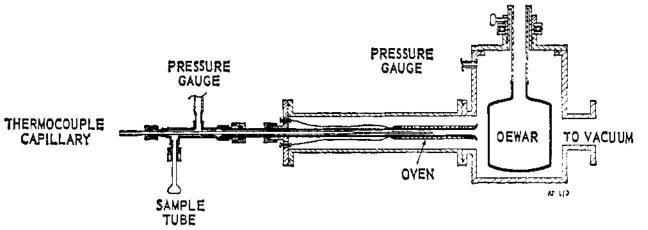

Figure 1. Flash vacuum pyrolysis apparatus.

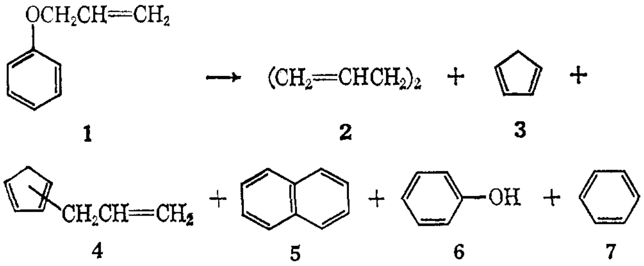

Table I. Flash Vacuum Pyrolysis of Allyl Phenyl Ether

P, μ[a]	Temp, °C	Yield[b]	Product distribution[c] 1	2	3	4	5	6	7	Other[d]
68	954	60.2	1.1	19.1	3.9	55.1	1.2	10.3	1.4	7.9
82	944[e]	24.2	1.9	25.0	9.8	3.2	6.8	28.6	8.2	16.5
62	857	62.6	1.6	22.9	1.7	38.9	1.6	16.7	0.3	16.3
185	750	51.9	2.6	42.6	0.6	16.2	0.5	32.4	1.1	4.0

[a] Approximate average pressure in radical gun; contact times were about 10^{-3} sec. [b] (Grams of volatiles/grams of allyl ether) × 100; does not include carbon monoxide or other noncondensable gases; in general, a small amount of an involatile amorphous residue was also obtained. [c] (Area of peak/total area of peaks) × 100 in gas chromatogram; Apiezon and Carbowax columns were used. [d] (Total area of unknown peaks/total area of peaks) × 100; in general, each unknown represented no more than 5% of the total area. [e] Pyrolysate was condensed in a cold trap about 1 ft from the tip of the radical gun.

2.8–3.2 m, 4.7 m, 5.1 m, and 5.5–6.4 m ppm in an area ratio of 4:1:1:4; infrared 3.25, 3.33, 3.48, 6.09, 6.21, and 14.8 br μ (neat); $\lambda_{\max}^{C_7H_{14}}$ (ϵ) 251 (940), 258 (790), 264 (730), 271 (720), and 278 (630). This material is probably a mixture of 1- and 2-substituted isomers.[7] The other products were characterized by direct comparison of mass, infrared, and nmr spectra and glpc retention times with those of authentic materials.

These data show that the mass spectral results of Lossing can be chemically duplicated in our apparatus on a preparative scale. Furthermore, the allylcyclopentadiene must be formed after condensation of the pyrolysate on the Dewar surface since the yield of this cross-coupling product is drastically reduced when condensation occurs instead in a liquid nitrogen trap located approximately 1 ft from the tip of the radical gun (second row, Table I). The radical-coupling reactions occurring either on condensation, or warming of the dewar surface, or both apparently lead to a statistical distribution of coupling products on the basis of allylcyclopentadiene:biallyl ratio (first row, Table I). The ultimate products resulting from coupling of two cyclopentadienyl radicals may include naphthalene, although more recent experiments[8] suggest that the dihydrofulvalene, which should be the initial product, may polymerize and thus lead in part to formation of nonvolatile residues. The over-all distribution of products indicates that the decarbonylation reaction of phenoxy radicals is an efficient process, as the mass spectral data also indicate. This remarkable reaction[9] was found to be significant at much lower temperatures, and its mechanism is a question of considerable interest.

The absence of Claisen rearrangement at the temperatures investigated here must result from an unfavorable activation entropy ($\Delta S^{\ddagger} = -12$ eu)[10] compared to that for homolysis, which overcomes the activation enthalpy difference which would clearly favor the former process. At 500° the Claisen rearrangement product (2-allylphenol) was detected by glpc.

We are currently investigating the FVP of a variety of phenyl ethers as well as other molecules and have already found that anisole[8] gives substantial yields of methylcyclopentadiene at 950°.

Acknowledgment. The authors are indebted to Dr. F. P. Lossing for important discussions, and also acknowledge the assistance of Mr. W. D. Bird in the construction of apparatus.

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(7) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

(8) E. Hedaya and D. McNeil, unpublished results.

(9) This reaction also occurs when phenols are flash photolyzed in the vapor: G. Porter and B. Ward, *Proc. Chem. Soc.*, 288 (1964).

(10) H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958).

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Flash Vacuum Pyrolysis. II. The Electronic, Vibrational, and Electron Spin Resonance Spectra of the Benzyl Radical

Sir:

In the preceding communication[1] it was demonstrated that flash vacuum pyrolysis (FVP) can be an efficient source of free radicals such that primary, stable reaction products can be isolated on a chemically significant scale. An important aspect of this work is the spectroscopic characterization of some of the free-radical intermediates whose existence has been demonstrated by the extensive research of Lossing and co-workers.[2] One approach suggested by studies[3] of the optical and esr spectra of simple radicals and high-temperature molecules would involve stabilization of the reactive free radicals by isolation in rare gas matrices at low temperatures. We have now found that a variety of reactive organic free radicals which are generated by FVP can in fact be stabilized in rare gas matrices which permits, in the most favorable cases, the observation of their ultraviolet, visible, infrared, and esr spectra *under essentially identical conditions;* such a

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(1) E. Hedaya and D. McNeil, *J. Am. Chem. Soc.*, **89**, 4213 (1967).

(2) (a) F. P. Lossing, P. Kebarle, and J. B. DeSousa, "Advances in Mass Spectrometry," Pergamon Press, London, 1959, p 431; (b) F. P. Lossing, *Ann. N. Y. Acad. Sci.* 67, 499 (1957); (c) A. G. Harrison, "Mass Spectroscopy of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 207.

(3) (a) W. Weltner, Jr., *Science*, **155**, 155 (1967); (b) C. K. Jen in "Formation and Trapping of Free Radicals," A. M. Bass and H. P. Broida, Ed., Academic Press Inc., New York, N. Y., 1960.

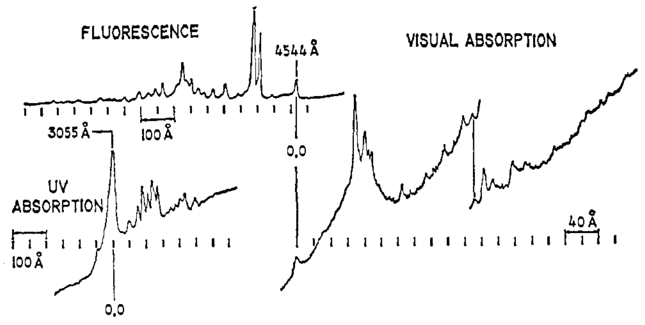

Figure 1. The visible and ultraviolet spectra of benzyl in a neon matrix.

spectral characterization of the benzyl radical is presented in this preliminary report.

Benzyl radicals were produced in the gas phase by the FVP of benzyl bromide in a radical gun similar to that previously described[1] at temperatures around 1000° and pressures of *ca.* 10–20 μ.[4] In these experiments, the radical gun was coupled to liquid helium dewars (which have also been previously described[3b,5]) where the neon matrix was formed either on a quartz or sapphire rod or a CsBr or CaF_2 plate in thermal contact with the bottom of the helium dewar. The dewar was fitted with appropriate windows for determination of optical spectra or alternatively the sapphire matrix support rod was lowered into a microwave cavity for determination of the esr spectra. In the optical experiments the amount of matrix formed was greater than that for the esr experiments because of the greater sensitivity of the detecting system for the latter case. However, the composition of the matrix was kept essentially constant for all experiments. The spectra obtained are reproduced in part in Figures 1 and 2.

In general there is a close correspondence between the visible emission and absorption (Figure 1) spectra of benzyl obtained in a neon matrix by FVP and those determined in the gas phase by flash photolysis.[6] For example, the 0,0 band for the $1\,^2A_2 \leftrightarrow 1\,^2B_2$ transition appears at 4544 A in both the visible absorption and emission spectra in the neon matrix while this same band also appears at 4544 A in the gas phase. Similarly, the 0,0 band for the $2\,^2A_2 \leftrightarrow 1\,^2B_2$ transition appears in the ultraviolet at 3055 A in the neon matrix and in the gas phase at 3053 A.[6b,7] In our case the spectrum in the ultraviolet region is more clearly defined than that observed by flash photolysis in the gas phase[6b] or in a toluene matrix,[8] especially below 3000 A. The recently reported[9] intense band at 258 mμ observed in a toluene matrix and assigned to a $3\,^2B_2 \leftrightarrow 1\,^2B_2$ transition apparently shifts in the neon matrix to a broad maximum at 245 mμ.

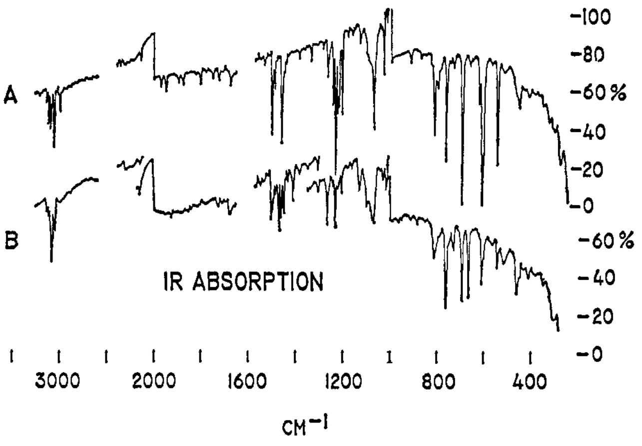

Figure 2. The infrared spectrum of benzyl in a neon matrix: (A) benzyl bromide; (B) benzyl.

The infrared spectrum for benzyl (Figure 2)[10] is especially important since it aids the assignment of many of the fundamental and combination bands which appear in the emission spectrum. Furthermore, the decreased bands due to benzyl bromide indicate that the decomposition was ~70% efficient. Molecules such as bibenzyl, toluene, and stilbene, which would be predicted to result from reactions of benzyl either in the gas phase or in the matrix, were not observed.

The esr spectrum for benzyl in a neon matrix was very similar to that observed for photolytically generated benzyl on silica gel,[11a] with the exception that our spectrum in neon was better resolved.[12] The approximate isotropic coupling constants which can be extracted from our spectrum are in agreement with those previously obtained.[11] A more precise assignment must await analysis of our spectrum in terms of both isotropic and anisotropic (dipole–dipole) coupling constants.

We believe that our techniques for what approaches a complete spectroscopic characterization of a reactive organic radical can have general utility, as exemplified by our results for the benzyl radical. We are currently investigating a number of reactive, chemically well-known, organic radicals both in order to define the scope of our methods and to obtain detailed spectral data which are required for a better theoretical understanding of these species.[13] Also, a detailed analysis of the data presented here is in progress, and the results will be discussed in future publications.[14]

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(4) From the work on benzyl pyrolytically generated from benzyl iodide, we inferred that benzyl bromide would also be a suitable source: F. P. Lossing, K. U. Ingold, and S. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1959).

(5) (a) W. Weltner, Jr., and D. McLeod, Jr., *ibid.*, **42**, 882 (1965); (b) P. H. Kasai, E. B. Whipple, and W. Weltner, Jr., *ibid.*, **44**, 2581 (1966).

(6) (a) L. Grajcar and S. Leach, *J. Chim. Phys.*, **61**, 1523 (1964); (b) G. Porter and B. Ward, *ibid.*, **61**, 1518 (1964).

(7) A similar correspondence between gas and neon-matrix electronic and vibrational frequencies has been noted for high-temperature molecules such as TiO: W. Weltner, Jr., and D. McLeod, Jr., *J. Phys. Chem.*, **69**, 3488 (1965); also see ref 3a.

(8) G. Porter and E. Strachan, *Spectrochim. Acta*, **12**, 299 (1958).

(9) G. Porter and M. I. Savadatti, *ibid.*, **22**, 803 (1966).

(10) A summary of the current status and limitations of the infrared detection of free radicals is given by G. C. Pimentel and K. C. Herr, *J. Chim. Phys.*, **61**, 1509 (1964); see W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.*, **44**, 2527 (1966), for infrared detection of methyl; apparently our spectrum for benzene is the first for a large organic radical.

(11) (a) V. A. Tolkachev, S. S. Chkheidze, and N. Ya. Buben, *Dokl. Akad. Nauk SSSR*, **47**, 643 (1962); W. D. Nixon and R. S. Norman, *J. Chem. Soc.*, 4857 (1964).

(12) The esr spectrum was obtained by W. D. Bird, whom we also acknowledge for very capable experimental assistance in other phases of this work.

(13) For example, the esr spectrum of the vinyl radical in a neon matrix has been recently obtained from vinyl iodide using the technique described here: P. Kasai and E. B. Whipple, *J. Am. Chem. Soc.*, **89**, 1033 (1967).

Acknowledgment. The very helpful advice and encouragement offered by Professor W. Weltner, Jr., in the early stages of this work is acknowledged.

[14] NOTE ADDED IN PROOF. Recent work on the polarization of the electronic bands of the benzyl radical indicates that the assignments quoted above might not be correct: P. M. Johnson and A. C. Albrecht, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, Sept 6–10, 1966, Abstract G3.

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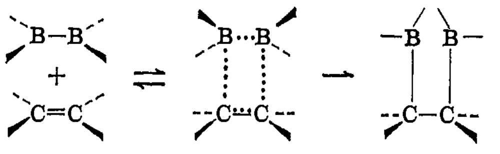
The Mechanism of Addition of Diboron Tetrachloride to Unsaturated Organic Compounds

Sir:

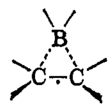
Holliday, *et al.*,[1,2] have postulated that diboron tetrachloride, B_2Cl_4, adds to unsaturated molecules through initial "π donation" from the unsaturated linkage to the two vacant p-type orbitals of the adjacent boron atoms in diboron tetrachloride. Subsequent B–B fission would result in *cis* addition of the $-BCl_2$ moieties across the unsaturated bond. Recently, Zeldin and Wartik[3] assumed *cis* addition of B_2Cl_4 to the π bonds of the conjugated systems in 1,3-cyclohexadiene and naphthalene. The rapidity of the reaction of many unsaturated species with diboron tetrachloride,[1-5] even at low temperatures, weighs against B–B bond rupture prior to addition. Nevertheless, the intuitively favored mechanism, the formation of an intermediate "π complex" leading to *cis* addition, has not been proven correct. In fact, Urry[6,7] has found the question of mechanism "somewhat puzzling" since, when cyclopentene is "diborated," the *trans*-bis(dichloroboryl) adduct is apparently formed.

In the present study the stereochemistry of certain B_2Cl_4 addition reactions was found to be stereospecific for *cis* addition. Such addition is consistent with a four-center transition state.

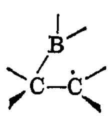


cis addition

Alternatively, B_2Cl_4 might dissociate prior to reaction. However, reasonable schemes involving $\cdot BCl_2$ would not be stereospecific for *cis* addition but present either (1) a bridged intermediate such as i which forces the second $\cdot BCl_2$ to add *trans*, or (2) a freely rotating intermediate such as ii which would allow random addition of the second $\cdot BCl_2$ and give no stereospecificity.



i



ii

When B_2Cl_4 and C_2H_2 were mixed as gases at 25° a pure compound identical with the originally reported $C_2H_2 \cdot B_2Cl_4$ was cleanly formed, as demonstrated by melting-point and vapor pressure checks. Since the *trans* form of $C_2H_2 \cdot B_2Cl_4$, *trans*-$(Cl_2B)HC{=}CH(BCl_2)$ [I (C_{2h})], possesses a center of symmetry, the "mutual exclusion rule"[8] should be obeyed in the infrared and Raman spectra of I. A comparison of the vibrational spectra (Table I) eliminates I because of the close agreement between infrared and Raman frequencies.

Table I. Infrared and Raman Spectra[a] of $(Cl_2B)HCCH(BCl_2)$

Frequency, cm^{-1}, and relative intensity Raman (liquid)	 Infrared (gas)	 Tentative assignment
109 s		ρ(BC)
159 s		ω(BC)
255 m		$\rho(BCl_2)$
274 m		$\omega(BCl_2)$
317 m, dp	332 vw	$\delta(BCl_2)$
371 m, p		$\delta(BCl_2)$
473 w		$\omega(BCl_2)$
496 m, p		$\omega(BCl_2)$
530 s	570 vw	δ(BCB)
680 w	694 m	ω(CH)
926 w	947 vs	$\nu(^{11}BCl)$
	984 s	$\nu(^{10}BCl)$
1025 w	1030 s	ν(BC)
1060 w	1068 s	$\nu(^{11}BC)$
	1089 w	$\nu(^{10}BC)$
1186 m	1193 vw	δ(CH)
	1322 vw	
1376 w, dp	1382 s	δ(CH)
1544 s, p	1598 s	ν(CC)
2915 w		Combination
2971 m, p		ν(CH)
3015 w, p	3010 vw	ν(CH)
	3028 vw	

[a] ν = stretch, δ = deformation, ω = wag, ρ = rock, v = very, s = strong, m = medium, w = weak, p = polarized, dp = depolarized; infrared determined between 4000 and 200 cm^{-1}. The slight shifts in line positions between the infrared and Raman spectra can be attributed to the necessity of determining the spectra in different phases.

The only alternative[9] is *cis*-1,2-bis(dichloroboryl)ethylene, *cis*-$(Cl_2B)HC{=}CH(BCl_2)$ [III (C_{2v})]. The presence of an infrared active C═C stretch alone is good evidence for III. However, the complementary Raman data listed in Table I show that the "mutual exclusion

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[1] A. K. Holliday and A. G. Massey, *J. Inorg. Nucl. Chem.*, **18**, 108 (1961).

[2] J. Feeney, A. K. Holliday, and F. J. Marsden, *J. Chem. Soc.*, 356 (1961).

[3] M. Zeldin and T. Wartik, *J. Am. Chem. Soc.*, **88**, 1336 (1966).

[4] G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger, *ibid.*, **76**, 5299 (1954).

[5] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, **81**, 6368 (1959).

[6] G. Urry in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., p 359.

[7] H. K. Saha, L. J. Glicenstein, and G. Urry, *J. Organometal. Chem.* (Amsterdam), **8**, 37 (1967).

[8] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945.

[9] Even though the asymmetric isomer, $(Cl_2B)_2C{=}CH_2$ [II (C_{2v})], might be consistent with the spectroscopic data it can be eliminated since X-ray [M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 605 (1959)] crystallography has shown that B_2Cl_4 adds across the unsaturated linkage. Also, the hydrogen atom migration necessary to form II is improbable.