

## MECHANISM OF THERMAL AROMATIZATION OF BUTADIENE-ETHYLENE AND BUTADIENE-PROPYLENE MIXTURES

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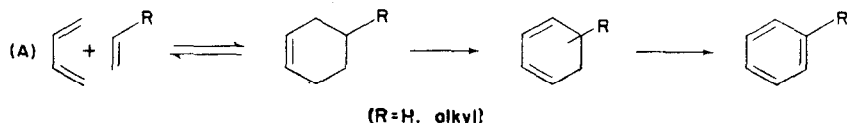
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**Abstract**—The thermal aromatization of butadiene–ethylene and butadiene–propylene mixtures was investigated at 550° in order to clarify the role of lower mono-olefins in the formation of aromatics by the Hague and Wheeler mechanism. The olefins react with butadiene to yield the Diels-Alder adducts—cyclohexene and 4-methylcyclohexene, respectively. On increasing the contact time from 4 to 8 sec a definite trend in the composition of the aromatic product was detected showing preferred formation of benzene in the presence of ethylene, and of toluene in the presence of propylene.

THE thermal decomposition of pure butadiene has been reexamined recently,<sup>3</sup> as part of an investigation on the mechanism of thermal aromatization of hydrocarbons. In the present paper a study on the role of aliphatic mono-olefins in the aromatization process is reported. According to Hague and Wheeler,<sup>4</sup> mono-olefins react with dienes to form cyclo-olefins, which then undergo dehydrogenation to aromatics. This scheme has been widely accepted,<sup>5,6</sup> although there is little unambiguous experimental evidence to support it. Thus, the data reported by Wheeler and Wood<sup>7</sup> establish only the formation of cyclohexene from ethylene and butadiene but do not prove the occurrence of *direct* thermal dehydrogenation of the cyclo-olefin to benzene, and furthermore no benzene was found in the decomposition products of cyclohexene at 500–600°.<sup>8</sup>

According to the Hague and Wheeler hypothesis, ethylene and propylene should react with butadiene as follows:



The detailed study<sup>3</sup> of the thermal decomposition of pure butadiene at 550° has shown that, contrary to the original assumption, the primary dimeric adduct, 4-vinylcyclohexene, does not form the skeletally related products, ethylbenzene and styrene, only.

Instead, a complex series of double bond and skeleton rearrangements, as well as carbon–carbon splitting reactions occur. As a result benzene and toluene, as well as the corresponding hydroaromatic products, i.e. the compounds expected in reaction sequence (A), are also formed from butadiene itself. Hence the occurrence of the

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<sup>3</sup> E. Gil-Av, J. Shabtai and F. Steckel, *Ind. Eng. Chem.* **52**, 31 (1960); <sup>b</sup> *J. Chem. Eng. Data* **5**, 98 (1960).

<sup>4</sup> E. N. Hague and R. V. Wheeler, *J. Chem. Soc.* 378 (1929).

<sup>5</sup> L. F. Fieser and M. Fieser, *Organic Chemistry* (2nd ed.), p. 568. Reinhold, New York (1950).

<sup>6</sup> R. E. Kinney and D. J. Crowley, *Ind. Eng. Chem.* **46**, 258 (1954).

<sup>7</sup> R. V. Wheeler and W. L. Wood, *J. Chem. Soc.* 1819 (1930).

<sup>8</sup> L. Kuchler, *Trans. Faraday Soc.* **35**, 874 (1939).

reactions of ethylene and propylene, postulated by Hague and Wheeler, cannot be proved by the examination of the reaction products of mixtures of butadiene and the olefins, unless a quantitative comparison is made with pure butadiene, treated in closely similar conditions. Parallel runs were therefore carried out with binary mixtures of butadiene plus either argon, ethylene, or propylene.

All experiments were performed at 550°. In accordance with previous experience,<sup>3</sup> aromatization is incomplete at this temperature, and intermediate compounds of the process can be isolated. Pure ethylene and propylene are practically unchanged in these conditions.<sup>9</sup>

Because of the weak dienophilic character of aliphatic mono-olefins, their addition to the diene proceeds far slower than the competing dimerization of butadiene. At 550° the rate constant was found to be equal to  $K = 1340 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$  for ethylene,<sup>10</sup> and  $K \approx 1000 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$  for propylene.<sup>3</sup> On the other hand the dimerization of butadiene<sup>10</sup> has a rate constant as high as  $K = 8000 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$  at the same temperature. A considerable excess (3.9:1) of the olefins over butadiene had therefore to be used in order to obtain a reasonable amount of products according to sequence (A).

The runs were carried out at atmospheric pressure, and the contact time was 4 sec in one set of experiments and 8 sec in another. The resulting products were worked up as shown in Fig. 1, essentially according to the procedure used in the study of butadiene.<sup>3</sup> The liquids formed were separated by repeated displacement chromatography over silica gel at 0° into the following three cuts: (1) alkylcyclohexenes plus most of the unconjugated cyclic diolefins (e.g. 4-vinylcyclohexene); (2) conjugated diolefins (e.g. ethyl- and dimethyl-1,3-cyclohexadienes) plus some 4-vinylcyclohexene; (3) aromatics, containing only a few percent of conjugated dienes. The chromatographic cuts were fractionally distilled and their composition determined quantitatively by a combination of catalytic hydrogenation and dehydrogenation, gas-liquid partition chromatography, infra-red and ultra-violet spectroscopy. Details on the methods used are given in the Experimental.

The results are presented in Table 1 and in Fig. II. Experiments 3 and 6 served to establish the distribution of the reaction products of butadiene itself, when diluted with argon to the same initial partial pressure (155 mm) as in the experiments with olefins. The addition of ethylene and propylene to butadiene has several effects. On the one hand the olefins, which are stable in comparable conditions in the pure state, undergo thermal decomposition to some extent, e.g., 6–7% at 4 sec contact time. On the other hand, the conversion of butadiene is decreased, particularly at the higher contact time, e.g., to 58.5% (Expt. 4) and 55.5% (Expt. 5), as compared with 77% (Expt. 6). Further, propylene, probably by its inhibiting action,<sup>11</sup> reduces the aromatization of the liquid product to 26.0% (Expt 2) and 31.6% (Expt. 5) as compared with 46.5% (Expt. 3) and 49% (Expt. 6), respectively.

However, the most important effect from the point of view of the present study, is the formation of cyclo-olefins corresponding to Diels-Alder reaction with butadiene. Cyclohexene is formed in considerable amounts in Expts 1 and 4, but only in traces in all other runs. On the other hand, the amount of 4-methylcyclohexene in Expts. 2

<sup>9</sup> For instance propylene was found to yield only 0.1% of aromatics at 690° and 20 sec contact time.

<sup>10</sup> D. Rowley and H. Steiner, *Disc. Faraday Soc.* **10**, 198 (1951).

<sup>11</sup> L. S. Echols and R. N. Pease, *J. Amer. Chem. Soc.* **61**, 208, 1024 (1939).

FIG. 1 Analysis of liquid products<sup>a</sup>.

		Component or group of isomers	Method of determination	
Liquid product	Repeated Displacement Chromatography	Cyclic mono-olefins and unconjugated semicyclic dienes	Fractional distillation	Aliphatic olefins Cyclohexene 1-Methylcyclohexene 3-Methylcyclohexene 4-Methylcyclohexene } <i>e</i>
			Fractional distillation	C <sub>8</sub> cyclohexenes 4-Vinylcyclohexene plus some double bond isomers } <i>b, c, d, g</i>
		Cyclodienes and conjugated semicyclic dienes	Fractional distillation	Cyclohexadienes Methylcyclohexadienes Ethyl- and dimethylcyclohexadienes Methylmethylenecyclohexenes 4-Vinylcyclohexene (small amount) } <i>b, d, g</i> <i>d, g</i> <i>b, c, d, f</i>
		Aromatics		Benzene Toluene Ethylbenzene <i>o</i> -Xylene <i>m</i> -Xylene <i>p</i> -Xylene Styrene } <i>h</i>

<sup>a</sup> For more details see ref. 3b Table 2.

<sup>b</sup> Hydrogenated to corresponding saturated compound, which was analyzed by IR.

<sup>c</sup> IR spectroscopy.

<sup>d</sup> Dehydrogenation to corresponding aromatic, which was analyzed by G.L.P.C. or IR.

<sup>e</sup> G.L.P.C. with a silver nitrate/glycol column<sup>20</sup>.

<sup>f</sup> More than 80% of the 4-vinylcyclohexene was contained in the first chromatographic cut.

<sup>g</sup> UV spectroscopy.

<sup>h</sup> G.L.P.C. with a benzylidiphenyl column (see Experimental).

and 5 is from 7–15 times higher than in the corresponding butadiene-argon experiments (Fig. 2). Whereas the reaction of butadiene with ethylene is well known, the formation of 4-methylcyclohexene from propylene and butadiene, at near atmospheric pressure, has been reported only recently.<sup>3</sup>

The rate of formation of the two cyclo-olefins agrees closely with available kinetic data.<sup>3,10</sup> However, equilibrium, as estimated from thermodynamic data, is far from being reached even at the higher contact time. The 4-methylcyclohexene formed showed little tendency to undergo double bond migration, as evidenced by the presence of only small amounts of the pertinent isomers (Table 1, Expts. 2 and 5). If rapid equilibration had been possible in the experimental conditions, considerable amounts of 1- and 3-methylcyclohexene would have resulted, according to extrapolation of equilibrium data for 25°<sup>12</sup> and 250°.<sup>13</sup>

According to reaction sequence (A), ethylene and propylene should enhance the formation of benzene and toluene, respectively. Comparison of the absolute amounts of these aromatics, formed in the different runs, does not permit to evaluate such an effect, because of the higher conversion of butadiene in Expts. 3 and 6, as compared

<sup>12</sup> E. Gil-Av and J. Herling, unpublished data.

<sup>13</sup> E. Gil-Av and J. Shabtai, *Chem. & Ind.* 1630 (1959).

TABLE 1. PRODUCTS OF THERMAL DECOMPOSITION<sup>a</sup> OF BUTADIENE-MONOOLEFIN AND BUTADIENE-ARGON MIXTURES, AT 550°

Experiment No.	1	2	3	4	5	6
Starting mixture	C <sub>2</sub> H <sub>4</sub> -C <sub>4</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub> -C <sub>4</sub> H <sub>6</sub>	A-C <sub>4</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub> -C <sub>4</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub> -C <sub>4</sub> H <sub>6</sub>	A-C <sub>4</sub> H <sub>6</sub>
Volume, <sup>b</sup> l.	195:50	195:50	195:50	195:50	195:50	195:50
Contact time, sec	4	4	4	8	8	8
Recovery, wt. %	95.5	94.8	92.7	94.0	96.5	95.3
Converted						
butadiene, %	45.0	40.8	45.5	58.5	55.0	77.0
Gaseous product, l.	229.0 <sup>c</sup>	224.8 <sup>d</sup>	236.0 <sup>e</sup>	212.0 <sup>f</sup>	224.0 <sup>g</sup>	233.5 <sup>h</sup>
Liquid product, g	29.7	31.0	22.5	59.6	52.2	56.1
Aromatics, wt. %	29.5 (40.5) <sup>i</sup>	22.6 (26.0) <sup>j</sup>	46.5	36.0 (49.0) <sup>k</sup>	26.1 (31.6) <sup>l</sup>	49.0
Olefins, g.	20.9	24.3	12.0	38.2	38.6	28.6
Composition, wt. %:						
Low-boiling fraction <sup>k</sup>	1.9	4.4	1.4	3.2	9.6	2.8
Cyclohexene	38.0	traces	traces	42.1	traces	traces
Methylcyclohexenes	3.0	24.8 <sup>l</sup>	3.3	3.2	29.1 <sup>m</sup>	5.5
Ethyl- & Dimethyl-cyclohexenes	3.3	7.3	7.1	4.3	8.1	12.8
Cyclohexadienes <sup>n</sup>	1.8	1.5	1.3	2.2	1.1	1.2
Methylcyclohexadienes <sup>o</sup>	2.1	2.8	2.5	1.8	3.0	1.9
4-Vinylcyclohexene plus C <sub>8</sub> isomers <sup>p</sup>	49.2	52.6	78.7	42.4	46.2	68.7
Undetermined <sup>q</sup>	0.7	6.6	5.7	0.8	2.9	7.1
Aromatics, g.	8.8	6.7	10.5	21.4	13.6	27.5
Composition, wt. %:						
Benzene	18.7	18.3	17.8	24.3	12.8	18.1
Toluene	24.1	31.9	29.0	24.9	36.5	26.9
Ethylbenzene	11.8	11.5	10.8	10.8	11.4	11.6
<i>m</i> - and <i>p</i> -Xylenes	11.3	11.0	11.8	10.9	13.8	11.9
<i>o</i> -Xylene	25.2	20.7	23.3	22.6	21.2	24.4
Styrene	8.9	6.6	7.3	6.5	4.3	7.1

<sup>a</sup> In an empty stainless steel reactor. <sup>b</sup> N.T.P. <sup>c</sup> Composition, Vol. %: H<sub>2</sub>, 2.2; CH<sub>4</sub>, 1.2; C<sub>2</sub>H<sub>4</sub>, 77.6; C<sub>3</sub>H<sub>6</sub>, 2.9; C<sub>3</sub>H<sub>8</sub>, 1.6; C<sub>3</sub>H<sub>8</sub>, 0.4; C<sub>4</sub>H<sub>6</sub>, 11.5; C<sub>4</sub>H<sub>8</sub>, 2.3; n-C<sub>4</sub>H<sub>10</sub>, 0.3. <sup>d</sup> Composition, Vol. %: H<sub>2</sub>, 1.9, CH<sub>4</sub>, 1.0; C<sub>2</sub>H<sub>4</sub>, 0.8; C<sub>3</sub>H<sub>6</sub>, 0.1; C<sub>3</sub>H<sub>8</sub>, 76.7; C<sub>3</sub>H<sub>8</sub>, 3.6; C<sub>4</sub>H<sub>6</sub>, 12.5; C<sub>4</sub>H<sub>8</sub>, 2.3, n-C<sub>4</sub>H<sub>10</sub>, 1.1. <sup>e</sup> Composition, Vol. %: H<sub>2</sub>, 5.0; A, 77.0; CH<sub>4</sub>, 2.4; C<sub>2</sub>H<sub>4</sub>, 1.7; C<sub>2</sub>H<sub>6</sub>, 0.3; C<sub>3</sub>H<sub>6</sub>, 0.4; C<sub>3</sub>H<sub>8</sub>, 0.1; C<sub>4</sub>H<sub>6</sub>, 11.0; C<sub>4</sub>H<sub>8</sub>, 1.6; n-C<sub>4</sub>H<sub>10</sub>, 0.5. <sup>f</sup> Composition, Vol. %: H<sub>2</sub>, 3.6; CH<sub>4</sub>, 1.2; C<sub>2</sub>H<sub>4</sub>, 78.5; C<sub>2</sub>H<sub>6</sub>, 4.3; C<sub>3</sub>H<sub>6</sub>, 0.7; C<sub>3</sub>H<sub>8</sub>, 0.2; C<sub>4</sub>H<sub>6</sub>, 9.2; C<sub>4</sub>H<sub>8</sub>, 1.6; n-C<sub>4</sub>H<sub>10</sub>, 0.7. <sup>g</sup> Composition, Vol. %: H<sub>2</sub>, 4.3; CH<sub>4</sub>, 1.1; C<sub>2</sub>H<sub>4</sub>, 0.4; C<sub>2</sub>H<sub>6</sub>, 0.1; C<sub>3</sub>H<sub>6</sub>, 76.5; C<sub>3</sub>H<sub>8</sub>, 6.4; C<sub>4</sub>H<sub>6</sub>, 9.6; C<sub>4</sub>H<sub>8</sub>, 1.0; n-C<sub>4</sub>H<sub>10</sub>, 0.6. <sup>h</sup> Composition, Vol. %: H<sub>2</sub>, 4.9; A, 80.0; CH<sub>4</sub>, 4.3; C<sub>2</sub>H<sub>4</sub>, 2.7; C<sub>3</sub>H<sub>6</sub>, 1.4; C<sub>3</sub>H<sub>8</sub>, 0.3; C<sub>3</sub>H<sub>8</sub>, 0.1; C<sub>4</sub>H<sub>6</sub>, 4.7; C<sub>4</sub>H<sub>8</sub>, 1.0; n-C<sub>4</sub>H<sub>10</sub>, 0.6. <sup>i</sup> Calculated on liquid product minus cyclohexene. <sup>j</sup> Calculated on liquid product minus methylcyclohexenes formed from propylene. <sup>k</sup> Open-chain C<sub>5</sub> and C<sub>6</sub> mono- and diolefins. <sup>l</sup> 1-Methylcyclohexene 0.6%, 3-methylcyclohexene 1.0%, 4-methylcyclohexene 98%, methylenecyclohexane <0.1%, ethylcyclopentene 0.4%. <sup>m</sup> 1-Methylcyclohexene 1.4%, 3-methylcyclohexene 4.0%, 4-methylcyclohexene 89%, methylenecyclohexane 0.2%, ethylcyclopentene 5.4%. <sup>n</sup> U.V. shows the presence of a 1,3-cyclohexadiene system. <sup>o</sup> Ethyl- and dimethyl-1,3-cyclohexadienes and methyl-methylenecyclohexenes (see ref. 3).

with the parallel runs, and the decrease of aromatization of the liquid products in the presence of propylene, mentioned above. On the other hand, the distribution of the individual components in the aromatic cut should reflect the influence of the added olefins. If the concentrations of ethylbenzene and the xylenes are compared (Table 1), it is seen that they are closely similar, and that the slight deviations which exceed the mean error ( $\pm 2-3\%$ ) are random. For benzene, at 4 sec contact time, the increase in the presence of ethylene hardly exceeds the analytical error (18.7 per cent Expt. 1, as compared with 17.8 per cent Expt. 3), whereas for toluene there is a small but definite increase in the presence of propylene from 29.0 per cent (Expt. 3) to 31.9 per cent (Expt. 2). At higher contact time, on the other hand, the slight trend found at 4 sec is much more marked for both the C<sub>6</sub> and the C<sub>7</sub> aromatics. At 8 sec the benzene

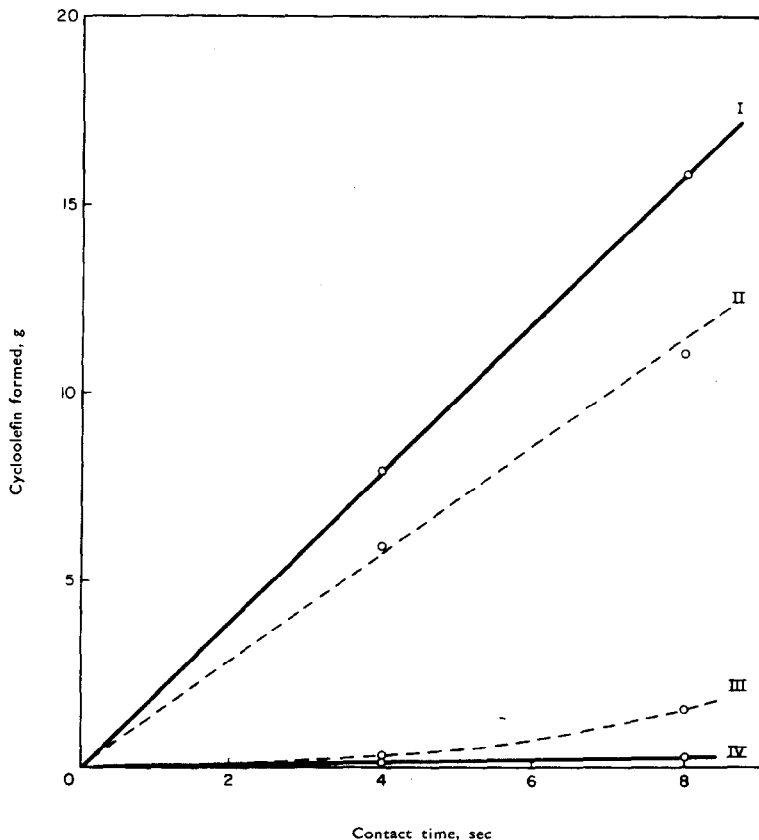


FIG. 2. Formation of cyclic olefins at 550°: cyclohexene (I) from butadiene and ethylene; 4-methylcyclohexene (II) from butadiene and propylene; methylcyclohexenes (III) and cyclohexene (IV) from butadiene in the presence of argon.

concentration is increased in fact from 18.1 per cent (Expt. 6) to 24.3% (Expt. 4) in the presence of ethylene, and the toluene concentration from 26.9 per cent (Expt. 6) to 36.5 per cent (Expt. 5) in the presence of propylene. These differences, and particularly the 10 per cent increase for toluene, are larger than any deviations observed in the composition of the aromatics in the six experiments, and are therefore significant.

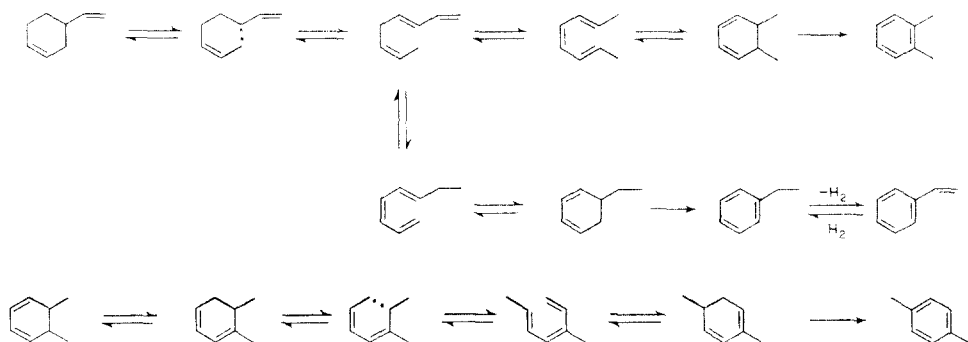
A further indication for the occurrence of reaction sequence (A) is found in the formation of more cyclohexadiene in the presence of ethylene, i.e., 0.84 g (Expt. 4), as compared with 0.3 g (Expt. 6), and correspondingly more methylcyclohexadienes in the presence of propylene, i.e., 1.2 g (Expt. 5), as compared with 0.5 g (Expt. 6). Important concentrations of these substances are not expected to form, because of the instability of the cyclohexadienes.

At higher contact time there is therefore a definite trend in the composition of the products, which is in accord with the reactions postulated by Hague and Wheeler. Further prolongation of contact time, and increase of the proportion of the olefins could raise the importance of this mechanism in the formation of aromatics. On the other hand, decrease of stability of the adducts limits the possibility of enhancing the occurrence of sequence (A) by higher temperatures. For testing further the proposed

mechanism and its contribution to the overall aromatization process, experiments with suitably labelled compounds are indicated.

The thermal conversion of cyclohexadienes to aromatics has been shown to proceed readily,<sup>14-16</sup> and a radical mechanism has been assumed.<sup>17</sup> A similar mechanism may be operative in the dehydrogenation of cyclohexenes to the corresponding cyclohexadienes according to sequence (A). The results obtained indicate, however, that this step of the reaction is a slow one. On the other hand, in the case of 4-vinylcyclohexene, the product of the competing dimerization of butadiene, the second double bond is already present in the molecule and therefore the transition to the cyclohexadiene structure could be accomplished by an isomerization step, requiring a lower activation energy.

In the present experiments the main part of the aromatics were formed via dimerization of butadiene to 4-vinylcyclohexene.<sup>3</sup> The biallylic biradical mechanism of Pines *et al.*<sup>14,15</sup> originally proposed to explain the thermal reactions of limonene, a homolog of 4-vinylcyclohexene, could be applied also in this case:



All stable intermediates required by this mechanism, including small amounts of normal octatrienes,<sup>3</sup> have been identified in the reaction products. The formation of ethylcyclohexadiene from the skeletally related 4-vinylcyclohexene can be equally well explained by double bond migration not involving a rupture of the ring system.<sup>3</sup>

In agreement with the biradical mechanism, *o*- and *p*-xylene have been found to predominate in the xylene fraction. 1,3-dimethylcyclohexadiene and *m*-xylene, were, however, also detected. Thus in Expt. 6, the dimethylcyclohexadienes contained 56 per cent *o*-, 31 per cent *p*-, and 13 per cent *m*-isomer. The xylene fraction obtained in the same experiment had the following composition, as determined by infra-red analysis: *o*-xylene, 67 per cent, *p*-xylene, 24 per cent and *m*-xylene, 9 per cent. This distribution pattern is clearly related to that of the dimethylcyclohexadienes, which have been shown to be easily dehydrogenated to the corresponding aromatics under thermal conditions. It was found previously<sup>3</sup> that xylenes do not isomerize under the experimental conditions used.

The Pines mechanism cannot account for the formation of the *m*-isomers, essentially because only monocyclic six membered ring compounds are supposed to act as

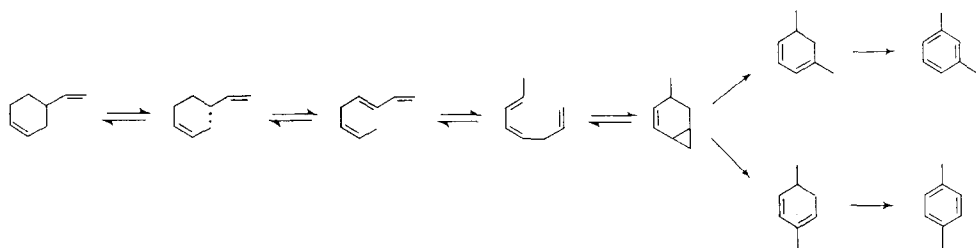
<sup>14</sup> H. Pines and J. Ryer, *J. Amer. Chem. Soc.* **77**, 4370 (1955).

<sup>15</sup> H. Pines and C. T. Chen, *J. Amer. Chem. Soc.* **81**, 928 (1959).

<sup>16</sup> G. J. Janz, *J. Chem. Phys.* **22**, 751 (1954).

<sup>17</sup> H. Pines and J. Kozłowski, *J. Amer. Chem. Soc.* **78**, 3776 (1956).

intermediates of skeleton rearrangement. However, consideration of other ring systems, less likely to occur because of lower stability, would explain the formation of the relatively small amounts of these isomers. Such an intermediate could for instance be methylnorcarene:



Formation of a norcarene derivative from 1,4,6-heptatriene-1,2-dicarboxylic acid diester has been observed by Alder and Bong.<sup>18</sup>

The formation of benzene and toluene by splitting reactions of the C<sub>8</sub> cyclohexadienes has been discussed elsewhere.<sup>3</sup>

## EXPERIMENTAL

**Apparatus and procedure.** The apparatus was similar to that used previously.<sup>3</sup> It consisted essentially of an empty stainless steel reactor, 80 cm long and 3.5 cm in internal diameter, a system for the drying and measuring of the starting mixture, and a combination of coolers, traps, a stripping column, and a gas holder of 250 l., for preliminary separation and collection of the products. The isothermal zone in the middle of the furnace had a minimum length of 40–45 cm. The system was purged with pure nitrogen at the beginning of each experiment. When the desired temp was approached, the gaseous mixture was introduced and the heating adjusted until a stable temp distribution was obtained. Collection of products was started after 1–2 hr observation had shown that the gas and liquid formation rate was approximately constant. After each run the C<sub>3</sub> and C<sub>4</sub> gases, which condensed mainly in the liquid products train, were stripped of heavier components in an ice cooled column, packed with Dixon fillings, and led into the gas holder; the small amount of residue resulting from this operation was added to the main part of the liquid product. A run carried out in an empty copper tube, but in otherwise identical conditions, gave the same results as obtained with the stainless steel reactor. Though the formation of carbon was very low, the tubes were cleaned after every experiment.

**Gas analysis.** The gaseous products were determined by gas chromatography using a Perkin Elmer Model 154 Vapor Fractometer.

Two different columns were used: (1) a 4 mm × 8 m copper tube packed with 60–80 mesh silica gel; (2) a 4 mm × 3 m glass tube packed with 30% tri-isobutylene on Johns-Manville C-22 firebrick. Helium was used as the mobile phase.

**Analysis of the liquid product.** The different classes of hydrocarbons present in the liquid were separated by repeated displacement chromatography over silica gel (28–200 mesh), as described previously.<sup>3</sup> The columns used had the dimensions of 1.5 cm × 3 m and 1.0 cm × 1.8 m and the rate of percolation was 20–40 ml per hour. Losses due to polymerization were reduced to about 5–10% by cooling the columns with iced water.

**Distillation.** The two olefinic cuts obtained by chromatography (Fig. 1) were fractionally distilled on a Piros-Glover spinning band column. The reflux ratio was 50–60:1, and the take-off rate 1–2 ml per hour. Polymerization losses were reduced by adding hydroquinone, and amounted to 5–10% for the first cut and 10–15% for the second cut. The fractions, composed of individual components or groups of isomers (see Fig. 1 and reference 3b, Table 2) were further examined by the methods described below.

<sup>18</sup> K. Alder and M. Schumacher, in *Anwendungen der Dien-Synthese für die Erforschung von Naturstoffen* Vol. X, p. 66. Springer Verlag, Wien (1953).

*Catalytic hydrogenation and dehydrogenation.* The number of double bonds per molecule was determined by micro-hydrogenation using Adam's platinum catalyst.

Catalytic dehydrogenation to aromatics in conjunction with gas-liquid partition chromatography or infra-red analysis of the compounds formed was used for determining the carbon skeleton of individual cyclo-olefins or for quantitative analysis of skeleton isomers (ethyl- and dimethylcyclohexenes; ethyl- and dimethylcyclohexadienes). Dehydrogenation was carried out in a semimicro-apparatus at 300° over 5% platinum on asbestos.

*Infra-red and ultra-violet spectroscopy.* Infra-red analysis of isolated components and of their hydrogenation or dehydrogenation products was carried out with a Perkin Elmer Model 12 C spectrophotometer. Comparison was made with published spectrograms,<sup>19</sup> in the region of 3 to 15  $\mu$ .

The presence of 1,3-cyclohexadienes, and the degree of substitution at the conjugated double bond system was determined<sup>3</sup> by ultra-violet absorption, which was measured with a Beckman DU spectrophotometer in a 1 cm cell, using 95% alcohol as the solvent.

*Gas chromatography.* Mixtures of isomeric cyclo-olefins were analyzed at 30° on a 2 m column with a silver nitrate/glycol solution on firebrick, as the stationary phase.<sup>20</sup>

The aromatics were analyzed at 110° on a benzyl-diphenyl column. In the range of product composition, the error, in percent of amount present, was found to be  $\pm 5\%$  for benzene, and  $\pm 2-3\%$  for toluene and the C<sub>8</sub> aromatics.

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<sup>19</sup> A. P. I. Infrared Spectral Catalog.

<sup>20</sup> E. Gil-Av, J. Herling and J. Shabtai, *J. Chromatog.* **1**, 508 (1958); J. Shabtai, J. Herling and E. Gil-Av, *Ibid.* **2**, 406 (1959).