82. The Ring Closure of Cyclopenta-1,3-dien-5-yl-carbene to Benzvalene. A Mechanistic Study of an Unusual Carbene Reaction[1])

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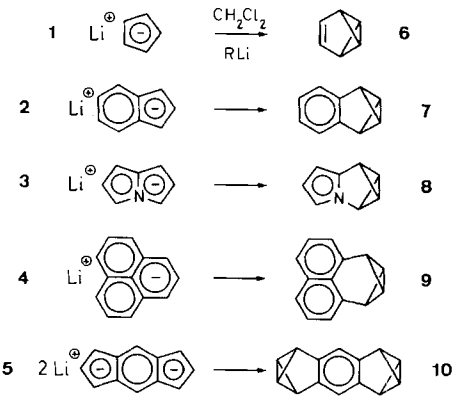
Summary

The base-induced α-elimination of hydrogen chloride from 5-chloromethyl-5-methylcyclopenta-1,3-diene (**19**) produces 1-methyltricyclo[3.1.0.$0^{2,6}$]hexene-3 (1-methylbenzvalene) (**21**) together with toluene and spiro[4.2]heptadiene (**23**). A common intermediate, 5-methylcyclopenta-1,3-dien-5-yl-carbene (**20**), accounts for these results by intramolecular 1,4-carbene addition, 1,2-carbon shift and CH-insertion, respectively. Independent synthesis of 2-methylbenzvalene (**24**) allows us to show that the classic intramolecular cyclopropanation is completely suppressed by the linear cheletropic ring closure. MINDO/3 predicts the key carbene to have a bisected conformation in its singlet ground state. This ideally fulfills the stereoelectronic conditions for a carbene reaction of least motion. The influence of the methyl substituent upon that process is discussed.

Introduction. – The range of carbene reactions has been enriched during the last decade by a particularly interesting type which consists in the reaction of lithium salts of aromatic anions, *e.g.* **1**–**5**, with monochlorocarbene (or carbenoid)[2]),

Scheme 1[3])



[1]) Preliminary note: [1].

[2]) For leading references concerning the carbenoid problem see [2] and ref. therein.

[3]) **6** [3a], **7** [3a], **8** [4a], **9** [5a] [6a], **10** [4b].

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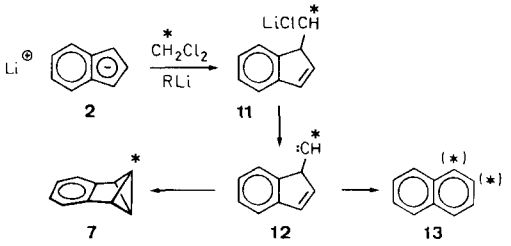
the latter being generated from methylene chloride/alkyllithium. Three new C-C bonds are formed and benzvalene-like molecules, *e.g.* **6**–**10**, result. The reaction, first applied by *Katz et al.* [3] to salts of simple carboaromatic anions, **1**, **2**, has since been demonstrated to allow construction of a wide variety of valence isomers of aromatic compounds [4–6]. *Scheme 1* shows a pertinent selection. For further examples and some border-line cases see [4c].

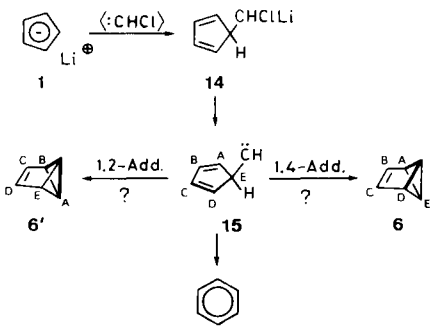
At first glance, all these reactions follow a unique mechanistic scheme; labelling experiments performed with indenyllithium (**2**) as a model have provided evidence that one new C-C bond is formed in the initial step producing the exocyclic carbene **12**[4]). The latter, competitively, undergoes intramolecular cyclopropanation to give the valene **7**, or expends to the fully aromatic isomer, naphthalene (**13**). Both vinyl and phenyl migration account for the ring expansion in this example [4d] *(Scheme 2)*.

Scheme 2[5])



These findings suggest that *sym*-cyclopentadienylcarbene (**15**) is the corresponding key intermediate in the reaction leading from cyclopentadienyllithium (**1**) to the parent benzvalene (**6**) *(Scheme 3)*. However, carbene **15**, unlike its analogues of lower symmetry, has two options for intramolecular ring closure. A classic cyclopropanation, as in the preceding indenyl example, or more interestingly,

Scheme 3[6])



4) This may be the result of an electrophilic addition of free chlorocarbene to the aromatic substrate or a substitution at dichloromethyllithium.

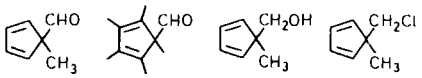
5) The asterisk shows the position of the deuterium label.

6) The new bonds of the intramolecular carbene addition are shown in bold face in **6** and **6'** respectively.

a 1,4-addition of the exocyclic carbene moiety to the *cisoid* butadiene unit can produce benzvalene (**1**→**6′** *vs.* **1**→**6**). We deal with this particular alternative in the present work. Will the title carbene **15** take advantage of its unique molecular geometry to undergo 1,4-cheletropic addition following a pathway of least motion?

In order to answer this question we decided to generate a carbene derived from structure **15**, labelled or substituted in such a way that we could unambiguously identify C-atom C^E in the resulting benzvalene and thereby distinguish 1,2- from 1,4-addition. Clearly, this excludes the use of an isotopically labelled version of *Scheme 3*. The latter starts from a species of C_{5v} symmetry and thus does not allow distinction of the ring C-atoms. Moreover, no carbene precursor having the exocyclic C-C bond preformed, *i.e.* a monosubstituted cyclopentadiene, can be expected to remain in the C_s form. The notoriously fast 1,5-hydride shift [7] would invariably lead to double bond isomerization and simultaneously scramble any peripheral label. Therefore, we had to start from a geminally disubstituted cyclopentadiene, one of the substituents serving as label for C-atom C^E, and the other providing a handle to generate the carbenic center.

The more economic routes to complex carbenes start from the corresponding carbonyl derivatives [8]. The appropriate aldehyde **16** however is unknown [9] and, keeping in mind that its pentamethyl derivative **17** [10] undergoes 1,5-formyl shift at a rate which is fast on the NMR.-time scale at RT., it is obvious that **16** would not be a suitable compound. We therefore must generate the desired carbene by a route shunning the intermediacy of an aldehyde.



16 **17** **18** **19**

The neopentyl-type alcohol **18** [11] is stable at RT., and so is the corresponding chloride **19**. The latter is obtained by reaction of **18** with excess triphenylphosphine in carbon tetrachloride [1]. We now reckoned that the most acidic H-atoms of **19** should be those of the chloromethyl grouping. If a suitable base could be found, then α-elimination of hydrogen chloride might be achieved. This direct approach to generate the desired carbene **20** turned out to be viable.

Results. – When a 0.5 M solution of the chloride **19** in ether was allowed to react at 25° in the presence of two mol-equivalents each of potassium tertiary butoxide, *n*-butyllithium and [18]-crown-[6] for 3 h, three isomeric hydrocarbons were obtained: 1-methylbenzvalene **21** (38%), toluene **22** (18%) and spiro[4.2]hepta-2,4-diene **23** (0.9%) *(Scheme 4)* and 23% of **19** was recovered[7]). All products were identified from their ^{1}H-NMR. spectra and compared with authentic samples. An independent synthesis of the yet unreported 1-methylbenzvalene (**21**) was readily achieved by reaction of 1-lithiobenzvalene [15] in ether with methyl iodide.

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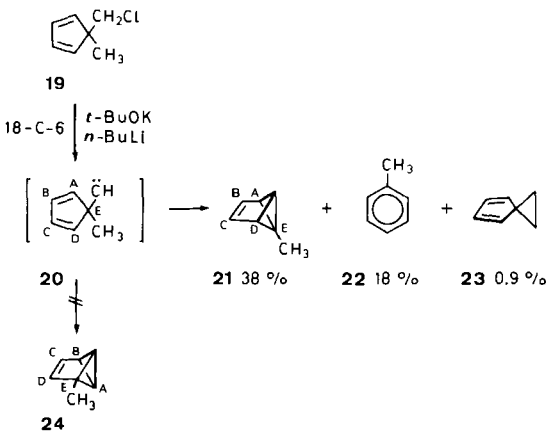
[7]) The combination KO*t*Bu/*n*BuLi is a well-documented metallating agent [12]. However, in the present example, addition of crown ether was essential. Without it we obtained only toluene from **19** in a sluggish reaction. *Moss & Pilkiewicz* [13] have shown that addition of crown ether to base-induced α-elimination reactions greatly favours formation of free carbene, as opposed to some sort of carbenoid. *Cf.* [14].

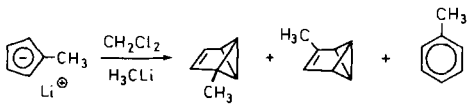
Scheme 4



In the key experiment outlined in *Scheme 4*, no 2-methylbenzvalene (**24**) resulting from classic cyclopropanation was detected. In order to make this finding, quite unambiguous, we synthesized **24** together with its 3-methyl isomer **25** and tested its stability. Apart from a little thermal decomposition *(vide infra)*, compound **24** was stable under the conditions of the α-elimination.

The isomers **24** and **25** were obtained in an analogous manner to the parent benzvalene **6** [3] in 38% and 18% yield respectively, by reaction of methylcyclopentadienyllithium (**26**) with dichloromethane and methyllithium in dimethyl ether at $-70°$. Toluene (7%) was also formed in this reaction, but remarkably, no 1-methylbenzvalene (**21**) *(Scheme 5)*. The structures of **24** and **25** follow from the ^{1}H-NMR. spectrum of the mixture; **24** is characterized particularly by the presence of two chemically non-equivalent olefinic protons, whereas **25** displays resonance of a single olefinic H-atom coupled to the methyl group.

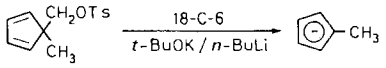
Scheme 5



Compounds **21**, **24** and **25** underwent thermal valence isomerization to toluene (**22**). At 30° in ether, the half-lives were respectively *ca.* 7, 13, and 35 h. Thus all methylbenzvalenes are less stable than the parent compound **6** for which, under identical conditions, a half-life of 48 h is observed[8]).

[8]) This destabilization by disymmetric methyl substitution is reminiscent of difficulties and failures encountered when syntheses of highly alkyl substituted benzvalenes were attempted. Only pentamethylbenzene with no benzvalene derivative could be detected when pentamethylcyclopentadienyllithium reacted with chlorocarbene at $-70°$ [16] [17].

Scheme 6



27 **26**

The base-induced α-elimination of trifluoromethane sulfonic acid provides convenient access to alkylidenecarbenes and vinylidencarbenes [14] [18]. With the intention of generating carbene **20** by an independent route, we treated the toluenesulfonate **27** [11][9]) with the powerful basic combination used above. Elimination did indeed occur, but methylcyclopentadienide (**26**), and not *p*-toluene sulfonate, took the role of the leaving group. Three prototropic isomers of methylcyclopentadiene were obtained from the aqueous work-up. This reaction *(Scheme 6)* proceeds probably by a fragmentation starting with nucleophilic attack on the S-atom [19].

MO calculations and discussion. – The formation of 1-methylbenzvalene (**21**) by α-elimination starting from the chloride **19** can hardly be understood otherwise than by admitting an intramolecular 1,4-carbene addition. And, as we are working in presence of a crown ether, we are dealing virtually with a 'free carbene in solution' [13].

Theory [20] states that the concerted linear cheletropic 1,4-addition of singlet carbene (*e.g.* σ^2-methylene) to *cisoid*-butadiene is allowed with respect to the conservation of MO symmetry. Clearly, this does not exclude the existence of a still more favourable reaction which, in the present context, is the *notorious* non-linear 1,2-addition, producing vinylcyclopropanes instead of the cyclopentene unit. Few examples of formal intermolecular 1,4-carbene additions are known [21]. Intramolecular reactions of this type are unknown.

Two factors have been invoked to account for this rarity. The first, being of entropic nature, can partially be matched by the proper choice of the diene geometry. This has first been demonstrated by *Jefford* and ourselves in a series of papers dealing with the isoelectronic homo-1,4-addition of halocarbenes to norbornadiene [22] [23]. The second factor believed to disfavour 1,4-carbene additions is the repulsive closed-shell interaction between the lower occupied π-orbital of the diene (*i.e.* the sub-$HOMO_{diene}$) and the lone pair of the approaching σ^2-carbene (*i.e.* the $HOMO_{carbene}$) [20].

Having discovered an example in which the classic cyclopropanation is entirely suppressed in favour of the unusual 1,4-addition, we performed the appropriate semi-empirical MO calculations using the MINDO/3 technique [24]. We wanted to know the conformations of carbenes **15** and **20** in their singlet ground state – certainly of great importance to the activation entropy of the ring closure. We also needed information about the activation barrier MINDO/3 assigns to the 1,4-addition and the role of the methyl group of **20** in this process. Is this substituent just a label or does it control the mode of addition?

The singlet ground state geometries computed by MINDO/3 for the carbenes **15** and **20** are shown in *Figure 1*. Both carbenes were found to be bisected, *i.e.* they belong to point group C_s. This result is obtained without any geometric restriction.

[9]) Attempts to synthesize the corresponding triflate invariably resulted in the formation of toluene.

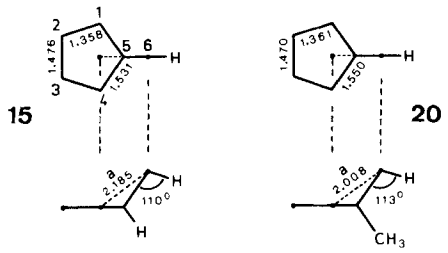


Fig. 1. *Geometries of carbenes* **15** (left) *and* **20** (right) *in top and side views computed by MINDO/3* (Distances are given in Å)

No other carbene conformation corresponds to a local minimum on the energy surface. Both **15** and **20** bear their carbenic H-atom in the *anti*-orientation as shown. The five-membered rings are planar and, with respect to bond lengths and angles, are normal cyclopentadienes [24]. However, a difference was found for the distance (a) from the carbenic center C(6) to the midpoint between C-atoms C(1) and C(4). For the unsubstituted carbene **15** this distance (2.185 Å) is somewhat bigger than for the methyl substituted derivative **20** (2.008 Å). We anticipate that this parameter (a) will be used below as reaction coordinate for the intramolecular 1,4-addition.

Clearly, these ground state conformations are the most favourable we can realize in order to minimize the entropy problem. Moreover, ideal symmetry relations of the frontier orbitals ensue *(Fig. 2)*. Both pairs of interacting orbitals, *i.e.* $LUMO_{carbene}$-$HOMO_{diene}$ and $LUMO_{diene}$-$HOMO_{carbene}$, have the correct symmetry required for 1,4-ring closure, and both interactions are co-operative[10]).

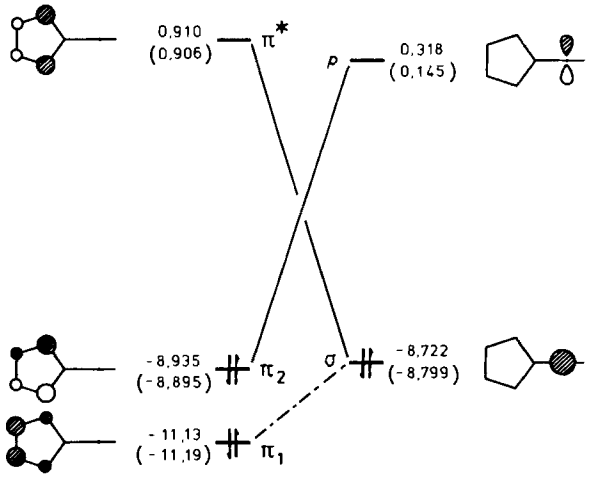


Fig. 2. *Symmetry of frontier orbitals of carbenes* **15** *and* **20**. Eigenvalues (eV) for **15** are given in parentheses. Left: diene moiety, right: carbene moiety in top view.

[10]) Analysis of net atomic charges reveals a slight charge transfer (0.029 charge units) to occur from the diene part of **20** to the carbenic center during 1,4-addition. This suggests that the interaction $LUMO_{carbene}$-$HOMO_{diene}$ is slightly more important than the $LUMO_{diene}$-$HOMO_{carbene}$ part.

We now have to look at the energy profile of the addition process. Distance (a) defined above and illustrated in *Figure 1* was chosen as reaction coordinate. When no geometric restriction was imposed on the process, shortening of this distance resulted for both carbenes **15** and **20** in aromatization; *i.e.* MINDO/3 predicted the minor products, benzene and toluene respectively. Only when the constraint of C_s symmetry was imposed were the corresponding benzvalenes **6** and **21** predicted. In doing so we clearly anticipate the 1,4-addition mode, and the activation barrier obtained is an estimate of an upper limit. The result is depicted in *Figure 3*. Ring closure of the carbene **20** following the pathway of least motion has, according to MINDO/3 and in full agreement with the experiment, a very small activation barrier ($\Delta H^+ = 0.7$ kcal/mol). A larger value is computed for the unsubstituted carbene **15** ($\Delta H^+ = 7.3$ kcal/mol). Thus the calculation does not allow us to extend the mechanism established for the *gem*-methyl substituted carbene **20** to the parent system **15** without further evidence.

The stereoselection encountered when methylcyclopentadienyllithium (**26**) reacted with dichloromethane/methyllithium is revealing. From the absence of 1-methylbenzvalene (**21**) in this experiment we can safely conclude that the carbene **20** is not implied *(Fig. 4)*. A glance at the π-electron densities computed for methylcyclopentadienide by simple *Hückel*-MO theory [25] (formula **26-A**) suggests that we are dealing with a charge-controlled process, *i.e.* initial C-C bond formation

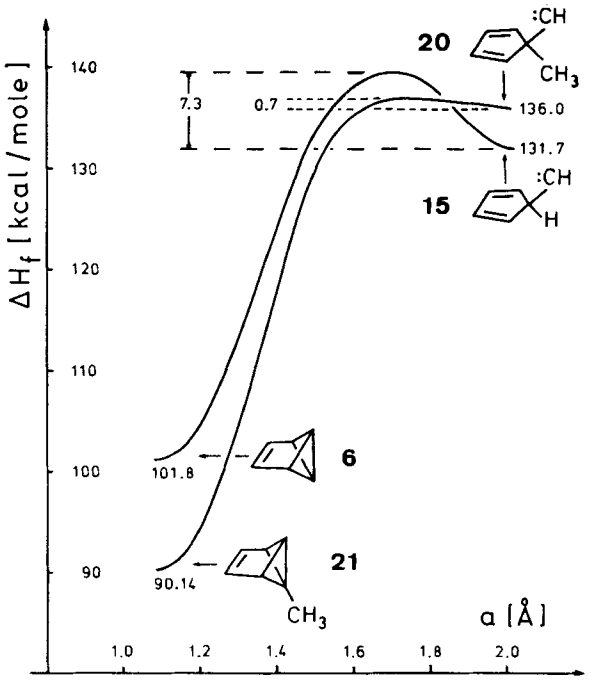


Fig. 3. *Computed barriers* (MIND/3) *for the linear cheletropic ring closure of carbenes* **15** *and* **20** *to the benzvalenes* **6** *and* **21**

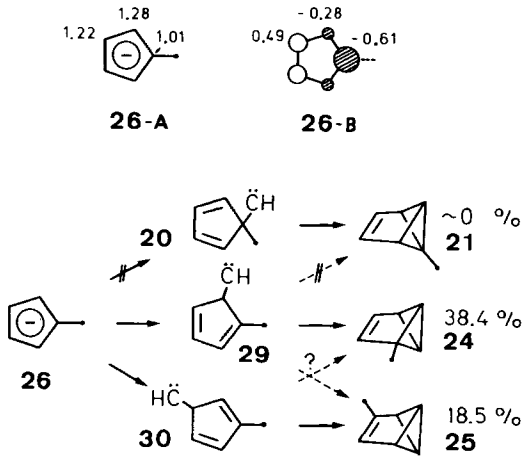


Fig. 4. *On the charge controlled formation of* **24** *and* **25** *from* **26**. **26-A**: π-electron densities, and **26-B**: coefficients of the HOMO of **26** computed by HMO.

occurs at C(2) and C(3) only[11]). Carbenes **29** and **30** are the outcome. Orbital control would result in the predominant formation of the carbene **20**. This is readily seen from the coefficients of the HOMO of **26** shown in formula **26-B**.

Once we admit that the carbene **29** is involved[12]) then intramolecular 1,4-addition – once again – is the easiest explanation of the overall result.

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Experimental Part

General remarks. All operations with benzvalene and its derivatives were performed under argon. Contact with metal instruments, *e.g.* injection needles, spatulas, etc. was avoided whenever possible. ^{1}H-NMR. spectra (δ [ppm] relative to internal TMS; multiplicity: *s* singlet, *d* doublet, *t* triplet, *m* multiplet, *J*(Hz) = apparent coupling constant): *Varian* XL-100 spectrometer operating at 100.1 MHz (pulsed mode). Mass spectra (MS.) (*m/z*, base peak in italics): *Varian* MAT-SMA spectrometer. Further abbreviations: RT. = room temperature; i.V. = *in vacuo*.

5-Chloromethyl-5-methyl-cyclopenta-1,3-diene (**19**). A solution of 2.0 g (18.5 mmol) of 5-hydroxymethyl-5-methyl-cyclopenta-1,3-diene (**18**) [11] in 6 ml CCl_4 was added under N_2 to a freshly prepared solution of 9.7 g (37 mmol) of triphenylphosphine in 30 ml CCl_4. The mixture was kept under reflux for 24 h and then passed together with the solvent through a column charged with 200 g of aluminum oxide (*Fluka*, type 5016-A, activity I) (bottom) and 50 g powdered $MgSO_4$ (top). Ether (200 ml) was used to complete elution of the product. After removal of the solvents i.V., 770 mg (32% yield) of chloride **19** was obtained as a colourless liquid, b.p. 48–50°/12 Torr. – ^{1}H-NMR. (CCl_4, 60 MHz): 6.3 (*s*, 4 H); 3.4 (*s*, 2 H) and 1.25 (*s*, 3 H). – *MS.* (C_7H_9Cl, 128.5): 130, 128, *93*, 77, 65.

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[11]) *Pagni et al.* [6b] have drawn attention to the fact the analogous reaction of benz[*de*]anthracenyllithium with chlorocarbene (or carbenoid) occurs under charge control.

[12]) The carbene **30** alone could account for both product **24** and **25** by virtue of intramolecular 1,2-addition. However, stereospecific formation of **30** from **26** seems quite unlikely, both for a charge controlled and for an orbital controlled reaction.

1-Methylbenzvalene (**21**) *from benzvalene* (**6**). To a 0.5N solution of **6** (10 ml, 5 mmol) in ether [3] in a *Schlenk* tube equipped with a magnetic stirrer and kept under argon, at $-10°$, was added 3.5 ml (5.6 mmol) of a 1.6N ethereal solution of *n*-butyllithium. The reaction mixture was stirred for 30 min at $-10°$, then 0.31 ml (5 mmol) of methyl iodide was injected. After 1 h, flash distillation at 15 Torr gave an ethereal solution of unreacted **6** (43%) and **21** (57%) which undergoes aromatization ($t_{1/2}/30° = 7$ h) much faster than the parent **6** ($t_{1/2}/30° = 48$ h).

^{1}H-NMR. of **21** (ether/benzene-d_6 9:1, 100 MHz): 5.80 (apparent *t*, 2 H, olefinic); 3.61 (*m*, 1 H, H–C(6)); 1.83 (*m*, 2 H, allylic bridgeheads); 1.60 (*s*, 3 H, methyl group).

1-Methylbenzvalene (**21**) *and spiro[4.2]hepta-2,4-diene* (**23**) *from* **19**. A narrow *Schlenk* tube, equipped with a magnetic stirrer and kept under argon, was charged with 520 mg (4.66 mmol) of freshly sublimed *t*-BuOK, 1.23 g (4.66 mmol) of [18]-crown-[6] and 2 ml of ether. A solution of 300 mg (2.34 mmol) of chloride **19** in 1 ml of ether was injected through a rubber septum. After stirring for 10 min, 3 ml of 1.6N *n*-butyllithium in ether (4.8 mmol) was introduced. The mixture was stirred for 3 h at RT. and then hydrolyzed at 0° by slow addition of 3 ml of water. The organic layer was pre-purified by flash distillation at RT./1 Torr, the trap being cooled with liquid N_2. Subsequent distillation at RT./12 Torr gave a liquid residue of unreacted **19** (69 mg, 23%) and an ethereal solution of the C_7H_8 products. Comparison with authentic samples by ^{1}H-NMR. showed the latter to be 1-methylbenzvalene (**21**) (38%), toluene (**22**) (18%) and spiro[4.2]hepta-2,4-diene (**23**) (0.9%) [26]. 2-Methylbenzvalene (**24**) was absent (^{1}H-NMR., threshold of detectability ~1%). Compounds **22** and **23** were also identified by GC. (double injection; 5% didecyl phthalate + 1.25% triethanolamine on Chromosorb, column temp. 50°). Compound **21** rearranges under these conditions to a mixture of isomeric monomethylfulvenes [27].

2-Methylbenzvalene (**24**) *and 3-methylbenzvalene* (**25**). A 200 ml reactor equipped with a dry ice condensor, a Teflon-coated mechanical stirrer, an injection septum and a gas inlet tube, was charged with 50 ml of a 1.34N ethereal solution of methyllithium (67 mmol) and kept under argon. Diethyl ether was removed i.V. at RT. and replaced after cooling to $-78°$ by 90 ml of dimethyl ether. After injection of 2.4 g (30 mmol) of methylcyclopentadiene (mixture of prototropic isomers), the temperature was raised to $-40°$ for 30 min and then lowered again to $-70°$. CH_2Cl_2 (2.0 ml, 31 mmol) was introduced dropwise under vigorous stirring. After 1 h dimethyl ether was evaporated (*ca.* $-40°$/12 Torr) and progressively replaced by 50 ml of diethyl ether (or THF). Flash distillation at RT./12 Torr gave an ethereal solution of **24** (38,4% yield), **25** (18.5%) and toluene (7%), the total concentration of benzvalenes being 4.5%. Both **24** ($t_{1/2}/30° = 13$ h) and **25** ($t_{1/2}/30° = 35$ h) in ethereal solution are less stable than the parent benzvalene **6** ($t_{1/2}/30° = 48$ h).

^{1}H-NMR. (data were obtained with the mixture of **24** + **25** in ether/benzene-d_6 9:1 at 100 MHz). *Data of* **24**: ABE_2M system, 5.99 (*m*, 1 H, $^3J = 5.3$ Hz); 5.80 (*m*, 1 H, $^3J = 5.3$ Hz); 3.55 (*d*, 2 H); 1.85 (*m*, 1 H, owing to overlap with resonances of **25** determined by INDOR); methyl group (in THF-d_8) 1.17 (*s*). **25**: 5.49 (*m*, 1 H olefinic, couples with the methyl group. $^4J = 1.8$ Hz); 3.64 (*t*, 2 H); 1,8–1,9 (*m*, 2 H); 1.78 (*d*, methyl group, $^4J = 1.8$ Hz).

Computational. Calculations were done on a *UNIVAC*-1110 computer using the standard MINDO/3 programme together with the associated *Davidon-Fletcher-Powell* (DFP) geometry procedure [24]. Heats of formation and geometries of individual molecules are found by minimizing the total energy with respect to all geometrical variables, no restrictions being imposed. Initial geometry parameters for the benzvalene skeleton are taken from [28]. Reaction paths were determined by minimization of the total energy with respect to geometrical variables other than the reaction coordinate, the latter being successively decremented. C_s symmetry is imposed on the carbon framework during this procedure.

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