A Fused Benzocyclooctene Ring System *via* an Aromatic *Cope* Rearrangement: Thermal Reactions of *trans*-1-Aryl-2-ethenylcyclobutanecarbonitriles

by **José Gustavo Ávila-Zárraga***[a]), **Adrián Vázquez-Sánchez**[a]), and **Luis Ángel Maldonado**[b])

[a]) Departamento de Química Orgánica, Facultad de Química, Universidad Nacional Autónoma de México, 04510, México

[b]) Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04360, México

The results of an aromatic *Cope* rearrangement of a *trans*-1-aryl-2-ethenylcyclobutanecarbonitrile are reported (*Scheme*). The use of this rearrangement for the construction of the fused benzocyclooctene ring system and a preliminary study of the electronic requirements to favor such a transformation are also described.

Introduction. – It is well known that the *Cope* rearrangement is quite challenging to achieve if one of the C=C bonds of the hexa-1,5-diene system is part of an aromatic ring. This is in contrast to the *Claisen* rearrangement, which undergoes the [3.3]-sigmatropic rearrangement relatively easily [1]. However, there are two reports that describe successful *Cope* transformations of this type [2]. For example, thermolysis of 4-phenylbut-1-ene does not lead to the *Cope*-rearrangement product [3][4], but on application of very specific conditions, such transformations may be carried out [2].

Several factors limit the success of *Cope* rearrangements, and the strategy most commonly used for promoting this transformation involves the insertion of a cyclopropane ring at positions 3 and 4 of the hexa-1,5-diene moiety, leading to the formation of a cycloheptane system [5]. This approach has been widely studied and is commonly employed, with its success being due to the release of the cyclopropane ring strain [6]. In a similar manner, the incorporation of a cyclobutane ring at the same positions allows cyclooctane-ring formation, a process that was described by *Vogel* in 1958 [7]. These kinds of reactions are called 1,2-diethenylcyclobutane rearrangements and have been studied by several research groups [8]. This particular sigmatropic rearrangement may occur as undesired reactions [9] or can be implemented as a serious strategy for the synthesis of natural products [10].

Another way to accelerate the [3.3]-sigmatropic rearrangement is the incorporation of an O-atom into the diene moiety, enriching the electron density of the entire system. This promotes what is known as 'oxy-*Cope*' rearrangement, a name that was first applied in 1964 by *Berson* [11]. Oxy-*Cope* rearrangements, in particular anionic oxy-*Cope* rearrangements, demonstrate many advantages, including high yields, controlled stereoselectivity, and tolerance to a wide range of functionalities, and consequently this strategy has been studied and applied in many syntheses [12].

The anionic oxy-*Cope* rearrangement, which relies on activation by an oxygen anion, has also been used in systems that contain aromatic moieties [13][14]. However, only one previous study has reported the incorporation of an O-atom into the aromatic structure, activating the *Cope* rearrangement at distance through the benzene portion of the hexa-1,5-diene moiety [2a], thereby making what could be termed an anionic aromatic oxy-*Cope* rearrangement. The presence of other electron-donating groups at the aromatic rings also favors a rate increase under appropriate conditions [15].

To the best of our knowledge, the extension of this methodology to the construction of fused benzocyclooctene systems through *Cope* rearrangements of a 1-aryl-2-ethenylcyclobutane precursor has not been reported, leaving some uncertainties about its scope and generality.

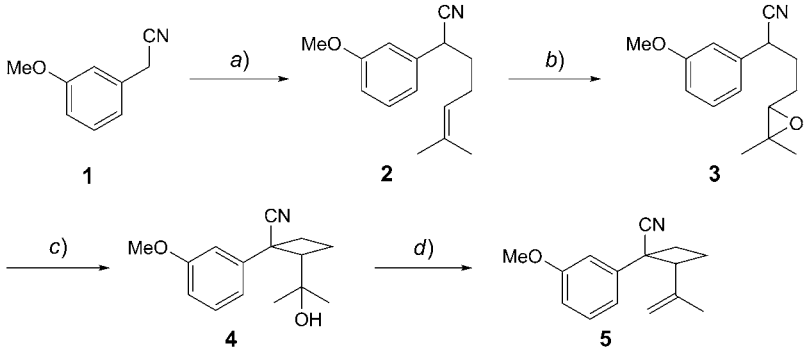
As a continuation of our previous studies on aromatic *Cope* rearrangements in the context of a cyclobutane ring at positions 3 and 4 of the hexa-1,5-diene moiety, we here present the results of a study of *trans*-1-aryl-2-ethenylcyclobutanecarbonitriles with *cis*-oriented aryl and ethenyl substituents, as precursors for systems of interest containing the benzocyclooctene ring system [16].

Restults and Discussion. – An earlier first attempt by our group to synthesize the benzocyclooctene natural product parvifoline by an aromatic oxy-*Cope* rearrangement was unsuccessful [17], and so, in the work presented here, the conditions required to achieve this kind of transformation were investigated.

For the construction of the starting *trans*-1-aryl-2-ethenylcyclobutanecarbonitrile **5**, the synthetic route shown in *Scheme 1* was chosen, which involves an intramolecular cyclization reaction of epoxynitrile **3**. Thus, 3-methoxybenzeneacetonitrile (**1**) was alkylated to generate 3-methoxy-α-(4-methylpent-4-en-1-yl)benzeneacetonitrile **2**, which was oxidized to give the corresponding epoxynitrile **3**, see [18]. In a previous report, we studied the cyclization reactions of α-aryl-δ,ε-epoxynitriles, which allowed for the determination of the optimal conditions to modulate 4-*exo* and 5-*endo* processes in a differentiated and stereoselective manner [18]. Following this strategy, a number of modifications were made to the original protocol to assess the effect on the regio- and stereoselectivity during the formation of the cyclobutanemethanol derivative (**4**). Significant improvements were made with respect to the previous results, resulting in higher yields of intermediate **4**, achieved without any modification of the configuration of the final product, which is essential for carrying out the subsequent sigmatropic shift in such systems (*Scheme 1*). With adduct **4** in hand, an elimination reaction was performed under very mild conditions, producing the *Hofmann*-type alkene derivative **5** in acceptable yields. Considering the structural complexity of **5**, the synthesis of the required 1-aryl-2-ethenylcyclobutane moiety exhibiting the diethenyl *cis*-configuration was highly successful.

Several different conditions were tested for the subsequent *Cope* rearrangement, as shown in *Scheme 2*. The presence of a MeO group in **5** as a potential activating group prevented in fact the reaction from occurring, which was, however, expected because of previous reports on such structures that revealed the importance of an oxy anion to facilitate the rearrangement [2a]. Thus, the generation of the corresponding phenoxide anion was investigated, and the sigmatropic rearrangement was studied *in situ* after LiSEt deprotection of the MeO group. Unfortunately, during the initial experiments,

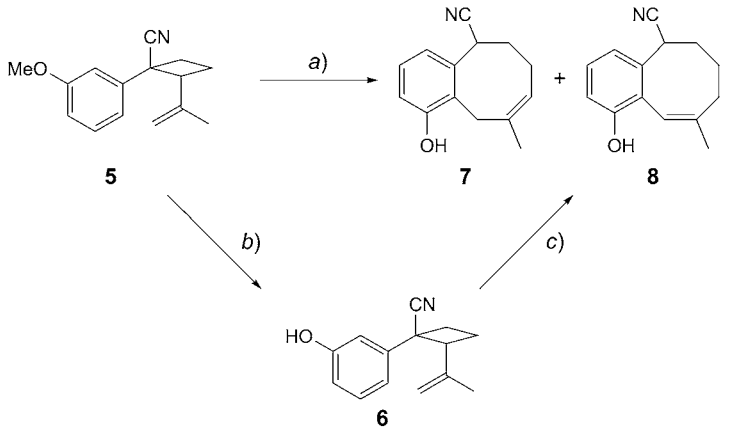
Scheme 1. *Synthesis of* trans-*1-Aryl-2-ethenylcyclobutanecarbonitrile* **5**



a) 1. BuLi, THF, – 78°; 2. 5-iodo-2-methylpent-2-ene; 80%. *b*) Acetone, *Oxone*®, $NaHCO_3$, H_2O; 95%. *c*) BuLi, Cs_2CO_3, THF, reflux 64%. *d*) $SOCl_2$, DABCO, benzene, 0°; 49%.

high proportions of decomposition were observed. Therefore, derivative **6** was first synthesized, followed by the ring expansion in a subsequent step. The results are shown in the *Table*. The *Cope* rearrangement to **7** did not occur in any of the experiments in which the solvent was THF, indicating that the energy barrier is high under these conditions. It was deduced that the presence of the aromatic ring in the system increased the thermal requirements for the reaction to proceed. On the other hand, the experiments conducted in DMF demonstrated a successful rearrangement in a regiospecific manner, with ring fusion at the *ortho* position. The C=C bond present in the cyclooctene moiety of product **7** underwent isomerization during the purification process, thus forming the conjugated tetrahydrobenzocyclooctene **8**.

Scheme 2. *Different Reaction Conditions for the Aromatic* Cope *Rearrangement of* **5** *and* **6**



a) LiSEt, DMF or THF. *b*) 1. BBr_3, CH_2Cl_2; 2. H_2O. *c*) 1. BuLi, THF; 2. DMF or THF.

Table. *Results of the Attempted Aromatic* Cope *Rearrangement of* **5** *and* **6**

	Method[a])	Solvent, temp.	Products (yield)
5	*A*	THF, 60°	no reaction
5	*A*	DMF, 120°	no reaction
5	*B*	THF, 60°	**6** (91%)
5	*B*	DMF, 120°	**7** (11%)[b]), **8** (20%)[b])
6	*A*	THF, 60°	No reaction
6	*A*	DMF, 120°	**7** (17%)[b]), **8** (11%)[b]) **7** (9%)[c]), **8** (18%)[c])
6	*C*	THF, 60°	no reaction
6	*C*	DMF, 120°	**7** (38%)[b]), **8** (27%)[b]) **7** (21%)[c]), **8** (45%)[c])

[a]) *Method A:* no deprotection. *Method B: i*) LiSEt, THF; *ii*) solvent. *Method C: i*) BuLi, THF; *ii*) solvent. [b]) Determined by ^{1}H-NMR. [c]) Obtained after chromatography.

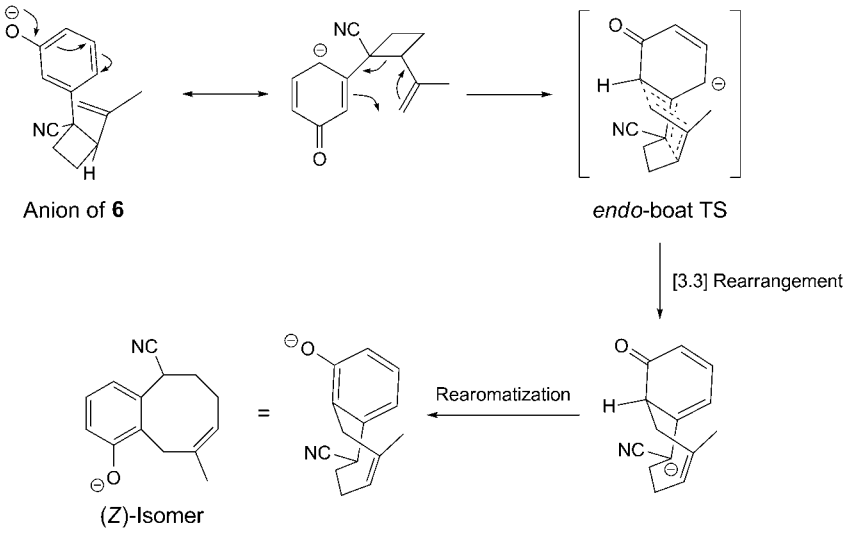
A fundamental condition for the *Cope* rearrangement to occur in the particular case of diethenylcyclobutanes is the conformation of the system; *i.e.*, the C=C bonds that make up the hexa-1,5-diene must be in the same plane [10][19]. There are also some electronic features that are considered to favor the rearrangement, *e.g.*, the presence of an anion in the diene structure [11c]. These two conditions are important for facilitating an effective rearrangement.

The mechanism of the *Cope* rearrangement has been the subject of extensive studies and discussions. Four mechanistic alternatives, which involve the following intermediates/transition states (TS), have been proposed: a pair of interacting allyl radicals, an aromatic neutral TS, a cyclohexane-1,4-diyl biradical, and a dipolar mechanism involving zwitterionic intermediates [20]. However, there is a recent consensus that the *Cope* rearrangement of hexa-1,5-dienes is likely to proceed *via* an aromatic chair TS. Substituents have a profound effect on the mechanism, and there is a mechanistic continuum between the biradical and concerted pathways, with the exact mechanism depending on the nature and position of substituents [21][22].

Theoretical studies on the possible TS structures in diethenylcyclobutane rearrangements favor an *endo*-boat-like TS because of the configuration required for the formation of the more stable final (*Z*,*Z*)-cyclooctene ring [23]. In the present work, the rearrangement was regio- and diastereospecific, resulting in only the (*Z*)-tetrahydrobenzocyclooctene ring system **7**. Based on these results, and those of previous reports, we propose that the diene moiety that comprises the isopropenyl group and the aromatic ring of the anion of **6** must be in the same plane. This fragment then reacts through an *endo*-boat-like TS, assisted by the O-anion at the appropriate *meta*-position of the aromatic ring thus inducing the anionic electronic activation of to the diene moiety (*Scheme 3*).

The best results were obtained from the rearrangement of **6** under basic conditions, thereby reinforcing the hypothesis that strong electron donation by the activating group is required for the reaction to proceed. We propose a concerted mechanism involving a remote oxy anion, a process analogous to that described by *Marvell* and *Lin* [2a]. Such a concentrated mechanism is suggested by the restrictions imposed by the

Scheme 3. *Possible Reaction Pathway Proposed for the* Cope *Rearrangement of the Anion of* **6**



final configuration of the (*Z*)-tetrahydrobenzocyclooctene ring system **7** [23], and chiefly, by the experimentally observed regio- and stereospecificity of the formation of **7**.

Conclusions. – These results show, for the first time, that the aromatic *Cope* rearrangement of a *trans*-1-aryl-2-ethenylcyclobutanecarbonitrile (with *cis*-orientation of the aryl and ethenyl substituents) is possible, making this approach a valuable tool for the construction of fused benzocyclooctene ring systems. Such transformations require relatively high temperatures (120°) and the presence of strong activating groups, such as the electron-rich phenoxide ion, to proceed effectively.

At present, we continue our study of such systems, which contain different groups at the aromatic ring.

This research was supported by the Facultad de Química UNAM (PAIP 4690–14), and the *CONACYT* through a M. S. scholarship for *Adrián Vázquez* (235256). We wish to thank to *Marisela Gutiérrez*, *Margarita Guzmán*, and *Georgina Duarte* for their assistance in acquiring the spectroscopic data.

Experimental Part

General. All chemicals and solvents were purchased from *Sigma–Aldrich*. The solvents were dried over the appropriate drying agents and distilled prior to use. Column chromatography (CC): silica gel (SiO_2; *Merck 60G*). IR Spectra: *Perkin-Elmer-Spectrum RX I* FT-IR spectrophotometer, $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Varian-Unity-Inova-300* spectrometer; at 300 and 75 MHz, resp., in $CDCl_3$; δ in ppm rel. to Me_4Si as an internal standard, *J* in Hz. HR-EI-MS: *Thermo-DFS* spectrometer; at 70 eV; in *m*/*z*.

trans-*2-(1-Hydroxy-1-methylethyl-2-yl)-1-(3-methoxyphenyl)cyclobutanecarbonitrile* (**4**; see [18]). To Cs_2CO_3 (1 g, 0.5 equiv., 3.06 mmol), under N_2, anh. THF (25 ml) was injected through a rubber

septum, and the mixture was stirred. Then, the flask was cooled in an ice/water bath for 10 min, before 1.6M BuLi in hexane (4.2 ml, 1.1 equiv., 6.73 mmol) was injected. The mixture was stirred for 5 min, and then epoxide **3** (1.5 g, 1.0 equiv., 6.12 mmol) [18] in THF (5 ml) was injected and the mixture stirred for a further 5 min. Then, the flask was removed from the ice bath, the reaction left to proceed at r.t., and then the flask placed in a preheated oil bath at 80°. Once the reflux was initiated, the mixture was stirred for 2 h and then left to cool to r.t. A 20% of NH_4Cl soln. (10 ml) was added and the mixture stirred for 5 min and then extracted with AcOEt (6 × 25 ml). The org. extracts were washed with $NaHCO_3$ soln. (2 × 10 ml), dried (Na_2SO_4), and concentrated. The final crude product was purified by prep. TLC (hexane/acetone): 960 mg (64%) of **4**. Amber liquid. Spectroscopy data: see [18].

trans-*1-(3-Methoxyphenyl)-2-(1-methylethyl)cyclobutanecarbonitrile* (**5**). Under N_2, anh. benzene (5 ml) was injected through a rubber septum with stirring to alcohol **4** (500 mg, 1 equiv., 2.04 mmol). The flask was placed in an ice/water bath for 5 min, and then $SOCl_2$ (0.22 ml, 1.5 equiv., 3.06 mmol) was slowly injected. The mixture was stirred for 5 min, followed by the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO; 450 mg, 2 equiv., 4.08 mmol) dissolved in benzene (2 ml). The reaction was carried out for 3.5 h, then 50% NH_4Cl soln. (10 ml) was added, and the mixture stirred for 5 min, and then extracted with AcOEt (4 × 15 ml). The org. extracts were washed with 15% HCl soln. (3 × 10 ml) and subsequently with 15% $NaHCO_3$ soln., dried (Na_2SO_4), and concentrated. The final crude product was purified by CC (hexane/acetone): 245 mg (49%) of **5**. Colorless liquid. IR (film): 3083, 2958, 2916, 2837, 2229, 1668, 1650. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.40–1.41 (*m*, 3 H); 2.23–2.33 (*m*, 1 H); 2.36–2.46 (*m*, 1 H); 2.51–2.58 (*m*, 1 H); 2.86 (*td*, *J* = 7.1, 9, 1 H); 3.74 (*t*, *J* = 6.9, 1 H); 3.81 (*s*, 3 H); 4.65–4.67 (*m*, 1 H); 4.77 (*dd*, *J* = 0.8, 1.2, 1 H); 6.83 (*ddd*, *J* = 0.9, 1.2, 7.8, 1 H); 7.0 (*t*, *J* = 1.5, 1 H); 7.06 (*ddd*, *J* = 0.8, 1.6, 7.5, 1 H); 7.27 (*t*, *J* = 7.9, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1; 21.7; 30.2; 43.2; 52.8; 55.4; 113.0; 113.2; 113.4; 119.4; 124.4; 129.5; 137.4; 142.1; 159.6. HR-EI-MS: 227.1303 (M^+, $C_{15}H_{17}NO^+$; calc. 227.1310).

trans-*1-(3-Hydroxyphenyl)-2-(1-methylethyl)cyclobutanecarbonitrile* (**6**). To compound **5** (250 mg, 1 equiv., 1.10 mmol) under N_2, anh. CH_2Cl_2 (5 ml) was added through a rubber septum. The mixture was cooled to −78° and stirred for 5 min. Then, BBr_3 (0.44 ml, 1.14 g, 2.50 equiv., 2.92 mmol) was slowly injected. The reaction was carried out for 4 h, during which time the mixture was allowed to warm to r.t. After cooling in an ice/water bath, sat. NH_4Cl soln. (10 ml) was slowly added and the mixture stirred for a further 5 min and then extracted with CH_2Cl_2 (5 × 15 ml). The org. phases were washed with sat. of soln. NaCl (3 × 10 ml), dried (Na_2SO_4), and concentrated. The resulting crude product was purified by CC (hexane/acetone): 229 mg (96%) of **6**. Slightly viscous colorless liquid. IR (film): 3381, 3084, 2957, 2923, 2855, 2236, 1706, 1650. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.40–1.41 (*m*, 3 H); 2.24–2.33 (*m*, 1 H); 2.36–2.43 (*m*, 1 H); 2.51–2.58 (*m*, 1 H); 2.83–2.90 (*m*, 1 H); 3.73 (*t*, *J* = 9.2, 1 H); 4.65–4.67 (*m*, 1 H); 4.77 (*dd*, *J* = 1.3, 2.7, 1 H); 5.19 (*s*, 1 H, exchange with D_2O); 6.83 (*ddd*, *J* = 0.9, 1.8, 8.1, 1 H); 7.0 (*t*, *J* = 1.5, 1 H); 7.06 (*ddd*, *J* = 0.9, 1.5, 7.9, 1 H); 7.27 (*t*, *J* = 7.8, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1; 21.7; 30.2; 43.2; 52.8; 55.4; 113.0; 113.2; 113.4; 119.4; 124.4; 129.5; 137.4; 142.1; 159.6. HR-EI-MS: 213.1150 (M^+, $C_{14}H_{15}NO^+$; calc. 213.1154).

(9Z)-5,6,7,10-Tetrahydro-1-hydroxy-9-methylbenzocyclooctene-5-carbonitrile (**7**) *and (9Z)-5,6,7,8-Tetrahydro-1-hydroxy-9-methylbenzocyclooctene-5-carbonitrile* (**8**). To **6** (100 mg, 1 equiv., 0.469 mmol) under N_2, anh. THF (3 ml) was injected through a rubber septum. The mixture was cooled to −78° and stirred for 5 min. Then, 1.6M BuLi in hexane (0.32 ml, 1.1 equiv., 0.510 mmol) was injected (→ immediate formation of a white suspended solid). The solvent was removed with a stream of N_2, and anh. DMF (3 ml) was injected under vigorous stirring. The mixture was placed in an oil bath preheated to 120° and the reaction continued for 24 h. Then, the mixture was cooled to r.t., a sat. NH_4Cl soln. (15 ml) added, and the mixture stirred for 5 min and extracted with AcOEt (5 × 10 ml). The org. phases were washed with sat. NaCl soln. (4 × 25 ml), dried (Na_2SO_4), and concentrated. The resulting crude product was purified by prep. TLC (7 elutions with hexane/acetone): 21 mg (21%) of **7** and 45 mg (45%) of **8**. *Data of* **7**: Colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.58 (*s*, 3 H); 1.71–1.76 (*m*, 1 H); 1.94–2.01 (*m*, 1 H); 2.13–2.19 (*m*, 2 H); 2.47 (*s*, 2 H); 4.10 (*dd*, *J* = 3.1, 11.1, 1 H); 5.07 (*s*, 1 H, exchange with D_2O); 5.56 (*s*, 1 H); 6.79 (*dd*, *J* = 2.1, 8.1, 1 H); 7.01 (*dd*, *J* = 1.8, 8.4, 1 H); 7.26 (*t*, *J* = 7.5, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.2; 28.3; 32.6; 33.2; 34.6; 113.1; 119.3; 120.4; 127.2; 132.8; 137.46; 154.7. HR-EI-MS: 213.1151 (M^+, $C_{14}H_{15}NO^+$; calc. 213.1154).

Data of **8**: Colorless liquid. IR (film): 3377, 3072, 3018, 1928, 2242, 1603. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.61 (*s*, 3 H); 1.72–1.78 (*m*, 2 H); 1.96 (*s*, 2 H); 1.98–2.10 (*m*, 2 H); 4.06 (*dd*, *J* = 3.3, 11.5, 1 H); 5.08 (*s*, 1 H, exchange with D_2O); 6.14 (*s*, 1 H); 6.79 (*dd*, *J* = 0.9, 8.1, 1 H); 7.03 (*dd*, *J* = 1.2, 8.4, 1 H); 7.25 (*t*, *J* = 8.4, 1 H). HR-EI-MS: 213.1152 (M^+, $C_{14}H_{15}NO^+$; calc. 213.1154).

REFERENCES

[1] A. C. Cope, L. Field, D. W. H. MacDowell, M. E. Wright, *J. Am. Chem. Soc.* **1956**, *78*, 2547.

[2] a) E. N. Marvell, C. Lin, *J. Am. Chem. Soc.* **1978**, *100*, 877; b) W. von E. Doering, R. A. Bragole, *Tetrahedron* **1966**, *22*, 385.

[3] D. C. Hurd, H. T. Bollman, *J. Am. Chem. Soc.* **1933**, *55*, 699; D. C. Hurd, H. T. Bollman, *J. Am. Chem. Soc.* **1934**, *56*, 447.

[4] A. C. Cope, J. E. Meili, D. W. H. MacDowell, *J. Am. Chem. Soc.* **1956**, *78*, 2551.

[5] W. von E. Doering, W. R. Roth, *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 115.

[6] E. Vogel, *Angew. Chem.* **1960**, *72*, 4; E. N. Marvell, S. W. Almond, *Tetrahedron Lett.* **1979**, *20*, 2777; E. N. Marvell, S. W. Almond, *Tetrahedron Lett.* **1979**, *20*, 2779.

[7] E. Vogel, *Justus Liebigs Ann. Chem*. **1958**, *615*, 1.

[8] J. A. Berson, P. B. Dervan, *J. Am. Chem. Soc.* **1972**, *94*, 7597; R. C. Gadwood, R. M. Lett, *J. Org. Chem*. **1982**, *47*, 2268; K. J. Shea, A. C. Greeley, S. Nguyen, P. D. Beauchamp, D. H. Aue, J. S. Witzeman, *J. Am. Chem. Soc*. **1986**, *108*, 5901; P. A. Wender, C. R. D. Correia, *J. Am. Chem. Soc*. **1987**, *109*, 2523.

[9] W. E. Billups, J. H. Cross, C. V. Smith, *J. Am. Chem. Soc.* **1973**, *95*, 3438.

[10] J. Limanto, M. L. Snapper, *J. Am. Chem. Soc.* **2000**, *122*, 8071.

[11] a) J. A. Berson, M. Jones, *J. Am. Chem. Soc*. **1964**, *86*, 5017; b) J. A. Berson, M. Jones, *J. Am. Chem. Soc.* **1964**, *86*, 5019; c) D. A. Evans , A. M. Golob, *J. Am. Chem. Soc.* **1975**, *97*, 4765; d) L. A. Paquette, *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 609.

[12] M. Sworin, K. C. Lin, *J. Am. Chem. Soc.* **1989**, *111*, 1815; M. E. Jung, G. L. Hatfield, *Tetrahedron Lett.* **1983**, *24*, 2931; P. Koch-Huber, R. W. Kunz, S. Bienz, *Molecules Online* **1999**, *3*, 9; L. Barriault, I. Denissova, N. Goulet, *Synthesis* **2012**, *44*, 1833; C. F. Weise, S. Immel, F. Richter, C. Schneider, *Eur. J. Org. Chem.* **2012**, 1520.

[13] M. E. Jung, J. P. Hudspeth, *J. Am. Chem. Soc.* **1978**, *100*, 4309; M. E. Jung, J. P. Hudspeth, *J. Am. Chem. Soc*. **1980**, *102*, 2463.

[14] S. S. Hussaini, A. R. N. Raj, C. A. M. A. Huq, *Tetrahedron Lett.* **2007**, *48*, 775.

[15] E. N. Marvell, T. H. C. Li, *J. Am. Chem. Soc.* **1978**, *100*, 883.

[16] R. Villagómez-Ibarra, C. Alvarez-Cisneros, P. Joseph-Nathan, *Tetrahedron* **1995**, *51*, 9285; J. J. Bucchignano, W.-S. Huang, P. R. Varanasi, R. R. Yu, to *IBM* (US) 'Fused Aromatic Structures and Methods for Photolithographic Applications', US Pat. 2009004596 (A1), 01.01.2009.

[17] J. G. Ávila-Zárraga, Ph. D. Thesis, Universidad Nacional Autónoma de México, 2000; J. G. Ávila-Zarraga, G. Ramirez-Galicia, M. Rubio, L. A. Maldonado-Graniel, *J. Mol. Struct. – THEOCHEM* **2000**, *531*, 301.

[18] J. A. Luján-Montelongo, A. Vázquez-Sánchez, J. G. Ávila-Zárraga, *Heterocycles* **2009**, *78*, 1955.

[19] K. J. Shea, R. B. Phillips, *J. Am. Chem. Soc*. **1980**, *102*, 3156.

[20] M. J. S. Dewar, L. E. Wade Jr., *J. Am. Chem. Soc.* **1977**, *99*, 4417; R. Wehrli, H. Schmid, D. Belluŝ, H.-J. Hansen, *Helv. Chim. Acta* **1977**, *60*, 1325; J. J. Gajewski, N. D. Conrad, *J. Am. Chem. Soc.* **1978**, *100*, 6268; J. J. Gajewski, N. D. Conrad, *J. Am. Chem. Soc.* **1978**, *100*, 6269; D. A. Hrovat, K. Morokuma, W. T. Borden, *J. Am. Chem. Soc.* **1994**, *116*, 1072; R. Gompper, W. R. Ulrich, *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 299; R. Gompper, W. R. Ulrich, *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 301.

[21] V. N. Staroverov, E. R. Davidson, *J. Am. Chem. Soc.* **2000**, *122*, 7377; K. N. Houk, J. González, Y. Li, *Acc. Chem. Res.* **1995**, *28*, 81; W. von E. Doering, Y. Wang, *J. Am. Chem. Soc.* **1999**, *121*, 10967; R. Hoffmann, W.-D. Stohrer, *J. Am. Chem. Soc.* **1971**, *93*, 6941.

[22] D. A. Hrovat, B. R. Beno, H. Lange, H.-Y. Yoo, K. N. Houk, W. T. Borden, *J. Am. Chem. Soc.* **1999**, *121*, 10529.
[23] M. Zora, I. Özkan, *J. Mol. Struct. – THEOCHEM* **2003**, *625*, 251.

Received July 9, 2012