The Photochemical Rearrangement of Benzene-1,3,5-d_3[1]

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Abstract: Irradiation of benzene-1,3,5-d_3, in the vapor phase and in solution, with light in the region of 2500 Å, has been found to produce isomeric trideuteriobenzenes. The extent of isomerization has been determined by mass spectrometry of *m*-dinitro derivatives. The rearrangements are intramolecular and probably proceed *via* valence isomerization. Quantum yields for an assumed benzvalene intermediate are 0.03 and 0.07 in the vapor phase at 2537 and "2480 Å," respectively; 0.05 in hexadecane solution at 2537 Å. The wavelength dependence in the vapor suggests that the intermediate is formed, at least in part, from a vibrationally excited species. The quantum yield for rearrangement in solution rules out the possibility that addition of olefins to benzene proceeds predominantly *via* a benzvalene intermediate, but is consistent with such an intermediate for the addition of alcohols.

In order to obtain further information on the role of valence isomerization[2-4] in the photochemistry of benzene, we have irradiated benzene-1,3,5-d_3 in the vapor phase and in solution, at wavelengths within its first electronic absorption band. Rearrangements to isomeric trideuteriobenzenes have been observed in both cases and approximate quantum yields have been measured. The results demonstrate that a previously undetected reaction occurs in benzene vapor, and that it may have to be considered in attempting to account[5] for the energy input.

The reactions do not involve intermolecular hydrogen transfer. It is likely[2-4] that they result from skeletal rearrangements and that they proceed by formation and rearomatization of a valence isomer of benzene. In solution the rearrangement must proceed at least in part *via* the tricyclic valence isomer, benzvalene.[4] Photochemical formation[4] of benzvalene from benzene and its rearomatization[6] have been observed in hydrocarbon solvents at 2537 Å; the transpositions[2] of adjacent carbon atoms which occur in half of these cycles would lead to isomerization of trideuteriobenzene. In the absence of evidence to the contrary, we have assumed that benzvalene is the only intermediate; we have calculated its yield from that of the isotopic rearrangement for comparison with yields of other photochemical[4,7,8] reactions of benzene in solutions. In the vapor phase there is no direct evidence as to the nature of the intermediate, since no isomers have been detected upon irradiation at 2537 Å. In this case, too, we have assumed that a benzvalene is the sole intermediate, since intermediates of this type best account[2] for the photochemical rearrangements of the xylenes[9] in the vapor phase. We have obtained some information as to the nature of the excited state leading to the intermediate by studying the effect of wavelength on rearrangement yields.

The rearrangement of benzene-1,3,5-d_3 has been followed by mass spectrometry of *m*-dinitro derivatives of irradiated samples. The *m*-dinitro derivative of the 1,3,5 isomer should contain only d_1 and d_3 species in essentially equal amounts,[10] whereas those of the 1,2,4 and 1,2,3 isomers should contain d_1, d_2, and d_3 species in the ratio of 1:4:1. Increases in the relative intensity of the parent peak (mass 170) of the d_2 species therefore provide a measure of the extent of rearrangement.

Partial mass spectra of *m*-dinitrobenzenes prepared from unirradiated benzene-1,3,5-d_3 and purified[11] by several procedures are shown in Table I. The intensity of the 170 peak relative to that of the 169 peak varies with the mode of purification but falls in the range of 16.0–17.3%. Most of this intensity is attributable to the ^{13}C and ^{15}N isotope peak (7.5%) from the d_1-dinitrobenzenes and to the presence of 6% benzene-d_2 in the starting material. As is indicated by the variation in intensity with the method of purification of the *m*-dinitrobenzene, residual amounts of *ortho* and *para* isomers may also contribute to the peak. The effect of

Table I. Partial Mass Spectra of Dinitro Derivatives of Unirradiated and Irradiated Benzene-1,3,5-d_3

	Method of purification[a]	Relative intensities (mass 169 = 100) 168	170	171	172	$C_6H_2D_2N_2O_4$, mole %
Unirradiated	A	2.75	16.99	90.13	6.82	4.76
	B	2.43	17.31	88.03	6.12	4.97
	C	2.73	16.06	88.79	6.23	4.35
Irradiated						
L-1	C	3.04	22.57	89.05	6.28	7.35
L-2	A	3.26	36.32	90.35	6.92	13.18
V-1	A	2.62	37.20	90.00	6.92	13.58
V-2	A	3.54	99.23	92.40	7.58	32.83
V-3	A	3.08	58.50	91.00	7.16	21.27
V-4	C	2.48	22.24	88.65	6.20	7.26
V-5	B	2.64	28.94	89.12	6.26	10.21

[a] A, recrystallized twice from 75% ethanol; B, gas chromatography on Carbowax 20M; C, recrystallized twice and chromatographed.

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(10) The nitration of benzene under the conditions used takes place without significant isotope effect or hydrogen exchange: L. Melander, *Arkiv Kemi*, **2**, 211 (1950).

(11) Crude dinitrobenzene prepared under our conditions contains 7% of the *ortho* and about 1% of the *para* isomers.

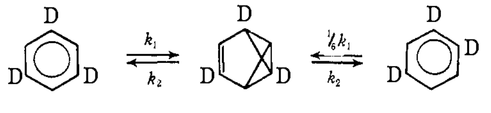
this contribution has been minimized by using the appropriate blanks for the irradiated samples. Table I also contains mass spectra of m-dinitrobenzenes from irradiated samples of benzene-1,3,5-d_3. The relative intensities of the 168 and 172 peaks are essentially unchanged and show that intermolecular hydrogen transfer has not occurred. The relative intensities of the 170 peaks, however, are all higher than in the blank. Increases in the mole fraction of dinitrobenzene-d_2 correspond to extents of rearrangement of 4.4–42%.

The number of molecules rearranged per quantum absorbed in benzene vapor at 2537 and "2480 Å" and in hexadecane solution at 2537 Å are shown in Table II. For low conversions, these values are essentially equal to the quantum yield for rearrangement; at higher conversions they are lower than the true quantum yield because of back reaction. Quantum yields for the assumed benzvalene intermediate (I) have been calculated on the basis that it is formed only one-sixth as readily from benzene-1,2,4-d_3 as from the 1,3,5 isomer and rearomatizes to both with equal probability.

Table II. Photochemical Yields in Rearrangement of Benzene-1,3,5-d_3

Run	Phase	Radiation, Å	Sample, mg	Dosage, quanta/molecule	Quantum yields	
					Rearrangement[a]	"Benzvalene"[b]
L-1	Soln	2537	90	1.8	0.025	0.051
L-2	Soln	2537	90	5.4	0.024	0.052
V-1	Vapor	2537	140	10	0.014	0.030
V-2	Vapor	2537	140	44	0.010	0.026
V-3	Vapor	2537	34.7	19	0.012	0.028
V-4	Vapor	2480[c]	17.4	1.30	0.034	0.068
V-5	Vapor	2480[c]	8.8	2.26	0.035	0.073

[a] Not corrected for back reaction. [b] Assumed intermediate; yields are those of rearrangement corrected for back reaction and multiplied by two. [c] See Experimental Section.



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The quantum yield for formation of this intermediate is about 0.03 in benzene vapor at 2537 Å and appears to be independent of pressure from 20 to 86 mm. The yield at "2480 Å," 0.07 at 14 and 28 mm, is more than twice as great. The fluorescence yield of benzene, however, varies in the opposite direction and has been reported[5] to be only 0.57 as great at 2480 as at 2537 Å. Since fluorescence yield is presumably proportional to the number of benzene molecules in the lowest vibrational level of the $^1B_{2u}$ state, it can be concluded that at least three-fourths of the isomerization at 2480 Å arises from a vibrationally excited state. Whether higher vibrational levels of the $^1B_{2u}$ state lead directly to the intermediate or whether they first undergo intersystem crossing or internal conversion cannot be determined from the present results. If the intermediate is formed only from singlet states, its yield must be added to fluorescence and triplet yields in considering energy balance[5] in benzene. Even if the intermediate is formed from a triplet, its yield might have to be included since a unimolecular isomerization might compete favorably with bimolecular processes involved in the measurement of triplet yields.

The calculated quantum yield for formation of the assumed benzvalene intermediate in hexadecane solution at 2537 Å is 0.05. This value is compared in Table III with the yields of some related reactions measured under comparable conditions. In an irradiation so short that photochemical and thermal rearomatization is completely negligible, the measured quantum yield of benzvalene[4] itself is only 0.02. A plausible explanation for the difference is that excited benzene isomerizes to benzvalene possessing so much excess energy that some of it is rearomatized before this energy is completely transferred to the solvent. This explanation could account for the failure to detect benzvalene in irradiated benzene vapor. The quantum yield for the 1,3 addition[4,7] of methanol to benzene is, within experimental error, equal to that calculated for the "benzvalene intermediate." Acidified methanol is known[4] to add efficiently to ground-state benzvalene. The present results suggest that it also reacts with benzvalene before deactivation has occurred. An alternative explanation is that the photochemical addition involves a transient species other than benzvalene, such as one recently proposed,[12] and that the similarity in the quantum yields is only coincidental. An investigation of this point is in progress. The quantum yield for 1,3 cycloaddition[8] of cyclopentene to benzene is five times that of the "benzvalene intermediate." Unless the formation of benzvalene is markedly solvent dependent, it would appear that the cycloaddition follows a different path. A diradical intermediate has been suggested[13] by Bryce-Smith, *et al.*

Table III. Photochemical Reactions of Benzene in Solution

Solvent	Product	Quantum yield
Hexadecane	"Benzvalene intermediate"	0.051[a]
Hexadecane	Benzvalene	0.020[b]
Methanol + 0.2% HCl	1,3 adducts	0.045
Cyclopentene	1,3 cycloadducts	0.25

[a] Calculated from rearrangement of benzene-1,3,5-d_3. [b] Initial yield measured by gas chromatography.

Experimental Section

Materials. Benzene-1,3,5-d_3 was obtained from Volk Radiochemical Co., 98% isotopic purity. A low-voltage mass spectrum indicated the presence of 6% benzene-d_2. Hexadecane, 99.5%, Chemical Samples Co., cyclopentene, Phillips Petroleum Co., Research Grade, and methanol, Eastman Organic Chemicals, Spectro Grade, were used. The cyclopentene was distilled before use; other chemicals were used without further purification.

Irradiations. Solutions, 2537 Å. A glass-stoppered rectangular quartz cell 2 cm × 10 cm with a path length of 1 cm was irradiated with an 8-w General Electric G8T5 germicidal lamp fitted with a cylindrical Vycor 7910 shield to filter out 1849-Å radiation. The lamp delivered 2.6×10^{20} quanta/hr of 2537-Å radiation to the cell, as measured by potassium ferrioxalate actinometry with appropriate filters.

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(12) D. Bryce-Smith, A. Gilbert, and H. C. Longuet-Higgins, *Chem. Commun.*, 240 (1967).

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Solutions of 100 μl of benzene-1,3,5-d_3 in 20 ml of hexadecane were irradiated at room temperature for periods of 5 and 17.5 hr after first flushing with nitrogen. The absorbance of the solutions at 2537 Å increased by 30% in the former case and by 100% in the latter. Reported values for the quanta absorbed per molecule of benzene were corrected for this effect. The irradiated benzene was recovered from the hexadecane solution by evacuation, ultimately at 50° and 10^{-4} mm. More than 90% of the initial benzene was recovered.

Similar irradiation procedures were employed to measure the rates of related reactions. The amount of benzvalene present after a 15-min irradiation of a solution of 100 μl of benzene in 20 ml of hexadecane was determined by gas chromatographic analysis[4] of the recovered benzene. The formation of methoxybicyclohexenes[4,7] in a 4-hr irradiation of 100 μl of benzene in 20 ml of acidified methanol (0.2% HCl) and of 1,3-cycloaddition products[8] in a 30-min irradiation of 100 μl of benzene in 20 ml of cyclopentene was also determined.

Vapor Phase, 2537 Å. A dewar-type cell was used to provide a large surface and thus minimize absorption by deposited polymer. The vessel had an inner wall of 43-mm o.d. Vycor 7910, an outer wall of 69-mm o.d. quartz, a path length of 1.1 cm, and a volume of 400 ml. A coiled low-pressure mercury lamp (Nester and Faust NFUV-300) within the well delivered 3.8×10^{21} quanta/hr of 2537-Å radiation to a solution of uranyl oxalate in the cell. Weighed benzene samples in vacuum-sealed fragile tubes were introduced into the cell before evacuation and seal-off. The absorption of light by the benzene was calculated using a measured molar extinction coefficient of 120. Transmission through the cell was observed to decrease during the irradiations. In view of the temperature gradient (*ca.* 20°) across the cell, it was assumed that most of the polymer deposition occurred on the outer wall, and that the intensity of the light available to benzene did not decrease. This assumption is supported by the correspondence of quantum yields in runs V-1 and V-2 in which exposures differed by a factor of 5. If the assumption is not correct, quantum yields may be somewhat greater than those reported. Recoveries of benzene were 95% in runs V-1 and V-3 and 80% in run V-2.

Vapor Phase, 2480 Å. A cylindrical quartz cell with a diameter of 43 mm, a volume of 145 ml, and a 10-cm light path was used. The light source was a Bausch and Lomb SP-200 super-pressure mercury lamp and high-intensity grating monochromator, set at 2480 Å. Although the slit widths permitted a band pass of 96 Å, almost all of the light was absorbed between 2465 and 2490 Å. The output of the lamp, *ca.* 1.5×10^{19} quanta/hr, was measured with a potassium ferrioxalate actinometer. Absorption by benzene was determined by measuring the light transmitted through the (evacuated) cell before and after the sealed sample tube was opened. During irradiation the cell was rotated continuously, and reversed once, in order to distribute the light, and the deposited polymer, over as large a surface as possible. Periodically, the cell was removed and the intensity of the incident light was remeasured. At these times, the benzene was condensed in a side arm, and the transmission of the cell at 2480 Å was measured in a Cary spectrophotometer.

(In run V-5 the lamp output decreased by 24% and the optical density of the cell increased by 0.21 during the 30-hr irradiation.) It was assumed, on the basis of visual examination, that the decreased transmission resulted from deposits on the incident window. Absorption of light by benzene in each interval was calculated from the average light intensity and the average transmission of the incident window. Recovery of benzene was 96% in run V-4 and 93% in run V-5.

Nitration. The procedure was adapted from that of Melander.[10] The recovered benzene was distilled *in vacuo* onto ten times its volume of nitrating mixture (1:2 HNO_3:H_2SO_4). The reaction tube was sealed off, warmed to room temperature, and shaken for 10 min. The contents were transferred to crushed ice and the crude dinitrobenzene was washed with water. All but the smallest sample were recrystallized twice from 75% ethanol. Those samples in which the extent of rearrangement was small were subjected to gas chromatography (Carbowax 20M, 155°) to further decrease the content of *o*-dinitrobenzene. The smallest sample (run V-5) was purified only by gas chromatography.

Samples of unirradiated benzene-1,3,5-d_3 were nitrated similarly, and the products were purified by each of the three procedures.

Mass Spectrometry. The purified samples of dinitrobenzene were analyzed on a 12-in. sector mass spectrometer with an ionizing potential of 70 v. The solid samples were introduced with a probe into the heated (150°) gas inlet system. The parent mass region was scanned repeatedly in both directions; reported intensities are averages of twelve scans. Mole fractions of the various deuterated dinitrobenzenes were calculated from the ratio of their parent peaks, corrected for ^{13}C, ^{15}N, and ^{18}O contributions from molecules of lower deuterium content, to the sum of all the corrected parent peaks. The mole fraction of rearranged trideuteriobenzene was assumed to be 1.5 times the increase in mole fraction of dideuteriodinitrobenzene in an irradiated sample over that in the blank.

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Electrochemistry of Organophosphorus Compounds. II. Electroreduction of Triphenylphosphine and Triphenylphosphine Oxide

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Abstract. The electrochemical reduction of triphenylphosphine (TPP) and triphenylphosphine oxide (TPPO) has been investigated using polarography, cyclic voltammetry, coulometry, and product analysis. The reduction of TPP proceeds by a one-electron transfer to form the anion radical which undergoes cleavage of a phenyl group.

Several recent papers have been concerned with the polarography of triphenylphosphine (TPP) and triphenylphosphine oxide (TPPO)[2,3] and the electron spin resonance (esr) spectroscopic investigation of radicals derived from alkali metal reduction of these. Hanna[4] claimed, partly on the basis of polarographic evidence of a one-electron reversible reduction,[2] that he

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[1] To whom correspondence and request for reprints should be directed.

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