phenones.[3] Since the total *difference* between solvent stabilization of the excited and ground states is changed very little with solvent, one would not expect the factor of steric hindrance to solvation near the alkyl group to greatly influence the excitation energy spreads from solvent to solvent. Certain minor trends possibly attributable to this factor may be discernible, although speculation seems unwarranted.

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SEATTLE 5, WASH.

[CONTRIBUTION FROM ATOMICS INTERNATIONAL, A DIVISION OF NORTH AMERICAN AVIATION, INC.]

Synthesis of Deuterated Biphenyls[1]

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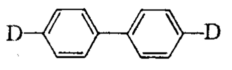
The preparation of four deuterated analogs of biphenyl, biphenyl-4,4'-d_2, biphenyl-3,3',5,5'-d_4, biphenyl-2,2',4,4',6,6'-d_6, and biphenyl-d_{10} is described. The first compound was synthesized from 4,4-dibromobiphenyl, and the other three were formed by coupling the Grignard reagent of the appropriate deuterated bromobenzene.

Deuterium labeling has proved of great value for studies of substitution reactions in organic compounds.[2] Examination of the fragmentation of organic compounds by ionizing radiation[3,4] and the determination of molecular configuration by infrared spectrometry[5] have also been facilitated by deuterium labeling. Furthermore, the use of properly deuterated molecules greatly simplifies the interpretation of mass spectra of organic molecules[4,6] by enabling identification of the ionized fragments produced and analysis of the processes taking place.

In this laboratory we are studying aromatic hydrocarbons of the polyphenyl type by several of the above methods—irradiation, vibrational analysis, and mass spectrometry. Biphenyl, which is the simplest member of the polyphenyl series, is the simplest aromatic compound containing only benzene rings which has nonequivalent carbon-hydrogen bonds. This nonequivalence has been demonstrated in the substitution reactions of biphenyl, since the rates of reaction differ at the positions *ortho*, *meta*, and *para* to the bond joining the two rings.[7] Replacing hydrogen atoms by deuterium atoms at various sites in the biphenyl molecule allows the techniques mentioned above to furnish more information about the molecule. Consequently we have prepared four deuterium-substituted biphenyls: biphenyl-4,4'-d_2 (I), which has deuterium atoms in the two *para* positions; biphenyl-3,3',5,5'-d_4 (II), which has deuterium atoms in the four *meta* positions; biphenyl-2,2',4,4',6,6'-d_6 (III), which has deuterium atoms in the four *ortho* and two *para* positions; and biphenyl-d_{10} (IV), which is completely deuterated. It can be seen that no molecular symmetry is lost in these deuterated biphenyls (in contrast to the case of the partially deuterated benzenes[5]), and therefore there is no increase in complexity of the vibrational spectra of the deuterated biphenyls over that of biphenyl itself.



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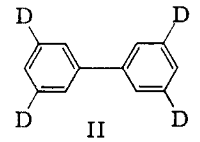

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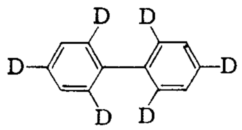

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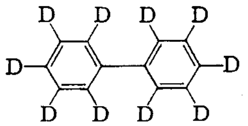

IV

Synthetic procedures. Deuterated benzenes and toluenes have been prepared by treatment of Grignard reagents[8] and organolithium compounds[9]

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(1) This work was performed under AEC Contract AT(11-1)-GEN-8.

(2) J. G. Burr, Jr., *Tracer Applications for the Study of Organic Reactions*, Interscience Publishers, Inc., New York, 1957; L. C. S. Melander, *The Use of Nuclides in the Determination of Organic Mechanisms*, University of Notre Dame Press, Notre Dame, Ind., 1955.

(3) S. Gordon and M. Burton, *Discussions Faraday Soc.*, No. 12, 88 (1952); P. V. Phung and M. Burton, *Radiation Research*, **7**, 199 (1957).

(4) J. G. Burr, *J. Phys. Chem.*, 61, 1477, 1481, 1483 (1957).

(5) W. R. Angus, C. R. Bailey, C. K. Ingold, and C. L. Wilson, *J. Chem. Soc.*, 912 (1936); C. R. Bailey, C. K. Ingold, H. G. Poole, and C. L. Wilson, *J. Chem. Soc.*, 222 (1946).

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(7) G. W. Wheland, *Resonance in Organic Chemistry*, J. Wiley & Sons, Inc., New York, 1955, pp. 493–494.

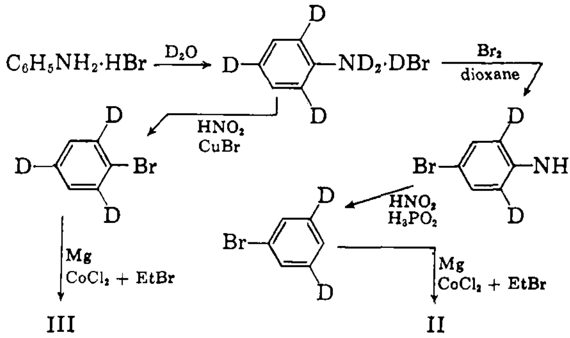
(8) L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, 235 (1946); J. Turkevich, H. A. McKenzie, L. Friedman, and R. Spurr, *J. Am. Chem. Soc.*, **71**, 4045 (1949); T. J. Prosser and E. L. Eliel, *J. Am. Chem. Soc.*, **79**, 2544 (1957).

(9) W. M. Lauer and W. E. Noland, *J. Am. Chem. Soc.*, **75**, 3689 (1953).

with deuterium oxide. Several attempts to prepare the difunctional Grignard reagent from 4,4'-dibromobiphenyl, either with magnesium iodide as promoter[10] or with ethyl iodide by the entrainment method, gave low yields. Dilithium compounds have been prepared previously from 4,4'-dibromobiphenyl[11] and 3,3'-dibromobiphenyl.[12] The exchange reaction between 4,4'-dibromobiphenyl and *n*-butyllithium reagent was first carried out in aliphatic hydrocarbon solvents.[11] Better yields and a purer product were obtained by the use of ethyl ether as the reaction solvent.[12] The 4,4'-dibromobiphenyl was treated with excess *n*-butyllithium reagent, and the reaction mixture hydrolyzed with 99.7% deuterium oxide; the yield of biphenyl 4,4'-d_2 was 63%.

The other three deuterated biphenyls were prepared by converting the appropriately deuterated bromobenzene to its Grignard reagent; this was coupled to form biphenyl by cobaltous chloride in the presence of ethyl bromide, according to the method of Kharasch and Fields.[13]

For the synthesis of biphenyl-3,3',5,5'-d_4, aniline hydrobromide was converted by six successive exchanges with 99.7% deuterium oxide to aniline-*N*,*N*,2,4,6-d_5 hydrobromide-d by a modification of the method of Best and Wilson.[14] Bromination to 2,4,6-tribromoaniline and examination of its infrared spectrum showed the absence of deuterium in the 3- and 5-positions of the deuterated aniline.[15] The aniline-*N*,*N*,2,4,6-d_5 hydrobromide-d was brominated by the bromine-dioxane complex[16] to 4-bromoaniline-2,6-d_2, which was diazotized and reduced by hypophosphorous acid to bromobenzene-3,5-d_2.[17] The Grignard reagent formed from this was then coupled to biphenyl-3,3',5,5'-d_4. The over-all yield for the bromination, reduction, and coupling was 22%.



The preparation of biphenyl-2,2',4,4',6,6'-d_6 has not been previously accomplished; Shatenshteĭn, Kalinachenko, and Varshavskiĭ[18] have determined, however, by measuring rates of exchange, that six hydrogens of biphenyl can be exchanged for deuterium in liquid deuterium bromide. No product was isolated, and the positions which underwent exchange (presumably the *ortho-* and *para-*positions) were not determined.

In the present work, biphenyl-2,2',4,4',6,6'-d_6 was prepared from aniline-*N*,*N*,2,4,6-d_5 hydrobromide-d. The deuterated aniline was converted by the Sandmeyer reaction[19] to bromobenzene-2,4,6-d_3. The Grignard reagent was prepared and and coupled as above. The yield for these two steps was 41%.

The completely deuterated compound, biphenyl-d_{10}, has been obtained by treating biphenyl in liquid ammonia-d_3 in the presence of potassium amide-d_2.[20] Several experiments were carried out[21] to determine if biphenyl-d_{10} could be synthesized by exchange between biphenyl and sulfuric acid-d_2. These included shaking biphenyl alone (at room temperature or above its melting point) or dissolved in benzene or carbon tetrachloride with sulfuric acid-d_2 of varying concentrations. In those cases where exchange took place, the rate of sulfonation of biphenyl was too great to permit isolation of sufficient deuterated material. Hence, benzene was converted by exchange with sulfuric acid-d_2 to benzene-d_6 by the procedure of Ingold, Raisin, and Wilson.[22] This was brominated by stirring with aqueous hypobromous acid to bromobenzene-d_5.[14] The Grignard reagent was prepared and coupled as above to biphenyl-d_{10}. The yield for the bromination and coupling was 38%.

The various deuterated biphenyls were analyzed by gas chromatography, and were found to be free of chemical impurities. The infrared spectra and the mass patterns were obtained. The isotopic content of the preparations was determined by mass spectrometry at an ionizing voltage great enough to ionize the molecules but too small to remove hydrogen atoms from the molecules.[23] The isotopic purities obtained in this manner are shown in

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[10] R. Gibert, *Compt. rend.*, **205**, 443 (1937).

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[12] H. R. Snyder, C. Weaver, and C. D. Marshall, *J. Am. Chem. Soc.*, **71**, 289 (1949).

[13] M. S. Kharasch and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941).

[14] A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 239 (1946).

[15] A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 28 (1938).

[16] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3596 (1953).

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[20] G. S. Landsberg, A. I. Shatenshteĭn, G. V. Peregudiv, E. A. Israilevich, and L. A. Novikova, *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **18**, 669 (1954); *Chem. Abstr.*, **50**, 7585h (1956).

[21] These experiments were conducted by Dr. R. H. Shudde of this laboratory.

[22] C. K. Ingold, C. G. Raisin, and C. L. Wilson, *J. Chem. Soc.*, 915 (1936).

[23] D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950).

Table I. Since the D_2O used in the preparations contained 0.3 atom % hydrogen, the theoretical maximum purity is given in the last column of Table I.

TABLE I

ISOTOPIC COMPOSITION OF DEUTERATED BIPHENYLS

Compound	Isotopic Composition	Theoretical Maximum Purity
Biphenyl-d_2	$C_{12}H_8D_2$- 97.4% $C_{12}H_9D$- 2.2% $C_{12}H_{10}$- 0.4%	99.4%
Biphenyl-d_4	$C_{12}H_6D_4$- 98.0% $C_{12}H_7D_3$- 1.8% $C_{12}H_8D_2$- 0.2%	98.8%
Biphenyl-d_6	$C_{12}H_4D_6$- 95.2% $C_{12}H_5D_5$- 4.6% $C_{12}H_6D_4$- 0.2%	98.2%
Biphenyl-d_{10}	$C_{12}D_{10}$- 95.1% $C_{12}HD_9$- 4.7% $C_{12}H_2D_8$- 0.2%	97.0%

EXPERIMENTAL[24]

4,4'-Dibromobiphenyl was prepared by bromination of biphenyl.[25]

n-Butyllithium reagent was prepared in ethyl ether[26] and used directly upon completion of the reaction. The reagent was analyzed only for the total base present.

Biphenyl-4,4'-d_2. To a mixture of 43.1 g. (0.138 mole) of 4,4'-dibromobiphenyl and 400 ml. of anhydrous ethyl ether in an inert atmosphere in a 3-neck flask was added rapidly, with stirring, 520 ml. of *n*-butyllithium reagent (containing 0.55 mole of total base). The mixture refluxed slowly for a short time. It was stirred 17 hr. at room temperature, refluxed for 1 hr., and treated, drop by drop, with approximately 20 ml. of 99.7% pure deuterium oxide. The ether phase was separated, washed twice with water, and dried over potassium carbonate. The solvent was evaporated and the residual material distilled twice *in vacuo*. The fraction collected (b.p. 120–121° at 11.5 mm., m.p. 64.5–66°) was sublimed *in vacuo*. A yield of 13.5 g. (63%) of white crystals m.p. 68–69°, was obtained.

Aniline-N,N,2,4,6-d_5 hydrobromide-d was prepared from aniline hydrobromide by the method used by Best and Wilson[14] to deuterate aniline hydrochloride. The progress of the deuteration was followed by converting samples to aniline and analyzing the infrared spectrum. The ratio of absorbance for C-D stretching to C-H stretching became constant during the last three equilibrations, indicating that maximum deuteration had been achieved. A sample of the final product was brominated to 2,4,6-tribromoaniline, and its infrared spectrum was examined; no C-D absorption was found, indicating that exchange takes place only in the *ortho-* and *para-* positions.

Bromobenzene-3,5-d_2. A mixture of 72.0 g. (0.400 mole) of aniline-*N*,*N*,2,4,6-d_5 hydrobromide-d and 120 ml. of dioxane was treated slowly with a solution of 44.8 g. (0.800 mole) of potassium hydroxide in 80 ml. of water. The mixture was cooled below 5° while a solution of 64 g. (0.40 mole) of bromine in 640 ml. of dioxane was added with stirring. The mixture was filtered, the filtrate was washed with 60 ml. of 40% (w/w) potassium hydroxide in water, and the solvent was distilled *in vacuo*. The dark, viscous residue was dissolved in anhydrous ethyl ether, and anhydrous hydrogen chloride was passed in until precipitate no longer formed. The precipitate was separated, washed with ethyl ether, and dried; it weighed 71.6 g. The crude hydrochloride in 50 ml. of water and 100 ml. of concentrated hydrochloric acid was diazotized with 24.7 g. of sodium nitrite in 60 ml. of water, the temperature being kept below 5°. The diazonium solution was treated with 530 ml. of cold 50% hypophosphorous acid (5.1 moles) and was kept at about 0° overnight. The lower organic phase was separated. The aqueous phase was extracted with ethyl ether, and the extract was combined with the organic phase, washed with sodium hydroxide solution and water, and dried over potassium carbonate. Distillation gave 21.8 g. (0.137 mole) of bromobenzene-3,5-d_2, a 34% yield.

Biphenyl-3,3',5,5'-d_4. The Grignard reagent prepared from 21.5 g. (0.135 mole) of bromobenzene-3,5-d_2, 4.1 g. (0.169 gram-atom) of magnesium, and 55 ml. of anhydrous ethyl ether, was added with stirring to a mixture of 1.6 g. (0.012 mole) of anhydrous cobaltous chloride, 16.3 g. (0.150 mole) of ethyl bromide, and 15 ml. of anhydrous ether at such a rate that the mixture refluxed. After the addition was completed, the reaction mixture was refluxed for another hour and then poured into ice and water. The mixture was treated with 20 ml. of acetic acid. The organic phase was separated, washed with sodium bicarbonate solution and water, and dried over potassium carbonate. The solvent was distilled, and the residue was sublimed *in vacuo*. The yield of 6.8 g. (0.043 mole) of biphenyl-3,3',5,5'-d_4, m.p. 68–69°, is 64%.

Bromobenzene-2,4,6-d_3. A mixture of 36.0 g. (0.2 mole) of aniline-*N*,*N*,2,4,6-d_5 hydrobromide-d and 48 ml. of 48% hydrobromic acid was treated with 13.8 g. of sodium nitrite in 25 ml. of water, the temperature being kept below 10°. The reaction mixture was added to a boiling mixture of 17.2 g. of cuprous bromide and 16 ml. of 48% hydrobromic acid at such a rate that the product steam distilled from the reaction mixture. The distillate was extracted with ethyl ether, and the extract was washed with dilute sulfuric acid, water, dilute sodium hydroxide solution, and water, and dried over potassium carbonate. Upon distillation, 20.2 g. (63%) of product (b.p. 155–156°) was obtained.

Biphenyl-2,2',4,4',6,6'-d_6 was prepared from bromobenzene-2,4,6-d_3 by the procedure used for biphenyl-3,3',5,5'-d_4.

Benzene-d_6 was prepared by shaking benzene several times with 51 mole % sulfuric acid-d_2 in 99.7% deuterium oxide until the hydrogen content was about 0.4 atom %. The product was analyzed by infrared spectrometry using standards analyzed by mass spectrometry.

Bromobenzene-d_5 was prepared by brominating benzene-d_6 by the method of Best and Wilson.[14]

Biphenyl-d_{10} was prepared from bromobenzene-d_5 by the procedure used for biphenyl-3,3',5,5'-d_4.

Gas chromatography. The various intermediates and the deuterated biphenyls were analyzed for chemical purity with a Perkin-Elmer model 154B Vapor Fractometer. Two columns, a two meter column of didecyl phthalate on Celite, and a two meter column of silicone oil on Celite, were used to analyze the biphenyls. The former column, on which biphenyl has a retention time of about 41 min. at 175°, was used to check for impurities more volatile than biphenyl, and the latter column, on which biphenyl has a retention time of about 8 min. at 150°, was used to check for impurities less volatile than biphenyl. The intermediates were analyzed on the first column. Under these conditions, biphenyl and the various deuterated biphenyls are not separated.

Infrared spectrometry. The infrared spectra were measured with a Perkin-Elmer model 21 double-beam recording infrared spectrophotometer. The strong absorption peaks found in the spectra of the deuterated biphenyls and biphenyl

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(24) Melting points and boiling points are uncorrected.

(25) R. E. Buckles and N. G. Wheeler, *Org. Syntheses*, **31**, 29 (1951).

(26) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 352 (1951).

TABLE II

INFRARED ABSORPTION PEAKS OF BIPHENYLS

Biphenyl	Biphenyl-d_2	Biphenyl-d_4	Biphenyl-d_6	Biphenyl-d_{10}
3.29 microns	3.29	3.26	3.28	4.41
6.27	4.41 (mod)[a]	4.42	4.43	7.44
6.75	5.22	5.46	5.44	7.60
6.98	6.29	6.32	7.03	
9.32	6.81	7.02	7.12	
9.58	7.16	7.22	7.27	
11.07	9.02	9.06	10.87	
	9.63	9.15		
		10.9–11.3 (band)		

[a] This absorption peak, caused by C-D stretching, is only moderately strong.

itself (measured in carbon tetrachloride solution, 200 mg. per ml. of solution) in the range 1.5–11.5 microns are given in Table II.

Mass spectrometry. The mass spectra of the deuterated biphenyls were determined with a modified Consolidated Electrodynamics Corporation model 21-620 mass spectrometer. The mass spectra of the compounds are discussed elsewhere.[27]

CANOGA PARK, CALIF.

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(27) J. M. Scarborough, J. G. Burr, and R. H. Shudde, to be published.

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

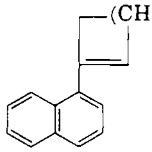
Syntheses and Ultraviolet Spectra of Eight Naphthylcycloalkenes[1-3]

L. H. KLEMM, B. T. HO, C. D. LIND, B. I. MACGOWAN,[4] AND E. Y. K. MAK[5]

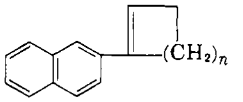
Received November 24, 1958

Syntheses of 1-(1- and 2-naphthyl)cycloheptenes and -cyclo-octenes and of 3-(1- and 2-naphthyl)cyclopentenes and -cyclohexenes are described. Correlation of ultraviolet spectra of these compounds with structure is made.

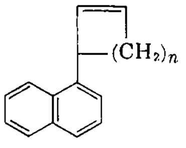
In previous papers[6-9] we reported syntheses and ultraviolet absorption spectra of a number of conjugated naphthylalkenes, including I–IV. The present paper concerns an extension of these studies to the higher homologs V–VIII and the unconjugated isomers IX–XII. Compounds V–VIII were prepared by dehydration of the carbinols resulting from interaction of the appropriate naphthyl-magnesium bromides and cycloalkanones, while IX–XII resulted from the same Grignard reagents acting on 3-bromocyclohexene and 3-chlorocyclopentene. That the double bond had not migrated into the conjugated position during the preparative process was indicated by the isolation of crystalline polynitroaromatic complexes of IX–XI which were different (as determined by melting point and mixture melting point) from the corresponding complexes of the conjugated isomers I–III and by the fact that the ultraviolet spectra of X and XII were significantly different from those of II and IV, respectively.



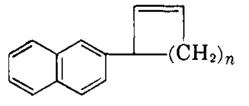
n = 2: I
n = 3: III
n = 4: V
n = 5: VII



II
IV
VI
VIII



n = 2: IX
n = 3: XI



X
XII

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(1) Presented, in part, at the Northwest Regional Meeting of the American Chemical Society, Portland, Ore., June 1958. Paper X in the series on Chemical Reactivities of Arylcycloalkenes. For paper IX see L. H. Klemm, D. Reed, and C. D. Lind, *J. Org. Chem.*, **22**, 739 (1957).

(2) Performed under the sponsorship of the Office of Ordnance Research, U. S. Army contract No. **DA-04-200-ORD-176.**

(3) Abstracted largely from the M.A. dissertation of B. T. Ho, University of Oregon, 1959, and the Ph.D. dissertation of C. D. Lind, University of Oregon, 1956.

(4) Research assistant, 1956.

(5) Research assistant, 1956–1957.

(6) L. H. Klemm and W. Hodes, *J. Am. Chem. Soc.*, **73**, 5181 (1951).

(7) L. H. Klemm and H. Ziffer, *J. Org. Chem.*, **20**, 182 (1955).

(8) L. H. Klemm, H. Ziffer, J. W. Sprague, and W. Hodes, *J. Org. Chem.*, **20**, 190 (1955).

(9) L. H. Klemm, J. W. Sprague, and E. Y. K. Mak, *J. Org. Chem.*, **22**, 161 (1957).