172. *The Thermal Co-dimerisation of Isoprene and Buta-1,3-diene.*

By R. A. W. JOHNSTONE and P. M. QUAN.

It is shown that copolymerisation of a mixture of isoprene and buta-1,3-diene yields all the nine possible dimers by Diels–Alder type addition. Also isolated were cyclo-octadienes and some octahydrobiphenyls.

IT has long been known that conjugated dienes, alone or with catalysts, form cyclic dimers when heated.[1] Thus isoprene yields dipentene,[1,2] *m*-mentha-1,8-diene,[3] dimethylcyclo-octa-1,5-dienes,[2] and a hydrocarbon suggested to be a mixture of 1,4- and 2,4-dimethyl-4-vinylcyclohexene.[4] The preparation of 1,4-dimethyl-4-vinylcyclohexene by another route has been reported.[5] Similarly, from the dimerisation of buta-1,3-diene, have been obtained 4-vinylcyclohexene,[2] *cis,cis*-cyclo-octa-1,5-diene,[6] and *trans*-1,2-divinylcyclobutane.[7]

The copolymerisation of isoprene and buta-1,3-diene at 150° has been reported to yield a co-dimer, 1-methyl-4-vinylcyclohexene, together with a trace of 1-methyl-5-vinylcyclohexene, although the evidence for these structures and their relative amounts is incomplete.[8]

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[1] Wallach, *Annalen*, 1895, **227**, 295.

[2] Lebedev, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949.

[3] Wagner-Juaregg, *Annalen*, 1931, **488**, 176.

[4] Lebedev and Mereshkovski, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249; Nazarov, Kuznetsova, and Kuznetsov, *Zhur. obshchei Khim.*, 1955, **25**, 307; Walling and Peisach, *J. Amer. Chem. Soc.*, 1958, **80**, 5819; Binder, Eberly, and Smith, *J. Polymer Sci.*, 1959, **38**, 229.

[5] Pummerer, *Sitzber. math.-naturw. Kl. bayer. Akad. Wiss. München*, 1954, 191.

[6] Ziegler and Wilms, *Annalen*, 1950, **567**, 1.

[7] Reed, *J.*, 1951, 685.

[8] Petrov and Shlyakhter, *Doklady Akad. Nauk S.S.S.R.*, 1950, **75**, 703.

We have repeated this copolymerisation and, by the use of preparative-scale gas–liquid chromatography, have fractionated the product into the wider range of substances shown in the Table. Also isolated were the cyclic trimers 4-4′-cyclohexenylcyclohexene, 4-4′-cyclohexenyl-3- and -4-methyl-cyclohexenes (fractions I, J).

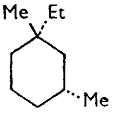
TABLE.

Fraction	R_V	Structure assigned	B. p.	P.W.
A	1·00	4-Vinylcyclohexene	131°	52
B	1·33	4-Methyl-4-vinylcyclohexene	145	3
C	1·56	1-Methyl-5-vinylcyclohexene 1-Methyl-4-vinylcyclohexene	150	22
D	1·65	*cis,cis*-Cyclo-octa-1,5-diene	152	4
E	1·80	4-Isopropenylcyclohexene	157	13
F	1·97	1,4-Dimethyl-4-vinylcyclohexene 2,4-Dimethyl-4-vinylcyclohexene	161	1·2
G	2·46	1-Methylcyclo-octa-1,5-diene	171	1·4
Ha	2·69	*m*-Mentha-1,8-diene	175	3·4
Hb	2·77	*p*-Mentha-1,8-diene	177	

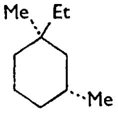
R_V = relative retention volume; P.W. = percentage weight of total dimers.

Each of the fractions A—H, corresponding to peaks on the gas chromatogram, absorbed two equivalents of hydrogen, indicating ring structures for the dimers. Information on the double-bond types in each substance was obtained from its comparative behaviour on gas chromatography through columns containing squalane and glycerol–silver nitrate. On the latter column, substances containing *cis*-disubstituted double bonds were much more strongly retained than those with trisubstituted or vinyl-type bonds. Complementary but more informative data were obtained by infrared spectroscopy in the 1000—650 cm.$^{-1}$ region. The small shift from 990 to 1000 cm.$^{-1}$ for a vinyl group adjacent to a fully substituted carbon atom [9] provided useful information in elucidating the structures of fractions B and F. The trisubstituted double bonds in *m*- and *p*-mentha-1,8-diene absorbed 13 cm.$^{-1}$ apart, and, similarly, there were two bands 16 cm.$^{-1}$ apart in the spectrum of the mixture of 1-methyl-4- and -5-vinylcyclohexene.

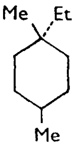
The structures of the six-membered ring compounds isolated were confirmed by catalytic hydrogenation or dehydrogenation to substances of known structure. Mild dehydrogenation of fractions A, C, E, and H yielded the expected substituted benzenes but fractions B and F were not aromatised under the same conditions. Hydrogenation of fraction B gave 1-ethyl-1-methylcyclohexane which has been synthesised by a different route.[10] Hydrogenation of fraction F yielded a product resolvable by gas chromatography into four components which were pairs of configurational isomers of 1-ethyl-1,3- and -1,4-dimethylcyclohexane (I)—(IV).[11] (I)—(IV) were present in the ratio 15 : 19 : 26 : 40, respectively.



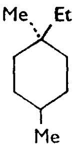
(I)



(II)



(III)



(IV)

These four hydrocarbons were synthesised separately and a mixture of them in the same proportions as the hydrogenated hydrocarbons from fraction F had an identical infrared spectrum. Fraction A, 4-vinylcyclohexene, was readily dehydrogenated to ethylbenzene. Fraction C could not be separated into its two components but their proportions were

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[9] Bellamy, " The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen & Co. Ltd., London, 1958, p. 49.

[10] Buck, Elsner, Forbes, Morrell, Smith, and Wallsgrove, *J. Inst. Petroleum*, 1948, **34**, 339; American Petroleum Institute Research Project 44, No. 1808 (1956).

[11] Johnstone and Quan, unpublished work.

obtained from the ratio of the 3- and 4-ethyltoluene obtained on dehydrogenation. Fractions Ha and Hb were recycled several times through the preparative gas-chromatography column to isolate pure *m*- and *p*-mentha-1,8-diene, the ratio of which was found from the infrared spectrum of the mixture of *m*- and *p*-cymene obtained on dehydrogenation. Fraction D, *cis,cis*-cyclo-octa-1,5-diene, appeared as a shoulder on fraction C and was separated from it by extraction with aqueous silver nitrate.[12] Fraction G was shown to be 1-methylcyclo-octa-1,5-diene by ozonolysis and oxidation of the ozonide to lævulic and succinic acids. A strong absorption band at 705 cm.$^{-1}$ showed the *cis*-configuration of the disubstituted double bond in this compound. Like *cis,cis*- but not *trans,trans*-cyclo-octa-1,5-diene there was also a strong, sharp band at 1490 cm.$^{-1}$ in the spectrum of G.

The small fractions I and J emerging after H were octahydrobiphenyls. Between peaks H, I, and J very small quantities of linear trimers were eluted. The latter absorbed three equivalents of hydrogen to yield saturated hydrocarbons having infrared spectra characteristic of long-chain paraffins.

EXPERIMENTAL

A mixture of buta-1,3-diene (100 ml. of liquid at $-70°$), isoprene (45 ml.), and pyrogallol (3 g.) was heated to 170—180° for 36 hr. in a steel autoclave, and the product was steam-distilled to give an oil X (60 g.) and a rubber-like residue. Gas chromatography of a sample of X on column 1 (see below) enabled the relative amounts of the dimer fractions A–H to be calculated. The very small amount of residual butadiene and isoprene, and a large proportion of the 4-vinylcyclohexene in X were removed by distillation through a Vigreux column and a liquid, Y, remained. A solution of Y (10 g.) in petrol (b. p. 40—42°) (100 ml.) was extracted with 20% aqueous silver nitrate solution (7 × 35 ml.). The extracts, made strongly alkaline with 15N-ammonium hydroxide, yielded an oil, Z.

Preparative-scale Gas Chromatography.—Samples (1 ml.) of Y and Z were placed on a 15 ft. × 1 in. column containing Celite brick-dust (Johns-Manville; 40—60 mesh) coated with 25% by weight of a silicone elastomer (Imperial Chemical Industries Limited; E 301) and eluted at 140° with 200 ml./min. of nitrogen. Samples of Y were split into the fractions A–H, but Z gave only fractions A, B, D, E, and G, *viz.* those components having a *cis*-disubstituted double bond in the molecule. By placing samples of Y on the column operated at 180° further small fractions I, J (less than 1% of total product, X) were eluted. All the fractions were collected by cooling the column effluent to $-70°$.

Analytical Gas Chromatography.—Column 1, a 200 ft. × 0·01 in. nylon capillary coated with squalane and operated at 83° with nitrogen carrier gas, was used to separate the saturated and unsaturated hydrocarbons. Column 2, a 4 ft. × $\frac{1}{4}$ in. copper column packed with 30—60 mesh Celite brick-dust coated with 40% by weight of glycerol saturated with silver nitrate, was operated at 57° and an argon flow of 45 ml./min. The relative retention volumes of the hydrocarbons on the two columns are given below:

Fraction	A	B	C	D	E	F	G	Ha	Hb
Column 1	1·00	1·13	1·34	1·34	1·49	1·65	2·13	2·45	2·50
Column 2		4·09	1·54	*	6·67	1·00			

* Not eluted after several hr.

Hydrogenation.—Each of the fractions A–J was hydrogenated completely in glacial acetic acid with platinic oxide catalyst at room temperature and atmospheric pressure.

Dehydrogenation.—Each of the fractions A–J was passed, in the vapour state in a slow stream of nitrogen, through a short tube at 250° packed with 30% palladium–charcoal catalyst. Fractions A, C, E, H, I, and J were aromatised on one passage through the tube, but fractions B and F resisted aromatisation even after several passages.

The absorption bands for the double bonds $R^1R^2C{=}CHR^3$ in cm.$^{-1}$ (R^1, R^2, R^3 = alkyl, unless otherwise stated) are given below.

Fraction A. Infrared spectrum identical with that of 4-vinylcyclohexene. *Fraction* B.

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[12] Cope, *J. Amer. Chem. Soc.*, 1950, **72**, 1131; 1952, **75**, 3212.

4-*Methyl*-4-*vinylcyclohexene* (Found: C, 87·9; H, 12·1. C_9H_{14} requires C, 88·4; H, 11·6%); $\nu_{max.}$ 1000, 915 (R^2, R^3 = H), and 765 cm.$^{-1}$ (R^2 = H, *cis*). *Fraction* C. Mixture of 1-methyl-4- and -5-vinylcyclohexene (Found: C, 88·4; H, 11·7. Calc. for C_9H_{14}: C, 88·4; H, 11·6%); $\nu_{max.}$ 991, 911 (R^2, R^3 = H), 798 and 782 cm.$^{-1}$. Dehydrogenation gave a product whose infrared spectrum was identical with that of a mixture of 3- and 4-ethyltoluene in the ratio 45 : 55. *Fraction* D. Infrared spectrum identical with that of authentic *cis,cis*-cyclo-octa-1,5-diene. *Fraction* E. 4-*Isopropenylcyclohexene* (Found: C, 88·7; H, 11·4. C_9H_{14} requires C, 88·4; H, 11·6%); $\nu_{max.}$ 891 (R^3 = H) and 724 cm.$^{-1}$ (R^2 = H, *cis*). It was dehydrogenated to isopropylbenzene. *Fraction* F. Mixture of 1,4- and 2,4-dimethyl-4-vinylcyclohexene (Found: C, 88·3; H, 11·8. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%); $\nu_{max.}$ 1000, 912 (R^2, R^3 = H), and 803 cm.$^{-1}$. Their ratio, 66 : 34, was derived from the proportions of the saturated hydrocarbons (III) + (IV) to (I) + (II). *Fraction* G. 1-*Methylcyclo-octa*-1,5-*diene* (Found: C, 88·5; H, 11·2. C_9H_{14} requires C, 88·4; H, 11·6%); it absorbed 2·0 mol. of hydrogen. Ozonolysis in carbon tetrachloride at 0° gave a colourless solid ozonide which, after removal of the solvent, was oxidised by warming with 5% hydrogen peroxide until all the solid had dissolved. The solution was concentrated under reduced pressure and, by chromatography on Whatman No. 1 paper using a liquid phase of butan-1-ol saturated with 1·5N-ammonium hydroxide, the residue was resolved into only succinic and lævulic acids. Strong absorption bands at 705 and 835 cm.$^{-1}$ confirm the presence of *cis*-disubstituted and trisubstituted bonds, respectively. *Fraction* H. On elution this was divided into two almost equal parts. The two parts were rechromatographed to give enriched fractions, Ha and Hb. Repetition of this process led to pure *m*-mentha-1,8-diene, $\nu_{max.}$ 888 (R^3 = H) and 784 cm.$^{-1}$, and *p*-mentha-1,8-diene, $\nu_{max.}$ 888 (R^3 = H) and 797 cm.$^{-1}$. Dehydrogenation yielded *m*- and *p*-cymene in the ratio 55 : 45, the same ratio as found by gas chromatography of the menthadienes themselves. *Fraction* I, b. p. 133° (air bath)/20 mm., absorbed 2·0 mol. of hydrogen to give a saturated hydrocarbon with an infrared spectrum identical with that of cyclohexylcyclohexane.[13] Dehydrogenation yielded biphenyl, m. p. and mixed m. p. 70°. *Fraction* J absorbed 2·0 mol. of hydrogen. On dehydrogenation it afforded a product with an infrared spectrum identical with that of a 1 : 1 mixture of 3- and 4-methylbiphenyl. Gas chromatography [14] showed only peaks corresponding to these methylbiphenyls.

1-Ethyl-1,3- and -1,4-dimethylcyclohexane were prepared by treating 1-chloro-1-ethyl-3- and -4-methylcyclohexane, respectively, with dimethylzinc under conditions similar to those used in the preparation of 1-ethyl-1-methylcyclohexane.[10] Each reaction yielded a pair of closely-boiling saturated hydrocarbons which were separated into the configurational isomers by preparative gas chromatography.

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MEDICAL RESEARCH COUNCIL UNIT,
WASHINGTON SINGER LABORATORIES,
THE UNIVERSITY, EXETER.

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[13] American Petroleum Institute Research Project 44, No. 1836 (1956).

[14] Beaven, James, and Johnson, *Nature*, 1957, **179**, 490.