carbonyl reagents. Reaction of II thermally with $Fe_2(CO)_9$[1b] or photolytically with $Fe(CO)_5$[13] leads only to very small isolated yields of VI along with several other complexes, while reaction of V with $Fe(CO)_5$ photolytically or $Fe_2(CO)_9$ thermally leads chiefly to cyclononatetraeneiron tricarbonyl, complex VIII, bicyclo[6.1.0]nonatrieneiron tricarbonyl, and none of complex VII.[8] In view of these examples, it is clear $BDAFe(CO)_3$ complements the reactions of iron carbonyl reagents and may offer general synthetic utility for selectively trapping various types of dienes. We are currently exploring the utility of this reagent in other tautomeric systems as well as the reasons for its remarkable selectivity.

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(13) G. Scholes and M. Brookhart, unpublished results.

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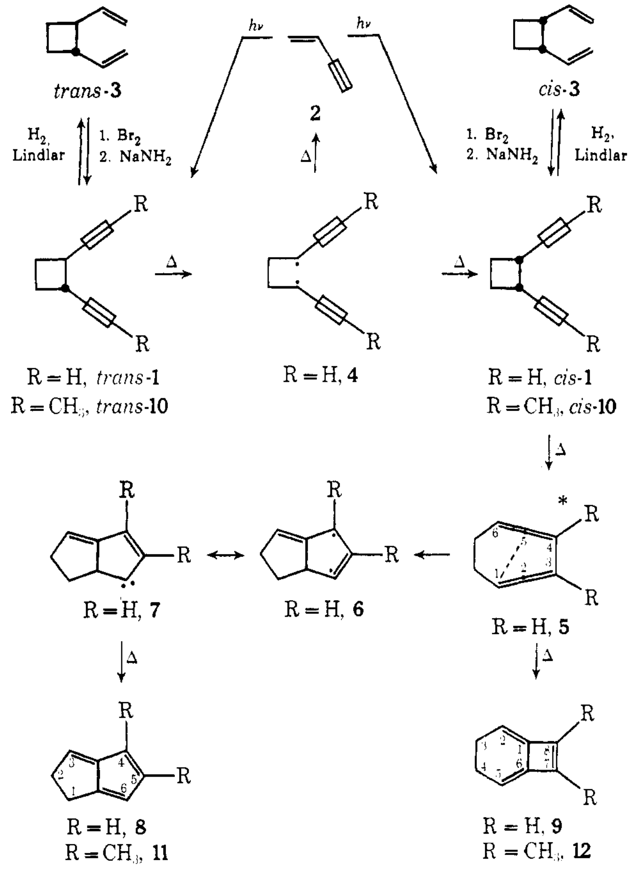
Gas Phase Pyrolysis of *trans*- and *cis*-1,2-Diethynylcyclobutane. A New Entry to the C_8H_8 Energy Surface

Sir:

Whereas thermal rearrangements of mono- and polyolefins have been extensively studied,[1,2] far less is known about the pyrolytic behavior of the corresponding alkynes.[3] Since their thermal isomerization reactions are expected to provide valuable preparative and mechanistic information, we have started a comprehensive study of the gas phase pyrolysis of acetylenes.[4] This communication reports the rearrangement of *trans*- and *cis*-1,2-diethynylcyclobutane (Scheme I, R = H, *trans*- and *cis*-**1**), the acetylenic pendants of the thoroughly investigated divinylcyclobutanes *trans*- and *cis*-**3**.[1,2,5] The isomeric bisalkynes are conveniently prepared in 84% yield by sensitized (Michler's ketone) photodimerization of vinylacetylene (**2**) using a 450-W Hannovia lamp (trans/cis ratio by glpc, 2.5:1). An alternative route, bromination of *trans*- and *cis*-**3** followed by dehydrobromination with sodium amide, affords the same compounds in lower yield (*trans*-**1**, 18%; *cis*-**1**, 9.6%). The isomerically pure hydrocarbons were obtained by preparative gas chromatography (6 ft DEGS column, 65°), and their structures were established by spectroscopic and chemical means.

The nmr spectrum ($CDCl_3$, int TMS) of *trans*-**1** shows three groups of protons at δ 3.25–2.85 (m, 2), 2.50 (d, J = 1.0 Hz, 2), and 2.40–1.90 (m, 4) which are easily recognized as the tertiary, acetylenic and methylene protons, respectively. In the cis isomer these signals are shifted to somewhat lower field: 3.45–3.05 (m, 2), 2.45–2.10 (m, 6). The ir ($CDCl_3$) shows the expected bands at 3310 and 2120 (–C≡C–H), 2958, 2878, and 1258 (cyclobutane ring) for *trans*-**1**, and at 3304, 2996, 2950, 2870, 2115, and 1250 cm^{-1} for *cis*-**1**.[6] Their relative stereochemistry is established by Lindlar hydrogenation to *trans*- and *cis*-**3** (Scheme I).

Scheme I



When *trans*-**1** is pyrolyzed in a stream of nitrogen at 500° (contact time approximately 28 sec) three products are formed: vinylacetylene (**2**, 52% by nmr analysis), 1,2-dihydropentalene (**8**, 43%), and bicyclo[4.2.0]octa-1,5,7-triene (**9**, 4.5%). Hydrocarbon **8** was identified by spectral comparison with an authentic sample. The structure of the previously unknown C_8H_8 isomer, **9**, rests on the following spectral data: its nmr (CCl_4, int TMS) shows a pseudo-singlet at 6.80 (H_7, H_8) a broad singlet at 5.18 (H_2, H_5), and a pseudo-triplet at 2.30 (H_3, H_4). In the ir (CCl_4) the main absorption bands appear at 3100 and 3050 (C=C—H), 2920, 2820, 1436, and 1336 (-CH_2), and at 1665 cm^{-1} (C=C).

Compound **9** (molecular weight 104 by mass spectral determination) is colorless after gas chromatographic separation (DEGS, 75°) and stable for a few hours at room temperature. Exposure to air causes rapid polymerization, and so far has prevented the determination of a quantitative uv spectrum. The qualitative spectrum (ethanol) with bands at 213 and 258 nm is in accordance with data for model compounds.[7] When

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(1) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

(2) M. R. Wilcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, **9**, 25 (1972).

(3) W. D. Huntsman, *Intra-Sci. Chem. Rep.*, **6**, 151 (1972).

(4) For Part V of this series see V. Dalacker and H. Hopf, *Tetrahedron Lett.*, 15 (1974).

(5) For new results on the thermal rearrangement of substituted divinylcyclobutanes, *cf.* J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 269 (1973).

(6) All new compounds had correct molecular weight (mass spectrum) and elemental analysis.

(7) 3,4-Bismethylenecyclobutene absorbs (isooctane) at 211.5 (10,000) and 248 nm (19,950).[8]

(8) A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc., London*, 332 (1961).

cis-**1** is pyrolyzed under the same conditions **8** and **9** are formed again, the former in nearly quantitative yield (95% and 2.5% yield, respectively), vinylacetylene (**2**), however, cannot be detected in the pyrolysate by glpc. At higher isomerization temperatures styrene is formed in increasing amounts and becomes the main product at 710° (72% from *trans*-, 95% from *cis*-**1**).

The following mechanism is proposed for this new entry to the C_8H_8 energy surface. In the first step the diradical **4** is formed from *trans*-**1**. This species may either dissociate to **2** or ring-close to the cis isomer, which subsequently rearranges to 1,2,4,5-cyclooctatetraene (**5**) by a [3,3] sigmatropic shift. Disrotatory cyclization of **5** leads to **9** and 1,5-carbon bridging to diradical **6**. Formation of **8** by an insertion reaction of the "carbene resonance form" of **6** (**7**) concludes the process. This mechanism is supported by the analogous conversion of 1,5-hexadiyne to 3,4-bismethylenecyclobutene,[9] for which 1,2,4,5-hexatetraene has been postulated as an intermediate,[10] as well as the thermal rearrangement of 3,4-bismethylenecyclobutene to benzene and fulvene which presumably proceeds *via* the same bisallenic intermediate.[11] More direct mechanistic evidence was obtained when the dimethyl derivatives of *trans*- and *cis*-**1** were pyrolyzed; at 480° *trans*- and *cis*-**10**[12] rearrange to **11** and **12**, hydrocarbons that lack the characteristic H_4, H_5 and H_7, H_8 resonance signals of **8** and **9**.

Finally, pyrolysis experiments in the 0.5–1 Torr pressure region hint that intermediate **5** may be a vibrationally excited species.[13,14] Under these conditions the concentration of **9** is increased to nearly 20% while that of **8** is reduced by the corresponding amount.

Acknowledgment. We thank Professor G. Wilke (Mülheim) for a generous sample of *cis*-1,2-divinylcyclobutane and Professor K. Hafner (Darmstadt) for the uv and nmr spectrum of 1,2-dihydropentalene. This work was supported by the Fonds der Chemischen Industrie.

(9) W. D. Huntsman and H. J. Wristers, *J. Amer. Chem. Soc.*, **89**, 342 (1967).

(10) H. Hopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 732 (1970).

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(12) These compounds[6] were prepared from the sodium salts of *cis*- and *trans*-**1** with methyl iodide in liquid ammonia and characterized by spectroscopic methods.

(13) M. B. D'Amore, R. G. Bergman, M. Kent, and E. Hedaya, *J. Chem. Soc., Chem. Commun.*, 49 (1972).

(14) M. C. Flowers, H. M. Frey, and H. Hopf, *J. Chem. Soc., Chem. Commun.*, 1284 (1972).

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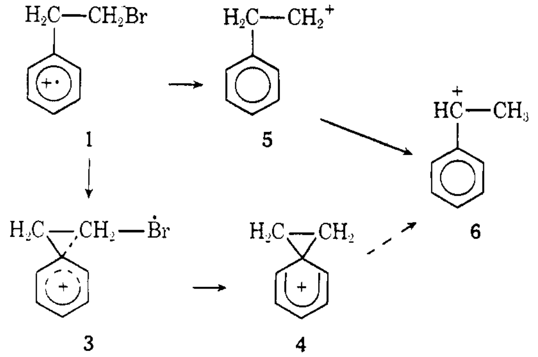
Long-Lived β-Phenylethyl and Ethylenebenzenium Cations in the Gas Phase[1]

Sir:

The $C_8H_9{}^+$ ion generated by unimolecular expulsion of Br· from $C_6H_5CH_2CH_2Br\cdot{}^+$ (**1**) is very abundant in comparison to $C_9H_{11}{}^+$ generated from $C_6H_5CH_2CH_2CH_2Br\cdot{}^+$ (**2**).[2] Based on a variety of evidence, Shapiro[3] has proposed that this is due to aryl participation (**3**), possibly to form the ethylenebenzenium ion (**4**) instead of the classical β-phenylethyl cation (**5**) (Scheme I).

Scheme I



Similar "phenonium" ion structures have been postulated to explain analogous mass spectral data.[4] However, Grützmacher[5] has argued against aryl participation, presenting evidence that losses of Br· from **1** and **2** have equal energy requirements (identity of ionization and appearance potential values).[6] From solution studies Olah[7] has given strong evidence for the formation from $C_6H_5CH_2CH_2Cl$ of **4** and the rearranged α-phenylethyl ion (**6**), but not of **5**; isotopic labeling is consistent with the formation of **6** from **5**, but not from **4**. Recently the homologous $C_7H_7{}^+$ ions, such as tropylium, benzyl, and tolyl, have been shown[8] to be stable in the gas phase utilizing collisional activation (CA) spectra.[9,10] We report here evidence from CA spectra for the formation of stable **4**, **5**, and **6** cations from **1**.

The $C_7(H,D)_5$-$C_7(H,D)_7$ region of the CA spectra[11] of **1**, $C_6H_5CH_2CD_2Br$ (**1b**), $C_6H_5CD_2CH_2Br$ (**1c**), and $C_6H_5CD_2CD_2Br$ (**1d**) (Table I) show dramatic changes with ionizing electron energy below 15 eV, indicating that a mixture of isomers is formed whose composition is sensitive to electron energy.[9] In contrast, $C_6H_5CH(CH_3)Br$ appears to give a single isomeric product, presumably **6**.[11] At the lowest electron energy at which measurements could be made (~11 eV), the spectra of the d_2 isomers **1b** and **1c** became identical within experimental error and consistent with that

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(1) Metastable Ion Characteristics. XXXIII. For paper XXXII see P. F. Bente, III, F. W. McLafferty, D. J. McAdoo, and C. Lifshitz, *J. Phys. Chem.*, submitted for publication.

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(3) R. H. Shapiro and T. F. Jenkins, *Org. Mass Spectrom.*, **2**, 771 (1969).

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(5) H.-Fr. Grützmacher, *Org. Mass Spectrom.*, **3**, 131 (1970).

(6) Labeling experiments are not definitive, as extensive isotopic scrambling accompanies decomposition[5]: N. M. M. Nibbering and Th. J. de Boer, *Org. Mass Spectrom.*, **2**, 157 (1969); A. Venema, N. M. M. Nibbering, and Th. J. de Boer, *ibid.*, **3**, 1589 (1970); A. Venema, N. M. M. Nibbering, K. H. Maurer, and U. Rapp, submitted for publication.

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(11) Lower mass peaks are much less characteristic; complete CA spectra of these and other $C_8H_9{}^+$ isomers will be discussed in the full paper.