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THE PHENYLCARBENE REARRANGEMENT REVISITED

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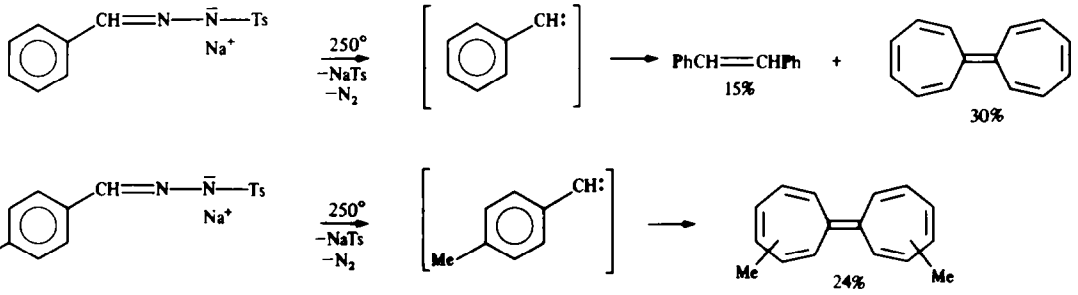
Abstract—The evolution of mechanistic ideas about the phenylcarbene rearrangement has been reviewed, and three closely linked problems have been identified toward whose solution this research has been aimed: 1. Why do the ratios of the stable end products from the rearrangements of *o*-, *m*- and *p*-tolylmethylene differ when all three reactions have been thought to pass through a common intermediate? 2. Why does the rearrangement of 2-methylcycloheptatrienylidene lead to exclusive formation of styrene? 3. What is the mechanism of styrene formation from *o*-tolylmethylene? New mechanisms have been proposed in which *m*- and *p*-tolylmethylene can rearrange to styrene without *necessarily* being converted to *o*-tolylmethylene. The formation of a small amount of 2,6-dimethylstyrene from the rearrangement of 3,4,5-trimethylphenylmethylene is viewed as evidence for such a mechanism, and a set of interconverting norcaradienylidenes are believed to be the crucial intermediates. Other alternatives are considered and rejected on the basis of the rearrangement products of 3,5-dimethyl- and 3,4,5-trimethylphenylmethylene.

INTRODUCTION

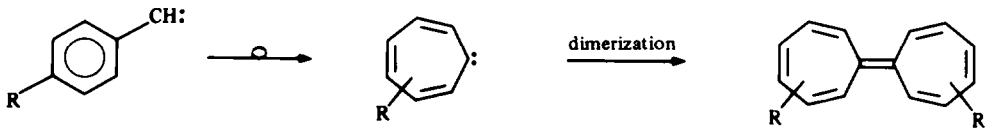
Recognition of the phenylcarbene rearrangement and the evolution of mechanistic postulates to explain it

The reaction called the phenylcarbene rearrangement by workers in the field came to be recognized through the observation by Jones *et al.* that the generation of phenylmethylene in the gas-phase leads to the formation of heptafulvalene.[1] Shortly thereafter



Hedaya *et al.* also reported the formation of heptafulvalene in the flash vacuum pyrolysis of phenyldiazomethane.[2]

The formation of heptafulvalenes was explained by suggesting that a phenylmethylene rearranges by ring expansion to a cycloheptatrienylidene which undergoes dimerization.

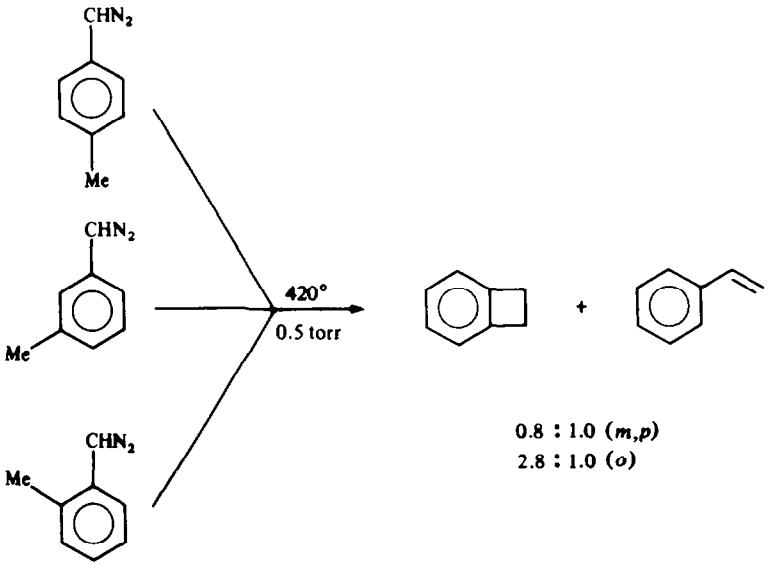


At the end of 1969 Crow and Wentrup predicted on the basis of their work on the interconversion of 2-pyridylcarbenes and phenylnitrenes, and N-scrambling in 2-pyridyl nitrene,[3] that phenylmethylene and cycloheptatrienylidene could be transformed into each other, with the ring contraction favored over ring expansion.[4]

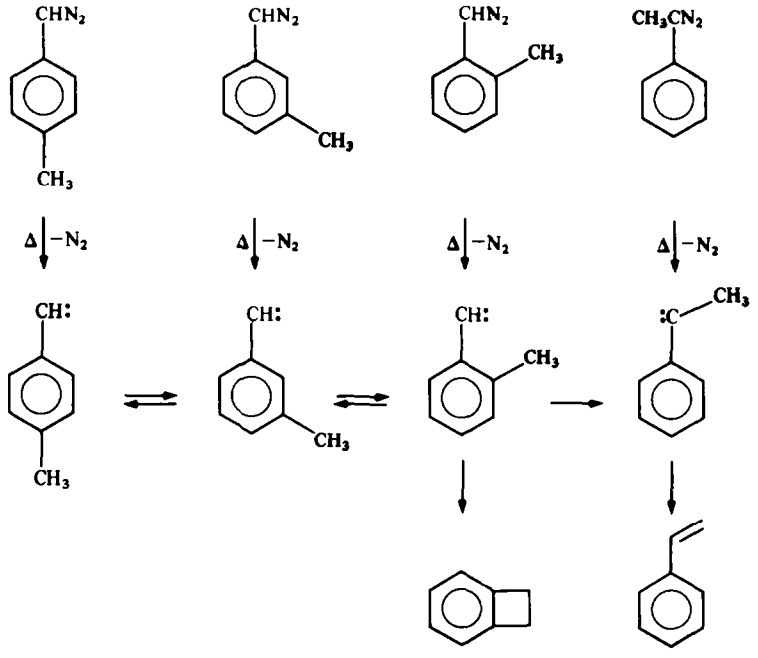
The reversibility of the phenylmethylene-to-cycloheptatrienylidene rearrangement, and hence the interconversion of substituted phenylmethylenes, was inferred by Baron *et al.* from the findings of Jones. This led to the prediction that *o*-, *m*-, and *p*-tolylmethylene would all stabilize themselves via intramolecular trapping by the methyl groups of *o*-tolyl and α-methylphenylmethylene. The formation of benzocyclobutene and styrene from the flow pyrolysis of *o*-, *m*-, and *p*-tolyldiazomethane dramatically confirmed this prediction.[5]

* Author to whom correspondence should be addressed.

† Taken in part from the doctoral dissertation of J.-P. Hsu, Washington University, August, 1981.

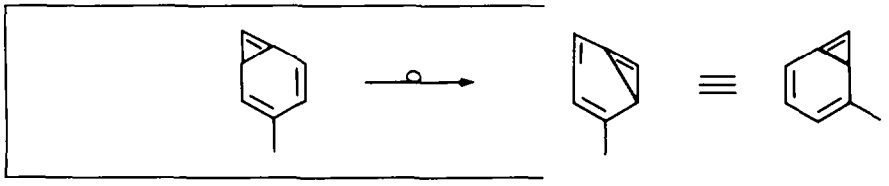


The following reaction scheme was postulated:



For the interconversion of the isomeric tolylmethylenes a mechanism was suggested (Fig. 1), which was based on the known cyclization of vinylmethylene to cyclopropene and its reversal.[6,7] A bicycloheptatriene intermediate in the conversion of phenylmethylene to cycloheptatrienylidene was also suggested by Hedaya *et al.*[2]

It was recognized that neither a bicycloheptatriene nor a cycloheptatrienylidene intermediate was demanded by the formation of benzocyclobutene and styrene, and indeed an alternative mechanism was written that circumvented cycloheptatrienylidenes by multiple degenerate vinyl cyclopropene rearrangements such as:[5]



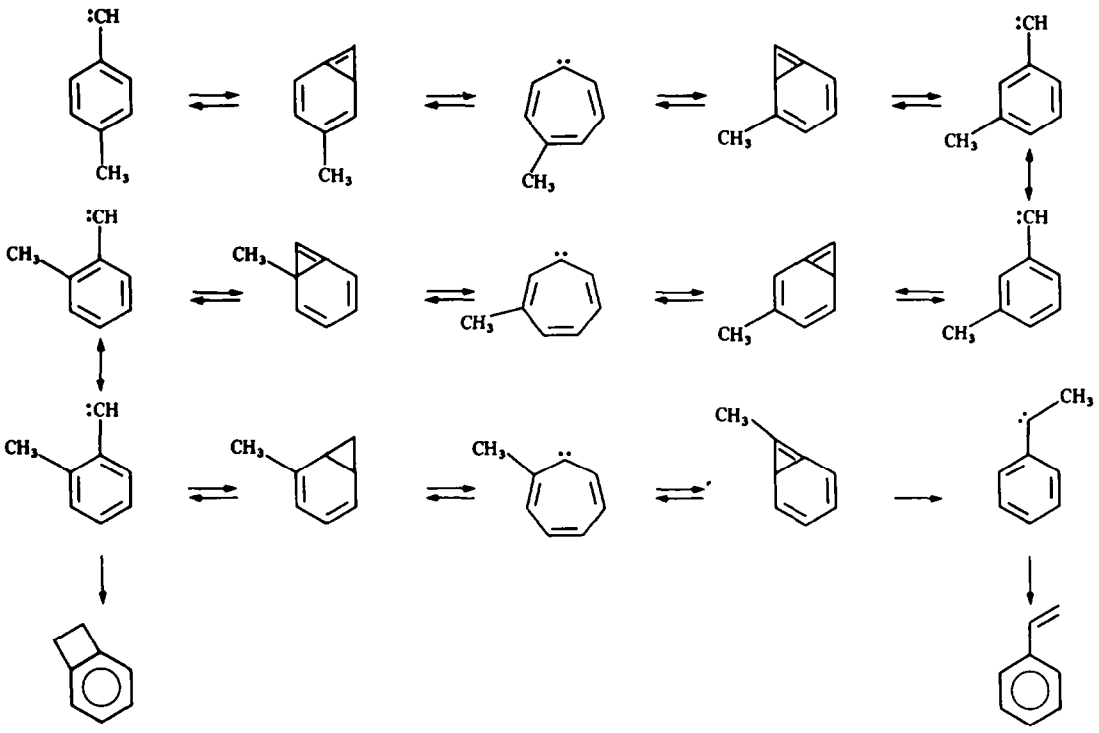
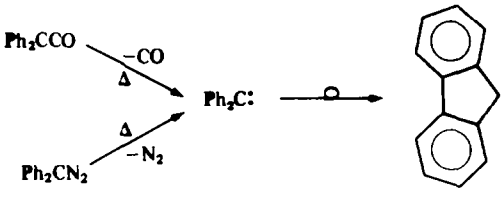


Fig. 1. The "Baron mechanism" for the interconversion of *ortho*-, *meta*- and *para*-tolylmethylenes via bicycloheptatriene and cycloheptatrienylidene intermediates. The stable products benzocyclobutene and styrene are viewed as being formed from *o*-tolylmethylene and α-methylphenylmethylene respectively, the former rearranging irreversibly to the latter (see ref. 5).

A process similar to this had been proposed in 1968 by Cadogan to account for the rearrangements of tolylnitrene intermediates in the deoxygenation of nitroso toluenes by trivalent P.[8] An important consequence of the proposed mechanism displayed in Fig. 1 was the prediction that phenylmethylene would undergo degenerate rearrangements in which each CH group could exchange roles with each of the others, but that their cyclic order would be maintained, and the interconversions would not mix the CH carbons with the unique quaternary carbon (C^1). The symmetry of the proposed phenylcarbene interconversion can be represented by a hexagon with the six CH groups (α, *o*, *m*, *p*, *m'*, *o'*) at the vertices and labelled with their original positions, and the unique C^1 in the center (Fig. 2). The allowed labelling for the six phenylmethylenes interconverted by the Baron mechanism can be generated from this mnemonic by the graphical operation of extrusion of a vertex by C^1. The six cycloheptatrienylidenes that occur as postulated intermediates in the Baron mechanism can be generated by inserting C^1 between each pair of adjacent vertices.

Tests of mechanism and further postulates

An early indication of the validity of this scheme, at least for the interconversion of phenylmethylenes, came in the work of Myers *et al.* who proposed a similar mechanism to solve a mystery then 57 years old: how is diphenylmethylene converted into fluorene?[9] Staudinger and Endle had obtained fluorene from gas-phase pyrolysis of diphenylketene in 1913 and suggested that diphenylmethylene was an intermediate and underwent H-migration.[10] Rice and Michaelson obtained the same result from diphenyldiazomethane.[11]



Myers *et al.* pointed out that H-migration would require that *p*-tolylphenyldiazomethane be transformed into 3-methylfluorene while a multiple carbene-to-carbene rearrangement sequence would yield 2-methylfluorene.[9]

That a 7-membered cyclic intermediate presumed to be phenylcycloheptatrienylidene (see below) was involved in the rearrangement of diphenylmethylene to fluorene was suggested by the formation of fluorene from pyrolysis of the sodium salt of the tosylhydrazone of 2-phenyltropone, and also by formation of products containing 7-membered rings from unsubstituted diphenylmethylene.[9]

The latter two products were ascribed to carbene–carbene combination reactions. Wentrup and Wilczek also pointed to carbene dimerization products as evidence for reversible phenylmethylene–cycloheptatrienylidene interconversion.[12] They found *cis*- and *trans*-stilbene and heptafulvalene as products from

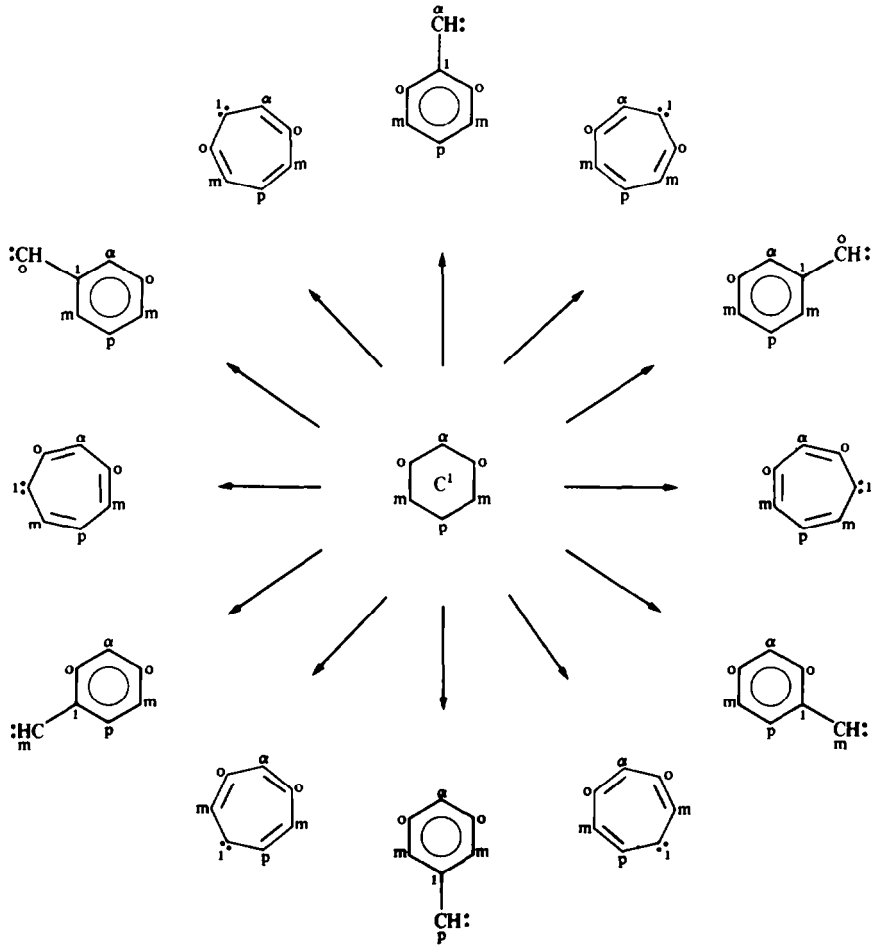
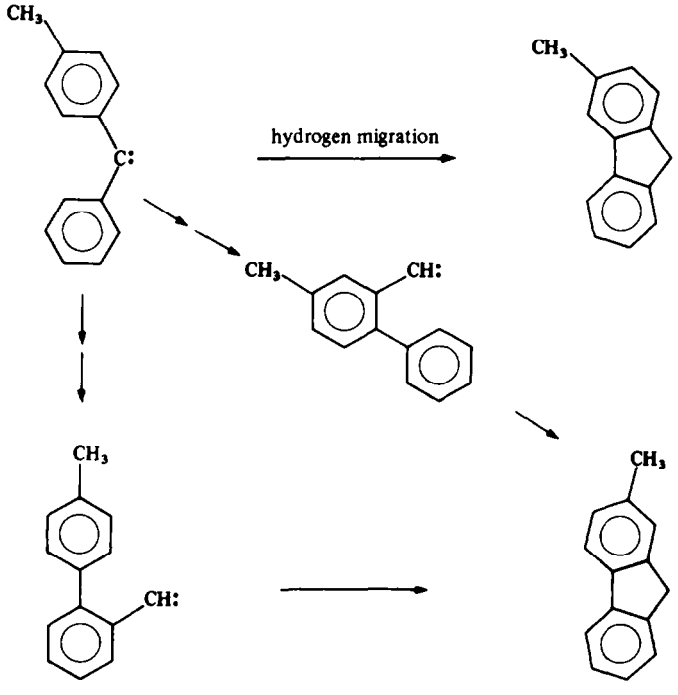
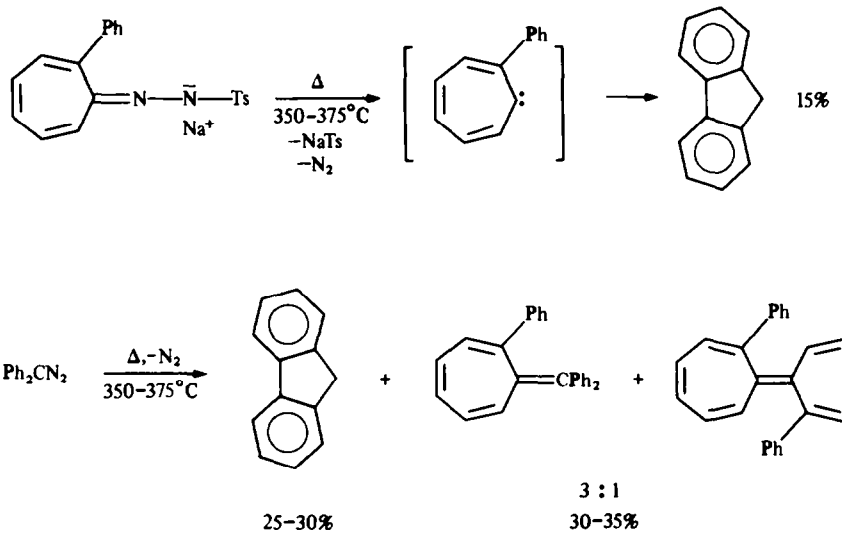
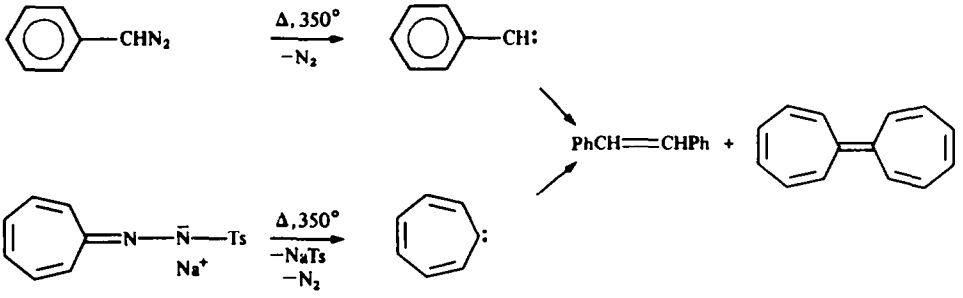


Fig. 2. The hexagon mnemonic for the labelling pattern predicted by the Baron mechanism. The vertices of the central hexagon represent the CH groups of the initially generated phenylmethylene shown at 12 o'clock. The Baron mechanism predicts that the cyclic order of these groups will be maintained and that rearrangement will lead to the six phenylmethylenes generated by the graphic device of displacing one of the vertices by the central carbon C^1 that represents the ipso carbon of each phenylmethylene. The mechanism also predicts that any cycloheptatrienylidene or cyclohepta-1,2,4,6-tetraene (not shown) intermediates will have a structure graphically generated by inserting C^1 between any two adjacent vertices of the central hexagon (see ref. 5).



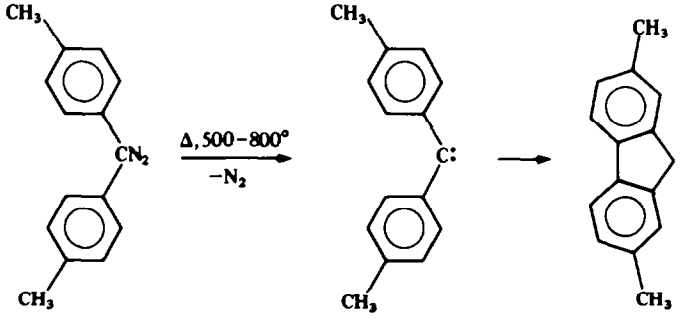


gas phase pyrolysis of both phenyldiazomethane and the sodium salt of tropone tosylhydrazone.



In an experiment similar to that of Myers *et al.*, the generation of *p,p'*-ditolylmethylene in the gas phase was found to give a 75% yield of 2,7-dimethylfluorene and thus lend support to a phenylmethylene-to-phenylmethylene interconversion formulated as occuring via cycloheptatrienylidene intermediates.

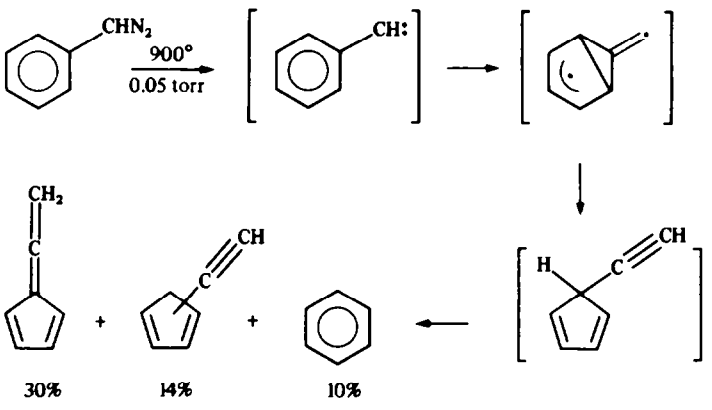
As Fig. 3 indicates, a mechanism can be written in which the vinylidene moiety undergoes a "walk" around a 5-membered ring, thus interconverting *p*-, *m*- and *o*-tolylmethylene. Simple intramolecular carbenic C—H insertion would give benzocyclobutene in which the original divalent carbon atom would be in one of the CH_2 groups. Further conversion of the *o*-tolylmethylene into styrene by the Baron mechanism would



The most direct test of the interconversion of the phenylmethylenes depicted in Fig. 2 was a labelling experiment carried out by Hedaya and Kent.[13] A bicyclic diradical had previously been proposed to account for the ring *contraction* of phenylmethylene to fulvenallene and vinylcyclopentadiene.[2] The ring contraction reactions of phenylmethylene have continued to receive attention.[14]

incorporate the original divalent carbon into a styrene *ortho*-position, while an insertion (considered by Hedaya!) into a C—C bond followed by ring opening and H-migration would give styrene labelled in the vinyl group. In the event, the label was found in the 4-position of benzocyclobutene and the *para*-position of styrene, just as predicted by the Baron mechanism.

Another pathway for the isomerization of *o*-



tolylmethylene to styrene which is consistent with Hedaya's labelling results was proposed by Vander Stouw *et al.* as a possible alternative to the Baron mechanism.[15] It is shown in Fig. 4. We see that the D-label employed does not distinguish the formation of styrene via a C—H insertion by the divalent C of 2-methylcycloheptatrienylidene into a methyl C—H bond followed by C—C valence tautomerism, from the H-shift in α-methylphenylmethylene proposed by Baron *et al.* In both reaction schemes the D ends up in an *ortho*-position of styrene. It is only in the permutation of one of the *ortho* carbons and the 1-

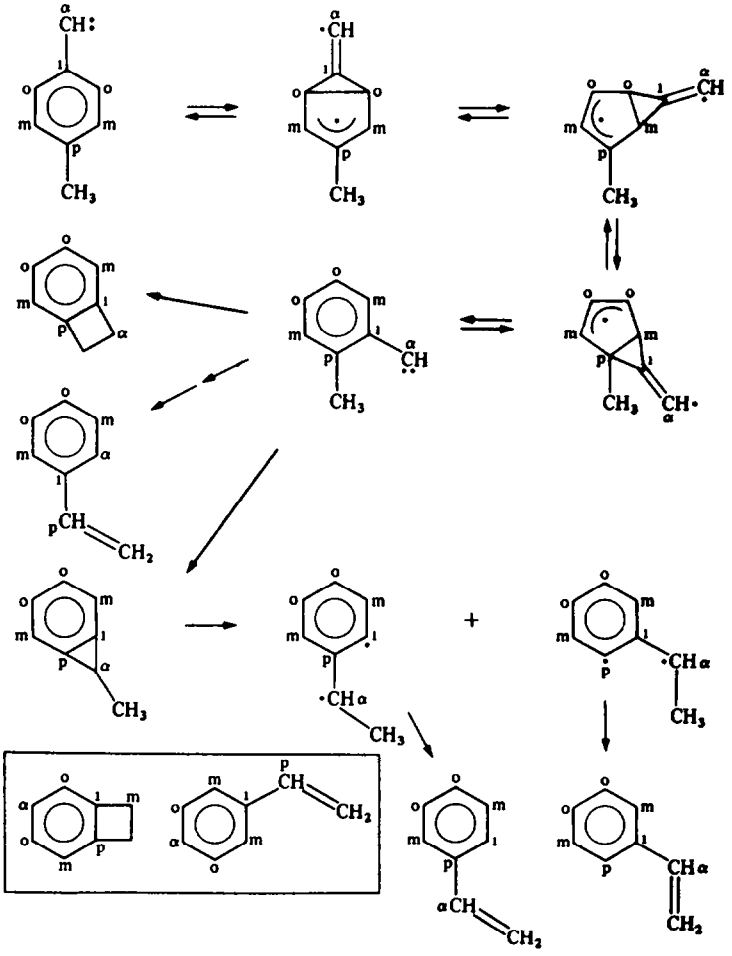


Fig. 3. The Hedaya–Kent mechanism (ref. 13) for the conversion of *p*-tolylmethylene to benzocyclobutene and styrene. The labels designate the positions of the initial *p*-tolylmethylene. Shown within the box is the labelling pattern predicted by the Baron mechanism.

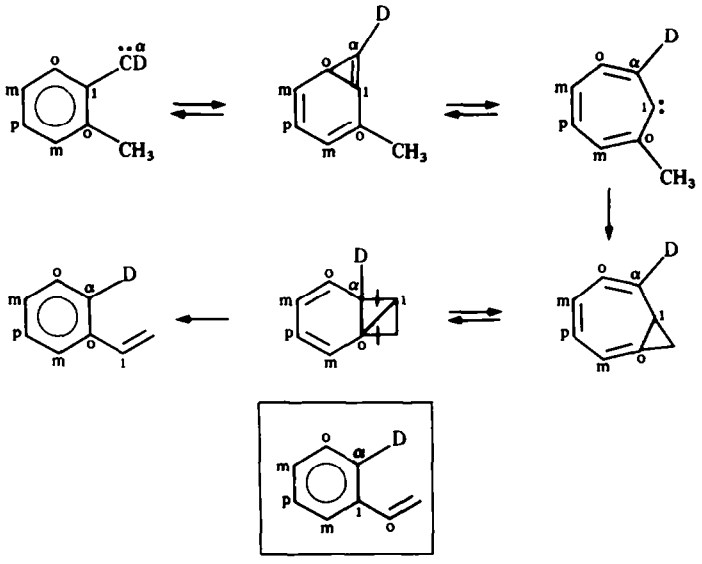


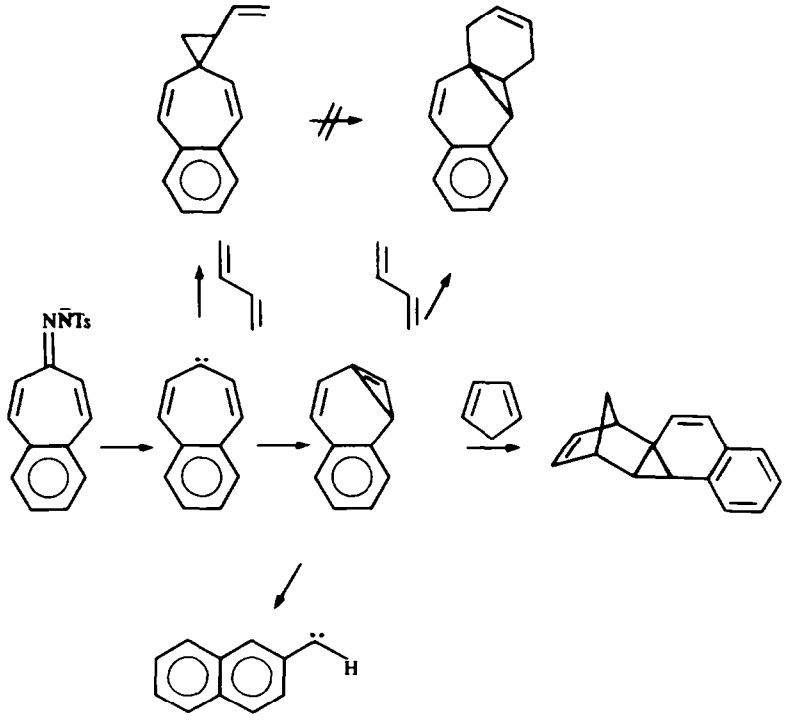
Fig. 4. The Vander Stouw–Kraska–Shechter mechanism (ref. 15) for the conversion of α-D-*o*-tolylmethylene to styrene. Shown within the box is the labelling pattern predicted by the Baron mechanism.

carbon of the *o*-tolylmethylene that the two mechanisms differ. Below we shall report a fair test of these two mechanistic possibilities.

Second thoughts about the vinylmethylene–cyclopropene mechanism for the phenylcarbene rearrangement

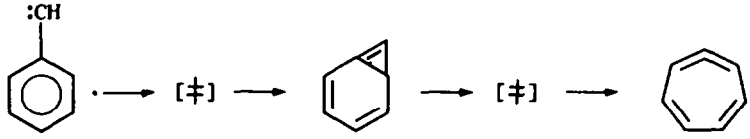
While the Baron mechanism has been described as recently as 1980 as being "generally accepted",[3a] in several aspects it has been justifiably criticized. In 1974 Wentrup estimated a value of $\geqslant 128$ kcal/mole for the heat of formation of the bicycloheptatriene intermediate, considerably higher than the *ca* 102 kcal/mole for phenylmethylene and *ca* 115 kcal/mole for cycloheptatrienylidene likewise estimated by the group additivity method.[16] At that time Wentrup stated of the bicycloheptatrienes: "There is no experimental fact that requires their existence".

In the same year however, Coburn and Jones trapped a substituted bicycloheptatriene formed from a benzocycloheptatrienylidene in competition with carbenic addition to butadiene and ring contraction to β-naphthylmethylene.[17] Jones inferred that the bicycloheptatriene is *lower* in energy than both phenylmethylene and cycloheptatrienylidene.[18]



Semiempirical calculations of the INDO type place cycloheptatrienylidene 7.8 kcal/mole lower in energy than phenylmethylene, and cyclohepta-1,2,4,6-tetraene, the cyclic allene valence isomer of cycloheptatrienylidene, 21.6 kcal lower than phenylmethylene.[19] Wentrup *et al.* had employed a CNDO/2 calculation and found phenylmethylene 11.6 kcal/mole more stable than cycloheptatrienylidene, and an extended Hückel treatment gave the same stability order with a larger energy difference of 16.4 kcal/mole.[20]

Dewar and Landman performed MINDO/3 calculations on the rearrangement of phenylmethylene to cycloheptatrienylidene and found that in the singlet manifold there is a decrease in energy from phenylmethylene (ΔH_f = 113.8 kcal/mole) to bicycloheptatriene (ΔH_f = 100.7 kcal/mole) to "cycloheptatrienylidene" (ΔH_f = 87.0 kcal/mole), but the calculation indicated that the 7-membered ring should be described as the 1,2,4,6-cycloheptatetraene.[21] The calculated activation barriers were 6.3 and 5.8 kcal/mole.



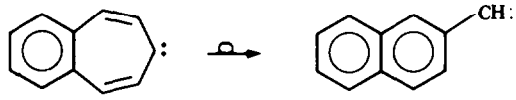
For both phenylmethylene and cycloheptatrienylidene a considerably lower degree of electron delocalization was found than in the corresponding benzyl and tropylium cations, because in the former charge separation accompanies delocalization.

The tendency for MINDO/3 to overestimate the stability of 3-membered rings led Dewar to suggest that conversion of phenylmethylene to bicycloheptatriene might be nearly thermoneutral rather than 13 kcal/mole exothermic as calculated. Thus in the rearrangement of phenylmethylene to cycloheptatrienylidene via the bicycloheptatriene the transition state for the overall conversion was believed to resemble that for the first step.

In the triplet manifold the exothermicity for isomerization of phenylmethylene to cycloheptatrienylidene was predicted to be much less (*ca* 8 kcal/mole) than in the singlet state reaction (26.5 kcal/mole), but for the triplet reaction a much larger barrier (ΔH_f° (‡) $\geq$ 120 kcal/mole, $E_a \geq$ 28.5 kcal/mole) was calculated.

An *ab initio* calculation by Radom *et al.* predicted that a nonplanar cycloheptatetraene is 17.9 kcal/mole more stable than planar cycloheptatrienylidene and 80.6 kcal/mole more stable than *planar* cycloheptatetraene, these values resulting from use of a minimal STO-3G basis set.[22] Energy optimization at the STO-3G geometry with a 4-31G basis altered these energy differences to 15.8 and 89.5 kcal/mole respectively. Singlet phenylmethylene and singlet cycloheptatrienylidene were predicted to be nearly isoenergetic (ΔE = 0.0008 au $\simeq$ 0.5 kcal/mole). Singlet and triplet phenylmethylene were also found to have nearly equal energies, but triplet cycloheptatrienylidene was indicated as lying 5 to 30 kcal/mole above the other species.

Krajca and Jones have presented evidence that in the rearrangement of benzocycloheptatrienylidene to 2-naphthylmethylene the naphthylcarbene is *formed* in



the singlet state.[23] They found that the stereospecifity of addition of the 2-naphthylmethylene to *cis*-2-butene increases with the concentration of added butadiene, which can compete with the olefin and with intersystem crossing for the triplet naphthylcarbene.

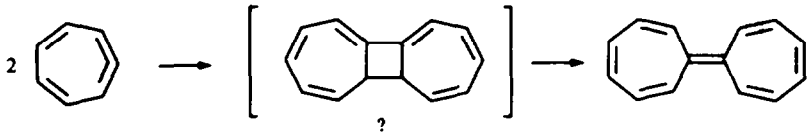
The role of 1,2,4,6-*cycloheptatetraene in the phenylcarbene rearrangement*

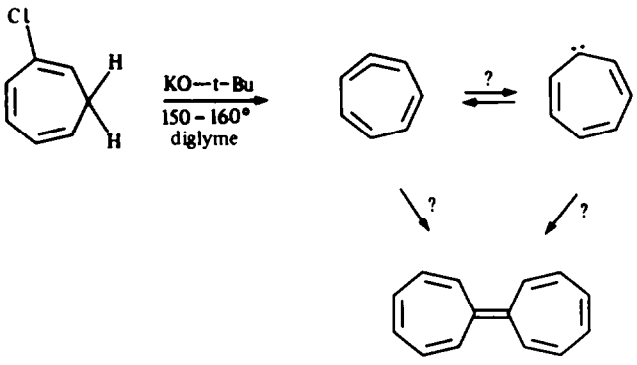
The role of the cyclic allene 1,2,4,6-cycloheptatetraene in the phenylcarbene rearrangement has received considerable attention recently. It was mentioned as a possible precursor of heptafulvalene by Jones in 1969,[1] and its dimerization would explain why the initial condensate from flow pyrolysis of benzaldehyde tosylhydrazone sodium salt was described as "light colored" and only turned to the black color of heptafulvalene on warming from the temperature of liquid nitrogen.

Heptafulvalene is obtained when 2-chlorocycloheptatriene is dehydrochlorinated, a process presumed to yield the cycloheptatetraene.[24,25] While the heptafulvalene may be formed via cycloheptatrienylidene it may also arise via the allene dimerization depicted above.

Although cycloheptatrienylidene is apparently trapped by addition to styrene in the thermolysis and photolysis of tropone tosylhydrazone sodium salt,[26] it is the cycloheptatetraene isomer that seems to be trapped by 1,2-diphenylbenzo[*c*]-furan, and anthracene.[27]

Saito *et al.* recognized that these adducts need *not* be





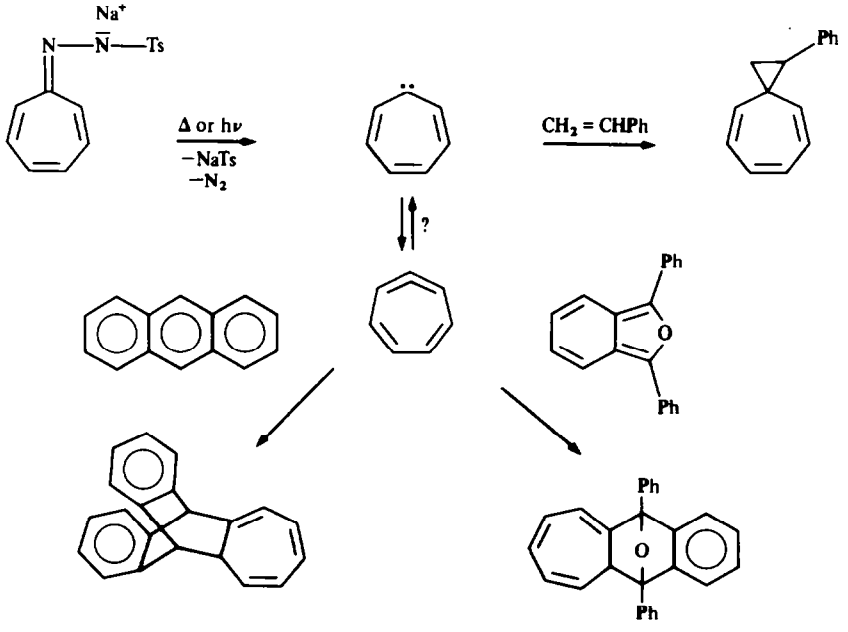
formed in concerted reactions and hence might not arise from the allene isomer, although this pathway seemed more likely.[27]

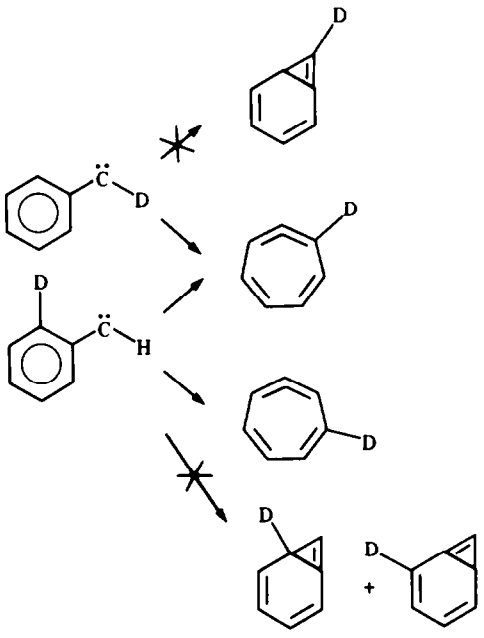
Harris and Jones have obtained optically active adducts from the dehydrohalogenation of bromocycloheptatrienes with an optically active base, and from optically active bromocycloheptatriene by dehydrohalogenation with an optically inactive base in the presence of diphenylisobenzofuran.[28] Since the allene is expected to be nonplanar and chiral and the carbene planar and achiral, this was strong evidence for addition of the cycloheptatetraene to the diphenylisobenzofuran in a Diels–Alder reaction. The styrene adduct, however, was found to be optically inactive, and this provided some evidence that it is formed from the carbene.

Kirmse has found that both the tropone tosylhydrazone decomposition and the halotropylidene dehydrohalogenation lead to intermediates whose reactions with methanol yield carbene rather than allene products.[29] Since Mayor and Jones had already demonstrated that the dehydrohalogenation gives the allene *directly*,[24] these findings suggest that the allene can be transformed to the carbene.

The detection of 1,2,4,6-cycloheptatetraene in a matrix isolation experiment has been reported by West *et al.*[30] Photolysis of phenyldiazomethane matrix-isolated in argon at 10 K with light of $\lambda > 478$ nm gave phenylmethylene, identified by conversion into phenylketene upon softening of an argon matrix doped with carbon monoxide. Further irradiation of phenylmethylene with radiation of $\lambda > 416$ nm led to its conversion into a new species also obtained from irradiation of phenyldiazirine in argon at 10 K and from matrix isolation of the 500° pyrolysis products of phenyldiazomethane. This new species does *not* produce a ketene on reaction with carbon monoxide and on this basis a cycloheptatrienylidene structure was considered unlikely. The bicycloheptatriene structure was excluded on the basis of its IR spectrum. Formation of the allene 1,2,4,6-cycloheptatetraene was presumed from the weak allene bands observed in the infrared spectrum and from the formation of a common product from rearrangement of α-deuteriophenylmethylene and *ortho*-deuteriophenylmethylene as observed in the IR spectrum.

It should be noted that no common intermediate would arise upon formation of bicycloheptatriene.





The problem

With this background we can now examine those aspects of the phenylcarbene rearrangement to which this research is addressed.

1. There is a significantly *different* ratio of benzocyclobutene to styrene formed from *o*-tolylmethylene on the one hand and the *m*- and *p*-isomers on the other.[3b,5] Under similar conditions the *o*-tolylmethylene gives nearly three times as much benzocyclobutene as styrene, while from the *m*- and *p*-tolylmethylenes the ratio is approximately 0.8.

The Baron mechanism, which became generally accepted on the basis of Hedaya's labelling experiment,[13] requires that the *m*- and *p*-tolylmethylenes rearrange to the *o*-tolylmethylene before any products are formed. Since the *o*-tolylmethylene is thus postulated to be a common intermediate that precedes the formation of benzocyclobutene and styrene from all three tolylmethylenes, the ratio of these products should be the same for each of the tolylmethylenes.

Modification of the Baron mechanism by replacement of the bicycloheptatriene and cycloheptatrienylidene intermediates by cycloheptatetraenes (Fig. 5), thus making the interconversion of isomeric tolylmethylene a reversible vinylmethylene-to-allene Wolff rearrangement, does not solve this problem.

Here too the *o*-tolylmethylene is a common intermediate in the formation of benzocyclobutene and styrene from the *m*- and *p*-tolylmethylenes, and hence the product ratio should be the same whether one enters the reaction sequence at the *o*-tolylmethylene or at its *m*- or *p*-isomers.

α-Methylphenylmethylene gives only styrene when generated from methylphenyldiazomethane, and the final step in the formation of styrene can be regarded as being irreversible.

Baron *et al.* had suggested the possibility that the larger yield of benzocyclobutene from *o*-tolylmethylene might be due to its formation in a geometry especially favorable for insertion of the carbene center

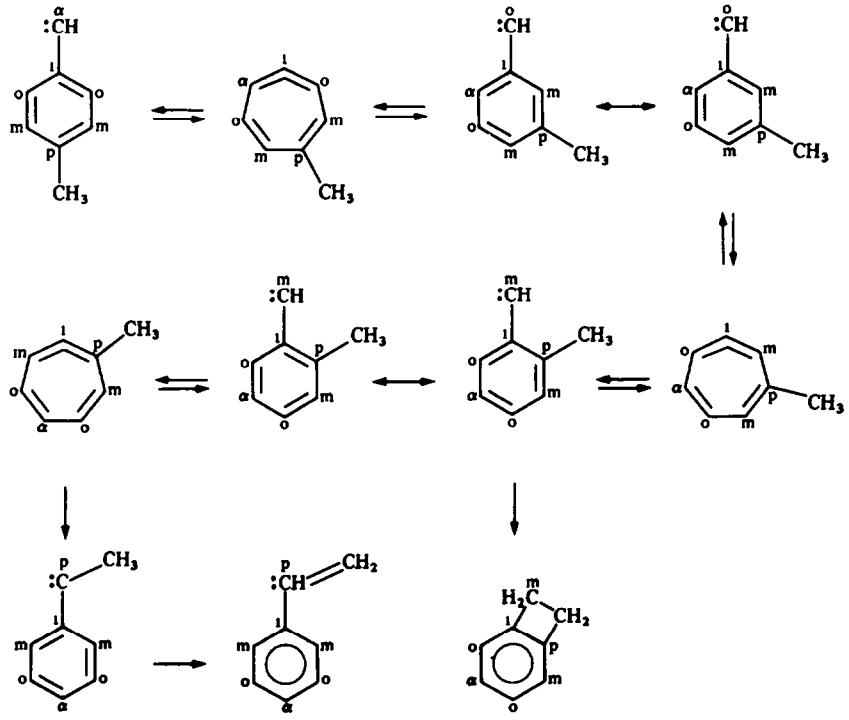


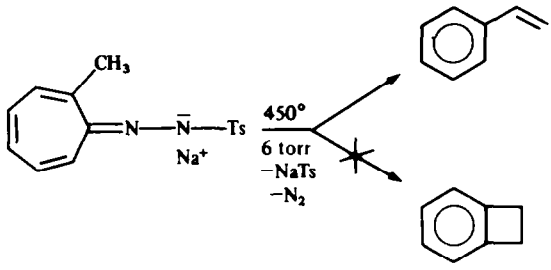
Fig. 5. The Baron mechanism for the conversion of *p*-tolylmethylene to benzocyclobutene and styrene, modified by replacement of the bicycloheptatriene and cycloheptatrienylidene intermediates by cyclohepta-1,2,4,6-tetraenes. The labelling pattern of the isomeric phenylmethylenes and of the stable products is unaffected by this alteration. The labels designate the positions of the initial *p*-tolylmethylene.

into the neighboring methyl group.[5] Gleiter *et al.* have provided a dynamic explanation,[31] but neither of these *ad hoc* devices is very convincing.

The latter workers carried out extended Hückel and CNDO/2 calculations on the ring expansion of phenylnitrene and extended their results to the phenylmethylene ring expansion. They pointed out that when formed by rearrangement from *m*- and *p*-tolylmethylene, the divalent carbon of *o*-tolylmethylene would be out of plane and moving *away* from the methyl with which it must react to form benzocyclobutane. Hence it has a good chance to rearrange further to styrene. When formed *directly*, however, the *o*-tolylmethylene is not dynamically biased against benzocyclobutene formation.

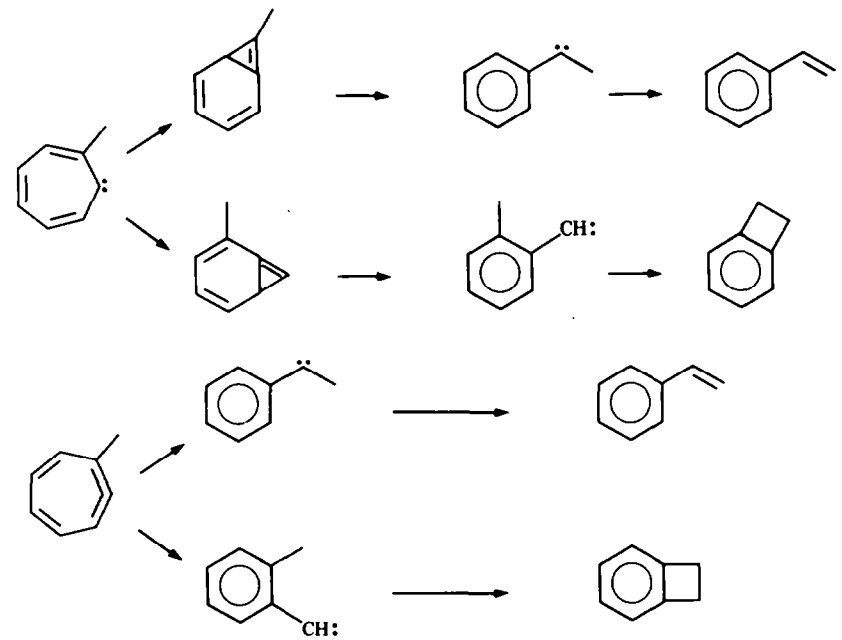
2. A second question for which no satisfactory answer has yet been found is why does the generation of 2-methylcyclohepta-2,4,6-trien-1-ylidene lead to the formation of styrene but apparently no benzocyclobutene.[32]

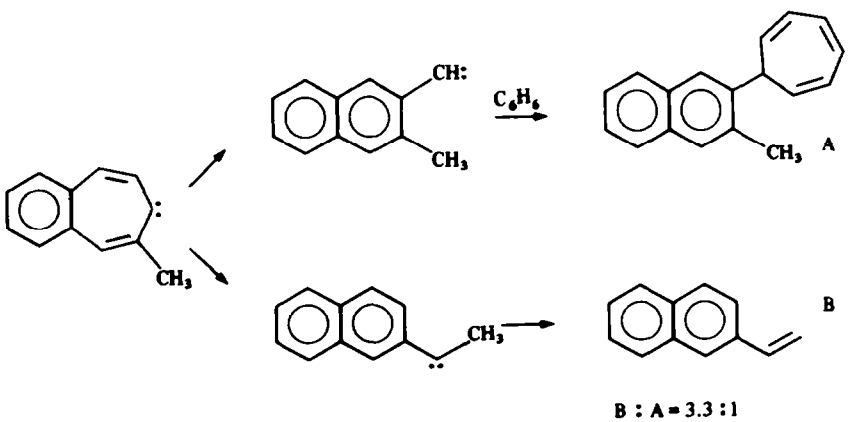
According to either the original Baron mechanism or the version shown above (Fig. 5) incorporating cycloheptatetraene intermediates, both products should be formed unless there is an irreversible step leading to the formation of methylphenylmethylene, or a



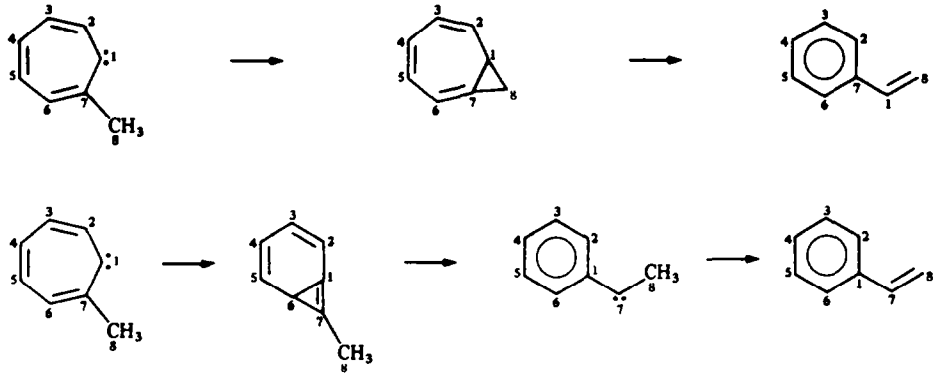
significant perturbation by a Me group of the reactivity of an adjacent double bond.

In the rearrangement of an annelated 2-methyl-4,5-benzocycloheptа-2,4,6-trien-1-ylidene the methyl group did affect the direction of rearrangement, a 3.3 : 1 product ratio having been obtained.[32]





3. A related, or presumably related question is the mechanism of styrene formation. We have seen that two different pathways have been proposed. Vander Stouw and Shechter have suggested that 2-methylcycloheptatrienylidene can undergo a C—H insertion and reorganization to styrene, while the Baron mechanism postulates a methylphenylmethylene intermediate. These paths differ in a single permutation of C atoms: mnemonic devised by Baron *et al.* to keep track of the permutation of atoms in their postulated rearrangement pathway takes on life as a real if evanescent molecule, a kind of carbon atom–toluene complex. One can write a mechanism in which this complex can reform a phenylmethylene by the now physical (rather than graphical) extrusion of one of the ring C atoms.[33]



RESULTS AND DISCUSSION

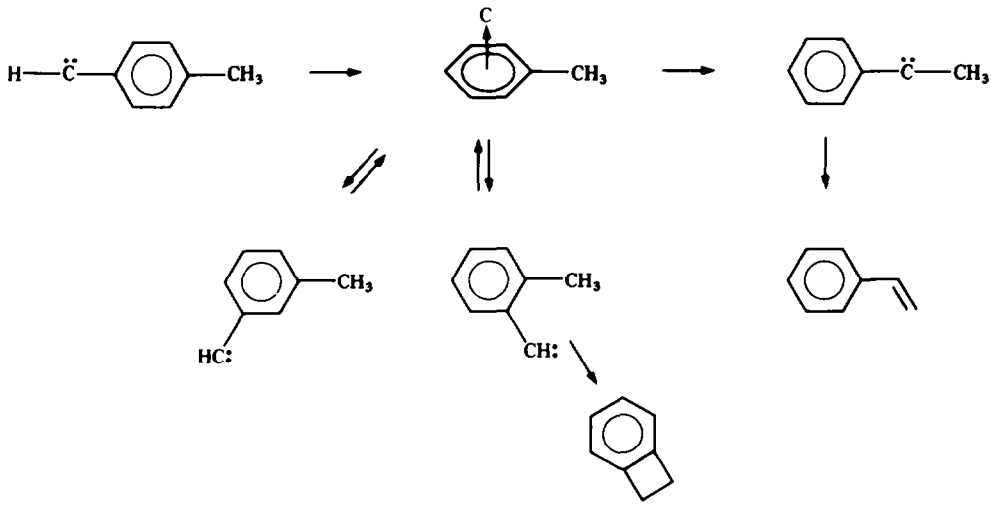
It is clear that to accommodate the formation of different ratios of benzocyclobutene and styrene from the rearrangements of *m*- and *p*-tolylmethylene on the one hand, and *o*-tolylmethylene on the other, a common intermediate must be avoided. That is, *m*- and *p*-tolylmethylene must rearrange to the immediate precursor of styrene by a pathway that can at least partially bypass *o*-tolylmethylene. This was accomplished in a dynamical sense by Wentrup's suggestion that when *o*-tolylmethylene is formed by rearrangement of *m*-tolylmethylene it is predisposed to further rearrangement.[31] This is not entirely satisfactory in that this dynamic memory suggests that the *o*-tolylmethylene has no time to exchange momentum with other molecules before it rearranges further and is therefore not a true intermediate.

More appealing is a mechanism in which styrene can be formed from *m*- and *p*-tolylmethylene without the necessary intermediacy of *o*-tolylmethylene. The simplest such mechanism is one in which the hexagon

In this reaction scheme the interconversion of *p*- and *o*-tolylmethylene is shortened to two steps and would account for the different product ratio from *p*- and *o*-tolylmethylenes, since this mechanism provides a pathway for styrene formation from *p*-tolylmethylene that does *not* pass through the *o*-tolylmethylene, which is formed in parallel with the α-methylphenylmethylene.

This mechanism has been tested by generation of 3,5-dimethylphenylmethylene. The mechanism with an intermediate (C atom)–(benzene ring) complex predicts the formation of 3-methylbenzocyclobutene as a major product along with 4-methylbenzocyclobutene and 3-methylstyrene; see Fig. 6.

The Baron mechanism on the other hand, presented in Fig. 7 in streamlined form with cycloheptatetraene intermediates, predicts that *no* 3-methylbenzocyclobutene will be formed since an α-methylphenylmethylene intervenes, and it should be quantitatively diverted to a styrene.



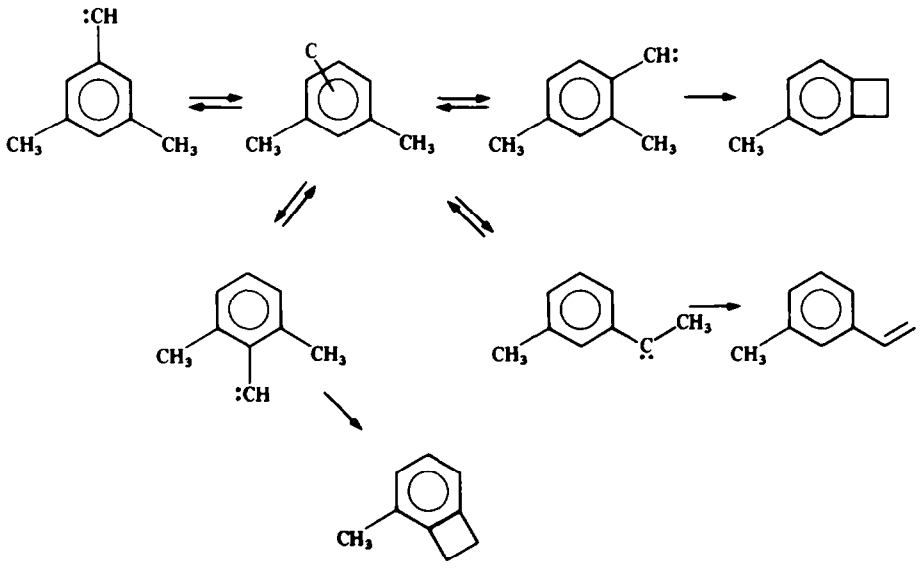


Fig. 6. A mechanism for the interconversion of isomeric xylylmethylenes in which a C atom–xylene complex is the only species that intervenes between the xylylmethylenes. It is a critical feature of this mechanism that 2,6-dimethylphenylmethylene is formed in parallel with α-methyl(*m*-tolyl)methylene.

In the event, none of the 3-methylbenzocyclobutene was obtained upon gas-phase pyrolysis of 3,5-dimethylphenyldiazomethane, the major products being the 4-methylbenzocyclobutene and 3-methylstyrene predicted by the Baron mechanism (Fig. 8).

While a loosely bound (C atom)–(xylene) complex seems ruled out as an important intermediate, a related mechanism in which a C atom is more tightly held in the form of a norcaradienylidene seems capable of explaining the absence of the 3-methylbenzocyclobutene product and yet accounting for the different benzocyclobutene–styrene product ratio from the isomeric tolylmethylenes.

The norcaradienylidene walk mechanism shown in Fig. 9 permits the formation of styrene starting from *p*- and *m*-tolylmethylene without necessarily passing through the *o*-tolylmethylene, although the latter species can be formed in a parallel process permitting

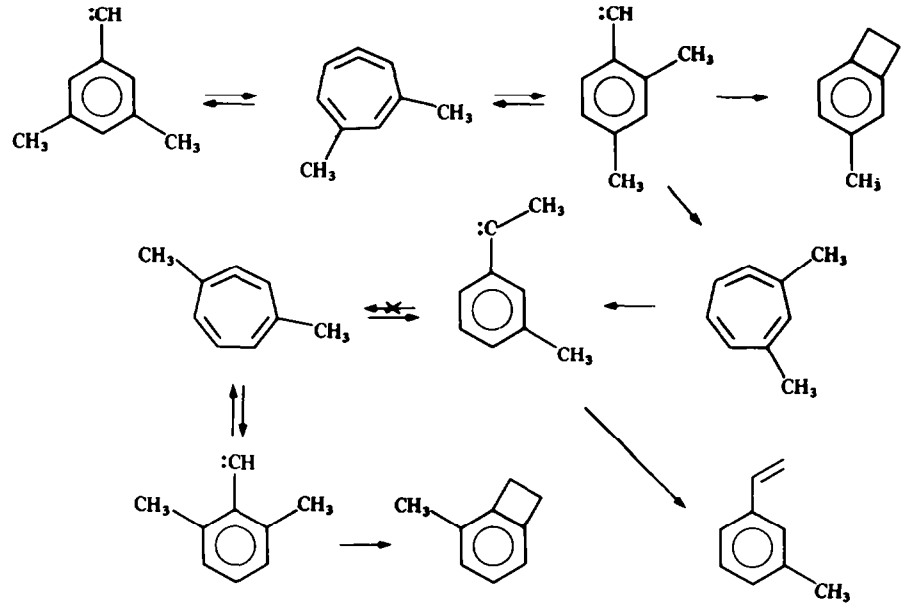
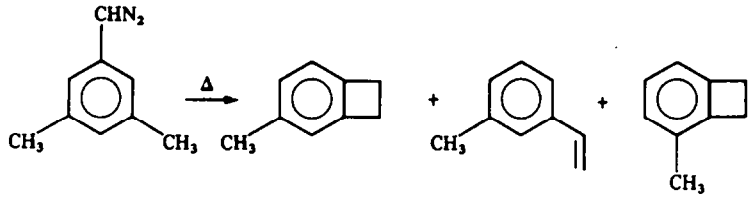


Fig. 7. A "modified Baron" mechanism for the rearrangement of 3,5-dimethylphenylmethylene. Here the isomeric dimethylphenylmethylenes are formed serially and no 2,6-dimethylphenylmethylene is expected to be formed via this mechanism, since its precursor α-methyl(*m*-tolylmethylene) should undergo rapid hydrogen migration, converting it irreversibly to 3-methylstyrene.



350°C	10%	12%	< 0.01%
475°C	24%	30%	< 0.01%
600°C	27%	40%	< 0.02%

Fig. 8. Product yields from the vacuum flow pyrolysis of 3,5-dimethylphenyldiazomethane at 350, 475 and 600°.

the formation of benzocyclobutene. A closer look at this mechanism reveals that it is capable of explaining why an extremely low yield of 3-methylbenzocyclobutene might be formed from 3,5-dimethylphenylmethylene. This is because the norcaradienylidene walk mechanism also presents opportunities for the diversion of intermediates on the way to 3-methylbenzocyclobutene (Fig. 10). Here the original Baron form of the phenylmethylene–cycloheptatrienylidene interconversion mechanism is drawn, but the same predictions would flow from (and same number of steps drawn for) a scheme in which a 1,2,4,6-cycloheptatetraene replaces each bicycloheptatriene intermediate.[36]

We see a norcaradienylidene W formed on the way to 3-methylbenzocyclobutene that must be presumed to be in equilibrium with a cycloheptatrienylidene X that contains a Me group α to the divalent C atom. We have already seen that Jones *et al.* reported that 2-methylcyclohepta-2,4,6-trien-1-ylidene gives only styrene and no benzocyclobutene rearrangement product.[32] Hence we would expect from this mechanism that most of W would be diverted to 3-methylstyrene.

Even if a fraction of W continues the norcaradienylidene walk to Y, the particular norcaradienylidene required as a precursor for 3-methylbenzocyclobutene, it too should be in equilibrium with a cycloheptatrienylidene Z that also contains an Me group adjacent to the divalent C and should therefore be diverted predominantly to the styrene.

Thus this mechanism suggests that the formation of a product *not* predicted by the Baron mechanism requires that *two* favorable detours be avoided. This number can be reduced to one by placement of an additional Me group on the rearranging carbene. We therefore studied the rearrangement of 3,4,5-trimethylphenylmethylene, for which a norcaradienylidene walk

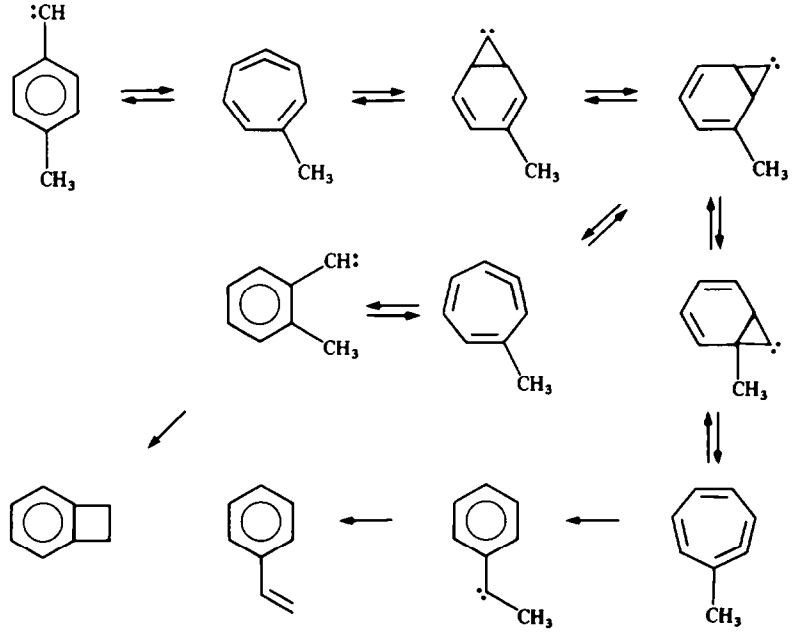


Fig. 9. A "norcaradienylidene walk" mechanism for the conversion of *p*-tolylmethylene to benzocyclobutene and styrene. A critical feature of this mechanism is that styrene formation does not *require* the prior formation of *o*-tolylmethylene. While cycloheptatetraenes are drawn as intermediates, their replacement by cycloheptatrienylidenes and bicycloheptatrienes would leave this important feature intact.

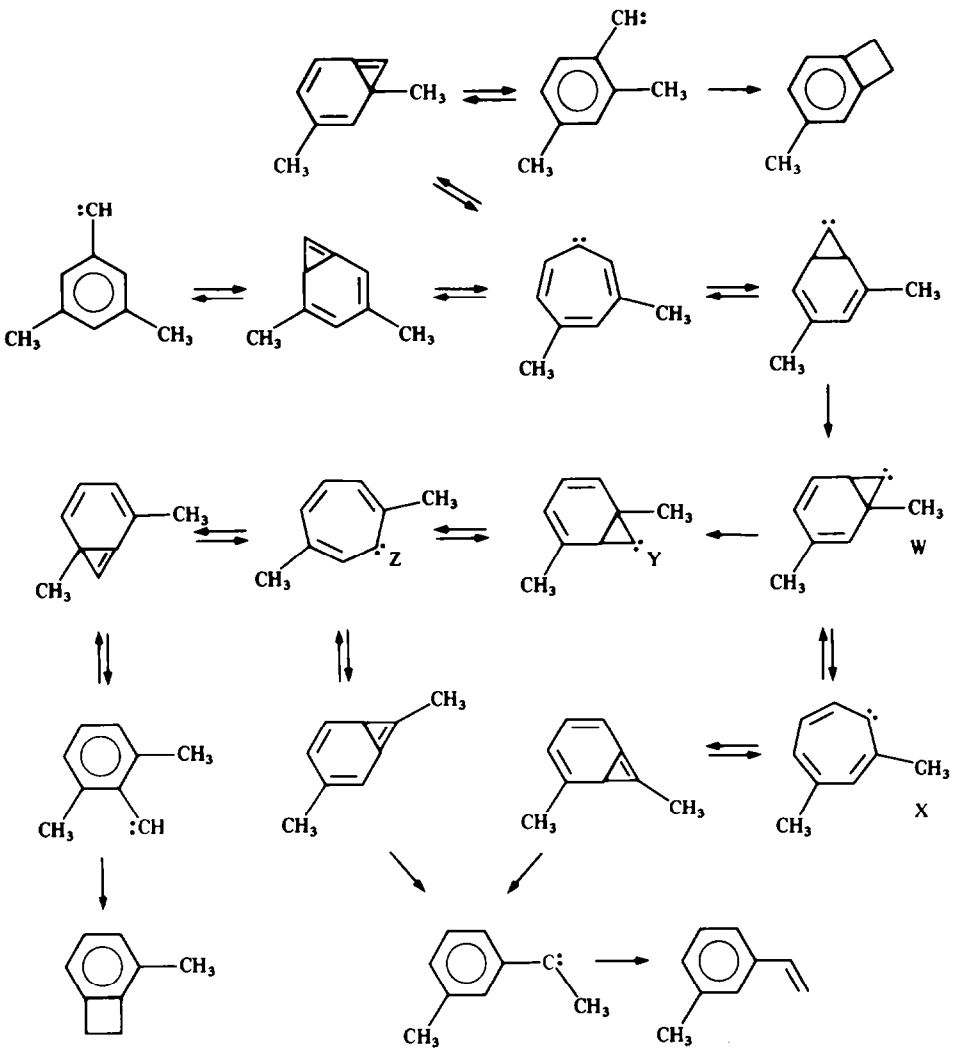


Fig. 10. A "norcaradienylidene walk" mechanism for the rearrangement of 3,5-dimethylphenylmethylene. Norcaradienylidenes W and Y are expected to be largely diverted to 3-methylstyrene via cycloheptatrienylidenes X and Z or their cycloheptatetraene tautomers (not shown).

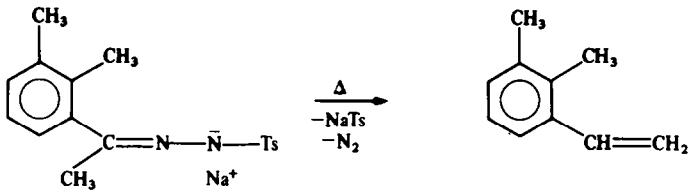
mechanism is shown in Fig. 11. Here cycloheptatetraene intermediates are drawn in place of the bicycloheptatrienes of Fig. 10, but this does not affect the outcome.

The product whose formation is not expected if the Baron mechanism is followed but *is* predicted by this norcaradienylidene walk mechanism is 2,6-dimethylstyrene M. Here too an intermediate norcaradienylidene K is formed whose partial diversion to the 2,3-dimethylstyrene N, predicted by the Baron mechanism to be along with 3,4-dimethylbenzocyclobutene a major product, is expected. The ultimate cycloheptatetraene precursor of 2,6-dimethylstyrene, L, can also yield 2,3-dimethylstyrene. Since it possesses an Me group on both ends of the allene, however, it seemed to have a fighting chance to yield at least some of the revealing product.

Figure 12 displays the predictions of the Baron mechanism: 3,4-dimethylbenzocyclobutene and 2,3-dimethylstyrene are predicted as the rearrangement products of 3,4,5-trimethylphenylmethylene. *No* 2,6-dimethylstyrene is predicted because 2,3-dimethylphenyl(α-methyl)methylene is expected to be transformed quantitatively into 2,3-dimethylstyrene rather than rearranging to 2,6-dimethylphenyl-α-methylmethylene, the precursor of 2,6-dimethylstyrene. To test this prediction 2,3-dimethylphenyl(α-methyl)-methylene was generated by pyrolysis of the tosylhydrazone sodium salt of 2,3-dimethylacetophenone. No 2,6-dimethylstyrene was detected under conditions whereby its presence in a ratio of 1 : 1000 to 2,3-dimethylstyrene could easily be found.

When 3,4,5-trimethylphenyldiazomethane was subjected to gas-phase pyrolysis a small amount of 2,6-dimethylstyrene *is* formed in addition to the major products 3,4-dimethylbenzocyclobutene and 2,3-dimethylstyrene. Product yields from pyrolyses at three temperatures and the results of control experiments are shown in Fig. 13.

While the yield of 2,6-dimethylstyrene is very small,



we are convinced it is real and comes from isomerization of the initially formed 3,4,5-trimethylphenylmethylene. We believe that its formation cannot be explained by a mechanism that *sequentially* interconverts phenylmethylene positional isomers. It *can* be explained by a mechanism that can bypass any of the phenylmethylenes, yet allow their formation as *side-products* as does the norcaradienylidene walk. In this mechanism the norcaradienylidenes whose interconversion allows particular methylphenylmethylenes to be bypassed are always just one step away from a cycloheptatrienylidene or cycloheptatetraene, and this mechanistic proximity led to the prediction that only a small amount of 2,6-dimethylstyrene would be formed.

Indeed the low yield of 2,6-dimethylstyrene from 3,4,5-trimethylphenylmethylene and the failure to observe 3-methylbenzocyclobutene as a product from 3,5-dimethylphenylmethylene permit a choice to be made between a norcaradienylidene walk and a related reaction involving a norbornadienylidene intermediate.

One can formulate the interconversion of the phenylmethylenes in terms of a reversible norcaradienylidene–norbornadienylidene transformation.

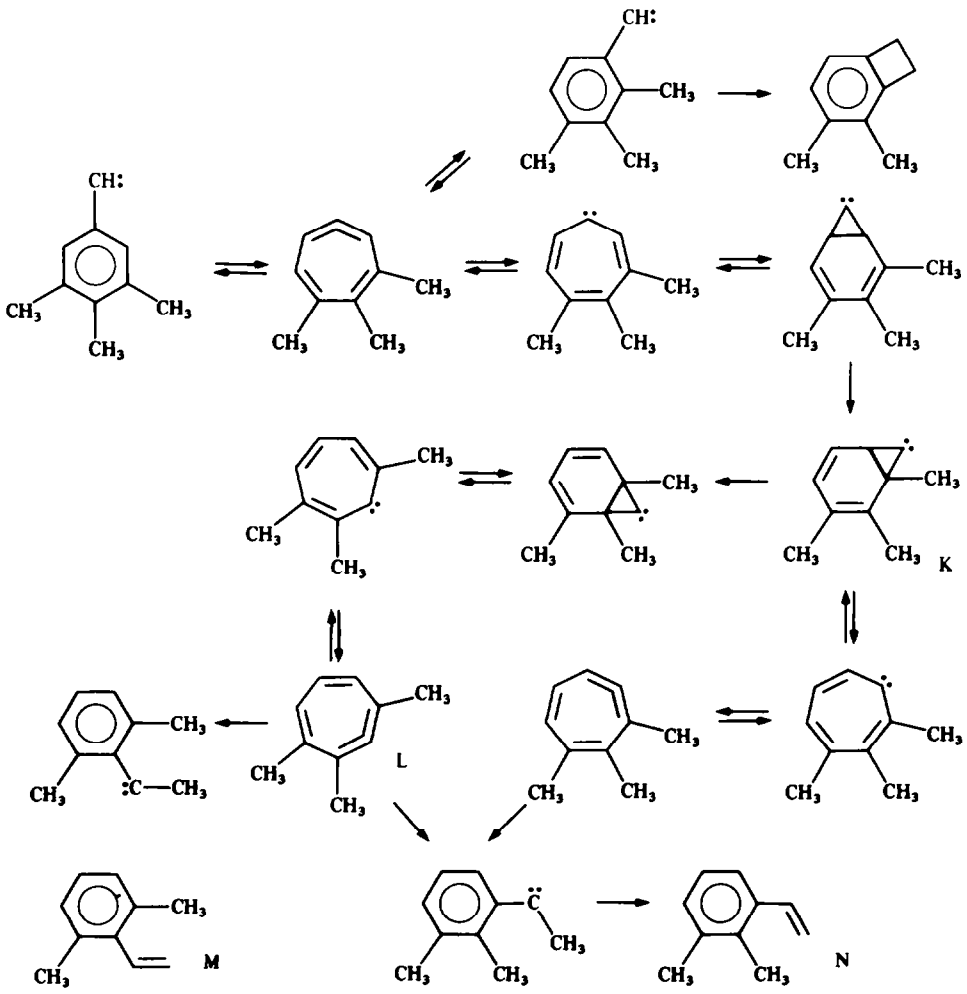


Fig. 11. A "norcaradienylidene walk" mechanism for the rearrangement of 3,4,5-trimethylphenylmethylene. While norcaradienylidene K is expected to be partially diverted to 2,3-dimethylstyrene N, some further rearrangement is likely to reach a cycloheptatrienylidene or its cycloheptatetraene tautomer L that can form either 2,6- or 2,3-dimethylstyrene (M and N respectively).

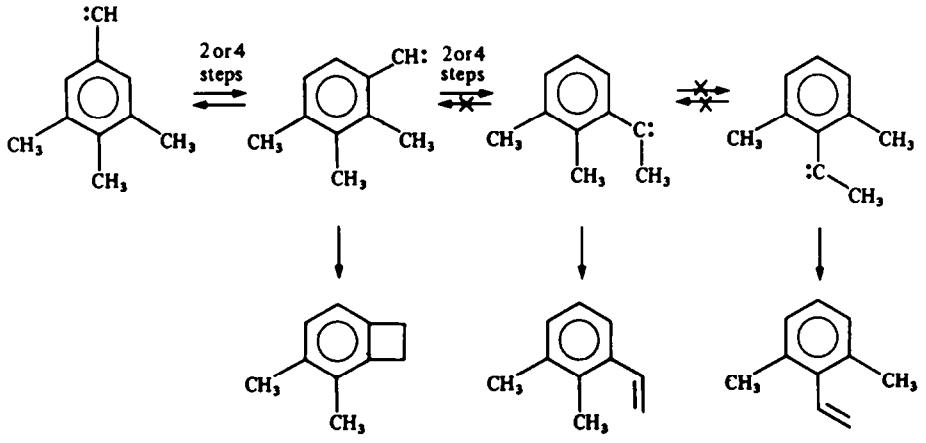
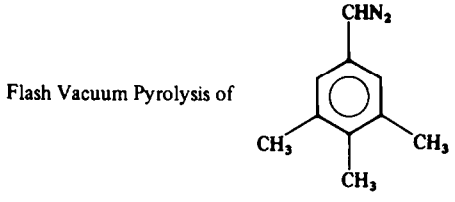
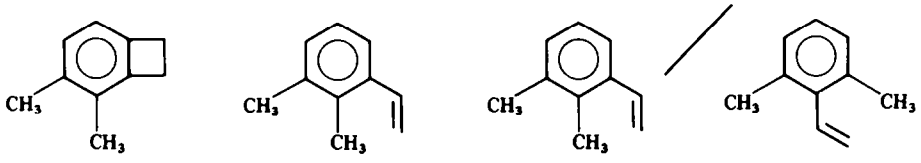


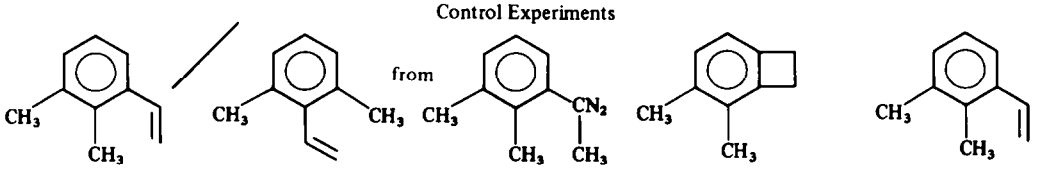
Fig. 12. The serial interconversion of 3,4,5- and 2,3,4-trimethylphenylmethylene and 2,3-dimethylphenyl(α-methyl)methylene predicted by the Baron mechanism. The rapid formation of 2,3-dimethylstyrene is expected to consume the 2,3-dimethylphenyl(α-methyl)methylene before rearrangement to 2,6-dimethylphenyl(α-methyl)methylene can occur, and thus according to this mechanistic scheme no 2,6-dimethylstyrene product is expected.





Temperature	Yield	Yield	Yield Ratio
350°C	47 ± 3%	11 ± 1%	135 ± 5
475	38	10	123 ± 13
600	47	13	102 ± 13

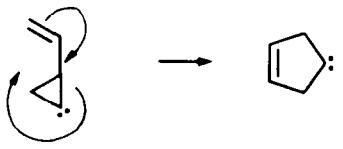
Control Experiments



Yield ratios in control experiments:	≥1000	≥3000	≥7600

Fig. 13. Product yields from the vacuum flow pyrolysis of 3,4,5-trimethylphenyldiazomethane at 350, 475 and 600°. The 2,3- to 2,6-dimethylstyrene product ratios are also reported from control reactions in which 1-(2,3-dimethylphenyl)diazoethane, 3,4-dimethylbenzocyclobutene and 2,3-dimethylstyrene were subjected to the pyrolysis conditions.

This mechanism is an example of the vinylcyclopropylidene-to-cyclopentenylidene rearrangement discovered by Skattebøl in 1962.[37]



When written for *p*-tolylmethylene in Fig. 14 it can be formulated as a norcaradienylidene "knight's walk". This reaction scheme represents a two-step interconversion of all the methylnorcaradienylidenes of Fig. 9 via the two isomeric methyl norbornadienylidenes accessible from the norcaradienylidene formed from *p*-tolylmethylene.

This has the effect of making any two norcaradienylidenes interconvertible without the intermediacy of the others. While this mechanism preserves the basic symmetry of the Baron mechanism it would lead to the prediction of a larger yield of the anomalous product 2,6-dimethylstyrene from 3,4,5-trimethylphenylmethylene because it provides two paths for the formation of norcaradienylidene O of Fig. 15 without the necessary intermediacy of norcaradienylidene K.

In this norcaradienylidene–norbornadienylidene interconversion mechanism there is less opportunity for diversion of the norcaradienylidenes to the intermediates of the Baron mechanism.

It is therefore our belief that the norcaradienylidene walk is the only mechanism thus far proposed that can account for a variation of the benzocyclobutene–styrene ratio with the entry point into the methylphenylmethylene interconversion sequence *without* observation of the "leap frogging" associated with a loose carbon atom aromatic ring complex or a norbornadienylidene intermediate.

One further question can be asked about the norcaradienylidene walk mechanism: is it thermodynamically feasible? This hinges on the energy difference between norcaradienylidene and the other C_7H_6 isomers. In Table 1 are given thermochemical estimates for the heat of formation of singlet and triplet norcaradienylidene together with values for singlet and triplet phenylmethylene, cycloheptatrienylidene and norbornadienylidene, and singlet bicycloheptatrinene, several of these values taken from Wentrup.[16] While both the absolute values and their ordering may be in error, they serve to indicate that norcaradienylidene is not so high in energy as to be inaccessible in a high temperature reaction.

Is the Vander Stouw mechanism the route to styrene?

The norcaradienylidene walk mechanism presented a possible explanation for the exclusive formation of styrene from intramolecular reaction of 2-methylcycloheptatrienylidene. As indicated in Fig. 4, Vander Stouw *et al.* proposed that 2-methylcycloheptatrienylidene could rearrange to styrene via a C—H insertion into the neighbouring Me group by the divalent C center of the cycloheptatrienylidene ring.[15] Unfortunately the D label employed did not distinguish this pathway from

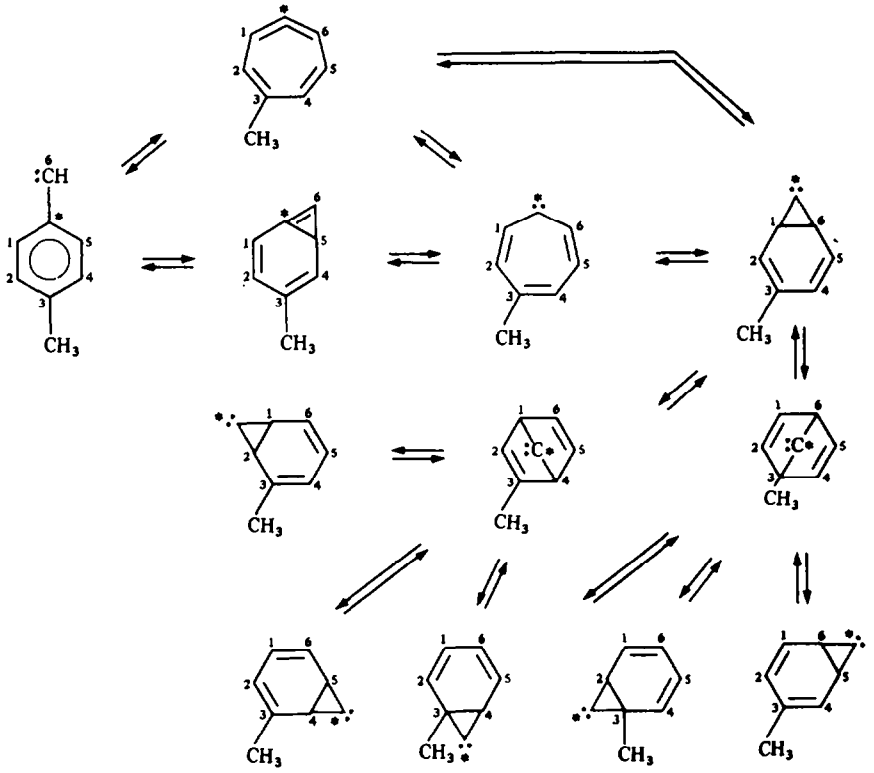


Fig. 14. A partial mechanism for reactions of *p*-tolylmethylene in which a reversible Skattebøl rearrangement interconverts norcaradienylidenes via norbornadienylidene intermediates.

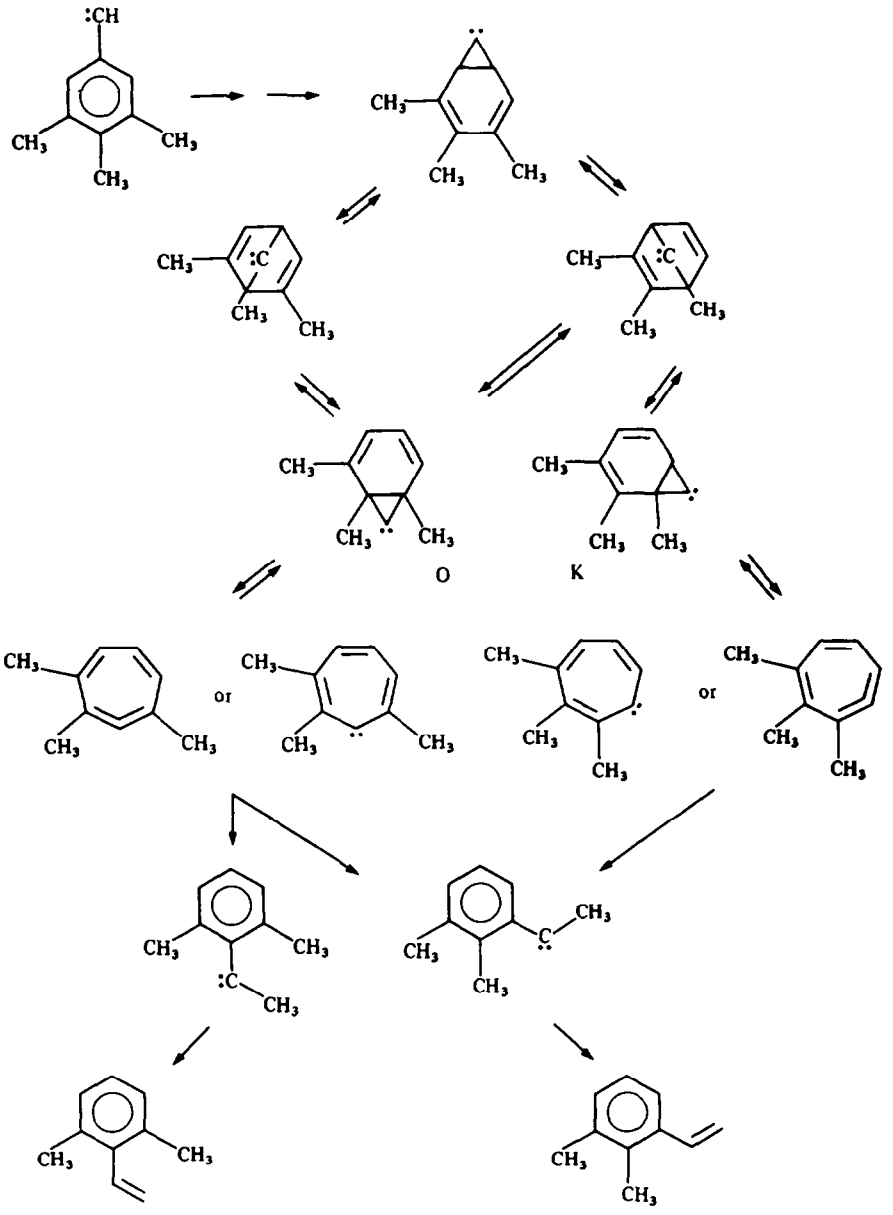


Fig. 15. A mechanism for the rearrangement of 3,4,5-trimethylphenylmethylene incorporating norbornadienylidene intermediates for the interconversion of norcaradienylidenes. This scheme predicts a larger yield of 2,6-dimethylstyrene than the mechanism of Fig. 11, since a Skattebøl mechanism allows parallel formation of the immediate precursors for 2,6- and 2,3-dimethylstyrene.

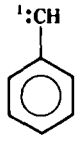
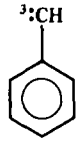
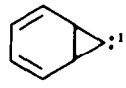
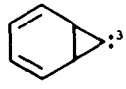
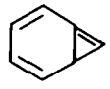
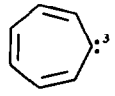
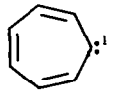
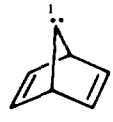
the Baron mechanism whose prediction is also shown. Only a strategically placed C label could differentiate the two mechanisms since their predictions differ only in the transposition of a single pair of carbons.

The work of Jones[38] has indicated that cycloheptatrienylidene is rather unreactive toward C—H bonds.[39] Norcaranylidenes are however known to undergo intramolecular C—H insertion yielding bicyclobutane structures. Hence one can reformulate the Vander Stouw mechanism to allow the norcaradienylidene to perform the critical intramolecular insertion.

There is precedent for conversion of a cyclic allene to a cyclopropylidine that can undergo the equivalent of intramolecular C—H insertion.[40] This was believed to be a triplet-photosensitized reaction, and direct irradiation takes another course.[41]

It was decided to determine whether the Vander Stouw mechanism was responsible for styrene formation in the rearrangement of *p*-tolylmethylene, since if this were the case it would provide independent evidence for norcaradienylidene intermediates. Figure 16 shows the predictions of both the Baron and Vander Stouw mechanism for the location of the ^{13}C label in the styrene formed from *p*-^{13}C-*p*-tolylmethylene. Figure 20 gives the synthetic scheme for the starting material.

Table 1. Estimated heats of formation for some possible intermediates in the phenylcarbene rearrangement[a]

Species	ΔH_f° (kcal/mol)	Source
	124 ± 9	$\Delta H_f^\circ(^3CH_2)^b + \Delta H_f^\circ(PhCH{=}CH_2)^c - \Delta H_f^\circ(CH_2{=}CH_2)^c$ – R.E. $(PhCH_2\cdot)^d$ $+ \Delta E_{S-T}(PhCH{:})^e = (92 \pm 1) + 35.2 - 12.5 - (13 \pm 3) + (22.3 \pm 5^f)$
	123 ± 11	$\Delta H_f^\circ(^3CH_2)^b + \Delta H_f^\circ(PhCHO)^c - \Delta H_f^\circ(CH_2O)^g$ – R.E.$(PhCH_2\cdot)^d + \Delta E_{S-T}(PhCH{:})^e =$ $(92 \pm 1) - 6 - (-27.7 \pm 2) - (13 \pm 3) + (22.3 \pm 5^f)$
	125 ± 8	$\Delta H_f^\circ(^3CH_2)^b + \Delta H_f^\circ(PhCH_2\cdot)^d - \Delta H_f^\circ(CH_3\cdot)^h + \Delta E_{S-T}(PhCH{:})^e = (92 \pm 1) + (45 \pm 1)$ $-(34 \pm 1) + (22.3 + 5^f)$
	120 ± 10	$\Delta H_f^\circ(PhCH_2\cdot)^d + DH^\circ(\cdot CH_2{-}H)^i - \Delta H_f^\circ(H\cdot)^g + \Delta E_{S-T}(PhCH{:})^e = (45 \pm 1) + (105 \pm 3)$ $-(52 \pm 1) + (22.3 \pm 5^f)$
	102 ± 4^a	$124 - \Delta E_{S-T}(PhCH{:})^e$
	101 ± 6^a	$123 - \Delta E_{S-T}(PhCH{:})^e$
	103 ± 3^a	$125 - \Delta E_{S-T}(PhCH{:})^e$
	98 ± 5^a	$120 - \Delta E_{S-T}(PhCH{:})^e$
	123 ± 6	$\Delta H_f^\circ(\text{◇▷})^a + \Delta H_f^\circ(\text{▷}{:}^1)^j - \Delta H_f^\circ(\text{▷})^c = (55.7 \pm 1) + (79.9 \pm 5^f) - 12.74$
	121 ± 6	$\Delta H_f^\circ(\text{◇▷})^a + \Delta H_f^\circ(\text{▷}{:}^3)^j - \Delta H_f^\circ(\text{▷})^c = (55.7 \pm 1) + (77.6 \pm 5^f) - 12.74$
	128 ± 7^a	$\Delta H_f^\circ(\text{◇▷})^a + \Delta H_f^\circ(\text{▷})^c - \Delta H_f^\circ(\text{▷})^c$ + extra strain$^{a,j} = (55.7 \pm 1) + (66.6 \pm 1) - 12.74$ $+ (18.5 \pm 5^f)$
	115 ± 17^a	$\Delta H_f^\circ(PhCH{:}^3) + \Delta H_f^\circ(\text{◯}{=}O)^a - \Delta H_f^\circ(PhCHO)^c$ + R.E.$(PhCH_2\cdot)^d$ + R.E.$(\text{◯}{=}O)^{k,l}$ $-$ R.E.$(\text{◎}) = (102 \pm 5) + (13 \pm 2^f) - (-6 \pm 1) + (12 \pm 2) + (13 \pm 3) - (31 \pm 4)$
	119 ± 17^a	$(115 \pm 17) + \Delta E_{S-T}(\text{⬡}{:})^e = (115 \pm 17) + 3.5$
	123 ± 5	$\Delta H_f^\circ(\text{△})^m + \Delta H_f^\circ(^1\ddot{\text{△}})^j - \Delta H_f^\circ(\text{△})^c = 55.7 + (79.9 \pm 5^f) - 12.74$
	121 ± 5	$\Delta H_f^\circ(\text{△})^m + \Delta H_f^\circ(^3\ddot{\text{△}})^j - \Delta H_f^\circ(\text{△})^c = 55.7 + (77.6 \pm 5^f) - 12.74$

[a] These thermochemical estimates follow in the spirit of Wentrup, ref. 16, and several of the values are his.

[b] *JANAF Thermochemical Tables*, 2nd edn (Edited by D. R. Stull *et al.*), NSRDS-NBS 37, U.S. Dept. of Commerce, Washington, 1971.

[c] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.* **69**, 279 (1969).

[d] S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, NSRDS-NBS 21, U.S. Dept. of Commerce, Washington, 1970.

[e] Ref. 21.

[f] Error estimated by the present authors.

[g] S. W. Benson, *J. Chem. Ed.* **42**, 502 (1965).

[h] D. M. Golden, R. Walsh and S. W. Benson, *J. Am. Chem. Soc.* **87**, 4053 (1965).

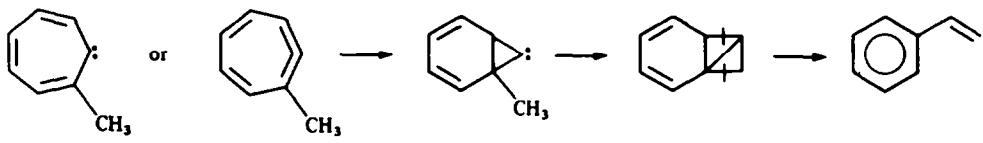
[i] H. M. Frey, *Progr. React. Kin.* **2**, 132 (1964).

[j] E. F. Ullman and E. Buncel, *J. Am. Chem. Soc.* **85**, 2106 (1963).

[k] G. Vincow, H. J. Dauben, F. R. Hunter and W. V. Volland, *J. Am. Chem. Soc.* **91**, 2823 (1969).

[l] R. B. Turner, W. R. Meador, W. v. E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, *J. Am. Chem. Soc.* **79**, 4127 (1957).

[m] W. V. Steele, *J. Chem. Thermodynam.* **10**, 919 (1978).



Omitted in Fig. 16 are the steps that intervene between *p*-tolylmethylene and 1-methylcyclohepta-1,2,4,6-tetraene or 2-methylcycloheptа-2,4,6-trien-1-ylidene, since the labelling is invariant to the mix of bicycloheptatriene, cycloheptatetraene, cycloheptatrienylidene and/or norcaradienylidene (and indeed norbornadienylidene) intermediates that intervene. The other major product benzocyclobutene is predicted by both the Baron and norcaradienylidene walk mechanism to arise from an *o*-tolylmethylene. A labelled C atom originally in the *p*-position of *p*-tolylmethylene is predicted to appear exclusively at the 1-position of benzocyclobutene, independent of whether the styrene is formed via the Baron or Vander Stouw mechanisms.

The Baron mechanism, in which styrene is formed by H-migration in α-methylphenylmethylene predicts that the ^{13}C label will appear in the vinyl group at the α-position of styrene, whereas the Vander Stouw mechanism places the label at the quaternary *ipso* position C in the aromatic ring.

Pyrolysis of the labelled precursor (30% ^{13}C at the *para* ring position) at 400° gave a 20% yield of benzocyclobutene and 21% yield of styrene. Figure 17 shows the results for the determination of the labelling position for both products. Peak intensities in the ^{13}C-NMR spectra of the labelled products were normalized by use of spectra of styrene and benzocyclobutene that were not enriched in ^{13}C over natural abundance. This procedure gave enrichment ratios that clearly indicated

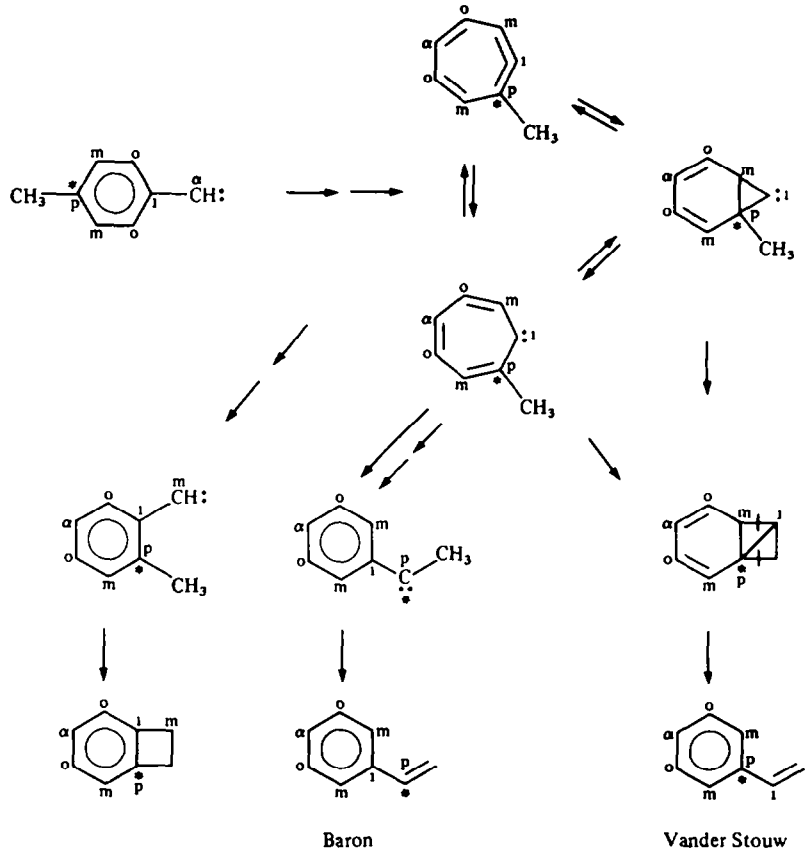
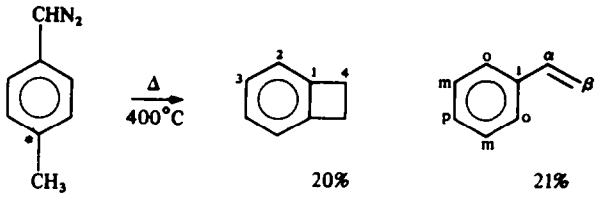


Fig. 16. Predictions of the Baron and the Vander Stouw–Kraska–Shechter mechanisms for the labelling pattern of styrene formed from the rearrangement of 4-^{13}C-*p*-tolymethylene. The positions of the initial *p*-tolylmethylene are indicated throughout with * denoting the ^{13}C label.



Carbon	^{13}C δ	Peak intensity (labelled product)	Peak intensity (natural substance)	Enrichment ratio C_α/C_n
Styrene				
α	136.9	100.0	36.48	1
β	113.7	2.00	36.22	33
1	137.6	1.66	20.23	28
o	126.2	12.96	100.0	24
m	128.5	6.06	86.50	31
p	127.8	2.45	42.35	34
Benzocyclobutene				C_1/C_n
1	145.7	100.0	42.6	1
2	122.4	21.97	91.5	29
3	126.6	13.49	100.0	35
4	29.7	17.65	42.6	30

Fig. 17. ^{13}C spectroscopic data and enrichment ratios for styrene and benzocyclobutene formed from vacuum pyrolysis of 4-^{13}C-*p*-tolyldiazomethane at 400°. The peaks in the ^{13}C spectra were attributed according to refs 57 and 58.

that the styrene was formed via α-methylphenylmethylene, i.e. the Baron mechanism, which predicts an enrichment ratio $C_\alpha/C_n = 30$ for all $n \neq \alpha$, in good agreement with the observed result 30.0 ± 4.1. The enrichment factors for benzocyclobutene $C_1/C_n (n \neq 1) = 31.3 \pm 3.2$ are also in good agreement with the proposed mechanism.

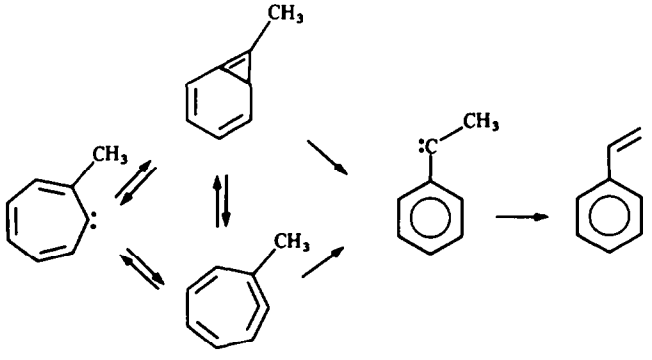
The apparent lack of a contribution from the Vander Stouw–Kraska–Shechter mechanism to styrene formation means that an *independent* probe for the participation of norcaradienylidene intermediates did not succeed, but it does not speak against the norcaradienylidene walk mechanism. It simply fails to prove it.

This result does, however, leave unanswered the question why direct generation of 2-methylcycloheptatrienylidene gives rise to styrene, but *not* benzocyclobutene.[32] Whether the key rearranging species is the cycloheptatrienylidene or instead its allene isomer, the Me group must play either an electronic or steric role in biasing the reaction in favor of the bond to which it is attached. Cadogan has proposed that an Me group can significantly stabilize intermediates such as the bicycloheptatriene in the following scheme.[8]

The role of the Me remains to be determined by manipulating the electronic supply on either side of the carbenic or central allenic carbon and by changing the size of the substituent, and this work is underway.

SUMMARY

It seems clear that the formation of different ratios of styrene and benzocyclobutene from the intramolecular reactions of *o*-tolylmethylene on the one hand and *m*- and *p*-tolylmethylene on the other precludes pathways in which formation of *o*-tolylmethylene *must* precede product formation from the *m*- and *p*-isomers. Three mechanisms have been considered that permit *parallel* formation from *m*- or *p*-tolylmethylene of the styrene precursor, 2-methylcycloheptatrienylidene or 1-methylcyclohepta-1,2,4,6-tetraene, and the benzocyclobutene precursor, *o*-tolylmethylene. Both a C atom–toluene π-complex and methylnorbornadienylidene intermediates have been rendered unlikely by the absence of the anomalous product 3-methylbenzocyclobutene from the rearrangement of 3,5-dimethylphenylmethylene and the low yield of 2,6-dimethylstyrene from the rearrangement of 3,4,5-



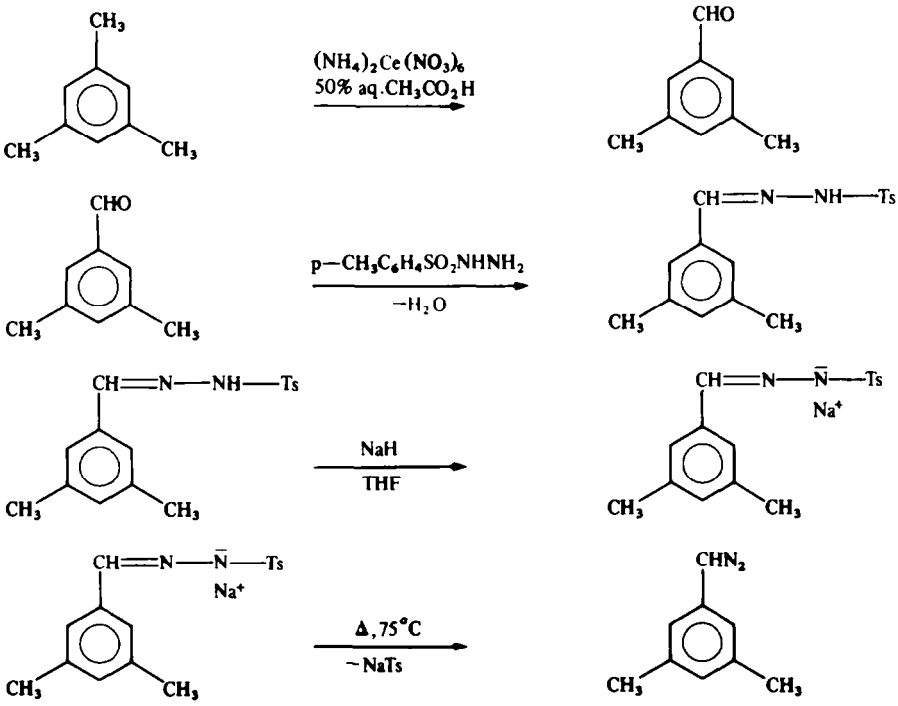


Fig. 18. Steps in the synthesis of 3,5-dimethylphenyldiazomethane.

trimethylphenylmethylene. Both these results are compatible, however, with a norcaradienylidene walk mechanism, which would have revealed itself unmistakably had styrene formation resulted from intramolecular C—H insertion by methylcycloheptatrienylidene carbene center. This is not the case however, and it has been demonstrated that α-methylphenylmethylene is the direct precursor of styrene.

EXPERIMENTAL

Instrumentation. M.ps were taken in a Thomas–Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Proton magnetic resonance spectra were recorded on a Hitachi Perkin–Elmer R-24B 60 MHz NMR spectrometer. Chemical shifts are reported in δ values from internal TMS standard. ^{13}C magnetic resonance spectra were recorded on a JEOL JNM-FX-100 FT NMR spectrometer. Samples were dissolved in $CDCl_3$. The D signal from the solvent was used to maintain the field frequency lock. Mass spectra were determined on a Varian MAT CH-7 mass spectrometer interfaced by a Biemann–Watson separator with a Varian Aerograph Moduline® 2700 Series gas chromatograph.

Synthesis of 3,5-dimethylbenzaldehyde tosylhydrazone. The synthetic sequence is shown in Fig. 18.

Synthesis of 3,5-dimethylbenzaldehyde. The method of Syper was employed.[42]

3,5-Dimethylbenzaldehyde tosylhydrazone. To a soln of 0.36 g (1.9×10^{-3} mol) of *p*-tosylhydrazine (97%, Aldrich) in 1 ml of hot reagent-grade MeOH was added 0.25 g (1.9×10^{-3} mol) 3,5-dimethylbenzaldehyde. The mixture was cooled to room temp and allowed to stand overnight. The resulting crystals were filtered and washed with several drops of MeOH, and dried in air for a day. The product weighed 0.48 g (84%) with m.p. 139–141° (dec). ^1H-NMR ($CDCl_3$): δ 2.20 (6H, s, 3,5-CH_3), 2.30 (3H, s, tosyl CH_3), 6.89 (1H, s, 4-H), 7.10 (2H, s, 2, 6-H), 7.27 (2H, d, J = 7.8 Hz, tosyl 2',6'-H), 7.69 (1H, s, —CH=N—), 7.94 (2H, d, J = 7.8 Hz, tosyl 3',5'-H), 8.66 (1H, br s, NH). Mass spectrum (70 eV) *m/e*: 302 (parent, 4%), 147 (22%), 146 (15%), 134 (18%), 133 (23%), 132 (15%), 124 (16%), 118 (34%), 117 (21%), 116 (22%), 105 (23%), 103 (14%), 92 (37%), 91 (100%), 79 (15%), 77 (28%), 65 (30%), 63 (17%), 51 (20%), 50 (10%). (Found: C, 63.56; H, 6.05; N, 9.30; S, 10.70. Calc for $C_{16}H_{18}N_2O_2S$: C, 63.58; H, 5.91; N, 9.27; S, 10.60%.)

Sodium salt of 3,5-dimethylbenzaldehyde tosylhydrazone. To 0.07 g of a 50% oil dispersion of NaH washed with Na-dried pentane in a 100 ml round-bottom flask was added a soln of 0.41 g (1.4 mmol) of 3,5-dimethylbenzaldehyde tosylhydrazone in 5 ml of THF distilled from $LiAlH_4$. The THF and residual pentane were removed from the jelly-like tosylhydrazone sodium salt that coated the wall of the reaction flask by vacuum suction overnight.

Formation and pyrolysis of 3,5-dimethylphenyldiazomethane. The flask containing the dried Na-salt of 3,5-dimethylbenzaldehyde tosylhydrazone coated on its walls was weighed and attached to a flow pyrolysis system consisting of a 25 cm section of 7 mm i.d. pyrex tube wrapped with asbestos paper and Chromel A wire (0.0253" diam.) embedded in a mixture of alundum cement and sodium silicate, oven-dried. The temp was measured with an iron–constantan thermocouple. The pyrolysis tube was connected to a trap cooled in liquid N_2 which in turn led to a vacuum line. The system was evacuated to 7 mTorr, the pyrolysis tube was heated to the desired temp (350, 475, and 600° respectively), and the flask containing the tosylhydrazone salt was immersed in an oil bath and gradually heated to 75°, slowly liberating 3,5-dimethylphenyldiazomethane which passed through the pyrolysis tube. The pressure increased to 10–20 mTorr due to the N_2 gas formed in the pyrolysis, whose termination was signalled by a fall in pressure back to 7 mTorr. Reweighing the flask in which the tosylhydrazone salt was prepared permitted the weight of diazocompound formed to be determined by difference. 0.133 ± 0.003 g 3,5-dimethylphenyldiazomethane (67% yield based on tosylhydrazone, average of two experiments) was formed and pyrolysed.

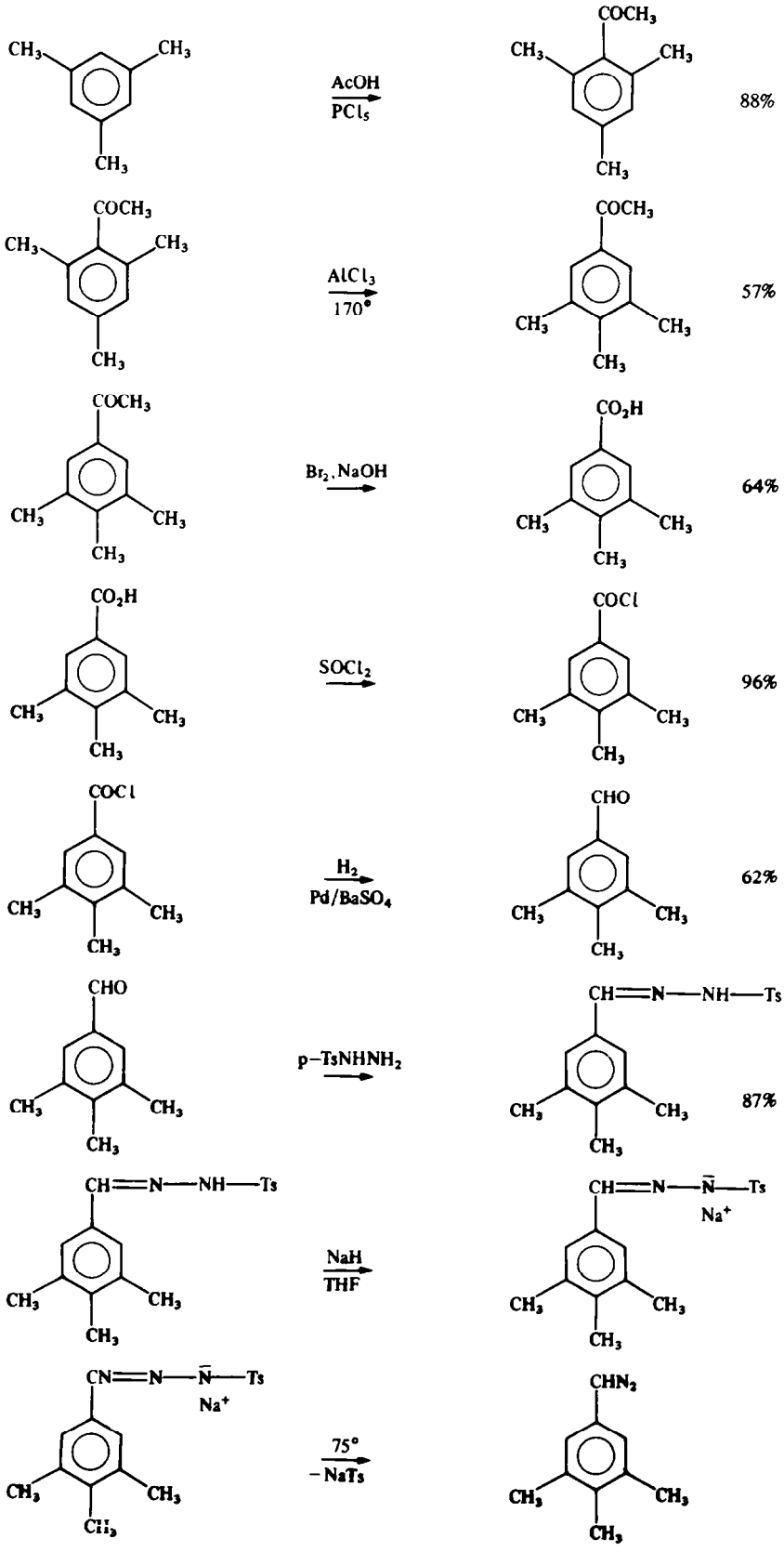


Fig. 19. Steps in the synthesis of 3,4,5-trimethylphenyldiazomethane.

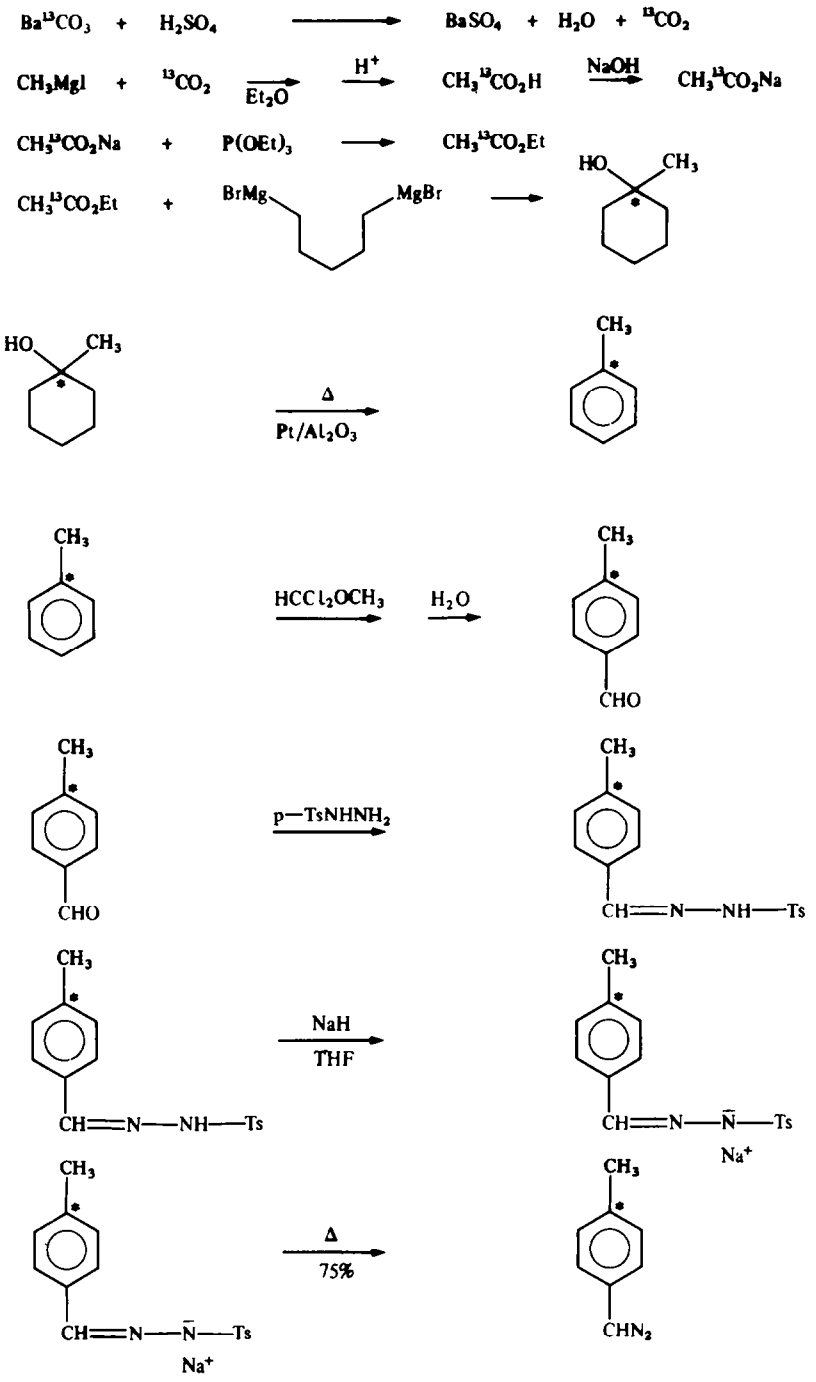


Fig. 20. Steps in the synthesis of 4-^{13}C-*p*-tolyldiazomethane.

Product was collected by washing the trap with CCl_4, and product yields were determined by ^{1}H-NMR spectroscopy using an internal standard method and confirmed by gas chromatography and combined gas chromatography–mass spectroscopy. The yields of 4-methylbenzocyclobutene and 3-methylstyrene are given in Fig. 8. While there was no gas chromatographic peak with retention time corresponding to 3-methylbenzocyclobutene in the product mixture from pyrolysis at 350°, a very small peak with nearly the same retention time (27.9 min on a 2 mm i.d. × 12′ glass column 10% OV-17 on chromosorb W AWDCMS, 80/100 mesh, 80°, 25 ml He/min, *versus* 23.2 min for 3-methylstyrene and 30.7 min for 4-methylbenzocyclobutane) was observed for pyrolyses at 475° and 600°, but the yield ratios 4-methyl- to 3-methylbenzocyclobutene were > 5000 and > 3000 respectively.

Authentic 3-methylbenzocyclobutene was isolated from the flow pyrolysis of 3,4-dimethylphenyldiazomethane carried out as described above with 3,4-dimethylbenzaldehyde tosylhydrazone sodium salt, prepared as described for the 3,5-isomer above.

4-Methylbenzocyclobutene, mass spectrum (70 eV) *m/e*: 118 (parent, 71%), 117 (base, 100%), 115 (68%), 103 (31%), 91 (76%), 77 (24%), 65 (25%), 63 (27%), 51 (39%).

3-Methylstyrene, mass spectrum (70 eV) *m/e*: 118 (parent,

base, 100%), 117 (91%), 115 (61%), 103 (17%), 91 (89%), 77 (25%), 65 (44%), 63 (50%), 51 (55%).

3-Methylbenzocyclobutane, ^{1}H-NMR (CCl_4): δ 2.08 (3H, s, CH_3), 3.00 (4H, s, CH_2), 6.67–7.18 (3H, m, aromatic H); mass spectrum (70 eV) *m/e*: 118 (parent, 89%), 117 (base, 100%), 115 (69%), 103 (19%), 91 (48%), 77 (27%), 65 (19%), 63 (20%), 51 (37%).

Synthesis of 3,4,5-*trimethylbenzaldehyde tosylhydrazone.* See Fig. 19.

2,4,6-*Trimethylacetophenone.* Mesitylene was acetylated by the method of Kosolapoff[43] in 88% yield (b.p. 83°, 1.6 Torr; 74°, 0.9 Torr; lit. 100–102°, 1 Torr); ^{1}H-NMR (CCl_4): δ 2.12 (6H, s, 2,6-CH_3), 2.19 (3H, s, 4-CH_3), 2.28 (3H, s, $COCH_3$), 6.67 (2H, s, aromatic H); ^{13}C-NMR ($CDCl_3$): δ 19.0 (2,6-CH_3, 53.85%), 20.9 (4-CH_3, 29.42%), 31.8 (α-CH_3, 31.99%), 128.6 (3,5-C, 100%), 132.3 (2,6-C, 37.05%), 138.0 (4-C, 21.12%), 140.5 (1-C, 9.03%), 206.8 (CO, 11.04%); mass spectrum (70 eV) *m/e*: 162 (parent, 98%), 147 (base, 100%), 119 (80%), 91 (25%), 77 (16%).

3,4,5-*Trimethylacetophenone.* Isomerization of 2,4,6- to 3,4,5-trimethylacetophenone was accomplished by heating with $AlCl_3$, the method of Baddeley[44] in 57% yield (only fraction with b.p. 89°, 0.9 Torr, collected in fractional distillation through 65 cm column packed with glass helices; lit. b.p. 138°, 20 Torr,[44] 101.5°, 3 Torr[45]): ^{1}H-NMR (CCl_4): as lit;[46] ^{13}C-NMR ($CDCl_3$): δ 15.7 (4-CH_3, 23.5%), 20.4 (3,5-CH_3, 69.1%), 26.2 (α-CH_3, 35.2%), 127.6 (2,6-C, 100%), 134.8 (4-C, 13.7%), 136.7 (3,5-C, 33.0%), 140.8 (1-C, 10.5%), 197.6 (CO, 10.7%); mass spectrum (70 eV) *m/e*: 162 (parent, 41%), 147 (base, 100%), 119 (66%), 91 (35%), 77 (10%), 65 (9%).

3,4,5-*Trimethylbenzoic acid.* 3,4,5-Trimethylacetophenone was converted to 3,4,5-trimethylbenzoic acid by the bromoform reaction, as described,[44] in 64% yield (m.p. of product recrystallized from EtOH, 215–218°, lit. 218–220°,[44] 125–126°[47]); ^{1}H-NMR ($CDCl_3$ and DMSO-d_6), 2.20 (3H, s, 4-CH_3), 2.30 (6H, s, 3,5-CH_3), 7.66 (2H, s, 2,6-CH), 9.46 (1H, br s, CO_2H); mass spectrum (70 eV) *m/e*: 164 (parent, 67%), 149 (25%), 147 (14%), 119 (base, 100%), 105 (53%), 91 (47%), 77 (32%).

3,4,5-*Trimethylbenzoyl chloride.* 3,4,5-Trimethylbenzoic acid was converted to the acid chloride by treatment with thionyl chloride in benzene.[44] 3,4,5-Trimethylbenzoyl chloride was isolated by vacuum distillation in 96% yield (b.p. 95°, 0.18 Torr; lit. 100–105°, 0.1 Torr[44]): ^{1}H-NMR (CCl_4): δ 2.21 (3H, s, 4-CH_3), 2.31 (6H, s, 3,5-CH_3), 7.59 (2H, s, 2,6-CH); mass spectrum (70 eV) *m/e*: 184 (parent, 5%), 182 (parent, 20%), 148 (22%), 147 (base, 100%), 120 (13%), 119 (98%), 117 (17%), 115 (17%), 104 (15%), 103 (20%), 91 (47%), 78 (11%), 77 (31%), 76 (12%), 66 (13%), 65 (16%).

3,4,5-*Trimethylbenzaldehyde.* 3,4,5-Trimethylbenzoyl chloride was subjected to a Rosemund reduction by a slight variation of a published procedure,[44] employing a 5% Pd on $BaSO_4$ catalyst poisoned with a S–quinoline soln, and xylene solvent. The course of the reduction was monitored by employing the H_2 stream used in the reduction to sweep the HCl formed from the mixture into a flask containing aqueous NaOH and phenolphthalein indicator. After consumption of each 5 ml aliquot of 1 N NaOH a fresh one was added. 3,4,5-Trimethylbenzaldehyde was isolated by vacuum distillation, b.p. 97°, 0.5 Torr (lit. 80–85°, 0.15 Torr[44]) and recrystallization from petroleum ether to afford a 52% yield of colorless needles, m.p. 58–59° (lit. 60–61°[44]); ^{1}H-NMR ($CDCl_3$): δ 2.20 (3H, s, 4-CH_3), 2.30 (6H, s, 3,5-CH_3), 7.43 (2H, s, 2, 6-CH), 9.81 (1H, s, CHO); mass spectrum (70 eV) *m/e*: 148 (parent, 97%), 147 (base, 100%), 119 (92%), 105 (33%), 103 (19%), 91 (40%), 77 (28%), 65 (22%), 63 (18%).

Vapor chromatographic analysis of the 3,4,5-trimethylbenzaldehyde on two columns of differing polarity (10% carbowax 20 M and 3% OV-17) indicated three small impurities each present in an amount less than 0.05 mol %. To make certain that these did not contribute to the formation of the mechanistically important product 2,6-dimethylstyrene formed in low yield from the pyrolysis of 3,4,5-trimethylphenyldiazomethane described below, a sample of 3,4,5-trimethylbenzaldehyde was purified by vapor chromatography (2 mm i.d. × 4′ 3% OV-17 glass column) and carried through the subsequent conversions. The product ratios were the same, within experimental error, as those obtained from the bulk of the 3,4,5-trimethylbenzaldehyde purified by vacuum distillation and recrystallization.

3,4,5-*Trimethylbenzaldehyde tosylhydrazone.* In 10 ml of hot reagent-grade methanol was dissolved 4.78 g (0.026 mol) of *p*-tosylhydrazine (97% Aldrich), and then 3.80 g (0.026 mol) of 3,4,5-trimethylbenzaldehyde was added. After the aldehyde dissolved the mixture was cooled to room temp and needle-like crystals appeared. After two recrystallizations from MeOH, 7.05 g (87% yield) of 3,4,5-trimethylbenzaldehyde tosylhydrazone was obtained, m.p. 164–167 (dec.); ^{1}H-NMR ($CDCl_3$): δ 2.01 (3H, s, 4-CH_3), 2.18 (6H, s, 3,5-CH_3), 2.32 (3H, s, tosyl-4-CH_3), 7.11 (2H, s, 2,6-CH), 7.22 (2H, AB d, J_{AB} = 7.8 Hz, tosyl-3′,5′-CH), 7.65 (1H, s, CH=N), 7.83 (2H, AB d, J_{AB} = 7.8 Hz, tosyl-2′,6′-CH), 8.40 (1H, br s, $NHSO_2$); mass spectrum (70 eV) *m/e*: 316 (parent 6%), 161 (26%), 148 (33%), 147 (48%), 146 (15%), 145 (17%), 131 (11%), 130 (35%), 124 (14%), 120 (11%), 119 (34%), 117 (19%), 115 (15%), 105 (24%), 103 (15%), 92 (24%), 91 (base, 100%), 79 (11%), 77 (31%), 65 (27%), 64 (14%), 63 (14%), 51 (21%). (Found: C, 64.26; H, 6.23; N, 8.86; S, 10.39. Calc for $C_{17}H_{20}N_2O_2S$: C, 64.56; H, 6.33; N, 8.86; S, 10.13%.)

Sodium salt of 3,4,5-*trimethylbenzaldehyde tosylhydrazone.* From 0.50 g 3,4,5-trimethylbenzaldehyde tosylhydrazone and 0.08 g 50% oil dispersion of NaH, the Na salt was prepared as described above for 3,5-dimethylbenzaldehyde tosylhydrazone.

Formation and pyrolysis of 3,4,5-*trimethylphenyldiazomethane.* The procedure was the same as that described above for 3,5-dimethylphenyldiazomethane. The average amount of 3,4,5-trimethylphenyldiazomethane pyrolysed in four experiments was 0.087 ± 0.023 g (weight by difference), representing a 34% yield of diazocompound based on tosylhydrazone. In Fig. 13 are given the yields obtained at three different pyrolysis temperatures 350°, 475° and 600° of the observed products which were isolated following vapor chromatographic separation. 3,4-Dimethylbenzocyclobutene, ^{1}H-NMR (CCl_4): δ 2.01 (3H, s, CH_3), 2.17 (3H, s, CH_3), 2.97 (4H, s, CH_2), 6.50–6.80 (2H, distorted AB dd, J_{AB} = 7.8 Hz, 5,6-CH); mass spectrum (70 eV) *m/e*: 132 (parent, 60%), 131 (15%), 117 (base, 100%), 116 (23%), 115 (76%), 91 (65%), 89 (15%), 79 (13%), 78 (16%), 77 (24%), 65 (28%), 63 (31%), 51 (62%). 2,3-Dimethylstyrene, ^{1}H-NMR (CCl_4): δ 2.17 (3H, s, CH_3), 2.21 (3H, s, CH_3), 5.16 (1H, m, vinyl H *trans* to Ar), 5.42 (1H, m, vinyl H *cis* to Ar), 6.66–7.20 (4H, m, aromatic H plus vinyl H *gem* to Ar); mass spectrum (70 eV) *m/e*: 132 (parent, 54%), 117 (base, 100%), 115 (70%), 91 (49%), 77 (30%), 65 (34%), 63 (29%), 51 (45%). The spectroscopic properties of 2,3-dimethylstyrene obtained from 3,4,5-trimethylphenyldiazomethane were identical with that formed from 1-(2,3-dimethylphenyl)diazoethane (see below). 2,6-Dimethylstyrene was identified by comparison of its vapor chromatographic retention time on three columns of differing polarity (Carbowax 20 M, silicone oil DC-200, and silicone oil OV-17) and of its mass spectrum with an authentic sample obtained from the Fairfield Chemical Co. whose identity was verified by its NMR spectrum. ^{1}H-NMR ($CDCl_3$): δ 2.26 (6H, s, 2,6-CH_3), 5.15 (1H, m, vinyl H *trans* to Ar), 5.43 (1H, m, vinyl H *cis* to Ar), 6.63 (1H, m, vinyl H *gem* to Ar), 6.96 (3H, s, aromatic); mass spectrum (70 eV) *m/e*: 132 (parent, 62%), 117 (base, 100%), 115 (84%), 91 (65%), 77 (27%), 65 (41%), 63 (53%), 51 (81%).

Synthesis of 2,3-*dimethylacetophenone tosylhydrazone.* *o*-Xylene was acetylated with glacial AcOH and P_2O_5, as described above for the preparation of 2,4,6-trimethylacetophenone. A *ca* 1:1 mixture of 2,3- and 3,4-dimethylacetophenone was collected as the fraction b.p. 68–78°, 0.7 Torr obtained upon distillation of the mixture through a 65 cm column packed with glass helices. Purification was by preparative vapor chromatography on a ¼″ o.d. × 20′ 15% DC-200 on ABS treated 40/50 mesh Anakrom. *Ca* 4 g (5% yield) of 2,3-dimethylacetophenone was obtained, con-

taminated with *ca* 7%, 3,4-dimethylacetophenone; 2,3-dimethylacetophenone: ^{1}H-NMR (neat): δ 2.13 (3H, s, ring-CH_3), 2.25 (3H, s, ring-CH_3), 2.40 (3H, s, $COCH_3$), 6.82–7.56 (3H, m, aromatic); mass spectrum (70 eV) *m/e*: 148 (parent, 44%), 133 (base, 100%), 105 (84%); 3,4-dimethylacetophenone, ^{1}H-NMR (neat): δ 2.09 (6H, s, ring-CH_3), 2.39 (3H, s, $COCH_3$), 6.90–7.69 (3H, m, aromatic).

The 2,3-dimethylacetophenone tosylhydrazone was produced from 0.26 g *p*-tosylhydrazine and 0.20 g 2,3-dimethylacetophenone as described above, yielding 0.39 g (86%), m.p. 147–151° (dec.); ^{1}H-NMR ($CDCl_3$): δ 1.91 (3H, s, α-CH_3), 2.13 (3H, s, 2-CH_3), 2.25 (3H, s, 3-CH_3), 2.43 (3H, s, tosyl-CH_3), 6.55–7.19 (4H, m, 4,5,6-CH and NHTs), 7.27 (2H, dd, J_{AB} = 7.8 Hz, tosyl 2',3',5',6'-CH); mass spectrum (70 eV) *m/e*: 316 (parent, 4%), 162 (10%), 161 (87%), 160 (16%), 146 (29%), 145 (11%), 133 (13%), 132 (53%), 131 (19%), 120 (33%), 117 (75%), 116 (17%), 115 (42%), 105 (17%), 103 (11%), 91 (base, 100%), 79 (13%), 77 (28%), 65 (32%), 64 (17%), 63 (16%), 58 (10%), 51 (21%). (Found: C, 64.22; H, 6.49; N, 8.82; S, 10.34. Calc for $C_{17}H_{20}N_2O_2S$: C, 64.56; H, 6.33; N, 8.86; S, 10.13%.)

Sodium salt of 2,3-dimethylacetophenone tosylhydrazone. From 0.39 g of 2,3-dimethylacetophenone tosylhydrazone and 0.06 g of 50% oil dispersion of NaH, the Na salt was prepared as previously described.

Formation and pyrolysis of 1-(2,3-*dimethylphenyl*)*diazoethane.* The procedure was the same as that described above for 3,5-dimethylphenyldiazomethane. In three separate experiments, the diazo compound was generated by heating the tosylhydrazone sodium salt in high vacuum ($p < 10$ mTorr) to 75°, and allowing the diazo compound to vaporize into the pyrolysis tube maintained at 350, 475 and 600° respectively. In all cases the only products detected were 2,3-dimethylstyrene and *ca* 3% 3,4-dimethylstyrene formed from the 3,4-dimethylacetophenone impurity in the 2,3-dimethylacetophenone (see above). No 2,6-dimethylstyrene was observed under conditions where it was demonstrated by its addition that it would be detected at ratios of 1,3- to 2,6-dimethylstyrene of $\leq 900:1$.

Control pyrolyses of 1,3-*dimethylstyrene and* 3,4-*dimethylbenzocyclobutene.* To make certain that the 2,6-dimethylstyrene product obtained from the pyrolysis of 3,4,5-trimethylphenyldiazomethane was *not* due to secondary pyrolysis of the major products, 2,3-dimethylstyrene and 3,4-dimethylbenzocyclobutene were subjected to the same pyrolysis conditions as the diazo compound. In separate experiments at 350, 475 and 600° no 2,6-dimethylstyrene was observed under conditions where it was demonstrated with added 2,6-dimethylstyrene that it could be detected at ratios 2,3-dimethylstyrene to 2,6-dimethylstyrene $\leq$ 7600 and 3,4-dimethylbenzocyclobutene to 2,6-dimethylstyrene $\leq$ 3000.

Synthesis of p-[4-^{13}C]*tolualdehyde tosylhydrazone.* See Fig. 20.

Sodium[1-^{13}C]*acetate.* From a mixture of 0.2143 g 99% Ba[^{13}C]CO_3 and 0.4324 g unlabelled $BaCO_3$, CO_2 was liberated and reacted with the Grignard reagent from 15.00 g MeI according to the procedure of Murray and Williams.[48] 0.239 g sodium[1-^{13}C]acetate (88.7% yield, enrichment 33%) was obtained. In two other runs the chemical yields were 77 and 57.3%.

Ethyl[1-^{13}C]*acetate.* Labelled NaOAc was treated with triethyl phosphite employing the method of Ropp.[49] From 0.36 g (4.4 mmol) of NaOAc, 0.38 g (4.3 mmol, 98% yield) was obtained; ^{1}H-NMR ($CDCl_3$): δ 1.24 (3H, t, J = 7.8 Hz, CH_3 of ethyl), 2.00 (3H, s and d, $J_{^{13}C-CH}$ = 6.9 Hz, CH_3 ^{13}CO, area of d is 33 ± 1% that of s + d and is the ^{13}C enrichment of the 1-position), 4.12 (2H, triplet of quartets, J_{CH-CH} = 7.8 Hz, $J_{^{13}C-O-CH_2} \simeq$ 3 Hz, CH_2).

1-*Methyl*[1-^{13}C]*cyclohexanol.* Labelled EtOAc (0.334 g, 3.78 mmol) was reacted with the di-Grignard reagent prepared from 2.86 g (12 mmol) pentamethylene dibromide in ether as described by Fields *et al.*[50] A 66% yield (0.284 g, 2.48 mmol) of 1-methyl[1-^{13}C]cyclohexanol was obtained; ^{1}H-NMR ($CDCl_3$): δ 1.20 (3H, s, and d, $J_{^{13}C-CH}$ = 4.2 Hz, CH_3, area of d is 33 ± 1% that of s + d and is the ^{13}C enrichment of the 1-position), 1.51 (10H, br, CH_2), 2.13 (1H, s, OH). Both the identity of the product and the enrichment of the 1-position were confirmed by comparison of the ^{13}C NMR spectra of labelled and unlabelled 1-methylcyclohexanol. The chemical shifts matched the lit. values.[51]

[1-^{13}C]*Toluene.* Labelled 1-methylcyclohexanol (0.87 g, 7.6 mmol) was dehydrogenated by the procedure of Steinberg and Sixma[52] over a Pt–alumina catalyst.[53] A 50% yield (0.35 g, 3.8 mmol) of [1-^{13}C]toluene was obtained; ^{1}H-NMR ($CDCl_3$): δ 2.22 (3H, s + d, $J_{^{13}C-CH}$ = 5.8 Hz, CH_3, area of d is 33 ± 1% that of s + d and is the ^{13}C enrichment of the 1-position), 7.03 (5H, m, aromatic H). The identity of the product and the enrichment were confirmed by ^{13}C-NMR spectroscopy.[54]

p-[4-^{13}C]*Tolualdehyde.* Labelled toluene (0.114 g, 1.24 mmol) was formylated with 0.48 g (4.2 mmol) dichloromethyl methyl ether[55] and 0.53 ml (5.3 mmol) $TiCl_4$ catalyst in CH_2Cl_2,[56] to yield, after separation from its *ortho* isomer by preparative gas chromatography, 62 mg (42% yield; 37% was obtained in another run) of *p*-[4-^{13}C]tolualdehyde: ^{1}H-NMR ($CDCl_3$): δ 2.36 (3H, s + d, $J_{^{13}C-CH}$ = 5.2 Hz, CH_3, area of d is 34 ± 1% that of s + d and is the ^{13}C enrichment of the 4-position), 7.18 (2H, d, J = 7.2 Hz, 3,5-CH), 7.70 (2H, d, J = 7.2 Hz, 2,6-CH), 9.85 (1H, s, CHO); ^{13}C-NMR ($CDCl_3$): see below (peak intensities for labelled and unlabelled *p*-tolualdehyde recorded under identical, white-noise decoupled, conditions).

Assignments	δ	Labelled intensities	Unlabelled intensities
CH_3	21.8	5.26	28.85
C-2,3,5,6	129.7	65.91	100.0
C-1	134.4	3.60	5.78
C-4	145.4	100.0	9.06
CHO	191.7	9.20	32.79

p-[4-^{13}C]*Tolualdehyde tosylhydrazone.* The tosylhydrazone was produced from 103 mg (0.86 mmol) *p*-[4-^{13}C]tolualdehyde and 166 mg (0.86 mmol) *p*-tosylhydrazine as previously described, yielding 210 mg (0.73 mmol, 85% yield), m.p. 145–146° (dec.).

Sodium salt of p-[4-^{13}C]*tolualdehyde tosylhydrazone.* From 0.21 g (0.73 mmol) of the tosylhydrazone and 0.04 g 50% NaH oil dispersion the sodium salt was prepared as previously described.

Formation and pyrolysis of p-[4-^{13}C]*tolyldiazomethane.* The procedure was as described above for 3,5-dimethylphenyldiazomethane, with the pyrolysis zone at 400°. The products, [α-^{13}C]styrene (16 mg, 21% yield) and [1-^{13}C]benzocyclobutene (15 mg, 20% yield) were isolated by preparative vapor chromatography on a $\frac{1}{4}$" × 20' 15% DC-200 column. The [α-^{13}C]styrene was further purified on a $\frac{1}{4}$" × 20' 15% Carbowax 6000 column. [α-^{13}C]Styrene, ^{1}H-NMR ($CDCl_3$): δ 5.17 (1H, dd, vinyl H *trans* to Ph), 5.65 (1H, dd, vinyl H *cis* to Ph), 6.67 (1H, dd, vinyl H *gem* to Ph) with satellites due to $J_{^{13}C-H}$ = 155 Hz); ^{13}C-NMR: see Fig. 17;[57] [1-^{13}C]benzocyclobutene, ^{13}C-NMR ($CDCl_3$): see Fig. 17.[58]

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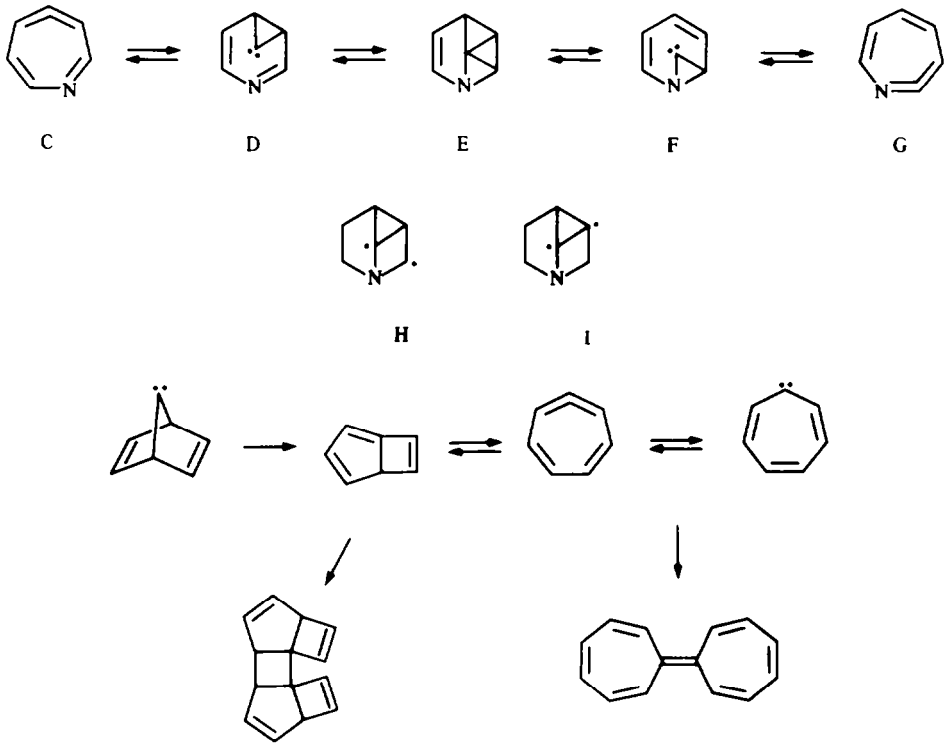

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