

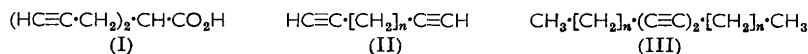
**497. Rearrangement of Diacetylenes to Aromatic Compounds.**

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Hepta-1,6-diyne-4-carboxylic acid (I) readily undergoes base-catalysed aromatisation in high yield to *m*-toluic acid. The rearrangement has been extended to diacetylenic hydrocarbons of types (II) and (III) which give mixtures consisting mainly of the correspondingly *o*-disubstituted and mono-substituted benzenes.<sup>1</sup>

By dehydrobromination and hydrolysis of diethyl di-(2-bromoallyl)malonate Perkin and Simonsen<sup>2</sup> isolated a crystalline acid, C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>, m. p. 47°, which they named “*ψ*-*m*-toluic acid.” They assigned to it the plausible structure hepta-1,6-diyne-4-carboxylic acid (I), and reported that it underwent a remarkable isomerisation by treatment with hot mineral acid, or even by boiling with water, to give *m*-toluic acid. Attempted repetition of Perkin and Simonsen’s route to this compound was uniformly unsuccessful in our hands. A preparation of authentic hepta-1,6-diyne-4-carboxylic acid, m. p. 45·5°, was carried out by dialkylation of diethyl malonate with prop-2-ynyl chloride followed by careful hydrolysis and decarboxylation.<sup>3</sup> This acid was substantially unaffected by boiling water and was only slowly attacked by mineral acid with the formation of lactonic products.<sup>4</sup> No indication could be found of the production of *m*-toluic acid or its derivatives under any of the conditions previously described.<sup>2</sup> However, when the diacetylenic acid was boiled with potassium hydroxide solution it was transformed virtually quantitatively into *m*-toluic acid.

Perkin and Simonsen suggested an unlikely mechanism involving hydration of the two triple bonds of hepta-1,6-diyne-4-carboxylic acid and aldolisation of the resulting diketoid acid. This latter acid has now been prepared by hydration of acid (I) but, as expected,



treatment with base produced only 3-methyl-5-oxocyclohex-3-ene-1-carboxylic acid,<sup>4</sup> with no trace of *m*-toluic acid. In order to examine the generality and structural requirements for this unusual rearrangement it was extended to a series of diacetylenic hydrocarbons. Preliminary experiments showed that potassium *t*-butoxide dispersed in boiling bis-(2-methoxyethyl) ether (diglyme) was a convenient basic medium. Treatment in this manner of the hydrocarbon most nearly related to (I), hepta-1,6-diyne (II; *n* = 3), rapidly caused substantial aromatisation to toluene. In a similar manner a variety of straight chain  $\alpha\omega$ -diacetylenes (II; *n* = 4, 5, 6, 10, 17) gave products consisting mainly of the isomeric *o*-dialkylbenzenes, the total conversion into aromatic compounds being in most cases around 65%. The rearrangement was not confined to terminal acetylenes; thus, nona-2,7-diyne gave the same proportions of *n*-propylbenzene and *o*-ethylmethylbenzene as did nona-1,8-diyne (II; *n* = 5). Conjugated diynes underwent the rearrangement with equal ease; thus, both octa-3,5-diyne and octa-1,7-diyne produced similar proportions of ethylbenzene and *o*-xylene.

<sup>1</sup> Eglinton, Raphael, and Willis, *Proc. Chem. Soc.*, 1960, 247.

<sup>2</sup> Perkin and Simonsen, *J.*, 1907, 816, 840, 848.

<sup>3</sup> Schulte and Reiss, *Chem. Ber.*, 1954, **87**, 964.

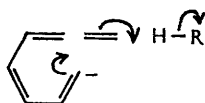
<sup>4</sup> Schulte and Nimke, *Arch. Pharm.*, 1957, **290**, 597; Schulte, Mleinek, and Schär, *ibid.*, 1958, **291**, 227.

To study the reaction in more detail the isomeric pair, deca-1,9-diyne and deca-4,6-diyne, were investigated. Analysis using a high-resolution capillary gas chromatography column calibrated with known synthetic mixtures revealed similar proportions of the expected benzenoid isomers, *n*-butylbenzene, *o*-methyl-*n*-propylbenzene, and *o*-diethylbenzene, the last two isomers predominating. However, these were by no means the only peaks to appear; at least six further products were indicated on the traces from both diynes. The ethylenic nature of these "abnormal" constituents was clearly shown by the nuclear magnetic resonance (n.m.r.) spectra of the total product. That at least some of these olefins were conjugated was demonstrated by differential ultraviolet (u.v.) spectroscopy. Infrared (i.r.) spectra showed strong indications of cyclic *cis*-double bonds (sharp band at 700 cm.<sup>-1</sup>). These olefinic properties disappeared completely when the mixture was catalytically hydrogenated (under conditions which left the benzenoid constituents unscathed). The absence of *n*-decane, demonstrated by gas-liquid chromatography (g.l.c.) of the hydrogenated mixture, showed conclusively that these olefinic constituents were certainly not straight-chain compounds but were most likely cyclic in nature. Certain unassigned peaks on the traces did not shift on hydrogenation; these almost certainly could not have corresponded to ethylenic compounds and this point is discussed below in connection with the C<sub>8</sub> diyne.

In view of the large number of isomeric possibilities for these C<sub>10</sub> by-products, detailed investigation of this aspect of the rearrangement was transferred to the C<sub>8</sub> system. Similar base-catalysed isomerisation of octa-1,7-diyne produced an eight-component mixture (capillary column). The expected ethylbenzene and *o*-xylene formed the two most important components of the mixture. As in the C<sub>10</sub> series, the spectral data (u.v., n.m.r., i.r.) clearly indicated conjugated ethylenic unsaturation (*cis*-CH=CH), and these characteristics vanished on hydrogenation. Examination by analytical and preparative g.l.c. of the hydrogenated mixture showed, of course, that the peaks due to ethylbenzene and *o*-xylene had not altered their position. However, most unexpectedly, a partly resolved double peak was also unaltered in position after hydrogenation, strongly suggesting the presence of two further aromatic isomers; these were identified by g.l.c. as *m*- and *p*-xylene! Two further components of the hydrogenated product proved to be cyclooctane and methylcycloheptane, identified by g.l.c. and n.m.r. Employment of milder rearrangement conditions (2% butoxide in diglyme for 2 hr.) gave a very similar product distribution, with the addition of two acyclic products tentatively identified as octa-1,3,5,7-tetraene and octa-2,6-diyne.

At this point it was found that a drastic simplification of this product complexity could be achieved by using carefully filtered butoxide solutions in diglyme. Even though the solution was extremely dilute (~0.2% butoxide), it effected very rapid and clean-cut isomerisation of octa-1,7-diyne to a 9:5 mixture of *o*-xylene and ethylbenzene with the formation of less than 1% of by-products. It would therefore seem at first sight that the formation of anomalous side-products in the isomerisation is associated with the presence of solid butoxide; this point is being further examined.

The simplest conception to account for the production of monoalkyl- and *o*-dialkylbenzenes from diacetylenes would seem to be a multiple prototropic rearrangement to a *cis*-allene diene of the type shown, followed by either an intramolecular Diels-Alder reaction<sup>1,5</sup> or internal attack on the allene by a terminal carbanion<sup>6</sup> as depicted. Such a mechanism would imply the necessary involvement of at least a seven-carbon chain and it is interesting to note that base-catalysed rearrangement of hexa-1,5-diyne under the above and other conditions<sup>7</sup> furnishes no detectable trace of benzene. Since the original announcement<sup>1</sup> of this aromatisation a number of allied base-catalysed transformations



<sup>5</sup> Alder and Brachel, *Annalen*, 1957, **608**, 195.

<sup>6</sup> Skattebøl and Sørensen, *Acta Chem. Scand.*, 1959, **13**, 2101.

<sup>7</sup> Sondheimer, Ben-Efraim, and Wolovsky, *J. Amer. Chem. Soc.*, 1961, **83**, 1675.

have been reported, *e.g.*, cyclo-octatetraene to benzocyclobutene,<sup>8</sup> non-conjugated macrocyclic diynes to 1,2-polymethylenebenzenes,<sup>9</sup> cyclododeca-1,3,7,9-tetrayne to biphenylene,<sup>10</sup> cyclohexadeca-1,9-dien-4,6,12,14-tetrayne to 10-diphenylsuccindene,<sup>11</sup> *cis*-oct-4-en-1,7-diyne to two dimers of *o*-dimethylenequinone,<sup>12</sup> cyclo-octadeca-1,3,7,9,13,15-hexayne to triphenylene,<sup>13</sup> and 1,6-dithiacyclodeca-3,8-diyne to 4,9-dithiabicyclo[5,3,0]deca-1(10)2,7-triene.<sup>14</sup>

Suggested mechanisms for the production of alicyclic products and *m*- and *p*-dialkylbenzenes in the non-homogeneous reactions would be premature at this stage. Certainly alkyl- and *o*-dialkylbenzenes remain unaffected under these conditions and therefore cannot be the source of the unexpected compounds. Further experiments are in hand to clarify these findings.

#### EXPERIMENTAL

Light petroleum had b. p. 30–40°. Diglyme [bis-(2-methoxyethyl) ether] was purified by heating under reflux over sodium and subsequent distillation. The g.l.c. studies were made with a Pye Argon chromatograph (packed columns) equipped with a strontium-90 detector and a Perkin-Elmer model 451 fractometer (50 m. Apiezon L capillary column and 2 m. packed columns) equipped with a flame-ionisation detector. The packed columns were also used for small-scale preparative separations, using a hot-wire detector. Peak areas were measured by means of a planimeter and standard solutions of the various aromatic hydrocarbons, singly and as mixtures, were used to evaluate the possible differing response of the detector; in practice these differences were found to be negligible.

Quantitative i.r. measurements were obtained with a Unicam S.P. 130 grating spectrophotometer and survey spectra with either a Perkin-Elmer 137 or 237 instrument. The u.v. spectra were measured with a Perkin-Elmer model 137 UV and with a Unicam S.P. 500 spectrophotometer. An Associated Electrical Industries model RS2 (60 megacycles) instrument was employed for the n.m.r. spectra, with tetramethylsilane as internal standard.

*Diethyl Di-(2-bromoallyl)malonate.*—The original method<sup>2</sup> from 1,2,3-tribromopropane was repeated but a much better yield was obtained by using 2,3-dibromoprop-1-ene as follows. The dibromopropene<sup>15</sup> (67 g.) was added dropwise to a stirred suspension of diethyl sodiomalonate [from sodium (7.8 g.) and diethyl malonate (29 g.)] in ethanol (125 ml.) at 60°, and the mixture heated under reflux for 30 min. The bulk of the solvent was removed under reduced pressure and the resulting suspension poured into dilute sulphuric acid. Isolation with ether and distillation, gave the ester as an oil (43 g.), b. p. 122–123°/0.1 mm.,  $n_D^{20}$  1.5010 (lit.,<sup>2</sup> b. p. 191°/11 mm.), which solidified to long needles, m. p. 7° (Found: C, 40.5; H, 4.6; Br, 39.3. Calc. for C<sub>13</sub>H<sub>18</sub>Br<sub>2</sub>O<sub>4</sub>: C, 39.3; H, 4.6; Br, 40.2%);  $\nu_{\max}$  (film) 1735s, 1616s, 1200s, and 855s cm<sup>-1</sup>. All attempts to convert this ester into “*ψ*-*m*-toluic acid” by the reported method<sup>2</sup> failed. It was noteworthy, however, that drastic alkaline treatment produced excellent yields of *m*-toluic acid.

*Hepta-1,6-diyne-4,4-dicarboxylic Acid.*—Dimethylhepta-1,6-diyne-4,4-dicarboxylate, m. p. 46°, was prepared in high yield by the dialkylation of diethyl malonate with prop-2-ynyl chloride<sup>4</sup> or bromide. This ester (7.5 g.), in methanol (20 ml.), was added to a warm solution of potassium hydroxide (5 g.) in 80% aqueous methanol (20 ml.). The resultant suspension was heated for 2 hr. on a steam-bath and diluted with methanol (20 ml.), the precipitated salt was collected, dissolved in water, and acidified, and the crude free acid was extracted; it (4.2 g.) had m. p. 139–140° [benzene–light petroleum (3 : 1)] (lit.,<sup>16</sup> 140°).

*Hepta-1,6-diyne-4-carboxylic Acid (I).*—The dicarboxylic acid (2.2 g.) was dissolved in pyridine (15 ml.), the solution heated under reflux for 90 min., and the solvent removed *in vacuo*. The residue was treated with dilute sulphuric acid (100 ml.); the resulting acid crystallised from light petroleum in large prisms (1.4 g.), m. p. 45.5° (lit.,<sup>18</sup> 45°).

<sup>8</sup> Eglinton, Raphael, and Willis, *Proc. Chem. Soc.*, 1962, 334.

<sup>9</sup> Dale, Hubert, and King, 1963, 73.

<sup>10</sup> Wolovsky and Sondheimer, *J. Amer. Chem. Soc.*, 1962, **84**, 2844.

<sup>11</sup> Sondheimer and Gaoni, *J. Amer. Chem. Soc.*, 1961, **83**, 4863.

<sup>12</sup> Ben-Efraim and Sondheimer, *Tetrahedron Letters*, 1963, 313.

<sup>13</sup> Amiel and Sondheimer, *Chem. and Ind.*, 1960, 1162.

<sup>14</sup> Eglinton, Lardy, Raphael, and Sim, *J.*, 1964, 1154.

<sup>15</sup> Lespieau and Bourguet, *Org. Synth.*, Coll. Vol. I, 209.

<sup>16</sup> Gaudemar, *Compt. rend.*, 1953, **237**, 71.

*Isomerisation of Acid (I) to m-Toluic Acid.*<sup>17,18</sup>—The action of boiling water, hot dilute sulphuric acid (10%), or hot potassium carbonate solution on the acid (I) produced no *m*-toluic acid, as indicated by the absence of its characteristic spectral properties. Successful isomerisation was carried out as follows. A solution of the acid (I) (590 mg.) in 10% aqueous potassium hydroxide (50 ml.) was heated under reflux for 4 hr. Acidification, and crystallisation of the product from water gave *m*-toluic acid (420 mg.), m. p. 111–112°, identical with an authentic sample.

*2,6-Dioxoheptane-4-carboxylic Acid.*<sup>7</sup>—A solution of the acid (I) (2.8 g.) in water (200 ml.) was heated under reflux with mercury-impregnated Amberlite IR-120 H resin (2.8 g.) for 30 min.<sup>19</sup> Isolation by means of ether yielded the *dioxo-acid* (2.6 g.) as needles, m. p. 72.5° (from ethyl acetate–light petroleum) (Found: C, 56.0; H, 6.8.  $C_8H_{12}O_4$  requires C, 55.8; H, 7.0%). Base treatment of this compound gave no *m*-toluic acid, but the product showed spectral properties in accord with the expected 3-methyl-5-oxocyclohex-3-ene-1-carboxylic acid.

*Preparation of Diacetylenes.*—Hexa-1,5-diyne,<sup>20</sup> hepta-1,6-diyne,<sup>21</sup> octa-1,7-diyne,<sup>22</sup> nona-1,8-diyne,<sup>23,24</sup> deca-1,9-diyne,<sup>23</sup> nona-2,7-diyne,<sup>25</sup> octa-3,5-diyne,<sup>26</sup> deca-4,6-diyne,<sup>26</sup> tetradeca-1,13-diyne<sup>27</sup> were prepared by standard literature methods.

Heneicosa-1,20-diyne was obtained as follows. Undeca-10-yn-1-yl chloride<sup>28</sup> (17.3 g.) in benzene (250 ml.) was treated with triethylamine (11 g.), set aside overnight at room temperature, then acidified with dilute sulphuric acid, and the diketene isolated with ether. The residue after removal of solvent was dissolved in aqueous ethanolic potassium hydroxide [potassium hydroxide (13 g.) water (10 ml.), ethanol (125 ml.)], set aside for 48 hr., and refluxed for 4 hr. The *heneicosa-1,20-diyne-11-one* (13.6 g.) separated from the cooled solution in plates, m. p. 46–47° (from aqueous methanol) (Found: C, 83.4; H, 11.0.  $C_{21}H_{34}O$  requires C, 83.4; H, 11.3%);  $\nu_{\max}$  (film) 3270, 2110 ( $-C\equiv C-H$ ), and 1700  $cm^{-1}$ . A mixture of the ketone (500 mg.), dioxan (10 ml.), water (20 ml.), concentrated hydrochloric acid, and zinc amalgam (10 g.) was heated under reflux for 6 hr., during which time a further quantity of acid (5 ml.) was added. Isolation by light petroleum and chromatography on alumina (grade V) gave *heneicosa-1,20-diyne* as a waxy solid, m. p. 47–48° (from methanol) (single peak on g.l.c.) (Found: C, 87.3; H, 12.6.  $C_{21}H_{36}$  requires C, 87.4; H, 12.6%);  $\nu_{\max}$  (film) 3300, 2110, and 725  $cm^{-1}$ .

*Aromatisation of Diynes (General Method).*—The basic medium was prepared just before use, as an opalescent dispersion, by refluxing freshly-prepared potassium *t*-butoxide (previously heated at 160° under reduced pressure until sublimation started) with ten times its weight of diglyme. The diyne (500 mg.) and this reagent (3 g. of butoxide in 30 ml. of solvent) were refluxed under nitrogen for the requisite period (4–15 hr.). The mixture was diluted with water and extracted with pentane. Repeated washing with water, drying ( $MgSO_4$ ), and evaporation of the extract gave the hydrocarbons.

The aromatic products were detected by the absorption bands,  $\gamma(CH)$ , near 750 and 690  $cm^{-1}$

Diacetylene	Main benzenoid products
Hexa-1,5-diyne (II; $n = 2$ )	—
Hepta-1,6-diyne (II; $n = 3$ )	Toluene
Octa-1,7-diyne (II; $n = 4$ )	} Ethylbenzene and <i>o</i> -xylene
Octa-3,5-diyne (III; $n = 1$ )	
Nona-1,8-diyne (II; $n = 5$ )	} <i>n</i> -Propylbenzene and <i>o</i> -ethyltoluene
Nona-2,7-diyne	
Deca-1,9-diyne (II; $n = 6$ )	} <i>n</i> -Butylbenzene, <i>o</i> - <i>n</i> -propyltoluene, and <i>o</i> -diethylbenzene
Deca-4,6-diyne (III; $n = 2$ )	
Tetradeca-1,13-diyne (II; $n = 10$ )	} Complex mixture of isomeric <i>o</i> -dialkylbenzenes
Heneicosa-1,20-diyne (II; $n = 17$ )	

<sup>17</sup> Harkin, B.Sc. Thesis, Glasgow University, 1955.

<sup>18</sup> Rosenfeld, B.Sc. Thesis, Glasgow University, 1959.

<sup>19</sup> Newman, *J. Amer. Chem. Soc.*, 1953, **75**, 4740.

<sup>20</sup> Raphael and Sondheimer, *J.*, 1950, 120.

<sup>21</sup> Kamm and Marvel, *Org. Synth.*, Coll. Vol. I, 25.

<sup>22</sup> Bader, Cross, Heilbron, and Jones, *J.*, 1949, 619.

<sup>23</sup> Everett and Kon, *J.*, 1950, 3131.

<sup>24</sup> Lespieau and Journaud, *Compt. rend.*, 1929, **188**, 1410.

<sup>25</sup> Henne and Greenlee, *J. Amer. Chem. Soc.*, 1945, **67**, 484.

<sup>26</sup> Armitage, Jones, and Whiting, *J.*, 1951, 44.

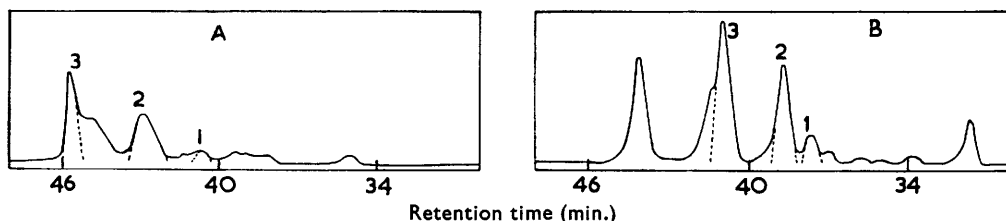
<sup>27</sup> Eglinton and Galbraith, *J.*, 1959, 889.

<sup>28</sup> Sauer, *J. Amer. Chem. Soc.*, 1947, **69**, 2444.

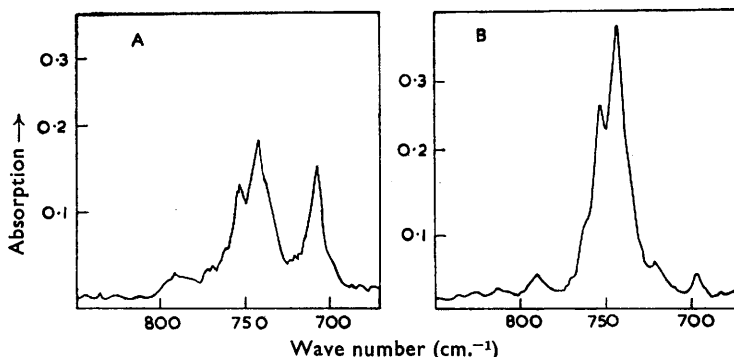
due to *o*-disubstituted and monosubstituted benzenes, respectively; by permanganate oxidation to phthalic and benzoic acids, respectively, and by comparative g.l.c. studies with authentic alkylbenzenes where feasible.

*Deca-1,9-diyne and Deca-4,6-diyne.*—The relevant hydrocarbon was heated under reflux as above for 8 hr., and the product examined by capillary g.l.c. and n.m.r., i.r., and u.v. spectroscopy. (A time study of the progress of the reaction of deca-4,6-diyne showed that no diyne was detectable after 1 hr.; after 25 hr. the g.l.c. pattern was essentially similar.) The product of hydrogenation with 10% palladium-charcoal in ethyl acetate was examined in exactly the same manner.

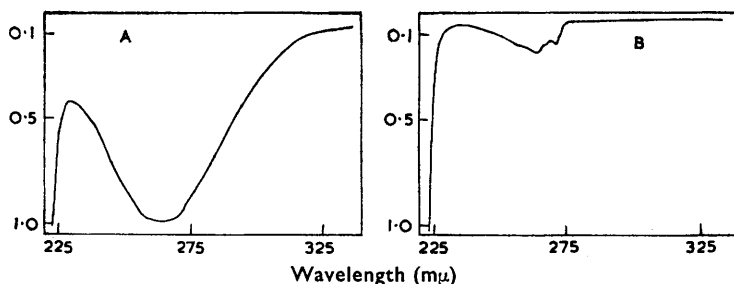
The "before" and "after" results for deca-1,9-diyne are illustrated in the Figure. The g.l.c. trace of the primary product showed a nine-component mixture, of which the three peaks indicated corresponded to *n*-butylbenzene, *o*-diethylbenzene, and *o*-*n*-propyltoluene in approximate proportions of 2 : 5 : 6; these identifications were made by direct comparison with



Apiezon L capillary column with flame-ionisation detector; 50 m.; 81°; 50 and 110 ml./min., respectively (total flow). 1. *n*-Butylbenzene. 2. *o*-*n*-Propyltoluene. 3. *o*-Diethylbenzene.



Cell path 0.51 cm.; concentrations 4.6 and 11.1 mg./ml., respectively, in carbon disulphide.



Cell paths 0.1 and 0.2 cm., respectively; concentrations 0.64 and 0.79 mg./ml., respectively, in cyclohexane.

G.l.c., i.r., and u.v. characteristics of the primary product (A) and the hydrogenated product (B) from the rearrangement of deca-1,9-diyne.

authentic samples (see Table). The hydrogenated product also showed the expected peaks for these aromatic isomers in the same proportions. Seven other components were detectable in the hydrogenation product but *n*-decane was not present.

Physical properties of aromatic reaction products.

		Bands in 800—650 cm. <sup>-1</sup> region (CS <sub>2</sub> ; 0.51 mm. cell)			<i>R</i> <sub>RT</sub>	$\lambda_{\text{max.}}$ (m $\mu$ ) (cyclohexane)	$\epsilon$
		$\gamma\text{CH}$	$\Delta\nu_{\frac{1}{2}}$	$\epsilon^a$			
<i>o</i> -Diethylbenzene	$\gamma\text{CH}$	753					
	$\Delta\nu_{\frac{1}{2}}$	8			1.00	265	175
	$\epsilon^a$	160					
<i>o</i> - <i>n</i> -Propyltoluene	$\gamma\text{CH}$		745				
	$\Delta\nu_{\frac{1}{2}}$		14		1.06	265	265
	$\epsilon^a$		150				
<i>n</i> -Butylbenzene	$\gamma\text{CH}$		744		696		
	$\Delta\nu_{\frac{1}{2}}$		18		7	262	215
	$\epsilon^a$		95		195		
Primary product from deca-1,9-diyne	$\gamma\text{CH}$	753	742	707	0.95		
	$\Delta\nu_{\frac{1}{2}}$	sh	~18	10	1.00	264	1905
	$\epsilon^a$	~65	100	80	1.06		
Hydrogenated product from deca-1,9-diyne	$\gamma\text{CH}$	753	742		697	0.97	
	$\Delta\nu_{\frac{1}{2}}$	sh	~8		~7	1.00	264
	$\epsilon^a$	55	90		5	1.06	115

*R*<sub>RT</sub> = Retention time relative to *o*-diethylbenzene (for conditions see Figure).

The n.m.r. spectrum of the primary product clearly showed the presence of ethylenic compounds (vinyllic proton absorption over the region  $\tau$  3.5—4.9) as well as aromatic products ( $\tau$  2.8—3). This was confirmed by the disappearance of the former absorption in the n.m.r. spectrum of the hydrogenated product. The i.r. absorption of the primary product clearly showed the presence of *o*-dialkylbenzenes (Table). The strong band at 707 cm.<sup>-1</sup> was found to be due predominantly to *cis*-ethylenic absorption, its sharpness being indicative of an endocyclic ethylene. This band vanished completely in the hydrogenation product revealing a small residual absorption at 697 cm.<sup>-1</sup> due to *n*-butylbenzene. The presence of conjugated ethylenic unsaturation in the primary product was revealed by the u.v. spectrum. In the hydrogenated product this band collapsed to reveal the weak absorption in the 260 m $\mu$  region characteristic of alkyl-benzenes.

The cognate rearrangement of deca-4,6-diyne gave substantially the same products (g.l.c., n.m.r., i.r., and u.v.). The relative proportions of the aromatic hydrocarbons were essentially the same, but there was a greater preponderance of ethylenic constituents.

From these results it would seem that the main products from these two isomeric diynes were the three expected aromatic isomers. At least some of the remaining unassigned g.l.c. peaks must correspond to a range of unsaturated conjugated cyclic hydrocarbons. As the isomeric possibilities for such structures of molecular formula C<sub>10</sub>H<sub>14</sub> are very numerous it was decided to obtain further insight into these by-products by obtaining analogous compounds from a hydrocarbon of lower molecular weight.

*Rearrangement of Octa-1,7-diyne.*—(a) The conditions of the preceding experiment were used; no further isomerisation could be detected after 2 hr. In these circumstances octa-1,7-diyne gave a primary product separated into eight components by capillary g.l.c. (Apiezon L; 50 m.; 81°; total flow rate 55 ml./min.). The two main components were identified as the expected *o*-xylene and ethylbenzene in a proportion of 5 : 3 (by direct area comparison).

However, most unexpectedly, a partly resolved double peak was present, which appeared to be due to *m*- and *p*-xylene. Preparative g.l.c. [poly(ethylene glycol) column, 20%; 2 m., 85°; 20 p.s.i. pressure] furnished a fraction which was shown by i.r. and analytical g.l.c. (20% of 7,8-benzoquinoline column; 2 m.; 80°; 65 ml./min.) to contain *m*- and *p*-xylene. The total aromatic constituents were shown to be present in the proportions of *o*-xylene : ethylbenzene : *m*-xylene + *p*-xylene = 5 : 3 : 2 (by peak area). The i.r. (film;  $\gamma\text{CH}$ , cm.<sup>-1</sup>) and g.l.c. (retention time; min.) identification data for the aromatic constituents were as follows. Product: 795w, 790w, 743vs, 707s, 697s; *R*<sub>t</sub> 17.85, 19.10, 20.35, 25.70. Ethylbenzene: 790vw, 772w, 697vs; *R*<sub>t</sub> 17.80. *m*-Xylene: 770vs, 695s; *R*<sub>t</sub> 19.00. *p*-Xylene: 795vs; *R*<sub>t</sub> 20.30. *o*-Xylene: 743vs; *R*<sub>t</sub> 25.65. The possibility that the *m*- and the *p*-isomer had arisen by isomerisation of *o*-xylene or ethylbenzene under these conditions was disproved by direct trial.

Examination of the primary product, using g.l.c., and n.m.r., i.r., and u.v. spectroscopy, showed the presence of conjugated ethylenic carbocycles. Hydrogenation of the primary product and g.l.c. (capillary column) showed the four aromatic peaks due to ethylbenzene and the three xylenes. Apart from these, four further peaks were obtained; the two predominant ones were isolated by preparative g.l.c. in the following manner. A poly(ethylene glycol) column (20% stationary phase; 2 m.; 80°; and 18 p.s.i. pressure) was used for the initial separation of the non-aromatic fraction, which was then subjected to further separation on an Apiezon L column (20% stationary phase; 2 m.; 85°; and 18 p.s.i. pressure). The two predominant fractions were collected and identified as cyclo-octane and methylcycloheptane by direct comparison (g.l.c., n.m.r.) with authentic samples.

(b) The use of a 2% butoxide dispersion for 2 hr. gave a similar spread of products with the addition of two further components. One was detected in the mixture by its strong absorption at 269 ( $\epsilon$  400), 280 ( $\epsilon$  400), 293 ( $\epsilon$  45), and 306  $m\mu$  ( $\epsilon$  305) (cyclohexane); this suggested the presence of a small percentage of the acyclic octa-1,3,5,7-tetraene [ $\lambda_{\text{max}}$ . (iso-octane) 267, 278, 290, and 304  $m\mu$ ].<sup>7</sup>

A second acyclic component, isolated by preparative g.l.c. [20% poly(ethylene glycol); 2 m.; 90°; and 18 p.s.i. pressure], possessed properties compatible with its tentative formulation as octa-2,6-diyne<sup>29</sup> (u.v., end absorption only)  $\nu_{\text{max}}$ . (film) 2338w, 2235w, 2050w, 1435s, 1375w, 1340m  $\text{cm}^{-1}$ . Hydrogenation with 10% palladium-charcoal gave a product identified by analytical g.l.c. as n-octane.

(c) A hot dispersion of 2% butoxide in diglyme was carefully filtered through a sintered-glass filter under nitrogen. Use of this filtrate for the isomerisation (2 hr.) gave a two-component mixture of *o*-xylene and ethylbenzene, as shown by g.l.c., with only traces of other components.

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<sup>29</sup> Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1.

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