Automerization in Vinylidenecyclopentadiene and Phenylcarbene

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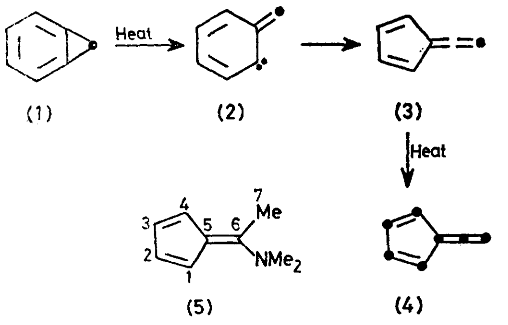
Summary Flash pyrolysis of vinylidenecyclopentadiene at 800—1050 °C results in carbon randomization; 2-methylvinylidenecyclopentadiene rearranges to styrene and benzocyclobutene, and [1-^{13}C]phenyldiazomethane yields vinylidenecyclopentadiene carrying excess label at C(5) at 590 °C and 5—7 mmHg of N_2, thus suggesting that the ring contraction is reversible and occurs *via* bicyclo-[3.2.0]hepta-1,3,6-triene.

Vinylidenecyclopentadiene (**3**) is the major product of the high temperature flash pyrolysis of benzocyclopropene, phthalide, indane-1,2-dione, homophthalic anhydride, indazole, phenyldiazomethane, and other precursors.[1] The pyrolysis of [1-^{13}C]phenyldiazomethane at 770 °C yields uniformly labelled (**3**).[2]



• = Carbon-12

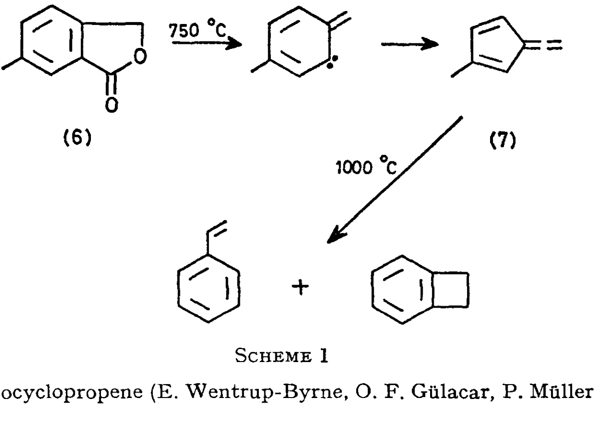
We now report that all the previously suggested mechanisms of this ring contraction[1–3] are untenable, since carbon randomization occurs in (**3**) itself, and our results suggest that this takes place *via* reversion to phenylcarbene. Furthermore, we have found conditions where carbon scrambling in [1-^{13}C]phenylcarbene is non-uniform.

[1-^{12}C]Benzocyclopropene (**1**)[4] (650 mg) was flash-pyrolysed at 800 °C at 10^{-3} mmHg. The yellow product containing (**3**) and ethynylcyclopentadiene[1–3] was converted with dimethylamine into the stable 6-dimethylamino-6-methylfulvene (**5**) [yield 62% based on (**1**)] whose ^{13}C n.m.r. spectrum has been analysed previously.[2,5] The spectrum shows a *ca.* 14·7% ^{13}C-peak for the methyl group at C(7) (*i.e.* a *ca.* 14·7% decrease of the ^{12}C-content) implying that *ca.* 83% of (**1**) contracts by the direct route, (**1**) → (**2**) → (**3**), and a scrambling process occurs to the extent of *ca.* 17%.

In a second experiment, (**1**) was flash-pyrolysed at 1000 °C at 10^{-3} mmHg and the derived fulvene (**5**) (58%) now showed *ca.* 80% scrambling of all carbon atoms (*i.e. ca.* 20% direct ring contraction).

In a third experiment, (**1**) was pyrolysed at 700 °C at 10^{-3} mmHg (*i.e.* under conditions expected to result in $<17\%$ scrambling). The vinylidenecyclopentadiene formed was then repyrolysed at 1050 °C at 10^{-3} mmHg and treated with dimethylamine to give (**5**) (42%) whose ^{13}C n.m.r. spectrum now demonstrated *ca.* 100% randomization of all carbon atoms. It is certain, therefore, that scrambling takes place after ring contraction [(**3**) → (**4**)].‡

From these experiments it is still not clear how the actual scrambling takes place. However, since [1-^{13}C]-phenylcarbene also yields automerized (**3**),[2] one possibility would involve a thermal interconversion of (**3**) and phenylcarbene. Such a process would demand that a methyl derivative of (**3**) reverts to a tolylcarbene, the latter in turn rearranging[1,6] to styrene and benzocyclobutene. Thus (**7**), which has been prepared previously by Wiersum[1,7] by



Scheme 1

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‡ Carbon randomization is also observed in the molecular ion of benzocyclopropene (E. Wentrup-Byrne, O. F. Gülacar, P. Müller, and A. Busch, *Org. Mass Spectrometry*, submitted for publication).

pyrolysis of 6-methylphthalide (**6**), was converted into styrene and benzocyclobutene when pyrolysed at 1000 °C (Scheme 1).[8]

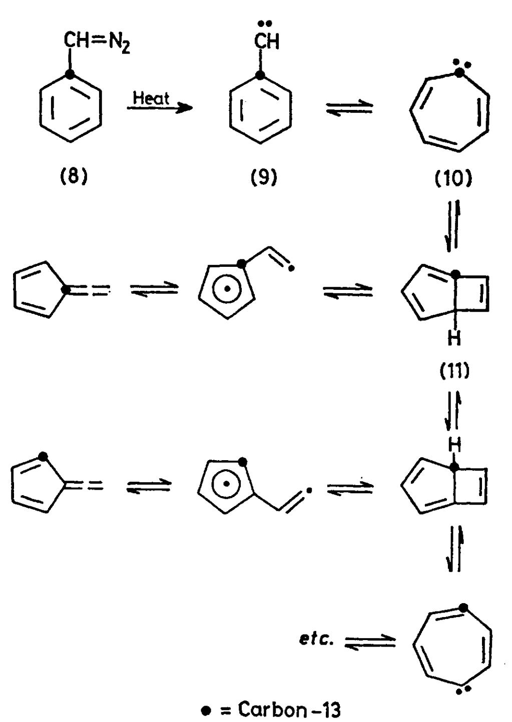
In order to investigate the path(s) connecting (**3**) and phenylcarbene, [1-^{13}C]phenyldiazomethane (**8**), prepared by standard procedures from [1-^{13}C]benzoic acid, was pyrolysed under the mildest possible conditions to give (**3**) (590 °C and 5—7 mmHg N_2 carrier gas).[1] The ^{13}C n.m.r. spectrum of the derived and recrystallized (**5**) (20 mg) showed that the quaternary C(5) was almost three times more labelled than any other carbon atom. The extent of ^{13}C-labelling decreased in the order: $C(5) > C(1)$ and $C(4) > C(2)$ and $C(3) > C(6) > C(7)$ [the attribution of peaks to C(1) and C(4) *vs.* C(2) and C(3) is tentative, based on the analysis by von Philipsborn *et al.*[5]].

When the pyrolysis of (**8**) was carried out at 700 °C and 10^{-3} mmHg, the excess of label at C(5) in (**5**) was hardly outside experimental error, and at 900 °C and 10^{-3} mmHg the ^{13}C n.m.r. spectrum was indistinguishable from that of unlabelled (**5**).

The excess label at C(5) in the 590 °C pyrolysis rules out any direct ring contraction in phenylcarbene (**9**) as well as pre-equilibrium interconversion of phenylcarbene and benzocyclopropene or methylene cyclohexadienylidene (**2**). The simplest mechanism explaining these results is shown in Scheme 2. Two features are important: (i) the results of experiments with (**1**) and (**7**) require that the whole sequence be reversible, and (ii) ring contraction appears to take place *via* bicyclo[3.2.0]hepta-1,3,6-triene (**11**), which is formed by electrocyclization in cycloheptatrienylidene (**10**).

In connection with this new mechanism it may be relevant to mention that the flash pyrolysis of norbornadien-7-yl acetate at 700 °C yields acetic acid and (**3**),[9] possibly *via* 7-norbornadienylidene[10] which rearranges to (unlabelled) (**11**). At 450 °C heptafulvalene, the dimer of (unlabelled) (**10**) is formed.[10]

It should be noted that the mechanisms of ring contraction in phenylnitrene[11] and phenylcarbene are quite different, and it is not possible (nor necessary) to force the two reactions to fit a single mechanistic scheme.



Scheme 2

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