Experimental and Theoretical Study of the Dimetalation of Phenylacetylene and (1-Naphthyl)acetylene

Peter A. A. Klusener,[1] Jaap C. Hanekamp, and Lambert Brandsma*

Department of Synthetic Organic Chemistry of the University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Paul von Ragué Schleyer*

Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, 8520 Erlangen, Bundes Republik Deutschland

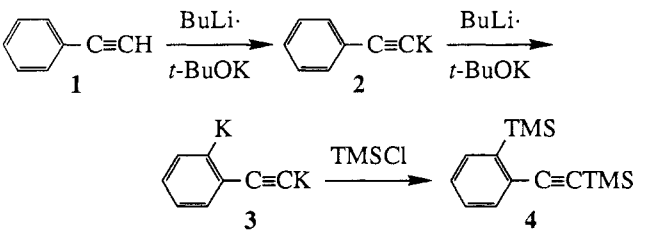
Received March 15, 1989

The direct dimetalation of phenylacetylene and of (1-naphthyl)acetylene at the acetylenic as well as the ortho position can be achieved by an equimolar mixture of *n*-butyllithium and potassium *tert*-butoxide. Metalation at the ortho position was shown by subsequent reaction with trimethylchlorosilane (TMSCl) resulting in the formation of the ortho-silylated disilyl compounds *o*-TMSC$_6$H$_4$C≡CTMS and 2-TMS-1-C$_{10}$H$_6$C≡CTMS. Under similar conditions C$_6$H$_5$C≡CBu^t and 1-C$_{10}$H$_7$C≡CBu^t gave the meta-silylated compound and a mixture of 3-, 4-, and 5-silylated derivatives, respectively. Ab initio calculations show that the ortho metalation of ethynylbenzene and 1-ethynylnaphthalene can be explained by the much higher coordination energy of the metalating reagent with the C≡CM rather than with the C≡CR moiety.

Introduction

The ortho metalation of aromatic compounds with hetero substituents such as OR, SR, NR_2, CH_2NR_2, $CH_2CH_2NR_2$, F, Cl, and CF_3 is a well-established and synthetically useful reaction.[2-8] During this position-specific deprotonation two mechanisms may be operative: (a) an acid–base mechanism; (b) a so-called coordination-only mechanism.[2] In the first case the activation is caused by inductive electron withdrawal, typical examples being the lithiations of fluorobenzene and (trifluoromethyl)-benzene.[2] The relatively smooth ortho lithiation of benzyldimethylamine ($PhCH_2NMe_2$) with *n*-butyllithium (BuLi) is explicable only by invoking mechanism b: in a preequilibrium BuLi is coordinated to nitrogen after which the ortho proton is abstracted. Another illustration is the dilithiation of benzyl alcohol,[9,10] the second lithium atom being introduced specifically into the position ortho to the CH_2OLi group. This lithiation requires the assistance of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The lithiation of the ortho position may be ascribed to the initial formation of a mixed aggregate of BuLi and $PhCH_2OLi$. Other dimetalations, such as the formation of 2,2'-dilithiobiphenyl[11-13] and 2,2'-dilithiodiphenyl ether[6,14] from BuLi·TMEDA and biphenyl and diphenyl ether, respectively, and the formation of 1,8-dilithionaphthalene[6,15] from 1-lithionaphthalene and BuLi·TMEDA, may be explained similarly. The addition of BuLi to the triple bond in diphenylacetylene, PhC≡CPh, and the subsequent ring metalation have been reported to give *o*-LiC$_6$H$_4$C(Bu)=C(Li)Ph.[13,16-20] The easy ring metalation is assumed to proceed through an aggregate of the initial adduct, PhC(Bu)=C(Li)Ph, and BuLi. These results are supported by NMR data and by MNDO calculations.[11,15,19,20] In a number of position-directed metalations, coordinative and electron-withdrawing effects cooperate; e.g., in the ortho metalation of aryl alkyl ethers, coordination to the ether oxygen by the metalating agent will enhance the inductive effect of the OR group and so increases the acidicity of the ortho proton(s).[2,4-6,8,21-24]

Scheme I

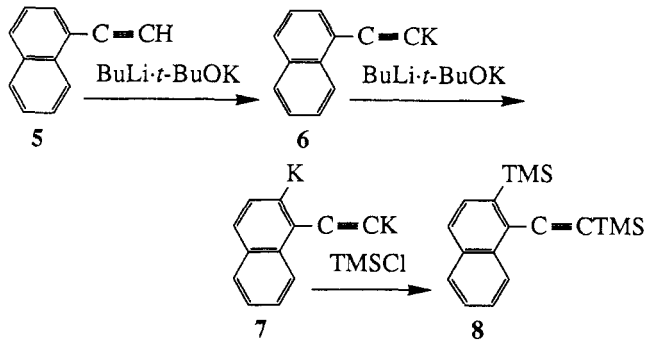


We observed that phenylacetylene can be dimetalated with a 2:1 molar mixture of BuLi and *t*-BuOK in THF/hexane at low temperature.[6,25-27] After the initial meta-

(1) Klusener, P. A. A. Ph.D. Thesis, University of Utrecht, 1989. Current address of P.A.A.K.: Koninklijke/Shell Laboratorium Amsterdam, P.O. 3003, 1003 AA Amsterdam, The Netherlands.
(2) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. Wardell, J. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, pp 54–59.
(3) Beak, P.; Sniekus, V. *Acc. Chem. Res.* **1982**, *15*, 306.
(4) Narasimhan, N. S.; Mali, R. S.; Kulkarni, B. K. *Tetrahedron* **1983**, *39*, 1975.
(5) Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 1, and references therein.
(6) Brandsma, L.; Verkruijsse, H. D. *Preparative Polar Organometallic Chemistry*; Springer-Verlag: Heidelberg, 1986; Vol. 1
(7) Bauer, W.; Klusener, P. A. A.; Harder, S.; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, L.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 552, and refs 1 and 2 cited therein.
(8) Simig, G.; Schlosser, M. *Tetrahedron Lett.* **1988**, *29*, 4277.
(9) Meyer, N.; Seebach, D. *Angew. Chem.* **1978**, *90*, 553; *Angew. Chem., Int. Ed.* **1978**, *17*, 521.
(10) Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1304.
(11) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1982**, *228*, 107.
(12) Schubert, U.; Neugebauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1184.
(13) See also: Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1962**, *84*, 1501.
(14) Gilman, H.; Miles, D. *J. Org. Chem.* **1958**, *23*, 1363.
(15) Neugebauer, W.; Clark, T.; Schleyer, P. v. R. *Chem. Ber.* **1983**, *116*, 3283.
(16) Mulvaney, J. E.; Gardlund, Z. G.; Gardlund, S. L.; Newton, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 476.
(17) Mulvaney, J. E.; Carr, L. J. *J. Org. Chem.* **1968**, *33*, 3286.
(18) Mulvaney, J. E.; Newton, D. J. *J. Org. Chem.* **1969**, *34*, 1936.
(19) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 6033.
(20) Bauer, W.; Schleyer, P. v. R. *Magn. Res. Chem.* **1988**, *26*, 827.
(21) Ellison, R. A.; Kotsonis, F. N. *Tetrahedron* **1973**, *29*, 805.
(22) Slocum, D. W.; Jennings, C. A. *J. Org. Chem.* **1976**, *41*, 3653.
(23) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Am. Chem. Soc.* **1983**, *105*, 7790.
(24) Crowther, G. P.; Sundberg, R. J.; Sarpeshkar, A. M. *J. Org. Chem.* **1984**, *49*, 4657.
(25) Hommes, H.; Verkruijsse, H. D.; Brandsma, L. *J. Chem. Soc., Chem. Commun.* **1981**, 366.

0022-3263/90/1955-1311$02.50/0

Scheme II



lation of the acetylenic function the second metal atom was specifically introduced into the position ortho to the C≡CLi group. The formation of the dimetalated intermediate was shown inter alia by the formation of the disilyl derivative **4** in excellent yields by quenching with trimethylchlorosilane (TMSCl). Useful applications of this dimetalation are the syntheses of some ortho-substituted phenylacetylenes and of fused heterocyclic compounds.[25-27]

In other metalation reactions, acetylide groups also exert a distinct directing effect by interaction with strongly basic reagents. Thus, in the reaction of vinylacetylene, HC≡CCH=CH_2, with 2 equiv of BuLi·*t*-BuOK in THF/hexane at −90 °C, the initial acetylide, KC≡CCH=CH_2, was deprotonated specifically in the 3-position to afford KC≡CC(K)=CH_2.[6,28] The acetylide group not only directs but also activates: under similar conditions ethene and benzene do not undergo metalation.

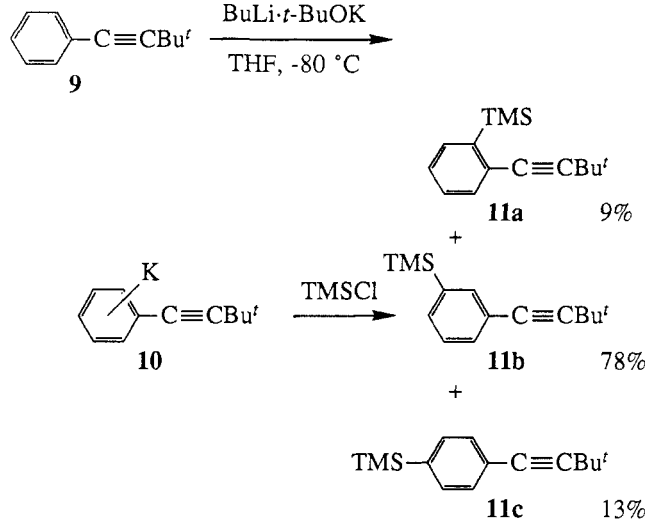
The present combined experimental and theoretical investigation was undertaken to gain more insight into the nature of the directing and activating effect of acetylenic functions in benzene and in naphthalene derivatives.

Experimental Results and Discussion

Dimetalation of Phenylacetylene and of (1-Naphthyl)acetylene. As reported earlier[6,25-27] almost quantitative conversion into the dimetalated compound, presumed to be *o*-$KC_6H_4C{\equiv}CLi$, can be achieved by treatment of phenylacetylene (**1**) with a 2:1 *molar* mixture of BuLi and *t*-BuOK in THF/hexane at ca. −70 °C. The dimetalation of phenylacetylene was performed here with 2 mol equiv of an *equimolar* mixture of BuLi·*t*-BuOK (usually 25% excess of "BuK"—formed by the reaction of BuLi with *t*-BuOK[29,30]—was employed to compensate for losses due to the competitive reaction with THF) in a 1:1 THF-hexane mixture in order to generate the dipotassio compound *o*-$KC_6H_4C{\equiv}CK$ (**3**; see Scheme I). Careful analysis (^1H and ^{13}C NMR, GC-MS, IR) of the TMSCl quench product showed it to consist of at least 95% of *o*-TMS-$C_6H_4C{\equiv}CTMS$ (**4**).

Other conditions for the dimetalation of phenylacetylene were shown to be less satisfactory. Thus, BuLi·TMEDA in THF at room temperature gives only monometalation at the acetylenic function.[25,27] Heating of a mixture of phenylacetylene and BuLi·TMEDA under reflux in hexane gave some meta and para metalation.[6,27] The complex mixture of BuLi·*t*-BuOK·TMEDA in hexane at −20 °C gave incomplete dimetalation (85%).[6]

Scheme III



Treatment of (1-naphthyl)acetylene under the optimum conditions for the dimetalation of phenylacetylene and subsequent quenching with TMSCl afforded the 2,2′-disilyl product **8** in an excellent yield (Scheme II). The absence of the 8-silylated isomer is both striking and unexpected, since a number of 1-naphthyl derivatives (e.g., naphthyl-CH_2NR_2, $-NR_2$, $-OR$, $-OLi$) are metalated preferentially at the 8-position by BuLi.[2,4-6,31-33]

Regiospecific functionalization reactions involving the intermediacy of **7** with electrophiles have been reported elsewhere.[34]

Metalations of PhC≡CR (R = *t*-Bu, (*t*-Bu)(Me)COK, Me_2COK, C≡CK) and of (*tert*-Butylethynyl)naphthalene. The activating and ortho-directing influence of the acetylide group (C≡CK) was compared with that of other acetylenic systems, viz., C≡CBu^t, C≡CC(Me)(R)OK, and C≡CC≡CK with regard to the metalation of benzene and naphthalene systems.

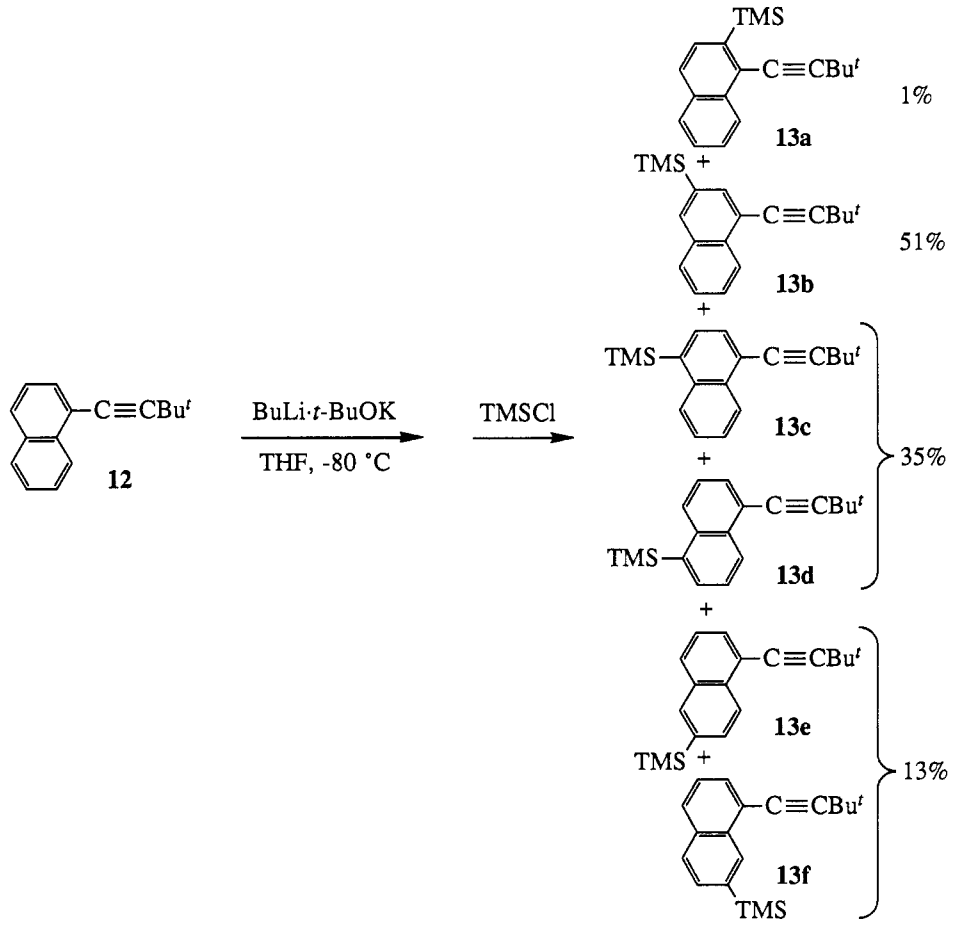
The *tert*-butyl group in the *t*-BuC≡C-aryl systems was chosen since it is inert toward metalation. This permits study of the effect of the acetylene (C≡C) function. Treatment of **9** with a molar equivalent of BuLi·*t*-BuOK in THF followed by addition of an excess of TMSCl gave in 87% yield a mixture of three isomers **11a–c** in a ratio of 9:78:13 (Scheme III). The isomers were identified and analyzed by GC-MS and ^{13}C NMR by reference to the authentic compounds whose syntheses are given in the experimental part (vide infra).

The deactivation of the ortho position in **9** toward metalation can hardly be due to steric hindrance. Since PhOBu^t and anisole have equal reactivity toward ortholithiation,[2] steric effects also are insignificant.

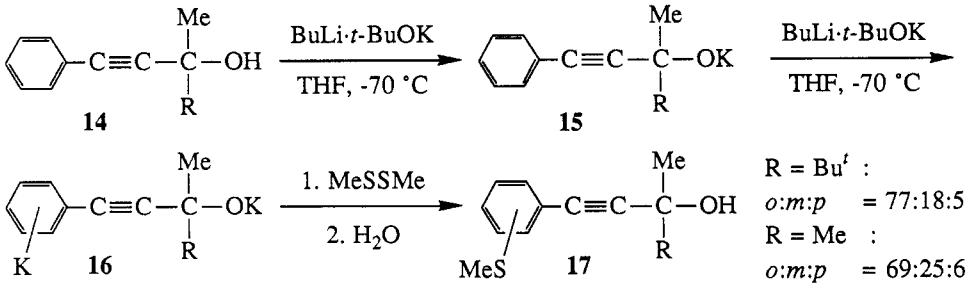
Treatment of the *tert*-butyl derivative of (1-naphthyl)acetylene **12** with the BuLi·*t*-BuOK reagent followed by quenching with TMSCl afforded a 90% yield of a mixture of isomeric silyl derivatives, comprised of **13b–d** as the main components (Scheme IV). The various silylated products were identified by GC-MS analysis and

(26) Hommes, H.; Verkruijsse, H. D.; Brandsma, L. *Tetrahedron Lett.* **1981**, *22*, 2495.
(27) Brandsma, L.; Hommes, H.; Verkruijsse, H. D.; de Jong, R. L. P. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 226.
(28) Brandsma, L.; Hommes, H.; Verkruijsse, H. D.; Kos, A. J.; Neugebauer, W.; Baumgärtner, W.; Schleyer, P. v. R. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 286.
(29) Pi, R.; Bauwer, W.; Brix, B.; Schade, C.; Schleyer, P. v. R. *J. Organomet. Chem.* **1986**, *306*, C1.
(30) Grovenstein, E., Jr. *Recent Advances in Anionic Polymerization*; Hogen-Esch, T. E., Smid, J., Eds.; Elsevier Science: Amsterdam, 1987; p 3.
(31) Barnes, R. A.; Nehmsmann L. *J. Org. Chem.* **1962**, *27*, 1939.
(32) Shirley, D. A.; Cheng, C. F. *J. Organomet. Chem.* **1969**, *20*, 251, and references therein.
(33) Coll, G.; Morey, J.; Costa, A.; Saá, J. M. *J. Org. Chem.* **1988**, *53*, 5345.
(34) Hanekamp, J. C.; Klusener, P. A. A.; Brandsma, L. *Synth. Commun.* **1989**, *19*, 2691.

Scheme IV



Scheme V



by ^{1}H and ^{13}C NMR spectroscopy on the two main fractions obtained by preparative gas chromatography of the mixture. The absence of the 8-silylated isomer was proven by comparison of the retention time of the separately synthesized 1-(*tert*-butylethynyl)-8-(trimethylsilyl)-naphthalene. The retention times of the other three silylated isomers implicated that only 1% ortho metalation had occurred. The two remaining peaks (8% and 5%) were assigned to the 6- and 7-silylated isomers.

We next investigated the reaction of the *carbinols* PhC≡CC(Me)(R)OH (R = Me or *t*-Bu) with the BuLi·*t*-BuOK reagent. It was expected that ring metalation could be directed toward the ortho position via a complex aggregate of the initial alkoxide and the second equivalent of the base. Treatment of the carbinols **14** (R = Me or *t*-Bu) with 2 equiv of BuLi·*t*-BuOK, followed by addition of dimethyl disulfide indeed gave mainly the ortho-methylthio derivative **17** (Scheme V).

The *distance* effect of the metalated triple bond to the ring was investigated by subjecting phenylbutadiyne (**19**) to the metalation conditions and quenching the reaction mixture with TMSCl. This experiment gave a mixture of bis(trimethylsilyl) derivatives **21** in 82% yield. GC-MS and NMR analysis showed that the ortho, meta, and para isomers had been formed in a ratio of 45:44:11 (Scheme VI).

Evidently, the ortho specificity is unique for an acetylide function that is attached *directly* to the aromatic ring.

Competition Experiments (See Table I). *Activating* effects (arising either from the inductive or from the coordinating properties of the acetylenic functions) have been investigated by competition experiments.

Treatment of a 1:1 molar mixture of PhC≡CK (**2**) and benzene with a deficiency of the BuLi·*t*-BuOK reagent at −80 °C and subsequent quenching with TMSCl showed that only the aromatic ring in **2** had reacted with the base ($PhSiMe_3$ was absent in the product mixture) to give the expected ortho-silylated derivative **4**. A similar experiment with (1-naphthyl)C≡CK (**6**) and naphthalene gave the bis-silylated naphthylacetylene derivative **8** and (trimethylsilyl)naphthalene in a ratio of 76:24. This lower selectivity with respect to the PhC≡CK/benzene meta-

Scheme VI

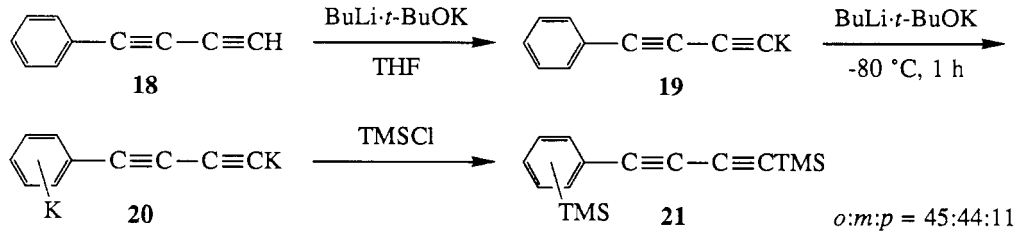


Table I. Competition Experiments[a]

competing substrates		mmolar amounts of				
A	B	A	B	BuLi·t-BuOK	TMSCl	products and molar ratio[c]
PhC≡CK[b]	benzene	50	50	100[b]	150	4:PhTMS[d] = 100:0
PhC≡CBu^t	benzene	20	20	20	50	11[e]:PhTMS = 100:0
PhC≡CK[b]	PhC≡CBu^t	20	20	40[b]	60	4:11[f] = 73:27
6[b]	naphthalene	10	10	20[b]	30	8:$C_{10}H_7$TMS[h] = 76:24
12	naphthalene	10	10	10	20	13[g]:$C_{10}H_7$TMS[h] = 70:30
6[b]	12	10	10	20[b]	30	8:13[g] = 65:35

[a] Reaction conditions: THF, −80 °C, 1 h. [b] In the cases of the substrates PhC≡CK and 6 half of the amount of BuLi·t-BuOK was consumed for the deprotonation of the acetylenic groups of PhC≡CH and 5, respectively. [c] Determined by GC and GC-MS analysis. [d] Under these conditions it is not possible to metalate benzene.[44] A competition experiment carried out −70 °C gave a metalation ratio of 90:10.[27] [e] Mixture of isomers; o:m:p = 11:74:15. [f] Mixture of isomers; o:m:p = 9:80:11. [g] Mixture of isomers. [h] Only one isomer of (trimethylsilyl)naphthalene was found with GC-MS analysis; from previous results we assume that this was the 2-isomer.[6]

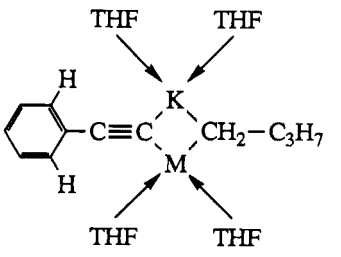
lation may be explained by a greater acidity of the various protons in naphthalene.[6]

From the similar metalation regiochemistry of **9** and **12** and of t-BuPh, i-C_3H_7Ph, EtPh, and c-C_3H_5Ph (weakly or non-coordinating groups) giving rise to (initial) meta and para metalation,[35-43] one might conclude that the t-BuC≡C group deactivates the ring for metalation (as do the alkyl groups mentioned). This conclusion is not justified, however, since in the competition between t-BuC≡CPh and benzene for the metalating agent, only the former compound had reacted (giving an ortho:meta:para ratio of 17:74:15).

In the experiment with the naphthalene compound **12** and naphthalene, the metalation ratio was 70:30. These experiments indicate that the t-BuC≡C group is capable of activating the ring (particularly the meta and 3 positions, respectively) for metalation.

In two final experiments **2** and **9**, and **6** and **12** were allowed to compete for the basic reagent. Analysis of the reaction mixtures obtained by quenching with TMSCl showed that the ring metalation ratios were 73:27 and 65:35, respectively. Thus the ortho activation by the C≡CK group is stronger than the meta activation by the C≡CBu^t group.

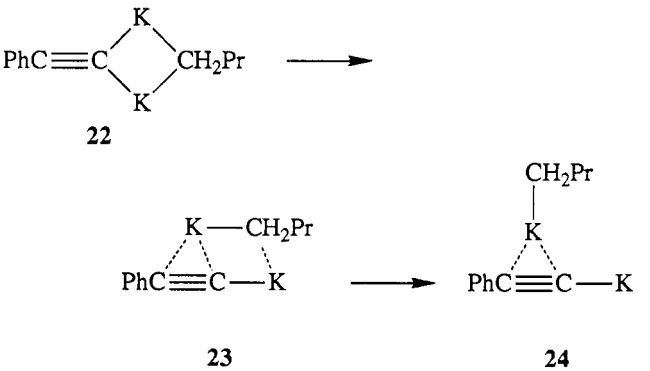
The meta-directing effect of the t-BuC≡C group in the metalations of **9** and **12** and the ortho-directing effect of the C≡CK (or C≡CLi) and of the C≡CC(Me)(R)OK



22

Figure 1.

Scheme VII



groups in the metalation reactions of **2**, **6** and **15** suggest that the presence of a metal atom is necessary for ortho metalation.

Seebach showed with ^{13}C NMR that in THF solution PhC≡CLi forms an aggregate with BuLi.[45] A reasonable assumption therefore is that the ortho metalation of PhC≡CM (M = K or Li) occurs within a comparable aggregate with BuK (Figure 1). However, specific ortho metalation seems hardly explicable with this model, because of the large distance between the ortho protons and the CH_2 center. With ^1H NMR we were unable to show any influence of the aggregating BuLi on the ortho protons: the aromatic patterns of BuLi·LiC≡CPh·$(THF)_n$ and of

(35) Bryce-Smith, D. *J. Chem. Soc.* **1954**, 1079.
(36) Morton, A. A.; Claff, C. E., Jr.; Collins, F. W. *J. Org. Chem.* **1955**, *20*, 428.
(37) Benkeser, R. A.; Foster, D. J.; Sauve, D. M.; Nobis, J. F. *Chem. Rev.* **1957**, *57*, 867.
(38) Bryce-Smith, D. *J. Chem. Soc.* **1963**, 5983.
(39) Benkeser, R. A.; Hooz, J.; Liston, T. V.; Trevillyan, A. E. *J. Am. Chem. Soc.* **1963**, *85*, 3984.
(40) Crimmins, T. F.; Chan, C. M. *J. Org. Chem.* **1976**, *41*, 1870.
(41) Crimmins, T. F.; Rather, E. M. *J. Org. Chem.* **1978**, *43*, 2170.
(42) Schlosser, M.; Schneider, P. *Helv. Chim. Acta* **1980**, *63*, 2403.
(43) Metalation of *tert*-butylbenzene in our laboratory with BuLi·t-BuONa·TMEDA in hexane at −20 °C and subsequent reaction with TMSCl afforded a mixture of meta- and para-silylated products [yield 50%, ratio m:p = 63:37]. Klusener, P. A. A. Unpublished results.
(44) At higher temperatures (ca. −50 °C) benzene undergoes metalation rapidly; however, at that temperature also THF reacts with BuLi·t-BuOK (ref 6, p 18). Without THF, benzene can be metalated for synthetic use: Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9. Reference 6, pp 192–3.
(45) Hässig, R.; Seebach, D. *Helv. Chim. Acta* **1983**, *66*, 2269.

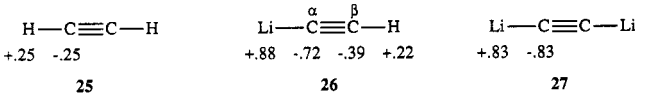


Figure 2. Natural changes of acetylene and lithiated acetylene. Geometries are optimized with 3-21G basis set using GAUSSIAN. Charges are obtained with NPA.

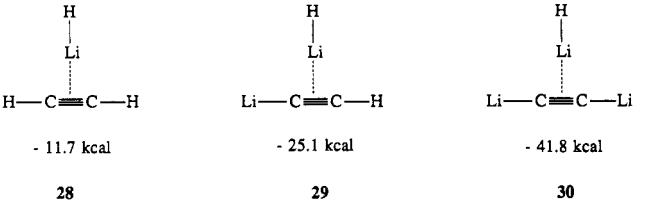


Figure 3. Association energies of (lithiated) acetylenes and lithium hydride. Association energies are in kcal/mol. Model calculations (3-21G//3-21G) using GAUSSIAN imposing C_{2v} symmetry in complexes **28** and **30** and a similar perpendicular geometry for system **29**.

$(PhC{\equiv}CLi)_2{\cdot}(THF)_n$[46] were similar. Crystal structures of **3**, *o*-$KC_6H_4C{\equiv}CLi$, or of *o*-Li-$C_6H_4C{\equiv}CLi$ would probably give more insight into the dimetalation, but attempts to isolate crystals from the reaction mixture or from *o*-$IC_6H_4C{\equiv}CLi$ and BuLi have been hitherto unsuccessful.

Model theoretical calculations provide a better understanding of the directing and activating effect of the C≡C group during the ring-metalation.

Theoretical Results and Discussion

Methods. Ab initio calculations were carried out using the 3-21G basis set,[47-49] generally adequate for organolithium compounds,[49] and the GAUSSIAN 82[49] or the GAMESS programs.[50-52] Charges were obtained by using natural population analysis (NPA).[53]

Association of LiH with the C≡C Bond. The first step in (di)metalations often involves coordination and/or aggregation of the metalating agent with the substrate.[6,11-20,28] However, the most likely aggregate (**22** as depicted in Scheme VII and in Figure 1) does not explain the exclusive second metalation at the ortho position of phenylacetylene. The metalating agent is too far from the reaction site. To facilitate ring metalation, the aggregated BuK needs to move toward the ring, e.g., by coordination of BuK with the π-system of the C≡C bond.

This is illustrated by **23** and **24** in Scheme VII, but these structures do not imply true intermediates (energy minima). Nevertheless, complex **23** can be compared with the crystal structures of RC≡CM (R = H, CH_3; M = Na, K).[54] Complexes **23** and **24** represent arrangements along the pathway leading to the transition state for metalation.

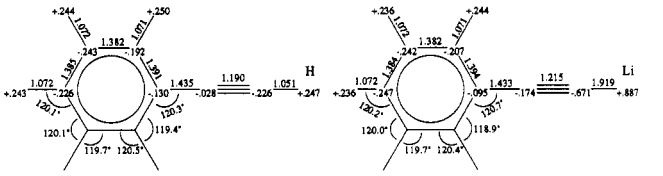


Figure 4. Ab initio calculations of phenylacetylene and of lithiophenylacetylene. Geometries optimized with the 3-21G basis set (C_{2v} symmetry). Distances in angstroms.

Since it would require a great deal of computer time to calculate these transition structures, we examined model systems instead.

As a model for the coordination complex **24**, association energies of (lithiated) acetylene with lithium hydride were calculated.[55] The negative natural charges of acetylene and the lithiated acetylenes, shown in Figure 2, show an increase at both C_α *and* C_β of HC≡CH (**25**), HC≡CLi (**26**), and LiC≡CLi (**27**).

This increase of charge density on both acetylenic carbons in **26** and **27** results in an increase of the association energies of the complexes of these acetylenes with LiH (Figure 3). Hence, the coordination energy in **24** (Scheme VII) should be large enough to direct ortho metalation. In contrast, in *t*-BuC≡CPh (low charge densities on C_α *and* C_β; compare **25** and **28**) this coordination is too weak to direct ortho metalation.

Ab Initio Calculations of PhC≡CH and PhC≡CLi. To assess the effects of the *t*-BuC≡C and of the C≡CM (M = Li or K) groups on the aromatic ring, ab initio calculations on phenylacetylene (the effects of the C≡CH and *t*-BuC≡C groups are assumed to be comparable) and on LiC≡CPh have been carried out. The geometries, optimized in C_{2v} symmetry, and the calculated charges are given in Figure 4.

The anionic acetylene also produces an increase in the negative charge density in remote positions. Polarization shifts the charge in the attached phenyl ring. This redistribution of negative charge in the π-system facilitates coordination with BuK and stabilizes the metalation transition state.

Thus, BuK can coordinate with the C≡C π-system as well as with the aromatic π-system of KC≡CPh. This is in agreement with what is known about the structures of benzyllithium and benzylpotassium. Whereas lithium prefers to be attached to the α (and the ipso) positions, the larger potassium prefers a site over the phenyl ring.[56] Such a poly-η coordination of BuK and KC≡CPh favors ortho metalation.

The association model of Figure 3 does not explain why the second metalation of (1-naphthyl)acetylene occurs only at the 2-position and not at the 8-position. The polarization of the negative charge density in monometalated (1-naphthyl)acetylene away from the metalated acetylenic function in the aromatic π-system might influence the attached ring more than the adjacent ring. Thus, the increase of negative charge at the 2-position caused by the metalated acetylene group may be larger than that of the 8-position. This would favor proton abstraction from the 2-position.

Experimental Section

a. General Remarks. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP200 or AC200 apparatus of solutions in deuter-

(46) The dimeric structure of PhC≡CLi in THF solution has been shown by cryoscopic measurements: Bauer, W.; Seebach, S. *Helv. Chim. Acta* **1984**, *67*, 1972.
(47) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
(48) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.
(49) Helene, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(50) Dupuis, M.; Spangler, D.; Wendoloski, J. J. GAMESS, Vol. I, NRCC Program QG01, 1980.
(51) Implementation of GAMESS: van Lenthe, J. H. *Supercomputer* **1985**, *5*, 33.
(52) See also: Guest, M. F.; Harrison, R. J.; van Lenthe, J. H.; van Corler, L. C. H. *Theor. Chim. Acta* **1987**, *71*, 117.
(53) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.
(54) Weiss, E.; Plass, H. *Chem. Ber.* **1968**, *101*, 2947.
(55) See also: Kaufmann, E.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 121.
(56) Gregory, P. Unpublished calculations, Erlangen.

iochloroform. Mass spectrometry was performed on a Kratos MS80 GC-MS combination apparatus equipped with a BP-1 column (25 m, i.d. 0.33 mm, film 0.5 μ). High-resolution mass spectrometry (HRMS) was performed with a resolution of 3000 and perfluorokerosine as reference. Preparative gas chromatography was carried out with a Hewlett-Packard 5750 gas chromatograph equipped with a 10% OV-17 column and a flame ionization detector. THF (Janssen Chimica) was distilled from lithium aluminum hydride and stored over sodium lead alloy under nitrogen. Potassium *tert*-butoxide (Chemetal), *n*-butyllithium (ca. 1.6 M hexane solution, Chemetal), and phenylacetylene (Janssen Chimica) are commercially available and were used as such. (1-Naphthyl)acetylene was prepared on 1 M scale as described by Hanekamp et al.[57] Phenylbutadiyne was prepared on 0.1 M scale as described by Brandsma.[58] Tetrakis(triphenylphosphino)paladium was prepared as described by Coulson.[59] TMEDA (Janssen Chimica) was distilled under reduced pressure from lithium aluminum hydride and stored under nitrogen. Trimethylchlorosilane (TMSCl, Merck) was distilled under nitrogen before use. All glassware was oven dried at 80 °C for 24 h. All reactions were carried out in an atmosphere of nitrogen.

b. Dimetalation of Phenylacetylene and Subsequent Silylation. A solution of 0.050 mol of phenylacetylene in 10 mL of THF was added at ca. −90 °C to a mechanically stirred solution of 0.125 mol of BuLi and 0.125 mol of *t*-BuOK in 80 mL of hexane and 80 mL of THF (this solution was prepared at <−90 °C; occasional cooling with liquid nitrogen was necessary). A suspension of **3** was formed gradually. The reaction mixture was stirred for an additional hour at −70 °C. (Subsequent regiospecific functionalizations of dimetalated phenylacetylene can be carried out as reported.[25-27,63])

To this suspension of **3** in THF was added at −70 °C 0.150 mol of trimethylchlorosilane (TMSCl), after which the temperature was allowed to rise to +30 °C. After an additional 10 min, 100 mL of water was added at 0 °C. Two extractions with pentane were carried out. The organic solutions were dried over magnesium sulfate and subsequently concentrated under reduced pressure.

Distillation of the remaining liquid gave *o*-$TMSC_6H_4C{\equiv}CTMS$ (**4**), 95% yield: bp 128 °C (12 mmHg), ca. 65 °C (0.1 mmHg); n^{20}_D 1.5145; ^1H NMR (CH_2Cl_2 δ 5.32 as internal standard) δ 7.62 (H^3 and H^6, m), 7.40 (H^4 and H^5, m), 0.55 (C_6H_4*TMS*, s), 0.42 (C≡CTMS, s); ^{13}C NMR data in Table II; mass spectrum, *m/e* (percent of base peak) 246 (M^+, 15), 231 (100), 215 (9), 191 (11), 145 (13), 108 (7), 73 (31); HRMS calcd for $[M^+]$ $^{12}C_{14}{}^1H_{22}{}^{28}Si_2$ 246.1260, found 246.1274.

c. Metalation of (*tert*-Butylethynyl)benzene (9) and Subsequent Silylation. To a solution of 0.030 mol of *t*-BuOK in 33 mL of THF were successively added at −90 °C a solution of 0.030 mol of BuLi in 20 mL of hexane and a solution of 0.030 mol of **9** in 23 mL of THF. After the mixture had been stirred for 2 h at −80 °C, 0.050 mol of TMSCl was added to the red solution. Workup as described in section b gave according to the GC-MS analysis a mixture of o, m, and p isomers of $TMSC_6H_4C{\equiv}CBu^t$ (**11**) in a ratio of 9:78:13 (in order of retention time) in 87% yield, bp 90 °C (0.1 mmHg): ^1H NMR (CH_2Cl_2 δ 5.32 as internal standard) δ **11b** 7.67 (H^2, m), 7.50 (H^4 and H^6, m), 7.36 (H^5, m), 1.45 (Bu^t, s), 0.38 (TMS, s), **11c** 7.49 (H^2, m), 7.52 (H^3, m), 1.44 (Bu^t, s), 0.37 (TMS, s); ^{13}C NMR data in Table II; mass spectra, *m/e* (percent of base peak) **11a** 230 (M^+, 49), 215 (100), 197 (8), 183 (5), 173 (13), 155 (25), 145 (22), 73 (22), 59 (37), **11b** and **11c** 230 (M^+, 34), 215 (100), 199 (19), 185 (4), 169 (2), 156 (6), 141 (2), 73 (7); HRMS calcd for $[M^+]$ $^{12}C_{15}{}^1H_{22}{}^{28}Si$ 230.1491, found 230.1531 (**11a**), 230.1505 (**11b**), 230.1496 (**11c**), calcd for $[M^+ - CH_3]$ $^{12}C_{14}{}^1H_{19}{}^{28}Si$ 215.1256, found 215.1271 (**11a**), 215.1253 (**11b**), 215.1242 (**11c**). (The identification was based on the comparison of the retention times of the separately synthesized isomers (vide infra) with those of the mixture. The order of retention times was in accordance with this identification.)[60]

d. Dimetalation of (1-Naphthyl)acetylene (5) and Subsequent Silylation. To a solution of 0.060 mol of *t*-BuOK in 50 mL of THF were successively added at −90 °C a mixture of 0.060 mol of BuLi in 40 mL of hexane and a solution of 0.020 mol of **5** in 10 mL of THF. The mixture was stirred for 1 h at −80 °C, after which the dark suspension was treated with 0.130 mol of TMSCl (excess). Workup as described in section b gave **8** in 86% yield, bp ca. 125 °C (0.005 mmHg) as a light brown liquid: n^{20}_D 1.5720; ^1H NMR data in Table III; ^{13}C NMR data in Table IV; mass spectrum, *m/e* (percent of base peak) 296 (M^+, 66), 281 (100), 265 (20), 207 (25), 195 (17), 183 (11), 165 (16), 133 (13), 97 (11), 73 (86), 59 (12), 45 (12); HRMS calcd for $[M^+]$ $^{12}C_{18}{}^1H_{24}{}^{28}Si_2$ 296.1416, found 296.1449.

e. Metalation of 1-(*tert*-Butylethynyl)naphthalene (12) and Subsequent Silylation. To a solution of 0.039 mol of *t*-BuOK in 50 mL of THF were successively added at −90 °C solutions of 0.039 mol of BuLi in 25 mL of hexane and 0.019 mol of **12** in 15 mL of THF. The dark reaction mixture was stirred for 1 h at −80 °C. After addition of 0.100 mol of TMSCl, workup was carried out as described in section b, giving a yellow mixture of isomers of **13**: 90% yield, bp 115–120 °C. The ratio of isomers according to the GC-MS analysis in order of retention time was 51:1:7:2:4:35.[61] All isomers had almost the same mass spectrum, *m/e* (percent of base peak) 280 (M^+, 56), 265 (100), 249 (14), 235 (5), 219 (3), 207 (6), 192 (4), 125 (5), 73 (12). Two fractions (1 and 2), obtained with preparative gas chromatography, were subjected to GC-MS and ^1H and ^{13}C NMR analysis (see Scheme IV and Tables III and IV). Fraction 1 consisted mainly of **13b** (73%), which was 51% of the distilled mixture, and consisted further of four other isomers, all in concentrations <7%. Fraction 2 consisted mostly (97%) of a ca. 1:1 mixture of two isomers **13c** and **13d**, whose retention times on the capillary column of the GC-MS apparatus were the same.

f. Dimetalations of 3-Methyl-1-phenyl-1-butyn-3-ol (14, R = Me) and of 3,4,4-Trimethyl-1-phenyl-1-pentyn-3-ol (14, R = *t*-Bu). To a solution of 0.075 mol of *t*-BuOK in 50 mL of THF were successively added at −90 °C a solution of 0.075 mol of BuLi in 50 mL of hexane and a solution of 0.025 mol of the carbinol **14** in 10 mL of THF. The mixture was stirred for 2 h at −70 °C, after which 0.050 mol of dimethyl disulfide was added in one portion. The temperature was allowed to rise to +5 °C. After an additional 10 min, 100 mL of a saturated aqueous solution of ammonium chloride was added. After three extractions with ether the organic solutions were combined and dried over magnesium sulfate and subsequently concentrated under reduced pressure, to give **17**:

17 (R = Me) ortho, meta and para in a ratio of 69:25:6:[60] 76% yield; ^1H NMR δ 6.98–7.37 (Ar H, m), 3.25 (OH, s), 2.42 (SMe, s), 1.65 (ortho Me_2C, s), 1.60 (meta and para Me_2C, 2 s); ^{13}C NMR data in Table II; mass spectra, *m/e* (percent of base peak) ortho 206 (M^+, 100), 191 (41), 188 (48), 173 (20), 171 (18), 163 (18), 159 (16), 149 (50), 148 (44), 147 (75), 134 (27), 116 (23), 115 (19), 89 (12), 43 (51), meta 206 (M^+, 65), 191 (100), 188 (35), 175 (6), 159 (11), 148 (20), 141 (8), 134 (7), 129 (8), 115 (20), 102 (5), 89 (7), 43 (21), para 206 (M^+, 30), 191 (79), 188 (100), 173 (37), 158 (11), 148 (19), 141 (12), 128 (12), 115 (21), 102 (5), 89 (11), 43 (26).

17 (R = *t*-Bu) ortho, meta and para in a ratio of 77:18:5:[60] 82% yield; ^1H NMR δ ortho 6.98–7.37 (Ar H, m), 2.43 (OH, s), 2.41 (SMe, s), 1.57 (CMe, s), 1.14 (Bu^t, s); meta and para 6.98–7.37 (Ar H, m), 2.43 (OH, s), 2.43 (meta SMe, s), 2.42 (para SMe, s), 1.52 (CMe, 2 s), 1.10 (Bu^t, 2 s); ^{13}C NMR data in Table II; mass spectra, *m/e* (percent of base peak) ortho 248 (M^+, 2), 233 (11), 215 (19), 191 (100), 149 (69), 134 (24), 116 (28), 89 (14), 57 (24), 43 (71), meta and para 248 (M^+, 4), 230 (8), 191 (100), 148 (14), 115 (9), 89 (5), 57 (14), 43 (17).

(57) Hanekamp, J. C.; Klusener, P. A. A. *Synth. Commun.* **1989**, *19*, 2677.

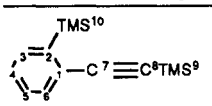
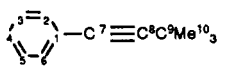
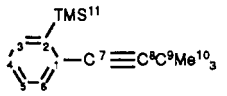
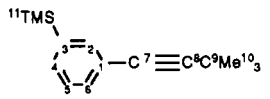
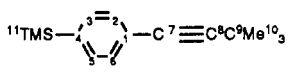
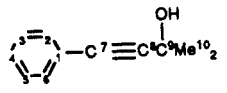
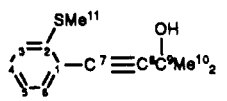
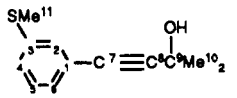
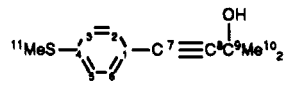
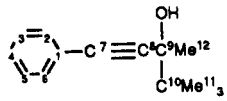
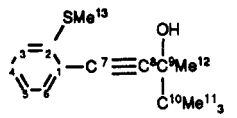
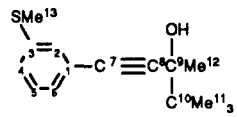
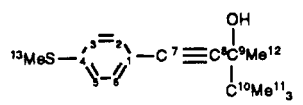
(58) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1971; p 156.

(59) Coulson, D. R. *Inorg. Synth.* **1972**, *8*, 121.

(60) In accordance with the GC-MS analysis. Here we used the empirical rules that the retention times increase in the order ortho < meta < para, being the same order as the boiling points, and that the mass spectrum of the ortho isomer is different from that of the meta and para isomers, whose mass spectra are very similar.

(61) The product was contaminated with 10% of a silylated compound with M^+ = 338 (*m/e*). We assume that this product was the result of an addition of BuLi to the C≡C bond and the subsequent reaction with TMSCl, namely, (1-naphthyl)(TMS)C=C(*n*-Bu)(*t*-Bu). This compound was not further investigated.

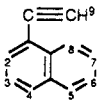
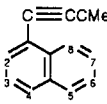
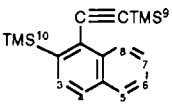
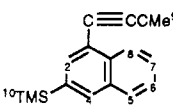
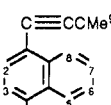
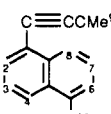
Table II. ^{13}C NMR Data of the Phenylacetylene Derivatives[a]

compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}
 **4**	128.3	142.6	133.8	127.7	128.6	132.9	106.9	96.9	−0.2	−1.1			
 **9**	124.1	131.5	128.1	127.3			79.1	98.3	27.8	31.0			
 **11a**	129.3	141.5	133.7	126.6	128.6	132.6	80.8	100.7	28.0	30.8	−1.0		
 **11b**	123.5	136.3	140.3	132.2	127.5	131.9	79.4	98.3	27.9	31.1	−1.2		
 **11c**	124.5	130.7	133.0	139.7			79.2	98.9	27.9	31.1	−1.2		
 **14**, R = Me	122.7	131.5	128.1	128.1			82.0	93.9	65.5	31.4			
 ***o*-17**	120.6	141.2	123.9	128.5	123.7	132.0	79.3	100.5	65.4	31.2	15.3		
 ***m*-17**	123.3	128.8	138.5	126.1	128.3	127.9	81.4	94.2	65.2	31.2	15.3		
 ***p*-17**	118.8	131.7	125.6	138.9			81.5	93.8	65.3	31.3	15.0		
 **14**, R = *t*-Bu	122.9	131.4	128.0	127.9			83.7	92.9	74.1	38.3	25.1	24.7	
 ***o*-17**	120.7	141.4	124.0	128.5	123.6	132.2	81.3	99.5	74.3	38.3	25.2	24.8	14.7
 ***m*-17**	122.8	129.0	138.6	126.1	128.4	128.0	83.2	93.3	74.1	38.3	25.1	24.6	15.4
 ***m*-17**	119.1	131.7	125.6	138.9			83.4	92.9	74.1	38.3	25.1	24.6	15.2

[a] δ values in ppm downfield from $SiMe_4$, and $CDCl_3$ as internal standard.

g. Dimetalation of Phenylbutadiyne (18) and Subsequent Silylation. To a solution of 0.050 mol of *t*-BuOK in 30 mL of THF were successively added at −90 °C a mixture of 0.050 mol of BuLi in 31 mL of hexane and a solution of 0.020 mol of phenylbutadiyne[58] in 20 mL of THF. The mixture was stirred for 1 h at −80 °C, after which the dark-colored solution was treated with 0.060 mol of TMSCl (excess). After warming the mixture to +30 °C workup was carried out as described in section b.

Table III. ^{1}H NMR Data of the (1-Naphthyl)acetylene Derivatives

compound	δ, ppm downfield from $SiMe_4$									^3J, Hz				
	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	H^{10}	23	34	56	67	78
 **5**	7.70	7.34	7.76	7.76	7.44	7.53	8.35	3.43		7.2	8.3	8.0	6.7	8.7
 **12**	7.59	7.30	7.66	7.73	7.41	7.51	8.31	1.40		7.2	8.2	8.0	6.8	8.3
 **13a**		7.54	7.73	7.75	7.45	7.54	8.43	0.34	0.46		8.2	8.0	6.8	8.3
 **13b**	7.77		7.96	7.87	7.53	7.63	8.34	1.50	0.40	6.9		7.0	6.8	7.8
 **13c**	7.62	7.57		8.10	7.62	7.62	8.41	1.47	0.49			7.5	7.2	8.0
 **13d**	7.73	7.43	8.05		7.59	7.54	8.41	1.47	0.49	7.0	8.5		6.1	7.9

Concentration of the organic solution in vacuo (0.1 mmHg) gave a mixture of o, m, and p isomers of **21** in a ratio of 45:44:11:[60] 82% yield;[62] ^{1}H NMR δ 7.66 (H^2 of *m*-**21**), 7.58–7.48 (H^3 and H^6 of *o*-**21**; H^4 and H^6 of *m*-**21**; H^2 and H^3 of *p*-**21**; H^2 of PhC≡CC≡CTMS[62]), 7.39–7.29 (H^4 and H^5 of *o*-**21**; H^5 of *m*-**22**; H^3 and H^4 of **23**), 0.44 (C_6H_4*TMS* of *o*-**21**), 0.32 (C_6H_4*TMS* of *m*-/*p*-**21**), 0.30 (C≡CTMS of **22** and PhC≡CC≡C*TMS*); ^{13}C NMR data in Table V; mass spectrum, *m*/*e* (percent of base peak) *o*-**21** 270 (M^+, 29), 255 (100), 241 (3), 255 (2), 215 (8), 195 (7), 120 (15), 97 (7), 73 (10); *m*-/*p*-**21** 270 (M^+, 30), 255 (100), 241 (5), 225 (2), 195 (2), 120 (21), 97 (2), 73 (29).

h. Competition Experiments. Typical Procedure for Phenylacetylene and Benzene. (Amounts of reactants and results are mentioned in Table I). To an efficiently stirred solution of 0.100 mol of *t*-BuOK in 90 mL of THF a solution of 0.100 mol of BuLi in 62 mL of hexane was added at −100 °C. After an additional 5 min at −100 °C a mixture of 0.050 mol of phenylacetylene, 0.050 mol of benzene, and 10 mL of THF was added dropwise at −100 °C in 1 min. (Terminal acetylenes were added dropwise, while occasionally cooling with liquid nitrogen was performed. The other additions were carried out in one portion.) The mixture was stirred for 1 h at −80 °C, after which the green suspension was treated with 0.150 mol of TMSCl. The mixture was warmed to +30 °C, after which water was added at 0 °C and extraction with pentane was carried out. Concentration in vacuo (0.1 mmHg) afforded an oil, which was subjected to GC and GC-MS analysis (data in Table I). In this case 12.1 g of a mixture of PhC≡CTMS (M^+ = 174 *m*/*e*) and **4** in a ratio of 17:83 was obtained.

i. Preparation of Starting Compounds. (*tert*-Butylethynyl)benzene (9) was prepared by $Pd(PPh_3)$[59]-catalyzed reaction of *t*-BuC≡CZnCl (prepared in situ as described by Brandsma)[64] with iodobenzene (Aldrich) following the procedure described by Negishi[65] in 60% yield; bp 85–90 °C (12 mmHg); n^{20}_D 1.5243; ^{1}H NMR δ 7.37 (H^2, m), 7.23 (H^3 and H^4, m), 1.31 (Bu^t, s); ^{13}C NMR data in Table II; mass spectrum, *m*/*e* (percent of base peak) 158 (M^+, 29), 143 (100), 128 (40), 115 (15), 103 (6), 77 (6); HRMS calcd for [M^+] $^{12}C_{12}{}^1H_{14}$ 158.1095, found 158.1067, calcd for [$M^+ - CH_3$] $^{12}C_{11}{}^1H_{11}$ 143.0861, found 143.0846.

1-(*tert*-Butylethynyl)naphthalene (12) was prepared following the method described by Brandsma[64,66] of $Pd(PPh_3)$-catalyzed reaction of aromatic *bromides* (here we used 1-bromonaphthalene, Aldrich) with *t*-BuC≡CZnCl (6-h reflux) in 67% yield; bp 106 °C (0.05 mmHg); n^{20}_D 1.5932; NMR data in Tables III and IV; mass spectrum, *m*/*e* (percent of base peak) 208 (M^+, 53), 193 (100), 178 (35), 165 (13), 152 (15); HRMS calcd for [M^+] $^{12}C_{16}{}^1H_{16}$ 208.1252, found 208.1297, calcd for [$M^+ - CH_3$] $^{12}C_{15}{}^1H_{13}$ 193.1018, found 193.1048.

3-Methyl-1-phenyl-1-butyn-3-ol (14, R = Me) and 3,4,4-Trimethyl-1-phenyl-1-pentyn-3-ol (14, R = *t*-Bu). A solution of 0.210 mol of BuLi in 140 mL of hexane was added in 2 min

(62) This yield is according to the GC-MS analysis. Other compounds were 16% of monosilylated product PhC≡CC≡CTMS (M^+ = 198 *m*/*e* and ^{13}C data in Table V) and 2% of a compound with M^+ = 328 *m*/*e*, probably Ph(Bu)C=C(TMS)C≡CTMS, formed by addition of BuLi to the C≡C bond and the subsequent reaction with TMSCl.

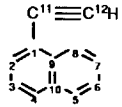
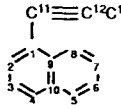
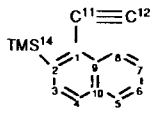
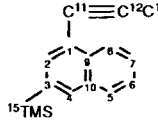
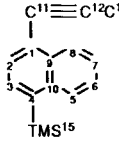
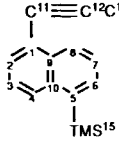
(63) Recently the regiospecific functionalization of *p*-LiC_6H_4C≡CLi has also been described: Furber, M.; Taylor, R. J. K.; Barford, S. C. *J. Organomet. Chem.* **1987**, *311*, C35.

(64) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; p 157.

(65) King, A. O.; Negishi, E.; Villani, F. J., Jr.; Silveira, A., Jr. *J. Org. Chem.* **1978**, *43*, 358.

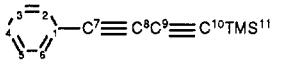
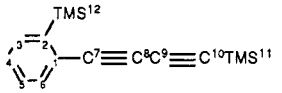
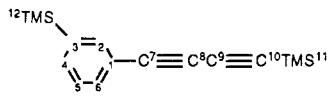
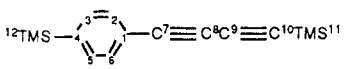
(66) van der Heiden, R.; Keegstra, B.; Klusener, P. A. A.; Brandsma, L. Unpublished results.

Table IV. ^{13}C NMR Data of the (1-Naphthyl)acetylene Derivatives[a]

compound		C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}
	δ	119.7	131.2	125.0	129.2	128.2	126.9	126.4	126.0	133.5	133.0	81.8	82.0			
	$^1J_{CH}$		163.9	163.3	156.8	160.2	160.3	161.3	160.9				251.3			
	$^3J_{CH^n}$	8.3^3	8.7^4		7.7^2	$5.7^{4,7}$	8.6^8	8.6^5	5.9^6	$7.2^{2,7}$	$\sim 6.5^{3,6,8}$	49.6^{12}				
		$4.3^{8,12}$			5.4^5					$6.0^{4,5}$		6.1^2				
5																
	δ	121.7	129.8	125.0	128.1[c]	127.8[c]	126.4[c]	126.0[c]	126.1	133.5	133.2	77.4	103.4	28.2	31.1	
	$^1J_{CH}$		163.7	163.4	160.5	161.3	159.7	160.5	160.3						127.3	
	$^3J_{CH^n}$	8.3^3	8.7^4		6.4^2	5.1^4	8.5^8	8.6^5	6.5^6	7.6^7	6.6^8	6.1^2	5.2^{14}	*d*	4.6^{14}	
		4.8^8		5.4^5	7.4^7				$7.1^{4,5}$							
12																
	δ	126.7	141.6	129.9	127.7	128.1	126.6[c]	126.8[c]	126.2	133.8	133.3	104.7	103.2	−0.8	−0.1	
	$^1J_{CH}$			159.9	159.8	160.2	160.5	160.6	161.0					119.5	120.0	
	$^3J_{CH^n}$	8.6^3	*b*		5.0^5	5.1^4	9.5^8	8.2^5	6.8^6	8.4^7	*b*			2.0^{13}	2.1^{14}	
		4.7^8				6.7^7				$5.8^{4,5}$						
13a																
	δ	120.8	133.8	137.3	133.6	128.3	126.1	126.8	126.2	132.6	133.6	77.3	103.5	28.4	31.3	−1.1
	$^1J_{CH}$		159.4		157.9	160.6	160.9	159.7	160.6						127.4	119.3
	$^3J_{CH^n}$	5.4^8	9.7^4		8.5^2	6.5^7	8.3^8	8.4^5	5.2^6	*b*	$\sim 6.1^{2,6,8}$	6.4^2	4.8^{14}	*d*	4.6^{14}	2.1^{15}
					5.1^5	4.9^4										
13b																
	δ	123.2	128.9	132.4	138.5	128.4	127.9	125.8	127.3	133.2	136.7	77.3	104.3	28.4	31.2	0.3
	$^1J_{CH}$		161.7	158.7		156.5	160.8	160.1	160.6						127.4	119.4
	$^3J_{CH^n}$	5.0^8			*b*	6.9^7	7.6^8	8.4^5	5.9^6	$\sim 6.7^{2,5,7}$	$7.7^{3,6}$	*b*	*b*	*d*	4.5^{14}	1.9^{15}
		8.8^3									6.8^8					
13c																
	δ	122.7	129.6	124.9	128.4	138.5	133.5	125.7	128.0	133.2	136.7	77.3	103.7	28.4	31.2	0.3
	$^1J_{CH}$		162.2	160.3	156.5		158.6	160.9	155.6						127.4	119.4
	$^3J_{CH^n}$	7.0^3	8.4^4		6.9^2	*b*	8.2^8		5.4^6	$6.7^{2,4,7}$	$7.7^{3,6}$	*b*	*b*	*d*	4.5^{14}	1.9^{15}
		5.0^8									6.8^8					
13d																

[a] δ values in ppm downfield from $SiMe_4$, and $CDCl_3$ as solvent and internal standard. J values in hertz. [b] Broadened signal. [c] The values of C^4, C^5, and/or C^6, C^7 may be interchanged. [d] $^2J_{C^{13}H^{14}} = 4.0$ Hz.

Table V. ^{13}C NMR Data of the Phenylbutadiyne Derivatives[a]

compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}
	121.2	132.5	128.3	129.2			76.6	74.3	90.3	88.0	−0.5	
 *o*-21	126.3	144.0	133.9	128.3	128.7	133.2	77.9	77.1	90.9	88.0	−0.3	−1.1
 *m*-21	120.8	137.5	140.9	133.9	127.7	132.7	76.7	74.2	90.3	88.0	−0.4	−1.4
 *p*-21	121.5	131.6	142.4	142.4			76.7	74.6	90.4	88.0	−0.4	−1.4

[a] δ values in ppm downfield from $SiMe_4$ and $CDCl_3$ as solvent and internal standard.

at −20 °C to a solution of 0.200 mol of phenylacetylene in 100 mL of THF. Next 0.240 mol of acetone (Merck, Pro Analysi) or pinacolon (Janssen Chimica) was added at −20 °C, and the temperature was allowed to rise to +20 °C. After this was cooled to 0 °C, 100 mL of water was added, and the aqueous layer was neutralized with hydrochloric acid. Three extractions with ether were carried out. Drying over magnesium sulfate, removal of the solvents in vacuo, and subsequent distillation gave the carbinol.

14 (R = Me): 90% yield; 80–95 °C (0.15 mmHg); n^{20}_D 1.5503; ^1H NMR δ 7.40 (H^2 and H^6, m), 7.26 (H^3, H^4 and H^5, m), 2.88 (OH, s), 1.61 (CMe_2, s); ^{13}C NMR data in Table II; mass spectrum, *m/e* (percent of base peak) 160 (M^+, 20), 145 (100), 129 (11), 115 (20), 102 (14), 77 (8), 43 (32);

14 (R = *t*-Bu): 80% yield; 95–100 °C (0.1 mmHg); n^{20}_D 1.5323; ^1H NMR δ 7.40 (H^2 and H^6, m), 7.24 (H^3, H^4 and H^5, m), 2.50 (OH, s), 1.53 (Me, s), 1.10 (Bu^t, s); ^{13}C NMR data in Table II; mass spectrum, *m/e* (percent of base peak) 202 (M^+, 0.5), 187 (2.5), 184 (5), 169 (3), 145 (100), 129 (13), 115 (6), 102 (9), 91 (4), 77 (4), 57 (11), 43 (21).

j. Preparation of Reference Compounds. *m*- and *p*-TMS-$C_6H_4C{\equiv}CBu^t$ (11b and 11c). To a solution of 0.050 mol of *m*- and *p*-dibromobenzene in 100 mL of THF a solution of 0.052 mol of BuLi in 34 mL of hexane was added at −80 °C over 10 min. The mixture was stirred for an additional 5 min at −80 °C, after which the white suspension was treated with 0.060 mol of TMSCl. After the mixture was warmed to +30 °C, aqueous workup, drying over magnesium sulfate, subsequent concentration in vacuo, and distillation gave *m*-TMS-C_6H_4Br in 100% yield [bp 50 °C (0.05 mmHg); n^{20}_D 1.5270] and *p*-TMS-C_6H_4Br in 93% yield [bp 50 °C (0.1 mmHg); n^{20}_D 1.5262]. To a solution of 0.025 mol of *t*-BuC≡CZnCl in 25 mL of THF and 17 mL of hexane (prepared as described by Brandsma)[64] were added 0.024 mol of *m*- or *p*-TMS-C_6H_4Br and a solution of 0.43 mmol of $Pd(PPh_3)_4$ (0.5 g) in 30 mL of THF. After the reaction mixture had been heated for 5 h at 40–50 °C, it was poured into 100 mL of a saturated aqueous solution of ammonium chloride. Pentane (50 mL) was added, and washing with an aqueous ammonium chloride solution was carried out until a slurry of palladium salts precipitated. The organic layer was decanted from this slurry, dried over magnesium sulfate, and subsequently concentrated in vacuo. Distillation gave **11b**: 60% yield; bp ca. 70 °C (0.1 mmHg); n^{20}_D 1.5142; ^1H NMR data in section c; ^{13}C NMR data in Table II; HRMS calcd for $[M^+]$ $^{12}C_{15}{}^1H_{22}{}^{28}Si$ 230.1491, found 230.1505, calcd for $[M^+ - CH_3]$ $^{12}C_{14}{}^1H_{19}{}^{28}Si$ 215.1256, found 215.1267.

11c: 50% yield; bp ca. 75 °C (0.1 mmHg); n^{20}_D 1.5162; ^1H NMR data in section c; ^{13}C NMR data in Table II; HRMS calcd for $[M^+]$ $^{12}C_{15}{}^1H_{22}{}^{28}Si$ 230.1491, found 230.1496, calcd for $[M^+ - CH_3]$ $^{12}C_{14}{}^1H_{19}{}^{28}Si$ 215.1256, found 215.1250.

***o*-TMS-$C_6H_4C{\equiv}CBu^t$ (11a).** To a mixture of 0.050 mol of *o*-dibromobenzene, 60 mL of THF, and 60 mL of diethyl ether was added at −118 °C a solution of 0.050 mol of BuLi in 33 mL of hexane. Immediately thereafter 0.070 mol of TMSCl was added in one portion and the temperature was allowed to rise. Aqueous workup, drying over magnesium sulfate, removal of the solvents under reduced pressure, and subsequent distillation afforded in 20% yield *o*-TMSC_6H_4Br [bp 38–40 °C (0.1 mmHg); n^{20}_D 1.5347; mass spectrum, *m/e* (percent of base peak) 230 + 228 (M^+, 12), 215 + 213 (100), 187 + 185 (21), 133 (50), 91 (41)]. Using 0.010 mol of *tert*-butylacetylene,[64] BuLi (0.010 mol in 7 mL of hexane), zinc chloride (0.010 mol), *o*-TMSC_6H_4Br (0.010 mol), 0.17 mmol of $Pd(PPh_3)_4$, and 35 mL of THF, following a procedure similar to that for **11a** and **11c** gave according to the GC-MS analysis a mixture of *o*-TMSC_6H_4Br and **11a** in a ratio of 70:30 in 90% overall yield (27% chemical yield of **11a**): bp 40 °C (0.1 mmHg); ^{13}C NMR data in Table II.

1-(*tert*-Butylethynyl)-8-(trimethylsilyl)naphthalene and 1-((Trimethylsilyl)ethynyl)-8-(trimethylsilyl)naphthalene. A solution of 1.25 mol of cyanogen bromide in 200 mL of diethyl ether was prepared by careful addition at 0 °C of 1.25 mol of bromine to a well-stirred mixture of 1.25 mol of potassium cyanide,[64] 160 mL of water, and 100 mL of diethyl ether, followed by two extractions with 50 mL of diethyl ether and subsequent successive dryings over magnesium sulfate and several portions of phosphorus pentoxide. This yellow solution was added at ca. −60 °C to an efficiently stirred mixture of 0.20 mol of 1,8-dilithionaphthalene, 0.40 mol of TMEDA, 200 mL of hexane, and 150 mL of THF (prepared as described by Brandsma).[6] The temperature of the light brown reaction mixture was allowed to rise to −30 °C, and 100 mL of water was added. The aqueous layer was extracted three times with methylene chloride. The combined organic layers were washed twice with an aqueous solution of hydrogen chloride (18%) and subsequently dried over magnesium sulfate. Removal of the solvents yielded a partly solid black residue, which was dissolved in 60 mL of boiling ethanol. Fast filtration over *diatomaceous earth* of the hot solution and subsequent crystallization afforded 1,8-dibromonaphthalene as white crystals: 34% yield;[67] mp 106 °C; bp 138–140 °C (0.1 mmHg); ^1H NMR[68] δ 7.82 (H^2, dd, J_{23} = 7.4 Hz, J_{24} = 1.2 Hz), 7.66 (H^4, dd, J_{43} = 8.3 Hz, J_{42} = 1.2 Hz), 7.13 (H^3, dd, J_{32} = 7.4, J_{34} = 8.3 Hz); ^{13}C NMR δ 136.9 (C^{10}), 135.2 ($C^{2/7}$), 129.5 ($C^{4/5}$), 128.7 (C^9), 126.3 ($C^{3/6}$), 119.4 ($C^{1/8}$); mass spectrum, *m/e* (percent of base peak) 288 + 286 + 284 (M^+, 50 + 100 + 50%, isotopic pattern of dibromo compounds), 207 + 205 ($M^+ - Br^\bullet$, 30), 126 ($M^+ - 2Br^\bullet$, 83).

To convert 1,8-dibromonaphthalene into 1-(*tert*-butylethynyl)-8-(trimethylsilyl)naphthalene, the same procedure was followed as for **11b** and **11c**; however, the palladium cross-coupling reaction was performed at ca. 50 °C during 17.5 h. After removal of the solvents under reduced pressure, a mixture was obtained, which according to the GC-MS analysis contained 1-bromo-8-(trimethylsilyl)naphthalene[69] and 1-(*tert*-butylethynyl)-8-(tri-

(67) Sometimes light green crystals were obtained, however with the same purity.

(68) Compare: Brügel, W. *Handbook of NMR Spectral Parameters*; Heyden and Son: London, 1979; Vol. II, p 460.

methylsilyl)naphthalene: 27% yield; mass spectrum, *m/e* (percent of base peak) 280 (M^+, 60), 265 (100), 223 (72), 193 (68), 179 (20), 165 (25), 73 (30), 22 (59); HRMS calcd for $[M^+]$ $^{12}C_{19}{}^{1}H_{24}{}^{28}Si$ 280.1647, found 280.1679, calcd for $[M^+ - CH_3]$ $^{12}C_{18}{}^{1}H_{21}{}^{28}Si$ 265.1413, found 265.1414.

1-((Trimethylsilyl)ethynyl)-8-(trimethylsilyl)naphthalene was prepared similarly by using TMSC≡CZnCl[64] in the Pd cross-coupling reaction: 10% yield; mass spectrum, *m/e* (percent of base peak) 296 (M^+, 17), 281 (100), 265 (29), 209 (15), 207 (16), 193 (29), 165 (14), 73 (66); HRMS calcd for $[M^+]$ $^{12}C_{18}{}^{1}H_{24}{}^{28}Si_2$ 296.1417, found 296.1442, calcd for $[M^+ - CH_3]$ $^{12}C_{17}{}^{1}H_{21}{}^{28}Si_2$ 281.1182, found 281.1205.

Acknowledgment. This work was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for Advancement of Research (NWO). We thank S. Harder (Department of Synthetic Organic Chemistry of the University of Utrecht) for carrying out the ab initio calculations of phenylacetylene and its lithium analogue and Dr. J. H. van Lenthe (Department of Theoretical Chemistry of the University of Utrecht) for his assistance and the disposal of computer time. We thank A. C. van der Kerk-van Hoof for carrying out the GC-MS analyses and for determining the exact masses.

Registry No. 1, 536-74-3; 2, 1122-79-8; 3, 124153-61-3; 4, 62618-20-6; 5, 15727-65-8; 8, 124153-63-5; 9, 4250-82-2; 11a, 124153-64-6; 11b, 124153-65-7; 11c, 124153-62-4; 12, 124153-66-8; 13a, 124153-73-7; 13b, 124153-74-8; 13c, 124153-75-9; 13d, 124153-76-0; 13e, 124153-77-1; 13f, 124153-78-2; 14 (R = Me), 1719-19-3; 14 (R = t-Bu), 85051-67-8; 17 (R = t-Bu, *o* isomer), 124153-67-9; 17 (R = t-Bu, *m* isomer), 124153-68-0; 17 (R = t-Bu, *p* isomer), 124153-69-1; 17 (R = Me, *o* isomer), 124153-79-3; 17 (R = Me, *m* isomer), 124153-80-6; 17 (R = Me, *p* isomer), 124153-81-7; 18, 5701-81-5; 21 (*o* isomer), 124153-70-4; 21 (*m* isomer), 124153-71-5; 21 (*p* isomer), 124153-72-6; 25, 74-86-2; 26, 1111-64-4; 27, 1070-75-3; 31, 4440-01-1; tBuC≡CZnCl, 89556-09-2; MeCOMe, 67-64-1; $H_3CCOC(CH_3)_3$, 75-97-8; *m*-BrC_6H_4Br, 108-36-1; *p*-BrC_6H_4Br, 106-37-6; *o*-BrC_6H_4Br, 583-53-9; *m*-$TMSC_6H_4Br$, 17878-47-6; *p*-$TMSC_6H_4Br$, 6999-03-7; *o*-$TMSC_6H_4Br$, 17878-37-4; tBuC≡CH, 917-92-0; TMSC≡CZnCl, 78389-87-4; LiH, 7580-67-8; 1-bromonaphthalene, 90-11-9; 1,8-dilithionaphthalene, 61767-59-7; 1,8-dibromonaphthalene, 17135-74-9; 1-bromo-8-(trimethylsilyl)naphthalene, 124153-82-8; 1-(*tert*-butylethynyl)-8-(trimethylsilyl)naphthalene, 124153-83-9; 1-[(trimethylsilyl)ethynyl]-8-(trimethylsilyl)naphthalene, 124153-84-0.

(69) 73% unreacted 1-bromo-8-(trimethylsilyl)naphthalene: bp ca. 115 °C (0.1 mmHg); mass spectrum, *m/e* (percent of base peak) 280 + 278 (M^+, 5.8), 265 + 263 ($M^+ - CH_3^\bullet$; 49), 183 ($M^+ - [CH_3 + Br^\bullet]$, 100), 167 (15), 155 (14), 141 (23), 115 (19).

The Mechanism of the Olefin-to-Carbene Rearrangement for 9-Phenyl-1(9)-homocubene

Philip E. Eaton* and Andrew J. White

Department of Chemistry, 5735 S. Ellis Avenue, The University of Chicago, Chicago, Illinois 60637

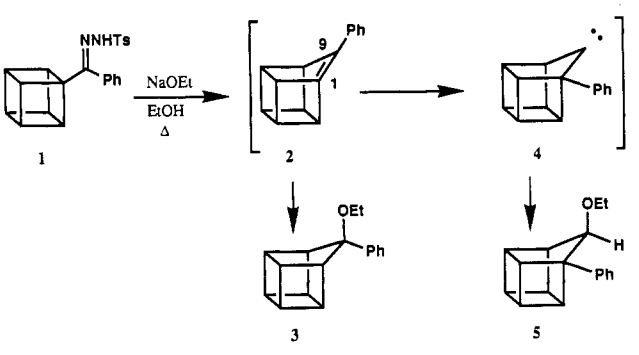
Received August 22, 1989

Two distinct mechanistic pathways exist for the olefin-to-carbene rearrangement of 9-phenyl-1(9)-homocubene to 1-phenyl-9-homocubylidene: a phenyl shift or a skeletal carbon–carbon bond shift. Cubane ^{13}C carboxylic acid was prepared and converted to cubyl phenyl ^{13}C ketone and its tosylhydrazone. Determination of the distribution of label in the ethers formed on decomposition of the tosylhydrazone in hot ethanolic base showed that the latter mechanism is operating.

Rearrangements of carbenes to olefins are well-documented in the literature.[1] However, as can be expected from simple energy considerations, only a few examples of the reverse reaction have been observed.[2] These olefin-to-carbene rearrangements apparently can occur only under drastic reaction conditions or when very strained, highly energetic olefins are involved. Little is known about the mechanism of such rearrangements.

Recently, Eaton and Hoffmann[2f] showed that decomposition of cubyl phenyl ketone tosylhydrazone (1) in ethanolic base generated 2, 9-phenyl-1(9)-homocubene, an extraordinarily strained bridgehead olefin. Regiospecific addition of ethanol across the twisted double bond of this very reactive intermediate was proposed to account for

Scheme I



formation of ether 3, one of the reaction products isolated. Rearrangement of olefin 2 to the singlet carbene 4, 1-phenyl-9-homocubylidene, and insertion of this carbene into the O–H bond of ethanol was invoked to account for formation of ether 5, the other isolated product (Scheme I). The ethers are formed in good yield in a ratio of approximately 1.7:1.

The rearrangement of an olefin *to a carbene* is an extraordinary event. How do the bonds reorganize? The p

(1) Gutsche, C. D.; Redmore, D. *Carbocyclic Ring Expansion Reactions*; Academic Press: New York, 1968; pp 111–117.

(2) (a) Billups, W. E.; Lin, L. P.; Chow, W. Y. *J. Am. Chem. Soc.* **1974**, *96*, 4026. (b) Landleer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1974**, 2813. (c) Hixson, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 1981. (d) Chan, T. H.; Massuda, D. *J. Am. Chem. Soc.* **1977**, *99*, 936. (e) Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* **1984**, *25*, 1661. (f) Eaton, P. E.; Hoffmann, K. L. *J. Am. Chem. Soc.* **1987**, *109*, 5285. (g) Chen, N.; Jones, M., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 305.

0022-3263/90/1955-1321$02.50/0