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Aromatic and Pseudoaromatic Non-benzenoid Systems. III. The Synthesis of Some Ten π-Electron Systems[1-3]

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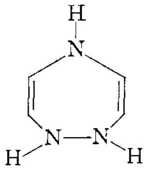
The synthesis of 2,3,6,7-dibenzo-1-methyl-1,4,5-triazacyclohepta-2,6-diene (IIb) and the 1-oxa, 1-thia, and 1-methylene analogs is reported. The first three compounds possess a ten π-electron system in the center ring, while the latter does not.

In 1931, Hückel published[5] the results of his quantum mechanical calculations on the conjugated cyclic polyenes. The general ideas of his molecular orbital method have been extensively elaborated and refined, and the method has been applied quite generally to a variety of systems.[6] The success of the method in its simplest form in predicting approximately various properties of the ground state for a wide variety of systems is now well known.

Hückel's rule that $(4n + 2)$ π-electrons yield stable systems in monocyclic cases has been proved to be a helpful guide to the stability of compounds which come within the scope of the simple theory. Various resonance stabilized compounds containing two or six π-electrons are known. The only ten π-electron system which appears to be known is the one formed by the addition of two electrons to cyclooctatetraene.[7] It was recently shown that this dianion is planar and aromatic.[8] Attempts to prepare other ten π-electron systems have met with no success.[9,10]

One of the difficulties in trying to devise a 10 π-electron system is to fit the large number of atoms involved together in some manner so they will not interfere sterically. Cyclodecapentaene has apparently never been prepared,[9] although its synthesis was claimed. Were it to be prepared it is expected to have its potential aromaticity reduced considerably because of the non-planarity of the system which will no doubt result from the steric interaction of the transannular hydrogens.[11] Blood and Noller attempted to avoid this undesirable steric effect by substituting nitrogen atoms for carbon atoms at the appropriate positions.[10] Their synthesis was not successful, but even if it had been it seems unlikely that the desired planarity would have been attained, since there is evidence that a lone pair of electrons on nitrogen is "larger" than the corresponding protonated species.[12]

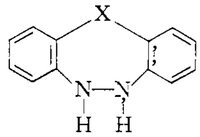


I

The system I pretty well avoids this steric problem, and numerical calculations by the simple molecular orbital method indicate a substantial resonance energy for the compound. The present paper describes the synthesis and properties of several similar compounds containing electronic systems as typified by I. A later paper[13] will discuss the theoretical studies which have been carried out on the compounds.

Discussion

Rather than to attempt the synthesis of I immediately, it appeared to be experimentally more feasible to prepare some benzenoid derivatives of I, such as the structures represented by IIa–IId.[14]



IIa = N–H
b = N–CH_3
c = O
d = S
e = CH_2

The synthesis of a hydroxyl derivative of IIc was first undertaken as outlined on the flowsheet.

Nucleophilic substitution by *m*-methoxyphenoxide ion on *o*-chloronitrobenzene gave the ether III. Simultaneous reduction of the nitro group and demethylation with hydriodic acid[15] yielded the aminophenol IV. The latter was diazotized and cyclized by treatment of the diazonium salt with base. The resulting azo compound V also contained an interesting potentially aromatic 8 π-electron system. Compound V could be reduced with hydrogen using a platinum catalyst in alcohol.

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(1) A preliminary description of this work has appeared in *Tetrahedron Letters*, **No. 9**, 10 (1959).

(2) Paper II, N. L. Allinger and G. A. Youngdale, *J. Org. Chem.*, **25**, 1509 (1960).

(3) Supported in part by a research grant from the National Science Foundation.

(4) National Science Foundation Predoctoral Fellow, 1956–1959.

(5) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(6) (a) C. A. Coulson, "Valence," Oxford Press, New York, N. Y., 1952, p. 238; (b) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955; (c) R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry, Methods and Applications," Interscience Publishers, Inc., New York, N. Y., 1959, p. 52.

(7) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

(8) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).

(9) (a) L. E. Craig and C. E. Larrabee, *ibid.*, **73**, 1191 (1951); (b) A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1195 (1951).

(10) A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 873 (1957).

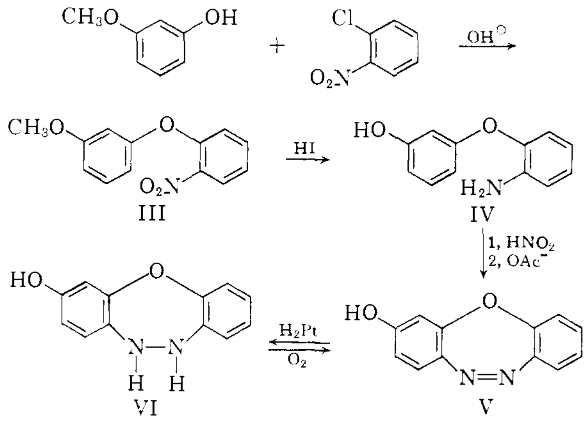
(11) K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).

(12) M. Aroney and R. J. W. LeFevre, *J. Chem. Soc.*, 3002 (1958).

(13) N. L. Allinger and R. B. Hermann, to be published.

(14) Compounds containing this basic ring system, particularly IIa, have been reported (P. C. Guha and M. K. De, *Quart. J. Indian Chem. Soc.*, **3**, 41 (1926)) in the literature. They were characterized solely by nitrogen analysis, and are reported to have melting points above 300° and to be insoluble in organic solvents except pyridine. The colors of these compounds, when reported, are given as red or black. In the course of the present work, two of these preparations were repeated, but only intractable products were formed. In view of the physical properties of these compounds as discussed below, the earlier structure assignments are regarded as overly optimistic.

(15) N. M. Cullinane, H. G. Davey and H. J. H. Padfield, *J. Chem. Soc.*, 716 (1934).

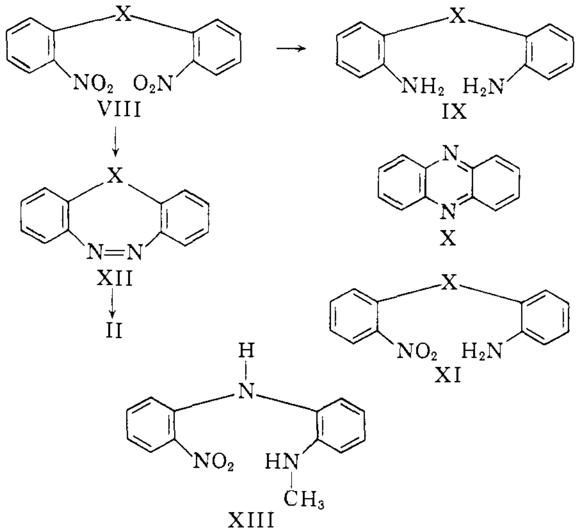


One mole of hydrogen was taken up, and the reaction stopped. The solution was essentially colorless and it seems likely that VI was in solution at this point. As soon as air was let into the system the solution began turning yellow. As the workup of the reaction mixture was carried out the solution became darker, and finally the crystalline product isolated proved to be V. It is presumed that VI was oxidized by oxygen in the air during the isolation procedure.

The reduction of V with other reducing agents was also investigated. With lithium aluminum hydride the starting material was again recovered, while tin and hydrochloric acid yielded no identifiable product. The reduction of V with zinc dust and ammonium chloride led to the corresponding diamine (VII).

An attempt was made to ring close the diazonium salt obtained from *o*-aminodiphenyl ether, but under mild conditions no reaction took place, while more strenuous conditions led only to a resinous product. The possibility of utilizing the diazonium salt for the ring closure was not further investigated, although the method did show some promise.

The synthetic scheme that ultimately proved successful for the preparation of the desired structures (IIa–d) began with the appropriate dinitro compound (VIII a-d). There are a number of reagents which have been used to reduce nitro compounds to azo or hydrazo compounds, and the action of several of these reagents was investigated.



The reduction of VIIIa with zinc and ammonium chloride[16] proceeded further than was desired, and reduced the dinitro compound all the way to the diamine IXa. With zinc and alkali,[17] the reaction yielded the same diamine together with phenazine (X). Sodium sulfide[18] reduced the nitro compound VIII to a mixture from which were isolated IX, X and the nitroamine XI. The most promising reducing agent tried was lithium aluminum hydride, which oridinarily reduces nitro compounds to azo compounds.[19] From this reduction there was isolated a crude yield (6%) of what appeared to be the azo compound XIIa. It was thought likely that the active hydrogen on the nitrogen in VIIIa might be interfering with the lithium aluminum hydride reduction, so the compound was methylated to give VIIIb, and the reduction of that compound was tried. In this case a 21% yield of pure azo compound XIIb was isolated.

From the sodium sulfide reduction of VIIIb there were obtained two compounds. One of these was the expected nitroamine XIb. The other compound was found to have structure XIII. The latter is probably formed from the former by way of a Smiles type rearrangement,[20] that is a nucleophilic displacement of $-NHCH_3$ by $-NH_2$ at a position *ortho* to a nitro group.

Several potential methods for reducing XIIb to IIb were tried. Catalytic hydrogenation of XIIb in the presence of Adams catalyst gave the diamine IXb, two moles of hydrogen being taken up. When the reaction was interrupted after one mole of hydrogen had been taken up, the product was found to be a mixture of the diamine IXb and the starting material XIIb. Lithium aluminum hydride[21] with a prolonged reaction time also reduced the azo compound to the diamine. No crystalline product was isolable from the reaction[22] of ethyl Grignard with XIIb, followed by hydrolysis.

The reduction of the azo compound XIIb to the hydrazo compound IIb was accomplished in 91% yield with hydrazine and Raney nickel.[23] The structure of the hydrazo compound was indicated by the N–H stretching bands at 3.0 and 3.1 μ in the infrared, and by elemental analysis and molecular weight. It could be reduced to the diamine IXb, and it could be oxidized to the azo compound XIIb with mercuric oxide in a yield of 95%. The compound was not very stable in air and darkened after a few days. The ultraviolet spectrum of the decomposition product indicated that it was largely the azo compound XIIb.

The syntheses of the analogous oxygen (IIc) and sulfur (IId) hydrazo compounds were carried out by

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(16) H. Duval, *Bull. soc. chim. France*, [4] **7**, 527 (1910).

(17) H. E. Bigelow and D. B. Robinson, "Organic Syntheses," Coll. Vol. III, J. Wiley and Sons, Inc., New York, N. Y., 1955, p. 103.

(18) F. E. King and T. J. King, *J. Chem. Soc.*, 824 (1945).

(19) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948).

(20) W. J. Evans and S. Smiles, *J. Chem. Soc.*, 181 (1935).

(21) For the reduction of azobenzene to hydrazobenzene in 90% yield, see F. Bohlmann, *Ber.*, **85**, 390 (1952).

(22) H. Gilman and R. M. Pickens, *J. Am. Chem. Soc.*, **47**, 2406 (1925).

(23) S. Hornsby and W. L. Peacock, *Chemistry & Industry*, 858 (1958).

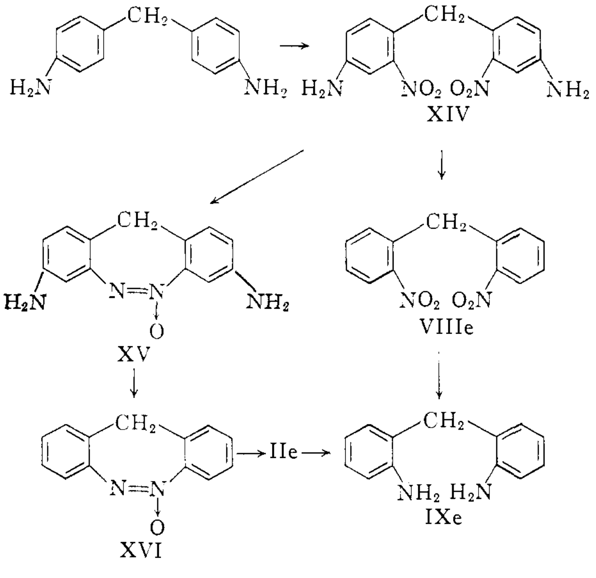
adaptations of the same general reaction sequence, and the structures were established as previously indicated. These hydrazo compounds all showed a close similarity in their infrared and ultraviolet spectra. The oxygen compound IIc appeared to be somewhat more stable toward air than its nitrogen analog, and the sulfur compound IId was stable in air indefinitely. The stability order is reminiscent of the related heterocyclic molecules, where thiophene is more stable and less reactive in most respects than furan and pyrrole.

To establish experimentally whether or not a compound possesses a substantial resonance energy, heat of combustion measurements are most useful. Such measurements require larger amounts of material than are easily available in the present case.

One method of detecting a considerable resonance energy in the hydrazo compounds II would be from X-ray crystallography.[24] The bond angles will be normal if the center ring is in the form of a boat,[25] while a large resonance energy would be expected to cause the system to flatten out.

Many other methods might be applicable to the determination of the presence or absence of resonance in the center ring, but these methods could be applied with greater certainty if a suitable model compound were available for comparison purposes.

An ideal model compound would appear to be IIe, which rather closely approximates the gross structure of the other hydrazo compounds, but lacks the essential feature of a cyclic conjugated structure. The synthesis of this compound is outlined. Compounds XIV and XV have been previously prepared and there seems to be no reason to question their structures.



Compound VIIIe is described in the literature,[26] m.p. 159°, and was obtained from XIV by allowing the latter to react with ethyl nitrite and ethanol. In the present work VIIIe was obtained from XIV by reaction in turn with nitrous acid, followed by hypophosphorous acid. The material obtained from the latter reaction had m.p. 85°, and was accompanied by only a 2% yield of material, m.p. 156°, similar to that described earlier.[26] The structure of the latter compound was not established, but the presence in the infrared spectrum of a strong doublet at 2.78 and 3.0 μ suggests that it is a phenol. Certainly it does not have structure VIIIe. That the compound m.p. 85° was in fact the dinitro compound VIIIe is shown by the fact that it was catalytically reduced to the diamine IXe. This amine was also obtained from XV *via* the azoxy compound, XVI and IIe. The molecular weight of IIe shows it to be monomeric and, together with the analytical data on the various compounds, leads to the structures indicated as uniquely compatible with the data.

The synthesis of IIe has recently been carried out independently by Theilacker and Korndörfer.[27] Where their work and ours overlap we are in good agreement.

To determine whether or not the center ring of II (a-d) was really an aromatic system, a number of methods were considered. The first of these, the ultraviolet spectrum, was used only in a qualitative way, since the actual complete calculation of the spectrum of II would be a very sizable undertaking. Since in IIe the methylene group fairly well interrupts the conjugation of the center ring, it might be guessed that compounds IIa-d, if aromatic, would have ultraviolet spectra similar to one another but different from IIe. If IIa-d had very little aromaticity in the center ring, all of the spectra would probably be similar. The latter situation is what was found (Table I). While transitions are more allowed in IIa-d than in IIe, the observable separation of energy levels does not show any dramatic contrast in IIe as compared to the others.

TABLE I

II	X =	Ultraviolet spectrum λ (log ϵ)		pK_a	N.m.r.
b	NMe	231(4.4)	302(3.9)	..	3.74
c	O	......	281(3.5)	..	..
d	S	239(4.4)	295(3.8)	2.81	4.17
e	CH_2	247(3.8)	289(3.3)	3.10	3.82

Another way in which aromaticity might be detected is by pK measurements. The hydrazine nitrogens of II are the most basic atoms in the system. When one is protonated, the cyclic conjugation is interrupted. Therefore if IIb-d were aromatic they should be more reluctant to protonate than IIe, and the latter should have a higher pK_a. Such a trend is found between IId and IIe, but the effect is not large enough to ascribe to any particular cause. Compound IIb was also titrated in an attempt to determine its pK_a, but even very mild acid treatment brought about an irreversible color change and made the pK_a determination impossible. The deep red color observed upon acid treatment suggested that the compound disproportionated to give the corresponding azo compound and the diamine, since hydrazo compounds typically undergo such a reaction.[28]

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(24) Such crystallographic studies have been undertaken by Professor K. N. Trueblood, University of California at Los Angeles.

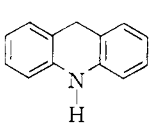
(25) The possiblity of a chair form need not be considered; see N. L. Allinger and G. Youngdale, *J. Org. Chem.*, **24**, 2059 (1959).

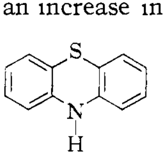
(26) K. Schnitzspahn, *J. prakt. Chem.*, [2] **65**, 315 (1902).

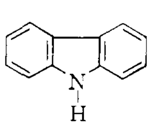
(27) W. Theilacker and O. Korndörfer, *Tetrahedron Letters*, No. **18**, 5 (1959).

Good evidence for or against aromaticity can often be obtained from n.m.r. data. A proton attached to an aromatic ring will in general resonate at a lower applied field by about 1.5 τ units than will a vinyl proton in an otherwise similar environment. This shift results from the magnetic field set up by the electron current which results from the application of a primary magnetic field to the cyclic system.[29] As models, the n.m.r. spectra of carbazole (XVII) and 9,10-dihydroacridine (XVIII) were compared. The protons on nitrogen were examined, and while the latter showed absorption at 2.02 γ, the corresponding absorption of the former was at 0.48 γ. The n.m.r. spectra of IIe and IIb were also compared. The hydrazo protons absorbed near 3.7 τ in both molecules (Table I), the observed shift with IIb being only about 5% that seen in carbazole.

When the n.m.r. spectrum of IId was examined, however, the situation was somewhat different. The n.m.r. spectrum of XVIII showed absorption at 2.02 τ, while XIX showed the corresponding absorption at 2.90 τ, an increase in the value of τ of 0.88 upon replacing the carbon by sulfur. Since IIe showed absorption at 3.82 τ, if there was no special resonance in IId, absorption of the latter would be predicted as coming at 3.82 + 0.88 = 4.70 τ. Actually the compound absorbs at 4.17 τ, and shows an aromatic shift of about one-third that of benzene.


XVIII


XIX


XVII

The experimental evidence therefore seems to indicate the absence of any special aromaticity in IIa-c relative to IIe, suggesting that this type of 10 π-electron system does not have the character that might have been expected. Compound IId, on the other hand, can accept electrons by contributing two electrons to the π-system together also with two orbitals.[30] The theory will be fully developed in a subsequent paper.[13]

Experimental

2-Nitro-3′-methoxydiphenyl Ether (III).—Potassium hydroxide, 6.7 g., was heated with 2 ml. of water until a clear melt was obtained. At the point of incipient crystallization 19 g. of *m*-methoxyphenol[31] was added rapidly with vigorous stirring, followed by 14 g. of *o*-chloronitrobenzene. The mixture was kept at 185–195° for 2 hours, and was then poured into ice-water containing sodium hydroxide. The solid which separated was collected and washed with water. The aqueous solution was extracted with ether. The ether solution and the solid were combined, washed with dilute aqueous alkali, then water. The ether was evaporated and the product was distilled, b.p. 197–199° (4 mm.). The distillate was crystallized from alcohol, and gave yellow needles, m.p. 56–57°, yield 72%.

Anal. Calcd. for $C_{13}H_{11}NO_4$: C, 63.64; H, 4.52. Found: C, 63.36; H, 4.67.

2-Amino-3′-hydroxydiphenyl Ether (IV).—Four grams of the nitro ether III and 80 ml. of 47% hydriodic acid were mixed and heated under reflux overnight. The resulting deep red solution was poured into dilute aqueous sodium hydroxide, and sulfur dioxide was passed in until the solution became yellow. Excess concentrated hydrochloric acid was added and the solution was neutralized with aqueous ammonia. The crystalline precipitate was collected, washed with water and recrystallized from aqueous alcohol (Norite). The product, obtained in the form of slightly colored needles, weighed 2.3 g. (71%), m.p. 132–133°.

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.64; H, 5.51. Found: C, 71.45; H, 5.37.

2,2′-Azo-5-hydroxydiphenyl Ether (V).—The amine IV, 16.1 g., was dissolved in a solution prepared from 26 ml. of concd. hydrochloric acid and 300 ml. of water. The solution was cooled to 2°, and a solution of 5.8 g. of sodium nitrite in 40 ml. of water was added dropwise. After the diazotization was complete, the solution was filtered leaving behind a small quantity of black tarry material. The solution of diazonium salt was poured with stirring into a beaker containing 70 g. of crystalline sodium acetate. A red solid precipitated which was collected and washed well with water. Recrystallization of this material from acetic acid–water yielded V as red needles, m.p. 216° dec., wt. 13 g. (77%). The ultraviolet spectrum showed λ_{max} 340 mμ, ε 7,150.

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.91; H, 3.80; mol. wt., 212. Found: C, 67.94; H, 3.88; mol. wt. (Rast), 212.

Catalytic Reduction of 2,2′-Azo-5-hydroxydiphenyl Ether (V).—A sample of the azo compound V was reduced with hydrogen in absolute ethanol in the presence of prereduced platinum oxide. The uptake of hydrogen ceased after 35 minutes and was equal to one molar equivalent. The solution was essentially colorless at this point. The solution was filtered and one-half the alcohol was removed under reduced pressure. The remaining solution, now light red in color, was diluted with water and extracted with ether. The ethereal solution was concentrated and diluted with benzene. The remainder of the ether was removed, and the flask was stoppered and allowed to stand overnight. The red solid was collected and was identified as V, m.p. 210° dec.

2,2′-Diamino-5-hydroxydiphenyl Ether.—A mixture of 1 g. of the azo compound V, 1 g. of zinc dust and 1 g. of ammonium chloride in 50 ml. of 80% ethanol was heated to boiling. Another gram of zinc dust was added, and heating was continued until the solution became colorless. The resulting solution was filtered, diluted with water and extracted with ether. The dried ether solution was concentrated and diluted with benzene. Upon cooling, a solid separated and was recrystallized from benzene to yield 0.1 g. (10%) of the diamine as a nearly colorless solid which darkened on exposure to air, m.p. 155–155.5°.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.60. Found: C, 66.97; H, 5.59.

Attempted Preparation of IIc *via* Diazonium Coupling.—*o*-Nitrophenylphenyl ether was prepared from *o*-chloronitrobenzene and potassium phenoxide.[32] Reduction of the nitro compound to the corresponding amine was carried out with zinc dust and calcium chloride.[33] The diazotization was carried out as described for the preparation of V, and the solution was poured onto sodium acetate. No reaction was observed. Upon warming the solution a brown tar separated. This material could not be crystallized.

Reduction of 2,2′-Dinitrodiphenylamine (VIIIa).—The dinitro-compound was obtained by the method of Eckert and Steiner[34]; m.p. 168–169°, reported m.p. 169°.

Method A. Reduction with Zinc and Alkali.—To a stirred mixture of 4.5 g. of VIII and 8 ml. of 12 *N* sodium hydroxide in 43 ml. of alcohol was added 14 g. of zinc dust in 1-g. portions at intervals of several minutes. The mixture was kept at about 90° for 2 hours, several ml. of saturated sodium bisulfite solution was added, and the resulting solution was filtered (Celite). The yellow crystalline material on the filter pad was taken up in ether. Evaporation of the ether yielded phenazine (X) as a yellow-brown crystalline solid, m.p. 170.5–171°. A mixture melting point with authentic phenazine showed no depression.

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[28] J. Stieglitz and G. O. Curme, *Ber.*, **46**, 911 (1913).

[29] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 180.

[30] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

[31] H. Brederek, I. Henning and W. Rau, *Ber.*, **86**, 1085 (1953).

[32] R. Q. Brewster and T. Groening, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 445.

[33] C. M. Suter, *J. Am. Chem. Soc.*, **51**, 2581 (1929).

[34] A. Eckert and K. Steiner, *Monatsh.*, **35**, 1153 (1914).

The filtrate was diluted with water, and the crystals which separated were recrystallized from ligroin to yield 2,2′-diaminodiphenylamine (IX) as purple prisms, m.p. 100–101° (literature[35] m.p. 101°).

Method B. Reduction with Zinc and Ammonium Chloride.—A mixture of 1 g. of 2,2′-dinitrodiphenylamine (VIIIa), 4 g. of *N* ammonium chloride and 2 g. of water in 20 ml. of alcohol was heated to boiling and 3 g. of zinc dust was added. When the solution was pale yellow it was filtered, and a rapid stream of air was passed through the filtrate for 10 minutes. Upon standing, the solution deposited crystals which were recrystallized from ligroin to yield the diamine IXa as purple prisms, m.p. 100–101° (literature[35] m.p. 101°).

Method C. Reduction with Sodium Sulfide.—A mixture of the dinitro compound VIIIa, 5 g., and sodium sulfide monohydrate, 18 g., in 100 ml. of 80% alcohol was heated under reflux for 1 hr., then poured into water. The resulting mixture was extracted with ether, and the ether solution was washed and dried. Evaporation of the ether yielded a red oil which was dissolved in 20 ml. of benzene. The solution was poured into a column containing 150 g. of activated alumina. Elution of the column with 2:1 hexane–ether gave a yellow solid. Further elution with 1:1 hexane–ether gave a red-orange solid, and with 1:1 ether–methanol gave a purple solid. The yellow solid was crystallized from aqueous alcohol and gave 0.09 g. of phenazine (X) as yellow needles, m.p. 166–168° (literature[35] m.p. 172°). The purple solid was crystallized from ether–hexane and gave 1.2 g. of 2,2′-diaminodiphenylamine (IXa), purple prisms, m.p. 100.5–101.5° (literature[35] m.p. 101°). The red-orange solid was recrystallized from ether–hexane, and gave 0.72 g. of 2-amino-2′-nitrodiphenylamine (XIa) as orange needles, m.p. 106–107° (literature[36] m.p. 103°). The infrared spectrum showed bands at 2.85 and 2.95 μ. The ultraviolet spectrum showed λ_{max} 232 mμ, ε 31,900; λ_{max} 280 mμ, ε 10,000; λ_{max} 418 mμ, ε 6,900.

Anal. Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.34; O, 13.96. Found: C, 62.71; H, 4.94; N, 18.16; O, 13.82.

Method D. Reduction with Lithium Aluminum Hydride.—Two grams of the dinitro compound VIIIa in 50 ml. of dry tetrahydrofuran was added during 30 minutes to a stirred suspension of lithium aluminum hydride, 1 g., in 50 ml. of dry tetrahydrofuran. The resulting mixture was then heated under reflux for 4 hours. The cooled mixture was treated carefully first with ethanol then with several ml. of water. The solids were removed by filtration and washed with ether. The filtrate and washings were combined and dried and the solvent was evaporated. The residual red oil was taken up in 20 ml. of benzene and adsorbed on a column of 100 g. of activated alumina. The column was eluted with hexane containing increasing amounts of ether. A solid was obtained from the 3:7 hexane–ether fractions. Recrystallization of the material from these combined fractions gave 62 mg. of red needles, m.p. 166–168°, which was thought to be the azo compound XIIa. The solid could not be recrystallized to constant melting point, and was not obtained pure.

Reduction of N-Methyl-2,2′-dinitrodiphenylamine (VIIIb).—The required compound VIIIb was prepared by the method of Hey and Mulley; m.p. 147–147.5° (reported[37] m.p. 147–148.5°).

Method E. Reduction with Zinc Dust and Calcium Chloride.—Nitro compound VIIIb, 2.1 g., together with 1.6 g. of calcium chloride and 6.4 g. of zinc dust in 50 ml. of 80% ethanol was heated on the steam-bath until the mixture was nearly colorless. The solution was filtered and diluted with water. The black solid which separated was collected and twice crystallized from ligroin (Norite). The product proved to be diamine IXb which was obtained as nearly colorless crystals, m.p. 127.5–128.5°, wt. 0.16 g. (10%).

Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09. Found: C, 73.16; H, 7.03.

Method C.—Reduction of 4 g. of VIIIb with sodium sulfide was carried out as described for the reduction of VIIIa. Chromatography of the crude reaction product on alumina gave an orange solid (eluted with hexane–ether 19:1) and red crystals (eluted with 9:1 hexane–ether). The orange solid was recrystallized from ether–hexane and gave 0.64 g. of 2-methylamino-2′-nitrodiphenylamine (XIII) as orange needles, m.p. 99.5–100.5° (literature[43] m.p. 99–100°). The red crystals were recrystallized from ether–hexane, and gave 0.13 g. of 2-amino-2′-nitro-N-methyldiphenylamine (XIb) as red prisms, m.p. 118–120° (literature[43] m.p. 118–119°).

Method D.—Lithium aluminum hydride reduction of 6 g. of VIIIb (as described for the reduction of VIIIa) gave 0.97 g. (21%) of pure azo compound XIIb as red needles, m.p. 140–140.5°. The ultraviolet spectrum showed λ_{max} 258 mμ, ε 30,500; λ_{max} 311 mμ, ε 7,200; λ_{max} 420 mμ, ε 1.140.

Anal. Calcd. for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.53; H, 5.59; N, 20.01.

Reduction of 2,3,6,7-Dibenzo-1-methyl-1,4,5-triazacyclohepta-2,4,6-triene (XIIb). Method F. Catalytic Reduction.—Azo compound XIIb, 0.2 g. in absolute ethanol, was reduced with hydrogen at atmospheric pressure in the presence of prereduced platinum. The reaction ceased after 35 minutes, when 2 molar equivalents had been taken up. No break in the rate of hydrogen uptake was noted. The solution was filtered and the solvent was evaporated under reduced pressure. The residue was crystallized from ether–hexane and gave 0.08 g. (39%) of diamine IXb as purple plates, m.p. 125–127°. The mixture melting point with an authentic sample was undepressed.

Method G. Lithium Aluminum Hydride Reduction.—A mixture containing 0.5 g. of lithium aluminum hydride and 0.5 g. of XIIb in 100 ml. of ether was heated under reflux for 2 days. The cooled reaction complex was then decomposed by the careful addition of saturated ammonium chloride solution. The ether layer was filtered, washed and dried, and diluted with hexane. The solution was further concentrated, and upon cooling the diamine IXb crystallized in nearly colorless plates, wt. 0.38 g. (74%), m.p. 129–130°. The mixture melting point with authentic IXb was undepressed.

Method H. Grignard Reduction.—The reduction of XIIb with ethyl Grignard was attempted using the method of Gilman and Pickens.[22] A resinous product was obtained which was chromatographed on alumina, but yielded no crystalline product.

Method I. Hydrazine Reduction.—A mixture of 0.5 g. of azo compound XIIb and 1 ml. of 95% hydrazine was dissolved in 30 ml. of warm ether. Raney nickel, 0.1 g., which had been aged for several months, was added, and the mixture was warmed sufficiently to maintain a vigorous evolution of nitrogen. After 3 hours an additional 0.1 g. of catalyst was added and the nearly colorless solution was heated under reflux for 15 minutes.

The catalyst was removed by filtration, and the bulk of the ether was evaporated. The solution was diluted with hexane and further concentrated. Upon cooling the solution in ice, the product crystallized as colorless needles, m.p. 93.5–95°, wt. 0.46 g. (91%). An analytical sample was recrystallized. m.p. 96.5–97.5° (vac.). The infrared spectrum showed peaks at 3.0 and 3.1 μ. The ultraviolet spectrum showed maxima at 231 and 302 mμ, with ε 24,300 and 8,230.

Anal. Calcd. for $C_{13}H_{13}N_3$: C, 73.91; H, 6.20; N, 19.89; mol. wt., 211. Found: C, 73.91; H, 6.18; N, 19.93; mol. wt., 219 (Rast),

The compound was found to discolor after several hours exposure to the air. After several days the compound was dark red-brown. The ultraviolet spectrum of this material indicated that it had been largely oxidized by the air to the azo compound XIIb.

Oxidation of IIb to XIIb.—A mixture of 0.5 g. of mercuric oxide and 0.25 g. of the hydrazo compound IIb in 20 ml. of ether was heated under reflux overnight. The solution was filtered, concentrated, diluted with hexane, concentrated again, and cooled. The azo compound XIIb crystallized as orange needles, m.p. 140–141.5°. A mixture melting point with authentic XIIb showed no depression.

Reduction of IIb to IXb.—The hydrazo compound, 0.4 g., was reduced with platinum and hydrogen at atmospheric pressure in tetrahydrofuran. One equivalent of hydrogen was taken up after several hours. The solution was filtered and the solvent was removed under reduced pressure. The residual oil solidified, was crystallized from ether–hexane and yielded purple plates, 0.30 g. (75%), m.p. 126–128°. The mixture melting point with authentic IXb was undepressed.

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(35) M. L. Tomlinson, *J. Chem. Soc.*, 158 (1939).

(36) F. Kehrmann and G. Steiner, *Ber.*, **34**, 3089 (1901).

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Reduction of 2,2′-Dinitrodiphenyl Ether (VIIIc).—The dinitro compound was obtained by a modification of a known procedure.[15] The yield was increased from 6 to 23%. The product was obtained as yellow-brown plates, m.p. 113.5–115° (reported[15] m.p. 116°).

Method C.—Reduction of 7.8 g. of the nitro compound VIIIc with sodium sulfide was carried out as described for the reduction of VIIIa except that the reflux period was extended to 3 hours. After diluting the solution with water the alcohol was removed under reduced pressure. The residue was continuously extracted with ether overnight, and the dried ether solution was poured onto a column of 250 g. of activated neutral alumina. The column was eluted with ether then with 1:1 ether–methanol. The solid obtained from the ether fractions was crystallized from ligroin and gave **2-hydroxy-2′-nitrodiphenylamine**, m.p. 140–142°, yield 0.42 g. (6%). For analysis a sample was twice recrystallized, red plates, m.p. 146–146.5°. The compound was soluble in dilute sodium hydroxide solution. The infrared spectrum showed strong bands at 2.80 and 2.98 μ. The ultraviolet spectrum showed maxima at 254 mμ, ϵ 16,900; 276 mμ, ϵ 11,200; and 418 mμ, ϵ 51,20.

Anal Calcd. for $C_{12}H_{10}N_2O_3$: C, 62.62; H, 4.38; N, 12.18. Found: C, 62.97; H, 4.49; N, 12.25.

The 1:1 ether–methanol eluate yielded 0.17 g. (3%) of 2-hydroxy-2′-aminodiphenylamine (from ligroin) as pale pink needles, m.p. 116–117.5°. The compound was soluble in dilute sodium hydroxide. The ultraviolet spectrum showed maxima at 270 and 295 mμ with ϵ 10,900 and 9,800.

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.96; H, 6.04; N, 13.99; O, 7.99. Found: C, 71.74; H, 5.98; N, 13.85; O, 7.74.

Method D.—Six grams of the nitro compound VIIIc was added *via* a Soxhlet extractor to 3 g. of lithium aluminum hydride in tetrahydrofuran. The mixture was heated under reflux for 4 hours after the addition was complete. The isolation procedure used was that described earlier. The azo compound XIIc was isolated and recrystallized from hexane to yield 0.5 g. (11%) of orange needles, m.p. 57.5–58.5°. The ultraviolet spectrum had λ_{max} 240 mμ, ϵ 10,300; λ_{max} 311 mμ, ϵ 7,920; λ_{max} 413 mμ, ϵ 975.

Anal. Calcd. for $C_{12}H_8N_2O$: C, 73.45; H, 4.11; N, 14.25. Found: C, 73.66; H, 3.85; N, 14.57.

2,3,6,7-Dibenzo-1-oxa-4,5-diazacyclohepta-2,6-diene (IIc).—From 0.30 g. of azo compound XIIc by reduction method I was obtained 0.27 g. (88%) of IIc as colorless needles, m.p. 97.5–98°. The analytical sample, recrystallized from ether–hexane, had m.p. 98.5–99°. The infrared spectrum showed maxima at 3.0 and 3.1 μ. The ultraviolet spectrum showed λ_{max} 281 mμ, ϵ 3,510.

After exposure to air for 10 days the compound became yellow. A sample sealed under nitrogen remained colorless.

Anal. Calcd. for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.09; N, 14.14; O, 8.07; mol. wt., 196. Found: C, 72.85; H, 4.96; N, 13.92; O, 8.33; mole wt., 210 (Rast).

A sample of IIc was oxidized with mercuric oxide to XIIc in 94% yield as described for the oxidation of IIb to XIIb. A sample of IIc was catalytically reduced to the diamine IXc as described for the reduction of IIb to IXb.

2,2′-Diaminodiphenyl Sulfide (IXd).—2,2′-Dinitrodiphenyl sulfide (VIIId) was prepared by a standard procedure[38]; m.p. 119–122° (reported[39] m.p. 122–123°). Reduction of the dinitro compound with zinc dust and calcium chloride (method E) gave the diamine as pale yellow needles, m.p. 84–85.5°, yield 44% (literature[39] m.p. 85–86°).

2,3,6,7-Dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene (XIId).—Reduction of 2 g. of VIIId with sodium sulfide was carried out as described previously (method C) except the reflux period was shortened to 5 minutes. The crude product was isolated as before and was chromatographed on alumina with hexane, benzene and ether in the usual way. From the 1:1 hexane–benzene fraction was obtained a yellow solid, and from the 2:1 benzene–ether fractions was obtained a brown solid. Recrystallization of the brown solid from ether–hexane gave 0.21 g. (13%) of diamine IXd, nearly colorless needles, m.p. 85.5–86.5°, no mixture melting point depression.

Recrystallization of the yellow solid from ether–hexane gave 0.05 g. (3%) of the azo compound XIId, yellow needles, m.p. 139.5–140°. The ultraviolet spectrum showed λ_{max} 244 mμ, ϵ 12,750; λ_{max} 311 mμ, ϵ 4,420; λ_{max} 420 mμ, ϵ 804.

Anal. Calcd. for $C_{12}H_8N_2S$: C, 67.89; H, 3.80; N, 13.20. Found: C, 68.02; H, 3.81; N, 13.02.

By Method D.—Azo compound XIId was also prepared by lithium aluminum hydride reduction of VIIId as described earlier except that the column was eluted with 9:1 hexene-ether and gave an orange solid. Recrystallization from ether–hexane gave XIId, orange needles, m.p. 139.5–140°, yield 6%. The mixture melting point with the material from the sodium sulfide reduction showed no depression.

2,3,6,7-Dibenzo-1-thia-4,5-diazacyclohepta-2,6-diene (IId).- The compound XIId, 0.70 g., was reduced with hydrazine (method I) as described except that 5% palladium-on-charcoal was used as the catalyst. There was obtained 0.60 g. (84%) of colorless crystalline product, m.p. 101–103°. The analytical sample was recrystallized from ether–hexane; m.p. 102–103°. The infrared spectrum showed absorption at 3.0 and 3.1 μ. The ultraviolet spectrum showed λ 239, ϵ_{max} 23,300, and λ_{max} 295, ϵ 5,760.

Anal. Calcd. for $C_{12}H_{10}N_2S$: C, 67.26; H, 4.71; N 13.08; S, 14.96; mol. wt., 214. Found: C, 67.50; H, 4.62; N, 13.03; S, 14.60; mol. wt., 223 (Rast).

The compound did not discolor appreciably from exposure to the atmosphere for 6 weeks. It was oxidized with mercuric oxide to IId in 96% yield, m.p. 140–141°, mixture melting point undepressed. It was reduced with platinum and hydrogen to IXd in 63% yield, m.p. 84–85.5°, mixture melting point undepressed.

2,2′-Dinitrodiphenylmethane (VIIIe).—2,2′-Dinitro-4,4′-diaminodiphenylmethane (XIV) was prepared by nitration of the amine according to Duval[16]; m.p. 205–206°, reported m.p. 205–206°. According to Schnitzspahn,[26] this amine can be diazotized with ethyl nitrite, and the diazonium salt can be reduced with ethanol to yield the dinitro compound VIIIe, m.p. 159°. In the present work no crystalline product could be isolated by this procedure. The general method of Kornblum, Kelly and Cooper[40] was therefore employed.

To 96 ml. of 96% sulfuric acid at 0° was added portionwise 50 g. of sodium nitrite. A solution of 32 g. of 2,2′-dinitro-4,4′-diaminodiphenylmethane in 96 ml. of 96% sulfuric acid was then added dropwise, the temperature being kept below 5°. The mixture was kept in an ice-bath with stirring for 4 hours, and was then poured with vigorous stirring into a mixture of 600 ml. of 30% hypophosphorous acid and 1840 g. of ice. The mixture was allowed to stand in an ice-bath for several hours and then at room temperature overnight. The red solid which formed was collected, wt. 31 g. An 8.25-g. portion of this material was ground up and extracted overnight in a Soxhlet apparatus with ligroin (b.p. 40–60°). There was thus obtained 0.75 g. of yellow crystals, m.p. 70–85°. Extraction of the residual red solid was then carried out overnight with ligroin (b.p. 69–80°). From this solvent was isolated 0.18 g. of yellow crystals, m.p. 155–156°. This material was soluble in dilute base, as described,[26] and showed intense bands in the infrared spectrum at 2.78 and 3.10μ. The identity of this compound was not established, but it seems likely that it is a phenol. It is clear that the compound does not have the structure assigned to it (VIIIe) by Schnitzspahn.[26]

The material having m.p. 70–85° was adsorbed on 50 g. of alumina from benzene, and was eluted with 4:1 hexane–ether. The yellow solid so obtained was recrystallized from ether–hexane and gave 0.49 g. (6%) of VIIIe as pale yellow needles, m p. 84–85°. The ultraviolet spectrum showed λ_{max} 257, ϵ 11,200.

Anal. Calcd. for $C_{13}H_{10}N_2O_4$: C, 60.46; H, 3.90. Found: C, 60.66; H, 4.00.

2,2′-Diaminodiphenylmethane (IXe).—The dinitro compound VIIIe was reduced with platinum and hydrogen in ethanol. The theoretical amount of hydrogen was taken up in 30 minutes. The catalyst was removed by filtration, the solvent was evaporated under vacuum, and the product was crystallized from ether–hexane as nearly colorless plates,

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(38) C. C. Price and G. W. Stacy, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 667.

(39) R Nietzki and H. Bothof. *Ber.*, **29**, 2774 (1896).

(40) N. Kornblum, A. E. Kelly and G. D. Cooper, *J. Am. Chem. Soc.*, **74**, 3074 (1952).

m.p. 134.5–136° (Bertram[41] assigned this structure to the reduction compound from what he incorrectly considered to be VIIIe; his reduction product is reported to melt at 160°). The infrared spectrum showed maxima at 2.94 and 3.01μ. The ultraviolet spectrum showed λ_{max} 233 mμ, ε 14,700; λ_{max} 286 mμ, ε 4.510.

Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.79; H, 7.15; N, 13.91.

2,2'-Azoxydiphenylmethane (XVI).—The dinitrodiamine XIV was converted to the cyclic azoxy compound XV according to Duval[16]; m.p 247° (reported[16] m.p. 273°). This compound was treated with nitrous acid followed by hypophosphorous acid as described for the preparation of VIIIe, except the reaction with hypophosphorous acid was allowed to continue for 45 hours at 0°. The reaction product was isolated by continuous extraction with ligroin (b.p. 40–60°) as before. There was obtained 1.86 g. (14%) of yellow needles, m.p. 130–132°. An analytical sample, twice recrystallized from petroleum ether, had m.p. 134.5–135.5°.

Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 74.26; H, 4.80; N, 13.33. Found: C, 74.24; H, 4.90; N, 13.40.

2,3,6,7-Dibenzo-4,5-diazacyclohepta-2,6-diene (IIe) Reduction of XVI with hydrazine (method I) gave IIe, pale yellow needles, m.p. 98–100°, yield 82%. The analytical sample was recrystallized from ether–hexane, m.p. 99–101°, m p. 105–105.5° (in vac.). The infrared spectrum showed bands at 3.0 and 3.1μ. The ultraviolet spectrum had λ_{max} 247, ε 6,550; λ_{max} 289, ε 1,810.

Anal. Calcd. for $C_{13}H_{12}N_2$: C, 79.56; H, 6.17; N, 14.28; mol. wt., 210. Found: C, 79.48; H, 6.40; N, 14.28; mol. wt., 187 (Rast).

The compound decomposed upon standing in air, but was stable when sealed under nitrogen. It was oxidized to the azo compound XIIe with mercuric oxide as described in 95% yield, and reduced to the diamine catalytically as described in 66% yield. These products were identified by lack of mixture melting point depression with authentic samples.

2,3,6,7-Dibenzo-4,5-diazacyclohepta-2,4,6-triene (XIIe).—Reduction of 0.66 g. of the azoxy compound XVI with sodium sulfide (method C) was carried out as described, but the reflux period was extended to 3 hours. Chromatography of the reaction product on alumina gave crude XIIe from the pentane–ether fractions, which was recrystallized from hexane and gave 0.10 g. (17%) as yellow needles, m.p. 111.5–112.5°. The mixture melting point with material from the lithium aluminum hydride reduction was undepressed.

From the ether fractions was also recovered a small amount of starting material, melting point and mixture melting point 135–136°.

Reduction of 0.70 g. of compound XVI was also carried out with lithium aluminum hydride (method D) except ether was used as the solvent and the mixture was heated under reflux for 3 days. Chromatography was carried out as described using benzene, ether and methanol in turn for the elution. From the methanol fractions was isolated 0.24 g. (36%) of 2,2'-diaminodiphenylmethane (IXe), m.p. and mixture m.p. 134.5–135.5°. From the benzene fractions after recrystallization from hexane was obtained 0.08 g. (12%) of XIIe as yellow needles, m.p. 111–112°. The analytical sample had m.p. 112.5–113.5°. The ultraviolet spectrum showed λ_{max} 242 mμ, ε 6,820; λ_{max} 314 mμ, ε 7,620; λ_{max} 423 mμ, ε 976.

Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.36; H, 5.19; N, 14.43. Found: C, 80.13; H, 5.14; N, 14.11.

N.m.r. Spectra.—All determinations were made in acetone solvent with a concentration of 5–10%. Compounds XVIII and XVII were run at 60 m.c. and referenced by external benzene. The protons on nitrogen appeared at −95 and −187 c.p.s. Compounds IIe and IIb were run at 60 mc. with internal tetramethylsilane as reference and showed absorption at −371 and −376 c.p.s. Compounds XIX and IId were run at 40 mc. with external methylene chloride reference, and showed resonance at −72 and −21 c.p.s. All values were corrected approximately to the τ scale by using[42] benzene = 3.60 τ, methylene chloride = 4.70 τ. No susceptibility corrections were made.

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[CONTRIBUTION FROM THE LABORATORIO DE QUIMICA ORGANICA, FACULTAD DE CIENCIAS EXACTAS Y NATURALES, UNIVERSIDAD NACIONAL DE BUENOS AIRES, BUENOS AIRES, ARGENTINA]

Polar Effects of Substituents on the Reaction Rates of 4-R- and 5-R-2-Nitrochlorobenzenes with Piperidine in Benzene

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The rate constants for the reaction of fourteen 4-R- and of twelve 5-R-2-nitrochlorobenzenes with piperidine in benzene have been determined. The reaction follows the Hammett relationship $\log k_R/k_H = \sigma^*\rho$ with a ρ-value of +3.80. Differences in rates are mainly determined by differences in activation energies.

The extensive literature on aromatic nucleophilic substitution, has been recently reviewed by Bunnett and Zahler,[3] Bunnett[4] and Sauer and Huisgen.[5] Miller,[6,7] Hammond and Hawthorne[8] and Kalberer,[9] have published partial reviews.

The nucleophilic substitution of halogen in 4-R-2-nitrohalogenobenzenes has been studied quantitatively by Berliner and Monack[10] in the solvolysis of 4-R-2-nitrobromobenzenes in piperidine; by Miller and coworkers,[11] by Bunnett and coworkers[12] and by Eliel and Nelson[13] in the reactions of 4-R-2-nitrochlorobenzenes with sodium methoxide in methanol. Bunnett and Snipes[14] studied the

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[1] Based in part on the D.Chem. thesis of W. G. (1960) and R. A. B. (1959).

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