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The Dimers of Isoprene*

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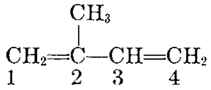
INTRODUCTION

In the infrared spectra of some types of polyisoprene, bands are found, particularly one at 8.7 μ, which cannot be ascribed to structures arising from the usual linear 1-2, 3-4, or 1-4 addition reactions of isoprene. A possible source of these bands is the formation of cyclic structures in the polymer chain; to investigate this possibility, the dimers of isoprene were prepared and their infrared spectra investigated. This work is reported here.

Isoprene



$$\underset{1}{CH_2}{=}\underset{2}{\overset{\overset{CH_3}{|}}{C}}{-}\underset{3}{CH}{=}\underset{4}{CH_2}$$

can dimerize in the following ways: by a 1,2–1,4, mechanism to yield 1,4- and 2,4-dimethyl-4-ethenyl-1-cyclohexenes; by a 3,4–1,4 mechanism to form 1- and 2-methyl-4-isopropenyl-1-cyclohexenes; by a 1,4-1,4 mechanism to produce *cis,cis'*-1,5- and 2,5-dimethyl-1,5-cyclooctadienes; by a 1,2–1,2 mechanism to form 1,2-dimethyl-1,2-diethenyl-cyclobutane and 1,4-dimethyl-1,3-diethenyl-cyclobutane could form; and by a 3,4–3,4 mechanism, to produce 1,2- and 1,3-diisopropenylcyclobutanes.[1] It seemed surprising that while Salomon et al.[2] have reported the preparation of cyclic C_6 dimers of isoprene, no mention was made of cyclic C_8 dimers, especially in view of the fact that butadiene dimerizes to yield *cis,cis*-1,5-cyclooctadiene, 1-ethenyl-1-cyclohexenes, and diethenylcyclobutane.[3] Ziegler and Wilms[1] and Cope, Pike, and Spencer[4] showed that only *cis,cis*-1,5-cyclooctadiene should be expected from the dimerization of butadiene, and Cope and Schmitz[5] found only 2,5-dichloro-1,5-cyclooctadiene resulting from the dimerization of chloroprene. Therefore *cis,cis*-2,5-dimethyl-1,5-cyclooctadiene should be expected as the only 8-membered ring compound from the dimerization of isoprene.

The main purpose of this was the synthesis of the heretofore unknown 8-membered rings by the dimerization of isoprene. Characterization of the 6-membered rings that emanated from isoprene was not of primary interest, as these compounds have been characterized by others.

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EXPERIMENTAL

Phillips Petroleum Co. pure isoprene, to which 0.1% by weight of hydroquinone was added, was heated in a steel bomb which had been filled with nitrogen for periods of time and temperatures indicated in Table I. After cooling, the liquid was distilled off under increasing vacuum until only viscous polymer remained. The polymer was dissolved in benzene and rubber precipitated from the solution with methanol. The material still dissolved in the benzene was recovered by adding water to the benzene-methanol mixture and fractionally distilling the recovered benzene layer. This residual organic liquid was added to the first distillate from the bomb and the whole fractionally distilled at a reflux ratio of at least 20:1 in a column packed with glass helices.

The products of dimerization of isoprene obtained in this manner are shown in Table I. No evidence of cyclobutanes was found, and they could not have amounted to more than 1% of the charge.

First Distillation Fraction

The first fraction from the fractionation of the high temperature dimerization mixture was a colorless liquid with the following physical properties: b.p. 67.3°/28.8 mm., 162°/751 mm.; congealed to a glass in liquid nitrogen; d_4^{20} 0.8319, n_D^{20} 1.4654. Lebedev[6] prepared a material by the dimerization of isoprene, which he identified as 2,4-dimethyl-4-ethenyl-1-cyclohexene, having the following properties: b.p. 44°/9 mm., 160–61°/760 mm., d_D^{20} 0.8331, n_D^{20} 1.4658. The first fraction therefore appears to be 2,4-dimethyl-4-ethenyl-1-cyclohexene.

The infrared spectrum of this fraction is shown in Figure 1 (as 2,4-dimethyl-4-ethenyl-1-cyclohexene). The bands at 10.08 μ and 11.00 μ show the presence of the ethenyl group, the two bands near 6μ show two kinds of double bonds, one due to the $CH_2{=}CH$ group and the other to the $C{=}C(CH_3)$ group. The bands in the 8–9 μ region also show the presence of the $C{=}C(CH_3)$ group and that it is probably both *cis* and *trans*. The spectrum itself shows that the molecule is not linear. Since there is no doubling of the bands in the 8–9 μ region, the substance is essentially uniform and hence there is little, if any, of the 1,4-dimethyl isomer present. The 1,4-dimethyl-4-ethenyl-1-cyclohexene compound has not been described in the literature.

Second Distillation Fraction

The next higher boiling fraction was a colorless liquid with the following physical properties: b.p. 63.5°/14.1 mm., 175.5°/751 mm.; congealed to a glass in liquid nitrogen; d_4^{20} 0.8444 and n_D^{20} 1.4734. The infrared spectrum of this fraction, shown in Figure 1 as 2-methyl and 1-methyl-4-isopropenyl-1-cyclohexene, indicated that it probably was a mixture by the doubling of the bands, particularly in the 8–9 μ region. Aschan[7] gives the following

TABLE 1
Dimerization of Isoprene at Various Temperatures

Temp. of dimerization, °C.	Period of dimerization, min.	Isoprene charged, g.	Isoprene recovered, g.	Total conv. of isoprene to dimers, %	Trimer and high polymer formed, g.	Ratio of individual dimers formed		
						2,4-Dimethyl-4-ethenyl-1-cyclohexene	Diprene[a]	*cis,cis*-1,5- and 2,-5-dimethyl-1,5-cyclo-octadienes
60	20,160	2145.0	1981	7.17	10.1	nil	100	nil
227	10	1253.4	112.95	80.19	135.3	28.15	62.4	9.45
240	3.5	1380.3	90.85	80.43	179.35	29.08	60.91	10.01

[a] Diprene proved to be, by comparison to pure 1-methyl-4-isopropenyl-1-cyclohexene (Dipentene), 2-methyl-4-isopropenyl-1-cyclohexene containing a little Dipentene.

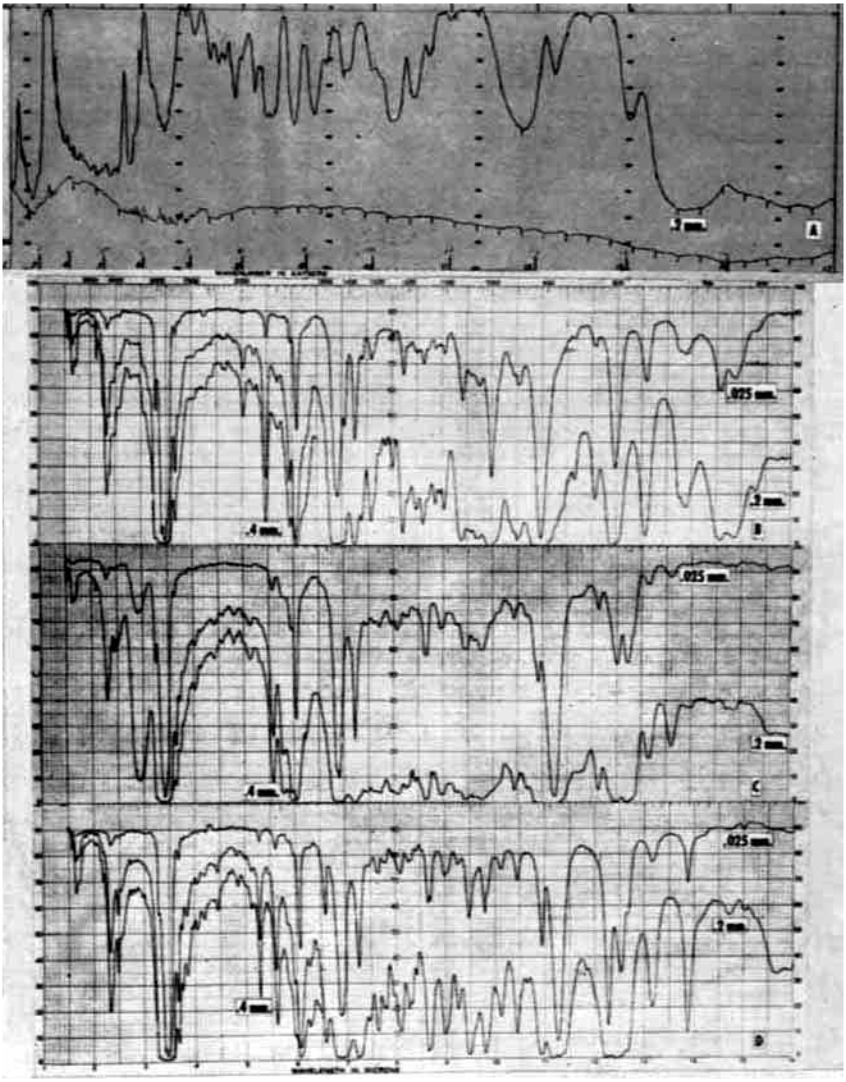


Fig. 1. Infrared spectra of (A) distillation fraction of Diprene and Dipentene, (B) 2,4-dimethyl-4-ethenyl-1-cyclohexene, (C) 2-methyl-4-isopropenyl-1-cyclohexene (Diprene), and (D) 1-methyl-4-isopropenyl-1-cyclohexene (Dipentene).

physical properties for Diprene or 2-methyl-4-isopropenyl-1-cyclohexene, which he identified: b.p. 68.5–69°/16 mm., 171.5–173°/752 mm., d_4^{20} 0.8476, $n_D^{23.2}$ 1.4695. Wagner-Jauregg[8] gives the following properties for the same compound: b.p. 172–174.5/752 mm., d_4^{19} 0.8454, and n_D^{17} 1.4754. Thus, the second fraction appears to be principally 2-methyl-4-isopropenyl-1-cyclohexene with some of the other likely isomer, 1-methyl-4-isopropenyl-1-cyclohexene or Dipentene.

The two isomers were separated by forming the silver nitrate complex, since Salomon et al.[2] state that 2-methyl-4-isopropenyl-1-cyclohexene forms a silver nitrate adduct, whereas the 1-methyl isomer does not. From 13.6 g. of this fraction, 4.6 g. of pure 2-methyl-4-isopropenyl-1-cyclohexene was obtained which had the following physical properties: congealed to a glass in liquid nitrogen, d_4^{20} 0.8451, and n_D^{20} 1.4734.

The infrared spectra of the 2-methyl-4-isopropenyl-1-cyclohexene thus prepared, and of 1-methyl-4-isopropenyl-1-cyclohexene obtained from Eastman, are also shown in Figure 1. The spectra of these two compounds show that the original fraction was a mixture, as was expected from the doubling of the bands. They also show the presence of the isopropenyl group (11.25 μ band), two different C=C groups (the two 6 μ bands), and the $C{=}C(CH_3)$ group (8.6–8.8 μ bands). It is also clear from the spectra that the molecules are not linear.

Third Distillation Fraction

The third fraction from the distillation was a colorless liquid having the following physical properties: b.p. 73.9°/15.9 mm., 182.5°/751 mm., congealed to a glass in liquid nitrogen, d_4^{20} 0.8713, and n_D^{20} 1.4890. Since all of the possible cyclic C_6 dimers had been accounted for, this fraction presumably contained the C_8 dimers. An analysis gave:

Calc. for $C_{10}H_{16}$: C, 88.16%; H, 11.84%
Found: C, 88.27%; H, 11.75%

Ozonolysis of 0.0748 mole of the fraction in chloroform at -25°C. yielded 0.0354 mole of levulinic acid as its phenylhydrazone and peroxide,[9] 0.0064 mole of succinic acid, and 0.0033 mole of 2,5-hexandione, as its bis-(*p*-nitrophenylhydrazone). An equimolecular mixture of this cyclic C_8 fraction and phenyl azide (n_D^{20} 1.5612) did not react in 15 days at 24°C.

The infrared spectrum of this fraction is shown in Figure 2 (as *cis,cis*-1,5-, and 2-5-dimethyl-1,5-cyclooctadiene). As in the case of the intermediate boiling cyclic C_6 fraction (Diprene), the doubling of the bands in the spectrum indicates that the material is a mixture. The bands near 8.8 μ show that $C{=}C(CH_3)$ groups are present, probaby *cis*, and the bands near 9.2 μ indicate that CH_3 groups are on the ring. Moreover, comparison with proven cyclooctadiene spectra shows that the substances examined are not linear molecules.

An attempt was made to resolve the mixture by forming the silver nitrate addition product. Although two layers separated, the infrared spectra of the hydrocarbon from each layer were identical. Hence no separation took place. Another attempt was made by forming the bromide, using 6.8 g. of the fraction and 18.4 g. of bromine at -30°C. After 96 hours, 22.3 g. of brominated product were formed (compared with a theoretical amount of 22.8 g. for $C_{10}H_{16}Br_4$). This could not be induced to crystallize at ice, dry ice, or liquid nitrogen temperatures, nor could it be crystallized from methanol. No separation of the isomers was effected.

To further identify the mixture, 20.45 g. of it were dissolved in methanol

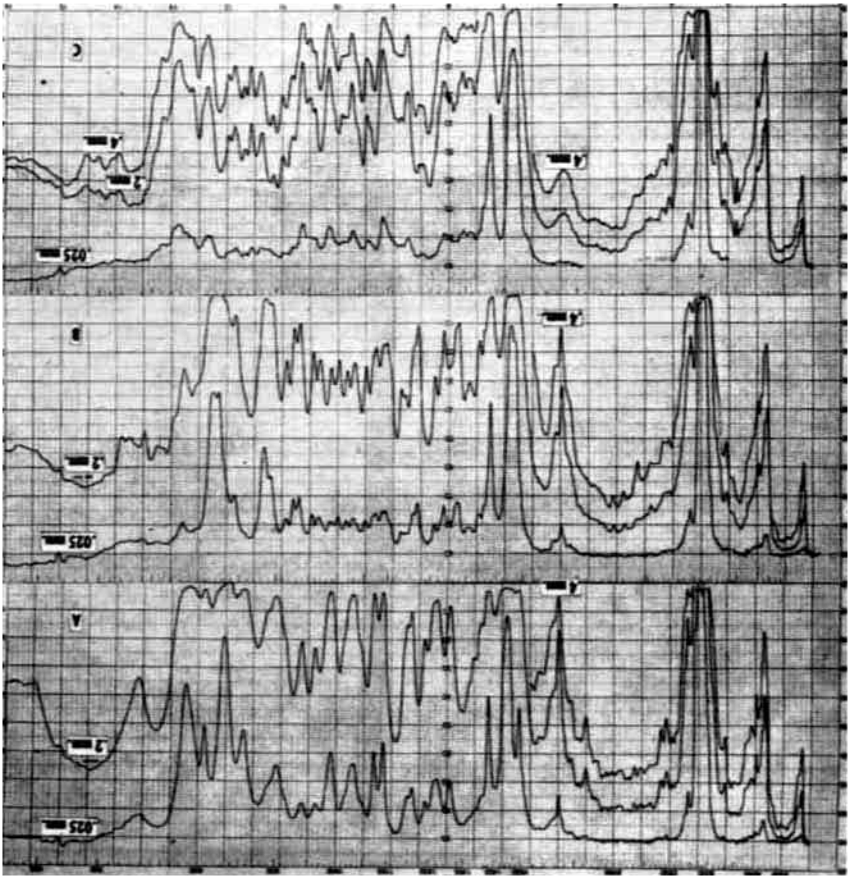


Fig. 2. Infrared spectra of (A) 1,5- and 2,5-dimethyl-1,5-cyclooctadienes, (B) 1,5- and 2,5-dimethyl-1-cyclooctene, and (C) 1,5- and 2,5-dimethylcyclooctane.

and hydrogenated at 43 p.s.i. gage and 24°C. with platinum oxide catalyst, until 0.150 mole of hydrogen were absorbed. A, colorless liquid 18.25 g., was recovered; this had the following properties: b.p. 178.0–178.8/729 mm., congealed to a glass in liquid nitrogen, d_4^{20} 0.8389, n_D^{20} 1.4664. Larrabee and Craig[1C] showed that vinylcyclooctatetraene did not completely hydrogenate in methanol solution. The analysis of the material obtained here is

Calc. for $C_{10}H_8$: C, 86.89%; H, 13.12%
Found: C, 86.85%; H, 13.15%

This analysis indicates a hydrogenation to the dimethyl-cyclo-octenes, and the infrared spectrum of this mixture is shown in Figure 2. Here again, the doubling of the band indicates a mixture, and the change in the spectrum in the 8–9 μ region, from that of the original mixture, indicates a change in the double bonds.

Cope, Pike, and Spencer[4] found that *cis*-1-cyclooctene did not dissolve in silver nitrate while the *trans* isomer did. When 10.0 g. of the hydrogenated mixture was shaken with 40% silver nitrate for 4.5 hr., 9.45 g. of the material remained undissolved. This liquid had the following properties: congealed to a glass in liquid nitrogen, n_D^{20} 1.4656. Moreover, an equimolar ratio of this hydrocarbon and phenyl azide did not react. Hence it is concluded that the material is the *cis* isomers of 1,5- and 2,5-dimethyl-1-cyclooctenes.

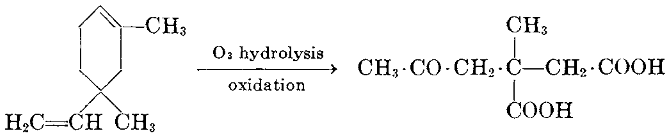
The semihydrogenated material was further hydrogenated in glacial acetic acid with platinum oxide catalyst. A colorless liquid, 3.0 g., was obtained from 3.2 g. of the starting material and had the following physical properties: b.p. 179°C./726 mm., congealed to a glass in liquid nitrogen, d_4^{20} 0.8221, n_D^{20} 1.4524. It did not decolorize an acetic acid solution of potassium permanganate. The analysis is:

Calc. for $C_{10}H_{20}$: C, 85.62%, H, 14.38%
Found: C, 85.31%, H, 14.33%

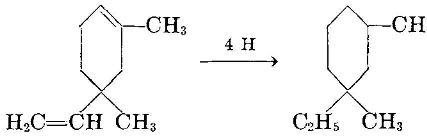
The infrared spectrum of this material presented in Figure 2 shows the absence of C=C bands and marked changes in the 8–9 μ region, as would be expected if the C=C bands were removed. A saturated, linear C_{10} hydrocarbon would be analyzed as $C_{10}H_{22}$ instead of $C_{10}H_{20}$. Thus the material is probably a mixture of 1,4- and 1,5-dimethylcyclooctanes.

Discussion

The properties of the lowest boiling fraction from dimerization of isoprene are almost identical with those of the compound which Lebedev[6] isolated and proved, by ozonolysis and hydrogenation, to be 2,4-dimethyl-4-ethenyl-1-cyclohexene.



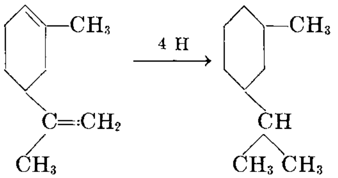
3-methylhexene-5-one-1,3-dicarboxylic acid



1,3-dimethyl-1,1-ethyl-cyclohexane

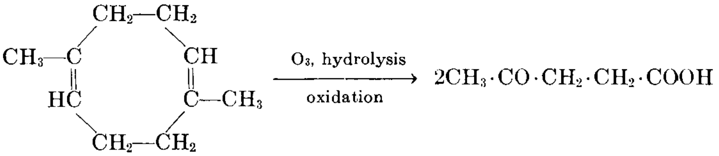
While the majority of this fraction is 2,4-dimethyl-4-ethenyl-1-cyclohexene there is the possibility that some 1,4-dimethyl-4-ethenyl-1-cyclohexene is also present, but the amount would be so small that it would not have substantially affected the physical properties of the 2,4-dimethyl-4-ethenyl-1-cyclohexene.

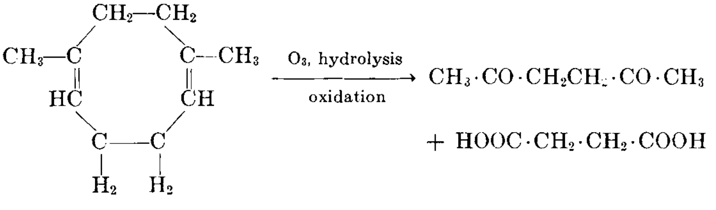
The intermediate boiling fraction appears to be very similar to the Diprene of Aschan[7] and Wagner-Jauregg.[8] Aschan showed that the crystalline dihydrochloride (m.p. 51.5–52°C.) from Diprene is not identical with that from Dipentene (1-methyl-4-isopropenyl-1-cyclohexene Wagner-Jauregg hydrogenated Diprene to yield *m*-menthane.



Boonstra et al.[2] showed that 2-methyl-4-isopropenyl-1-cyclohexene gives a crystalline silver nitrate adduct while the 1-methyl isomer does not. This was the basis of the separation of the two isomers which the infrared spectra show was accomplished. The infrared spectrum of the original fraction can be duplicated by adding the spectrum obtained as above for the pure 2-methyl isomer to that of the 1-methyl isomer which was obtained from Eastman.

It seemed most likely that the highest boiling fraction should contain cyclic C_8 or higher molecular weight compounds; the carbon and hydrogen analysis showed it to be $(C_5H_8)_n$. Ozonolysis of 0.748 mole of the fraction gave 0.0354 mole of levulinic acid, 0.0064 mole of succinic acid, and 0.0033 mole of 2,5-hexanedione; this shows that the fraction was principally 1,5-dimethyl-1,5-cyclooctadiene with some of the 2,5-dimethyl isomer.





Since the doubling of the bands in the Diprene fraction was due to the presence of two substances, it seems likely that the similar doubling of the bands observed in the spectrum of this fraction was due to the presence of two substances. Unfortunately, this doubling makes it difficult, if not impossible, to say now whether the $HC{=}C(CH_3)$ groups are *cis* or *trans*, since it is known from polyisoprene spectra that the positions of the *cis* and *trans* $H{-}C{=}C(CH_3)$ bands in the 8–9 μ region depends upon the neighboring configuration.

The physical properties of the fully hydrogenated high boiling fraction compare well with those of known dimers of isoprene and closely related cyclic C_8 compounds which are given in Table II. Because of the method of preparation, the starting material must have been unsaturated cyclic C_8

compounds. The infrared spectra bear out this conclusion, since there is a C=C band (not conjugated) at 6 μ.

TABLE II
Physical Properties of Cyclic C_8 Compounds

Compound	B.p., °C./mm.	d_4	n_d
1,3-Dimethyl-1-ethylcyclohexane[12]	165–165.5/758	0.8005^{20}	1.4419^{20}
m-Menthane	166–8/756	0.7965^{24}	1.4420^{20}
cis-p-Menthane	168.5	0.816^{20}	1.45149^{20}
trans-p-Menthane	161	0.792^{20}	1.43931^{20}
Ethylcyclooctane[13,14]	191.3	0.8348	1.4593^{25}
	83/30		1.4568^{25}
1,2-Dimethylcyclooctane[15]	99–105/70		1.4558^{25}

The *cis,cis* configuration is established by comparison with the work of Ziegler and Wilms[1] who showed that *cis,cis*-1,5-cyclo-octadiene and *cis*-cyclo-octene (stable forms) did not react with phenyl azide while the *trans* (labile form) did. The high boiling fraction and the half-hydrogenated product did not react with phenyl azide. This plus the above results led to the conclusion that the original fraction is a mixture of *cis,cis*-1,5- and 2,5-dimethyl-1,5-cyclooctadienes, that the half-hydrogenated material is *cis*-1,5- and -2,5-dimethyl-1-cyclooctenes, and that the fully hydrogenated product is 1,5- and 1,4-dimethylcyclooctanes.

No specific attempt was made to prepare or isolate the cyclic C_4 dimers; if they were formed here they occurred in very small amounts, as the material balance of the fractionation indicates.

In connection with the formation of the Diprene fraction, it was found that only this is formed when isoprene is dimerized at 60°C., but that at 227–240°C., the dimers described here were formed. These observations also agree with those of Ziegler and Wilms[1] on 1,3-butadiene which showed that at 120°C., 2.2% of 1,5-cyclooctadiene and 97.8% of ethenyl-cyclohexene formed, but at 270°C., 10% of 1,5-cyclooctadiene formed.

The assignments of the vinyl ($CH_2{=}CH$) and isopropenyl ($CH_2{=}C\cdot{-}CH_3{—}$) group to bands at 10.98 μ and 11.25 μ, respectively, are as well established as the C=C group and C=C conjugated group to bands at or near 6 μ and 6.25 μ, respectively. The assignments of the *cis* and *trans* $—C\cdot CH_3{=}CH—$ groups to bands 8.84 μ and 8.68 μ in linear polyisoprenes appears to be well established from work on the microstructures of polyisoprenes.[11] While bands at 9.2 μ in the spectra of these compounds appear to be due to methyl groups on a ring, this correlation is not definitely established.

Conclusions

In the thermal dimerization of isoprene 2,4-dimethyl-4-ethenyl-1-cyclohexene, 2-methyl-4-isopropenyl-1-cyclohexene (Diprene), 1-methyl-4-isopropenyl-1-cyclohexene (Dipentene) and a mixture of *cis,cis*-1,5- and -2,5-dimethyl-1,5-cyclooctadienes are formed. This mixture was not resolved.

No evidence for the formation of the possible cyclobutanes could be found. If formed, the amount was less than 1%.

The infrared spectra of these dimers confirm the structures expected from chemical evidence.

Since this work was done and reported it has come to our attention that Russian workers[16] have reported similar work with the same conclusions as given here, except that they also obtained 1,4-dimethyl-4-ethenyl-1-cyclohexene. They did not, however, obtain the infrared spectra of the substances.

We are indebted to Prof. A. C. Cope of the Massachusetts Institute of Technology for supplying us with his spectra of cyclohexenes, cyclo-octene, and cyclo-octadienes.

We wish to thank H. C. Ransaw who recorded the spectra given here and express our appreciation to Dr. F. W. Stavely for his interest in this work.

References

1. K. Ziegler and H. Wilms, *Naturwiss.*, **35**, 157 (1948); *Ann.*, 1 (1950).
2. G. Salomon, B. B. S. Boonstra, S. vander Meer, and A. J. Ultee, *Rubber Chem. and Technol.*, **22**, 956 (1949).
3. H. W. B. Reed, *J. Chem. Soc.*, **1951**, 685–87.
4. A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).
5. A. C. Cope and W. R. Schmitz, *J. Am. Chem. Soc.*, **72**, 3056 (1950).
6. S. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913); C (1914) I, 1406.
7. O. Aschan, *Ann.*, **439**, 221 (1924); *Ber.*, **57**, 1961 (1924).
8. T. Wagner-Jauregg, *Ann.*, **488**, 176 (1931).
9. R. Pummerer, G. Ebermayer, and K. Gerlach, *Rubber Chem. and Technol.*, **4**, 381 (1931).
10. C. E. Larrabee and L. E. Craig, *J. Am. Chem. Soc.*, **73**, 5471 (1951).
11. J. L. Binder and H. C. Ransaw, *Anal. Chem.*, **29**, 503 (1957).
12. R. Lavina, N. Shusherina, K. Gir, and E. Treshchova, *Zhur. Obshcheĭ Khim.* (*U.S.S.R.*), **24**, 1551 (1914).
13. L. Craig and C. Larrabee, *J. Am. Chem. Soc.*, **73**, 1191 (1951).
14. A. Cope and H. Van Orden, *J. Am. Chem. Soc.*, **74**, 175 (1952).
15. A. Cope and H. Campbell, *J. Am. Chem. Soc* , **74**, 179 (1952).
16. I. Nazarov, A. Kuznetsova, and N. Kuznetsov, *Zhur. Obshcheĭ Khim.* (*U.S.S.R.*), **25**, 291 (1955).

Synopsis

The cyclic C_6 and C_8 dimers of isoprene have been prepared by thermal dimerization and their physical and chemical properties obtained. The infrared spectra of these substances are also given and are used to confirm the structures deduced chemically.

Résumé

On a préparé les dimères cycliques en C_6 et C_8 de l'isoprène par dimérisation thermique et on a déterminé leur propriétés chimiques et physiques. On donne aussi les spectres infra-rouges de ces substances et on les utilise pour confirmer les structures déduites chimiquement.

Zusammenfassung

Die cyklischen C_6- und C_8-Dimeren von Isopren wurden durch thermische Dimerisation dargestellt und ihre physikalischen und chemischen Eigenschaften bestimmt. Die Infrarotspektren der beiden Substanzen werden ebenfalls mitgeteilt und zur Bestätigung der auf chemischem Weg abgeleiteten Strukturen benützt.

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