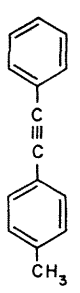
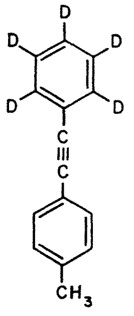
Hydrogen Randomization between Phenyl Groups in the Electron Impact-induced Fragmentation of Substituted Diphenylacetylenes

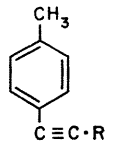
By S. SAFE

(*Atlantic Regional Laboratory, National Research Council of Canada, Halifax, Nova Scotia, Canada*)

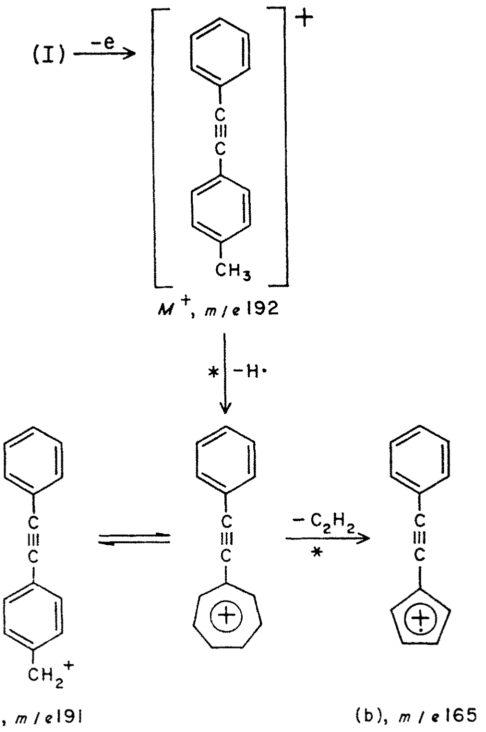
THE scrambling of aromatic hydrogens upon electron impact has been amply demonstrated with benzene[1] and its substituted derivatives[2] as well as in some bicyclic aromatic compounds.[3] Alkylbenzene derivatives have been thoroughly investigated[4] and in most cases hydrogen scrambling is thought to occur after rearrangement to a seven-membered ring.


(I)

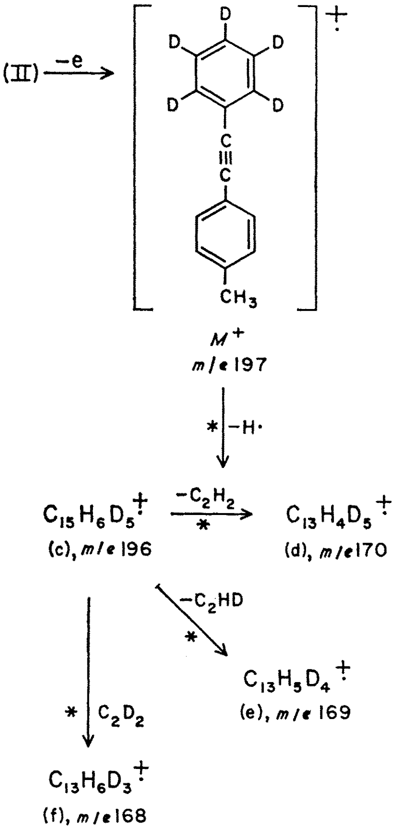

(II)


(III; R = H,D)
(IV; R=CH_2OH,CHDOH)

Although hydrogen scrambling in aliphatic acetylenic compounds has been reported[5] very little information is available concerning the fragmentation of aromatic acetylene derivatives upon electron impact. The methyl substituted diphenylacetylene (I) and its deuteriated analogue (II) were prepared by the coupling[6] of iodobenzene and the copper(I) derivative of 4-methylphenylacetylene and their mass spectra were recorded.†



Equation 1



Equation 2

The fragmentation pathway suggested for the substituted diphenylacetylene (I) is shown (equation 1) and not unexpectedly the loss of a proton to give the ion (a) at *m/e* 191 followed by expulsion of C_2H_2 to give ion (b) at *m/e* 165 is observed. This is typical of the mass spectra of substituted alkylbenzenes.[4] The fragmentation pattern of the deuteriated acetylene (II)‡ is shown (equation 2). The loss of a proton to give the $C_{15}H_6D_5$ ion (c) at *m/e* 196 occurs without any prior hydrogen scrambling. The fragment ion (c) loses a C_2H_2 fragment to give the $C_{13}H_4D_5$ ion (d) at *m/e* 170 and also loses C_2HD and C_2D_2. The metastable peaks at *m/e* 147·5, 145·7, and 144·0 confirm that these fragmentation reactions occur. These results are in contrast with the

---

† Mass spectra were measured with a Consolidated Electrodynamics Corporation 21-110B instrument at 70 ev with an inlet temperature of 46°.

‡ The isotopic purity of the $C_{15}H_7D_5$ acetylene (II) was >97%.

TABLE

Unlabelled acetylene (I)		Labelled acetylene (II)			
Mass	Relative abundance	Mass	Relative abundance	Mass measurement	
				Calculated	Found
193	17	198	16		
192	100	197	100		
191	26	196	24		
190	4	195	6		
166	1·5	171	0·6		
165	9·0	170	4·5	170·1018 ($C_{13}H_4D_5$)	170·1018
164	1·3	169	4·7	169·0954 ($C_{13}H_5D_4$)	169·0955
163	2·7	168	3·3	168·0893 ($C_{13}H_6D_3$)	168·0893
162	—	167	1·5		

data obtained for the aromatic acetylenes (III; R = H, D) and (IV; R = CH_2OH, CHDOH) which were prepared by conventional methods. Comparison of the mass spectra indicated that in the loss of acetylene from the analogous $R{\cdot}C_7H_6^+$ ions, expulsion of C_2HD was not detected.

Comparison of the data (Table) obtained for the acetylenes (I) and (II) shows that for the deuteriated diphenylacetylene (II) there is a marked decrease in the ion current for the $(M - 1)^+ - C_2H_2$ ion (d) and an increase in the $(M - 1)^+ - C_2HD$ and $(M - 1)^+ - C_2D_2$ ion currents. Normalization of the data shown indicates that about 50% hydrogen scrambling between the two phenyl rings occurs in the $C_{15}H_6D_5$ ion (c) prior to acetylene elimination. Mass measurement of the ions at *m/e* 170, 169, and 168 (see Table) supports the above results and the fragmentation pathway shown (equation 2).

These data clearly support a ready equilibration of the protons of the phenyl groups in the mass spectrum of the acetylenes (I) and (II) and favour a mechanism by which C–H (or C–D) bonds are broken in the randomization process rather than by a pathway which involves intermediates similar to those generated in a photochemical excitation.[2c] The hydrogen randomization probably occurs *via* the acetylene bridge since direct interaction between the protons of the two phenyl rings is unlikely.

I thank Dr. W. D. Jamieson and Mr. D. Embree for their assistance in recording the mass spectra.

(*Received, March* 24*th*, 1969; *Com.* 416.)

[1] K. Jennings, *Z. Naturforsch.*, 1967, **22a**, 454.

[2] (a) R. G. Cooks, R. S. Ward, and D. H. Williams, *Chem. Comm.*, 1967, 850; (b) I. R. King and G. W. Kirby, *J. Chem. Soc.* (*C*), 1966, 1334; (c) D. H. Williams, S. W. Tams, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 2150.

[3] R. G. Cooks, I. Howe, S. W. Tams, and D. H. Williams, *J. Amer. Chem. Soc.*, 1968, **90**, 4064.

[4] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," ed. F. W. McLafferty, Academic Press, New York, 1963, ch. 10.

[5] R. T. Alpin and S. Safe, *Canad. J. Chem.*, 1969, in the press.

[6] R. E. Atkinson, R. F. Curtis, D. M. Jones, and J. A. Taylor, *Chem. Comm.*, 1967, 718.