As already mentioned **3** decomposed readily under a variety of conditions to hexamethylbenzene and $PdCl_2$; this indicates that a ligand made up of only three acetylenes is coordinated to each palladium. In both $CDCl_3$ and C_6H_6 **3** reacted with Ph_3P to give a small amount of hexamethylbenzene and two organic compounds formulated as the vinylpentamethylcyclopentadienes **6** and **7** on the basis of their analyses and spectroscopic properties;[9] in addition, $(Ph_3P)_2PdCl_2$ was also obtained quantitatively from the lower temperature reactions where **6** was the main product. The formation of **7** lends support to a structure for **3** which has a vinylic Cl in the organic ligand.[10]

The infrared spectrum of **4** is very similar to that of **3** in the region 500–4000 cm^{-1} and suggests that a very similar organic ligand is present and that the extra $PdCl_2$ is not coordinated to a double bond but rather to the PdCl in **3**.[11]

Our observation that the rate of synthesis of **4** is not dependent on the butyne concentration suggests that the rate-determining step is probably a rearrangement. One reasonable such rearrangement would be "*cis* insertion" of the acetylene in **5** into a Pd–Cl bond, which would then be followed by two further very fast "*cis* insertions" of coordinated acetylenes into the Pd–C-(vinyl) bond, eventually yielding **4**.[12] The extra $PdCl_2$ present must assist these processes in some way not yet clear, either by coordinating another acetylene or by activating the one present in **5**. We have previously shown that $PdCl_2$ will catalyze the decomposition of dewar hexamethylbenzenepalladium chloride to hexamethylbenzene and $PdCl_2$;[13] it also appears to catalyze the decomposition of **3** in $CDCl_3$, and this seems to be a general phenomenon.[14]

The evidence presented here makes it clear that the reactions which occur between **1** and **2** are of a type quite different to those which have previously been considered to account for metal-catalyzed trimerization reactions.[15] Further details of these processes are under investigation and will be reported in detail shortly.

Acknowledgment. We thank the National Research Council of Canada for supporting this work and Johnson, Matthey and Mallory for the loan of $PdCl_2$.

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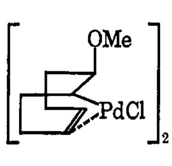
242 and 273 (m) (asymmetric $PdCl_2Pd^8$), 487 (w) and 530 (m) (ν_{Pd-C}), 772 (s) (ν_{C-Cl}), 1512 (m) (coordinated C=C), and 1624 cm^{-1} (mw) (uncoordinated C=C).

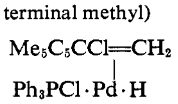
(8) J. Powell and B. L. Shaw, *J. Chem. Soc., A*, 583 (1968), found that in $[(allyl)_2RhCl]_2$ complexes, where the bridging Rh–Cl bonds have been shown to have very different lengths, the two predicted ν_{Rh-Cl} bands were quite widely different, whereas in $[(allyl)PdCl]_2$ where the bridging Pd–Cl bond lengths are equal, the two ν_{Pd-Cl}'s are very close together. For comparison we have examined the low-frequency infrared spectrum of



and find again two very different ν_{PdCl}'s at 222 and 272 cm^{-1}. This is to be expected in both this complex and in **3** since in both cases one Pd–Cl is *trans* to a Pd–C σ bond and hence is expected to be very long, whereas the other, *trans* to a Pd–olefin bond, will be nearly normal.

(9) The mass spectra show molecular ion peaks at 162.139930 (for **6**) and 196.10326 and 198.100317 (for **7**). Calcd for $C_{12}H_{18}$ (**6**): 162.140844; calcd for $C_{12}H_{17}{}^{35}Cl$: 196.101872; calcd for $C_{12}H_{17}{}^{37}Cl$: 198.098922 (**7**). The mass spectroscopic cracking patterns also support the assigned structures. The pmr spectra show the following resonances: for **6** at τ 9.00 (singlet, bridgehead methyl), 8.34 (doublet at 100 Mc, separation 0.9 cps, diene methyls), 8.22 (doublet at 100 Mc, separation 0.8 cps, diene methyls), and 4.96 (multiplet, vinyl protons) with intensity ratios 3:6:6:3. For **7**, resonances appear at τ 8.90 (singlet), 8.33 (doublet at 100 Mc; $J = 1.0$ cps), 8.22 (doublet at 100 Mc; $J = 0.85$ cps), and 4.75 (double doublet, $J = 4$ cps, vinyl protons) with intensity ratio 3:6:6:2. The infrared spectra of **6** and **7** also agree well with the proposed structures and show, apart from bands due to vibrations associated with the methyls, bands at 3080 (m), 3050 (w) (vinylic CH), 1655 (w), 1625 (s), and 906 (s) cm^{-1} for **6** and at 3110 (w), 1660 (m), 1625 (s), 1620 (sh), 882 (vs), and 708 (s) (C–Cl) cm^{-1} for **7**.

(10) Formation of **6** and **7** from **3** can be rationalized in terms of an insertion of the coordinated C=C bond in **3** into the Pd–C bond to give $Me_5C_5CCl(PdCl(PPh_3))Me$. This is converted to another π complex by H abstraction from the terminal methyl)



$$\begin{array}{c} Me_5C_5CCl{=}CH_2 \\ | \\ Ph_3PCl \cdot Pd \cdot H \end{array}$$

which can then either lose $HPdCl(PPh_3)_x$ to give **7**, or add Pd–H to the double bond to give $Me_5C_5CClH \cdot CH_2PdCl(PPh_3)_x$ which on elimination of $(Ph_3P)_2PdCl_2$ gives **6**.

(11) There are many examples of chloropalladium complexes adding extra $PdCl_2$ molecules (*e.g.*, R. Hüttel and H. J. Neugebauer, *Tetrahedron Letters*, 3541 (1964); P. M. Maitlis, D. F. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, 43, 470 (1965); M. Donati and F. Conti, *Inorg. Nucl. Chem. Letters.*, **2**, 343 (1966)), but the mode of bonding is not clear.

(12) R. Heck (private communication) has shown that compounds in which Pd–C bonds are present react very rapidly with olefins. We feel that the reaction studied here largely finishes after 3 moles of acetylene has been added for steric reasons. Molecular models show that the structure represented by **3** is very favorable and strain free; further, the coordinated olefin has the alternative of either lying in the coordination plane of the metal or perpendicular to it. The former arrangement would obviously facilitate the further intramolecular *cis* insertion postulated above.[10]

(13) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967); however, we have no evidence which indicates that either a dewar benzene- or a cyclobutadiene–metal complex is an intermediate in the reactions described here.

(14) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **147**, 399 (1962), have observed that in the absence of excess chloride ion, the $PdCl_2$-catalyzed oxidation of ethylene to acetaldehyde is second order in Pd(II).

(15) These mechanisms have been of two broad types, those involving "concerted" reactions[2g,16] and those in which five-membered metallocycles have been isolated as intermediates.[2d,e,h] Stepwise reactions involving insertion of acetylenes into $M{\leftarrow}C{\equiv}CR$ bonds have been postulated to occur for reactions involving monosubstituted acetylenes.[2f 17] A trimerization reaction which appears to proceed *via* a binuclear complex is that which occurs between acetylenes and $Co_2(CO)_8$, but the probable intermediate, $(acetylene)_3Co_2(CO)_4$,[2b] is of quite a different type to the one postulated here and is also much more stable.

(16) G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem.*, **76**, 28 (1964).

(17) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, 27, 3930 (1962).

(18) Fellow of the Alfred P. Sloan Foundation and author to whom inquiries should be addressed.

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Novel Reactions of Benzyne with Acetylenic Ethers

Sir:

The reaction of benzyne with ethoxyacetylene (Ia) to form 2-ethoxyphenylacetylene, reported earlier by Stiles,[1] represents an unusual rearrangement in benzyne–acetylene chemistry.[2,3] We now wish to report further novel transformations in this series arising from the reaction of benzyne with ethoxypropyne (Ib) and with the thioacetylenes IIa–d.

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(1) M. Stiles, U. Burckhardt, and A. Haag, *J. Org. Chem.*, 27, 4715 (1962).

(2) V. Franzen and H. I. Joschek, *Ann.*, 703, 90 (1967).

(3) S. F. Dyke, A. R. Marshall, and J. P. Watson, *Tetrahedron*, 22, 2515 (1966).

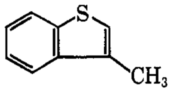
$R_1OC{\equiv}CR_2$
Ia, $R_1 = C_2H_5$; $R_2 = H$
b, $R_2 = C_2H_5$; $R_2 = CH_3$

$R_1SC{\equiv}CR_2$
IIa, $R_1 = C_2H_5$; $R_2 = H$
b, $R_1 = C_2H_5$; $R_2 = CH_3$
c, $R_1 = C_6H_5CH_2$; $R_2 = CH_3$
d, $R_1 = C_7H_{15}$; $R_2 = CH_3$

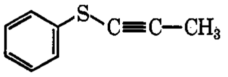
Benzenediazonium-2-carboxylate[4] was warmed with 1-ethoxypropyne[5] (Ib) in refluxing methylene chloride for 2 hr. Separation of the reaction mixture by distillation, glpc, and column chromatography (silica gel) yielded the following products: 3-methylbenzofuran (III; 20%); 1-(2-ethoxyphenyl)-1-propyne (IV; 10%); ethoxyphenylmethylenebenzocyclobutene (V) (a mixture of *cis* and *trans* isomers); and 1-ethoxy-1-phenyl-2-methylenebenzocyclobutene (VI).

The structures of III and IV were established by nmr spectral data and by comparison with authentic samples. The benzofuran III was prepared from phenoxyacetone by cyclization–dehydration (P_2O_5)[6] while the acetylenic ether IV was obtained by methylation of 2-ethoxyphenylacetylene. The mixture of benzocyclobutenes V shows a parent mass spectral peak at *m/e* 236 and on ozonolysis followed by hydrogenation (Pd–C) yielded only benzocyclobutenone[7] and ethyl benzoate. One of the isomers (1%), mp 67.5–68.2°, obtained in a pure state (fractional crystallization from cold petroleum ether, bp 30–60°) shows a nmr spectrum which is nearly indistinguishable from that of the parent mixture. *Anal.* Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.64; H, 7.04. The nmr spectrum (CCl_4) shows peaks at τ 2.35–2.95 (m, 9 H), 6.08 (q, 2 H), 6.23 (s, 2 H), and 8.62 (t, 3 H). Product VI (1%) has a parent mass spectral peak at *m/e* 236 and nmr peaks (CCl_4) at τ 2.50–2.90 (m, 9 H), 4.79 (d, 1 H), 5.07 (d, 1 H), 6.30–6.80 (m, 2 H), and 8.80 (t, 3 H). The infrared spectrum shows $\lambda_{max}^{CCl_4}$ 1670 cm^{-1} (shoulder at 1678).[8] The ultraviolet spectrum of VI, λ_{max}^{EtOH} 213 mμ (log ϵ 4.25), 247 (4.00), 280 (3.40), 288 (3.53), 291 (3.53), and 298 (3.52), is nearly identical with that of methylenebenzocyclobutene.[8]

When the thioacetylenes IIb–d were allowed to react with benzyne under the above conditions, the main products in each case (*ca.* 30%) were 3-methylbenzothiophene (VII)[9] and 1-phenylthio-1-propyne (VIII).[10,11]



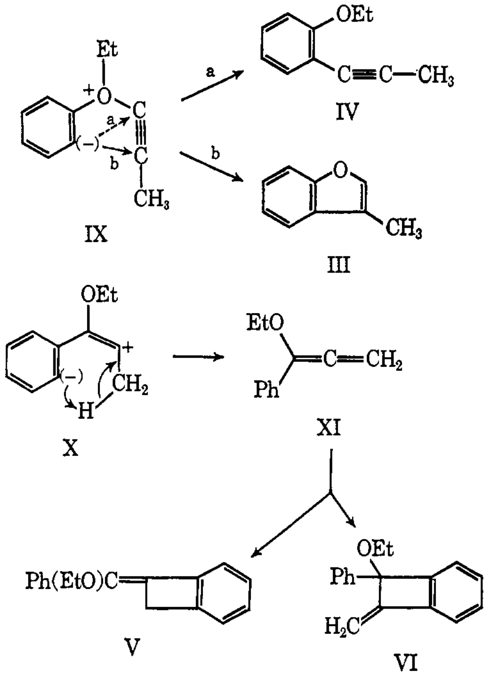
VII



VIII

With thioacetylene (IIa) only benzothiophene (13%) and diphenyl sulfide (6%) were obtained.

The above results are consistent with the view that benzyne is an electrophilic species[12] which may attack one of the electron-rich sites of the alkoxyacetylene. Formation of the dipolar intermediate IX would lead to IV (path a) or to III (path b).[13] Alternatively, the dipolar species X may undergo hydrogen transfer, producing the allene XI[14–16] which on cycloaddition with benzyne yields V or VI.



Acknowledgments. This work was supported by Grant GM 07874 from the National Institutes of Health. We wish to thank Drs. S. Lipsky and W. McMurray for their help in determining the mass spectra.

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[4] Benzyne was generated from benzenediazonium-2-carboxylate according to the procedure of Stiles and coworkers: M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963). We thank Professor Stiles for a personal communication describing revised details of this procedure.

[5] D. E. Farnum, M. A. T. Heybey, and B. Webster, *J. Am. Chem. Soc.*, **86**, 673 (1964).

[6] R. Stoermer, *Ber.*, **28**, 1253 (1895).

[7] M. P. Cava and K. Muth, *J. Am. Chem. Soc.*, **82**, 652 (1960).

[8] This infrared absorption is characteristic of the exocyclic methylene group: M. P. Cava and M. J. Mitchell, *J. Org. Chem.*, **27**, 631 (1962).

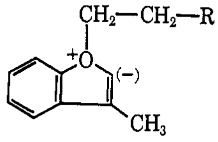
[9] E. G. G. Werner, *Rec. Trav. Chim.*, **68**, 509 (1949).

[10] C. J. M. Stirling, *J. Chem. Soc.*, 5856 (1964).

[11] This ether is analogous to the products formed in the reactions of benzyne with alkyl sulfides: H. Hellmann and D. Eberle, *Ann.*, **662**, 188 (1963); V. Franzen, H. I. Joschek, and C. Mertz, *ibid.*, **654**, 82 (1962).

[12] See, for example: G. Wittig and E. Benz, *Chem. Ber.*, **92**, 1999 (1959); H. H. Wasserman and J. Solodar, *J. Am. Chem. Soc.*, **87**, 4002 (1965).

[13] Loss of the ethyl group during this reaction appears to involve the intermediate ylide IXa, which may decompose by a number of pathways

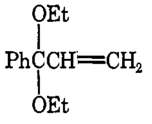


IXa

including intramolecular removal of a β proton (olefin formation) or an α proton (carbene formation) or by intermolecular proton abstraction. Thus far, we have not observed olefin formation when R = H or C_6H_{11}.

[14] Another case of allene formation in a benzyne–acetylene reaction has been reported by M. Stiles and A. Haag: R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 198.

[15] Isolation in low yield of the diethyl ketal of acrylophenone (XII)



$$PhC(OEt)_2CH{=}CH_2$$

XII

from this reaction provides further evidence for the intermediacy of the allene XI, which appears to incorporate ethanol carried over from the preparation of the benzyne precursor. The structure of XII was verified by an independent synthesis from 3,3-dichloro-1-phenylpropene using the method of L. I. Zakharkin and V. V. Korneva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1344 (1957); *Chem. Abstr.*, **52**, 7176*i* (1958).

[16] Further studies on cycloaddition reactions of benzyne with allenes will be reported separately.

[17] National Institutes of Health Predoctoral Fellow, 1964–1968.

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