Tetrahedron Letters No. 12, pp 911 - 914, 1973. Pergamon Press. Printed in Great Britain.

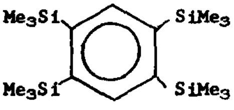
PHOTOLYSIS OF 1,2,4,5-TETRAKIS(TRIMETHYLSILYL)BENZENE[1]

Robert West, Masaoki Furue and V. N. Mallikarjuna Rao
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706, U.S.A.

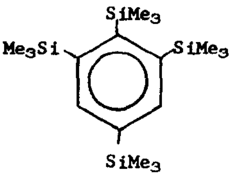
(Received in USA 2 January 1973; received in UK for publication 6 February 1973)

Many valence bond isomers of benzene and alkylated or halogenated benzenes have been prepared,[2] but such isomers have not been reported for silyl substituted benzenes. Photolysis[3] of 1,2,4,5-tetrakis(trimethylsilyl)benzene[4] (1) in ether or 2-methylbutane gives a distribution of isomers rather different from that obtained for other substituted benzenes. Five isomeric products are produced: the 1,2,3,5-tetrasubstituted benzene 2, the benzvalenes 3 and 4, the fulvene 5 and a second fulvene (6) having structure 6a or 6b; no prismanes or Dewar benzenes were observed.

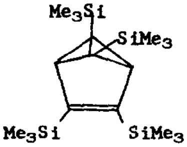
Compound 2 exhibited no infrared absorption characteristic of an olefinic bond, cyclopropane ring or vinylic hydrogen. The nmr spectrum showed a singlet at 2.38 (2H) τ and three singlets for trimethylsilyl groups at 9.61 (9H), 9.64 (18H) and 9.73 (9H) τ, establishing its structure as 1,2,3,5-tetrakis(trimethylsilyl)benzene.[5] Compound 3 showed a cyclopropane ring deformation mode at 1025 cm^{-1} in the infrared[6] and an absorption in the double bond region at 1520 cm^{-1}.[7] The nmr spectrum consisted of two singlets in the trimethylsilyl region at 9.91 (18H) and 9.92 (18H) τ and a singlet for the methine protons at 8.30 (2H) τ.[8] The symmetrical benzvalene structure 3 is consistent with these observations and was further confirmed by the cmr spectrum. The formation of 3 from 1 requires no cleavage of the sigma bond framework. When heated at 120° in hexachlorobutadiene for 22 hr, 3 is converted to a mixture of 1, 2 and 5 in the ratio 5:3:2.



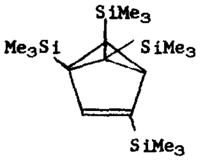
1



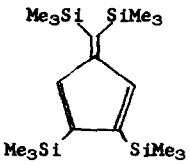
2



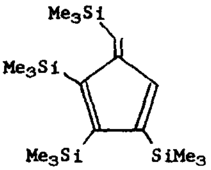
3



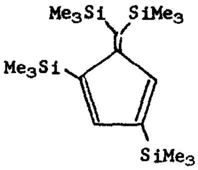
4



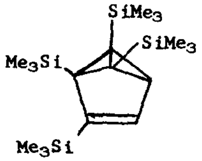
5



6a



6b



7

Compound 4 was also assigned a benzvalene structure on the basis of the following evidence. The infrared spectrum showed an absorption at 1550 cm^{-1} for a double bond[7] and an absorption at 1000 cm^{-1} for the ring deformation mode of cyclopropane.[6] The nmr spectrum consisted of three singlets in the trimethylsilyl region at 9.86 (18H), 9.94 (9H) and 9.98 (9H) τ and two doublets at 8.50 (1H) and 4.12 (1H) τ,[8] J = 2.0 Hz. When heated at 90° for 1 hr, 4 is completely converted to 2. The spectral data as well as the facile conversion to 2 is consistent with structure 4 rather than 7 for this compound.

Compound 5 is a yellow crystalline solid, mp 111-112°. In the ultraviolet, it showed absorptions at 323 (ϵ = 1200) 283 (ϵ = 13,000) and 233 (ϵ = 3600) nm. The infrared spectrum showed a strong band at 1469 cm^{-1} consistent with a conjugated carbon-carbon double bond carrying silyl substituents. Two singlets were observed for trimethylsilyl groups in the nmr spectrum at 9.70 (18H) and 9.78 (18H) τ and a singlet at 3.35 (2H) τ for olefinic protons. The symmetrical fulvene structure 5 is quite consistent with these observations.

The second fulvene is a reddish orange solid which has not yet been obtained completely free of 2. The best samples were about 90% pure. The infrared spectrum of this mixture showed absorptions at 1480 and 1435 cm^{-1}. The nmr spectrum showed four singlets in the trimethylsilyl region at 9.70 (9H), 9.72 (9H), 9.81 (9H) and 9.82 (9H) τ and two doublets at 2.94 (1H) and 3.80 (1H) τ, J = 1.2 Hz. Structures 6a or 6b are in keeping with these observations, and an unambiguous choice between the two is not possible on the basis of presently available evidence.[9]

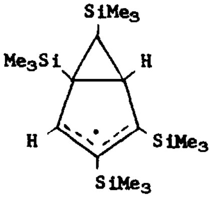
In the early stages of photolysis the product mixture consisted mainly of 1, 3 and 4 (Table I). Further irradiation produced 2, 5 and 6 while the concentration of 3 decreased steadily. Photolysis of 3 produced 4 and 5 in addition to small amounts of 1 and 2, while 4 produced 2 and 6 and a small amount of 3. These observations may mean that 3 is an intermediate in the photo conversion of 1 to 2, 4, 5 and 6. The reaction might take place through diradical intermediates[10] such as 8 which may also be involved in the symmetry forbidden[11] rearomatization of 3 and 4 to 1 and 2. However, 3, 4, 5 and 6 might alternatively be formed via a symmetry allowed concerted process from excited states of 1.[11]

TABLE I

Photolysis of 1 in Ether

Time, hr	Product Composition %					
	1	2	3	4	5	6
1.5	86	tr[a]	7	7	tr	0
4.5	25	tr	25	50	tr	tr
9	12	12	19	47	5	5
12	13	9	13	46	9	9
24	0	14	0	42	16	29

[a] tr = trace



8

We hope to carry out additional experiments with this and other systems which may shed further light on the mechanism.

FOOTNOTES AND REFERENCES

1. Research sponsored by the Air Force Office of Scientific Research (NC) O.A.R., USAF, Grant Nos. AF-AFOSR, 69-1772 and 70-1904.
2. For reviews on this subject, see L. T. Scott and M. Jones, Jr., Chem. Reviews, 72, 181 (1972) and E. E. van Tamelen, Accounts Chem. Res., 5, 186 (1972).
3. Dilute solutions (0.5%) in ether or 2-methylbutane were photolyzed through quartz using a Nester-Faust medium pressure ultraviolet lamp at room temperature.
4. T. Brennan and H. Gilman, Chem. Ind. (London), 1489 (1967).
5. A similar rearrangement to the 1,2,3,5-isomer has been observed in the photolysis of 1,2,-4,5-tetra-*t*-butylbenzene, but no benzvalenes or fulvenes have been reported. See E. M. Arnett and J. M. Bollinger, Tetrahedron Letters, 3803 (1964).
6. L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N.Y., p. 29.
7. Absorption in this region seems to be characteristic of polysilylated ethylenes. See H. Bock and H. Siedl, J. Organometal. Chem., 13, 87 (1968); H. Bock and H. Siedl, J. Amer. Chem. Soc., 90, 5964 (1968).
8. K. E. Wilzbach, J. S. Ritscher and L. Kaplan, ibid., 89, 1031 (1967).
9. Based on the coupling constants, other possible structures for this isomer can be eliminated. See D. Meuche, M. Neuenschwander, H. Schaltegger and H. U. Schulunegger, Helv. Chim. Acta, 47, 1211 (1964); M. Neuenschwander, D. Meuche and H. Schaltegger, ibid., 47, 1022 (1964).
10. D. Bryce-Smith and H. C. Longuet-Higgins, J. C. S. Chem. Comm., 593 (1966).
11. R. Hoffmann and R. B. Woodward, Accounts Chem. Res., 1, 17 (1968) and references cited therein.