and washed three times with benzene. The filtrate was returned to the reaction flask and refluxed for 6 hr. more to give an additional 9.7 g. of tan solid. The over-all yield of crude material, m.p. 245–246° dec., was 89%.

The solid was recrystallized from acetonitrile as nearly white crystals, m.p. 245–246° dec. The crystals darkened above 230°.

Anal. Calcd. for $C_{23}H_{17}N_2PS_2$: C, 66.32; H, 4.12; N, 6.73; S, 15.40; P, 7.45; mol. wt., 417. Found: C, 66.62; H, 4.23; N, 6.59; S, 15.85; P, 7.60; mol. wt. (boiling point elevation of acetone), 465 and 483.

The infrared spectrum had absorption at 2200, 2180, 1575, and 1490 cm.$^{-1}$. The ultraviolet spectrum in acetonitrile had maxima at 342 mμ (ε 18,300) and 275 (9940). The proton magnetic resonance spectrum (60 Mc., tetramethylsilane as internal reference) in dimethyl sulfoxide showed absorption at 470, 443, and 347 c.p.s. The latter was a doublet (J = 8 c.p.s.). The ratio of the combined areas of the absorption at 470 and 443 c.p.s. to the absorption at 347 c.p.s. was 15:2.

The phosphonium zwitterion was soluble in dimethyl sulfoxide, acetone, acetonitrile, hot chloroform, and nitromethane. It was slightly soluble in ether, dioxane, and ethyl actetate, and it was insoluble in water, acetic acid, benzene, and ethanol.

Acknowledgment.—We wish to thank Dr. Owen Webster and Dr. B. C. McKusick for helpful discussions.

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2,4-*p*-Menthadiene. A New Monoterpene from Valencia Orange Oil

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During an investigation of the constituents of cold-pressed orange oil, a new terpene hydrocarbon was isolated. Catalytic reduction yielded *cis-* and *trans-*

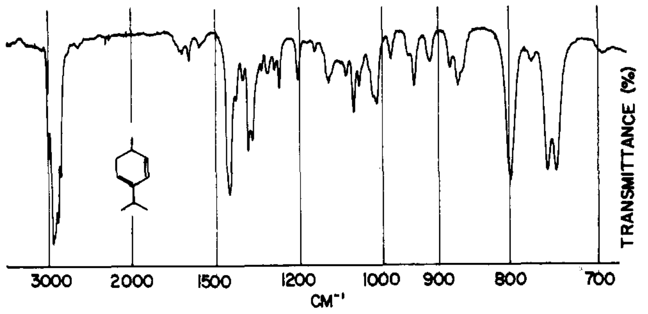

Fig. 1.—Infrared spectrum of 2,4-*p*-menthadiene.

p-menthane. Spectroscopic data indicated the presence of a triply substituted conjugated homoannular diene which was shown not to be 1,5-*p*-menthadiene (*p*-mentha-1,8-diene) by comparative infrared analysis. This previously uncharacterized terpene was identified as 2,4-*p*-menthadiene (*p*-mentha-2,4-diene).

The new terpene was synthetically obtained following dehydrohalogenation of 3,4-dibromo-*p*-menthane which resulted from the bromination of *p*-menth-3-ene. It was separated from both the orange oil and products of dehydrohalogenation by preparative gas chromatography.

Experimental

Isolation of 2,4-*p*-menthadiene.—Cold-pressed Valencia orange oil (300 ml.) was slowly added with stirring to 540 g. of silica gel in 500 ml. of hexane. The temperature was maintained at 5° throughout the addition. Upon complete addition the hexane solution was decanted and the silica gel washed three times with 300-ml. portions of hexane. The combined hexane solutions were distilled in a 5-ft. vacuum-jacketed packed column to give 30 ml. of material that boiled from 130–174°. Redistillation in a semimicro spinning-band column gave 10 ml. that boiled from 150–174°. The fourth peak of a gas chromatographic separation[1] of this fraction, having a retention time of 16 min. and following camphene, was collected to give the infrared spectrum shown in Fig. 1. Absorption at 795 cm.$^{-1}$ showed the presence of a triply substituted double bond and that at 750 cm.$^{-1}$ a *cis*-disubstituted double bond. The material was reduced with platinum black to yield *cis*- and *trans*-*p*-menthane. Its ultraviolet absorption at $\lambda_{\max}^{\text{ethanol}}$ 260 mμ shows it to be a homoannular diene having at least two alkyl constituents by Woodward's rule.[3] Comparative infrared spectroscopy ruled out 1,5-*p*-menthadiene, the only *p*-menthadiene whose structural characteristics are similar. The parent mass spectral peak occurred at 136. 2,4-*p*-Menthadiene appears in the oil in trace amounts.

3,4-Dibromo-*p*-menthane.—*p*-Menth-3-ene was dissolved in ether and treated with equimolar amounts of bromine with stirring. The temperature was maintained at 25° by controlling the rate of bromine addition. The solution was washed with sodium bisulfite, extracted with ether, and distilled; b.p. 85–90° (0.025 mm.), $n^{23}\text{D}$ 1.5276; lit.[4] $n^{20}\text{D}$ 1.5260.

2,4-*p*-Menthadiene.—3,4-Dibromo-*p*-menthane was added to absolute ethanol containing an excess of potassium hydroxide and heated on a steam bath for 30 min. The mixture was filtered, neutralized with dilute hydrochloric acid, and then gas chromatogrammed to give a major peak having a retention time of 16 min.; $n^{23}\text{D}$ 1.4660; ultraviolet, $\lambda_{\max}$ 260 mμ; the infrared spectra was identical with that shown in Fig. 1 (b.p. 56° at 25 mm. by the method of Garcia[5]). The compound gave *p*-menth-3-ene upon treatment with sodium and alcohol. Molecular weight by mass spectrometry was 136.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 88.20; H, 11.80.

Acknowledgment.—The authors thank G. S. Fisher, Naval Stores Laboratory, Olustee, Florida, for the 3-*p*-menthene.

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[1] Column, 0.5 in. × 36 ft., containing 30% Carbowax 20M[2] on Chromosorb-W; flow rate, 200 ml./min.; temperature, 145°.

[2] Mention of brand names is for identification of type of material and does not constitute endorsement.

[3] L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Co., New York, N. Y., 1959, p. 17.

[4] N. L. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952).

[5] C. R. Garcia, *Ind. Eng. Chem., Anal. Ed.*, **15**, 648 (1943).

Synthesis and Spectra of Derivatives of α-Bromo-*p*-phenylisobutyrophenone. A Comment upon the Mechanism of Quasi-Favorskiĭ Rearrangement

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Silver nitrate in acetonitrile has for several years been recognized as a useful reagent for conversion of alkyl halides into alkyl nitrates.[2] It has been found that this reagent is very selective towards a direct replacement of halogen. Tertiary α-bromo ketones, very sensitive to rearrangement or dehydrobromination, will react with this reagent to give an excellent yield of the corresponding α-nitrato ketone.

Although reaction of tetraethylammonium nitrate with α-bromo-*p*-phenylisobutyrophenone (I) leads to a complex mixture of products, reaction of silver nitrate with an acetonitrile solution of I has been found to give an excellent yield of the direct replacement product, α-nitrato-*p*-phenylisobutyrophenone (II), with no evidence for any significant amount of rearrangement or elimination product. For instance, from reaction at 92° was isolated a 77% yield of II and about 8% of a high melting point material[3] with an infrared spectrum indicating the absence of nitrate groups. The structure of II was confirmed by conversion to the known[4] 1,2-epoxy-2-methyl-1-methoxy-1-(4-biphenylyl)-propane (III) and α-hydroxy-*p*-phenylisobutyrophenone (IV). Spectral characteristics of III, of IV, and of α-acetoxy-*p*-phenylisobutyrophenone (V) are reported for the first time.

In acetonitrile solution, under identical conditions, silver nitrate was found to react with α-bromo ketone I at 130 times the rate of silver perchlorate and at 13 times the rate of tetraethylammonium nitrate. These results represent over-all initial rates, and the kinetics were not further investigated, but it is possible that in the rate-determining stage of the silver nitrate reaction, both electrophilic assistance by silver ion and nucleophilic assistance by nitrate ion are operative.

Reaction of α-bromo ketone I with silver nitrate in aqueous ethanol previously has been shown to give a 69% yield of 2-(4-biphenylyl)-2-methylpropanoic acid (VI)[5] formed by a Favorskiĭ rearrangement. α-Bromoisobutyrophenone similarly has been shown[6]

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[1] To whom communications concerning this paper should be addressed.

[2] L. F. Fieser and W. Von E. Doering, *J. Am. Chem. Soc.*, **68**, 2252 (1946).

[3] This product probably represents a small amount of reaction involving solvent participation; see, for example, J. Cast and T. S. Stevens, *J. Chem. Soc.*, 4180 (1953).

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[6] A. C. Cope and E. S. Graham, *ibid.*, **73**, 4702 (1951).