[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY]

Aromatic and Pseudoaromatic Nonbenzenoid Systems. IV. Cyclooctatetraene[1,2]

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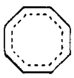
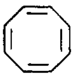
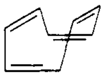
Calculations by the Pariser-Parr method indicate that the alternating long and short bond structure is of lower energy for cyclooctatetraene than is the symmetrical (D_{8h}) one, while the reverse is true for the dianion. The energy barrier to the inversion of cyclooctatetraene is predicted to be quite low. It is concluded that the method is not very satisfactory for making such predictions, and improvement in the values of some of the empirical constants ordinarily used can probably be made.

The Hückel method has been widely used for the calculation of properties of conjugated systems, and with considerable success.[3] Explicit methods such as the Goeppert-Mayer and Sklar calculation[4] are on a much stronger theoretical foundation, but give numerically unsatisfactory results. Daudel, Lefebvre, and Moser have mentioned that the success of the Pariser and Parr[5] method suggests it is most suitable for aromatic hydrocarbons and related molecules, and that it seems to be "the middle ground between the very rapid, sometimes incoherent but often successful Hückel theory, and the tedious, coherent and unfortunately disappointing non-empirical calculations."[6] With this thought in mind we have attempted to apply the method to cyclooctatetraene and its dianion, with the hope of determining the ground state energies for various possible geometries of these compounds, and hence the molecular geometry itself. It seems important to establish the suitability of the method, and of the empirically evaluated resonance and Coulomb integrals, for the calculation of ground state energies. The method has been used in a similar way previously.[7] The pi system of cyclooctatetraene itself has previously been treated by the Pariser-Parr method.[8,9] The energy levels calculated earlier were found to be in good agreement with the observed spectrum of the substance.

It was assumed at the outset that the structures of cyclooctatetraene and of its dianion could be reasonably approximated by one of three structures; a planar, symmetrical highly resonance stabilized form (I), a planar form with alternating long and short bonds (II), or a nonplanar tub form (III).


I


II


III

Cyclooctatetraene is known to have structure III,[10] while for the dianion I seems likely, although II does not appear to be definitely excluded.[11] Coulson has predicted[12] on the basis of the Hückel method that the symmetrical form of the dianion is the more stable.

We have applied the method of Pariser and Parr with only minor modifications of some numerical values to the three types of systems with the assumed geometries indicated. Properly, the sum of the π and σ energies of the ground state for a given geometry, say I, should be minimized by adjusting the bond lengths, and this would necessarily mean a self-consistent treatment.[13] To keep the calculations from becoming unduly lengthy, the problem was simplified by assuming that I would exhibit a bond length of 1.397 Å (like benzene), and that II and III would have alternating bond lengths of 1.334 and 1.462 Å (the known bond lengths in cyclooctatetraene). For I and II, Coulomb integrals of the type $(pp|qq)$ were evaluated from a curve drawn through a plot of $(pp|qq)$ *vs.* distance, using the Pariser-Parr values. In the case of III, the angles between the orbitals were measured on a carefully constructed scale model,[14] and each vector was resolved into π, $\bar{\pi}$, and σ components. The interactions between the various components were

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(1) Paper III, N. L. Allinger and G. A. Youngdale, *J. Am. Chem. Soc., in press.*

(2) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) For a recent review, see R. Daudel, R. Lefebvre, and C. Moser, *Quantum Chemistry, Methods and Applications,* Interscience Publishers, Inc., New York, 1959, p. 52.

(4) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.,* **6,** 645 (1938).

(5) R. Pariser and R. G. Parr, *J. Chem. Phys.,* **21,** 466, 767 (1953).

(6) Ref. 3, p. 517.

(7) M. J. S. Dewar and L. Paoloni, *Trans. Faraday Soc.,* **53,** 261 (1957).

(8) P. Schiess and A. Pullman, *J. Chim. phys.,* **53,** 101 (1956).

(9) H. C. Longuet-Higgens, *J. Chem. Phys.,* **24,** 771 (1956); *J. Chem. Phys.,* **26,** 722 (1957).

(10) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.,* **27,** 1311 (1957).

(11) T. J. Katz, *J. Am. Chem. Soc.,* **82,** 3784, 3785 (1960).

(12) C. A. Coulson, *Tetrahedron,* **12,** 193 (1961).

(13) J. A. Pople, *J. Phys. Chem.,* **61,** 6 (1957).

(14) In this case the required angles can be determined rather easily by trigonometric methods (see ref. 8 for details). We have used models in more complicated cases where the trigonometric method is excessively laborious, and having found it simple and satisfactory, we have employed it here.

TABLE I

Molecular Integrals (e.v.)

I	J_{11} 5.946	$(11\|11)$	10.53	β_{12} − 2.428	
	J_{22} 6.196	$(11\|22)$	7.30	α − 50.65	
	J_{23} 5.697	$(11\|33)$	5.18	(1:22) 1.193	
	K_{12} 1.399	$(11\|44)$	4.13		
	K_{14} 0.499	$(11\|55)$	3.82		
	K_{16} 0.278	I_1	−55.506		
	K_{18} 0.231	I_2	−54.084		
	K_{23} 0.249	I_4	−50.650		
	K_{24} 0.839	I_6	−47.216		
	K_{27} 0.481	I_8	−45.794		
II	J_{11} 5.929	$(11\|11)$	10.53	β_{12} − 1.994	
	J_{22} 6.079	$(11\|22)$	7.16	β_{18} − 2.940	
	J_{23} 5.779	$(11\|33)$	5.17	α − 50.43	
	K_{12} 1.395	$(11\|44)$	4.09	(1:22) 0.939	
	K_{14} 0.519	$(11\|55)$	3.79	(1:88) 1.371	
	K_{15} 0.476	$(11\|66)$	4.14		
	K_{16} 0.290	$(11\|88)$	7.38		
	K_{18} 0.236	I_1	−55.364		
	K_{23} 0.355	I_2	−53.982		
	K_{24} 0.971	I_4	−51.376		
	K_{25} 0.714	I_5	−49.484		
	K_{26} 0.326	I_6	−46.878		
	K_{27} 0.400	I_8	−45.496		
III	J_{11} 6.111	$(11\|11)$	10.53	β_{12} − 1.027	
	J_{22} 6.156	$(11\|22)$	7.03	β_{18} − 2.940	
	J_{23} 6.066	$(11\|33)$	5.38	α − 51.89	
	K_{12} 1.222	$(11\|44)$	4.64	(1:22) 0.939	
	K_{14} 0.584	$(11\|55)$	4.23	(1:88) 1.371	
	K_{15} 0.416	$(11\|66)$	4.32		
	K_{16} 0.352	$(11\|88)$	7.38		
	K_{18} 0.269	I_1	−55.857		
	K_{23} 0.520	I_2	−55.004		
	K_{24} 0.999	I_4	−53.803		
	K_{25} 0.576	I_5	−49.977		
	K_{26} 0.371	I_6	−48.776		
	K_{27} 0.332	I_8	−47.923		
IV	J_{11} 6.805	$(11\|11)$	10.53	β_{12} − 2.940	
	J_{22} 7.079	$(11\|22)$	7.38	β_{16} − 1.994	
	J_{23} 6.531	$(11\|33)$	5.44	α − 43.83	
	K_{12} 1.236	$(11\|44)$	4.88	(1:22) 1.371	
	K_{14} 0.460	$(11\|66)$	7.16	(1:66) 0.939	
	K_{16} 0.332	I_1	−48.764		
	K_{23} 0.274	I_2	−46.429		
	K_{24} 0.574	I_4	−41.231		
	K_{25} 0.906	I_6	−38.896		
V	J_{11} 6.825	$(11\|11)$	10.53	β_{12} − 2.428	
	J_{22} 7.047	$(11\|22)$	7.30	α − 44.03	
	J_{23} 6.602	$(11\|33)$	5.46	(1:22) 1.193	
	K_{12} 1.245	$(11\|44)$	4.90		
	K_{14} 0.445	I_1	−48.886		
	K_{16} 0.325	I_2	−46.458		
	K_{23} 0.222	I_4	−41.602		
	K_{24} 0.622	I_6	−39.174		
	K_{25} 0.947				

each evaluated from Roothaan's Tables,[15] and the theoretical value for the Coulomb integral was obtained. The integral $(\pi\pi|\pi\pi)$ was also evaluated at that distance, and the factor necessary to convert the theoretical value to the Pariser-Parr value was calculated. The actual integral was then correspondingly reduced in value. The molecular integrals actually used in the calculations are summarized in Table I.

In preliminary calculations resonance integrals used were those originally given[5] for benzene (−2.39 e.v. at 1.39 Å), and butadiene (−2.92 e.v. at 1.35 Å and −1.68 e.v. at 1.46 Å). Since the long bond of the tub form (III) has the π orbitals at opposite ends rotated through a dihedral angle of 59°, the resonance integral was reduced proportionally to the reduced overlap integral, and −0.87 e.v. was used. Resonance integrals between nonadjacent atoms were neglected.

Actually at the time of the original development of the Pariser-Parr method the bond lengths of benzene and ethylene were not accurately known. Using inaccurate bond lengths, it was found necessary to empirically adjust the values of the resonance integrals of ethylene and benzene to fit the observed spectra. It turns out that these empirical values and the theoretical values given by Pariser and Parr for these integrals are almost exactly the same for benzene and ethylene if the correct bond lengths are used. Consequently the theoretical values[5] for β of −2.80 e.v. at 1.35 Å and −2.48 e.v. at 1.39 Å were accepted, and an exponential curve was calculated which gave these values. The resonance integrals $(2p\pi - 2p\pi)$ for various distances were obtained from this curve (1), where β is in electron volts, r in Angstroms.

$$\beta = -167.9e^{-3.0323r} \qquad (1)$$

Penetration integrals for adjacent carbons were evaluated theoretically according to Scrocco and Salvetti,[16] and the theoretical values were used (see Table I). For atoms other than adjacent carbons, penetration integrals were neglected.

The orbitals used in each case were obtained by diagonalizing (by the Jacobi method)[17] the Hückel matrix obtained using for the off-diagonal elements the appropriate resonance integrals and setting the diagonal elements equal to zero. The orbitals which are not determined by symmetry are given in Table II.

The calculations were carried out utilizing an IBM 650 computer and previously described programs.[18]

The ground state π energy was thus found for I, II, and III, for 7,8,9,10, and 11 π-electrons (Table III). The trends are consistent with the fact that cyclooctatetraene adds chemically two electrons

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[15] C. C. Roothaan, "Tables of Two-center Coulomb Integrals between 1*s*, 2*s*, and 2*p* orbitals," Special Technical Report, Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, 1955.

[16] E. Scrocco and O. Salvetti, *La Ricera Scientifica*, **23**, 98 (1953).

[17] H. H. Harmon, *Modern Factor Analysis*, University of Chicago Press, Chicago, 1960, p. 180.

[18] R. B. Hermann, *J. Org. Chem.*, **27**, 441 (1962).

TABLE II

Wave Functions Used in the Calculations

Structure		χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8
II	ϕ_1	0.35355	0.35355	0.35355	0.35355	0.35355	0.35355	0.35355	0.35355
	ϕ_2	−0.44177	−0.44177	−0.23417	0.23417	0.44177	0.44177	0.23417	−0.23417
	ϕ_3	0.23417	−0.23417	−0.44177	−0.44177	−0.23417	0.23417	0.44177	0.44177
	ϕ_4	−0.35355	0.35355	0.35355	−0.35355	−0.35355	0.35355	0.35355	−0.35355
	ϕ_5	−0.35355	−0.35355	0.35355	0.35355	−0.35355	−0.35355	0.35355	0.35355
	ϕ_6	−0.23417	−0.23417	0.44177	−0.44177	0.23417	0.23417	−0.44177	0.44177
	ϕ_7	−0.44177	0.44177	−0.23417	−0.23417	0.44177	−0.44177	0.23417	0.23417
	ϕ_8	−0.35355	0.35355	−0.35355	0.35355	−0.35355	0.35355	−0.35355	0.35355
III	ϕ_1	0.35355	0.35355	0.35355	0.35355	0.35355	0.35355	0.35355	0.35355
	ϕ_2	−0.40770	−0.40770	−0.28944	0.28944	0.40770	0.40770	0.28944	−0.28944
	ϕ_3	0.28944	−0.28944	−0.40770	−0.40770	−0.28944	0.28944	0.40770	0.40770
	ϕ_4	−0.35355	0.35355	0.35355	−0.35355	−0.35355	0.35355	0.35355	−0.35355
	ϕ_5	−0.35355	−0.35355	0.35355	0.35355	−0.35355	−0.35355	0.35355	0.35355
	ϕ_6	−0.28944	−0.28944	0.40770	−0.40770	0.28944	0.28944	−0.40770	0.40770
	ϕ_7	−0.40770	0.40770	−0.28944	−0.28944	0.40770	−0.40770	0.28944	0.28944
	ϕ_8	−0.35355	0.35355	−0.35355	0.35355	−0.35355	0.35355	−0.35355	0.35355
IV	ϕ_1	0.40825	0.40825	0.40825	0.40825	0.40825	0.40825		
	ϕ_2	−0.56960	−0.36312	0.36645	0.57029	0.20315	−0.20716		
	ϕ_3	−0.09428	−0.44886	−0.44615	0.09004	0.54043	0.53890		
	ϕ_4	0.07936	−0.43922	0.45557	−0.10491	−0.53494	0.54413		
	ϕ_5	0.57187	−0.37473	−0.35467	0.56774	−0.21720	−0.19301		
	ϕ_6	−0.40825	0.40825	−0.40825	0.40825	−0.40825	0.40825		

TABLE III

π Energies (e.v.) of Cyclooctatetraene and Cyclohexatriene Systems Containing Various Numbers of Electrons[a]

No.	System				
Electrons	I	II	III	IV	V
5	—	—	—	−82.124	−81.816
6	—	—	—	−96.313	−95.839
7	−113.736	−114.980	−112.361	−98.654	−98.506
8	−124.938	−127.316	−125.967	−93.916	−94.126
9	−130.426	−131.510	−128.891	—	—
10	−129.967	−129.776	−125.703	—	—
11	−120.407	−120.067	−115.997	—	—

[a] Electrons all paired in lowest orbitals (or in the same orbital if there are two or more of the same energy).

quite easily, but will not add a third, while benzene adds two electrons with reluctance.[19]

The transition energy for the $^1A_1 \rightarrow {}^1A_2$ band was calculated to be 5.11 e.v. (without configuration interaction), in fair agreement with earlier calculations,[8] and with experiment (4.42 e.v.).

The σ-energies of the systems can be obtained fairly easily in principle. Both compression and bending must be accounted for. It is clear how compression should be treated, but the long accepted numerical conclusions[20] are now considered to be inaccurate,[21] and following Dewar's suggestion regarding the bond length of an sp^2-sp^2 pure single bond, Coulson[12] has given numerical quantities for carrying out such a calculation. While the exact numerical values used are of unpublished origin, it seems unlikely that more accurate values would significantly affect the results. The difference in compression energy between I and II is not large, the former arrangement is more stable by 10.9 kcal./mole. Bond angle bending is also present to a considerable extent in I and II. If a composite bending constant of 0.8×10^{-11} erg/radian^2 for the C=C—C bond angle is adopted[22] and the geometry of minimum energy is taken to be that of ethylene (H—C—H angle,[23] 117°), the bending energies for I and II are calculated to be some 25.5 kcal./mole, while for III the bending energy amounts to only 3.5 kcal./mole. The σ-π interaction energies (first and second order hyperconjugation) were also included.[24] When these various energies are added to the π-energies, relative total molecular energies are obtained for the 8 and 10 electron systems and are given in Table IV.

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(19) See ref. 11 for a summary of the pertinent chemical properties of cyclooctatetraene.

(20) R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951).

(21) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

(22) F. H. Westheimer in M. S. Newman, *Steric Effects in Organic Chemistry*, J. H. Wiley and Sons, New York, 1956, p. 523.

(23) (a) H. C. Allen, Jr., and E. K. Plyler, *J. Am. Chem. Soc.*, **80**, 2673 (1958); (b) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957).

(24) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959).

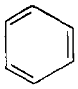
TABLE IV

Relative Energies of Various Structures

Energy of Structure	I	II	III	IV	V
(8π electrons)	+54.9	0.0	+31.1	0.0	+10.9
Compression	+29.3	+40.2	+40.2	+30.2	+22.0
Bond bending	+25.5	+25.5	+3.5	0.0	0.0
$\sigma - \pi$	−3.6	−3.6	−8.1	0.0	0.0
Total	+106.1	+62.1	+66.7	+30.2	+32.9
(10π electrons)	0.0	+4.4	+98.2		
Compression	+29.3	+40.2	+40.2		
Bond bending	+25.5	+25.5	+3.5		
$\sigma - \pi$	−3.6	−3.6	−8.1		
Total	+51.2	+66.5	+133.8		

Certain features here are of interest. It can be seen that with 8π electrons, the system of alternating single and double bonds is of considerably lower energy than that of equal bond lengths. Addition of one or two electrons lowers the total energy, and for the dianion the symmetrical structure is of lowest energy. In general these conclusions are in only fair agreement with experiment.[11,25] The calculations indicate, however, that for cyclooctatetraene itself the planar form with alternating bond lengths (II) is more stable than the tub (III) by 4.6 kcal./mole. They also indicate that the monoanion radical (9 electrons) is planar, and that alternating long and short bonds give a structure 14.1 kcal./mole more stable than one with equivalent bonds. The experimental evidence has been interpreted[11] as indicating a flat molecule and appears more consistent with equivalent bonds.

To obtain a reference point from which to work, analogous calculations were carried out for benzene, considering two possible structures, equal bond lengths (V), and alternating long and short bonds (IV) as before. There is little difference in



IV

V

π-energy in this case, the symmetrical structure being less stable by 10.9 kcal./mole. The compression energy favors the symmetrical structure by 8.2 kcal./mole, and this still leaves the alternating long and short bond structure more stable, but by only 2.7 kcal./mole. Such a prediction is not entirely satisfying, but one may regard this number as too small to be meaningful.

The thermochemical resonance energy is also of interest. This energy was calculated for benzene by taking the difference in energy between the real structure and the Kekulé form. To find the energy of the latter, the total Hamiltonian used was the same as for the long and short bond benzene, except the resonance integrals across each long bond were set equal to zero, and three isolated ethylenic orbitals were used. The resonance energy[26] of the real benzene was thus calculated to be 40.2 kcal./mole. The energy of benzene is also lowered (relative to the Kekulé form) by compression, and hence a conjugation energy of 48.4 kcal./mole is predicted. The resonance energy of the real cyclooctatetraene was likewise calculated to be 11.7 kcal./mole. There is no general agreement as to the exact interpretation of the experimental data and hence the agreement with "experiment" is somewhat arbitrary. However, if we follow Dewar,[27] the conjugation energy of benzene from heat of hydrogenation data is 49.1 kcal./mole. For cyclooctatetraene, using Turner's value for the heat of hydrogenation of the substance in acetic acid (98.0 kcal./mole[28]) adding 6.0 kcal. to correct to the gas phase (four times the value for cyclohexene[29]) gives 104.0 kcal./mole as an experimental quantity. The classical Kekulé form would be predicted to give four times the ethylene value (124.2 kcal./mole), but since the cyclooctane formed is strained relative to cyclohexane by 9.9 kcal./mole,[30] this amount must be subtracted, giving 114.3 kcal./mole. The conjugation energy is thus calculated to be 10.3 kcal./mole, or 21% that of benzene. This interpretation of the experimental data gives excellent agreement with the theoretical values.

Although the general qualitative results of the calculations carried out in this work are in agreement with known facts, some of the quantitative

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[25] One cannot (and does not) obtain more than a qualitative idea of the relative energies of the ions involved because the calculations refer to isolated ions and the experimental data is for solvated ion pairs.

[26] "Resonance energy" is taken to mean the lowering of π-energy relative to the classical cyclohexatriene (ref. 21). Conjugation or thermochemical energy is resonance energy plus compression energy.

[27] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

[28] R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *J. Am. Chem. Soc.*, **79**, 4127 (1957); and references given therein.

[29] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

[30] S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).

results are not. While the calculations correctly indicate that cyclooctatetraene will have alternating long and short bonds, II is predicted to be more stable than III, while the reverse is unquestionably true. The dianion, on the other hand, is definitely predicted to be planar and symmetrical, while the radical ion is predicted to be planar, but with bonds of alternating length.

For benzene the alternating bond length structure is predicted to be of lower energy than the symmetrical structure, but only by 2.7 kcal./mole. If configuration interaction of the singly excited configurations were to be included in the calculation, the alternating bond-form would be stabilized somewhat, but the symmetrical form, since the orbitals are already self-consistent, would not be. Hence, agreement with experiment would not be improved. In the present approximation, therefore, it would seem that the best that can be done is to say errors of perhaps 5–10 kcal./mole are to be expected, and in order to make a prediction as to whether or not a certain system has one configuration or another, the safest way is to compare with other known cases. Thus, the planar alternating bond structure of cyclooctatetraene is calculated to be more favorable than the symmetrical one by 44.0 kcal./mole, which shows the correct trend relative to benzene where the difference is only 2.7 kcal./mole.

There are various adjustments that might be made to improve the agreement between calculation and experiment, but any arbitrary adjustments would not lead to anything useful unless it was reasonably certain that such adjustments would carry over from one molecule to another. To raise the energy of the alternating bond structure of benzene above that calculated for the regular structure, one might try to have β fall off more slowly with distance. This would also lead to a lessening of the importance of resonance in the alternating bond structures of cyclooctatetraene and would tend to destabilize the planar form relative to the nonplanar, which would also be consistent with experiment. The inclusion of nonadjacent resonance integrals in III, although it causes some shifting about of energy levels, does not affect significantly the energy of the ground state. In any case, one can now see a possible reason for the fact previously considered anomalous,[24,31] namely that the long bonds in cyclooctatetraene are shorter than the long bond in butadiene (1.462 *vs.* 1.483 Å). The amount of resonance energy in cyclooctatetraene, while small compared to benzene, is still large compared to butadiene. Since very little compression energy is involved in going from 1.483 to 1.462 Å (0.4 kcal./bond) it is not too surprising that such a contraction occurs here, but not in butadiene. The fact that the C=C—C angle is 126.5° in cyclooctatetraene, compared to 121.5° in ethylene, can be attributed to a similar cause. The bond angle widens with increasing strain, but also increasing overlap across the long bond and increasing resonance. These two effects find a balance with the observed bond angle.

Since the method used seems in principle to be theoretically adequate, the discrepancy between theory and experiment is blamed on inaccurate empirically evaluated numerical quantities, and improvements in this direction will be considered in a subsequent paper.

DETROIT 2, MICH.

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[31] B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.*, **33**, 418 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

The Swamping Catalyst Effect. IV. The Halogenation of Anilines[1]

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The halogenation of the aluminum chloride–hydrogen chloride complex of aniline and dimethylaniline gave monohalogenated products in the ratio 50–60% *meta* to 25–30% *para*. Without hydrogen halide, other than that from substitution, less *meta* substitution (*ca.* 25%) was obtained. The halogenation of the aluminum chloride–hydrogen chloride complexes of *p*-alkyl- and *p*-haloanilines gave good yields of 3-halo-4-alkyl- (or halo)-anilines and is the method of choice for preparation of these compounds.

The objective of this work was to investigate means of changing the orientation of the powerfully *o*- and *p*-directing amino group in anilines so that preparative amounts of *meta*-haloanilines could be obtained by direct substitution. The most successful previous effort in this regard was the work of Gorvin[3] in which he found that bromination of dimethylaniline in concentrated sulfuric acid containing silver sulfate gave a mixture of *ca.* 60% 3-bromo- and 20% 4-bromodimethylaniline

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[1] Paper III, D. E. Pearson, W. W. Hargrove, J. K. T. Chow, and B. R. Suthers, *J. Org. Chem.*, **26**, 789 (1961).

[2] Taken in part from Ph.D. theses, Vanderbilt University, 1961.

[3] J. H. Gorvin, *J. Chem. Soc.*, 1237 (1953).