Tetrahedron. Vol. 30, pp. 1301 to 1311. Pergamon Press 1974. Printed in Great Britain

THERMOCHEMISTRY OF CARBENE AND NITRENE REARRANGEMENTS[a]

CURT WENTRUP
Institut de Chimie Organique, Université de Lausanne, Rue de la Barre 2,
CH-1005 Lausanne, Switzerland

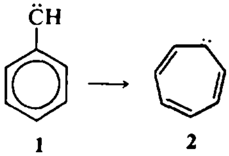
(*Received in the UK* 28 *June* 1973; *Accepted for publication* 9 *October* 1973)

Abstract—Thermochemical estimates for aromatic carbenes and nitrenes and their interconversions are reported and allow a unifying explanation of the majority of the experimental data published to date. Chemical activation is a very important, but hitherto ignored factor in these rearrangements. This has given rise to several misinterpretations in the literature, which are now corrected.

The rearrangements of aromatic carbenes and nitrenes are being extensively discussed in the current literature. It is the purpose of the present paper to present thermochemical estimates[1] which support recent semi-empirical calculations[2] and clarify the mechanistic speculation on the subject. Heat of formation data and the means of their calculation are indicated in Table 1.

1. *The phenylcarbene–cycloheptatrienylidene and related rearrangements*

The interconversion of phenylcarbene (**1**) and cycloheptatrienylidene (**2**) occurs in the gas-phase at 250–800°,[3] but even the direction of the equilibrium is a matter for conjecture.[3a,bd] Consider the forward reaction:



(1)

From the values in Table 1 the calculated enthalpy change for reaction (1) is *ca* + 13 kcal/mol for the *triplet* species, in good agreement with three different semi-empirical calculations for the *singlets* (Table 2), indicating that all four methods may reliably be used to estimate *qualitative* energy differences for carbenes.

Since it is the first excited singlet carbenes which are thought to be involved in rearrangements, it is important to estimate their relative energies. It is assumed throughout this paper that estimated energy *differences* for triplet carbenes (and nitrenes) are not significantly different from those for the singlets. The smaller the singlet–triplet separation the more correct this assumption will be. For methylene the singlet–triplet separation is converging on a value of ≈ 8–9 kcal/mol,[20,*] and since due to resonance, singlet phenylcarbene ($^1\mathbf{1}$) should be relatively more stabilized than $^1CH_2$, a maximum value of $\Delta H_f^0(^1\mathbf{1}) \simeq 110$ kcal/mol is obtained. This is in good agreement with the result of a MINDO/2 calculation[16] (107 kcal/mol). Singlet cycloheptatrienylidene ($^1\mathbf{2}$) is expected[21] to have some tropylium ion-like stabilization, although the ground state is probably still a triplet, hence $115 \leq \Delta H_f^0(^1\mathbf{2}) < 123$ kcal/mol. For diarylcarbenes the singlet–triplet separation may be as low as 5 kcal/mol.[20c] If the ground state of cycloheptatrienylidene is a singlet, the heat of reaction **1** may be less than 13 kcal/mol.

In order to test the predictive power of the thermochemical estimates, consider the model reactions of phenyl-2-naphthylcarbene (**3a**) (Scheme 1). The carbene **3** can in theory undergo three different ring expansion reactions, (2)–(4). Clearly, reaction (2), formally an insertion into the 1,2-bond in naphthalene is favoured on thermochemical grounds,† and this in fact is the only reaction observed in the unsubstituted 2-naphthylcarbene[22] (*vide infra*). This was interpreted[22] as evidence for reaction *via* the bicyclic intermediate **7**, because it was felt that an *electrophilic*‡ carbene would add preferentially to the 1,2-bond, which has the highest bond order. Since, however, "insertion" into the 2,3-bond would be *ca* 15 kcal/mol more endothermic (reaction (3)), a thermochemical explanation will suffice, and there is as yet little basis for

---

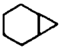
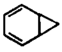
[a] This work was presented in parts in a series of seminars at Scandinavian Universities in March 1973.

*For a review of theoretical values, see M. J. S. Dewar, R. C. Haddon and P. K. Weiner, *J. Am. Chem. Soc.* **96**, 253 (1974). The experimental ΔH_f^0's given by N. Bodor, M. J. S. Dewar and J. S. Wasson, *Ibid.* **94**, 9095 (1972), are in error.

†This requires bond alternation. A CNDO/2 study agrees.[2a]

‡Ring expansion in aromatic carbenes may rather be regarded as a nucleophilic process of the carbene.[2a] E.g. phenyl-4-pyridylcarbene undergoes *ca* 11 times more expansion of the pyridine than of the benzene ring.[23]

Table 1. Heat of formation data[a]

Compound	ΔH_f°(kcal/mol)	Source
$^3CH_2$	92 ± 1	ref.[4]
^{3}**1**	102·2 ± 1	from $\Delta H_f^\circ(^3\mathbf{1}) \cong \Delta H_f^\circ(^3CH_2) + \Delta H_f^\circ$(styrene)[1] − ΔH_f°(ethylene)[1] − R.E.(benzyl)[4c] = 92 ± 1 + 35·2 − 12·5 − 12·5
	101·5 ± 1	from $\Delta H_f^\circ(^3\mathbf{1}) \cong \Delta H_f^\circ(^3CH_2) + \Delta H_f^\circ(\phi CHO)$[1] − $\Delta H_f^\circ(CH_2O)$[6] − R. E. (benzyl)[4c] = 92 ± 1 − 6 + 28 − 12·5
	103	from $^3CH_2(92) + \phi\text{–}\dot{C}H_2(44{\cdot}9) = \dot{C}H_3(34) + {}^3\phi\text{–}\ddot{C}H$
	98 ± 4	from $\phi\text{–}\dot{C}H_2$(45 ± 1[4c]) → $\phi\text{–}\ddot{C}H + H\cdot$(52·1[6]) + $DH^\circ(\dot{C}H_2\text{–}H)$[5] (105 ± 3)
^{3}**2**	115·5	from $\Delta H_f^\circ(^3\mathbf{2}) \cong \Delta H_f^\circ(^3\mathbf{1}) + \Delta H_f^\circ$(tropone)[b] − $\Delta H_f^\circ(\phi CHO)$[1] + R. E. (benzyl)[4c] + R. E. (tropone)[8,9] − R. E. ($c\text{-}C_7H_7\cdot$)[9] = 102 + 13·1 + 6 + 12·5 + 11·9 − 30
	116	from $\Delta H_f^\circ(^3\mathbf{2}) = \Delta H_f^\circ(c\text{-}C_7H_7\cdot)$[9] + [$\Delta H_f^\circ(C_7H_7\cdot$ non-resonating) − $\Delta H_f^\circ(c\text{-}C_7H_8)$][9] = 96 + 20
$^3\phi_2C$:	~ 108	from $\phi_2\dot{C}H$(60[4c]) → $\phi_2C: + H\cdot$(52·1[6]) + $DH^\circ(\phi_2\dot{C}\text{–}H)$[c] (100)
	≤ 110	from $\Delta H_f^\circ(^3\phi_2C:) \cong \Delta H_f^\circ(^3\phi\ddot{C}H) + \Delta H_f^\circ(\phi_2CO)$[1] − $\Delta H_f^\circ(\phi CHO)$[1] − R. E. (benzyl)[d]
^{3}**3a**	≤ 126	from $\Delta H_f^\circ(\phi_2C:)$ and group equivalents.
^{3}**4a**	140	from ΔH_f°(benzo[d]tropone)[b] = 16·2 and group equivalents.
^{3}**5a**	155	from ΔH_f°(benzo[c]tropone)[b] = 31·4 and group equivalents.
^{3}**6a**	153	from $\Delta H_f^\circ(^3\mathbf{2})$ and group equivalents.
^{3}**8**	~ 118	from $\Delta H_f^\circ(^3\mathbf{1})$ and group equivalents.
^{3}**9**	~ 118	from the benzotropones (*vide supra*) and group equivalents.
^{3}**10**	~ 116	
^{3}**11**	~ 133	
	0·4 ± 1	ref.[10]
	55·7 ± 1	from 0·4 ± 1 + $\Delta\Delta H_f^\circ$( − )[1]
12	≥ 128	from 55·7 ± 1 + $\Delta\Delta H_f^\circ$( )[1] + extra strain[11] ≥ 55·7 + 53·9 + 18·5
13	≥ 87 ± 5[h]	from $\Delta H_f^\circ(\mathbf{12})$ − R. E. (ϕH) ≥ 128 − 36 = 92
		and $\Delta H_f^\circ(\mathbf{14})$ − DH°(ArC–C)[6] + E_{strain}()[12] + extra strain[11] ≥ 105 − 93 + 52 + 18·5 = 82.
^{3}**14**	105 ± 2	from $\Delta H_f^\circ(\phi\text{–}\dot{C}H_2)$[4c] + $\Delta\Delta H_f^\circ(\phi\ \ - \phi H)$[4c] = 45 ± 1 + 80 ± 1 − 20
15	~ 80	from $\Delta H_f^\circ \cong \Delta H_f^\circ$(fulvene)[e] + $\Delta\Delta H_f^\circ$(allene − ethylene)[1] ~ 45·5 + 34·5
	88	ref.[13]: from group equivalents; apparently from ΔH_f°(cyclopentadiene) + $\Delta\Delta H_f^\circ$(butadiene − propene) + $\Delta\Delta H_f^\circ$(allene − ethylene).
16	~ 81	from group equivalents.[1]
17	≃ 98	from ΔH_f°(cryst)[14] + ΔH°(subl)[g] ≃ 70 + 28
$CH_2{=}N_2$	65 ± 5[f]	ref.[1,4b–c]
18	~ 87 ± 5	from CH_2N_2 and group equivalents.
29	~ 110	from $\Delta H_f^\circ(\mathbf{17})$ and group equivalents.
30	89·5 ± 8	from kinetics; see text
31	~ 99 ± 5	from $\Delta H_f^\circ(\phi CHN_2)$ and group equivalents.
^{3}**32**	114	from $\Delta H_f^\circ(^3\mathbf{1}) + \Delta\Delta H_f^\circ$(pyridine − benzene)[1] ≈ 102 + 12
^{3}**33**	125	from $\Delta H_f^\circ(^3\mathbf{2}) + \Delta\Delta H_f^\circ$(imine − alkene)[1] ≈ 115 + 10
$NH(^3\Sigma^-)$	≈ 90	ref.[15]
^{3}**34**	≈ 100	from $\Delta H_f^\circ \cong \Delta H_f^\circ(^3\mathbf{1}) + \Delta H_f^\circ(NH) - \Delta H_f^\circ(CH_2)$
	100 ± 4	from $\phi\text{–}N{=}N\text{–}\phi \to 2\phi\text{–}N + DH^\circ(N{=}N)$[6,17] ~ 97[16] 100 ± 4
^{3}**35**	~ 115	from $\Delta H_f^\circ(\phi\text{–}\dot{N}H)$[4c] ~ 53 and from $\Delta H_f^\circ(\mathbf{14})$, and group equivalents.
$\phi\text{–}N_3$	97 ± 2	from CH_3N_3, $C_2H_5N_3$,[4c] and group equivalents; and Refs 18, 19
37	~ 64	from group equivalents.[1]

[a] Estimated values by the group additivity method.[1] All values refer to the ideal gas state at 298 K.

[b] Calculated from heat of atomization data.[7]

[c] Precise data are lacking; *cf* ref.[5,6]

[d] This second benzyl resonance in ϕ_2C: is presumably < 12·5 kcal/mol due to non-linearity of the molecule.[4c]

[e] N. C. Baird and M. J. S. Dewar (*J. Chem. Phys.* **50**, 1262 (1969)) estimate ΔH_f°(fulvene) ≈ 44 kcal/mol, and quote ΔH_f°(6,6-dimethylfulvene) = 31 kcal/mol. From the latter and group equivalents[1] ΔH_f°(fulvene) ~ 47 kcal/mol is obtained.

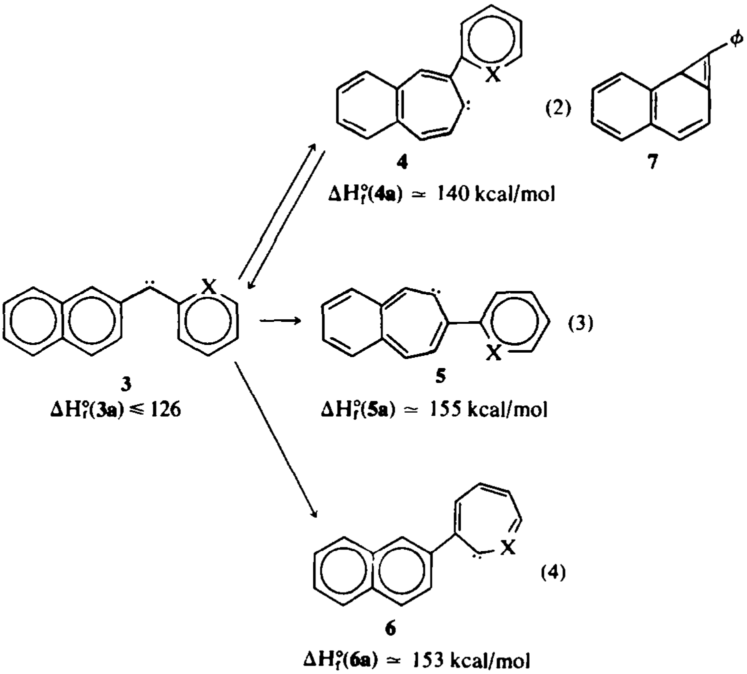
[f] Values between 49 and 103 kcal/mol have been suggested for $\Delta H_f^\circ(CH_2N_2)$; see W. Kirmse, Carbene Chemistry, second edition, Academic Press 1971, p. 25.

[g] The value of ΔH°(subl) is an assumed one; compare however ref.[14]

[h] Note added in proof: new experimental value derived from W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, J. L. Margrave, R. L. Sass, J. J. Shieh, P. G. Werness, and J. L. Wood (*J. Am. Chem. Soc.* **95**, 7879 (1973)) is 89 ± 1 kcal/mol.

Table 2. Enthalpy change ($\Delta H_r(1)$) for reaction (1)

Method	$\Delta H_r(1)$ (kcal/mol)	Ref
CNDO/2	11·5	2*a*
Extended Hückel	16·4	2*a*
MINDO/2	13·0	16
Thermochemical	~ 13	this work



SCHEME 1. **a**: X = CH; **b**: X = N

mechanistic discussion in terms of intermediates such as **7**.

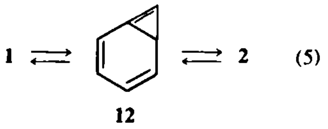
In 2-pyridyl 2-naphthylcarbene (**3b**) we also found [2a] that reaction (2) was favoured over reaction (4), and reaction (3) was not observed (in these reactions all ΔH_f^0's would be *ca* 12 kcal/mol higher than for **3a**–**6a**).

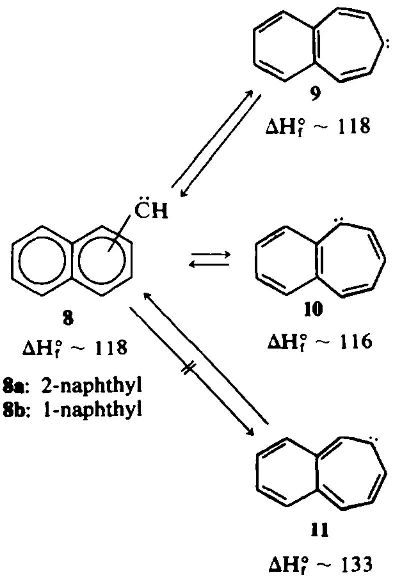
The naphthylcarbenes and the isomeric benzocycloheptatrienylidenes are indicated in Table 1 and Scheme 2.

The experimentally observed[22] facile interconversion of **8a** and **9**, even in solution, and the absence of the reaction **8a** → **11**, is in agreement with the thermochemistry.* It may be further noted that **11** may be expected to rearrange to **8** (**a** or **b**), and that 1-naphthylcarbene (**8b**) might rearrange to **10**. At present no information on these reactions is available.

2. *The question of bicyclic intermediates*

Many assumptions of the existence of bicyclic intermediates (e.g. **7** and **12**) in the ring expansion reactions are found in the literature (for Refs see e.g. [2a]):



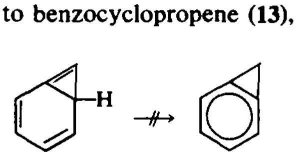


SCHEME 2

---

*This requires bond alternation. A CNDO/2 study agrees.[2a]

There is no experimental fact which requires their existence, but there is some evidence against them. If **12** were an intermediate, it might be expected to rearrange to benzocyclopropene (**13**),



(6)

12 $\Delta H_f^\circ \geq 128$ **13** $\Delta H_f^\circ \geq 87 \pm 5$

as this reaction should be very exothermic (*cf* Table 1), and the bond dissociation energy for the migrating proton in **12** should be very low. However, no **13** is obtained from phenylcarbene[3] under conditions (300–500°) where **13** is isolable[24a] and where the phenylcarbene–cycloheptatrienylidene rearrangement does take place.[3b] The intense and unpleasant smell of **13** would have allowed subjective detection of as little as 10^{-4}%. It could be argued that the very exothermicity of reaction (6) would mitigate against the isolation of **13**; i.e. it could suffer chemically activated ring opening and consequent ring contraction[24] to fulvenallene and ethynylcyclopentadiene (**15** and **16**; see Fig 1 and sections 3, 4). These products are not, however, isolable below 500°; nor are the dimers of **14** (Fig 1), anthracene and phenenthrene.[24a] As a consequence, benzocyclopropene is not formed even as a transient intermediate from phenylcarbene below 500°, and the existence of the bicyclic species **12** as a long-lived intermediate can be ruled out.

The same argument may be applied to the rearrangements of tolylcarbenes.[25] These reactions[25a,d] were carried out at a relatively high pressure (up to 1 atm) and low temperature (down to 150°), where collisional deactivation of any benzocyclopropenes formed might have been expected.

The heat of formation of **12** is estimated in Table 1 from that of norcarane. Disregarding any additional strain due to the bridgehead double bond, ΔH_f^0 would be $109{\cdot}6 \pm 1$ kcal/mol. The extra strain in benzocyclopropene (**13**) due to angle deformation has been estimated as $\geq 18{\cdot}5$ kcal/mol.[11] If the strain in **12** is at least as much as in **13**, the value of $\Delta H_f^0(\mathbf{12}) \geq 128$ kcal/mol is obtained.* This is at least 5 kcal/mol higher than $\Delta H_f^0(^1\mathbf{2})$ for singlet cycloheptatrienylidene. If the ground state of cycloheptatrienylidene is in fact a singlet, the difference in energy between **2** and **12** will be even higher. Although this estimate is somewhat uncertain, it does indicate the impropability of finding the *intermediate* **12** in reaction (5).

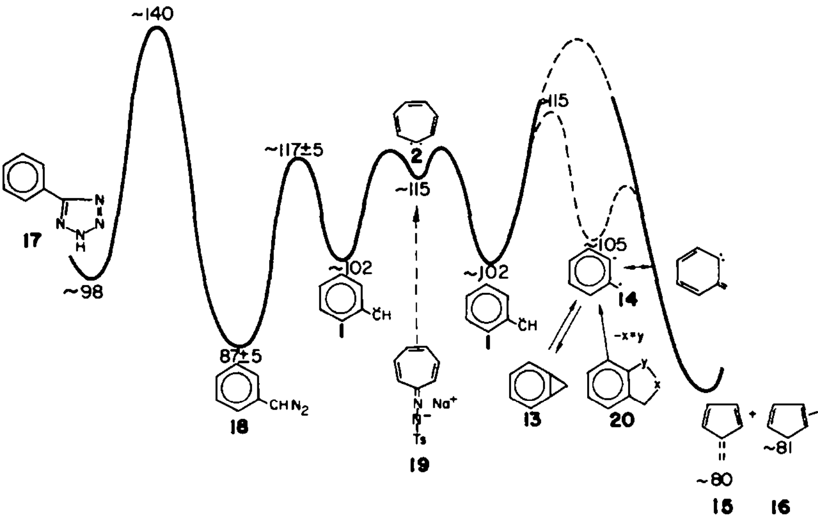


Fig 1. The C_7H_6 energy profile (values in kcal/mol).

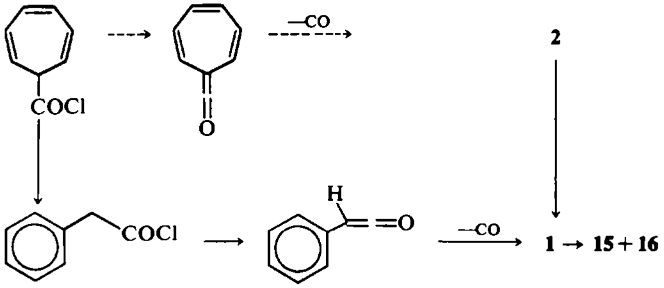
3. *The* C_7H_6 *energy profile*

The formation and rearrangements of the C_7H_6 species are depicted in Fig 1. The precursors, 5-phenyltetrazole (**17**) and phenyldiazomethane (**18**) are considered. In analogy with compound **29** (see section 6) the activation energy for decomposition of **17** is taken as *ca* 41·5 kcal/mol, and it is assumed that **18** is an intermediate. The activation energy for decomposition of **18** does not appear to have been measured. However, from the rate constant in acetonitrile at 85° ($7{\cdot}83\,.\,10^{-6}\,s^{-1}$)[27] and using the A-factor for diphenyldiazomethane in the same solvent ($10^{13\cdot2}$)[28] we get $Ea(\phi CHN_2) = 30{\cdot}0$ kcal/mol. From Fig 1 it is now clear that when the reactions

---

*For comparison, the extra strain in bicyclo[3.3.1]non-1-ene, due to a bridgehead double bond in a six-membered ring is *ca* 12 kcal/mol.[26]

are carried out in the gas-phase at low pressure, where collisional deactivation will be slow, the carbene formed from phenyldiazomethane (**18**) may possess just about enough energy to undergo ring expansion to **2**. This is in agreement with the fact that this rearrangement has been observed under very mild conditions (as low as 250° in a flow-system[3b]) in the gas-phase, but not in solution. The carbene (**1**) formed from **17** will, however, be chemically activated by as much as 40 kcal/mol plus a part of the thermal energy carried by **17**. If the carbene is not quickly deactivated, this energy may be used to cross the barrier to ring contraction (**1** → **15** + **16**). Experimentally, phenyldiazomethane (**18**) yields **15** + **16** above *ca* 600°,[3c,24a] in low yield, after previous interconversion with **2**.[3e] This reaction should be easier for the carbene from 5-phenyltetrazole (**17**) (*cf.* the reaction of **29**, section 6), a point which is difficult to ascertain because **17** undergoes preferentially a retro-1,3-dipolar-addition reaction to give benzonitrile and hydrazoic acid.[31] The activation energy for ring contraction in phenylcarbene may be estimated as lying between 15 and 40 kcal/mole (*cf* Fig 1), and in view of the high temperature required, Ea is likely to be considerably more than 15 kcal/mol.



SCHEME 3

It is now very simple to explain why cycloheptatrienylidene (**2**) (from the sodium salt of tropone tosylhydrazone (**19**)) itself does not undergo double ring contraction to **15** + **16**, or does so only to a very small extent.[3d,e] The activation energy for elimination of N_2 from diazocycloheptatriene is apparently so low that this compound decomposes spontaneously when formed by pyrolysis of the salt **19** at 90°.[30] The cycloheptatrienylidene (**2**) so formed reacts largely in the solid state (*cf* the yields[3d]), and if it arrives in the gas-phase at all, it will not be chemically or thermally activated. At most it can contract to phenylcarbene[3d] which will not be able to pass the barrier to fulvenallene (**15**) and **16**.

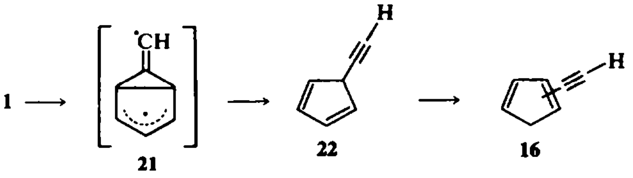
There exists another set of reactions where the importance of chemical activation in the formation and ring contraction of **1** is demonstrated:[31] cycloheptatriene - 7 - carbonyl chloride at $600°/10^{-2}$ mm yields benzyl chloride and fulvenallene (**15**) (*cf* the analogous elimination of CO and HBr from acetyl bromide[32]). Under the same conditions phenylacetyl chloride does not react.

Irrespective of the sequence of the rearrangements (Scheme 3), the higher amount of energy available in the thermolysis of cycloheptatriene-7-carbonyl chloride must come from chemical activation. (The rearrangement of cycloheptatriene to toluene is exothermic by *ca* 32 kcal/mol,[1,4c] and the Ea is *ca* 52 kcal/mol.[4c] Ea for decomposition of ketene is *ca* 59·3 kcal/mol.[33])

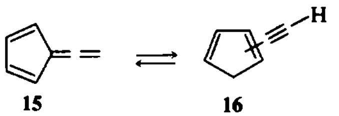
The contention that it is a vibrationally "hot" (*i.e.* thermally or chemically activated) phenylcarbene which undergoes ring contraction was first put forward by us in 1970.[34] This fact was unfortunately overlooked by Crow and Paddon-Row[3e] in their review of our conclusions.

4. *The ring contraction reaction*

It has usually been assumed that ring contraction in aromatic carbenes and nitrenes takes place *via* an intermediate or transition state, **21** (see e.g. Ref 2*a*,*b*):



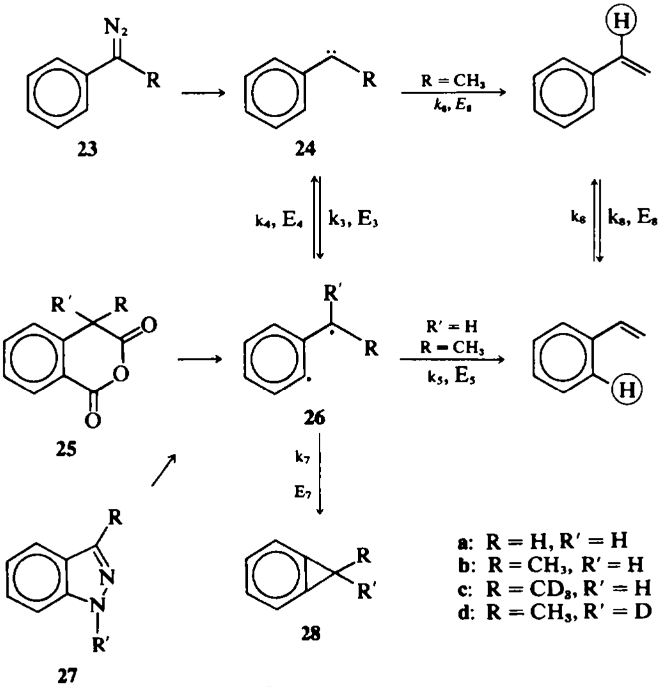
However, if this were the case, **22** would be the primary product, and this would be expected to rearrange to the conjugated ethynylcyclopentadienes **16**. Experimentally, however, fulvenallene (**15**; Fig 1) is the predominant product from phenylcarbene, even at the lowest temperature (590°) where the reaction can be observed.[3c,24a] Since the interconversion is estimated to be almost thermoneutral[24c] (Table 1) (or exothermic towards **16** if Bergman's[13] ΔH_f^0(**15**) is used); since the interconversion occurs only at elevated temperatures,[24,35] and since the ratio **16**:**15** increases with the temperature,[3c,24a]* it is difficult to avoid the conclusion that fulvenallene (**15**) is the primary product from phenylcarbene, and the most reasonable way to explain its formation is by the postulate that phenylcarbene first rearranges to methylenecyclohexadienylidene (**14**; Fig 1). It is most likely that the latter intermediate is also formed from compounds of the type **20** and benzocyclopropene (**13**) (Fig 1) which are known to yield fulvenallene as the primary product.[24] The ring contraction reaction then becomes a unifying process of the Wolff-rearrangement type[2a,36,37] through which many different carbene, nitrene, and diradical precursors pass (for nitrenes, see section 6).



15 **16**

Compounds like **20** and **13** give much better yields of fulvenallene than does phenyldiazomethane (**18**). The barrier between **1** and **14** must then be higher than the one between **14** and **15** (Fig 1). There will then be little impetus for the diradical **14** to rearrange to the carbene **1**. This is not to say that the reaction **14**→**1** cannot take place: it depends on the amount of energy available to **14**.

From Fig 1 it is seen that when fulvenallene originates from phenylcarbene (**1**) it will be more highly chemically activated (by 40–60 kcal/mol) than when it originates from **20** or **13**. This explains why, even at the lowest temperatures, phenylcarbene gives some "residual" enthynylcyclopentadiene (**16**); more so than does **13** or **20**.[3c,24a]



SCHEME 4

5. *On the interconversion of arylcarbenes and* 1,3-*diradicals*

It was recently reported [38]† that arylcarbenes and isomeric 1,3-diradicals interconvert in the gas-phase at 630–720°/~ 0·05 mm (e.g. $1 \rightleftarrows 14$ or

---

*Repeated pyrolyses of a mixture of **15** and **16** at 1000°/10^{-2} mm causes the ratio to change towards a value of *ca* 1:4,[24a] which is compatible with both thermodynamic and kinetic equilibrium if the heats of formation of **15** and **16** are about equal, and the tautomeric nature of **16** results in the existence of 4 different molecules of **16** per molecule of **15**.

†There appears to be a typing error in Ref 38: the compound numbers (2) and (3) in the Table should be interchanged.

24 ⇆ **26**; Scheme 4). In order to avoid too much confusion it is necessary to point out that this conclusion, as well as one published previously,[39] is not secure on the basis of the experiments published so far.

The conclusion[38] was was based on the fact that 5–9% ring-deuterated styrenes (presumably[38] *ortho*) were formed in the thermolyses of the carbene and diradical precursors **23c** and **25d** (Scheme 4). Previously, the formation of 15–18% ring-deuterated styrenes in the thermolysis of 1D-3-methylindazole (**27d**) was interpreted as evidence for either the interconversion **24** ⇆ **26**, or the occurrence of H shifts in the starting material.[39]

Using the authors' terminology, assumptions and yields,[38] one easily calculates for the carbene **24** at 720°:

$$\frac{\%\ \text{carbene product}}{\%\ \text{diradical product}} = k_6/k_4(1 + k_3/k_5) \cong k_6/k_4\,.\,1{\cdot}09$$

$$k_6/k_4\,.\,1{\cdot}09 \cong 94{\cdot}8/5{\cdot}2$$
$$k_6/k_4 \cong 16{\cdot}75$$

If the Arrhenius equation were applicable under the conditions of the experiments,[38] and if the A-factors corresponding to k_4 and k_6 were equal, one would then have for the difference in activation energies: $E_4 - E_6 = 5{\cdot}56$ kcal/mol.

The magnitude of E_6 can be obtained from recent theoretical calculations which indicate that the isomerization of ethylidene to ethylene has virtually no activation energy.[40] If as an upper limit we choose $E_6 = 5$ kcal/mol,[40b] we get $E_4 \sim 11$ kcal/mol. This figure must be taken with great reservation, since the Arrhenius equation will not be strictly applicable to the experiment (~ 0·05 mm; short contact time), and the A-factors may not be equal. If the value of $E_4 \sim 11$ kcal/mol is accepted, however, it is clearly at variance with the conclusion reached in section 3, that the barrier between **1** and **14** (**24a** and **26a**) must be considerably more than 15 kcal/mol.

Irrespective of the reliability of E_4, the Crow–Paddon-Row scheme suggests that phenylcarbene (**24a**) and the 1,3-diradical (**26a**) must interconvert rapidly at temperatures of 300–500° (that is, at temperatures where phenylcarbene does not yet undergo ring contraction, and where benzocyclopropene (**28**) is stable). As a consequence, phenylcarbene should be observed to rearrange quantitatively to benzocyclopropene.* None of these reactions are observed.[24a,25c]

An alternative explanation of the reported[38] Deuterium scrambling comes from the observation[38] that styrene itself undergoes such scrambling under the reaction conditions: 0·6% at 720°, and 15% at 800°. Assuming that the flow-rates were the same in these two experiments, a very rough estimate of the activation energy for H-scrambling in styrene is obtained: $E_8 = 84$–90 kcal/mol. The slightly higher yields of H-scrambled styrenes from **23c** and **25d** (5–9% at 630–720°) are readily accounted for by chemical activation.[42] The reaction **24b** → styrene is probably exothermic by more than 55 kcal/mol to which comes any excess chemical and thermal activation carried by the carbene **24**. When the isomerization of styrene itself does take place (0·6%) at 720°, then it is not surprising that **24b** gives a higher yield of this reaction (5·2%) at the same temperature. If the pressure were lowered, higher yields of styrene scrambling would be expected. The observation of a higher yield in the thermolysis of 1D-3-methylindazole[39] (**27d**) could be due, wholly or in part, to a lower effective pressure or a higher degree of chemical activation† carried by the initial 1,3-diradical **26d**. Other things being equal, the effective pressure in the thermolysis of **25** will be higher than for **27** for the simple reason that three molecules are formed from **25**, but only two from **27**.

CONCLUSION

The reports[38,39] have no bearing on the question of interconversion of arylcarbenes and 1,3-diradicals. None of the mechanisms suggested for H-migration in the thermolysis of 3-methylindazole[39] are required. H-shifts may occur at any place along the reaction coordinate in the thermolyses of unsubstituted indazole and pyrazolo [3, 4 - *b*] pyridine.[43]

6. *The* C_6H_5N *energy profile*

Phenylnitrene (**34**), 2-azepinylidene (**33**), and 2-pyridylcarbene (**32**) interconvert in the gas-phase, and the equilibrium is strongly in favour of the nitrene.[2a–c,29,44] The intermediates and precursors are shown in Fig 2.

The required heats of formation are estimated in Table 1. 2 - Pyridyldiazomethane (**31**) cannot be isolated as it cyclizes to *vic*-triazolo - [1, 5 - *a*] pyridine (**30**). However, both **30** and 2 - (5 - tetrazolyl)pyridine (**29**) can be used as precursors for 2-pyridylcarbene,[2a,29,44a] and the fact that **30** can be isolated[2a] from the thermolysis of **29** shows that 2-pyridyldiazomethane (**31**) is an intermediate.

The heat of formation of **30** is estimated from kinetic measurements. The activation energy for its decomposition in diphenylether and in nitrobenzene at 180–220° was E_a[30] = 43·5 ± 1 kcal/mol. If the activation energy for decomposition of 2-pyridyldiazomethane (**31**) is the same as for phenyldiazomethane (30 kcal/mol; see section 3), the heat of formation of **30** will be *ca* 13·5 kcal/mol lower than that of **31** (in solution), or 85·5 ± 5 kcal/mol. Confirmation of this comes from the decomposition of **30** in the

---

*From the report[41] that triplet diradicals of the type **26** disappear above 77–100 K, and that benzocyclopropenes are isolated on warming to room temperature, E_7 for ring closure in the singlet diradical **26** can hardly be more than 10 kcal/mol.

†An indication that the latter effect is operating comes from the discovery[43] that pyrazolo [3,4 - *b*] pyridine yields 1 - cyanocyclopentadiene (**37**), probably *via* 3-pyridylcarbene and phenylnitrene (**34**); and this reaction requires chemical activation (see section 6 and Fig 2).

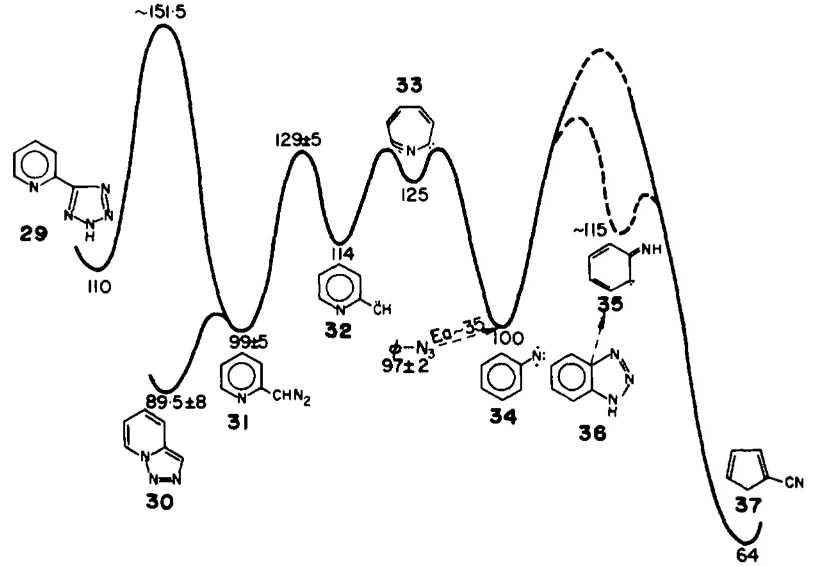


Fig 2. The C_6H_5N energy profile (values in kcal/mol).

presence of excess fumaronitrile (F), when an induced pseudo-first order reaction occurred, following a steady-state expression $k_{obs} = k_1k_2[F]/k_{-1} + k_2[F])$ with $E_{a(obs)} \sim$ 16 kcal/mol (*cf* Scheme 5). Thus $E_1(\mathbf{30} \rightarrow \mathbf{31}) <$ 16 kcal/mol. Assuming $E_1 = 14 \pm 2$ kcal/mol and using $E_{obs} = E_1 - E_{-1} + E_2$, where $E_2 \sim 8$ kcal/mol[45] we get $E_{-1} \sim 6 \pm 2$ kcal/mol, and the heat of diazo-tautomerization in **30** ~ 8 ± 3 kcal/mol. Since **31** cannot be observed by NMR at 150°, we can further limit E_{-1} to $4{\cdot}5 \pm 2$ kcal/mol, and the heat of tautomerization to $9{\cdot}5 \pm 3$, yielding $\Delta H_f^0(\mathbf{30}) = 89{\cdot}5 \pm 8$ kcal/mol, depending on the estimate for **31**.

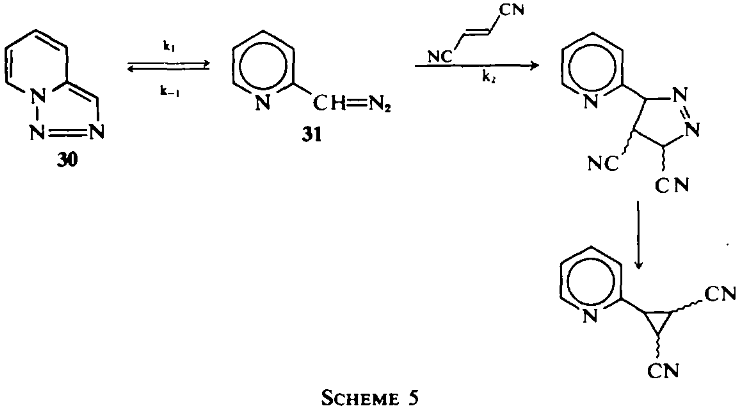
The pyrazoline formed by reaction of **31** with fumaronitrile decomposed under the reaction conditions (150–180°) giving a 2-pyridylcyclopropane (Scheme 5).*

The decomposition of tetrazolylpyridine (**29**) in diphenylether had $E_a^{29} = 41{\cdot}5 \pm 1$ kcal/mol and was independent of added fumaronitrile; hence the rate determining step is elimination of the first molecule of N_2.

From Fig 2 it is seen that the important difference between **29** and **30** as precursors of 2-pyridylcarbene is that **29** has both a higher heat of formation and a higher absolute activation energy for decomposition than **30**. When the thermolyses are carried out in the gas-phase at low pressure[2a,29,44] the carbene **32** generated from **29** will possess *ca* 20 kcal/mol more energy than the one from **30**. Provided that the ensuing rearrangements are faster than collisional deactivation, the carbene from **29** will be energetic enough to pass both the barriers to 2-azepinylidene and to phenylnitrene, and further on to 1 - cyanocyclopentadiene (**37**). This is true at pressures below *ca* 10^{-2} mm, where ring contraction to **37** is much more facile for **29** than for **30** or for phenylnitrene itself from phenyl azide.[2a,29,44] At pressure ≥ 10^{-1} mm the phenylnitrene generated from 2-, 3-, or 4 - (5 - tetrazolyl)pyridine can be collisionally deactivated, thus suppressing the for-

---

*Detailed kinetic experiments and data for 2 - pyridylcyclopropanes will be published in *Helv. Chim. Acta.*



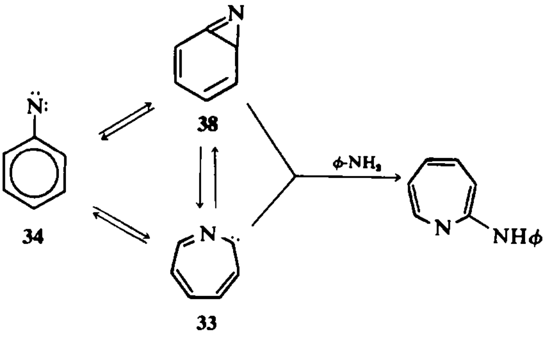
SCHEME 5

mation of **37** and yielding azobenzene instead.[46]

$2\phi\text{-N}\xrightarrow{\text{deactivation}}\phi\text{-N=N-}\phi$. The reaction temperature has relatively little influence on the reactivity of phenylnitrene: ring contraction to **37** is observable in the pyrolysis of **29** at $400°/10^{-3}$ mm,[2a] and rises to *ca* 60% at higher temperatures.[29] However, at $600°/10^{-1}$ mm **37** has almost disappeared, and azobenzene is isolated instead.[46]

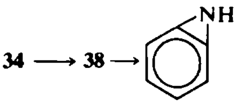
These experiments indicate the importance of chemical activation in the ring contraction of phenylnitrene, and an upper limit for the activation energy for ring contraction can now be given as $E_a(\mathbf{34}\rightarrow\mathbf{37})\leq 51$ kcal/mol (*cf* Fig 2). It is also seen from Fig 2 that when 2 - pyridylcarbene is generated from **30**, it may reach a point of 129 ± 5 kcal/mol at the transition state for its formation, *i.e.* enough to expand immediately to 2-azepinylidene (**33**) and to contract again to phenylnitrene, provided that the energy barriers to ring contraction in 2-azepinylidene are small. This reaction is observed,[44] but the phenylnitrene so formed has barely enough energy to contract to **37**. Thus the lower limit of $E_a(\mathbf{34}\rightarrow\mathbf{37})\geq 30\pm 5$ kcal/mol is obtained. Since the thermochemistry explains the observed reactions,[2a,29,44,47] there is no need for more obscure mechanistic explanations[29] invoking different spin states in the reactions of **29** and **30**. It should be remembered that phenylnitrene when generated directly from phenyl azide requires strong thermal activation in order to contract to **37**;[48] this is provided by rapid introduction of the azide into the furnace, which induces an explosive reaction.[48,49]

The activation energy for decomposition of phenyl azide itself is *ca* 35 kcal/mol,[50] *i.e.* enough to allow expansion to 2-azepinylidene.[44] The formation of azepines from thermolysis[51] or photolysis[52] of phenyl azides in aniline and other nucleophilic solvents could thus in principle involve the azepinylidene **33** rather than a fused azirine, **38**:



The wavelength-dependence reported by Odum and Wolf[52] for azepine formation is consistent with the endothermic reactions **34** → **33** or **34** → **38**.

As in the case of phenylcarbene (section 2) there is as yet no evidence for the existence of the azirine **38**. We have shown that the reaction

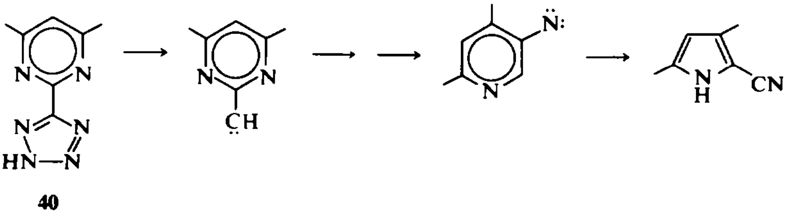


39

does not occur under conditions where 1*H*-benzazirine (**39**) appears to be capable of existence, and where the phenylnitrene-2-pyridylcarbene interconversion does take place.[53]

The ring contraction of phenylnitrene to cyanocyclopentadiene (**37**) is depicted in Fig 2 as a Wolff-type rearrangement *via* iminocyclohexadienylidene **35** (*cf* discussion in section 4).* It is known that benzotriazole (**36**) ring contracts to **37** much easier than phenylnitrene and in almost quantitative yield,[36] and that the intermediate **35** does not isomerise to phenylnitrene.[36,53] Therefore, the barrier between **34** and **35** is higher than the one between **35** and **37**. The high activation energy (30–50 kcal/mol) for the ring contraction of phenylnitrene would be rather unusual for such an exothermic reaction, if it were concerted. The postulated intermediacy of **35** thus seems energetically reasonable.†

This mechanism would explain why phenylnitrenes which lack *o*-hydrogens do not undergo ring



40

SCHEME 6

---

*An extended-Hückel calculation[54] indicates that singlet *syn*-**35** is about 18 kcal/mol higher in energy than singlet **34**. The thermochemical estimate (Table 1) gives 15 kcal/mol.

†When the transition state for ring contraction can be lowered by aromatic stabilization, as in *α*-hetarylnitrenes, the reaction may take place concertedly, without H-shift.[2b]

contraction: 2, 6 - dimethylphenyl azide does not give any cyanocyclopentadiene, although the three tolyl azides do.[44b,49,31] The three monofluorophenyl azides all contract to fluorocyanocyclopentadienes,[49] while it has been suggested that pentafluorophenyl azide undergoes ring expansion rather than ring contraction.[55]

The strongly exothermic nature of the ring contraction reaction causes the final product (**37**) to be chemically activated, and more so when originating from a nitrene (**34**) than from benzotriazole (**36**). This is also observed experimentally, for methylcyanocyclopentadienes undergo CN- and Me-group migrations much more readily in the thermolysis of tolyl azides[49] than in the thermolysis of methylbenzotriazoles.[36] The same is true for CN-group migration in cyanopyrroles obtained from pyridylnitrenes[3a,31] and 1*H* - 1, 2, 3 - pyridotriazoles, respectively.[36] Furthermore, cyanopyrroles are obtained from chemically activated pyridylnitrenes, which themselves are formed by rearrangement of 2- or 4-pyrimidyl- or 2-pyrazinylcarbenes from the corresponding 5-tetrazolyldiazines (e.g. **40**, Scheme 6). Not only does the ring contraction to cyanopyrroles occur under very mild conditions ($\geq 400°/10^{-2}$ mm) where the pyridyl azides themselves give only azopyridines; but in addition, both CN- and Me-group migrations occur in the products. The Me migration probably has an activation energy above 50 kcal/mol (*cf* methylcyclopentadienes[4c]). These group migrations can be suppressed by increasing the pressure, and therewith the rate of collisional deactivation.[56]

7. *Non-aromatic systems*

There are reactions known in which non-aromatic carbenes or nitrenes do yield strained bicyclic compounds, *e.g.* aza-analogues[57] of the cyclopropenes **41** and **42** indicated in Scheme 7.

The heats of formation in Scheme 7 are calculated by group additivity[1] from methylene and the required hydrocarbons.[1,10,58] No attempt has been made to optimize the values. The extra strain assigned to **41** is ≤ 10 kcal/mol; to **42** ≤ 20 kcal/mol. It is seen that these reactions become the less favoured the more unsaturation is introduced into the rings.[59] Even the reaction[60] **43** → **44** is estimated to be thermochemically feasible (using ΔH_f°(cyclopropyl) = $64 \pm 3{\cdot}5$ kcal/mol from the bond dissociation energy,[61] and $\Delta H_f^\circ(c\text{-}C_7H_9) = 46{\cdot}5 \pm 2$ extrapolated from cyclohexadienyl[6]). The instability of bicyclo [4.1.0] hepta - 2, 4, 6 - triene (**12**; section 2) can now be looked upon as due essentially to the loss of the benzene resonance.

Acknowledgement—This work was supported by the Schweizerischer Nationalfonds (Project No. 2.241.70).

REFERENCES

[1] 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)

[2a] C. Wentrup, C. Mayor and R. Gleiter, *Helv. Chim. Acta* **55**, 2628, 3066 (1972); [b] C. Wentrup, C. Thétaz and R. Gleiter, *Ibid.* **55**, 2633 (1972); [c] C. Wentrup, *Chimia Switz.* **26**, 654 (1972)

[3a] W. D. Crow and C. Wentrup, *Chem. Commun.* 1387 (1969); [b] R. C. Joines, A. B. Turner and W. M. Jones, *J. Am. Chem. Soc.* **91**, 7754 (1969); [c] P. Schissel, M. E. Kent, D. J. McAdoo and E. Hedaya, *Ibid.* **92**, 2147 (1970); [d] C. Wentrup and K. Wilczek, *Helv. Chim. Acta* **53**, 1459 (1970); [e] W. D. Crow and M. N. Paddon-Row, *J. Am. Chem. Soc.* **94**, 4746 (1972)

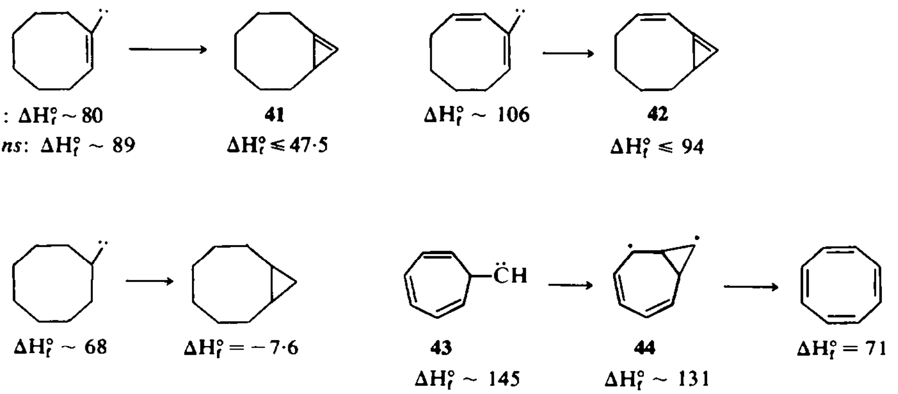
[4a] *JANAF Thermochemical Tables* (second Edition) D. R. Stull and H. Prophet *et al.*, NSRDS-NBS 37, U.S. Department of Commerce (1971); [b] A. H. Laufer and H. Okabe, *J. Phys. Chem.* **76**, 3504 (1972); *J. Am. Chem. Soc.* **93**, 4137 (1971); [c] S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, NSRDS-NBS 21, U.S. Department of Commerce (1970)

[5a] H. M. Frey, *Progr. React. Kinetics* **2**, 132 (1964); [b] G. v. Bünau, P. Potzinger and G. O. Schenck, *Tetrahedron* **21**, 1293 (1965)

[6] S. W. Benson, *J. Chem. Educ.* **42**, 502 (1965)

[7] M. J. S. Dewar and N. Trinajstić, *Croat. Chim. Acta* **42**, 1 (1970)

[8] 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)



SCHEME 7

[9] G. Vincow, H. J. Dauben, F. R. Hunter and W. V. Volland, *Ibid.* **91**, 2823 (1969)

[10] S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey and R. H. Boyd, *Ibid.* **92**, 3109 (1970)

[11] E. F. Ullman and E. Buncel, *Ibid.* **85**, 2106 (1963)

[12] R. B. Turner, P. Goebel, B. J. Mallon, W. v. E. Doering, J. F. Coburn, Jr., and M. Pomeranz, *Ibid.* **90**, 4315 (1968)

[13] R. G. Bergman, *Accounts Chem. Res.* **6**, 25 (1973)

[14] W. S. McEwan and M. W. Rigg, *J. Am. Chem. Soc.* **73**, 4725 (1951); M. M. Williams, W. S. McEwan and R. A. Henry, *J. Phys. Chem.* **61**, 261 (1957)

[15] K. F. Seal and A. G. Gaydon, *Proc. Phys. Soc.* **89**, 459 (1966); D. H. Stedman, *J. Chem. Phys.* **52**, 3966 (1970)

[16] E. Haselbach, Universität Basel, personal communication 1973, with permission to cite; preliminary calculation without minimization

[17] T. L. Cottrell, *The strengths of Chemical Bonds*, p. 278. Butterworths (1958)

[18] P. Gray and T. C. Waddington, *Proc. Roy. Soc.* **A235**, 481 (1956); B. L. Ewans, A. D. Yoffe and P. Gray, *Chem. Rev.* **59**, 515 (1959).

[19] H. Okabe and A. Mele, *J. Chem. Phys.* **51**, 2100 (1969)

[20a] H. M. Frey, *Chem. Commun.* 1024 (1972); [b] W. L. Hase, R. J. Phillips and J. W. Simons, *Chem. Phys. Letters* **12**, 161 (1971); [c] Z. Simon, *Acad. Rep. Pop. Roumaine, Studi si Cercetări Chim.* **11**, 171 (1963)

[21] R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.* **90**, 5457 (1968)

[22] T. Mitsuhashi and W. M. Jones, *Ibid.* **94**, 677 (1972); W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis and A. B. Turner, *Ibid.* **95**, 826 (1973)

[23] C. Wentrup and C. Mayor, *Schweir. Chem. Ges.* Autumn Meeting, Lugano, October, (1973)

[24a] C. Wentrup and P. Müller, *Tetrahedron Letters* 2915 (1973); [b] E. Hedaya and M. E. Kent, *J. Am. Chem. Soc.* **92**, 2149 (1970); [c] C. Wentrup, *Tetrahedron Letters* 2919 (1973)

[25a] W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *J. Am. Chem. Soc.* **92**, 4739 (1970); [b] E. Hedaya and M. E. Kent, *Ibid.* **93**, 3283 (1971); [c] U. E. Wiersum and T. Niewenhuis, *Tetrahedron Letters* 2581 (1973); footnote 12, and personal communication; [d] G. G. Vander Stouw, A. R. Kraska and H. Shechter, *J. Am. Chem. Soc.* **94**, 1655 (1972)

[26] P. M. Lesko and R. B. Turner, *J. Am. Chem. Soc.* **90**, 6888 (1968)

[27] D. Bethell and D. Whittaker, *J. Chem. Soc.* (B) 778 (1966)

[28] D. Bethell, D. Whittaker and J. D. Callister, *Ibid* 2466 (1965)

[29] W. D. Crow, M. N. Paddon-Row and D. S. Sutherland, *Tetrahedron Letters* 2239 (1972)

[30] W. M. Jones, Florida, personal communication (1971)

[31] C. Wentrup, to be published

[32] M. Szwarc and J. Murawski, *Trans. Faraday Soc.* **47**, 269 (1951)

[33] H. G. Wagner and F. Zabel, *Ber. Bunsenges. Phys. Chem.* **75**, 114 (1971)

[34] See Ref 3*d*, p. 1461, lines 17–18

[35] T. J. Henry and R. G. Bergman, *J. Am. Chem. Soc.* **94**, 5103 (1972)

[36] C. Wentrup and W. D. Crow, *Tetrahedron* **26**, 3965 (1970); *Ibid.* **27**, 880 (1971)

[37] *Cf* also O. Süs, H. Steppan and R. Dietrich, *Liebig's Ann.* **617**, 20 (1958), and earlier papers; H. J. Hageman and U. E. Wiersum, *Chem. in Britain* **9**, 206 (1973)

[38] W. D. Crow and M. N. Paddon-Row, *Tetrahedron Letters* 2217 (1973)

[39] W. D. Crow and M. N. Paddon-Row, *Ibid.* 3207 (1972)

[40a] N. Bodor and M. J. S. Dewar, *J. Am. Chem. Soc.* **94**, 9103 (1972); [b] V. Menéndez and J. M. Figuera, *Chem. Phys. Letters* **18**, 426 (1973)

[41] G. L. Closs, L. R. Kaplan and V. I. Bendall, *J. Am. Chem. Soc.* **89**, 3376 (1967)

[42] *Cf* B. S. Rabinovitch and M. C. Flowers, *Quart. Rev. Chem. Soc.* 122 (1964) and Ref 5*a*

[43] W. D. Crow, A. R. Lea and M. N. Paddon-Row, *Tetrahedron Letters* 2235 (1972)

[44a] W. D. Crow and C. Wentrup, *Ibid.* 6149 (1968); [b] C. Wentrup, *Chem. Commun.* 1386 (1969)

[45] R. Huisgen, R. Grashey and J. Sauer, *The Chemistry of Alkenes* p. 739. (Edited by S. Patai) Interscience (1964)

[46] C. Wentrup and R. Harder, unpublished results

[47] *Cf* also S. R. Suter, *Diss. Abstracts* **32**, 4502-B (1972)

[48] W. D. Crow and C. Wentrup, *Tetrahedron Letters* 4379 (1967)

[49] W. D. Crow and C. Wentrup, *Ibid.* 5569 (1968)

[50] M. Appl and R. Huisgen, *Chem. Ber.* **92**, 2961 (1959)

[51] R. Huisgen, D. Vossius and M. Appl, *Ibid.* **91**, 1 (1958)

[52] W. v. E. Doering and R. A. Odum, *Tetrahedron* **22**, 81 (1966); R. A. Odum and G. Wolf, *Chem. Commun.* 360 (1973)

[53] C. Wentrup, *Helv. Chim. Acta* **55**, 1613 (1972)

[54] R. Gleiter, Basel and Darmstadt, personal communication (1972)

[55] R. E. Banks and E. Prakash, *Tetrahedron Letters* 99 (1973)

[56] Nguyen Mong Lan, Diploma Thesis, Lausanne (1973)

[57] A. Hassner and F. W. Fowler, *Tetrahedron Letters* 1545 (1967)

[58] J. D. Cox, *Tetrahedron* **19**, 1175 (1963)

[59] *Cf* G. Köbrich, *Angew. Chem.* **85**, 494 (1973)

[60] H. E. Zimmerman and L. R. Sousa, *J. Am. Chem. Soc.* **94**, 834 (1972)

[61] D. F. McMillen, D. M. Golden and S. W. Benson, *Internat. J. Chem. Kin.* **4**, 487 (1972); J. A. Kerr, *Chem. Rev.* **66**, 465 (1966)