methyl the resonance state involves hyperconjugation[11] with a correspondingly high energy for the ionic state of biphenyl itself. In the case of the dihalogen derivatives, Fig. 9, the number of resonance states is the same for all derivatives, and the different energy of the ionic state and the wave length shift are solely due to the differences in the polarizability of the halogens.

The Correlation of Extinction Coefficient with Polarizability.—In the introduction it was stated that the extinction coefficient depends somewhat indirectly upon the polarizability and that, in general, changes in extinction coefficient and wave length of maximum absorption should parallel each other. The polarizability of a substituent group is directly proportional to the molecular refraction which may be calculated for the group with which we are concerned. We have prepared Table II in which molecular refraction and extinction coefficient are compared. It will be noted that the correlation is good with two or three exceptions. It is probable that these exceptions are due to the appearance of resonance forms in biphenyl which will increase the polarizability to a larger value than is observed in the non-resonating molecule. It should be noted that the extinction coefficient of molecules such as a 4,4′-substituted biphenyl does not depend upon the polarity of the substituent group but upon the polarizability, that is, the change in polarity when the molecule is excited to the ionic state.

TABLE II

Group	Mol. refr.	Max., ϵ(p,p'-biphenyl)
F	0.881	17,000
H	1.051	16,500
OH	2.572	22,400
NH_2	5.312	23,200
CH_3	5.654	21,100
Cl	5.998	21,700
NO_2	7.30	24,000
OCH_3	7.337	21,700
Br	8.927	23,300
$COOCH_3$	12.125	30,000
I	14.12	30,000

The authors wish to acknowledge their indebtedness to Professor Roger Adams and other members of the organic division for their helpful discussions and advice on the preparation of some of the compounds studied. For the preparation and purification of some of the samples we are indebted to Mr. E. C. Dunlop of the State Water Survey and Dr. G. C. Finger of the State Geological Survey.

Summary

The effect of type and position of substituent in the biphenyls upon their ultraviolet absorption has been investigated in a number of cases. Excellent correlation has been obtained in most cases between the possible resonance structures and values for extinction coefficient and wave length of maximum absorption. Evidence has been obtained for increasing departure from coplanarity with increasing size of group in the ortho positions. The difference in the behavior of ortho-para- and meta-directing groups is particularly interesting.

URBANA, ILL. RECEIVED AUGUST 4, 1941

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[11] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Photochemical Studies. XXXIV. The Photochemical Decomposition of Benzene

BY JOSEPH E. WILSON[1] AND W. ALBERT NOYES, JR.

The photochemical decomposition of benzene vapor, both direct[2,3] and sensitized by mercury vapor,[4] has been reported. In the direct decomposition radiation from the aluminum spark, presumably lying below 2000 Å., was found to be particularly effective. Hydrogen was identified as a product, and biphenyl was assumed to be formed. Definite proof was not given, however, for the formation of biphenyl. The products of the sensitized reaction were not completely analyzed, but hydrogen and methane were reported. Bates and Taylor[4] also mention a strong odor of biphenyl and state that the formation of such large amounts of hydrocarbon (40% of the gaseous products) must mean that excited mercury atoms can bring about a complete rupture of the benzene ring.

In a recent article Forbes and Cline[5] found that benzene vapor is decomposed by mercury atoms

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[1] Holder, during 1939–1940, of the Eastman Kodak Company Fellowship in Photochemistry at the University of Rochester.

[2] Krassina, *Acta physicochim. U. R. S. S.*, **10**, 189 (1939).

[3] Prilezhaeva, *ibid.*, **10**, 193 (1939).

[4] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

[5] Forbes and Cline, *ibid.*, **63**, 1713 (1941).

excited by the resonance radiation of wave length 1849.6 Å. They conclude also that an unsensitized reaction is brought about by wave lengths below 2000 Å. However, the latter statement is presumably based on experiments by these authors in which mercury vapor had been trapped out "pretty completely" at −8°. It should be pointed out that absorption by mercury vapor of the 1849.6 Å. line is so high that reducing the mercury vapor pressure to that at −8° would probably have no effect on the amount of reaction.

Forbes and Cline[5] found mixtures of hydrogen and benzene with mercury irradiated by the resonance radiation to give cyclohexadiene and hydrogenated biphenyls. Thus there is evidence that hydrogen atoms will react with benzene vapor, although little is known about the rates of the various steps.

Knowledge of the direct photochemical decomposition of benzene is fragmentary and unsatisfactory. Irradiation in the region of the near ultraviolet bands seems to produce no reaction.[6,7] That something happens at shorter wave lengths seems probable, but the nature of the products other than hydrogen does not seem to have been determined.

Experimental

Benzene vapor shows diffuse absorption bands below 2200 Å. and a continuum below 1850 Å.[8] In agreement with earlier work on the photochemical decomposition, the spectroscopic evidence would indicate that wave lengths below 2200 Å. and perhaps below 1850 Å. would be necessary to cause the photochemical decomposition of benzene. Several different light sources were used in the preliminary work, but the iron and aluminum sparks were found to be the most satisfactory. The latter was used almost exclusively in the present experiments.

The benzene was thiophene free and was fractionated several times at low pressures.

The reaction vessel was of quartz which had been shown in other experiments to transmit some radiation down to wave lengths of about 1600 Å.

A brown deposit was formed on the face of the reaction vessel nearest the spark. This deposit was insoluble in all of the ordinary organic solvents, in concentrated nitric acid, in hydrochloric acid, and in aqua regia. It could be removed by hot cleaning solution. It charred but did not melt at 350°. The general behavior of this material was similar to that of cuprene.[9]

A gaseous fraction uncondensed at 142°K. (pentane mush) included a fraction uncondensed by liquid nitrogen. The latter might be hydrogen, carbon monoxide, or methane. Carbon monoxide might have been formed in some way by a reaction with the silica of the walls or from traces of oxygen. Attempts to oxidize this gas with cupric oxide showed complete reaction at 250° and a negligible reaction at 155°. While this type of evidence is not conclusive, this gas behaves like hydrogen. The small quantities made further identification difficult.

The gaseous fraction uncondensed at 142°K. but condensed by liquid nitrogen was shown by combustion to give two molecules of carbon dioxide for each molecule burned. Moreover this fraction was absorbed by solid cuprous chloride. These two facts and the character of the polymer on the walls all indicate that this fraction is acetylene.

No evidence in this work could be found for the formation of biphenyl. This may be due, however, to the small amount of reaction and should not be taken as conclusive proof that no biphenyl is formed. Extraction with various solvents showed no solid to be produced in detectable amount other than the cuprene-like material referred to above.

Attempts to measure the quantum yield were made using the hydrogen bromide actinometer. Due to the deposition of solid on the window and the small amount of reaction the value is certainly not very precise. The technique has been described.[10] The group of aluminum lines between 1855 and 2000 Å. was separated by focal isolation. Corrections were made for the thermal reaction of hydrogen bromide with mercury vapor, but corrections for the transmissions of the windows were difficult to make.

The results showed 2×10^{-4} mm. of hydrogen to be produced from the benzene in 500 min. and the amount of hydrogen produced from the hydrogen bromide in the same length of time corresponding to the radiation absorbed by the benzene was equivalent (in the same volume) to 6.8×10^{-2} mm. The quantum yield of hydrogen formation from benzene, using these figures, is 3×10^{-3}. However it is not known whether all of the aluminum lines absorbed by the benzene are effective in producing reaction. We feel safe in stating, therefore, that the quantum yield for the entire group of lines is low and is of the order of magnitude of 0.01 to 0.001.

Some rate experiments were made in which the spark was placed about 3.3 cm. from the window of the reaction vessel. The polymer caused the rate to decrease after the start of the exposure. Figure 1 shows points obtained for 100 min. exposures at various pressures of benzene. The volume of the reaction vessel was 25.93 cc. and the volume of the entire system 375 cc. The open points were obtained when the vessel was cut off from the rest of the system by a mercury cut-off. Thus when diffusion permits some of the products to escape there is a slight but probably definite tendency for the amount of acetylene to increase and the amount of hydrogen to decrease.

Some exchange reactions with deuterium were attempted.[11] Approximately 0.1 mm. of deuterium was present with the benzene. Three runs were made. The average percentage of hydrogen in the deuterium due to the addition of the products of the reaction to the deu-

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[6] Lane and Noyes, This Journal, **54**, 161 (1932).

[7] West, *ibid.*, **57**, 1931 (1935).

[8] Carr and Stücklen, *Z. physik. Chem.*, **B25**, 57 (1934); *J. Chem. Phys.*, **4**, 760 (1936).

[9] Lind and Livingston, This Journal, **54**, 94 (1932).

[10] See Howe and Noyes, *ibid.*, **58**, 1406 (1936).

[11] See Herr, Matheson and Walters, *ibid.*, **63**, 1464 (1941), for description of the method.

terium should have been 0.5. The average found experimentally was 0.7. Within experimental error, therefore there proved to be no exchange with deuterium.

Discussion

While no conclusive evidence has been found for or against the formation of biphenyl in the present work, the amount must be small. On the other hand definite evidence for the production of hydrogen, of acetylene, and of a solid substance which may be a polymerized acetylene or a cuprene has been found.

Due to the exceedingly small amount of reaction, no detailed kinetic studies were possible and definite statements concerning mechanism are not possible. The absence of much exchange with deuterium means that if the primary process is

$$C_6H_6 + h\nu = C_6H_5 + H \qquad (1)$$

hydrogen atoms must react very rapidly with benzene. Forbes and Cline[5] have suggested the reaction

$$H + C_6H_6 = C_6H_7 \qquad (2)$$

but little is known concerning the rate. Also it may be stated that if (1) is the primary process, the reaction

$$C_6H_5 + D_2 = C_6H_5D + D \qquad (3)$$

must be slow compared to other reactions involving phenyl radicals. Had exchange been observed, the mechanism might be in doubt, but the absence of exchange is contributory evidence that primary process (1) is not important.

While the addition of a hydrogen molecule to a benzene molecule is endothermic and involves a positive free energy change,[12] the same is not true for the addition of two hydrogen atoms. Probably (2) would be an exothermic step and the rate might be fairly high.

Little can be said concerning the probable rate of (3). This reaction may be slightly endothermic and the heat of activation may be high enough to permit phenyl radicals to react with each other either in the gas phase or on the walls. Since no evidence for biphenyl formation was forthcoming, however, it seems probable that the absence of exchange is fairly conclusive proof that primary process (1) does not take place to a large extent.

The mechanism of acetylene formation is uncertain. From available data[13] one finds

$$C_6H_6(g) = 3C_2H_2(g);\ \Delta H = 147{,}000 \text{ cal.} \qquad (4)$$

This heat of reaction corresponds to a wave length of about 1950 Å. The coincidence between the calculated and the observed wave lengths constitutes no real evidence that (4) occurs as a primary process. We merely present this as a tentative conclusion.

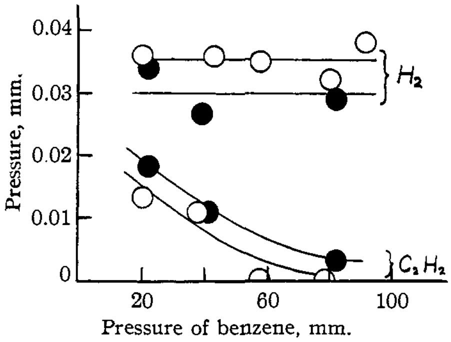

Fig. 1.—Time of exposure is 100 min. for each point.

The polymerization of the acetylene may occur in several ways: (1) by collision of the second kind with excited benzene molecules; (2) by absorption of radiation.[9] The acetylene polymer has approximately the empirical formula $(CH)_2$ but is slightly deficient in hydrogen.[14] The amount of hydrogen produced is independent of benzene pressure (see Fig. 1), while the amount of acetylene left in the gas phase decreases at high benzene pressures. These facts are consistent with a mechanism in which activated molecules are produced in the primary step; the activated molecules either dissociate directly into acetylene, are deactivated by collision, or by collision of the second kind induce the polymerization of acetylene. Little more can be said about mechanism at the present time.

Some of the hydrogen may result from the overall reaction

$$2C_6H_6 = (C_6H_5)_2 + H_2 \qquad (5)$$

but by the picture given the majority of the hydrogen would be produced indirectly from the acetylene.

In conclusion the authors wish to express their appreciation to Dr. Winston D. Walters for help with the experiments on deuterium exchange and for useful discussions.

Summary

1. Acetylene, hydrogen, and a solid resembling cuprene are produced when benzene is exposed to radiation of wave length less than 2000 Å.

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[12] Conant and Kistiakowsky, *Chem. Rev.*, **20**, 189 (1937).

[13] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, N. Y., 1932, pp. 84 and 90.

[14] Lind and Livingston, THIS JOURNAL, **56**, 1550 (1934).

2. The quantum yield of hydrogen formation has not been precisely determined but is very low.

3. Attempts to produce photochemical exchange reactions between benzene and deuterium were unsuccessful.

4. While definite conclusions concerning mechanism are not possible, the best explanation of the data is based on a small amount of primary dissociation of benzene molecules into acetylene.

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[CONTRIBUTION FROM THE MEDICAL-RESEARCH DIVISION, SHARP AND DOHME, INC.]

Sulfonamido Derivatives of Pyrimidines

BY JAMES M. SPRAGUE, L. W. KISSINGER AND ROBERT M. LINCOLN

The substitution of pyridyl and thiazolyl radicals into the N^1 position of sulfanilamide has resulted in compounds of improved therapeutic value. In continuing our study[1] of heterocyclic derivatives of sulfanilamide a number of sulfonamidopyrimidines[2] have been synthesized and a preliminary evaluation of their therapeutic activity in experimental infections has been made.

These compounds are 2- and 4-sulfonamidopyrimidines (Table I) and, in general, were prepared by the reaction of a sulfonyl chloride on 2- or 4-aminopyrimidines. 4-Alkyl or 4,5-dialkyl substituted 2-aminopyrimidines are conveniently prepared, although in low yields, from the reaction of guanidine with α-formyl, or hydroxymethylene ketones which are obtained by the condensation of methyl alkyl ketones with ethyl formate.[3] However, ketones of the type RCH_2COCH_3 may give rise to isomeric formyl derivatives, RCH_2COCH_2CHO I or $RCH(CHO)COCH_3$ II, depending on whether the ethyl formate condenses with the methyl or methylene group.[4] On condensing with guanidine these isomeric formyl derivatives would produce 4-alkyl- and 5-alkyl-4-methyl-2-aminopyrimidines, respectively. Benary[5] has shown that methyl ethyl ketone on condensation with ethyl formate, gives a mixture of the two formyl derivatives, I and II ($R = CH_3$), while methyl *n*-propyl ketone and methylheptenone[6] give only the methyl condensation product (I, $R = C_3H_7$, $(CH_3)_2C{=}CH(CH_2)_2$—). Recently, Tracy and Elderfield[7] have shown that, insofar as the structure of pyridine derivatives may be taken as evidence, the formyl methyl ethyl ketone has the structure II ($R = CH_3$) and point out that it is difficult to reconcile this fact with the report[5] that the next higher homolog, methyl *n*-propyl ketone, gives exclusively a formyl derivative of structure I.

Since, in the present study, the formyl derivatives of methyl *n*-propyl and methyl *n*-hexyl ketone were used in the preparation of 4-propyl and 4-*n*-hexyl-2-aminopyrimidine, respectively, it was desirable to prove the structures of these pyrimidines. Proof was obtained in two ways. 2-Amino-4-methyl-5-ethyl- and 2-amino-4-methyl-5-*n*-amylpyrimidine, which would arise if the formyl derivatives of methyl *n*-propyl ketone and methyl *n*-hexyl ketone had structure II, were synthesized from ethyl ethylacetoacetate and ethyl *n*-amylacetoacetate, respectively. These pyrimidines were found to be entirely different from the products derived from the formyl ketones. Further evidence was obtained by the synthesis of 2-amino-4-*n*-hexylpyrimidine from *n*-propyl heptanoylacetate. This product was found to be identical with the pyrimidine obtained from formyl methyl *n*-hexyl ketone. Therefore, from the structure of the aminopyrimidines, it is concluded that the formyl derivatives of methyl *n*-propyl ketone and methyl *n*-hexyl ketone have the structure I resulting from condensation on the methyl group.

Since the conclusion of this work, Caldwell, Kornfeld and Donnell[2b] have reported on the condensation of methyl *n*-hexyl ketone with ethyl formate and the 2-aminopyrimidine derived from the resulting formyl derivative. From the results of a nitric acid oxidation they concluded that the pyrimidine was 2-amino-4-methyl-5-*n*-amylpyrimidine and, therefore, that the formyl methyl *n*-hexyl ketone had the structure II resulting from reaction at the methylene group. This conclusion is not in agreement with our results.

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(1) Sprague and Kissinger, THIS JOURNAL, **63**, 578 (1941).

(2) Since this work was started some sulfanilamidopyrimidines have been reported by (a) Roblin, Williams, Winnek and English, *ibid.*, **62**, 2002 (1940), and by (b) Caldwell, Kornfeld and Donnell, *ibid.*, **63**, 2188 (1941).

(3) Benary, *Ber.*, **63**, 2601 (1930).

(4) Benary, Meyer and Charisius, *ibid.*, **59**, 108 (1926).

(5) Benary, *ibid.*, **59**, 2198 (1926).

(6) Leser, *Compt. rend.*, **128**, 108, 371 (1899).

(7) Tracy and Elderfield, *J. Org. Chem.*, **6**, 63 (1941).