Formation of Benzyne and Analogous Species from Benzo-2,1,3-selenadiazoles upon Electron Impact

By N. P. BUU-HOÏ, P. JACQUIGNON, and M. MANGANE

[*Institut de Chimie des Substances Naturelles du Centre National de la Recherche Scientifique, Gif-sur-Yvette (S.-et-O.), France*]

SEVERAL benzoheterocycles in the molecule of which the heterocycle is linked to the benzene nucleus by two easily split bonds (*e.g.*, benzo-1,2,3-thiadiazole 1,1-dioxide,[1] phthalic anhydride,[2]

[1] G. Wittig and R. W. Hoffmann, *Chem. Ber.*, 1962, **95**, 2718.
[2] F. W. McLafferty and R. J. Gohlke, *Analyt. Chem.*, 1959, **31**, 2076.

diphenyliodonium-2-carboxylate[3]) are generators of benzyne when submitted to energetic physical agents (pyrolysis, photolysis, and electron impact). We report here that benzo-2,1,3-selenadiazole (I) in spite of its chemical stability, behaves in a similar way upon electron impact. Its 70-volt (40 μA) mass spectrogram, taken with an Atlas CH4 spectrometer (temperature of introduction: 220°; of ionisation: 280°), did indeed show remarkable stability of the molecule, the main peak being the molecular peak $m/e = 184$ corresponding to ^{80}Se (with 4 satellite molecular peaks at 186, 182, 181, and 180 appearing in proportion to the relative isotopic abundances of ^{82}Se, ^{78}Se, ^{77}Se, and ^{76}Se); the peak $m/e = 76$, corresponding to the benzyne ion, nevertheless represented as much as 25% of the base peak. This type of decomposition is characteristic of the family of benzo-2,1,3-selenadiazoles, as the following examples show:

(a) 5-Methylbenzo-2,1,3-selenadiazole (II): the peak $m/e = 90$ corresponding to the methylbenzyne species (IV) represented 25% of the main molecular peak $m/e = 198$;

(b) 4,5,6-Trimethylbenzo-2,1,3-selenadiazole[4] (III): the peak $m/e = 118$ corresponding to the trimethylbenzyne species (VI) was 27% of the main molecular peak $m/e = 226$;

(c) Phenanthro(1′,2′)2,1,3-selenadiazole[5] (VII): the 1,2-phenanthryne (VIII) peak $m/e = 176$ was 25% of the main molecular peak $m/e = 284$.

Since in the similar case of phthalic anhydride Fields and Meyerson have recently shown a parallelism between benzyne formation upon electron impact and on pyrolysis,[6] it is to be expected that benzo-2,1,3-selenadiazoles would also generate benzyne and related species under drastic pyrolytic processes.

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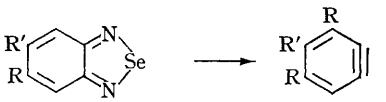
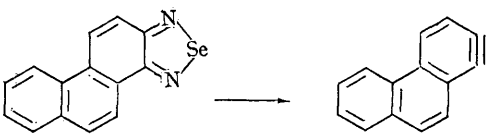


(I) R = R′ = H (IV) R = R′ = H
(II) R = H; R′ = Me (V) R = H; R′ = Me
(III) R = R′ = Me (VI) R = R′ = Me



(VII) (VIII)

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[3] E. Le Goff, *J. Amer. Chem. Soc.*, 1962, **84**, 3786.
[4] N. P. Buu-Hoï, P. Jacquignon, and O. Roussel, *Compt. rend.*, 1963, **257**, 4193.
[5] S. V. Bogdanov and L. S. Shibryaeva, *Zhur. Vsesoyuz. Khim. obshch. im. D. I. Mendeleeva*, 1960, **5**, 345; D. C. Thang, N. P. Buu-Hoï, and N. D. Xuong, *J. Chem. Soc.*, 1965, 4585.
[6] E. K. Fields and S. Meyerson, *Chem. Comm.*, 1965, 474.