Tetrahedron Letters No.49, pp. 4457-4464, 1965. Pergamon Press Ltd.
Printed in Great Britain.

DIMERIZATION OF ISOPRENE WITH AQUEOUS SULFURIC ACID

T. Aikawa, H. Izutani, I. Shiihara and H. Sano
Government Industrial Research Institute,
Osaka, Japan

(Received 8 October 1965)

Contrary to the literature that isoprene was dimerized to the mixture of dipentene and an aliphatic dimer in the presence of sulfuric acid (1), we can now report that the major products in this reaction are unsaturated and saturated cyclic ethers.

In our experiments, isoprene was stirred at 20 or 30°C in contact with 40-50 % sulfuric acid (acid to isoprene ratio was 3:1) for the periods between thirty minutes to five hours. The reaction product separated into an upper oily layer and a lower aqueous acid layer. The oily layer was treated with sodium carbonate and distilled. From the aqueous layer, an oily layer was obtained upon neutralization with sodium hydroxide, followed by extraction with ether. The experimental results are given in TABLE I.

The dimer fraction from the upper layer and the ether extraction from aqueous layer were then analysed separately by GLC (FIG. I). These products were then subjected to preparative-type GLC (Column P.E.G.-6000, 10mm×9m, temp. 180 °C) and purified by liquid column chromatography.

TABLE I.

Experimental Results

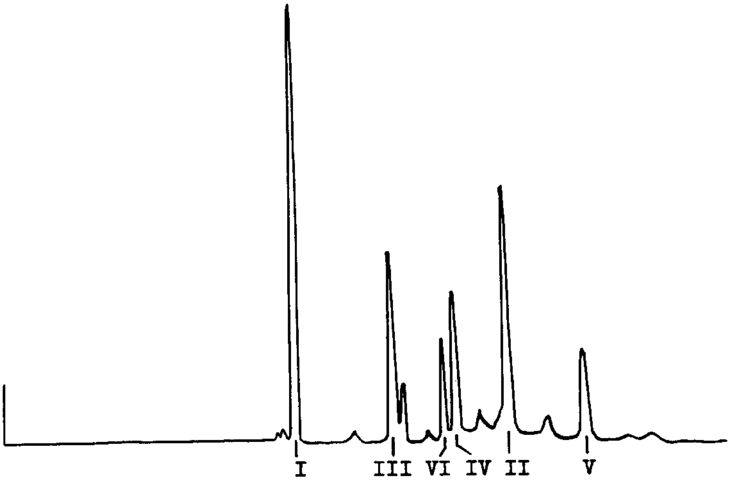
Acid concn. (%)	React. temp. (C^{o})	React. period (min.)	Unreact. isoprene (%)	Dimer b.p.50-120^{o}C (20mmHg) (%)	Polymer b.p.>120^{o}C (20mmHg) (%)
40	30	300	62	26	12
45	20	300	52	24	24
45	30	40	79	17	4
50	30	30	40	35	25

The components thus obtained were identified as 2,2,6-trimethyl-6-vinyl-tetrahydropyran(I), 2,2-dimethyl-5-(2-methylpropenyl)-tetrahydrofuran(II_a), 1,4-cineol(III), 1,8-cineol(IV), terpinolene(V), dipentene(VI), linalool(VII) and α,β,γ-terpineol(VIII). From the ether extraction of the aqueous layer, cis-1,8-terpinmonohydrate(IX) was identified as the principal product. The relative ratios of each product were dependent upon the reaction conditions used. In general, mild conditions yielded unsaturated ethers(I,II) predominantly, while stronger conditions favored the formation of saturated ethers(III,IV).

All compounds mentioned above with the exception of (II_a) were identified by comparison with authentic samples by GLC, IR, n.m.r., or mass-spectrum. Compound (I) was recently isolated from natural substances (2), but this is the first instance of it's preparation from isoprene. Compound (II_a) is an entirely new substance, and has the following properties $^{20}_{D}$ 1.4490, d_4^{20} 0.8799, b.p. 175^{o}C. It's structure was

FIG. 1.

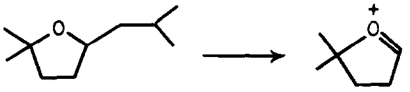
GLC of the fraction of Ethers



note; Golay column, P.P.G. 25m, temp. 110°C

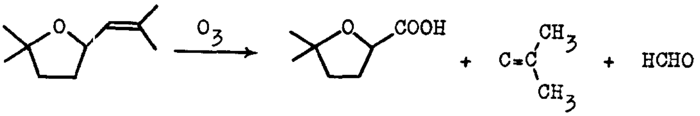
arrived at in the following manner. The mass-spectrum of this fraction showed the parent peak at m/e 154 and the relative intensities of P, P+1 and P+2 peaks (100, 11.23 and 0.84, respectively) supported the formula $C_{10}H_{18}O$. (Found: C, 77.55; H, 11.79. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76.) The IR showed the following: trisubstituted double bond (C=C 1665, C-H 820 cm^{-1}), gemdimethyl group (1362, 1375 cm^{-1}) and ether ring (C-O 1024 cm^{-1}) was found. The n.m.r. signals were $-O-C{<}^{CH_3}_{CH_3}$ 1.23 p.p.m., $-\overset{|}{C}=\overset{|}{C}-CH_3$ 1.57 p.p.m., $-O-\underset{\underset{C=C-}{|}}{\overset{|}{C}}-H$ 4.25, 4.33 p.p.m., $-\overset{|}{C}=\overset{|}{C}-H$ 5.50, 5.58 p.p.m., $-CH_2-CH_2-$ (ring methylene) 1.5 - 2.1 p.p.m., and the integrals of the area under the curve are in the ratio of 6:6:1:1:4 in the order mentioned.

Further support for this structure were arrived at from the hydrogenation and ozonolysis studies of (II_a). Hydrogenation of (II_a) with platinum oxide catalyst in gracial acetic acid was found to absorb one mole hydrogen per one molecule. The molecular weight of this hydrogenation product (II_b) was shown to be 156 by mass-spectrum, corresponding to the molecular formula of $C_{10}H_{20}O$. (Found: C, 77.29; H, 12.97. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90.) Both IR and n.m.r. spectra substantiated the proposed structure of (II_b), especially the mass-spectrum was favourable in the fact that there appeared the strong base peak at m/e 99 despite the existance of a weak parent ion at m/e 156. This ion could have originated from fragmentation by the easy bond cleavage at the overlapped point of α-position to ring and β-position to oxygen.



(II_b)
m/e 156 m/e 99

Ozonization of (II_a) followed by decomposition with water yielded acetone, formaldehyde and a monocarboxylic acid (II_c).



(II_a) (II_c)

Molecular weight of (II_c) was obtained as 144 from the mass-spectrum data which also reveals a prominent peak at m/e 99.

On these basis one can confidently conclude that the structure of (II_a) is as postulated.

Finally, we can reasonably present the dimerization process as undergoing the steps shown in FIG. 2. It is evident that the major products arise from the "head-to-tail" addition intermediate (A) which in turn is hydrated mainly to a diol or sulfuric monoesters and then to (I) by dehydration. Compound (I) can also be prepared by the treatment of linalool (VII) with sulfuric acid, but this process apparently is not the main reaction. (A) is partially cyclized and this may then lead to the intermediate (B), from which are then formed cyclic hydrocarbons(V,VI). At the same time compounds (VIII, IX) which are obtained by hydration of (B), lead to cineol (III,IV) upon dehydration.

The formation of furan type ether(II_a) is expected by the "tail-to-tail" addition of isoprene followed by an allylic rearrangement (3) process as shown in FIG. 3.

FIG. 2

" Head-to-tail " process

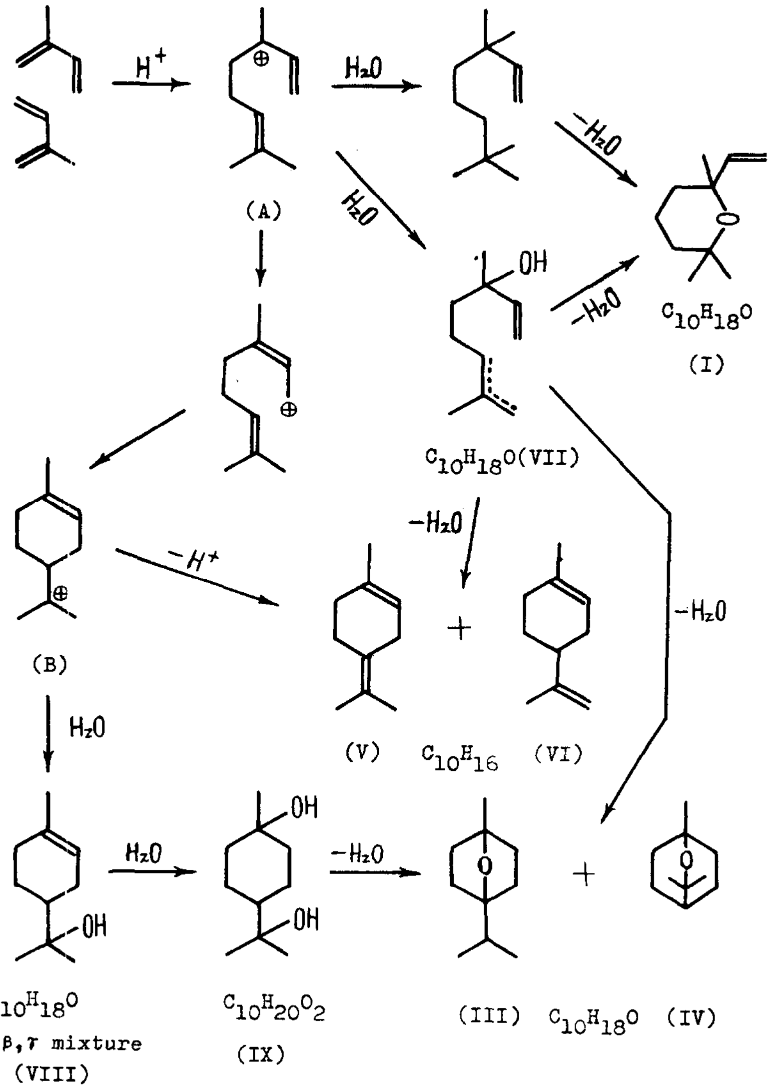
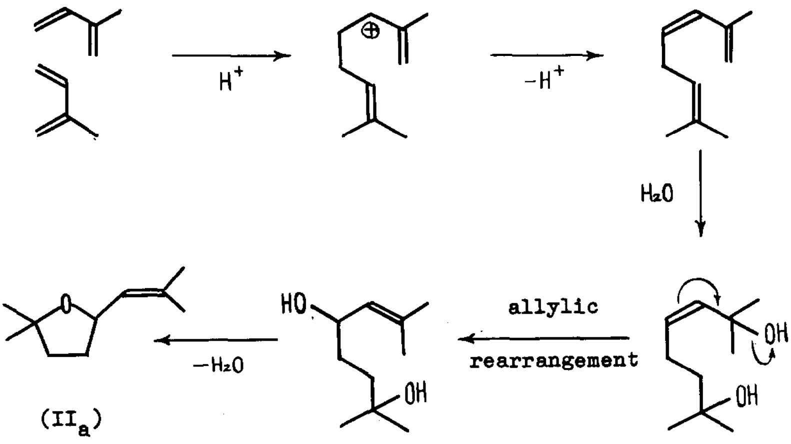


FIG. 3

" Tail-to-tail " process



(II$_a$)

Acknowledgements.

The authers are grateful to Y. Hirose, K. Nishimura and N. Tsubaki of the Institute of Food Chemistry, Osaka, Japan, for the kind help on the mass-spectra and Golay column.
Our thanks are also due to Y. Asahi and M. Nishikawa of the Takeda Chemical Resarch Laboratory, Osaka, Japan, for the n.m.r. spectra and the elemental analysis.

References.

(1) V. I. Komarewsky and C. C. Shin, J. Amer. Chem. Soc. 72, 1562 (1950).

(2) E. sz. Kovats, Helv. Chim. Acta. 46, 2705 (1963).
Y. Ohta, K. Nishimura and Y. Hirose, Agr. Biol. Chem. Japan 28, 5 (1964).

(3) G. Ohloff, E. Klein and G. O. Schenk, Angew. Chem. 73, 576 (1961).