10. **Di-*p*-tolyl Telluroxide and Sulfoxide.**[24]—Simple eutectic system with eutectic point at 84.5° and 6% of telluroxide.

TABLE X

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	92.1	93.1	48.7	84.5	127.6
3.4	84.5	88.0	70.2	84.6	146.0
11.0	84.4	90.9	89.8	84.6	160.5
20.9	84.6	100.9	95.0	84.8	164.1
34.7	84.5	114.7	100.0	166.3	167.2

11. **Di-*p*-tolyl Telluroxide and Sulfone.**[24]—Simple eutectic system with eutectic point at 134.3° and 40% of the telluroxide.

TABLE XI

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	157.3	158.1	60.4	134.2	148.8
5.0	134.2	157.0	76.0	134.4	157.1
14.2	134.1	153.2	88.5	134.5	162.5
26.3	134.3	145.8	95.4	134.5	165.4
34.3	134.3	139.1	100.0	166.3	167.2
47.8	134.3	140.8			

12. **Di-*p*-tolyl Telluroxide and Telluride.**—Simple eutectic system with eutectic point at 59.2° and 3% of telluroxide.

TABLE XII

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	62.8	63.6	40.6	59.4	117.1
4.3	59.1	63.5	59.9	59.3	135.6
11.9	59.0	78.7	80.2	59.4	152.0
17.1	59.0	87.3	95.4	59.6	164.7
26.1	59.2	100.0	100.0	166.3	167.2

Summary

1. It is shown by the thermal analysis method that diphenyl and di-*p*-tolyl telluroxide form with the pertaining selenoxides continuous mixed crystal series of the ascendant type (type I). Diphenyl telluroxide gives with the corresponding selenone a continuous series of mixed crystals of the type with minimum (type III). Di-*p*-tolyl telluride do not give mixed crystals with the pertaining telluroxide.

These facts lead to the conclusion that telluroxides must have the same steric configuration as the corresponding selenoxides or selenones. In accordance with our previous studies on the configuration of selenoxides[3] and sulfoxides[5] the tetrahedral configuration of telluroxides is postulated.

2. Diphenyl and di-*p*-tolyl telluroxide form with the corresponding sulfoxides and sulfones only simple eutectic systems without even a limited formation of mixed crystals. Di-*p*-tolyl selenoxide gives however with the corresponding sulfoxide a continuous mixed crystal series of type I and with the sulfone a series of type III; di-*p*-tolyl telluride forms with the corresponding selenide a continuous mixed crystal series of type I, and with the sulfide a series of type III.

These facts are explained by the admission that the bond angles in the telluroxides and the corresponding sulfoxides differ already in such an amount that the tetrahedral forms of these molecules are no more commensurable.

SÃO PAULO, BRAZIL RECEIVED JANUARY 29, 1947

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

cis- and *trans*-Piperylenes[1,2]

BY ROBERT L. FRANK, ROBERT D. EMMICK AND RAYNER S. JOHNSON

Piperylene is perhaps the most readily available diene existing in *cis* and *trans* forms. As shown by Craig[3] and by Robey, Morrell and Wiese,[4] the two isomers differ markedly in their reactions. Further study of their preparation and reactions, carried out because of increased interest in piperylene as a by-product in the cracking process for isoprene, is described in this paper.

Because one of the reactions we desired to study was the polymerization of *cis-* and *trans*-piperylenes, and since traces of impurities have a marked effect on such reactions,[5] it was considered necessary to obtain the material in high purity. Indeed, one of the most likely impurities in piperylene from cracked petroleum, cyclopentadiene, is also one of the most powerful polymerization inhibitors among hydrocarbons.[5]

Means of purification involving solid intermediates which might be purified by recrystallization are not available for piperylene. For example, the cyclic sulfone, although useful, is not crystalline as in the case of isoprene sulfone.[5a] Cuprous chloride complexes are likewise not obtainable as crystalline solids.[3] Another derivative, the tetrabromide, can be obtained as the crystalline isomer only in yields of approximately 20%.[3] A fourth means of purification, regeneration by pyrolysis of the maleic anhydride adduct

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(1) Presented before the Organic Division at the Chicago meeting of the American Chemical Society, September 9–13, 1946.

(2) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(3) Craig, THIS JOURNAL, **65**, 1006 (1943); U. S. Patent 2,403,054 (July 2, 1946).

(4) Robey, Morrell and Wiese, *ibid.*, **63**, 627 (1941); Robey, *Science*, **96**, 470 (1942); Robey and Wiese, U. S. Patent 2,357,910 (Sept. 12, 1944).

(5) (a) Frank, Adams, Blegen, Deanin and Smith, *Ind. Eng. Chem.*, **39**, 887 (1947); (b) Frank, Blegen, Inskeep and Smith, *ibid.*, **39**, 893 (1947).

of *trans*-piperylene, gave a 37% yield of piperylene (mostly *trans*), but this was contaminated by other hydrocarbons.

Technical piperylene can be purified, however, by the reaction with maleic anhydride. This removes *trans*-piperylene and cyclopentadiene. Efficient fractional distillation then removes traces of 1,4-pentadiene and other hydrocarbons, and the product is pure *cis*-piperylene.[6] This can then be converted to the *trans* isomer.

The conversion of *cis*- to *trans*-piperylene has been effected by Craig[3] by means of the cyclic sulfone, which gives on pyrolysis only the *trans* form. Isomerization can also be accomplished by refluxing with a trace of iodine. This results in an equilibrium mixture containing 86 ± 2% *trans* and 14 ± 2% *cis*-piperylene,[7] starting with either pure isomer. Establishment of the equilibrium was proved by reaction of the mixture with maleic anhydride. The *trans* form reacted; the *cis* isomer was subsequently distilled and characterized by refractive index, as described in detail in the Experimental Part.

Isomerization did not occur when sulfur was used as the catalyst, nor was ultraviolet light effective when tested on the *trans* isomer.

Both isomers are converted in 75% yield at 600° to an approximately 3:4 mixture of the *cis* and *trans* forms.

At present the best means of preparing pure *trans*-piperylene from the *cis*-isomer or from mixtures rich in the *cis* isomer appears to be to isomerize with iodine first, then complete the conversion by means of the cyclic sulfone. The reason for the preliminary iodine treatment is that *cis*-piperylene reacts only sluggishly with sulfur dioxide in the thermal cyclic sulfone synthesis.[3]

To verify the purity of the piperylenes obtained by the above means, especially with respect to cyclopentadiene, the following synthesis was carried out in 58% over-all yield

$$\underset{\text{I}}{CH_3COCH_2COCH_3} \xrightarrow[\text{Ni}]{H_2}$$

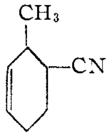
$$\underset{\text{II}}{CH_3CHOHCH_2CHOHCH_3} \xrightarrow[\text{anhydride}]{\text{acetic}}$$

$$\underset{\text{III}}{CH_3CH(OCOCH_3)CH_2CH(OCOCH_3)CH_3} \xrightarrow{575\text{–}600°}$$

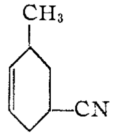
$$\underset{\text{IV}}{CH_2{=}CHCH{=}CHCH_3}$$

The pyrolysis products were *cis*- and *trans*-piperylenes (74%) (mostly *trans*) and 1,4-pentadiene (8%). These were separated by careful fractional distillation. The boiling points, refractive indices and polymerization rates of these synthetic isomers were identical with those of the products obtained from technical piperylene, and the physical constants were essentially the same as those reported by Craig.[3] We consider the polymerization rate to be a sensitive criterion of purity.[5]

The diene synthesis[8] has previously been shown to occur between *trans*-piperylene and maleic anhydride but to fail with the *cis* isomer.[3,4] Further experiments confirm this. For example, acrylonitrile gave a 56% yield of adduct with *trans*-piperylene; no reaction occurred with *cis*-piperylene. The adduct was shown by sulfur dehydrogenation and subsequent hydrolysis to the corresponding toluic acids to be a mixture containing mainly (> 60%) 2-methyl-1,2,5,6-tetrahydrobenzonitrile (V) along with a smaller amount of 3-methyl-1,2,3,6-tetrahydrobenzonitrile (VI)



V



VI

Dimerization of piperylene, again a diene synthesis, occurs only with the *trans* isomer and takes place slowly at 50°.[9]

In the emulsion polymerization of the piperylenes the *cis* isomer reacts considerably faster than the *trans*,[10] either alone or copolymerized with styrene (Fig. 1). This is perhaps to be expected, as the isomerization experiments have shown the *cis* isomer to be the less stable form. Either isomer polymerizes much slower than butadiene.[5b] It may further be noted from Fig. 1 that the *trans* isomer does not completely polymerize, but stops after a conversion of approximately 42%. This retardation is most likely due to the formation of piperylene dimer during the polymerization reaction, since the latter is known to be a retarder of addition polymerization.[5] Additional evidence is provided by an accelerated polymerization of the piperylenes. Points 1 and 2 in Fig. 1 represent the conversions of the *cis* and *trans* isomers, respectively. In this case the time of reaction was much shorter, less *trans*-piperylene could be converted to the dimer, and less retardation resulted.

Polymers obtained from the two piperylenes are rubbery and appear similar in physical proper-

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(6) Dr. David Craig of The B. F. Goodrich Company has reported a sample of this *cis*-piperylene to be free of cyclopentene, judging from tests with cuprous chloride.

(7) The presence of *cis*-piperylene in the product after iodine isomerization was first pointed out to us in private communications by Drs. H. L. Trumbull of the B. F. Goodrich Company and F. D. Rossini of the National Bureau of Standards on the basis of infrared spectra of piperylene samples submitted to them.

(8) *Cf.* Diels and Alder, *Ann.*, **470**, 102 (1929); I. G. Farbenindustrie, *Chem. Zentr.*, **102**, I, 2939 (1931); Arbuzov, Zinov'eva and Fink, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 2278 (1937); *C. A.*, **32**, 507 (1938); Fieser and Seligman, *Ber.*, **68B**, 1747 (1935); Arbuzov and Nikanorov, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 649 (1940); *C. A.*, **34**, 7896 (1940); Arbuzov and Spekterman, *Trans. Kirov. Inst. Chem. Tech. Kazan*, No. 8, 21 (1940); *C. A.*, **35**, 2498 (1941).

(9) *Cf.* Lebedev and Merezhkovskii, *J. Russ. Phys.-Chem. Soc.*, **45**, 1249 (1913), *C. A.*, **8**, 321 (1914).

(10) The *trans*-piperylene used for the polymerization experiments was that obtained by iodine isomerization of the *cis* isomer. Thus it contained approximately 14% of the latter.

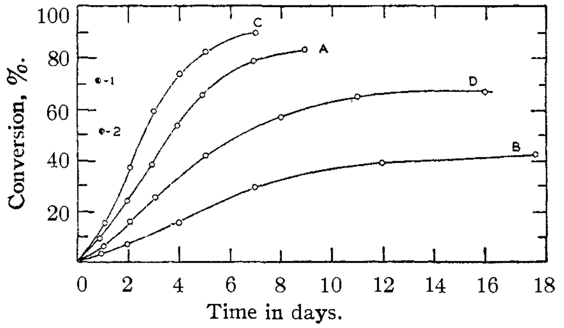

Fig. 1.—Emulsion polymerization rates of piperylene and piperylene–styrene mixtures; A, *cis*-piperylene; B, *trans*-piperylene; C, 75:*cis*-piperylene–25:styrene; D, 75:*trans*-piperylene–25:styrene; point 1, *cis*-piperylene in accelerated recipe; point 2, *trans*-piperylene in accelerated recipe.

ties. Infrared absorption spectra (Fig. 2) of the polymers are also essentially identical, perhaps indicating that the activated monomer during polymerization is the same for either isomer. No evidence was obtained to show a *cis* or *trans* structure in the final polymer.

Copolymers of the two isomers with styrene (monomer ratio 75:25) were also rubbery and quite similar, although ultraviolet analyses have shown that styrene enters the copolymer to a greater extent with *trans*-piperylene (25.4%) than with *cis*-piperylene (19.6%).

Experimental

***cis*-Piperylene from Technical Piperylene.**—In a 1-liter, three-necked flask fitted with a reflux condenser, Hershberg stirrer and dropping funnel were placed 245 g. (2.50 moles) of maleic anhydride and 3 g. of picric acid. The mixture was heated to 55° with an oil-bath to melt the maleic anhydride. Stirring was started and 272 g. (4.00 moles) of distilled Koppers Co. piperylene (b. p. 42.0–43.0°, n^{20}D 1.4328) was added at such a rate that the mixture refluxed gently. The addition required one hour and the mixture was heated under reflux with stirring for two hours more. The unreacted piperylene (120 g.) was removed by distillation, n^{20}D 1.4354. It was again refluxed with 25 g. of maleic anhydride in the presence of a small amount of trinitrobenzene for one-half hour. Redistillation of the final product through a 2-ft., glass, helix-packed column gave 111 g. of *cis*-piperylene, b. p. 43.5°, n^{20}D 1.4360. Its freezing point, in air at 1 atmosphere pressure, was −140.92°, kindly furnished by Dr. F. D. Rossini of the National Bureau of Standards.

Some technical piperylene contains ethyl ether which cannot be separated by fractional distillation (an azeotrope probably exists). In such cases the ether may be readily removed by continuous extraction with water in a counter-current, spinner extractor similar to that described by Ney and Lochte.[11] The piperylene is introduced at the bottom of the water-containing tower, rises to the top, overflows into a receiver from which it siphons into a distilling flask, and is then volatilized. The vapors are condensed so that the liquid flows through a tube to the inlet jet at the bottom of the washing cylinder, thus completing the cycle. A downward flow of fresh water is maintained in the tower.

3-Methyl-1,2,3,6-tetrahydrophthalic Anhydride.—In a 1-liter, round-bottomed flask fitted with a reflux condenser were placed 98 g. (1.00 mole) of maleic anhydride, 136 g. (2.00 moles) of redistilled technical piperylene (n^{20}D 1.4328), 500 ml. of benzene and 0.5 g. of picric acid. The mixture was heated to start the reaction which then proceeded with the evolution of considerable heat. The mixture was further heated under gentle reflux for twenty hours. The benzene and unreacted piperylene were removed by distillation under diminished pressure. The residue which crystallized when cooled was heated with 250 ml. of petroleum ether (90–110°) and enough benzene to effect solution. After treatment with Norite, 116 g. (70%) of product crystallized as colorless needles, m. p. 61° (cor.) (lit.[12] 61°).

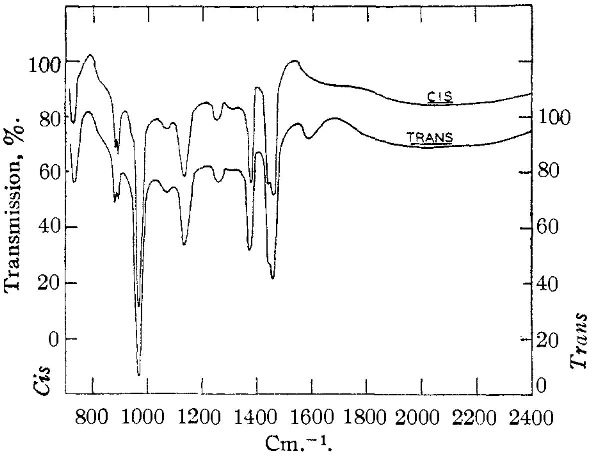

Fig. 2.—Infrared spectra of emulsion polymers from *cis*- and *trans*-piperylenes.

Pyrolysis of 3-Methyl-1,2,3,6-tetrahydrophthalic Anhydride.—Four hundred and fifteen grams (2.50 moles) of 3-methyl-1,2,3,6-tetrahydrophthalic anhydride was pyrolyzed by passing it through a vertical, 18-mm., Pyrex tube filled with glass beads and heated to 575–600° by means of a 12-in. combustion furnace. The pyrolyzate dropped into a receiver containing an excess of aqueous sodium carbonate solution maintained at 60–70°. The purpose of this solution was to dissolve the maleic anhydride formed and thus prevent it from recombining with the piperylene. The volatile material leaving the receiver was collected in a Dry Ice trap and redistilled to give 63 g. (37%) of impure piperylene, b. p. 41.0–42.0°, n^{20}D 1.4315.

Interconversion of *cis*- and *trans*-Piperylenes: *cis*-Piperylene and Iodine.—A mixture of 90 g. of *cis*-piperylene (n^{20}D 1.4360) and 1 g. of iodine was refluxed with a trace of trinitrobenzene for eighteen hours after which the piperylene was removed by distillation through a 6-in. Vigreux column to give 86 g. of mixed product, b. p. 42.0°, n^{20}D 1.4308. Its freezing point, in air at 1 atmosphere pressure, was −94.14°, kindly furnished by Dr. F. D. Rossini of the National Bureau of Standards. Starch–iodide and alcoholic silver nitrate tests indicated that no iodine nor iodide was carried over with the piperylene. Refluxing for as long as twenty-one days gave material of the same refractive index, thus indicating that equilibrium had been reached after eighteen hours.

The technical mixture of piperylene isomers (n^{20}D 1.4328) was likewise converted to a product of (n^{20}D 1.4308).

The refractive index (n^{20}D 1.4308) indicates an 87:13 ratio of *trans*- to *cis*-piperylenes. To determine more surely the presence and amount of *cis*-piperylene, 5.086 g. (0.0519 mole) of maleic anhydride, 4.251 g. (0.0625 mole) of the piperylene and 0.403 g. of picric acid were sealed in a glass tube and shaken for three hours in a water bath at 50°. The tube was opened and the unreacted piperylene distilled at 1 mm. pressure by fusing the

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(11) Ney and Lochte, *Ind. Eng. Chem.*, **33**, 825 (1941).

(12) Farmer and Warren, *J. Chem. Soc.*, 3221 (1931).

reaction mixture on a steam cone. The piperylene was collected in a Dry Ice trap and redistilled at atmospheric pressure, b. p. 43°, $n^{20}\mathrm{D}$ 1.4342. A recovery of 0.592 g. (82% of the theoretical amount assuming complete reaction of maleic anhydride) was obtained. Calculation ((0.0625 − 0.0519) × 42 × 100 ÷ 0.0625 × 60) indicates an original *cis*-piperylene content of 12%.

Preparation of Pure *trans*-Piperylene.—A quantity of pure *trans*-piperylene was prepared through the cyclic sulfone by the method of Craig.[3] From 128 g. (2.00 moles) of liquid sulfur dioxide, 68 g. (1.00 mole) of piperylene ($n^{20}\mathrm{D}$ 1.4308) and 5 g. of hydroquinone was obtained 107 g. (81%) of clear oily sulfone. This was decomposed at 95–120° to give 36 g. (65% from the sulfone) of *trans*-piperylene, b. p. 42.0°, $n^{20}\mathrm{D}$ 1.4300. Proof that this material contained no *cis* isomer was obtained by heating in a sealed tube at 50° for twenty-four hours 0.919 g. (0.0094 mole) of maleic anhydride, 1.082 g. (0.0159 mole) of the piperylene and 0.021 g. of trinitrobenzene. The unreacted piperylene was redistilled to give 0.348 g. (79% of the theoretical recovery assuming complete reaction of maleic anhydride), b. p. 42°, $n^{20}\mathrm{D}$ 1.4300. Any *cis*-piperylene present would have been concentrated by this treatment with consequent increase in refractive index.

***trans*-Piperylene and Iodine.**—To a mixture of 8.0 g. (0.12 mole) of *trans*-piperylene ($n^{20}\mathrm{D}$ 1.4300) and 0.5 g. of picric acid was slowly added 0.1 g. of iodine and the mixture sealed in a glass tube and heated at 50° for twenty-four hours. The piperylene was distilled from the mixture, shaken with zinc dust, and redistilled to give 5.5 g. (69% recovery), b. p. 42.5°, $n^{20}\mathrm{D}$ 1.4308.

Determination of *cis*-piperylene in this sample was carried out by heating 5.265 g. (0.0774 mole) with 4.998 g. (0.0510 mole) of maleic anhydride and 0.418 g. of picric acid in a glass tube for four hours at 50°. The unreacted piperylene, removed by distillation and redistilled, weighed 1.467 g. (82% recovery), b. p. 43°, $n^{20}\mathrm{D}$ 1.4328. Calculation ((0.0774 − 0.0510) × 28 × 100 ÷ 0.0774 × 60) indicates an original *cis*-piperylene content of 16%. A check run on the same mixture gave a value of 14%.

To show further the presence of *cis*-piperylene, this isomer was obtained pure by complete reaction of the *trans* form with maleic anhydride. A mixture of 1.258 g. (0.0185 mole) of the above piperylene ($n^{20}\mathrm{D}$ 1.4328), 4.113 g. (0.0419 mole) of maleic anhydride and 0.171 g. of picric acid was heated in a sealed tube at 56° for four hours. Redistillation of the recovered piperylene gave 0.473 g. (81% of the theoretical recovery), b. p. 44°, $n^{20}\mathrm{D}$ 1.4360.

Effect of Sulfur.—Refluxing with sulfur in place of iodine gave no isomerization after eighteen hours.

Effect of Heat.—Eighty-eight grams (1.29 moles) of *trans*-piperylene was passed through a vertical Pyrex tube packed with glass beads at 600° during a one and one-quarter hour period. Distillation of the product gave, in addition to a 7-g. fore-run, b. p. 38.0–41.7°, 67 g. (75% recovery) of a mixture of piperylenes, b. p. 41.7–43.2°, $n^{20}\mathrm{D}$ 1.4327. On the basis of its refractive index it contained 45% of the *cis* isomer. At temperatures below 500° no isomerization was detected. At temperatures above 650° the recovery of piperylene was diminished.

A similar experiment starting with *cis*-piperylene gave a 74% recovery, $n^{20}\mathrm{D}$ 1.4324, containing, on the basis of its refractive index, 40% of the *cis* isomer.

Effect of Ultraviolet Light.—Ultraviolet irradiation of *trans*-piperylene caused no change in refractive index after one hundred eight hours.

2,4-Pentanediol.—The method of Sprague and Adkins[13] was used, with 400 g. (4.00 moles) of acetylacetone in 800 ml. of dry ether to give 352 g. (85%) of product, b. p. 96–97° (11 mm.), $n^{20}\mathrm{D}$ 1.4348.

Diacetate of 2,4-Pentanediol.—In a 3-liter flask fitted with a reflux condenser were placed 352 g. (3.38 moles) of 2,4-pentanediol and 898 g. (8.80 moles) of acetic anhydride. The mixture was heated carefully until the initial exothermic reaction was over and then refluxed for eight hours. Fractional distillation through a 10-in., helix-packed column gave 599 g. (94%) of diacetate, b. p. 88–91° (11 mm.), $n^{20}\mathrm{D}$ 1.4160.

Pyrolysis of Diacetate of 2,4-Pentanediol.—The pyrolysis of 3243 g. (17.23 moles) of the diacetate was conducted by passing it at a rate of about one drop per second through an 18-mm., Pyrex tube filled with glass beads and heated to 575–600°. The pyrolyzate was condensed in an ice-cooled receiver and redistilled, after the addition of 1 g. of trinitrobenzene through a 48-in., helix-packed column equipped with a magnetic total reflux-partial take-off head at a reflux ratio of 130:1. There was obtained 89.5 g. (7.6%) of nearly pure 1,4-pentadiene, b. p. 24–28°, $n^{20}\mathrm{D}$ 1.3906, and 867.5 g. (74%) of mixed piperylenes, b. p. 41–44°, $n^{20}\mathrm{D}$ 1.4313. The piperylenes were carefully refractionated to give 375.0 g. of nearly pure *trans* isomer, b. p. 42.0–42.2°, $n^{20}\mathrm{D}$ 1.4308, and 59.0 g. of pure *cis* isomer, b. p. 44.0°, $n^{20}\mathrm{D}$ 1.4360, as well as a large intermediate fraction.

A sample of the *cis* isomer was refluxed for one and one-half hours over maleic anhydride and redistilled. The refractive index was unchanged after this treatment, indicating the absence of *trans* isomer.

Adduct of *trans*-Piperylene with Acrylonitrile.—A mixture of 13.6 g. (0.20 mole) of *trans*-piperylene, 10.6 g. (0.20 mole) of acrylonitrile, and a trace of trinitrobenzene was placed in a steel reaction vessel and heated on a steam cone for twenty-four hours. Fractional distillation of the product gave 13.5 g. (56%) of adduct, b. p. 72–74° (9 mm.), $n^{20}\mathrm{D}$ 1.4682.

Anal. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15. Found: C, 79.37; H, 9.02.

To 22.0 g. (0.182 mole) of the adduct in a 100-ml., round-bottomed flask fitted with a reflux condenser was added 11.6 g. (0.364 gram atom) of sulfur. The mixture was heated in a Wood's metal-bath at 200° for thirty minutes and then at 250° for thirty minutes. A little zinc dust was added and the mixture reheated at 225° for fifteen minutes. Distillation gave 8.0 g. of product, b. p. 85° (13 mm.), $n^{20}\mathrm{D}$ 1.5193.

To 3.0 g. of the dehydrogenated adduct was added 50 ml. of 10% aqueous sodium hydroxide and the mixture was refluxed for twelve hours. Dilute hydrochloric acid was added and the white precipitate which formed was recrystallized from 100 ml. of aqueous ethanol. The 2.2 g. of pure white crystals obtained, m. p. 104–105° (cor.), gave no depression in m. p. when mixed with an authentic sample of *o*-toluic acid. By concentration of the mother liquor from the recrystallization there was obtained 0.3 g. of a white solid, which on recrystallization from water melted at 110–111° (cor.). A mixed m. p. with an authentic sample of *m*-toluic acid was not depressed.

A similar mixture of *cis*-piperylene and acrylonitrile gave a complete recovery of the starting material and no trace of the adduct.

Dimerization of *trans*-Piperylene.—When 15.0 g. of *trans*-piperylene containing a trace of trinitrobenzene was kept in a sealed tube at 50° for 17 days and then evaporated a residue of less than 1 g. was obtained, $n^{20}\mathrm{D}$ 1.4713 (after distillation). No such residue was obtained with the *cis* isomer.

Polymerization of the Piperylenes.—Polymerizations were carried out in 4-oz., screw-cap bottles, using the recipe and technique described by Frank, Adams, Blegen, Deanin and Smith[5] with 20 g. of *cis*- or *trans*-piperylene, or in copolymerizations 15 g. of piperylene and 5 g. of styrene. Their technique of sampling and determination of yield were also employed. The accelerated polymerizations represented by points 1 and 2 in Fig. 1 were obtained with the following recipe: 50.0 g. of piperylene, 0.250 g. of benzoyl peroxide, 0.250 g. of ferrous sulfate heptahydrate, 0.350 g. of *l*-sorbose, 2.500 g. of sodium pyrophosphate decahydrate, 102.5 g. of a mixture of 6.0 g. of Procter and Gamble SF soap flakes and 240 g. of conductivity water.

In all polymerizations the piperylenes were distilled immediately before use.

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(13) Sprague and Adkins, THIS JOURNAL, **56**, 2669 (1934).

Ultraviolet and Infrared Absorption Spectra.—Samples were prepared for absorption studies by coagulation with 500 ml. of ethanol of polymerized lattices from 20 g. of monomer. No antioxidant was added. The polymers were washed with ethanol and dried *in vacuo* at room temperature.

Ultraviolet analyses for styrene content[14] were determined by the method of Meehan.[15]

The infrared absorption spectra[14] (Fig. 2) are considered to be identical. The difference at 1580 cm.$^{-1}$ is attributed to an experimental error.

Acknowledgment.—The authors are indebted to Dr. David Craig of The B. F. Goodrich Company for helpful suggestions in the preparation of the manuscript and to Dr. B. M. Vanderbilt of Esso Laboratories for a generous supply of piperylene.

Summary

The preparation and properties of *cis*- and *trans*-piperylenes (1,3-pentadienes) have been investigated.

The pyrolysis of 2,4-diacetoxypentane results in a mixture of *cis*- and *trans*-piperylenes which can be separated by careful fractional distillation.

Both *cis*- and *trans*- piperylenes are converted to a 14:86-*cis*:*trans* mixture by refluxing with iodine. Thermal isomerization at 600° results in an approximately 3:4-*cis*:*trans* mixture. Sulfur and ultraviolet light do not effect isomerization.

The adduct of *trans*-piperylene with acrylonitrile has been shown to be chiefly 2-methyl-1,2,5,6-tetrahydrobenzonitrile and partly 3-methyl-1,2,3,6-tetrahydrobenzonitrile. The *cis* isomer does not react with acrylonitrile.

Emulsion polymerization of *cis*-piperylene is much faster than that of *trans*-piperylene, with or without styrene as a comonomer. The polymers are rubbery. Emulsion polymers of the *cis* and *trans* isomers appear to be identical in respect to infrared absorption.

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[14] Ultraviolet analyses were carried out by Mr. J. S. Nelson and Miss Ruth Johnston. Infrared absorption spectra were determined by Mr. W. B. Treumann and Mrs. J. L. Johnson.

[15] Meehan, *J. Polymer Sci.*, **1**, 175 (1946).

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The Structure of the Branched Chain Fatty Acids in Wool Fat. An X-Ray Diffraction Study[1]

BY SIDNEY F. VELICK

The branched chain fatty acids of wool fat contain, in addition to the usual homologous series of normal acids with even numbered carbon chains, two homologous series of branched chain acids.[2] One of these, the iso series, consists of members with odd numbered carbon chains and a branching methyl group in the penultimate position, the location of which was determined by conversion of the C_{16} and C_{18} members to the previously known 17-methyloctadecanoic acid. The second, or so-called anteiso series, consists of members with even numbered chains and a branching methyl group in the antepenultimate position. One member of the anteiso series, *d*-14-methylhexadecanoic acid, has been synthesized in the optically active form, confirming the proposed structure and configuration.[3] In both cases the homology of the remaining members of the series was inferred from the neutralization equivalents, characteristic crystal habits, and orderly sequence of melting points. The present X-ray study was undertaken with the object of establishing homology by independent means, and of investigating the observation that the melting points of the amides, as the series are ascended, do not lie on a smooth curve but exhibit a periodic relationship.

Long chain aliphatic compounds tend to crystallize in the form of thin leaflets with the molecules either perpendicular to the leaflet surface or tilted at characteristic angles.[4] Consequently the spacings of the crystal planes parallel to the leaflet's surface are functions of the molecular length. If the members of a homologous series form an isomorphous series of crystals, which is usually the case, the spacing increments as the series is ascended are approximately constant or show a simple periodicity which is a function of the arrangement of the chain carbon atoms. Thus the increments in spacing between adjacent members of the normal fatty acid series show a simple alternation which arises from the zig-zag configuration of the tilted chains.[5] The differences in the orientation of the terminal groups of odd and even members with respect to the chain axis affects not only the spacing increment but also the melting points and is responsible for the well known alternation of melting points between odd and even members of the series.[6]

The Homology of the Iso Acids.—Since both the *iso* and *anteiso* series of acids from wool fat are built up by units of 2 carbon atoms it was to be expected, if the series were homologous and isomorphous, that the long spacings would increase

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[1] Part of the work reported here was done in 1945 at the Sterling Chemistry Laboratory, Yale University.

[2] A. W. Weitkamp, THIS JOURNAL, **67**, 447 (1945).

[3] S. F. Velick and J. English, Jr., *J. Biol. Chem.*, **160**, 473 (1945).

[4] Th. Schoon, *Z. physik. Chem.*, **39B**, 385 (1939).

[5] F. Francis and S. H. Piper, THIS JOURNAL, **61**, 577 (1939).

[6] T. Malkin, *Trans. Faraday Soc.*, **29**, 977 (1933).