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]

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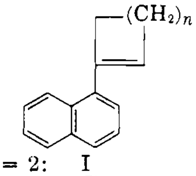
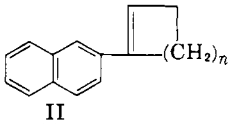
Syntheses of 1-(1- and 2-naphthyl)cycloheptenes and -cyclo-octenes and of 3-(1- and 2-naphthyl)cyclopentenes and -cyclohexenes are described. Correlation of ultraviolet spectra of these compounds with structure is made.

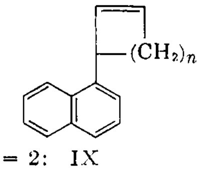
In previous papers[6-9] we reported syntheses and ultraviolet absorption spectra of a number of conjugated naphthylalkenes, including I–IV. The present paper concerns an extension of these studies to the higher homologs V–VIII and the unconjugated isomers IX–XII. Compounds V–VIII were prepared by dehydration 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.



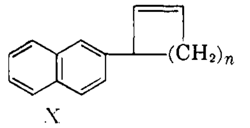
n = 2: I
n = 3: III
n = 4: V
n = 5: VII



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).

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA FOR EIGHT NAPHTHYLCYCLOALKENES[a]

V[b]		VI[c]		VII[d]		VIII[d]		IX[d]		X[d]		XI[b]		XII[d]	
λ_{max}, mμ	log ε	λ_{max}, mμ	log ε	λ_{max}, mμ	log ε	λ_{max}, mμ	log ε	λ_{max}, mμ	log ε	λ_{max}, mμ	log ε	λ_{max}, mμ	log ε	λ_{max}, mμ	log ε
225	4.78			224.5	4.79	(225)	4.70	224	4.87	226	5.04	226	4.94	227	5.13
		246	4.54			243–245	4.96								
								268	3.60	(270)	3.71	(263)	3.63	(268)	3.54
(273)	3.99	278	3.96	(273)	3.92	277	4.37	275	3.68	276	3.74	273	3.84	275–276	3.72
283	4.07	286	3.98	281–282	3.99	286	4.43	285	3.79	(284)	3.59	283	3.92	(284)	3.58
(294)	4.02	298	3.89	(291)	3.93	298	4.34	(290–293)	3.62			(292)	3.74		
								315	2.60	306[e]	2.67	315[f]	2.74	304[e]	2.66

[a] Determined on analytically pure samples by means of a Beckman DU spectrophotometer for V, VI, and IX–XII and a Beckman DK-2 spectrophotometer for VII and VIII. Parenthesized values of λ_{max} represent shoulders rather than true maxima. [b] Solvent, cyclohexane. [c] Solvent, 95% ethanol. [d] Solvent, isooctane. [e] Spectrum investigated only to 310 mμ; others, to 320 mμ. [f] This value is approximate only.

Pertinent data on the ultraviolet absorption maxima of V–XII are presented in Table I. As expected,[8] the spectra of IX and XI are virtually superimposable on the spectrum of 1-methylnaphthalene[10]; and those of X and XII, likewise on the spectrum of 2-methylnaphthalene.[10] The only clear difference between the spectrum of 1-methylnaphthalene and the nearly identical spectra of the 1-compounds I, III, V, and VII is the presence of the minor maximum at about 313 mμ in 1-methylnaphthalene. This close similarity is consistent with the suggestion[8] that electronic conjugation[11] is virtually absent in these structurally conjugated 1-compounds due to the presence of large angles of twist (between the planes of the naphthalene ring and the cycloalkenyl double bond) in the molecules. On the other hand the spectra of the 2-compounds II, IV, VI, and VIII differ markedly from the spectrum of 1-methylnaphthalene in the region of their major maxima (220–260 mμ). Of the spectra for this group, II exhibits the most fine structure, IV and VI are virtually identical, and VIII differs from IV principally only in having a shoulder at 225 mμ. Following our earlier interpretations[8] we then propose that VI and VIII should have θ'-distributions (sterically unrestricted angles of twist) similar to those of IV but with detectably increased prevalence (225 mμ shoulder) of molecules in the $90° - \beta$ to $90° + \beta$ spectral region for the cycloöctenyl compound VIII.

EXPERIMENTAL[12]

Titration of picrates. For those cases where neutral equivalents of picrates are reported these were determined on 0.2- to 0.4-g. samples dissolved in 125 ml. of 40% (by volume) acetone, using 0.1*N* sodium hydroxide and ethyl bis(2,4-dinitrophenyl)acetate as indicator.[13]

1-(2-Naphthyl)cycloheptene (VI). To the Grignard reagent prepared from 20 g. (0.097 mole) of 2-bromonaphthalene, 2.4 g. (0.099 g.-atom) of magnesium turnings, and 60 ml. of ether was added slowly, at room temperature, a solution of 11 g. (0.098 mole) of cycloheptanone[14] in 25 ml. of ether. The reaction mixture was stirred for 1 hr., hydrolyzed with cold aqueous ammonium chloride, and extracted with ether. The residue from evaporation of the dried (magnesium sulfate) ethereal extract was dehydrated by stirring with 30 ml. of anhydrous formic acid for 20 min. at room temperature and then for 1 hr. on a steam bath. Combined ethereal extracts of the diluted acidic mixture were washed with 10% aqueous sodium hydroxide and evaporated. The residue was steam distilled to remove naphthalene, collected in ether (dried), and fractionally distilled twice, yield 8 g. (37%) of almost colorless liquid, b.p. 140–145° (1 mm.). Treatment with an equimolar quantity of picric acid in absolute ethanol solution precipitated the picrate, recrystallized from methanol to constant m.p. 82–84°, obtained as orange needles.

Anal. Calcd. for $C_{17}H_{18} \cdot C_6H_3N_3O_7$: Neut. equiv. 451.4. Found: Neut. equiv. 457.

Chromatographic dissociation of the picrate *via* silicic acid–celite[7] and three fractional distillations of the effluent in an atmosphere of nitrogen produced purified VI, b.p. 146.5–147.5° (0.8 mm.), m.p. *ca.* 30°.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 92.09; H, 8.09.

1-(1-Naphthyl)cycloheptene (V). Repetition of the foregoing procedure but with 1-bromonaphthalene instead of its 2-isomer gave 19 g. (88%) of light yellow liquid, b.p. 139–144° (0.9 mm.), converted to the picrate, obtained as orange needles from methanol, m.p. 107–109°.

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(10) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, 1951.

(11) For clarity we have used the terms "conjugation" or "structural conjugation" in the classical sense of denoting alternate single and double bonds. The term "electronic conjugation" has been reserved for those structurally conjugated molecules which display special electronic properties due to such bond alternation.

(12) Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(13) Adapted from the method of the Staff of Hopkin and Williams Research Laboratory, *Organic Reagents for Organic Analysis*, Chemical Publishing Co., Brooklyn, 1950, pp. 112–13.

(14) H. J. Dauben, H. J. Ringold, R. H. Wade, D. L. Pearson, and A. G. Anderson, *Org. Syntheses*, **34**, 19 (1954).

Anal. Calcd. for $C_{17}H_{18}\cdot C_6H_3N_3O_7$: Neut. equiv. 451.4. Found: Neut. equiv. 459.

Chromatographic dissociation of the picrate *via* alumina-Celite[9] and two fractional distillations of the effluent gave purified V, b.p. 146–147° (1.0 mm.).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.57; H, 8.31.

1-(1-Naphthyl)cyclo-octene (VII). Following the general procedure for VI, but with 0.079-molar quantities of magnesium, 1-bromonaphthalene, and cyclo-octanone (10 g., Fluka), gave 4.5 g. (24%) of liquid, b.p. 141–148° (0.3 mm.), converted to the picrate, obtained as yellow prisms from absolute ethanol, m.p. 114–115° (not analytically pure). Purified VII boiled at 139–142° (0.3 mm.).

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.49; H, 8.73.

1-(2-Naphthyl)cyclo-octene (VIII). By the preceding method (but with 2-bromonaphthalene instead of its isomer) there was obtained 8.8 g. (47%) of crude liquid. After purification (picrate obtained as bright orange prisms from absolute ethanol, m.p. 79–110°) the product boiled at 148–152° (0.3 mm.).

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.22; H, 8.71.

3-(2-Naphthyl)cyclopentene (X). To the cold (−20°), stirred Grignard reagent prepared from 11 g. (0.45 g.-atom) of magnesium turnings, 93.2 g. (0.45 mole) of 2-bromonaphthalene, and 400 ml. of ether was added slowly (over 1–1.5 hr.) a freshly prepared, cold (Dry Ice bath temperature) solution of crude 3-chlorocyclopentene[15] (*ca.* 47 g.) in 150 ml. of ether. The mixture was allowed to warm to room temperature and then was added, with stirring, to a mixture of 30 g. of ammonium chloride, ice, and water. The ethereal layer was washed first with saturated aqueous sodium carbonate solution and then with water and evaporated. The residue was steam distilled. The ethereal extract of the nonvolatile organic residue was dried and distilled twice, yield 25.8 g. (30%) of liquid, b.p. 123–136° (1.2 mm.). One recrystallization from absolute ethanol of the picrate, which was formed in the same solvent, gave 26.5 g. (14% over-all) of orange needles, m.p. 86–87.5°, mixture m.p. with an authentic sample of II picrate[6] (m.p. 103–104°) 81–96°.

Anal. Calcd. for $C_{21}H_{17}N_3O_7$: C, 59.57; H, 4.05; N, 9.93. Found: C, 59.26, H, 4.13; N, 10.08.

Chromatographic dissociation[9] of the picrate gave purified X, b.p. 110.5–111.5° (0.6 mm.).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.48; H, 7.29.

3-(1-Naphthyl)cyclopentene (IX). Using the same procedure as for X, except with 1-bromonaphthalene rather than 2-bromonaphthalene and without steam distillation, there was obtained 25.7 g. (30%) of pale yellow liquid, b.p. 96–102° (0.15 mm.). It was stored as its 1,3,5-trinitrobenzene derivative, m.p. 75–110° (not analytically pure). The recovered[9] purified IX was colorless, b.p. 106–107° (0.15 mm.).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.47; H, 7.38.

In a small-scale preliminary run (which could not be reproduced) the trinitrobenzene derivative of IX was obtained as yellow needles, m.p. 72.5–74.5°, after one recrystallization from methanol, mixture m.p. with the correspondingly formed trinitrobenzene derivative of I (m.p. 79–80°) 70–75.5°.

Anal. Calcd. for $C_{21}H_{17}N_3O_6$: C, 61.91; H, 4.21; N, 10.32. Found: C, 62.27; H, 4.26; N, 10.23.

3-(1-Naphthyl)cyclohexene (XI). This preparation was conducted in a manner similar to that used for IX. From 68.7 g. (0.33 mole) of 1-bromonaphthalene, 8.1 g. (0.33 g.-atom) of magnesium shavings, and 53.4 g. (0.33 mole) of freshly prepared, distilled 3-bromocyclohexene[16] (used instead of 3-chlorocylopentene) was obtained 39.7 g. (58%) of pale yellow liquid, b.p. 144–157° (1.3 mm.). The picrate, formed in glacial acetic acid, was recrystallized thrice from the same solvent to give orange prisms, m.p. 99.5–100.5°, depressed on admixture with III picrate[6] of m.p. 126.5–127°.

Anal. Calcd. for $C_{16}H_{16}\cdot C_6H_3N_3O_7$: Neut. equiv. 437.3. Found: Neut. equiv. 443.

The purified hydrocarbon (colorless) boiled at 140–141° (1.6 mm.).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.38; H, 7.64.

3-(2-Naphthyl)cyclohexene (XII). This compound, prepared in a manner analogous to that used for XI, was obtained as a pale yellow liquid, b.p. 137–148° (1 mm.), yield 21.1 g. (31%), converted to a yellow picrate, m.p. 81–107°, after two recrystallizations from absolute ethanol.

Anal. Calcd. for $C_{16}H_{16}\cdot C_6H_3N_3O_7$: Neut. equiv. 437.3. Found: Neut. equiv. 427.

The purified hydrocarbon (colorless) boiled at 119.5–121.5° (1 mm.).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.43; H, 7.82.

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[15] R. B. Moffett, *Org. Syntheses*, **32**, 41 (1952).

[16] K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 80 (1942).