Comparison between Unimolecular Gas Phase Pyrolysis and Electron Impact Fragmentation. Part II.¹ The Gas Phase Pyrolysis of Tetralin and some Related Hetereocycles

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The thermal fragmentation of tetralin, chroman, isochroman, thiochroman, isothiochroman, 1,2,3,4-tetrahydroquincline and 1,2,3,4-tetrahydroisoquinoline has been investigated and compared with the fragmentation under electron impact reported in the preceding paper. Many similarities as well as some differences are noted. As a result of this work a new synthesis of the o-quinodimethane-benzocyclobutene system has been developed and the reactions of the former isomer with unreactive dienophiles are reported.

This work was carried out in order to investigate further the similarities and differences between thermal and electron-impact fragmentation processes.² Details of the latter processes in the case of the compounds discussed here have already been reported.¹

Since the fragmentation processes observed in an electron-impact mass spectrometer are essentially unimolecular for this type of comparison to have any meaning, it is necessary first to decide whether the first stage in the production of the thermal degradation product is almost unimolecular. The occurrence of subsequent bimolecular processes may then lead to different products in the thermal case. This difference may also occur due to the stability of even-electron species since in the case of the fragmentation of a molecular ion this is achieved by expulsion of a radical

whereas in the case of a neutral molecule this requires the expulsion of a neutral molecule, or components thereof. Although it is desirable to determine the nature of the primary thermal fragmentation this really requires a detailed kinetic study of the mode of formation of each species discussed. Even this, which was not practical in this case, may not determine the nature of this primary fragmentation. However to try and distinguish in this work between intramolecular and free-radical processes these compounds were thermally degraded in two different systems. The first was a conventional static system ³ which, having a long contact time and low temperatures, would be expected to favour radical and other consecutive processes. The second was a simple flow system (see Experimental section) which with higher temperatures and lower contact times (ca. 1 sec.) would be expected to favour almost completely non-radical mechanisms.

⁸ (a) A. Maccoll, 'Techniques of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 1961, vol. VIII, ch. x; (b) H. Melville and B. G. Gowenlock, 'Experimental Methods in Gas Reactions,' Macmillan, London, 1964.

¹ Part I, A. G. Loudon, A. Maccoll, and S. K. Wong, pre-

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The compounds studied were tetralin and compounds of the type (I) or (II). The pyrolysis of tetralin has already been reported in part.⁴ The products from



these reactions were identified by n.m.r., mass spectrometry, and g.l.c. The last technique was used also for the quantitative analysis of the product mixtures.

TABLE 2

Activation energies *‡ for the major ions formed by electron impact

	$\lceil M -$	M -	[M -	
Molecule Ic	on: [H]+	$CH_3]^+$	$XH]^+$	§ [R.D.A.]+
Tetralin †	$3 \cdot 1$	$2 \cdot 9$	2.9	$2 \cdot 6$
Isochroman	1.9	¶	¶.	$1 \cdot 0$
1,2,3,4-Tetrahydro-	0.6	9	ſ	$2 \cdot 5$
isoquinoline				
Isothiochroman	$2 \cdot 0$	1.5	$2 \cdot 4$	$2 \cdot 1$
Chroman	$3 \cdot 2$	$3 \cdot 1$	9	2.8
1,2,3,4-Tetrahydro-	$3 \cdot 9$	$4 \cdot 2$	Ŷ	ſ
quinoline				
Thiochroman	2.3	$2 \cdot 8$	3.8	2.8

* These are probably not significant to more than 0.4 eV. [†] Literature values for the appearance potentials of tetralin agree within experimental error. The reported ionisation potential seems low (see ref. 1). [‡] Activation energy is defined as the difference between the appearance and ionisation potentials.⁵ § Retro-Diels-Alder reaction. ¶ Ion not observed.

The mixtures obtained by the pyrolysis of these compounds under various conditions are summarised in Table 1.

energies 5 for the various primary processes occurring under electron impact are summarised in Table 2 in order to investigate this hypothesis.

It should be pointed out * that an apparently high activation energy for an electron-impact process can correspond to two different situations. The first is a reaction of the electronic ground-state of the molecular ion, with a genuine high activation energy. The second is that the reaction may occur from an isolated electronically excited state and that most of the apparent activation energy 1 is involved in producing this excited state. Since thermal reactions occur from the ground-state thermal equivalents of the second type of reaction would not be expected, but as discussed in the companion paper¹ it is not always easy to detect the presence of such excited states.

If the approach of Dougherty^{2a} is adopted, then those reactions occurring under electron impact which have a metastable peak should have thermal equivalents. In the majority of the reactions considered here (Table 3) metastables are observed and thus these reactions would seem to come from the ground electronic state of the molecular ion.

It should also be noted that if the comparison between a thermal reaction involving the net expulsion of a molecule and an electron-impact reaction involving the expulsion of a radical is to have any meaning, the rate-determining step in the thermal case must be the expulsion, including any rearrangement, of the same radical. The latter will not always be the case.

In order further to facilitate comparison, Table 3 is included. It should be noted that this Table is a summary and therefore of necessity is somewhat simplified.⁺ As in the preceding paper the thermal fragmentation

A comparison between the	electron i	mpact a	and the	rmal fra	agment	ation o	f the co	mpoun	ls discu	ssed in t	his pap	ber
Fragmentation	R.D.	A. (3)	M -	CH3	M -	- XH	M - H	$(n \leq 2)$	M - H	$I_m(m>2)$	' Styr	ene ' ª
Mole % of total products	Th.	E.I.	Th.	E.I.	Th.	E.I.	Th.	E.I.	Th.	E.I.	Th.	E.I.
Tetralin	2	73 °	20	180	20	180	36	9	25		10	73 4
Isochroman	80	66						12			11	3
1,2,3,4-Tetrahydroisoquinoline	66	46		80			7	34	4	13	7	3
Isothiochroman	38	375		14	58	27		7			1	3
Chroman	17	28	39	17		10	24	46			11 f	
1,2,3,4-Tetrahydroquinoline	4	3	22	2			36	52	11	19	16	4
Thiochroman	4	25	39	34	23	17	5	91		5^{f}	12	10

TABLE 3

In all cases except for styrene, the column headings refer to the electron impact fragmentation and the figures for the electron impact case include any subsequent loss of hydrogen (H₂,H) in columns 1, 2, and 3. In the case of column 2 the thermal fragment-ation is the loss of methane, column 3 the loss of H₂X and in columns 4 and 5 n = 2, m = 4 respectively.

In all cases the thermal figures are the results for the lowest % pyrolysis as determined in the flow system.

^a See ref. 1 for discussion of mechanism in E.I. case. ^b This is the same fragmentation in this case. ^c Retro-Diels-Alder reaction, in thermal case includes figures for *o*-xylene produced. ^d Formation of C_8H_8 by reaction other than retro-Diels-Alder, in the thermal case. ^e In this case $(M - CH_4)^+$. ^f No metastable for formation of this ion. X = O, NH or S as in text.

Superficially it might be expected that the unimolecular processes seen under thermal conditions might correspond to those processes having a low activation energy under electron impact. The activation

* This discussion was prompted by a remark of one of the referees.

† This table was included at the request of both of the referees.

of these compounds will be reported under the type of reaction being considered rather than each compound being treated separately. This should facilitate the comparison between the two papers and also between

⁴ P. Brown, J. Amer. Chem. Soc., 1968, **90**, 4459. ⁵ (a) G. M. Badger and R. W. L. Kimber, J. Chem. Soc., 1966, 266; (b) G. M. Badger, R. W. L. Kimber, and J. Novotny, Austral. J. Chem., 1962, **15**, 616.

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the compounds studied. Tetralin is here treated as a type (I) compound.

DISCUSSION

The Retro-Diels-Alder Reaction: The Origin of the Loss of $CH_2=X$ in the Type (I) Compounds.—o-Quinodimethane, the primary product of this reaction in the iso-compounds is unstable at the temperatures employed for pyrolysis. Thus to show its production it is necessary to stop it reacting further. This can be done by trapping it by a subsequent reaction, often an olefin (q.v.) was used. Alternatively short reaction times can be employed when the relatively more stable isomer benzocyclobutene could be isolated. This system of isomers will be referred to as benzocyclobutene unless the specific reaction of the other isomer is concerned.

Tetralin.—Even in the flow system there is only a little benzocyclobutene produced and the major product formed by the loss of ethylene is styrene. The work of Badger *et al.*^{4b} on the pyrolysis of the 1-¹⁴C compound showed that the styrene produced contained either C-1 or C-4 but not both carbons. Thus the styrene produced does not come as a result of isomerisation of benzocyclobutene, although this isomerisation occurs at these temperatures as has been shown in the course of this work.

The production, mainly of styrene, only in the case of this compound, is in line with the observation that in tetralin the activation energy for the electron-impact production of $[C_8H_8]^+$ which contains C-1 or C-4 is the same as that for the production of the $[C_8H_8]^+$ cation containing C-1 and C-4.

Isochroman.—The retro-Diels-Alder reaction is very important in the pyrolysis of this compound both in the static and flow systems. In the static system studies at low percentage reaction suggest that ca. 80% of this compound decomposes to give benzocyclobutene. A similar figure is obtained in the case of the flow system. In the static system the other retro-Diels-Alder, formaldehyde, as well as its expected decomposition products at this temperature, carbon monoxide and hydrogen, were detected. Although the pyrolysis of isochroman in the presence of propene gave rise to 2-methyltetralin (the expected product of o-quinodimethane and propene) this cannot be taken as evidence that o-quinodimethane is the intermediate in the production of benzocyclobutene, since at the temperatures used the equilibrium between the two isomers is very quickly established.6

1,2,3,4-*Tetrahydroisoquinoline.*—Under the conditions used the production of benzocyclobutene is small in the static system, but in the flow system it is the major product. However if this compound is pyrolysed in the static system in the presence of propene 2-methyltetralin is again isolated. There is no trace in this case of the other retro-Diels-Alder reaction product formaldehyde

imine but its probable decomposition products hydrogen and hydrogen cyanide were detected in the static system. In the static system as with isochroman the percentage of *o*-xylene produced increases with time and is much smaller when propene is added. This suggests that in the presence of free radicals benzocyclobutene is rapidly attacked to give *o*-xylene. For both compounds only small amounts of styrene and ethylbenzene (a possible final product of styrene) are observed and this could correspond with the observation of a minor process involving the loss of C-1 in $CH_2=X$ under electron impact in the case of these two molecules.

Isothiochroman.—This compound behaves rather differently in the static system as compared with the previous compounds in that only a trace of any product which might come from a retro-Diels-Alder reaction can be observed. In the flow system the second major product is however benzocyclobutene, in agreement with the behaviour of these three compounds under electron impact.

Type (II) Compounds.—In general in these compounds the retro-Diels-Alder reaction under electron impact is not very important. For chroman and 1,2,3,4-tetrahydroquinoline there is no trace of the product expected from the thermal retro-Diels-Alder reaction although it could be the precursor for the observed products in these two cases, o-cresol and o-toluidine respectively. For thiochroman this reaction seems even less likely as o-thiocresol was not observed. It should be said that both the amine and the cresol could also be formed in other ways.

Thus, as far as the retro-Diels-Alder reaction is concerned the electron-impact and thermal-induced behaviour seem to be similar.

Dehydrogenation.—This reaction will be compared with the formation of $M - H_x$ (x = 1—3) ions under electron impact.

Tetralin.—Previously the formation of naphthalene by the pyrolysis of tetralin has been reported.⁴ In this work we have detected the dehydrogenation of tetralin to 1,2-dihydronaphthalene. The ratio of the latter compound to the former in the pyrolysis products decreases with time which suggests that the latter is the precursor of the former. The thermal mechanism of this process is not clear but its occurrence in both the flow and static systems along with the knowledge that the similar dehydrogenation of cyclohexene to cyclohexa-1,3-diene ⁷ is unimolecular suggests that this may be a molecular process. The fact that the $[M - H]^+$ ion for tetralin can be formed either by a loss of hydrogen from C-1 or C-2 is consistent with this idea.

Isochroman.—No simple dehydrogenation products are seen amongst the products of the pyrolysis of this molecule. This is in contrast with the mass spectrum where the loss of hydrogen from elsewhere than C-1

⁶ F. R. Jensen, W. E. Coleman, and A. J. Belin, *Tetrahedron Letters*, 1962, 1, 15.

⁷ (a) R. Smith and A. S. Gordon, J. Phys. Chem., 1964, **65**, 1124; (b) M. Uchiya, T. Tomioka, and A. Amano, 1964, **68**, 1878.

occurs. Loss of a hydrogen from C-1 could not give rise to any dehydrogenation products without skeletal rearrangement, which might explain why no thermal dehydrogenation involving C-1 occurs. It is possible that the ethylbenzene observed in the static system could be formed by a free-radical reaction involving the initial loss of a hydrogen atom, most likely from C-1.

1,2,3,4-Tetrahydroisoquinoline.-The major product corresponding to a loss of hydrogen in both static and flow systems, is o-ethylbenzonitrile. The importance of this reaction in the thermal degradation of tetrahydroisoquinoline is in keeping with the low activation energy for the formation of $[M - 2H]^+$ under electron impact. This ion is reasonably intense in this case and is connected to the molecular ion by a metastable, which strongly suggests the expulsion of a molecule of hydrogen from the molecular ion as opposed to the stepwise expulsion of two hydrogen atoms. Thus these two processes are probably both unimolecular onestep reactions. The rather unusual nature of this reaction as compared with the rest of the compounds studied, except tetrahydroquinoline, suggests that it is a case where the process is somewhat independent of whether the starting material is an ion or a neutral molecule,^{2a,8} and depends more on the properties of the nitrogen atom. A simple mechanism is outlined below. The rearrangement process for the sulphur- and oxygencontaining molecules would, however, lead only to a rearranged form of the molecular ion since a subsequent expulsion of a hydrogen molecule as depicted in this scheme is not possible.



Chroman.—There is no major process involving a thermal expulsion of hydrogen.

1,2,3,4-Tetrahydroquinoline.—Expulsion of hydrogen in this case leads, after isomerisation 9 to o-ethylbenzonitrile. This is probably a unimolecular process since it occurs also in the flow system. As with tetrahydroisoquinoline there is a relatively large $[M - 2H]^+$ ion accompanied by an appropriate metastable suggesting an expulsion of a molecule of hydrogen.

Thiochroman.—There is little evidence for the loss of hydrogen being a major process in the pyrolysis of this compound. The $[M - H]^+/[M]^{+}$ ratio in the mass spectrum of this compound is the lowest of all the compounds discussed and the activation energy the highest, so this is perhaps not a surprising result.

Loss of XH₂: The Formation of Indene.—This should be compared formally with the formation of the ion at m/e 117 in the mass spectra of these compounds.

Tetralin. Both indene and 2-methylindane are observed as pyrolysis products under both static and flow conditions. The ratio of indene to 2-methylindane increases with time which suggests that the former could be a precursor of the latter. These observations

Isochroman. There is no indene formed in the pyrolysis of this compound, which is in keeping with the virtual absence of an ion at m/e 117 in the mass spectrum of this molecule.

Isothiochroman.⁶ The production of indene is one of the major paths of pyrolysis of this compound; no trace of any rearranged intermediate was found. From the limited labelling evidence it is not clear what the mechanism of formation of the ion at m/e 117 under electron impact is, but there is probably more than one mechanism in operation.

Tetrahydroisoquinoline and Tetrahydroquinoline.—In neither case is there any indene formed on pyrolysis which is in keeping with the absence of $M - \mathrm{NH}_2$ ions in the mass spectra of these compounds.

Chroman. There is no indene found in the pyrolysis products of this compound although there is a small ion at m/e 117 in its mass spectrum.

Thiochroman. There is a large amount of indene produced on pyrolysis in both systems. This is perhaps a little surprising since the production of the ion at m/e117 in the mass spectrum of this compound requires the highest activation energy of all the processes measured in this compound. In particular the loss of methyl under electron impact has a much lower activation energy whereas the thermal loss of methane (q.v.)is not much greater than the loss of hydrogen sulphide. This seems a case where the superficial similarities may be misleading.

Expulsion of Methane.—This should be compared with the $[M - \text{Me}]^+$ and $[M - \text{CH}_4]^+$ ions observed in the mass spectra.

Tetralin. This has been discussed under the previous heading.

Isochroman and Tetrahydroisoquinoline. This process does not occur in either compound nor are $[M - Me]^+$ ions observed. For tetrahydroisoquinoline there is a small $[M - CH_4]^+$ ion but this comes from the $[M - H]^+$ ion.

Chroman, Thiochroman, and Tetrahydroquinoline. In all cases the thermal expulsion of methane is an important process under both static and flow conditions, and thus is probably a unimolecular process. In every case corresponding $[M - Me]^+$ ions are formed with relatively low activation energies and so two processes may be comparable. The mechanism of loss of methyl

⁸ R. G. Cooks, Org. Mass Spectrometry, 1969, 2, 481.

⁹ (a) G. Kohimaier and B. S. Babinovitch, *J. Phys. Chem.*, 1959, **68**, 1793; (b) F. W. Schneider and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1962, **84**, 4215; (c) F. W. Schneider and B. S. Rabinovitch, *ibid.*, 1963, **85**, 2365.

in the first and last compound seems complicated from the deuterium-labelling evidence and carbon labelling may be necessary, in this case, to provide unambiguous results.

From this study alone it could be said that if a particular fragmentation does not occur under electron impact, e.g. the loss of a hydroxyl radical from isochroman then the corresponding process, namely, the formation of indene, is unlikely to occur. However this does not seem a general conclusion especially when skeletal rearrangement is involved.⁸ In as far as this is true the higher excess energy imparted by electron impact is a crude explanation of this observation.

More important is the fact that apparent similarities between electron impact and thermal processes must be treated with care.^{2a} Such reactions as the retro-Diels-Alder reaction may, in fact, depend little on whether the reactant is a molecule or an $ion.^{2a}$ Others which since they are ready, apparently are low-energy processes in thermolysis, e.g. the loss of hydrogen sulphide from isothiochroman, may correspond to processes under electron impact which have high activation energies, for example the expulsion of the thivl radical from isothiochroman, which has the highest activation energy of the five processes studied. In other cases although the products may be the same, the mechanisms may well be different, e.g. in tetralin in the process involving the expulsion of a methyl radical or methane. Considerable care must, therefore, be taken before any detailed comparison between the two processes are made. In particular, it must not be assumed that the mechanism in one case is similar to the other; in our present state of knowledge, a detailed study of both mechanisms is still essential.

However even with this warning certain practical advantages can be derived from an application of the results of one method of fragmentation to prediction of fragmentation under the other conditions and another example ¹⁰ of this forms the subject of the next section of this paper. In this the application of these ideas to the problem of producing a neat synthesis of benzocyclobutene is reported, together with an outline of the usefulness of that compound as a precursor for reactions involving o-quinodimethane.6* The reactivity of o-quinodimethane to dienophiles has been noted 6,11 and this work has shown its reactivity to nonactivated dienophiles leading easily to some relatively inaccessible tetralin derivatives. Such reactions are summarised in Table 3.

Previous synthesises 12 of benzocyclobutene although giving high yields were tedious. In view of the recogni-

tion of six-centred transition states in the gas phase 13 it was decided to try and form the compound by the pyrolysis of an appropriately substituted o-xylene. Several compounds were investigated in the mass spectrometer attention being paid in particular to see if the substituent was lost under electron impact. α -Chloro-o-xylene under electron impact showed a large $[M - Cl]^+$ ion and since it was commercially available it was chosen for further study. The pyrolysis of this compound in the flow system at 630 °C gave benzocyclobutene in 70% yield. It is interesting to note that the kinetics ¹² in the static system suggest a unimolecular mechanism.14

Before discussing the reactions with benzocyclobutene as an intermediate in the production of o-quinodimethane, those reactions in which the o-quinodimethane was produced and reacted in situ (summarised in Table 3) should be mentioned. In these cases the structure

TABLE 4

A summary of the preliminary experiments on the Diels-Alder reaction of o-quinodimethane with unactivated dienophiles

o-Quinodimethane		
precursor	Dienophile	Product
Isochroman	Propene	2-Methyltetralin
α-Chloro-o-xylene	But-1-ene	2-Ethyltetralin
α-Chloro-o-xylene	Cyclohexene	1,2,3,4,5,6,9,10-Octahydro-
		anthracene
α-Chloro-o-xylene	Formaldehyde	Isochroman

of the adducts were established by mass measurement of the molecular ions produced under electron impact and their subsequent fragmentation patterns. In the case of 2-methyltetralin preparative g.l.c. allowed the isolation of this material from the crude reaction products from both precursors. This compound was then identified by comparison of is retention times on several g.l.c. columns, its mass spectrum, n.m.r. and i.r. spectrum with those of an authentic sample.

Reactions with Benzocyclobutene as a Precursor.—The dienophiles used were cis-but-2-ene, trans-but-2-ene and vinyl chloride. In all cases the reaction products included 1,2:5,6-dibenzocyclo-octadiene; this was the only product obtained in the acetone experiment which is a very poor dienophile. The other products were identified as described below; in all cases the mass spectrum of the crude products showed, as proved by low electron voltage runs and mass measurement, the correct molecular ions. In the first two cases the n.m.r. of the crude reaction products agreed, after subtraction of the spectrum of dibenzocyclo-octadiene, very well with the published spectra of cis- and trans-2,3-di-

^{*} In order to avoid the high temperatures necessary to generate o-quinodimethane directly it was decided to trap out benzocyclobutene since the latter is the stable isomer at lower temperatures.6

 ¹⁰ R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, and R. K. Solly, *Chem. Comm.*, 1966, 407; (b) Austral. J. Chem., 1969, 20, 1917; (c) M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. V. Van Fossen, *Tetrahedron Letters*, 1966, 2947.
 ¹¹ M. P. Cava and A. A. Deaner, J. Amer. Chem. Soc., 1959, 01, 4066.

^{81, 4266.}

¹² (a) K. Alder and M. Fremery, Tetrahedron, 1961, 14, 190;
(b) J. A. Olivier and P. A. Ongley, Chem. and Ind., 1965, 1024;
(c) J. M. Garrett and G. J. Fonken, Tetrahedron Letters, 1969, 8,

 ¹⁹ C. J. Harding, A. G. Loudon, A. Maccoll, P. G. Rodgers, R. A. Ross, S. K. Wong, J. Shapiro, E. S. Swinbourne, V. R. Stimson, and P. J. Thomas, *Chem. Comm.*, 1967, 1187.

¹⁴ A. G. Loudon, A. Maccoll, and S. K. Wong, J. Amer. Chem. Soc., 1969, 91, in the press.

methyltetralin.¹⁵ This retention of configuration is in accordance with the mechanism of the Diels-Alder reaction.¹⁶ An estimate of the yields from these spectra suggested that they were as good as in the earlier preparation.¹⁵ The n.m.r. of the crude product of the reaction involving vinyl chloride was consistent with the proposed structure, 2-chlorotetralin.

These preliminary experiments suggest that this is a potentially useful route to substituted tetralin derivatives and indicated the use of a mass spectrometer in selecting synthetic routes.

EXPERIMENTAL

The analytical apparatus and preparative g.l.c. used have been described in the preceding paper,¹ the relative responses of the detector of the analytical g.l.c. machines to the various compounds detected by them was also determined. The preparation of the compounds studied in the first half of this paper are also described in the other paper.¹ The purification of α -chloro-o-xylene is reported elsewhere.12

¹⁵ H. Peter, R. Archer, and H. S. Moshem, J. Org. Chem., 1967, 32, 1382.
 ¹⁶ K. Alder and G. Stein, Angew. Chem., 1937, 50, 510.

Flow Pyrolysis System.-This consisted of a silica tube (24 in \times 1 in)), packed with small silica tubes (1 in \times in), surrounded by a furnace. The temperatures at the middle and the end of this could be measured and the temperature at the centre, which is the one quoted herein, was ca. 40 °C higher than at the ends. The whole system including the sample were degassed and flushed with oxygenfree nitrogen. The sample was then blown through the tube by a stream of nitrogen and assisted by gentle warming of the sample. The products were trapped in glass vessels, held at liquid-nitrogen temperatures.

Static System.—See ref. 3.

Reaction of Benzocyclobutene with Various Olefins .----Benzocyclobutene (0.02 mole) and the olefin (0.01 mole)were placed together in a sealed tube and heated at 200 °C for 15 hr. The crystals of impure dibenzocyclo-octadiene were separated and recrystallised from ethanol to give the pure compound, m.p. 109-110° (lit.,¹⁷ 109.5-110°). The n.m.r. spectra of the crude reaction product was determined in carbon tetrachloride.

2-Methyltetralin .--- This was prepared by the reduction of 2-methylnaphthalene with sodium in boiling pentyl alcohol.

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17 A. C. Cooper and S. W. Fenton, J. Amer. Chem. Soc., 1951, 78, 1688.