1301. *Cyclobutadienes. Part III.*[1] *The Dimer of Tetraphenylcyclobutadiene*

By J. H. Beynon, R. C. Cookson, R. R. Hill, D. W. Jones, R. A. Saunders, and A. E. Williams

The tetraphenylcyclobutadiene dimer of very high melting point is pyrolysed to hexaphenylbenzene and diphenylacetylene, and dehydrogenated with palladium on charcoal to a mixture of two hydrocarbons, $C_{56}H_{38}$. The mass spectra of these and related hydrocarbons are described. Although the evidence is not quite clear, we conclude that the chemical and spectral properties of the dimer indicate that it is probably octaphenylcyclo-octatetraene,* not octaphenylcubane as suggested by Freedman.

At 185° tetraphenylcyclobutadienepalladium dichloride complex evolves a vapour of molecular weight 356, showing that monomeric tetraphenylcyclobutadiene exists in the gas phase.

Several reactions that might have been expected to form tetraphenylcyclobutadiene have yielded a very insoluble, high-melting dimer: (1) Removal of palladium from tetraphenylcyclobutadienepalladium dichloride (I) (in absence of oxygen) with a tertiary phosphine [1,2] at room temperature or above (quantitative yield). (2) Elimination of dimethyltin dibromide from the butadiene derivative [3] (II) at about 150° (85% yield). (3) Oxidation of the dilithium derivative (III) with cupric bromide [4] (15% yield). (4) Elimination of sulphur dioxide from tetraphenylthiophen dioxide [5] (IV). (5) Reaction of diphenylacetylene with

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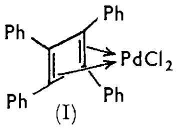
* Since this Paper was submitted, two independent groups have shown by X-ray analysis that the dimer is indeed octaphenylcyclo-octatetraene (H. P. Throndsen, P. J. Wheatley, and H. Zeiss, *Proc. Chem. Soc.*, 1964, 357; G. S. Pawley, W. N. Lipscomb, and H. H. Freedman, *J. Amer. Chem. Soc.*, 1964, **86**, 4725).

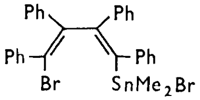
[1] R. C. Cookson and D. W. Jones, *Proc. Chem. Soc.*, 1963, 115; Part II, *J.*, 1965, 1881.
[2] P. M. Maitlis and F. G. A. Stone, *Proc. Chem. Soc.*, 1962, 330.
[3] H. H. Freedman, *J. Amer. Chem. Soc.*, 1961, **83**, 2195.
[4] E. H. Braye, W. Hübel, and I. Caplier, *J. Amer. Chem. Soc.*, 1961, **83**, 4406.
[5] C. E. Berkoff, R. C. Cookson, J. Hudec, D. W. Jones, and R. O. Williams, *J.*, 1965, 194.

phenylmagnesium bromide[6] (7·5% yield). (6) Ultraviolet irradiation of diphenylacetylene[7] (0·065% yield).

In the first two reactions,[1,3] a reactive monomer appears to be formed first, that will add to oxygen or to double or triple bonds, although it is not yet clear whether it is the singlet (Va) or triplet cyclobutadiene (Vb) or even the butadiene diradical (Vc): no adduct has yet been isolated with the cyclobutene ring intact.



(I)



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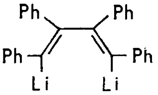

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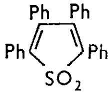

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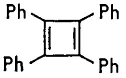
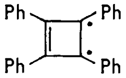
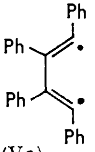


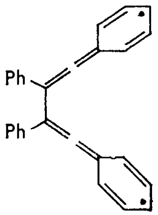
(Va)



(Vb)



(Vc)

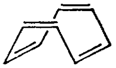


(Vd)

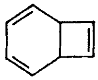
As possible structures still containing eight phenyl groups we considered the simple valency tautomers (VI—X) and other structures that can be derived by formation of bonds across an eight-membered ring (XI—XVI), as well as (XVII) which could be simply derived from (XII).

The high-melting dimer was too insoluble for measurement of its proton magnetic resonance spectrum or for convenient examination of its chemical reactions. It dissolved only in boiling diphenyl ether[8] or tetrahydrothiophen dioxide (sulpholane). Although the hot solutions were yellow, the colourless dimer crystallised on cooling leaving a colourless solvent, and there was no reaction with maleic anhydride. It dissolved in cold sulphuric acid and, less so, in trifluoroacetic acid to give deep violet solutions.

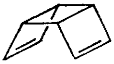
The significant properties of the dimer are: (1) $\lambda_{\text{max.}}$ 267 mμ (ε 44,600) in tetrahydrofuran;[1,4] (2) The absence of a Raman band[8] from the crystalline dimer in the C=C stretching region above 1605 cm.$^{-1}$; (3) Preliminary analysis of *X*-ray[8] diffraction patterns indicates that individual molecules have an alternating tetrad axis.



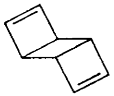
(VI)



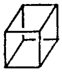
(VII)



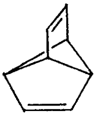
(VIII)



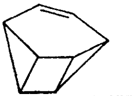
(IX)



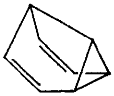
(X)



(XI)



(XII)



(XIII)

On the face of it, the u.v. spectrum (1) eliminates a tetraphenylcyclohexadiene group, which absorbs at about 312 mμ,[1,5] [(VII) and (XVI)], and structures containing no formal conjugation [(X), (XIV), and (XV)]. It allows a twisted *cis*-stilbene unit, which might occur in structures (VI), (VIII), (IX), (XI), (XII), (XIII), or (XVII).

The absence of a non-aromatic C=C bond (2) would eliminate structures (VI), (VII), (VIII), (IX), (XI), (XII), (XIII), (XVI), and (XVII), leaving only the saturated isomers (X), (XIV), and (XV).

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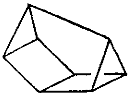
[6] H.-P. Throndsen and H. Zeiss, *J. Organometallic Chem.*, 1964, **1**, 301; see also M. Tsutsui, *Chem. and Ind.*, 1962, 780.

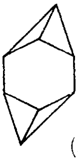
[7] G. Büchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, 1962, **27**, 4106.

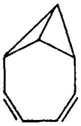
[8] H. H. Freedman and D. R. Petersen, *J. Amer. Chem. Soc.*, 1962, **84**, 2837.

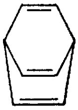
The alternating tetrad axis (3) eliminates all structures but (VI) and (X).

In short, straight-forward interpretation of the data excludes all possible isomers of Ph_8C_8: either some of the data or their interpretation must be wrong, or else the dimer is not Ph_8C_8. Considering the second possibility, and noting that the u.v. spectrum was nearly four times that of 9,10-dihydrophenanthrene, we suggested structure (XVIII) as an additional possibility.[1] It could have arisen by plausible mechanisms, and explained all the data.


(XIV)


(XV)


(XVI)


(XVII)

In formulæ (VI)—(XVII) each C atom carries a phenyl group

Hardly had our Note appeared[1] than we excluded structure (XVIII) by finding that the dimer formed diphenylacetylene and hexaphenylbenzene on pyrolysis. Apart from the very remote possibility of reversible hydrogen shifts, that means that the dimer *does* contain eight phenyl groups. Also it can be oxidised to benzoic acid with chromic acid[9] and to *p*-nitrobenzoic acid with nitric acid.[6] If we accept the *X*-ray evidence, the problem thus reduces to a direct conflict between interpretation of the u.v. and Raman spectra. While one cannot be quite sure that the bent bonds in the saturated isomers (XIV), (XV), and especially (X) might not allow enough conjugation to explain the u.v. spectrum, the absence of such absorption in, *e.g.*, diphenylcyclopropane makes one very sceptical. The u.v. spectrum ($\lambda_{\text{max.}}$ 267 mμ, log ε 4·65) is very like that of 1,2-diphenyl-[10] ($\lambda_{\text{max.}}$ 260 mμ, log ε 4·4), and 1,2,4,7-tetraphenyl-cyclo-octatetraene[11] ($\lambda_{\text{max.}}$ 263 mμ, log ε 4·66). On the other hand, the dimer is reported[8] to show no Raman band in the C=C stretching region at higher frequency than the phenyl absorption at 1605 cm.$^{-1}$, whereas several 1,2-diphenylcyclobutenes [(XX),[8] (XXI)[12] and the hexaphenyldifluoro-derivative of (IX)[12]] have strong bands at 1637 ± 10 cm.$^{-1}$. While that is an important observation, it does not constitute "quite compelling" evidence[8,6] for (X). This Raman band appears at 1650 cm.$^{-1}$ for cyclo-octatetraene[13] and at 1630 cm.$^{-1}$ for *cis*-stilbene,[14] about 30 cm.$^{-1}$ lower than that of most *cis*-alkenes.[15] It seems at least possible that (VI) might have its C=C Raman band below 1605 cm.$^{-1}$ where it would be obscured by the phenyl groups. The Raman spectral evidence is, then, even more ambiguous than that from the ultraviolet spectrum, especially when one considers the difficulty of obtaining reliable Raman spectra of the solid.

Freedman and Petersen[8] have tentatively identified as (VI) or (VIII) the hydrocarbon produced by condensation of the di-iodide (XIX) with the dilithium derivative (III) (40% yield) or by treatment of the dibromide (XX) with phenyl-lithium (80% yield). This isomer does have a Raman band at 1650 cm.$^{-1}$, and passes into the high-melting dimer we have been discussing even at room temperature in the solid state. In both reactions it might have been produced by dimerisation of tetraphenylcyclobutadiene first formed.

Removal of palladium from tetraphenylcyclobutadienepalladium dichloride (I) with phosphines in the presence of olefins has always yielded as adducts tetraphenylcyclohexadienes, rather than the valency-tautomeric bicyclohexenes that were possible intermediates.[1]

[9] H. H. Freedman and R. S. Gohlke, *Proc. Chem. Soc.*, 1963, 249; *Chem. and Ind.*, 1963, 946.

[10] A. C. Cope and D. S. Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 5136.

[11] E. H. White and H. C. Dunathan, *J. Amer. Chem. Soc.*, 1964, **86**, 453.

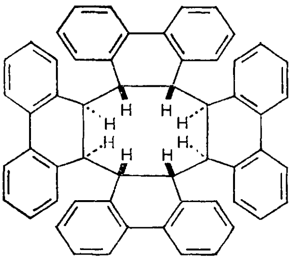
[12] K. Nagarajan, M. C. Caserio, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 449.

[13] E. R. Lippincott and R. C. Lord, *J. Amer. Chem. Soc.*, 1946, **68**, 1863; *J. Chem. Phys.*, 1948, **16**, 548.

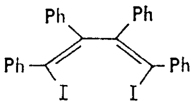
[14] E. Dallwigk, B. Susz, and E. Briner, *Helv. Chim. Acta*, 1952, **35**, 2145.

[15] J. Goubeau, *Annalen*, 1950, **567**, 214; S. V. Markova, P. A. Bazhulin, and M. M. Sushchinskii, *Optika i Spektroskopiya*, 1956, **1**, No. 1, 41; F. F. Cleveland, M. J. Murray, and W. S. Gallaway, *J. Chem. Phys.*, 1947, **15**, 742; K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, 1961, **83**, 1226.

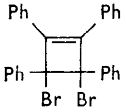
In the dimerisation in inert solvents [1] Freedman and Petersen's new hydrocarbon may well have been an unisolated intermediate. It seems unlikely that another cyclobutane ring would be formed, far more likely that one would be opened as before, giving structure (VI) from (VIII) *via* (VII) or directly. The reactions then (neglecting possible intervention of intermediate organopalladium compounds) become exactly analogous to the course followed in the dimerisation of 1,3-diphenylcyclobutadiene,[11] which first gives the tricyclo-octadienes (cf. VIII or IX) with the two possible orientations of the phenyl groups, that isomerise at room temperature to the cyclo-octatetraenes (cf. VI). Pyrolysis can then be formulated as valency-isomerisation of the cyclo-octatetraene (VI) to the bicyclo-octatriene (VII), which splits into hexaphenylbenzene and diphenylacetylene. In the octamethyl series [16] structure (VII) is more stable than (VI), (VIII), or (IX).



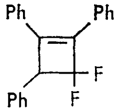
(XVIII)



(XIX)



(XX)



(XXI)

On balance, therefore, we are inclined to accept that the dimer is octaphenylcyclo-octatetraene (VI), in spite of its lacking a Raman band above 1605 cm.$^{-1}$. Since benzoic acid is nitrated to *m*-nitrobenzoic acid, oxidation of the dimer with nitric acid to the *para*-isomer must involve nitration at an earlier stage. Compound (VI) would be expected to be nitrated at the *para*-position, but so presumably would the cubane (X) if it would survive in acid.

Dehydrogenation of the dimer with palladium on charcoal in boiling diphenyl ether for several days formed two isomeric hydrocarbons, $C_{56}H_{38}$ (*i.e.*, dimer-H_2), one melting at 290° and the other at 305°, the structures of which have not been determined.

Mass Spectra.—The mass spectrum of the dimer was obtained by direct insertion [17,18] into the ion-source of the A.E.I. MS 9 mass spectrometer. This showed the "parent" peak, p, to correspond to a molecular weight of $712{\cdot}313 \pm 0{\cdot}002$, which is that of a compound $C_{56}H_{40}$. The formula was confirmed by the observed intensities of the isotope peaks at 713, 714, and 715 (61·8, 18·9, and 3·6%) compared with those calculated for the formula $C_{56}H_{40}$ (62·3, 18·8, and 3·6%). The spectrum was almost identical with that of a sample later supplied by Dr. R. S. Gohlke, made from the tin compound (II) and thought to be octaphenylcubane.[8,9] It differed, however, in several respects from the spectrum of the same compound reported by Freedman and Gohlke: [9] an ion corresponding to loss of a phenyl group, *i.e.*, $(p - C_6H_5)^+$ of mass 635, was detected, and also ions of mass 356, $(p)^{2+}$ or $(\frac{1}{2}p)^+$, and 178, (diphenylacetylene)$^+$ or (phenanthrene)$^+$, but almost all the other principal peaks in the spectrum occurred at mass numbers 1 to 5 units different from those reported previously.[9] The relative intensities were also somewhat different, but this is to be expected as the spectrum of Freedman and Gohlke was recorded on a time-of-flight mass spectrometer. The discrepancy between the masses of the ions in the two spectra is the more serious and due, no doubt, to the inferior resolution of the time-of-flight instrument. The principal peaks in the two spectra are given in Table 1 for comparison.

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[16] R. Criegee, W.-D. Wirth, W. Engel, and H. A. Brune, *Chem. Ber.*, 1963, **96**, 2230.
[17] R. I. Reed, *J.*, 1958, 3432.
[18] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Appl. Spectroscopy*, 1963, **17**, 63.

TABLE 1

Principal ions in mass spectrum of tetraphenylcyclobutadiene dimer

MS 9 Spectrum recorded at 120°	Mass no.	Freedman and Gohlke's spectrum	Mass no.
$p - C_6H_5$	635	$p - C_6H_5$	635
$p - C_6H_5 - CH_2$	621	$p - C_6H_5 - C$	623
$p - (C_6H_5)_2 - H$	557	$p - (C_6H_5)_2$	558
$p - (C_6H_5)_2 - CH$	545	$p - (C_6H_5)_2 - CH_2$	546
$p - (C_6H_4)[CH_2]_2(C_6H_4) - H$	533		
$p - (C_6H_5)_3 - H$	480	$p - (C_6H_5)_3$	481
$p - (C_6H_4)_3 - 4H$			
$p - (C_6H_5)_3 - H - CH_2$	467	$p - (C_6H_5)_3 - CH$	469
$p - (C_6H_4)_3 - 4H - CH_2$			
$p - (C_6H_4)_3 - 4H - C_2H_2$	455	$p - (C_6H_5)_3 - C_2H$	457
$p - (C_6H_5)_4 - 2H$			
$p - (C_6H_4)_4 - 6H$	402	$p - (C_6H_5)_4$	404
$p - (C_6H_5)_4 - 2H$			
$p - (C_6H_5)_4 - 2H - CH$	389	$p - (C_6H_5)_4 - C$	392
$p - (C_6H_4)_4 - 6H - CH$			
$p - (C_6H_5)_4 - C_2H_2$	378	$p - (C_6H_5)_4 - C_2$	380
$p - (C_6H_4)_4 - 4H - C_2H_2$			
$p - (C_6H_5)_4 - C_3H$	367	$p - (C_6H_5)_4 - C_3$	368
$p - (C_6H_4)_4 - 2H - C_3H_3$			
p^{++} and/or $\frac{1}{2}p$	356	p^{2+} and/or $\frac{1}{2}p$	356
$p - (C_6H_5)_4 - C_5H$	343		
$p - (C_6H_4)_4 - C_5H_5$			
$(C_6H_4)_4 + C_3H_3$			
$(C_6H_4)_3 + C_5H_3$	291	$(C_6H_5)_3 + C_5H_2$	293
$(C_6H_5)_3 + C_5$			
$(C_6H_4)_3 + C_4H_2$	278	$(C_6H_5)_3 + C_4H_2$	281
$(C_6H_4)_3 + C_3H_3$	267	$(C_6H_5)_3 + C_3H_2$	269
$(C_6H_4)_3 + C_2$	252	$(C_6H_5)_3 + C_2H_2$	257
$(C_6H_4)_3 + CH_3$	243	$(C_6H_5)_3 + CH_2$	245
$(C_6H_4)_2 + C_6H_3 + C$	239	$(C_6H_5)_3$	231
$(C_6H_4)_2 + C_3H_3$	191	$(C_6H_5)_2 + C_3$	190
Phenanthrene or $(C_6H_5)_2 + C_2$	178	Phenanthrene or $(C_6H_5)_2 + C_2$	178

Thus, although there *is* a peak at 635 from loss of a phenyl group from the parent molecular ion, the peaks that Freedman and Gohlke thought appeared at 558, 481, and 404, from loss of two, three, and four phenyl groups, really have masses of 557, 480, and 402, corresponding to elimination of additional hydrogen atoms. Again, their peak at 623 ($p - C_6H_5C$: from chipping off a corner of the cube?) really has a mass number of 621, and their peaks at 392, 380, and 368, which would have indicated loss of four phenyl groups with one, two, or three carbon atoms, actually have masses three, two, and one unit lower, respectively. As Freedman and Gohlke implied, many of their peaks, such as those just mentioned, could have arisen from a simple break-up of the unrearranged cubane. The correct masses, however, can be explained only by rearrangement and transfer of hydrogen atoms during fragmentation, whether the cubane (X) or cyclo-octatetraene (VI) structure is assumed, and the spectrum cannot be said to favour the former.

One can follow some of the paths of fragmentation by analysis of the " metastable " peaks, eight of which occur in the spectrum (Table 2). The formulæ given in the Table are intended only to illustrate compositions for the ions that add up to the right mass, and not to imply any particular structure. For example, the ion of mass 534 is probably the molecular ion of hexaphenylbenzene.

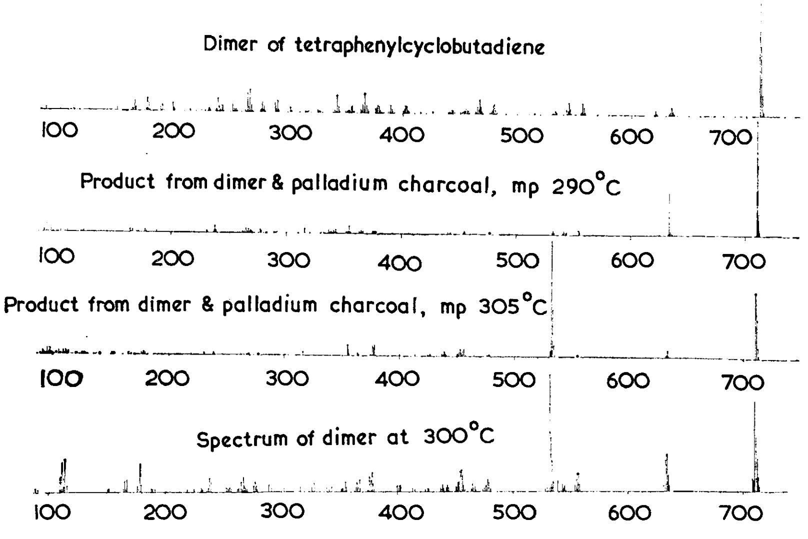
If the spectrum was obtained not at the lowest possible temperature (120°), but in the conventional way from the sample in a reservoir held at 300°, an entirely different spectrum resulted (Table 3). The most prominent heavy ion was then $(C_{56}H_{38})^+$ with a smaller amount of $(C_{56}H_{40})^+$ hidden in the isotopes. Prolonged heating of the dimer thus produced reaction, either to form an isomer (or isomers) that lost H_2 with extraordinary ease on electron

TABLE 2

Metastable transitions in mass spectrum of tetraphenylcyclobutadiene dimer recorded at 120°

Mass no.		Transition
543	$712^+ \longrightarrow 622^+ + 90$	$p^+ \longrightarrow [p - (C_6H_5 + CH)]^+ + C_7H_6$
		$\searrow [p - (C_6H_4 + CH_2)]^+ + C_7H_6$
478	$621^+ \longrightarrow 545^+ + 76$	$(p - C_7H_6)^+ \longrightarrow [(p - C_7H_6) - C_6H_4]^+ + C_6H_4$
464	$635^+ \longrightarrow 543^+ + 92$	$(p - C_6H_5)^+ \longrightarrow [(p - C_6H_5) - (C_6H_5 + CH)]^+ + C_7H_6$
		$\searrow [(p - C_6H_5) - (C_6H_4 + CH_2)]^+ + C_7H_6$
401	$712^+ \longrightarrow 534^+ + 178$	$p^+ \longrightarrow [p - C_6H_4(CH)_2C_6H_4]^+ + C_{14}H_{10}$
		$\searrow [p - C_6H_5C_2C_6H_5]^+ + C_{14}H_{10}$
376	$402^+ \longrightarrow 389^+ + 13$	$\{p - [(C_6H_5)_4 + 2H]\}^+ \longrightarrow \{p - [(C_6H_5)_4 + 2H + CH]\}^+ + CH$
338	$480^+ \longrightarrow 403^+ + 77$	$\{p - [(C_6H_5)_3 + H]\}^+ \longrightarrow \{p - [(C_6H_5)_3 + H + C_6H_5]\}^+ + C_6H_5$
264	$480^+ \longrightarrow 355^+ + 125$	$\{p - [(C_6H_5)_3 + H]\}^+ \longrightarrow \{p - [(C_6H_5)_3 + H + C_6H_5 + 4C]\}^+ + C_{10}H_5$
238	$635^+ \longrightarrow 389^+ + 246$	$(p - C_6H_5)^+ \longrightarrow \{(p - C_6H_5) - [(C_6H_5)_3 + 2H + CH]\}^+ + C_{19}H_{18}$

impact,* or more likely to produce rearrangement and pyrolytic loss of H_2. There was a prominent peak at 634 from loss of C_6H_4, but the most intense, in sharp contrast with the spectrum at low temperature, occurred at 532 from loss of Ph_2C_2. [Pyrolysis at relatively high pressure and short time gave only diphenylacetylene and hexaphenylbenzene (about 20% yield). At the much lower pressure and longer time in the reservoir of the spectrometer this cannot be an important reaction.]


Dimer of tetraphenylcyclobutadiene

Product from dimer & palladium charcoal, mp 290°C

Product from dimer & palladium charcoal, mp 305°C

Spectrum of dimer at 300°C

The spectrum of the hydrocarbon, m. p. 290°, from dehydrogenation with palladium showed the peak at 634, and the spectrum of the one, m. p. 305°, showed the peak at 532 with high intensity. In fact, the high-temperature spectrum of the dimer resembled a mixture of these two spectra, suggesting that it may have been produced by the two isomers. This can be seen from the Figure. [The small amount of metal in the glass inlet system may possibly have caused heterogeneous dehydrogenation.]

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* For example, even 1,2,3,4,5-pentaphenylcyclohexa-1,3-diene gave a peak for p^+ at 460 with an intensity 4·5% (after allowance for heavy isotopes) of the base peak's at 458, presumably from $(Ph_5C_6H)^+$ [Reservoir at about 95°, ionisation chamber at about 25°].

TABLE 3

Mass spectra of some related hydrocarbons

(C_4Ph_4 = tetraphenylcyclobutadiene; C_6Ph_6 = hexaphenylbenzene; C_2Ph_2 = diphenylacetylene)

Mass no.	Dimer of C_4Ph_4 at 120°	At 300°	$C_{56}H_{38}$, m. p. 290°	$C_{56}H_{38}$, m. p. 305°	C_6Ph_6	C_2Ph_2
	Percentages					
12					12·8	
17	0·96					
18	3·5					
26	0·58				1·85	1·09
27	0·58	2·54			9·6	1·22
28	2·23					0·32
29					2·35	
30		9·15			1·47	
31						0·46
32		4·23				
34			2·27		1·00	
36		4·74	3·1			
37			3·2			
37½			0·89			
38		2·20	5·41		0·73	0·62
39	1·2		19·41		3·45	5·16
40		2·03	16·47		0·88	0·32
41	0·62		27·06		5·67	0·49
42			31·77		2·05	
43			42·35		4·35	
44	1·48	29·23				
45			12·58		17·16	
46			4·13		5·67	
47			0·91	1·64		
48			0·93	1·52		
49			0·53	1·62		
50			13·67	9·10	1·17	4·28
51	1·37		16·47	13·28	1·4	6·85
52	1·68		18·82	14·41	0·97	2·28
53			2·7	2·44	0·88	
54			1·28	1·76	0·6	
55			10·58	11·57	1·14	
56		2·54	12·35	7·64	2·2	
57		4·91	21·18	16·69	3·4	
58		2·2		0·89		
61			0·64	0·63		0·69
61½						0·36
62				0·97		2·41
62½						0·39
63	0·62		3·13	1·81		8·10
63½						0·46
64		9·32	0·94	1·58	1·1	0·62
65			0·69	1·08	0·53	7·95
66		5·08		0·75		
67			3·13	5·01	1·93	
68		3·56	1·28	2·11	0·85	
69			5·55	8·3	2·76	
70			5·41	4·28	1·49	
71			10·81	8·54	2·02	
72			2·56	1·28		
73			1·99	1·48		
74	0·51		5·41	3·89		4·19
75			2·48	1·80		5·71
75½						1·28
76	0·55	3·05	5·73	6·52	0·56	6·09
76½						2·57
77	2·16		22·49	18·97	2·42	2·41
78	5·15	5·59	*100·00*	76·58	3·81	0·92
79	0·65		8·38	7·91	1·32	
80			0·94	1·38		
81			3·13	5·47	2·05	
81½						0·42
82			1·53	2·96	1·05	
83			3·41	5·93	1·98	
84			1·42	2·08	0·78	
85			2·99	4·81	1·17	0·32
86			1·33	0·95		1·71
87						3·20
87½						0·39
88				0·61		6·66
88½						1·32
89	0·58	3·39		1·17		16·07
89½						2·24
90						0·39
91	2·58	2·88	2·96	3·43	2·93	
92	0·78		0·94	1·34	0·97	
93			1·03	1·78	0·73	
94			0·79	1·38	0·68	
95			2·70	5·14	1·83	
96			1·28	2·37	0·88	
97			2·85	5·60	1·71	
98			0·84	1·46	0·61	2·01
99			1·08	1·88	0·58	1·35
100						0·92
101						0·72
102						2.11
103	1·13		1·13	2·04	1·10	0·49
104			0·56	0·68		
105			1·43	3·10	0·80	4·95
106			0·69	1·01		0·52
107			0·79	1·38		
108			0·59	1·03		
109			1·89	3·43	1·39	
110		12·87	0·79	1·36		0·56
111		13·38	1·99	3·56	1·03	0·65
112		25·07	0·84	1·88		
113		12·87	0·74	2·47		1·09
114		27·84		0·51		
115	1·24		0·55	0·87	0·66	1·25
116		6·6				
117			0·59	0·84		
118				0·60		
119			0·84	1·49		
120				0·85		
121			0·69	1·23		
122				0·66		0 43
123			1·18	2·28	0·70	
124			0·53			
125			1·18	1·94	0·63	0·62
126			0·64	1·3		4·47
127			0·69	1·45		1·23
128			0·59	1·07	0·61	0·99
129			0·54	0·84		
131			0·5	0·76		
133			0·62			
134				0·59		
135			0·62	1·08		
136				0·53		
137				1·36	0·61	0·76
138				0·60		0·95
139			0·59	0·99	0·58	3·07
140				0·59		0·32
141	0·55			1·32		
143				0·57		
145				0·79		
146						
147				0·56		
149			0·55	0·91		0·59
150				0·79		4·09
151	0·58	2·03	0·52	1·68	9·0	7·90
152	2·99	2·71	0·76	1·40	1·54	8·85
153	0.79			1·12	0·3	1·32
154			0·54		0·56	
155				0·86		
157				0·50		
159				0·52		
163				0·65		0·89
164		2·37				
165	5·98	9·15		1·60	2·91	
166	8·04	2·71	0·69	0·50	0·66	
167	8·14	10·0	2·56	1·01	4·01	
168	3·92				0·63	
169				0·85		
174						0·82
175				0·51		2·05
175½					0·88	
176	0·96	5·25		1·39		16·75
176½					1·49	
177	1·20	3·22		0·93	5·30	8·75
178	11·55	23·66	2·56	2·36	1·07	*100·00*
179	6·91	6·94	1·42	1·84	1·85	16·07
180	1·13			0·62		1·47
180½					0·58	
181					0·53	
181½					1·93	
182				0·68	2·91	
187				0·60	1·41	
187½					0·83	
188	0·69	3·22	1·58	0·95	3·52	
188½			0·54		1·22	
189	2·58	2·03		0·56	2·07	
189½					1·22	
190	0·69					
191	5·88	2·54	0·89		0·85	
192	1·03					
193½					1·22	
194					0·88	
194½					0·63	
195					0·90	
199					0·90	
199½					0·58	
200	7·22	4·74		0·52	3·10	

TABLE 3 (*Continued*)

	Dimer of C_4Ph_4 at 120°	At 300°	$C_{56}H_{38}$, m. p. 290°	$C_{56}H_{38}$, m. p. 305°	C_6Ph_6	C_2Ph_2
Mass no.			Percentages			
200½	3·13	2·54			2·02	
201	2·0				1·32	
202	1·44					
203	0·76					
205½					1·95	
206					1·90	
206½					4·25	
207					1·46	
207½					1·88	
208					0·92	
210					0·70	
211					0·70	
211½						
212				0·71	3·54	
212½					2·83	
213				0·58	4·54	
213½					2·10	
214					1·76	
214½					2·44	
215	1·92				1·98	
217½					2·05	
218				0·52	1·63	
218½	0·62	2·03		0·97	3·49	
219	0·58	2·2		1·05	3·76	
219½				0·68	2·44	
220					3·53	
220½					2·39	
221					3·49	
224	0·51			0·65	3·27	
224½	0·55				2·44	
225	1·58	2·71	0·69	0·75	3·49	
225½	0·82	2·03			1·46	
226	0·93				1·58	
226½					0·80	
227				0·52	0·92	
228	1·17				2·22	
228½					0·83	
229	0·58					
229½					0·68	
230					0·92	
230½	0·86		1·43	1·34	2·49	
231	2·65	3·39	1·18	1·13	3·61	
231½	3·61	3·56		0·53	2·00	
232	2·23	2·37			1·93	
232½	0·76				0·92	
234					0·53	
236				0·64	1·22	
236½					1·14	
237	0·62	3·22	1·82		2·54	
237½	0·55	3·56	5·97		1·88	
238	2·61	11·69	2·85	1·05	2·59	
238½	2·40	5·93		2·04	1·85	
239	12·03	8·13	1·53	1·05	1·66	
239½	5·15	2·54				
240	2·68				0·53	
241	1·61					
242	0·55					
242½					0·82	
243	5·15				0·90	
243½					0·92	
244	1·06			0·57	1·29	
244½					0·88	
245					1·17	
245½					0·75	
246					2·20	
246½					1·02	
248						
249				0·59		
250				0·57	0·78	
251	0·51				0·61	
252	6·19	3·73		0·65	1·71	
253	3·57	3·22			1·05	
254	2·47	2·03				
255	3·37	2·71	0·64	0·62		
255½			0·64	0·77		
256	1·24	2·03	0·79	0·81		
256½	0·51					
257	0·82					
259						
261			0·54	0·64		
261½			0·54	0·55		
262	0·51	2·37	1·03	1·07		
262½			0·89	0·75		
263	1·99	3·73	1·08	1·07		
264	1·06					
265	16·49	8·98	3·7	1·03	3·32	
266	5·98	2·71	1·14		1·27	
267	19·93	12·87	3·14	2·04	3·00	
268	6·49	5·08	1·42	1·07	0·53	
268½		2·2	2·99	0·8		
269	1·24	3·56	1·56	1·34		
269½		2·71	1·42	1·29		
270	0·96	2·37	0·89	0·73		
270½	0·86					
275				0·59		
275½		2·03				
276	2·1	5·08	0·59	1·15	1·85	
276½		2·54		0·59		
277	2·51	8·64		1·07	1·05	
277½	0·51	3·73	2·85	2·18		
278	8·14	5·76	1·56	0·91	1·35	
278½	2·34					
279	5·15	2·71	0·74		1·07	
280	1·34					
289	8·25	5·59	1·43	0·69	1·95	
290	3·33		0·54		0·70	
291	10·1	3·39	1·18		1·22	
292	2·54					
300	0·58				0·78	
301	0·51				4·89	
302	4·23	3·22	0·54	0·52	0·83	
303	2·37				0·92	
304	4·86					
313	1·27				0·53	
314	0·55					
315	1·61	2·54				
316	0·65	4·06	3·56	2·64		
316½		2·37				
317	1·92		0·64	0·52		
317½	0·72					
326	2·16	4·4	0·89		1·00	
327	1·48				0·56	
328	1·31	7·62				
329	0·62	2·71				
337			2·71			
339	2·4	3·56	1·28	0·52	1·71	
340	1·37		0·64		0·51	
341	2·27	2·54	2·36			
342	1·06		0·84			
343	15·12	4·06	3·10			
344	5·67		0·94			
345	1·03					
350	1·03		0·64	0·97	1·44	
351	1·31	2·03	0·54	0·63	1·10	
352	2·89	3·39	1·18	0·69	1·88	
353	2·44	3·05	1·18	0·49	1·17	
354	2·82	4·06	1·48	0·52	0·56	
355	5·15	8·81	3·10	9·49	0·92	
355½		3·39	1·28	5·47		
356	5·98	4·74	0·98	1·80		
356½	1·04					
357	1·79					
363	3·5	5·93	1·38	2·50	3·66	
364	2·4	4·57	0·94	1·23	2·49	
365	7·32	8·81	2·27	0·59	5·67	
366	3·47	4·23	0·94	0·68	2·66	
367	17·53	10·16	1·85	0·62	2·16	
368	6·8	3·22	0·79		0·70	
369	3·54					
370	1·27					
374		2·03		1·34	0·95	
375		2·2		1·19	0·78	
376	4·23	13·55	1·99	8·35	3·64	
377	4·64	10·67	1·71	7·97	3·57	
378	6·60	16·60	1·85	9·49	3·91	
379	6·29	7·28	0·89	0·71	4·59	
380	3·09	2·54		0·65	2·07	
381	1·10					
387	1·35				0·75	
388	1·17					
389	6·91	4·40	0·74	0·65	0·88	
390	3·81					
391	1·44				0·68	
392	0·72					
400	2·37	5·25	0·74	1·31	1·27	
401	3·50	3·90	0·62	0·81	1·10	
402	6·49	5·25		0·81	1·19	
403	5·36	4·23			1·22	
404	2·82				0·61	
405	0·89					
411						
413	0·96	2·88		1·11	1·80	
414	0·51			0·64	0·92	
415	1·17	2·03			2·64	
416					1·32	
424		2·03		1·17	0·73	
425				0·77	0·68	
426	1·17	2·71		1·52	1·12	
427	0·93	2·88		1·19	1·49	
428	0·89			0·69	1·27	

TABLE 3 (*Continued*)

Mass no.	Dimer of C_4Ph_4 at 120°	At 300°	$C_{56}H_{38}$, m. p. 290°	$C_{56}H_{58}$, m. p. 305°	C_6Ph_6	C_2Ph_2
	Percentages					
429	0·62		0·64		1·02	
431	0·62					
437	0·96	3·73		2·06	1·07	
438	0·69	2·37		1·38	0·73	
439	2·27	6·27		4·09	1·90	
440	1·37	3·56		2·57	1·17	
441	1·89	4·74	1·03	1·19	3·49	
442	1·10		0·64		2·34	
443	3·5	5·76	1·85	1·09	1·77	
444	2·78	4·57	0·79		0·56	
445	1·44					
446	0·72	2·03				
448				0·83		
449				0·75		
450	1·1	4·74	0·76	2·24	0·70	
451	1·31	4·4	0·69	2·24	0·68	
452	2·06	8·81	0·84	4·02	0·68	
453	2·30	9·48	0·98	6·20	0·88	
454	3·47	17·95	1·13	3·49	0·86	
455	4·74	18·8	2·41	4·81		
456	3·57	14·9	1·08	6·00		
457	3·16	6·61		1·36	5·13	
458	1·24	2·03			1·76	
463	2·10	4·91	1·28	1·97		
464	1·51	2·88	0·79			
465	6·56	6·61	2·22	1·27		
466	4·02	3·56	1·03	0·59		
467	12·71	4·91	0·59			
468	6·8	2·2				
469	2·51				0·66	
470	0·89					
474		2·7		0·81		
475		3·39	0·59	0·83		
476	1·27	5·42	0·98	1·31		
477	2·16	6·94	1·58	1·34		
478	3·37	10·33	1·82	1·62	0·56	
479	8·14	8·64	0·59	1·01	0·63	
480	8·66	5·42			0·70	
481	3·85	2·71				
482	1·00					
491	0·55			0·50	0·70	
493					2·73	
494					1·98	
505					0·63	
506						
515	1·06			0·79		
516	0·55			0·59		
517	0·76					
518	0·51					
519					0·95	
526						
527						
528	0·58	2·37				
529	0·72			0·61		
530	0·69	3·73		1·44		
531	1·03	7·45	1·09	5·47		
532	1·03	*100·0%*	3·21	*100·00*	0·92	
533	2·40	46·41	1·19	40·61	2·59	
534	1·72	27·84		10·06	*100·00*	
535	0·65	9·32		1·68	43·03	
536					9·31	
537					1·36	
539		9·32				
541	1·13	3·73		0·890		
542		3·05		0·57		
543	4·64	6·61		0·91		
544	3·57	3·39	1·18			
545	10·82	5·08				
546	5·15	2·71				
547	1·27					
552						
553			0·54	0·59		
554		5·76	0·59	0·79		
555	1·68	10·5	3·41	1·90		
556	2·71	15·58	1·85	1·78		
557	10·0	15·41		0·68		
558	6·80	6·6		0·17		
559	2·20					
560	0·58					
619		2·03				
620	0·86	2·89	0·94	0·44		
621	3·30	3·39		0·23		
622	1·65					
631		5·59				
632		7·79		1·31		
633	1·24	26·91	0·94	2·57		
634	3·30	31·66	11·91	36·45		
635	7·01	14·40	6·62	2·56		
636	3·44	4·57	1·85	0·45		
637	1·03		1·00			
708		11·52				
709		9·82	1·05	0·75		
710		76·66	*100·00*	56·98		
711	90·62	46·4	60·92	34·71		
712	*100·00*	28·30	18·32	10·44		
713	61·8	12·53	3·14	2·18		
714	18·9	4·23	0·42	0·31		
715	3·61					

TABLE 4

Mass spectrum of tetraphenylcyclobutadienepalladium dichloride at 185°

Mass no.	%	Mass no.	%	Mass no.	%	Mass no.	%
71	7·05	138	10·34	178	*100·0*	313	38·22
73	2·07	138½	5·12	179	18·64	314	14·61
74	2·32	139	9·60	191	2·00	315	14·92
75	2·35	139½	5·23	200	3·29	326	10·18
76	3·04	149	2·07	201	2·60	327	9·98
77	2·25	150	6·62	203	5·76	339	2·69
78	3·41	151	9·06	204	2·50	340	8·86
82	1·85	156	2·44	239	3·19	341	3·16
83	38·22	156½	4·91	250	3·32	350	5·23
84	2·19	157	2·67	252	20·51	351	4·27
85	25·17	162	4·69	253	2·85	352	7·68
87	4·0	163½	2·44	263	4·70	353	8·54
89	2·63	164	2·38	264	2·04	354	18·64
91	5·28	165	8·32	265	2·43	355	17·56
92	2·13	166	2·00	266	2·91	356	87·31
93	2·47	167	4·37	267	9·77	357	29·52
96	2·60	168½	5·98	268	2·60	358	7·79
97	2·11	169	6·26	274	5·12	372	2·79
102	2·32	169½	6·48	275	2·44	388	2·76
103	2·32	170	5·98	276	25·17	390	11·63
105	3·14	174	3·32	277	19·58	391	34·49
109	4·48	175	7·90	278	45·21	392	13·45
113	2·25	175½	2·98	279	29·21	393	12·60
115	2·82	176	19·27	280	8·11	394	3·69
119	3·31	176½	2·72	281	2·25	426	7·58
125	2·35	177	11·81	288	2·82	427	2·69
137	3·85	177½	2·22	312	2·76	428	5·12

Tetraphenylcyclobutadienepalladium dichloride (I) gave a mass spectrum (Table 4) with a very intense peak at 356, corresponding to tetraphenylcyclobutadiene less an electron. At higher mass numbers were peaks from $[C_4(C_6H_5)_4Cl]^+$ and $[C_4(C_6H_5)_4Cl_2]^+$. [Preparative vacuum sublimation of the complex yields geometrical isomers of 1,4-dichlorotetraphenylbutadiene and diphenylindenoindene, having two less hydrogen atoms than tetraphenylcyclobutadiene.[1]] It is impossible to tell, of course, whether the most intense peak at 178 is due only to the diphenylacetylene, or even phenanthrene, cation-radical formed by splitting of the tetraphenylcyclobutadiene cation-radical, or whether there is also a contribution from the Hückel aromatic tetraphenylcyclobutadiene dication. In the presence of water vapour and oxygen (*i.e.*, when the spectrum was run without prolonged evacuation of the sample) the peaks at 391 and 426 from the chlorinated ions were replaced by ones at 372 and 388, indicating reaction to form tetraphenylfuran and *cis*-dibenzoylstilbene. The solutions produced by treatment of the palladium complex (I) with tertiary phosphines at room temperature,[1] or pyrolysis of the tin compound (II) at 150°,[3] react in the same way, suggesting that the same reactive species may be present in solution and in the gas. This can hardly be other than tetraphenylcyclobutadiene (singlet Va or triplet Vb) or its open tautomer (planar Vc or non-planar Vd).

Monomeric tetraphenylcyclobutadiene has, therefore, been produced in the gas phase.

EXPERIMENTAL

Pyrolysis of Dimer.—The dimer (0·5 g.) was sublimed *in vacuo* through a column of glass beads at 670°. A dark sublimate collected in the head of the column and a yellow oil (17 mg.), smelling strongly of tolan, in the cold trap. The sublimate was dissolved in chloroform, and dimer (73 mg.) recovered by filtration. The concentrated filtrate afforded a white solid on dilution with ethanol, and more on evaporation and crystallisation from benzene–petrol. The combined solids (111 mg.) were sublimed *in vacuo* at 280°, and the sublimate was crystallised from benzene–petrol. The white crystals, m. p. >300°, had an i.r. spectrum identical with that of hexaphenylbenzene.

Alternatively the dimer (100 mg.) suspended in benzene (7 ml.) was dropped in a stream of nitrogen during 10 min. through a silica tube. At 600° most of the dimer was recovered. A benzene solution of the product of pyrolysis at 740° deposited hexaphenylbenzene (20 mg.): examination of thin-layer chromatograms by u.v. fluorescence showed the absence of significant amounts of phenanthrene. (Benzene alone at 740° gave only diphenyl.)

Dehydrogenation of the Dimer.—The dimer (0·45 g.) in diphenyl ether (30 ml.) containing 30% palladium on charcoal (0·6 g.) was boiled under nitrogen for a week. By repeated crystallisation and chromatography on silica gel the following products were separated: unchanged dimer (90 mg.), A (20 mg.), B (100 mg.), C (60 mg.), D (5 mg.).

Product C was a fluorescent oil, derived from the solvent and therefore not further examined. It deposited white crystals (5 mg.), m. p. 153—155°. The orange crystals of product D, m. p. 285—290°, were obviously impure.

Product A had m. p. 300—305°; $\nu_{\text{max.}}$ 3078, 3048, 1490, and 1440 in C_4Cl_6, 723, 704, and 695 cm.$^{-1}$ in Nujol; $\lambda_{\text{max.}}$ 270 (26,000) and shoulder at 300 mμ (10,000) in methyl cyanide (Found: C, 95·0; H, 5·7. Calc. for $C_{56}H_{38}$: C, 94·6; H, 5·4%).

Product B had m. p. 290°; $\nu_{\text{max.}}$ 3060, 3025, 1486, and 1440 in C_4Cl_6, 1595, 1028, 766, 755, 731, and 698 cm.$^{-1}$ in Nujol; shoulders at 260 (30,800) and 291 (17,300); $\lambda_{\text{max.}}$ 377·5 mμ (130) in C_6H_{12} (Found: C, 94·5; H, 5·5%).

R. R. H. acknowledges with thanks a Union Carbide Research Fellowship. We also thank Shell Research Ltd. for a grant.

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[*Received, November 9th*, 1964.]