Non-aromatic Products from the Base-catalysed Isomerisation of Octa-1,7-diyne

By **G. Eglinton, R. A. Raphael,*** and **J. A. Zabkiewicz,** Department of Chemistry, University of Glasgow, Glasgow W.2

The non-aromatic cyclic products from base treatment of octa-1,7-diyne have been characterised as 1-, 2-, and 3-methylcyclohepta-1,3,5-trienes and cyclo-octa-1,3,5-triene. A logical scheme to encompass the formation of these compounds, ethylbenzene, and all the isomeric xylenes is suggested.

IT has been demonstrated [1] that the base-catalysed rearrangements of linear diacetylenes (using a very dilute solution of potassium t-butoxide in diglyme) yield mixtures of the mono- and *o*-di-substituted benzenes of the same molecular formula. In the simplest case benzene and *o*-xylene are formed from octa-1,7-diyne. However, under non-homogeneous conditions, careful examination of the reaction products disclosed that *m*- and *p*-xylenes were also produced, together with non-aromatic carbocycles which yielded cyclo-octane and methylcycloheptane on hydrogenation.[1] It was obviously desirable to determine the precise structure of these unsaturated cyclo-octane and cycloheptane derivatives formed in the isomerisation and to determine their role in the overall process, *i.e.*, whether they were intermediates in the aromatisation sequence or merely adventitious by-products.

Treatment of octa-1,7-diyne with the standard heterogeneous basic medium [potassium t-butoxide dispersed in boiling diglyme, di-(2-methoxyethyl) ether] in a molar ratio of 1 : 5 of diyne to base, for 8 hours, yielded an oil with the expected spectral characteristics. Initial separation into aromatic and ethylenic constituents was achieved by chromatography on a silver nitrate–silica gel column. The fractions containing the non-aromatic compounds were combined and concentrated, then subjected to preparative gas–liquid chromatography (g.l.c.). The fraction of longest retention time had infrared (i.r.)

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[1] G. Eglinton, R. A. Raphael, R. G. Willis, and J. A. Zabkiewicz, *J. Chem. Soc.*, 1964, 2597.

and ultraviolet (u.v.) absorption identical with published data for cyclo-octa-1,3,5-triene, and broad singlets at τ 4·16, 4·3, 7·57 in the nuclear magnetic resonance (n.m.r.) spectrum provided further indication of this structural assignment. Direct comparison with a prepared authentic sample provided final proof. The penultimate and ante-penultimate fractions had spectral characteristics which strongly indicated that the former was predominantly 1-methylcyclohepta-1,3,5-triene (with about 25% of the 3-methyl isomer) and the latter 2-methylcyclohepta-1,3,5-triene (with a similar proportion of the 3-methyl isomer).

The isolation and characterisation of these compounds prompted the large-scale preparation of these and other possible unsaturated precursors in order to study their behaviour on base-catalysed isomerisation.

7-Methylcycloheptatriene was prepared in 52% yield by the action of methylmagnesium iodide on tropylium bromide.[2] The three other isomeric methylcycloheptatrienes were obtained simultaneously from the solvolysis of the toluene-*p*-sulphonyl derivative of 1,4-dihydro-2-methylbenzyl alcohol and obtained pure by preparative g.l.c. Each isomer was identified spectroscopically by comparison with published data.[3] Allylic monobromination of cyclo-octa-1,5-diene and dehydrohalogenation by base yielded cyclo-octa-1,3,5-triene.[4]

These, and other selected unsaturated hydrocarbons, were subjected to the same isomerisation conditions as the octa-1,7-diyne. The results may be summarised as follows.

(*i*) Neither *m*- nor *p*-xylene was produced by any of the following: *o*-xylene; ethylbenzene; cyclo-octa-1,3,5-triene or any of the isomeric methylcycloheptatrienes.

(*ii*) Cyclo-octa-1,5-diene was readily converted into cyclo-octa-1,3-diene (80%) by the standard reagent; similar treatment of cyclo-octa-1,3,5-triene yielded ethylbenzene (10%), bicyclo[4,2,0]octa-2,4-diene (28%) and starting material.

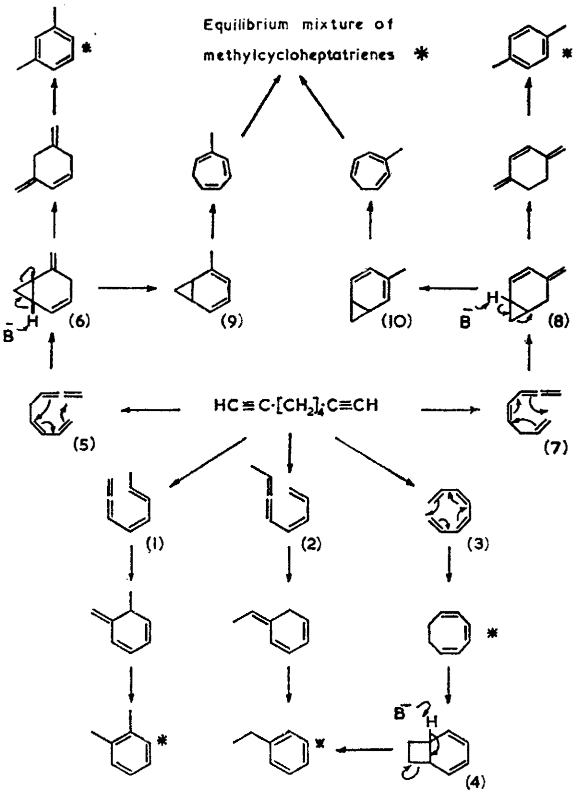
(*iii*) Neither cycloheptatriene nor the methylcycloheptatrienes produced any aromatic compounds, either by treatment with base or by simply heating under reflux in the solvent. With base, all the methylcycloheptatrienes formed the same equilibrium mixture of the four isomers, irrespective of the starting compound (see Experimental section, Table 5). Heating without base produced from each isomer an individual mixture of isomers whose composition can be explained by sequential 1,5 hydrogen migration in accordance with the Woodward–Hoffmann rules,[5] and are fully compatible with the results obtained for the methoxy-,[6] phenyl-,[7] and deuteriated [8] cycloheptatrienes.

(*iv*) When octa-1,7-diyne was heated under reflux without base, no isomerisation occurred.

The rationalisation of all these rearrangement products of octa-1,7-diyne can be postulated in terms of known base-catalysed reactions of alkynes and alkenes and thermal reorganisations of the unsaturated systems thus produced. This is shown in the flowsheet which suggests a self-consistent rationale of the experimental findings.

The base-catalysed rearrangement of alkynes to alkadienes and the base-catalysed isomerisation of alkenes are very well established phenomena, and their multiple occurrence to produce polyenes of types (1), (2), (3), (5), and (7) may be readily envisaged. Internal Diels–Alder type reactions involving the *cis*-allenedienes (1) and (2) as previously discussed,[1] provide a plausible pathway to *o*-xylene and ethylbenzene respectively. In this connection it is interesting to note the reported dominance of *cis*-products in the base-catalysed rearrangement of certain alkenes.[9] Prototropic isomerisation of octa-1,7-diyne to the *cis*,*cis*-octa-1,3,5,7-tetraene

Proposed routes for the base-catalysed formation of the isomeric xylenes, ethylbenzene, cyclo-octa-1,3,5-triene, and the methylcycloheptatrienes from octa-1,7-diyne



* Compounds actually isolated.

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[2] E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 1958, 4559.

[3] N. A. Nelson, J. H. Fassnacht, and J. U. Piper, *J. Amer. Chem. Soc.*, 1961, **83**, 206.

[4] A. C. Cope, C. L. Stevens, and F. A. Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2510.

[5] R. B. Woodward, 'Aromaticity,' *Chem. Soc. Special Publ.*, No. 21, 1967, p. 217: R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395.

[6] E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 1964, 59.

[7] A. P. Ter Borg and H. Kloosterziel, *Rec. Trav. chim.*, 1963, **82**, 741.

[8] A. P. Ter Borg, H. Kloosterziel, and N. Van Meurs, *Rec. Trav. chim.*, 1963, **82**, 717.

[9] S. Bank, A. Schriesheim, and C. A. Rowe, *J. Amer. Chem. Soc.*, 1965, **87**, 3244.

(3) followed by an electrocyclisation provides a plausible pathway to cyclo-octa-1,3,5-triene.[10,11] The earlier detection[1] of the all-*trans*-octatetraene in the base-catalysed reaction products lends further support to the scheme (this product cannot of course undergo electrocyclisation). The equilibration of cyclo-octa-1,3,5-triene and bicyclo[4,2,0]octa-2,4-diene is well established[12] and a base-catalysed deprotonation–protonation process as shown with (4) provides a further source of ethylbenzene. An electrocyclic reaction involving the 'skipped' allenediene (5) leads directly to the non-conjugated *exo*-methylenenorcarene (6). Base-catalysed deprotonation involving the cyclopropyl hydrogen shown, followed by the rearrangement indicated, leads to *m*-xylene (similar attack at the other cyclopropyl methine hydrogen would lead to further *o*-xylene). By an analogous series of transformations the isomeric allenediene (7) is convertible into *p*-xylene (and *m*-xylene by a corresponding alternative attack). It is pertinent to note in this connection the reported conversion of 3,4-dibromocarane into *p*-cymene.[13] The two *exo*-methylenenorcarenes (6) and (8) are capable of conversion under these reaction conditions into the two isomeric norcaradienes (9) and (10), and their valence tautomers 2- and 3-methylcycloheptatrienes. Each of these last, as demonstrated in the present work, is capable of base-catalysed conversion into the equilibrium mixture of the 1-, 2-, and 3-methylcycloheptatrienes actually isolated from the reaction mixture. Purely thermal isomerisation of the methylcycloheptatrienes to aromatics is extremely unlikely at these reaction temperatures (less than 200°) as such isomerisations proceed at measurable rates only above 300°.[14]

Although purely a paper rationalisation the above scheme does represent logical and plausible pathways which are compatible with the experimental findings for this complex series of rearrangements.

EXPERIMENTAL

Unless otherwise stated, the following experimental conditions apply throughout. Quantitative infrared (i.r.) spectra were obtained with a Unicam SP 130 grating spectrophotometer (accuracy ± 1 cm.$^{-1}$), and survey spectra with Perkin-Elmer 137, 237, or Unicam SP 200 (accuracy ± 10 cm.$^{-1}$). All survey spectra are corrected to the 1603 cm.$^{-1}$ band of polystyrene. Ultraviolet (u.v.) spectra were measured on either a Unicam SP 500, 800, or Perkin-Elmer 137 u.v. Nuclear magnetic resonance spectra (n.m.r.) spectra were recorded (in carbon tetrachloride unless otherwise stated) on a Perkin-Elmer R10 60 Mc. instrument. Tetramethylsilane was used as the internal standard throughout.

Gas–liquid chromatographic analyses were conducted on a variety of instruments and columns. Operating conditions, columns, and detectors are quoted where necessary; all quantitative work was done with a flame ionisation detector, using peak area or peak heights; no corrections were made for differences in detector response. Pye Argon Chromatographs (equipped with a closed injection system and flash preheater) and a Perkin-Elmer 451 Fraktometer were used for analytical isothermal runs, and the Fraktometers or a Varian Aerograph Autoprep 700 for preparative work.

Alumina (neutral) of activity determined by the method of Brockmann[15] was used; silica gel was normally from B.D.H. unless indicated otherwise. Silver nitrate on silica gel was prepared by a published method.[16] Melting points were taken on a Kofler hot-stage. Unless indicated otherwise, magnesium sulphate was used as drying agent throughout. Diglyme[di-(2-methoxyethyl) ether] was purified by heating under reflux over sodium and subsequent distillation.

*Isomerisation of Octa-*1,7*-diyne.*[1] *Standard Procedure.*—The diyne (2 g.) was heated under reflux (8 hr.) in di-(2-methoxyethyl) ether (120 ml.) with the basic system (potassium t-butoxide, from 3·8 g. of potassium) under nitrogen in the molar ratio 1 : 5, to give after extraction, 0·35 g. (35%) of a yellow oil; ν(film) 1652w, 1624w, 1605w, 1498s, 743s, 709s, 698s, cm.$^{-1}$; $\lambda_{\text{max.}}$ (cyclohexane) 251—256 mμ (ε 2530); n.m.r. τ 2·45—2·9 (m), 3·2—3·7 (m), 4·1—4·9 (m), 7·2—7·8 (m), 8·0—8·2 (m), 8·7—9·1 (m). Aliquots removed in the course of the reaction, and examined by g.l.c. showed that equilibrium was attained after 2 hr.

Analytical g.l.c. (50 m. Apiezon L capillary, 81°, 17 lb./in.^{2}/5·8, total flow 52 ml./min.) showed that eight components were present. The two main components were identified by R_T values and co-chromatography as *o*-xylene and ethylbenzene in a proportion of 5 : 3 (by direct area comparison), and comprising about 60% of the total reaction product.

In a typical experiment, the reaction products (3 g.) from the base-catalysed isomerisation of octa-1,7-diyne (10 g.) were chromatographed on a 10% silver nitrate–silica gel column (40 g.) using pentane and diethyl ether as eluants (gradient elution 5 ml. fractions collected). The ultraviolet spectra of initial fractions were aromatic in character, and the appropriate fractions (20—29) were combined; later fractions (33—50) had more diffuse spectra consistent with diene chromophores, and these in turn were combined, and subjected to preparative g.l.c.

Utilising a poly(ethylene glycol) column (20%, 2 m. × $\frac{1}{4}$ in. o.d., 81°, 55 ml./min.) five fractions were taken. The first two consisted of solvent and trace impurities, and were discarded. Fractions 3 and 4 were obtained in sufficient quantity to be identified by their spectral characteristics as mixtures of mainly 2-methylcyclohepta-1,3,5-triene (plus 3-methylcyclohepta-1,3,5-triene), and 1-methylcyclohepta-1,3,5-triene (plus 3-methylcyclohepta-1,3,5-triene) respectively. These three isomers, as well as 7-methylcyclohepta-1,3,5-triene were synthesised by a published route[2,3] and a comparison of their spectral characteristics and those of fractions 3 and 4 is shown in tabular form (Tables 1—3). The fifth fraction was obtained pure, and identified spectroscopically as cyclo-octa-1,3,5-triene $\nu_{\text{max.}}$ (film) 3010vs, 2935vs, 2885m, 843m, 815m, 775vs, 742m,

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[15] H. Brockmann and H. Schodder, *Ber.*, 1941, **74**, 73.

[16] E. Haahti, T. Nikkari, and K. Juva, *Acta Chem. Scand.*, 1963, **17**, 538.

TABLE 1

Infrared spectral data for the isomeric methylcyclohepta-1,3,5-trienes and fractions 3 and 4 from preparative g.l.c. of isomeric octa-1,7-diyne

Fraction 3	Fraction 4	1-Me	2-Me	3-Me	7-Me
	3200				
3022		3026	3028	3026	
			3012	2992	3014
2970	2965	2970	2970	2980	2962
2925			2944	2942	2930
		2911		2920	
2880	2885	2886	2882	2884	2874
2835	2840	2838	2836	2840	2852
	1650				
1625	1620	1633		1627	
1610				1604	
1500	1535	1540	1550	1550	
1380	1375	1380	1378	1375	1377
	1360				
1298	1295			1295	1290
1145	1190				
1080	1080				1059
1040					
1025	1010			1015	1016
942	915				
	855	854		858	
825			822		
790	795	795	790		
765	760	769		760	
740	735		737	737	742
720			719		
705	705	708		705	707
					671

Values quoted are ν (film) in cm.$^{-1}$. Fractions 3 and 4 run on PE 237, all others on Unicam SP 130.

TABLE 2

Ultraviolet data for the isomeric methylcyclohepta-1,3,5-trienes and fractions 3 and 4 from preparative g.l.c. of isomerised octa 1,7-diyne

Fraction 3	Fraction 4	1-Me	2-Me	3-Me	7-Me
259	264—266	269	258	260	258
ε 2200	ε 2750	ε 3400	ε 2600	ε 3800	ε 3310

Values for 1-, 2-, and 3-methyl isomers are $\lambda_{max.}$ (EtOH); all others are $\lambda_{max.}$ (cyclohexane).

TABLE 3

^{1}H n.m.r. data for the isomeric methylcyclohepta-1,3,5-trienes and fractions 3 and 4 from preparative g.l.c. of isomerised octa-1,7-diyne

Fraction 3	Fraction 4	1-Me	2-Me	3-Me	7-Me
3·53 doublet	3·55 triplet	3·6 triplet	3·55 doublet	3·6 doublet	3·4 triplet
3·95 mult.	3·95 mult.	3·98 mult.	3·98 mult.	4·01 triplet	3·93 doublet
4·75 mult.	4·7 quartet	4·74 quartet	4·72 mult.	4·75 mult.	4·97 quartet
7·86 triplet	7·7 doublet	7·75 doublet	7·85 triplet	7·75 mult.	8·4 mult.
8·16 doublet	8·0 doublet	8·05 singlet	8·15 singlet	7·96 triplet	8·65 doublet

All samples run in carbon tetrachloride with Me_4Si as internal reference. Only mid-points of multiplets are quoted (τ).

702vs, 647vs cm.$^{-1}$, identical with a published spectrum;[17] $\lambda_{max.}$ (cyclohexane) 263 mμ (ε 3000) [lit.,[12] $\lambda_{max.}$ (cyclohexane) 265 mμ (ε 3600)]. A more efficient column [25% poly(ethylene glycol) 600, 12 ft. × $\frac{3}{8}$ in. o.d., 70°, 180 ml./min.] installed in an Aerograph Autoprep instrument yielded a more convenient separation. Fractions were better separated, the fifth fraction being obtained in an amount sufficient for an n.m.r. spectrum; this showed broad singlets at 4·16, 4·3, 7·57 identical with that of a synthetic sample of cyclo-octa-1,3,5-triene. Comparison of these fractions by analytical g.l.c. (20% Cyano P, 4 ft. × $\frac{1}{4}$ in. o.d., 50°, 38 ml./min.) with synthetic materials showed that fraction 3 contained four components, the two major ones being 2- and 3-methylcyclohepta-1,3,5-triene respectively. Fraction 4 contained the 3- and 1-methyl isomers (major), while fraction 5 contained only cyclo-octa-1,3,5-triene.

Preparation of Methylcycloheptatrienes.—(i) 7-*Methylcycloheptatriene.* Tropylium bromide was prepared by the standard literature method;[18] $\nu_{max.}$ (Nujol) 1250m, 1210m, 1040m, 980m, 670s, 650s cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 210, 245 mμ (both broad, ε 1660 and 1130). Treatment of this (4 g.) with methylmagnesium iodide in ether (75 ml.; from 0·8 g. of magnesium and 4·7 g. of methyl iodide) yielded 1·3 g. (52%) of an oil, which was purified by preparative g.l.c. (25% Cyano P, 15 ft. × $\frac{3}{8}$ in. column, 75°, 190 ml./min.) to give pure 7-methylcyclohepta-1,3,5-triene. The physical characteristics were in agreement with literature values.[2]

(ii) 1-, 2-, and 3-*Methylcycloheptatrienes.* These were prepared simultaneously by the solvolysis of the toluene-*p*-sulphonyl derivative of 1,4-dihydro-2-methylbenzyl alcohol.[3] Purification by column chromatography and preparative g.l.c. (conditions as above) yielded the pure 1-, 2-, and 3-methylcycloheptatrienes. Each was identified by comparison of its spectral properties (i.r., u.v., n.m.r.) with published data.

Preparation of Cyclo-octa-1,3,5-*triene.*[4]—Cyclo-octa-1,5-diene (47 g., 0·44 mole), *N*-bromosuccinimide (53 g., 0·3 mole), and benzoyl peroxide (2 g.) in carbon tetrachloride (250 ml.), were heated under reflux for 3 hr. to yield a yellow oil (after removal of the precipitated succinimide by filtration, and concentration of the solution). Owing to difficulties in purification, the crude 3-bromocyclo-octa-1,5-diene (8 g.) was dehybrominated directly by heating under reflux (3 hr.) with potassium t-butoxide in t-butyl alcohol (from 2 g. of potassium in 50 ml. of t-butyl alcohol). The reaction mixture was cooled, water added, the mixture extracted with ether, and the ether extracts were dried and concentrated to give a yellow oil. Chromatography of this product over alumina (grade I) with pentane as eluant gave a colourless oil. Analytical g.l.c. [25% poly(ethylene glycol), 12 ft. × $\frac{1}{4}$ in. column, 80°, 45 ml./min.] revealed one minor and two major components. The two major components were obtained by preparative g.l.c. [25% poly(ethylene glycol), 12 ft. × $\frac{3}{8}$ in., 75°, 80 ml./min.]; cyclo-octa-1,5-diene was eluted first and identified by its i.r. spectrum. The major compound, of longer R_T, was shown to be cyclo-octa-1,3,5-triene by its spectral properties identical with published data.[4,17]

Base-catalysed Isomerisation of C_8H_{10} *Hydrocarbons and Related Species. General Procedure.*—The hydrocarbon under examination was heated under reflux (~160°) in a dispersion of potassium t-butoxide in diglyme (molar ratio of hydrocarbon to base 1 : 2) for 3—4 hr. under nitrogen. The isolation procedure was identical to that described in

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[17] Documentation of Molecular Spectra, Butterworths, London.

[18] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 352.

the isomerisation of octa-1,7-diyne. The products were examined by i.r. and analytical g.l.c. [50 m. poly(ethylene glycol) capillary column], which gave a quantitative evaluation (using peak heights). A summary of the results is given in Table 4.

TABLE 4

Isomerisation conditions and products of C_8H_{10} hydrocarbons and related species

Starting material	Conditions	Products (% composition)
o-Xylene	KOBu^t/diglyme [a]	Starting material
Ethylbenzene	KOBu^t/diglyme [a]	Starting material
Cyclo-octa-1,5-diene	KOBu^t/diglyme [a]	Cyclo-octa-1,5-diene 38%, cyclo-octa-1,3-diene 60%, others 2%
Cyclo-octa-1,5-diene	KOH/diglyme [a]	Cyclo-octa-1,5-diene, 60%, cyclo-octa-1,3-diene 38%, others 2%
Cyclo-octa-1,5-diene	KOBu^t/Bu^{t}OH [b]	Starting material
Cyclohepta-1,3,5-triene	KOBu^t/diglyme [a]	Starting material
Methylcyclohepta-1,3,5-trienes	KOBu^t/diglyme [a]	Equilibrium mixture; see Table 5
Methylcyclohepta-1,3,5-trienes	No base [a]	Equilibrium mixture; see Table 5
Cyclo-octa-1,3,5-triene	KOBu^t/diglyme [a]	Cyclo-octa-1,3,5-triene 52%, ethylbenzene 10%, bicyclo-[4,2,0]octa-2,4-diene 28%, others 10%
Octa-1,7-diyne	No base [c]	Starting material

Conditions. [a] 160°; 3—4 hr. [b] 80°; 3—4 hr. [c] 160°; 8 hr.

The molar ratio of base, when used, to initial hydrocarbon was 2 : 1 throughout.

o-*Xylene and Ethylbenzene*. These hydrocarbons were recovered unchanged; *m*- and *p*-xylene were absent.

Cyclo-octa-1,5-*diene*. On heating under reflux with the above reagent this hydrocarbon yielded cyclo-octa-1,3-diene (60%), starting material (38%), and others (2%). Reaction with potassium hydroxide in diglyme for 3 hr. produced starting material (60%), the conjugated diene (38%), and others (2%) as before. Reaction with potassium t-butoxide in t-butyl alcohol for 4 hr. yielded only starting material.

Cyclohepta-1,3,5-*triene*. The standard treatment for 3 hr. yielded unchanged cycloheptatriene. Heating in diglyme without base did not cause isomerisation either.

Methylcyclohepta-1,3,5-*trienes*. Each of the methylcycloheptatriene isomers (*i.e.*, 7-, 1-, 2-, and 3-methyl) was heated under reflux with the basic medium to form an identical equilibrium mixture in each case (Table 5). Aromatic products were not detected.

These same methylcycloheptatrienes, when heated under reflux (without base) under identical conditions again produced mixtures, but of varying composition, probably due to incomplete equilibration (Table 5).

TABLE 5

Base-catalysed isomerisation of methylcyclohepta-1,3,5-trienes

	Isomers in product (% composition)			
Starting isomer	7-Me	1-Me	2-Me	3-Me
7-Methyl	2	61	15	20
1-Methyl	3	55	15	23
2-Methyl	2	58	14	19
3-Methyl	2	62	15	20

Thermal isomerisation of methylcyclohepta-1,3,5-trienes

	Isomers in product (% composition)			
Starting isomer	7-Me	1-Me	2-Me	3-Me
7-Methyl	32	14	0	55
1-Methyl	4	86	5	5
2-Methyl	4	50	33	4
3-Methyl	6	31	4	56

Cyclo-octa-1,3,5-*triene*. The triene, on treatment with the standard reagents, was recovered largely unchanged (52%). However, by analytical g.l.c. on several columns [20% silver nitrate–tri(ethylene glycol); 5% Bentone 34—5% dinonyl phthalate; 50 m. poly(ethylene glycol) capillary] it was shown that ethylbenzene (10%) was also produced, along with bicyclo[4,2,0]octa-2,4-diene (28% the valence tautomer of cyclo-octa-1,3,5-triene), and several other minor compounds (11% of total).

Octa-1,7-*diyne*. The diyne, when heated under reflux (8 hr.) in diglyme without base was recovered unchanged.

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