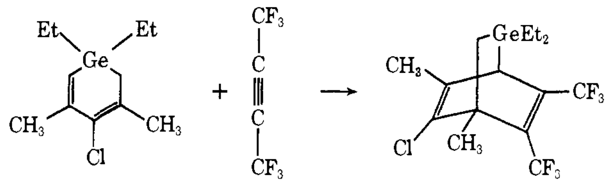
Evidence for a Germanium–Carbon (p–p)π Double Bond

Sir:

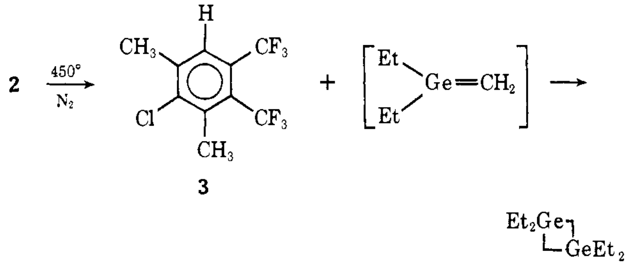
Once thought to be nonexistent,[1] considerable evidence for the transient existence of compounds containing a silicon–carbon,[2] silicon–silicon,[3] or silicon–oxygen[4] (p–p)π double bond has recently accrued. However, we are aware of only one case where (p–p)π bonding between germanium and carbon has been invoked (this in an attempt to explain the much greater acidity of pentaphenylgermole relative to triphenylgermane).[5] A single report has appeared of an attempt to generate a "pure" germanium–carbon (p–p)π double bond, and the route employed, pyrolysis of a germacyclobutane, proved unsuccessful.[6] We report here strong evidence for the intermediacy of a molecule containing a germanium–carbon (p–p)π double bond.

Germacyclohexadiene (**1**)[7] reacted in a sealed tube (overnight at 25° and then 5 hr at 70–80°) with a twofold excess of perfluoro-2-butyne to provide quantitative conversion (by nmr, 80–90% isolated) to the expected Diels–Alder adduct **2**:[8] a colorless, viscous liquid [nmr (CCl_4) δ 0.7 (s, 2 H, CH_2), 0.9–1.2 (m, 10 H, $GeEt_2$), 1.8–1.9 (overlapping Me singlet with Me quartet split by one CF_3, J_{HF} = 2.6 Hz), 3.75 (s, 1 H, bridgehead CH)].[9]



1 **2**

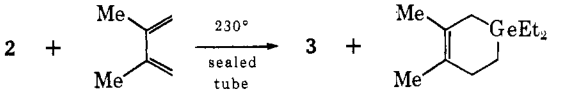
Complete pyrolysis of **2** was conducted in a nitrogen flow system (0.5 Torr, 450°) and the pyrolysate collected at −196°. Analysis of the pyrolysate by gas chromatography revealed only two components and a total absence of **2**. Separation of the two products by preparative gas chromatography afforded pure samples of **3** [50%; nmr (CCl_4) δ 2.45 (s) and 2.55 (d, J = 2.4 Hz) (6 H), 7.48 (br s, 1 H); mass spectrum m/e calcd for $C_{10}H_7{}^{35}ClF_6$ 276.0140, found 276.0125][8] and **5** [35%; nmr (CCl_4) δ 0.5 (s, 4 H, ring CH_2),[10] 0.9–1.1 (m, 20 H, Et); m/e calcd for $C_{10}H_{24}{}^{74}Ge_2$ 292.0302, found 292.0302][8] as colorless, viscous liquids.



3 **5**

The formation of 1,1,3,3-tetraethyl-1,3-digermacyclobutane (**5**) strongly argues for the intermediacy of 2-ethyl-2-germabutene (**4**), a compound containing the germanium–carbon (p–p)π double bond. Formation of 1,3-disilacyclobutanes from various thermal precursors has often been cited as evidence for silaalkene intermediates. Indeed the gas-phase thermal decomposition of the silabicyclo[2.2.2]octadiene system proceeds in a fashion exactly analogous to that described here for **2**.[2f]

Although trapping of **4** with anything other than itself has proven much more difficult than in the case of silaalkenes, we have been successful in one case. The copyrolysis of **2** and an excess of 2,3-dimethylbutadiene (sealed tube, 230°, 20 min) cleanly afforded the Diels–Alder adduct **6**[8] [59%; nmr ($DCCl_3$) δ 0.50–1.15 (m, 12 H, CH_2GeEt_2), 1.36 (br s, 2 H, $GeCH_2$), 1.73 (br s, 6 H, CH_3), 2.0–2.25 (br t, 2 H, CH_2); mass spectrum m/e calcd for $C_{11}H_{22}{}^{74}Ge$ 228.09334, found 228.09214]. This same product is formed, albeit in lower yield, in the flow gas-phase copyrolysis.



6

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(1) W. E. Dasent, "Nonexistent Compounds," Marcel Dekker, New York, N, Y., 1965.

(2) (a) N. S. Nametkin, V. M. Vdovin, L. E. Gusel'nikov, and V. I. Zavyalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3, 584 (1966); (b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968); (c) R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson, and J. Stevenson, *J. Organometal. Chem.*, **34**, 53 (1972); (d) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, 882 (1971); (e) T. J. Barton and C. L. McIntosh, *Chem. Commun.*, 861 (1972); (f) T. J. Barton and E. A. Kline, *J. Organometal. Chem.*, 42, C21 (1972); (g) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, **94**, 7926 (1972); (h) P. Boudjouk and L. H. Sommer, *Chem. Commun.*, 54 (1973).

(3) D. N. Roark and G. J. D. Peddle, *J. Amer. Chem. Soc.*, **94**, 5837 (1972).

(4) L. E. Gusel'nikov, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **6**, 84 (1971); I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971). Copyrolysis of 1,1-dimethylsilacyclobutane and benzaldehyde affords good yields of styrene, hexamethylcyclotrisiloxane, and octamethylcyclotetrasiloxane; T. J. Barton and E. A. Kline, unpublished observation. We believe that this results from the cycloaddition of $Me_2Si{=}CH_2$ to the carbonyl group to form an unstable silaoxetane which thermally decomposed to styrene and $Me_2Si{=}O$ which undergoes cyclic oligomerization. A similar reaction with heptanal has recently been mentioned in the literature: ref 2h, footnote 5. A single attempt to perform an analogous reaction with 2 and benzaldehyde was unsuccessful in our hands.

(5) M. D. Curtis, *J. Amer. Chem. Soc.*, **91**, 6011 (1969).

(6) N. S. Nametkin, *et al.*, *Dokl. Akad. Nauk SSSR*, **194**, 1096 (1970). Although no germanium-containing products were found which could be attributed to the intervention of a "germaalkene," the formation of ethylene leaves open the question whether such a species is involved in at least part of this thermal decompositon.

(7) D. Seyferth, *et al.*, *J. Amer. Chem. Soc.*, **92**, 657 (1970).

(8) Satisfactory (±0.2%) analyses for C and H were obtained for compounds 2 (also Cl), 3 (also Cl), 5, and 6.

(9) The spectral information on 2 does not totally exclude certain isomeric structures, some of which could conceivably thermally extrude **4**. The likelihood that this combination took a course other than the 2 + 4 addition is small in our opinion. A detailed discussion of this point will be included in the complete paper.

(10) The chemical shift of the ring-methylene protons of **5** is quite similar to the value of δ 0.64 for the only reported analogous ring system, 1,1,3,3-tetramethyl-1,3-digermacyclobutane: V. F. Mironov, T. K. Gar, and S. A. Mikhailyants, *Dokl. Akad. Nauk SSSR*, **188** (1), 120 (1969).

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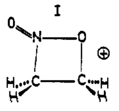
A Mechanism for Electrophilic Nitration

Sir:

Although electrophilic aromatic nitration has received an overwhelming amount of attention, little agreement about its mechanistic details has thus far been reached. This is in great part due to the variety of solvent systems in which the reaction has been studied, giving rise to a multitude of different product and rate data and unfortunately an almost equal number of varied interpretations.[1] To rectify this dilemma, electrophilic nitration reactions could be (and have been) studied in the gas phase through mass spectrometric and ion cyclotron resonance (icr) techniques. These, however, suffer from the disadvantages that structural information is not easily derived and that detailed product analyses are nearly impossible to obtain because of the minute quantities of material involved. An alternative approach would be the use of theoretical molecular orbital methods; it is the results of such a study that we report in this communication.

Using single determinant *ab initio* molecular orbital theory,[2] we have explored in some detail that section of the geometric potential surface corresponding to the interaction of ethylene with the nitronium ion NO_2^+, as a model for the electrophilic nitration of benzene. We have located three local minima on this potential: an asymmetric NO bridge (I) and symmetric ONO bridge (II) structures of nearly equal energy and a *bisected* open form (III) some 60 kcal/mol less stable. The relative disfavor of the "classical" form (III) is surprising in light of the interpretation given to the proton and carbon-13 nuclear magnetic resonance spectra of nitronium adducts of hexamethyl and trifluorotrimethylbenzene by Olah and coworkers.[6] We believe this discrepancy to be due not only to a large differential solvation and to our use of an ethylene substrate instead of benzene but also to the ability of methyl and fluoro substituents to stabilize such "classical" forms as III in preference to the bridged molecules.[7] Symmetric nitrogen-bridged forms (IV and V) and a perpendicular open structure (VI) were also investigated but were found to be unstable with respect to at least one of the three local minima (I–III).

I



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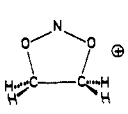
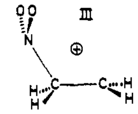


III



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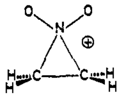

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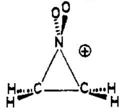
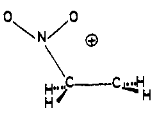


VI

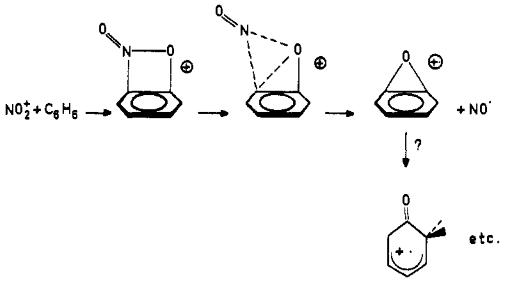


The results of recent ion cyclotron resonance investigations by Benezra, Hoffmann, and Bursey[8] and Dunbar, Shen, and Olah[9] indicate that the reaction of benzene with NO_2^+ does not lead to the formation of a stable complex but rather to a radical ion of formula $C_6H_6O\cdot^+$ presumably accompanied by loss of NO·.

$$NO\cdot + C_6H_6O\cdot^+ \longrightarrow C_6H_6 + NO_2^+ \not\longrightarrow \{C_6H_6\cdots NO_2\}^+$$

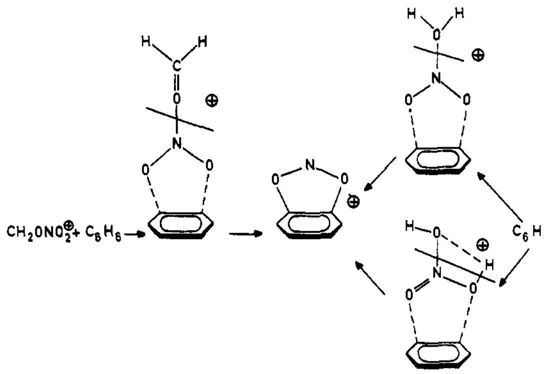
This observation might be rationalized in terms of the formation of an asymmetric NO bridged ion (corresponding to I), followed by rapid loss of NO· to give the stable oxygen-bridged radical.[10] The latter would presumably rearrange *via* 1,2-hydrogen shifts to a more favorable structure (Scheme I).

Scheme I



Bursey and coworkers[8] do observe, however, the formation of a stable nitronium–benzene complex when the aromatic is allowed to react with any of the ions, $H_2ONO_2^+$, $CH_2ONO_2^+$, and $CH_3CHONO_2^+$, formed in the icr chemistry of the alkyl nitrates.[11] In each of these cases direct nitrogen attack is blocked and the formation of the asymmetric NO complexes corresponding to I (or "classical" adducts as in III) is seemingly impossible. Instead we suggest attack by oxygen and the formation of an INO bridged ion (corresponding to II) similar to the proposal made by Dunbar and coworkers[9] to account for an abnormal (nucleophilic rather than electrophilic) ordering of substituent effects in the icr nitration experiment. We further suggest, however, that such an ONO bridged ion is stable and may not easily rearrange to give a nitrogen bonded adduct as a final product (Scheme II).

Scheme II



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(1) For reviews, see (a) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, New York, N. Y., 1965; (b) G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971); (c) J. H. Ridd, *ibid.*, **4**, 248 (1971).

(2) Calculations using the minimal STO-3G[3] and extended 4-31G[4] Gaussian basis sets have been performed with the Gaussian 70 series of computer programs.[5] Detailed structural and energy data will be presented in a forthcoming full report.

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(4) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

(5) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, submitted to Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(6) G. A. Olah, H. C. Lin, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3667 (1972).

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(8) S. A. Benezra, M. K. Hoffmann, and M. M. Bursey, *J. Amer. Chem. Soc.*, **92**, 7501 (1970).

(9) R. C. Dunbar, J. Shen, and G. A. Olah, *ibid.*, **94**, 6862 (1972).

(10) Preliminary findings of investigations in progress indicate that such a process requires considerably less activation energy than rearrangement to either an ONO bridged or open "classical" structure.

(11) P. Kriemler and S. E. Buttrill, Jr., *J. Amer. Chem. Soc.*, **92**, 1123 (1970).

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A Convenient and General Synthesis of Acetylenes *via* the Reaction of Iodine with Lithium 1-Alkynyltriorganoborates

Sir:

Treatment of lithium 1-alkynyltriorganoborates with iodine under mild conditions produces the corresponding alkyne in essentially quantitative yields (eq 1–3).

$$HC{\equiv}CR + n\text{-BuLi} \longrightarrow LiC{\equiv}CR + n\text{-BuH} \tag{1}$$

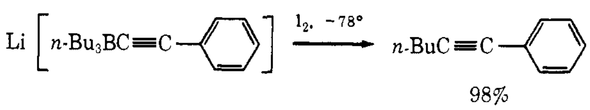
$$R'_3B + LiC{\equiv}CR \longrightarrow Li[R'_3BC{\equiv}CR] \tag{2}$$

$$Li[R'_3BC{\equiv}CR] + I_2 \longrightarrow R'C{\equiv}CR + R_2BI + LiI \tag{3}$$

The reaction is applicable to a wide variety of alkyl and aryl acetylenes and organoboranes. Consequently, unlike conventional methods for the preparation of acetylenes based on nucleophilic substitution reactions of the alkali metal acetylides, the present procedure readily permits the introduction of both primary and secondary alkyl groups and can even be extended to the introduction of aryl groups. This procedure, with its exceptionally broad range of applicability, provides a new simple, general synthesis of acetylenes.

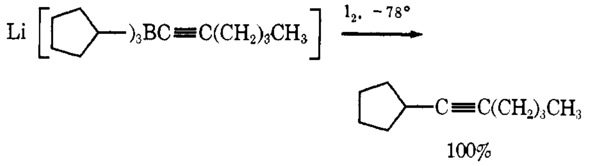
Trialkylboranes, readily prepared *via* hydroboration,[1] react with alkali metal acetylides to produce the corresponding alkali metal 1-alkynyltrialkylborates (eq 2).[2] Such compounds react with a variety of electrophiles, such as acids and acid halides, to induce transfer of an alkyl group from boron to carbon.[2c,d,3] Treatment of similar complexes of vinylorganoboranes with iodine results in an alkyl migration from boron to carbon, followed by a spontaneous deiodoboronation of the intermediate, to provide a highly convenient synthesis of olefins.[4] We undertook to explore the possibility of utilizing the reaction of iodine with alkali metal 1-alkynyltriorganoborates as a possible route to the corresponding alkynes.

Addition of a solution of iodine in tetrahydrofuran (THF) to a solution of the complex from tri-*n*-butylborane and phenylethyne in THF at 0° resulted in the immediate disappearance of the iodine color. After stirring the reaction mixture for 0.5 hr, glpc analysis revealed a 67% yield of 1-phenyl-1-hexyne. At −78° the reaction of the iodine was much slower. However, stirring for 1 hr, followed by gradual warming to room temperature, brought the reaction to completion. A 98% yield of the desired alkyne was produced (eq 4).



(4)

There appears to be no difficulty in introducing secondary alkyl groups, such as *sec*-butyl, cyclopentyl, or cyclohexyl (eq 5). Finally, even aryl groups are readily introduced (eq 6).



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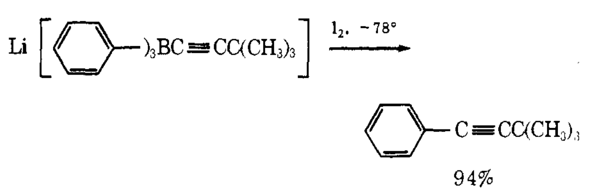

(6)

The results of representative reactions are summarized in Table I.

Table I. The Synthesis of Acetylenes *via* the Reaction of Iodine with Lithium 1-Alkynyltriorganoborates

Acetylene[a]	Organoborane,[a] R$_3$B, R =	Product	Yield,[b] %
1-Hexyne	*n*-Butyl	5-Decyne	96
	Isobutyl	2-Methyl-4-nonyne	98
	sec-Butyl	3-Methyl-4-nonyne	98
	Cyclopentyl	1-Cyclopentyl-1-hexyne	100
	Cyclohexyl	1-Cyclohexyl-1-hexyne	99
	Phenyl	1-Phenyl-1-hexyne	98
Phenylethyne	*n*-Butyl	1-Phenyl-1-hexyne	98
	Isobutyl	1-Phenyl-4-methyl-1-pentyne	96
	sec-Butyl	1-Phenyl-3-methyl-1-pentyne	95
	Phenyl	Diphenylacetylene	95
3,3-Dimethyl-1-butyne	*n*-Butyl	2,2-Dimethyl-3-octyne	91
	Isobutyl	2,2,6-Trimethyl-3-heptyne	93
	Phenyl	1-Phenyl-3,3-dimethyl-1-butyne	94

[a] 10 mmol in 10 ml of THF. [b] By glpc based on acetylene.

The following procedure for the preparation of 1-phenyl-3,3-dimethyl-1-butyne is representative. A dry 500-ml flask equipped with a magnetic stirring bar, septum inlet, and dropping funnel was flushed with nitrogen. The flask was charged under nitrogen with 7.47 g (30.8 mmol) of triphenylborane and 25 ml of dry THF, then cooled to 0°. In another dry nitrogen-flushed flask equipped with a magnetic stirring bar and septum inlet was placed 50 ml of THF and 2.54 g (31 mmol) of 3,3-dimethyl-1-butyne. The flask was cooled in an ice bath and 16.4 ml (30.8 mmol) of a 1.88 *M* solution of *n*-butyllithium in hexane was added to form

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(1) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972.

(2) (a) G. Wittig and P. Raff, *Justus Liebigs Ann. Chem.*, **573**, 195 (1951); (b) G. Wittig and D. Wittenberg, *ibid.*, **606**, 1 (1957); (c) P. Binger, G. Benedikt, G. W. Rotermund, and R. Köster, *ibid.*, **717**, 21 (1968); (d) P. Binger and R. Köster, *Tetrahedron Lett.*, 1901 (1965).

(3) M. Noruse, T. Tomita, K. Uchimoto, and H. Nozaki, Abstracts of the 27th Annual Meeting of the Chemical Society of Japan, Part I, 148 (1972).

(4) G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 3652 (1967).