methyl acrylate. Both mass (without solvent) and solution (20% in ethyl acetate) polymerization techniques were employed. The effects produced by the allyl and methallyl esters were similar, although that of the allyl ester was somewhat more pronounced. When the monomer mixture contained 1% or more of the allyl or methallyl ester, the polymer was noticeably harder and tougher than polymethyl acrylate and was insoluble in acetone or ethyl acetate. Some change in hardness and solubility of the polymer was detectable when only 0.1% of the allyl or methallyl methacrylate was present.

Summary

1. Satisfactory methods were developed for preparing allyl and methallyl α-hydroxyisobutyrates from hydroxyisobutyric acid and the appropriate alcohol.

2. The hydroxy esters were converted into allyl and methallyl α-acetoxyisobutyrates by treatment with acetic anhydride.

3. Under milder conditions than those required for the thermal decomposition of the corresponding acetoxypropionates, allyl and methallyl acetoxyisobutyrates were transformed satisfactorily by pyrolysis into allyl and methallyl methacrylates.

4. These results and data previously reported indicate that (1) esters of α-acetoxyisobutyric acid yield unsaturated esters more readily when pyrolyzed than do corresponding lactic acid derivatives and (2) that esters prepared from allyl and methallyl alcohols are more stable than those prepared from *n*-butyl and β-phenoxyethyl alcohols but less stable than esters prepared from methyl, benzyl and ethyl alcohols. Allyl, methallyl and β-methoxyethyl esters appear to have approximately the same thermal stability.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE B. F. GOODRICH COMPANY AND THE HYCAR CHEMICAL COMPANY]

The Geometric Isomers of Piperylene

BY DAVID CRAIG

During a current study of dienes in this Laboratory, it has been possible to effect the separation of the piperylene isomers by a variety of chemical methods and also by fractional distillation. The isomers thus secured have been found to have the properties shown in Table I. The assignment of the *trans* configuration to the lower boiling isomer, prepared but not identified by Dolliver, Kistiakowsky and Vaughan,[1] is based on the method of preparation from piperylene sulfone and on analogy to work by other investigators on the pentene-2 isomers. The assignment of *cis* configuration to the higher boiling isomer is confirmed by its behavior toward sulfur dioxide and maleic anhydride.

TABLE I

THE PROPERTIES OF THE PIPERYLENE ISOMERS

Isomer	Boiling point °C.	Boiling point Mm.	d^{20}_{20}	n^{20}_{D}	Diene content, % By hydrogenation	Diene content, % By Diels Alder reaction
cis	43.8	750	0.6916	1.4360	100	0
trans	41.7	745	.6771	1.4300	100	99+

In addition to its preparation from the sulfone *trans*-piperylene was prepared according to Lurji, *et al.*,[2] by the decomposition of the cuprous chloride addition compound. This solid derivative was secured from a C_5 fraction of a petroleum pyrolyzate by reaction with cuprous ammonium chloride. In a similar manner the corresponding solid addition compound of the *cis* isomer was secured from a higher boiling fraction. The debromination of the 1,2,3,4-tetrabromopentane racemate (m. p. 114°) supplied a mixture containing approximately equal amounts of the isomers. In agreement with Robey, Morrell and Weiss[3] *trans*-piperylene was found to react more rapidly with maleic anhydride than *cis*, thus affording a means of isolating the latter isomer. Mixtures of the isomers were also resolved by reaction with sulfur dioxide, the *cis*-isomer again reacting more slowly. These reactions are described below in considerable detail.

The presence of cyclopentene in many piperylene preparations may have escaped the attention of earlier investigators. Cyclopentene, which is also a C_5H_8 hydrocarbon, was found to form a constant boiling mixture with *cis*-piperylene.

The Chemical Properties of the Piperylene Isomers

cis-Piperylene vapor is absorbed slowly but

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[1] Dolliver, Kistiakowsky and Vaughan, THIS JOURNAL, **59**, 833, 837 (1937).

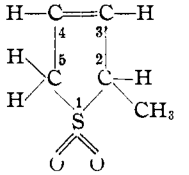
[2] Lurji, *et al.*, *Synthetic Rubber* (U. S. S. R.), **3**, No. 6, 13 (1934); *Chem. Zentr.*, **106**, II, 1977 (1935).

[3] Robey, Morrell and Weiss, THIS JOURNAL, **63**, 627 (1941).

completely by maleic anhydride at 100°. When sealed tube reactions were conducted a polymeric reaction product was formed from which none of the expected methyl tetrahydrophthalic anhydride could be isolated. The apparent conflict between this behavior and that reported by Robey, *et al.*,[3] can probably be explained on the basis that their preparation contained a low refractive impurity.

trans-Piperylene reacts rapidly and completely (99% in about three minutes) with maleic anhydride at 100°. As shown by reaction in sealed tubes 3-methyl-1,2,3,6-tetrahydrophthalic anhydride is formed in nearly the theoretical yield. Not more than traces of polymeric material are formed. This observation is in partial agreement with the work of Farmer and Warren,[4] who reported a 95% yield of the methyl tetrahydrophthalic anhydride from what now appears to be largely *trans*-piperylene.

While *cis*-piperylene thus far has displayed no ring forming tendency with maleic anhydride, it does react sluggishly with sulfur dioxide to form piperylene sulfone (2,5-dihydro-2-methylthiophene-1-dioxide). This compound (Formula I) is formed more readily from *trans*-piperylene. With both isomers the yield is enhanced by the presence of phenyl-β-naphthylamine or of a polyhydric phenol[5] which represses the yield of polysulfone. The presence of an inert solvent lowers the conversion to sulfone while an excess of sulfur dioxide, in which the dienes and sulfones are very soluble, increases it.



I

Since both *cis*- and *trans*-piperylene react with sulfur dioxide to form the same sulfone which on decomposition gives solely *trans*-piperylene, this reaction serves as a means for isomerizing the *cis*-piperylene to the *trans*.

Piperylene sulfone is a water-soluble oil. It differs from some other diene sulfones such as those from 1,3-butadiene or isoprene in that it decomposes at a somewhat lower temperature.

Both piperylenes may be hydrogenated quantitatively to *n*-pentane at room temperature.

Both isomers react with bromine to form a mixture of 1,2,3,4-tetrabromopentane racemates of which four are possible. *cis*-Piperylene is characterized by the relatively high yield of solid tetrabromide (m. p. 114°) that may be obtained. The solid is higher boiling than the other tetrabromides and can be concentrated by fractional distillation.

Both piperylenes react at room temperatures with the cuprous ammonium chloride solutions of Lurji, *et al.*,[2] to form solids which are stabilized by the presence of sufficient cuprous chloride to keep the aqueous phase saturated. Of special interest from the viewpoint of purification procedures (see Table IV) is the fact that no inversion of configuration occurs when the complexes are decomposed by heating to 60 to 90°. Thus the view of Hel'man[6] that complex formation does not involve a disturbance of the diene structure is confirmed. The C_5 alkenes and alkanes boil below 50° and, therefore, if present, can be distilled from the complexes, although in a single stage the separation of the piperylenes thus realized is not quantitative.

In connection with the application of the cuprous ammonium chloride treatment (Table IV) to the problem of separating the isomers it is to be noted that very little separation occurs if mixtures containing up to about 50% of the *cis*-isomer are used, and that which does occur favors the concentration of the *trans*-isomer as the least volatile portion. From a mixture containing 75% of *cis*-piperylene, however, there is a strong tendency to form a mixture containing somewhat less than 50% of the *cis*-isomer as the most volatile portion and the pure *cis*-isomer as the least volatile portion, revealing that the *cis*-isomer has been obtained almost configurationally pure. Likewise the cuprous chloride treatment when applied to the piperylene mixture secured by the debromination of the solid tetrabromide showed that the mixture is free of hydrocarbons other than diolefins, since very little separation could be observed.

The Correlation of Structure with the Properties of the Piperylene Isomers.—There are four structures to be considered if the possibility of restricted rotation around the single bond of the conjugated system is postulated. These are indicated by Formulas IIIa, IIIb, IVa and IVb, but are more accurately represented by molecular models. Only the models for *cis*-piperylene (IIIa and IIIb) indicate restriction to rotation around

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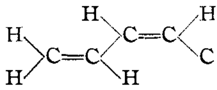
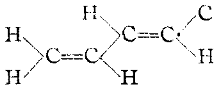
(4) Farmer and Warren, *J. Chem. Soc.*, 3224 (1931).

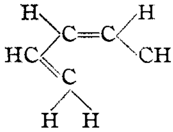
(5) Staudinger and Ritzenthaler, *Ber.*, **68**, 455 (1935).

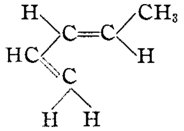
(6) Hel'man, *Compt. rend. acad. sci.* (U. S. S. R.), **23**, 532 (1939). See also Winstein and Lucas, THIS JOURNAL, **60**, 836 (1938).

the single bond of the diene system. But even in the case of butadiene Pauling and co-workers[7] as a result of electron diffraction studies assign an appreciable double bond character to this single bond and consider that the molecule is coplanar and *trans*; *i. e.*, it has the chair form as in IIIa and IVa. The steric hindrance around the single bond of the *cis*-piperylene model makes it seem reasonable to predict the chair form for this molecule.


IIIa, Chair form


IVa, Chair form

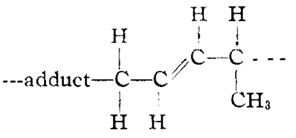

IIIb, Boat form, *cis*-Piperylene

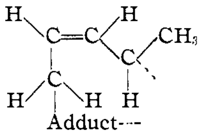

IVb, Boat form, *trans*-Piperylene

Both chair and boat forms of the isomers would be expected to undergo reactions which do not involve ring formation such as hydrogenation, bromination, polymerization and complex formation with cuprous chloride. Both piperylenes undergo these reactions but at least in the case of complex formation *trans*-piperylene seems to form a slightly more stable derivative than *cis*-piperylene. This is shown by the data in Table IV.

There is a striking difference between *cis*-piperylene and the other C_4 and C_5 dienes so far as reaction with ring forming addenda is concerned. However, the failure of *cis*-piperylene to form 3-methyl-1,2,3,6-tetrahydrophthalic anhydride by reaction with maleic anhydride is to be expected of this isomer since, as reported by several investigators,[8] a 1,3-diene such as 4-methyl-1,3-pentadiene which necessarily must have a hydrocarbon radical in the *cis* position will react to form a copolymer rather than a tetrahydrophthalic anhydride. The other dienes give good yields of the expected crystalline product.

Ring formation of *cis*-piperylene with sulfur dioxide and lack of it with maleic anhydride can be explained by assuming the formation of bivalent free radicals VIa and VIb as intermediates. In these molecules the diene single bond becomes a double bond and the double bonds assume a single bond character. Examination of the molecular model for VIa indicates that it could be formed from the chair forms of the piperylenes with no hindrance due to steric effects. On the other hand VIb would be expected directly from the boat form of *trans*-piperylene but only by rearrangement from the other piperylene forms. The reactions expected of VIa are reversion to a mixture of *cis*- and *trans*-piperylenes and polymerization. With VIb the reactions expected are *trans*-piperylene formation and ring closure. The relative rates of these reactions will determine the yields of the products.


VIa


VIb

Thus from *cis*-piperylene in the presence of maleic anhydride the high yield of polymer and absence of *trans*-isomer formation could be explained by assuming the formation of VIa and its rapid polymerization. With sulfur dioxide the rate of polymerization is relatively slow in comparison to reversion to the mixture of *cis*- and *trans*-piperylenes. Therefore, since VIb can be formed readily from the *trans*-piperylene, a certain amount of the cyclic sulfone is formed along with *trans*-piperylene itself. The rate of polymerization of VIa and also of VIb in comparison to reversion to the piperylenes should be lowered by dilution with sulfur dioxide as well as by the presence of polymerization inhibitors and, as already stated, these conditions are desirable for securing a good yield of the sulfone.

The sulfone I on decomposition yields essentially pure *trans*-piperylene as noted earlier. Probably VIb is a precursor of the diene in this transformation and VIa is not since it has not been possible to isolate the *cis*-isomer from the decomposition product or find evidence of its presence there. The bond between positions 2 and 3 as a part of the coplanar ring of the sulfone must be *trans* and, due to steric effects of the adduct radical and methyl group, this bond should tend to be *trans* in the free radical VIb. The inference can then be made that it will become a *trans* double bond when the free radical is cleaved to form the diene. The methyl group in the sulfone probably weakens the bond between carbon atom 2 and the sulfur atom since among the sulfones of the dienes those that have methyl groups in the 2

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[7] See Schomaker and Pauling, THIS JOURNAL, **61**, 1773 (1939), for discussion and bibliography.

[8] (a) Bachman and Goebel, *ibid.*, **64**, 787 (1942); (b) Henne and Turk, *ibid.*, **64**, 827 (1942).

position decompose at a lower temperature. This effect is indicated by Table II in which the decomposition temperatures are those required to give approximately equal rates of decomposition.

TABLE II

Sulfone from	Decomposition temperature, °C.
2,3-Dimethylbutadiene-1,3	140
Butadiene-1,3	125
Isoprene	125
Piperylene	100
4-Methylpentadiene-1,3	100

The bromination of the piperylenes and debromination of the bromides in a general way supports the structure which has been deduced from consideration of reactions with ring forming addenda. The addition of the first molecule of bromine probably forms a mixture of *cis* and *trans* dibromo-2-pentenes. The addition of the second molecule of bromine should then occur after the fashion of the bromination of 2-pentenes as studied by Lucas, Schlatter and Jones,[9] who presented evidence that the bromination of *cis*-2-pentene gave at least a 97% yield of *threo* dibromide and the *trans* isomer gave at least a 98% yield of *erythro* dibromide. The *threo* dibromide is the higher melting. Thus from the dibromides of the *cis*-piperylene, which should contain a preponderance of the *trans*-dibromide, it would be expected that two *threo* tetrabromides would be obtained. These should be higher melting than the corresponding *erythro* tetrabromides obtained from *trans*-piperylene by an analogous mechanism. It is thus suggested that the tetrabromide melting at 114° is a *threo* tetrabromide.

Since the debromination of a *threo* or an *erythro* dibromide forms a *cis* or a *trans*-olefin, respectively, according to Lucas and co-workers, it is notable that the debromination of piperylene tetrabromide melting at 114° gives nearly a 50% mixture of the two piperylenes. This is readily explained if it is assumed that debromination occurs first at the 2 and 3 positions to form a racemic 1,4-dibromo-*trans*- or *cis*-2-pentene. Debromination of this, regardless of whether it is *cis* or *trans* should then give a mixture of the piperylenes after the fashion of the rearrangement with sulfur dioxide. It should be noted here that the reversion of VIb to the *trans*-isomer occurs under the orienting influence of ring formation and decomposition which accounts for the lack of the formation of the *cis*-isomer, whereas, the removal of bromine from a racemic 1,4-dibromo-2-pentene occurs without any such influence and hence both isomers are expected which indeed has been found to be in accord with experimental fact.

Acknowledgment should be made to Dr. W. L. Semon, who directed this research, and to others in the Goodrich laboratory and that of the Phillips Petroleum Company including Mr. Fred Frey who suggested the possibility of cyclopentene as an impurity and Mr. Hillyer who suggested the Orsat pipet for measuring of diene content. Dr. A. L. Ward kindly contributed the volumetric hydrogenation values in Table I. The preliminary distillation was conducted under the direction of Wendell K. Fitch.

Experimental Part

A piperylene concentrate was purchased from the United Gas Improvement Company at Philadelphia.[10] It was subjected to a preliminary distillation through a pilot plant column having approximately thirty theoretical plates. The eight fractions (Fractions A through H) thus secured were collected between 32 and 43.4°. The index of refraction, $n^{20}D$, varied between 1.4030 and 1.4326. The fractions were contacted with a variety of diene reagents including maleic anhydride, sulfur dioxide, and cuprous ammonium chloride. Isoprene and the piperylene isomers were thereby isolated and identified.

The Determination of Diene Content.—This was done with gas samples prepared by diluting 40 ml. of nitrogen with sufficient of the vaporized C_5 mixtures to be analyzed to cause an increase in volume of 15 to 20.0 ml. The pipet was an Orsat type with a steam jacket around it. The absorbent consisted of about 2.5 g. of maleic anhydride floating on mercury which was used as the confining liquid. At least one "saturating absorption" was made before each analysis. The gas was allowed in the pipet for only about one minute for each transfer to and from the buret for measuring the contraction in volume. The diene content of Fraction A containing isoprene was 78% and of Fractions F, G and H which contained the piperylenes was found to be 70 to 75%.

The Isolation of the *cis*-Piperylene by Cuprous Ammonium Chloride Treatment.—A mixture of 1600 g. (8.1 moles) of cuprous chloride, 800 g. (15.1 moles) of ammonium chloride, 2000 g. of water, 100 ml. of concentrated hydrochloric acid, and 50 g. of copper wool was prepared in a five-liter, 3-necked flask equipped with a stirrer and thermometer. The flask was stoppered and the mixture stirred for thirty minutes and then allowed to stand overnight. The flask was placed in a 25° water-bath and 300 g. (4.4 moles) of Fraction H from the preliminary distillation was added. This fraction had been collected at

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[9] Lucas, Schlatter and Jones, THIS JOURNAL, **63**, 22 (1941).

[10] According to information supplied through Dr. A. L. Ward of U. G. I. this product was prepared by a high temperature petroleum cracking process involving checkerwork. The concentrate as supplied comprised the C_5 fraction of the pyrolyzate from which most of the isoprene, cyclopentadiene and monoölefins originally present had been removed.

42.5 to 43.4° and had $n^{20}D$ 1.4326. The stirrer was started and the reaction began immediately, as evidenced by the formation of a bulky solid and the partial disappearance of the hydrocarbon layer. The evolution of heat was slight. When considerable amounts of monoölefins and paraffins are present the liquid layer does not disappear entirely. The flask was connected to a dry-ice cooled trap by means of a 2.5 × 40 cm. vertical glass tube. The temperature of the slurry was raised gradually in order to effect the progressive decomposition of the addition compounds and concurrent distillation of the hydrocarbons. The data collected are summarized in Table III, in which the temperatures listed are those of the decomposing liquid.

TABLE III

Temperature, °C.	Fraction	Weight, g.	B. p., °C.	$n^{20}D$
43-48	a	88		1.4260
48-54	b	19		1.4287
54-64	c	53		1.4234
64-65	d	47	43.4-43.9	1.4357
65-65.5	e	35	43.6-44.0	1.4361
65-97	f	65	43.4-44.0	1.4359

The decomposition accompanied by foaming required from four to eight hours for 300 g. of hydrocarbon. The addition of pentanol-1 reduced the foaming but in several experiments it was found preferable to decrease the size of the charge of both slurry and hydrocarbon by about 30%. The fractions contained a total of approximately 10 g. of water which was removed with a pipet and drying over calcium chloride before determining the boiling points and refractive indices. Fractions e and f from the treatment of Fraction H were united and 78.5 g. distilled through a 1.5 m. x 8 mm. coil column at approximately 10/1 reflux. A moist forerunnings (13.5 g.) came over at 43 to 43.8°. The main fraction (51.5 g.) distilled at 43.8° (750 mm.) and had the properties given in Table I for *cis*-piperylene.

Anal. Calcd. for C_5H_8: C, 88.12; H, 11.84. Found: C, 88.12, 88.16; H, 11.78, 11.78.

The efficiency of cuprous ammonim chloride treatment increases with the excess of cuprous chloride and to some extent with the size of the runs and with the time allowed for the decomposition. Table IV contains data from several small-scale runs in which the slurry was prepared from 110 g. (0.55 mole) of cuprous chloride, 74 g. of ammonium chloride, 200 g. of water, 20 ml. of concentrated hydrochloric acid and 10 g. of copper wool. These data are discussed elsewhere in this paper.

TABLE IV

SUMMARY OF THE TREATMENT OF MISCELLANEOUS PIPERYLENE MIXTURES WITH CUPROUS AMMONIUM CHLORIDE

Mixture treated	$n^{20}D$ of mixture	$n^{20}D$ and weight of fractions produced a	b	c	d
10 g. *cis*-Piperylene	1.4360	1.4354 2.0 g.	1.4359 3.8 g.	1.4360 1.8 g.	1.4361 2.3 g.
10 g. *trans*-Piperylene (from the sulfone)	1.4300	1.4291 1.7 g.	1.4301 2.5 g.	1.4301 2.3 g.	1.4301 2.8 g.
50 g. *cis*-Piperylene 50 g. *trans*-Piperylene	1.4327	1.4327 2.8 g.	1.4327 1.9 g.	1.4327 2.0 g.	1.4326 3.0 g.
75 g. *cis*-Piperylene 2.5 g. *trans*-Piperylene	1.4347	1.4328 3.8 g.	1.4339 1.8 g.	1.4352 1.6 g.	1.4354 2.5 g.
3.0 g. *cis*-Piperylene 9.0 g. *trans*-Piperylene	1.4318	1.4320 3.4 g.	1.4319 2.4 g.	1.4317 2.1 g.	1.4315 3.2 g.
12.0 g. Piperylene from the tetrabromide	1.4327	1.4328 4.5 g.	1.4328 3.5 g.	1.4325 4.0 g.	..
4.0 g. *cis*-Piperylene 4.0 g. *trans*-Piperylene 3.0 g. cyclopentene	1.4303	1.4258 1.1 g.	1.4274 2.0 g.	1.4302 3.0 g.	1.4322 4.1 g.
12.0 g. Fraction H	1.4328	1.4283 3.5 g.	1.4303 2.3 g.	1.4340 3.1 g.	1.4358 3.3 g.

The diene recovered by the cuprous chloride treatment of Fraction D was identified as *trans*-piperylene essentially free of the *cis*-isomer by the rapid reaction to form nearly a theoretical yield of the expected Diels–Alder adduct with maleic anhydride. It also gave the correct carbon and hydrogen values for a C_5H_8 hydrocarbon and agreed in all respects with the hydrocarbon prepared by the decomposition of piperylene sulfone.

The Sulfone Method of Diene Purification.—The apparatus usually used for this consisted of a 320 ml. stainless steel autoclave. It was provided with a needle valve for releasing unreacted gases. A typical experiment with Fraction H will be described. The autoclave was charged with 75 g. (1.1 moles) of Fraction H and 5 g. of phenyl-β-naphthylamine. It was then cooled with dry-ice and 211 g. (3.3 moles) of liquid sulfur dioxide added. The autoclave was closed and heated in a water-bath at 80 to 85° for two hours with occasional shaking. The autoclave was then placed in a water-bath at 60° and unreacted starting materials amounting to 220 g. were released to a dry-ice–acetone cooled trap. The sulfur dioxide was almost completely removed by distillation through a 6 mm. × 75 cm. refrigerated coil column in the presence of 0.5 g. of phenyl-β-naphthylamine. Since the amine and sulfur dioxide form a compound with a red color, the disappearance of this color was a convenient indication of the end-point of the distillation. The sulfone and polysulfone formation which occurred in the column was appreciable but not serious. The final traces of sulfur dioxide as well as small amounts of sulfone were removed from the unreacted hydrocarbon (36 g.) by washing with dilute sodium hydroxide. The crude sulfone amounting to 66 g. was transferred to a 100-ml. flask provided with a thermometer extending into the liquid and a connection to a dry-ice cooled receiver. The flask was then heated in an oil-bath the temperature of which was gradually raised. A forerunnings fraction was collected at 60 to 85° which amounted to 4 g. Then the main fraction was collected at 85 to 120° which amounted to 39 g. The remaining material which presumably was a polysulfone was a viscous liquid when hot and a solid when cold. It weighed 22 g. The main fraction was separated into 19.5 g. of *trans*-piperylene and sulfur dioxide by the method given for the unreacted hydrocarbon. The diene content of the *trans*-piperylene thus secured was approximately 95% as indicated by absorption which was complete after about ten minutes. By repurification through the sulfone the diene content was increased to 99% with the time required for constant absorption reduced to four minutes. This behavior on repurification was observed with very little change in the refractive index and boiling point. Some impurity was indicated whose removal was relatively difficult. By extraction of the crude sulfone with water with subsequent evaporation of the water from the extract at reduced pressure it was found possible to obtain the sulfone as a nearly colorless oil with a faint pleasant odor. One hundred forty-six grams of this preparation underwent 91% decomposition in an oil-bath at 95 to 105° during two hours. The diene recovered in the usual way had the properties listed in Table I.

Anal. Calcd. for C_5H_8: C, 88.16; H, 11.85. Found: C, 88.12, 88.05; H, 11.82, 11.85.

Under similar conditions the sulfones of butadiene, isoprene, 2,3-dimethylbutadiene and 4-methylpentadiene required the temperature indicated in Table II. In the preliminary examination of the piperylene concentrate use was made of the relatively high temperature required for the decomposition of isoprene sulfone. In one experiment the crude sulfone from the concentrate was heated in an oil-bath to 110° to effect the decomposition of the piperylene sulfone. The remaining mixture, which was semicrystalline at room temperature, was extracted with hot water and the extract clarified with decolorizing carbon. When cooled it deposited colorless plates of isoprene sulfone which were identified by melting point and mixed melting point with an authentic specimen and by decomposition to isoprene and sulfur dioxide.

For the rearrangement of *cis*-piperylene 34 g. (0.5 mole) of this isomer was mixed in an autoclave with 162 g. (2.53 moles) of sulfur dioxide and 5 g. phenyl-β-naphthylamine. The autoclave was heated for four hours in a steam-bath after which it was cooled in a 60° water-bath. The unreacted starting materials were then collected in a dry-ice cooled trap and were found to weigh 136 g. This was separated by distillation into a mixture of 128 g. of sulfur dioxide and 7 g. of hydrocarbon which after the removal of a trace of sulfur dioxide distilled at 43.2 to 43.6° and had $n^{20}D$ 1.4345. The crude sulfone remaining in the autoclave was extracted with two 200-ml. portions of water at 25°. The undissolved portion was a sticky resin and was discarded. The water extracts were united and extracted with nine 10-ml. portions of chloroform. The chloroform extracts were united and the solvent removed at reduced pressure. The yield of sulfone amounted to 30.2 g. That this was piperylene sulfone was proved by the decomposition of 26 g. in an oil-bath at 97 to 102° with the subsequent identification of the sulfur dioxide free hydrocarbon. The constants observed for this hydrocarbon were: b. p. 41.8–41.9° (745 mm.) and $n^{20}D$ 1.4301. A mixture was prepared by weighing into a Pyrex tube the following compounds in the order named: 0.01 g. of phenyl-β-naphthylamine, 5.58 g. (0.057 mole) of maleic anhydride and 3.22 g. (0.047 mole) of the hydrocarbon. The tube was cooled in a dry ice-acetone bath and sealed. It was then brought to room temperature. After a few minutes a vigorous reaction set in. The tube was heated for two and one-half hours in a steam-bath, opened, and then heated for thirty minutes in a steam-bath. Finally it was heated for ten minutes in a steam-bath at an approximate pressure of 40 mm. There was no loss in weight, indicating that all of the hydrocarbon had reacted. The melting point of the mixture was 47–49°. The mixture was distilled through a short column at about 3 mm. pressure. The first fraction which amounted to 1.2 g. distilled at 54 to 118° and contained a considerable quantity of maleic anhydride. The main fraction weighed 7.4 g. and distilled at 118 to 120°. The holdup and residue were crystalline and weighed 0.2 g. The main fraction melted at 57 to 60°. By recrystallization from a mixture of benzene and petroleum ether a yield of 6.5 g. of 3-methyl-1,2,3,6-tetrahydrophthalic anhydride was secured. The compound melted at 61 to 63° alone or when mixed with a sample of this derivative prepared several months earlier which was found to melt to 60 to 61°, resolidify and then remelt at 61 to 63°. Two crystalline forms of this derivative are thus indicated.

The reaction of *cis*-piperylene with maleic anhydride at room temperature to 100° in sealed tubes (in contrast to the above described reaction of the *trans*-isomer) has thus far yielded polymeric material and nearly pure unreacted maleic anhydride. For example, 12 g. (0.12 mole) of maleic anhydride, 6.8 g. (0.10 mole) of *cis*-piperylene, 5 g. of phenyl-β-naphthylamine and 50 ml. of benzene were heated for four and one-half hours at 100°. Unreacted piperylene and benzene were distilled from the reaction mixture at atmospheric pressure. Then 7.5 g. of nearly pure maleic anhydride distilled at 102° at a pressure of about 32 mm. It had a freezing point of 51 to 54° which was strongly depressed by the addition of 3-methyl-1,2,3,6-tetrahydrophthalic anhydride. The residue weighed 9.0 g. and was a very viscous liquid. It was extracted with boiling water. The extract on cooling deposited a few crystals that melted at 158–160°. No methyltetrahydrophthalic acid could be isolated. In another experiment 7.8 g. of a mixture of the piperylene isomers ($n^{20}D$ 1.4340) containing approximately 67% of *cis*-piperylene was heated with maleic anhydride in a sealed tube submerged in a water-bath at 55–60°. A vigorous reaction occurred within a few minutes. After a period of one and one-half hours polymer began to separate. The tube was then cooled, opened and 2 g. of unreacted hydrocarbon distilled off at reduced pressure. This was identified by index of refraction, $n^{20}D$ 1.4360, as *cis*-piperylene.

Cyclopentene was isolated from Fraction H by consecutive treatments with cuprous ammonium chloride, sulfur dioxide and maleic anhydride. The constants found for the unreacted hydrocarbon were: b. p. 43.6–43.8° (740 mm.); $n^{20}D$ 1.4231. The refractive index was lowered to 1.4220 by purification through the dibromide which melted at 12.2°. Final identification was secured by preparation of *p*-cyclopentylacetanilide according to the procedure of Ipatieff and Schmerling.[11] The constants given by Carr and Stücklen[12] are b. p. 44.02 and $n^{20}D$ 1.4420. The index of refraction given by these authors may be a typographical error.

The Bromination of the Piperylene Isomers.—A solution of 242 g. (1.51 moles) of bromine in 300 g. of chloroform was prepared in a 1-liter flask fitted with a stirrer, thermometer and dropping funnel. It was cooled in a water-bath while a solution of 53.6 g. (0.8 mole) of *cis*-piperylene in 100 g. of chloroform was added gradually during two hours. The temperature at the beginning of the addition was 3° and toward the end was 30°. At this time a weak bromine color remained and only a trace of the solid tetrabromide remained undissolved. The mixture was distilled until the temperature of the liquid reached 67°. Up to this point 82 g. of distillate including some hydrogen bromide was collected and discarded. The mixture was poured into 400

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[11] Ipatieff and Schmerling, THIS JOURNAL, **60**, 1479 (1938).

[12] Carr and Stücklen, *J. Chem. Phys.*, **6**, 56 (1938).

ml. of alcohol and cooled in an ice-bath to 1°. The crystals melted at 112–113°. The yield was 116 g. or 38% based on the piperylene. The melting point after recrystallization was 114° as often reported for the solid tetrabromide. The filtrate was distilled at reduced pressure through a 2 × 50 cm. indented glass column. After the mixture of solvents was collected a fraction (14 g.) distilled at 45 to 46° at 1.5 mm. The next fraction was collected at approximately 93° at this pressure. It amounted to 121 g. The remainder which amounted to 38 g. was crystalline at room temperature and consisted of a mixture of tetrabromides. The fraction distilling at 93° could not be made to crystallize alone or when mixed with several common solvents. It is also a mixture of tetrabromides.

Anal. Calcd. for $C_5H_8Br_4$: C, 15.48; H, 2.08; Br, 82.46. Found: C, 15.70, 15.68; H, 2.30, 2.23; Br, 82.17, 81.97.

When the method just described was applied to the bromination of *trans*-piperylenes the yield of solid tetrabromide amounted to 13.8%.

It was found that the dibromide of cyclopentene could be isolated by distilling the mixture of bromides produced from mixtures of this hydrocarbon and the piperylenes and then recrystallizing the dibromide fraction from methanol.

The Debromination of the Solid Piperylene Tetrabromide.—A one-liter, 3-necked flask was equipped with a 30-cm. water-cooled reflux condenser, stirrer and a device for adding the solid tetrabromide. This consisted of a rubber tube with two pinch clamps capable of holding about 5 g. of the solid at one filling. The top of the reflux condenser was connected to an 8 × 8 mm. coil column cooled with dry-ice which in turn was connected to a dry-ice trap for collecting the piperylene–alcohol azeotrope. The flask was charged with 49.1 g. (0.75 mole) of 20-mesh zinc and 225 ml. of alcohol. The tetrabromide (110 g. or 0.284 mole) was added from time to time to the refluxing alcohol–zinc mixture during twenty minutes. The reaction was vigorous causing part of the piperylene–alcohol azeotrope to distil along with some alcohol at 39–45° during this period. The remainder of the azeotrope was distilled making a total of 20 g. that was collected in the dry-ice trap. The alcohol was removed by washing with three portions of strong calcium chloride solution. The hydrocarbon then was dried over calcium chloride; yield, 14.8 g. It distilled at 42.1 to 42.3° and displayed an index of refraction $n^{20}\text{D}$ 1.4327 corresponding to slightly more than 50% of *trans*-piperylene. The presence of *trans*-piperylene was established by the preparation in benzene solution of 3-methyl-1,2,3,6-tetrahydrophthalic anhydride in a sealed tube at 100°. A large quantity of polymer was also formed. By conducting the reaction at room temperature very little polymerization took place and it was possible to isolate unreacted hydrocarbon which distilled at 43°. It displayed an index of refraction of 1.4351, thus indicating the presence of residual *trans*-piperylene, and gave the solid tetrabromide in good yield melting at 114°. That the hydrocarbon from the debromination was free of mono-olefins was established by the data for the cuprous chloride treatment given in Table IV. This experiment differs in a non-essential way from the others reported in the table in that the amount of cuprous chloride that was used was less. Thus for this experiment 30 g. (0.15) mole) of cuprous chloride, 37 g. (0.69 mole) of ammonium chloride, 100 ml. of water, 10 ml. of concentrated hydrochloric acid and 5 g. copper wool were used in preparing the slurry.

The Hydrogenation of the Piperylene Isomers.—A mixture of 25 g. of *cis*-piperylene, 150 ml. of 95% alcohol and 10 g. of Raney nickel catalyst was shaken in an Adkins type hydrogenator under a pressure of approximately 35 atmospheres at 29 to 35° for one and three-tenths hours. The reaction mixture was filtered and distilled through a 6 mm. × 40 cm. coil column. 17.5 g. was collected at 32.8°. This fraction presumably consisted of the *n*-pentane–alcohol azeotrope. It was washed three times with strong calcium chloride solution and the hydrocarbon finally dried over calcium chloride. It then distilled at 35.7° (745 mm.) and possessed a refractive index $n^{20}\text{D}$ 1.3578. These values are in good agreement with those for *n*-pentane given by Deansley and Carleton.[13] Under similar conditions *trans*-piperylene yielded a reduction product which distilled at 32.6°. On removal of alcohol the hydrocarbon that remained distilled at 35.4° and had an index of refraction $n^{20}\text{D}$ 1.3579.

Summary

1. A method for separating the *cis* and *trans* piperylene isomers from mono olefinic or paraffinic hydrocarbons and from each other has been found. This method which involves the preparation and subsequent decomposition of the piperylene complexes with cuprous chloride was found to have no effect on the configuration of the dienes.

2. The sulfone method of purification of dienes has been applied to the preparation of *trans*-piperylene.

3. *cis*-Piperylene has been rearranged to *trans*-piperylene by sulfone formation and decomposition.

4. The solid piperylene tetrabromide, obtained by the bromination of either isomer, was debrominated to form a mixture of the piperylene isomers.

5. *cis*-Piperylene was found to form a minimum boiling mixture with cyclopentene.

6. Moderately efficient fractionation combined with the cuprous chloride treatment has been shown to be an efficient method for investigating the compositon of five carbon hydrocarbon fractions containing dienes.

7. *cis*-Piperylene was found to react with maleic anhydride to form a polymer rather than 3-methyl-1,2,3,6-tetrahydrophthalic anhydride. On the other hand the *trans*-isomer gave nearly the theoretical yield of this derivative.

8. Evidence was secured which indicates the

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(13) Deansley and Carleton, *J. Phys. Chem.*, **45**, 1108 (1941).

"chair" form as the most probable structure for at least the *cis*-isomer of piperylene. The *trans*-isomer apparently reacts largely in the "boat" form.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK & CO., INC.]

Hydrogenolysis of Sulfur Compounds by Raney Nickel Catalyst

BY RALPH MOZINGO, DONALD E. WOLF, STANTON A. HARRIS AND KARL FOLKERS

Contemplated investigations of the structures of natural products containing sulfur[1] have led us to study the action of Raney nickel catalyst on representative sulfur compounds. The present paper describes the hydrogenolysis of aliphatic and aromatic sulfides and disulfides and the extension of the reaction to sulfones and sulfoxides.

Raney nickel catalyst prepared in the usual way[2] contains hydrogen which is not lost when the nickel is stored in the absence of oxygen, and this hydrogen is fully capable of reaction with hydrogen acceptors. The hydrogen may be collected as the gas by heating the catalyst in the absence of oxygen. Whether this hydrogen is held by simple solution in the nickel, by chemical combination as nickel hydride,[3] or by so-called "adsorption" on the surface of the nickel is not known. The hydrogen is present, however, in considerable amount varying with the method of preparing the catalyst. It was found that 4 g. of Raney nickel catalyst may contain between 170 and 460 ml. of hydrogen depending upon the final temperature used in its preparation. It is hydrogenolysis by this hydrogen which is the basis of the present investigation.

It has been known that traces of catalyst poisons may be removed by treating compounds containing them with pyrophoric Raney nickel catalyst at room temperature or slightly above.[4] However, the fate of the sulfur containing compounds, when these are the poisons, has not been determined.

Recently, it was reported that Raney nickel catalyst in neutral or alkaline solution removes sulfur from aliphatic sulfhydryl compounds and disulfides, forming first nickel mercaptides which then decompose to yield sulfur-free compounds.[5] In the present work, it was found that an active Raney nickel catalyst alone, in the presence of a solvent at moderate temperature, removes either reduced or oxidized sulfur by cleavage from the remainder of the organic molecule. Two courses for the reaction of a sulfide may be postulated. In the first of these the nickel is considered to function as a metal, removing the sulfur in a Wurtz-type reaction according to equation (a). Alternately, in the presence of sufficient Raney nickel catalyst to contain an excess of hydrogen, the reaction may take the course represented by equation (b).

$$\mathrm{R{-}S{-}R^1 + Ni(H)} \begin{array}{l} \xrightarrow{\text{(a)}} \mathrm{R{-}R^1 + R{-}R + R^1{-}R^1} \\ \xrightarrow[\text{(b)}]{} \mathrm{R{-}H + R^1{-}H} \end{array}$$

Similar paths could be postulated for the reactions of disulfides, sulfoxides and sulfones. Using aliphatic and aromatic sulfides, disulfides, sulfoxides and sulfones with sufficient Raney nickel catalyst to contain a large excess of hydrogen only the reaction (b) has been observed. That is, in every case, the rupture of the carbon–sulfur bond was accompanied by the formation of a new carbon–hydrogen bond and combination of the organic radicals did not occur. Sulfhydryl compounds would, of course, give the same product by either mechanism (a) or (b) since R^1 is a hydrogen atom.

When benzyl sulfide (I) was treated with Raney nickel catalyst in boiling ethanol, but in the absence of a hydrogen atmosphere, an 85% yield of toluene was obtained. Compounds of more complicated structure such as benzoylmethionine

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(1) During a collaborative study of biotin by Dr. du Vigneaud and his co-workers of the Biochemistry Staff of the Cornell University Medical College and certain members of the Research staff of Merck & Co., Inc., it was thought that the application of a method for the replacement of sulfur by hydrogen atoms, under study in our laboratories, might be applied to the structural investigation of biotin. For the description of the use of this reaction in the preparation of desthiobiotin from biotin and the role of this compound in the final determination of the structure of biotin, see du Vigneaud, Melville, Folkers, Wolf, Mozingo, Keresztesy and Harris, *J. Biol. Chem.*, **146**, 475 (1942).

(2) "Organic Syntheses," **21**, 15 (1941).

(3) Bougault, Cattelain and Chabrier, *Bull. soc. chim.*, [5] **5**, 1699 (1938).

(4) Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937, p. 28.

(5) Bougault, Cattelain and Chabrier, *Bull. soc. chim.*, [5] **7**, 781 (1940).