added to a solution of potassium cyanide (0.380 g.), nickel chloride (0.300 g.), and anhydrous sodium carbonate (0.1 g.) in water (10 ml.) at 15° with stirring. The mixture allowed to stand for 2 hr. and then heated at 70° for 0.5 hr. The cooled reaction solution was extracted with ether (4 × 25 ml.); the combined ether extract dried over anhydrous sodium sulfate and ether removed by distillation to give a gum. The gum was refluxed with aqueous caustic potash (20 ml.; 10%) for 5 hr., cooled, and acidified with concentrated hydrochloric acid (Congo red). The acidified solution was filtered from insoluble matter and repeatedly extracted with chloroform; the combined extracts were dried over anhydrous sodium sulfate. Evaporation of the solvent gave a gum which slowly solidified in an ice chest, m.p. 65–66°. Vacuum sublimation at 110–115°/0.05 mm. yielded a white solid, m.p. 86–88°. It was crystallized from petroleum ether (b.p. 40–60°) with a few drops of chloroform (ice chest) when *3,4-dihydro-7,8-dimethoxyisocoumarin* (V) was obtained as rectangular prisms (0.130 g.; 50.6%), m.p. 92°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.4; H, 5.8. Found: C, 63.2; H, 5.8.

The infrared spectrum (chloroform solvent) had a band at 5.88 μ (conjugated δ-lactone.).

Acknowledgment. We are grateful to Dr. Tapan. K. Mukherjee, Retina Foundation, Boston 14, Mass., for the infrared data of the dihydroisocoumarin (V).

MUZAFFARPUR, INDIA

[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

Chlorination of Biphenyl

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Biphenyl was chlorinated under a wide range of conditions. The *ortho-para* ratios were observed to rise sharply with increasing *meta-para* ratio. Explanations are discussed.

Although the halogenation of biphenyl has received only moderate attention in the past thirty years,[1–3] we felt it would be a convenient system with which to study the chlorination process. In this paper we report the results of a detailed examination of the chlorination of biphenyl, 2-chlorobiphenyl, and 4-chlorobiphenyl. These results have permitted us further insights into the electrophilic aromatic substitution process.

RESULTS AND DISCUSSION

Biphenyl, 2-chlorobiphenyl, and 4-chlorobiphenyl were chlorinated under a wide range of conditions and the results are recorded in Tables I, II, and III, respectively.

Table I is arranged in descending order of $^1/_2$ m/p ratios and represents, therefore, a scale of chlorinating agent reactivity[4] and Lewis acid strength. The order of Lewis acid strength is in good agreement with previous reports.[5–7] Attention should be called to the sulfuric acid–silver sulfate system which falls in the middle portion of the scale. This system has been reported to involve a positive specie as chlorinating agent[8] and seems to be similar, at least in $^1/_2$ m/p ratio, to acid-catalyzed halogenation by hypohalous acids.[2,9] Since the $^1/_2$ m/p ratios in Table I continue to increase, it is unlikely that chloronium ion is involved in this system or in any of the examples. Some form of complexing between chlorine molecule and acid is probably involved in each case.

Changes in $^1/_2$ m/p ratio can be correlated with $^1/_2$ o/p ratio changes. As the $^1/_2$ m/p ratio increases, the $^1/_2$ o/p ratio increases precipitously, then levels out just below unity (Fig. I). This relationship can be rationalized in several ways. One explanation is based on the arguments of Ingold,[10] Waters,[11] Remick,[12] and DeLaMare,[13] suggesting that the transition state for substitution *para* to an *ortho-para*-directing conjugative substituent is more stable than the *ortho* transition state as a result of conjugative effects. The magnitude of this *para* preference would be approximated by the examples at the bottom of Table I where conjugative effects are expected to be large. If the above assumption is correct the $^1/_2$ o/p ratio should gradually rise with increasingly reactive chlorinating agents, and this

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[1] R. L. Jenkins, R. McCullough and C. F. Booth, *Ind. Eng. Chem.*, **22**, 31 (1930).

[2] P. B. D. DeLaMare and M. Hassan, *J. Chem. Soc.*, 3004 (1957).

[3] P. S. Varma and M. Krishnamurti, *J. Indian Chem. Soc.*, **14**, 156 (1937).

[4] H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

[5] D. L. Hawke and J. Steigman, *Anal. Chem.*, **26**, 1989 (1954).

[6] O. C. Dermer, D. M. Wilson, F. M. Johnson, and V. H. Dermer, *J. Am. Chem. Soc.*, **63**, 2881 (1941).

[7] J. L. Cotter and A. G. Evans, *J. Chem. Soc.*, 2988 (1959).

[8] J. H. Gorvin, *Chem. & Ind.*, 910 (1951).

[9] P. B. D. De La Mare and J. H. Ridd, *Aromatic Substitution*, Academic Press, New York, 1959, Chap. 9.

[10] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell Univ. Press, Ithaca, New York, 1953, pp. 267–269.

[11] W. A. Waters, *J. Chem. Soc.*, 727 (1948).

[12] A. E. Remick, *Electronic Interpretations of Organic Chemistry*, Wiley, New York, 2nd ed., 1949, pp. 366–369.

[13] Ref. 9, pp. 145 and 167.

TABLE I

CHLORINATION OF BIPHENYL

Chlorinating System	% o	% m	% p	$^1/_2$ o/p	$^1/_2$ m/p
$AlCl_3$, Cl_2, 40°, in benzene	55.7[a]	6.0	38.4	0.73	0.08
$GaCl_3$, Cl_2, 0°, in ODCB	62.5	4.3	33.4	0.93	0.065
$AlBr_3$, Cl_2, 0°, in ODCB	61.1	4.5	34.5	0.89	0.065
$FeCl_3$, Cl_2, 40°, in benzene	56.5	2.5	41.0	0.69	0.03
$SbCl_5$, Cl_2, 40°, in benzene	62.7	1.5	35.8	0.88	0.02
$SnCl_4$, Cl_2, 40°, in benzene	62.1	1.0	37.0	0.83	0.015
H_2SO_4, Ag_2SO_4, Cl_2, 0°, in CCl_4	59.1	0.8	40.2	0.73	0.01
$BF_3O(C_2H_5)_2$, Cl_2, R.T., in CCl_4	42.0	1.0	57.0	0.37	0.009
HOAc, Cl_2, R.T.	34.6	0.6	64.8	0.26	0.005
HOAc:CCl_4 (1:3), Cl_2, R.T.	28.1	1.0	70.3	0.2	0.007

[a] The *ortho* and *para* values are generally within ±3% while the *meta* are within ±0.5%.

TABLE II

2-CHLOROBIPHENYL CHLORINATION

Chlorinating System	2,2'-	2,6-	2,5-	2,4-	2,3'-	2,3-	2,4'-	$^1/_2$ o/p	$^1/_2$ m/p
$AlCl_3$, Cl_2, 40°, in benzene	35.8[a]	3.4	7.6	2.5	18.6	3.8	28.4	0.63	0.33
$FeCl_3$, Cl_2, 40°, in benzene	38.4	2.5	6.1	2.0	15.3	2.9	32.7	0.58	0.23
$SnCl_4$, Cl_2, 40°, in benzene	44.2	0.6	2.1	0.6	9.7	0.8	42.0	0.53	0.11
HOAc:CCl_4, Cl_2, R.T.	20.5	1.3	2.6	1.5	6.1	1.1	66.8	0.16	0.045

[a] The larger values are generally within ±3%, the smaller within ±0.4%.

TABLE III

4-CHLOROBIPHENYL CHLORINATION

Chlorinating system	2,4-	2,4'-	3,4-	3,4'-	4,4'-	$^1/_2$ o/p	$^1/_2$ m/p
$AlCl_3$, Cl_2, 40°, in benzene	1.3[a]	34.3	Trace	1.5	62.9	0.28	0.012
$FeCl_3$, Cl_2, 40°, in benzene	0.85	46.4	Trace	0.56	52.1	0.45	0.006
$SnCl_4$, Cl_2, 40°, in benzene	1.5	56.0	Trace	0.56	41.5	0.68	0.007
HOAc:CCl_4, Cl_2, R.T.	<0.73	29.5	Trace	0.59	69.2	0.21	0.004

[a] See note in Table II.

is expressed graphically by the dotted line in Fig. 1. The dotted line is a plot of $^1/_2$ *o/p vs.* $^1/_2$ *m/p* ratios calculated from the equation.[14,15]

$$\log k_{o(m)}/k_p = \beta_x'(N_{o(m)} - N_p)/RT$$

Experimentally, however, the $^1/_2$ *o/p* ratio does not gradually rise; it rises sharply as shown by the solid line in Fig. 1. Another piece of evidence contrary to the hypothesis of conjugative *para* preference is the similarity of the $^1/_2$ *o/p* ratio for chlorination in carbon tetrachloride-acetic acid of biphenyl (Table I) and 2-chlorobiphenyl (Table II). The substitution of a chlorine atom in the 2-position of biphenyl should significantly enlarge the angle between the rings, decreasing the activity of *ortho* and *para* relative to *meta* positions and the *para* relative to *ortho* positions.[16] The former does occur, the $^1/_2$ *m/p* ratio jumps nearly an order of magnitude, but the latter does not. In other words, chlorination under conditions extremely sensitive to conjugative

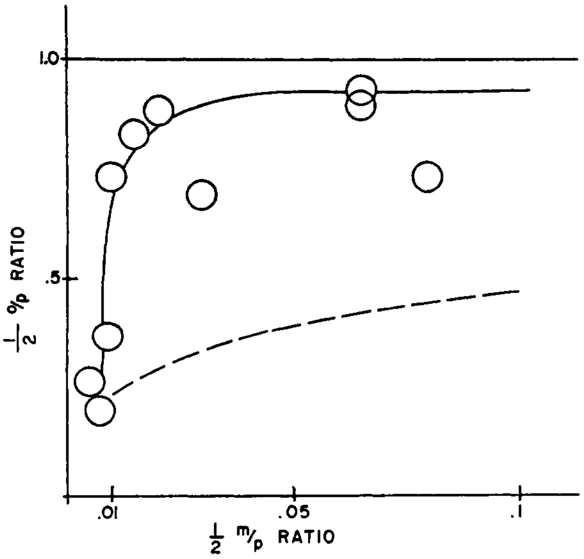

Figure 1

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[14] M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

[15] The ($N_{o(m)} - N_p$) values were computed using a β_x' of −13 kcal. (ref. 14) and the $^1/_2$ *o/p* and $^1/_2$ *m/p* ratios obtained experimentally for the chlorination in carbon tetrachloride–acetic acid. The $^1/_2$ *o(m)/p* ratios were then calculated by substituting other appropriate values for β_x'.

[16] R. D. Brown, *J. Am. Chem. Soc.*, 75, 4077 (1953).

changes in a system known to have undergone significant conjugative change (biphenyl to 2-chlorobiphenyl) nets no $^1/_2$ o/p ratio increase. It seems doubtful that conjugative effects are responsible for the observed $^1/_2$ o/p ratios.

We propose an alternative explanation based on the suggestion of Dewar[17] that the $^1/_2$ o/p ratio should be nearly unity for anionoid electromeric (+E)[18] substituents having a small electron affinity (−I).[18] If this assumption is correct, the most important factor determining $^1/_2$ o/p ratios in biphenyl substitution is steric.[16] The transition state formed by reaction with the more selective chlorinating agents will be similar to the Wheland intermediate. As the reagent becomes more reactive the forming carbon-chlorine bond becomes longer and its direction becomes more orthogonal to the plane of the phenyl ring[19,20] in the transition state, and the hybridization around the carbon being substituted[14] becomes less sp^3 and more sp^2 (see Fig. 2).

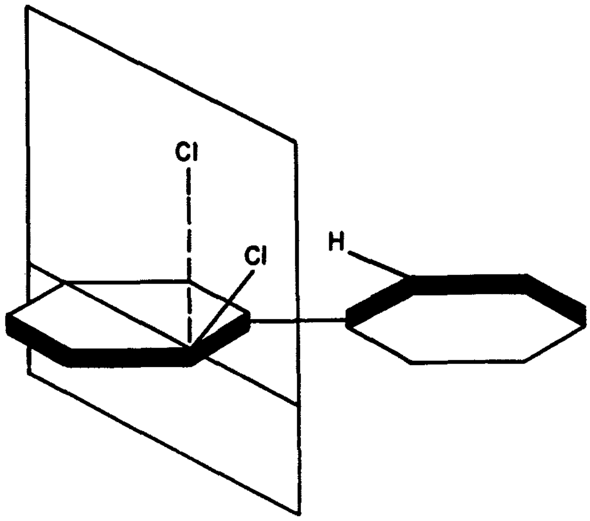

Figure 2

This change in bond length and direction should decrease steric interactions very rapidly causing a sharp rise in $^1/_2$ o/p ratios with increasing chlorinating agent activity, which is what we observe.[21]

A third possible explanation based on the conclusion of R. D. Brown[16] must also be considered. Brown suggests the $^1/_2$ o/p ratio should be greater than unity in the absence of steric effects. Our experimental results and rational will fit this assumption as well as the preceeding one. Table II offers some support for this hypothesis as the 2,6/2,4 ratios for the more reactive chlorinating systems are greater than unity. Presumably the larger angle between the rings provides further relief of steric interactions. One advantage of this third explanation is that it allows a more satisfactory unification of electrophilic and homolitic substitution mechanisms. The latter, carried out with extremely reactive, relatively nonpolar species such as phenyl radicals, tends to give a preponderance of *ortho* substitution.[22]

Thus far we have not discussed inductive effects which we expect to be relatively small in biphenyl. The results recorded in Table III allow a clear-cut example of inductive influence to be examined. The substitution of a chlorine atom in the 4-position has no effect on the $^1/_2$ o/p ratio for the low reactivity reagents but has a marked lowering effect on the $^1/_2$ o/p ratios for the more reactive species. This probably means as the reagent increases in activity and the positive charge in the transition state is distributed less in the rings and localized more on the incoming chlorine atom, inductive effects become dominant.[23,24] Inductive effects in the chlorination of biphenyl by highly reactive agents may account, in part, for the leveling of the curve below unity in Fig. 1.

EXPERIMENTAL

The solvents, catalysts and other reagents were the best commercial grades available. The gallium trichloride was kindly supplied by Robert I. Stearns, Monsanto Chemical Co., Dayton, Ohio. The 2- and 4-chlorobiphenyls were prepared *via* the Gomberg route.

Chlorination method A. Biphenyl or monochlorobiphenyl 0.01 to 0.02 mole, was placed in a 10-ml. amber volumetric flask and dissolved in about 5 ml. of solvent (carbon tetrachloride: acetic acid, 3:1; acetic acid or carbon tetrachloride). A solution of 0.001 to 0.005 mole of chlorine in 4 ml. of cold solvent was then added. (To the reaction in carbon tetrachloride 20 drops of boron trifluoride etherate was also added.) The volume was brought to the calibration line, the flask shaken and stored in the dark at room temperature. After an appropriate amount of time an aliquot was removed and from it most of the solvent was evaporated. The residue was used directly for gas chromatographic analysis.

Chlorination method B. To a cold solution of 0.6 g. of silver sulfate in 30 ml. of sulfuric acid and 3 ml. of water was added 0.02 mole of biphenyl. To this cold solution was added a solution of 0.003 mole of chlorine in 20 ml. of carbon tetrachloride. The reaction mixture was shaken vigorously in an ice bath for 5 min. then poured into ice. The aqueous layer was decanted and the organic layer was filtered to remove silver chloride. The organic layer was then washed with bicarbonate solution, water, dried over magnesium sulfate, filtered, and most of the solvent removed. The concentrate was used directly for gas chromatographic analysis.

Chlorination method C. Biphenyl, 0.02 mole, was dissolved in 10 ml. of o-dichlorobenzene and cooled in an ice bath. To

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(17) M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949).

(18) The sign convention is that of Ingold, *Chem. Revs.*, **15**, 225 (1934).

(19) J. H. Binks, J. Gresser and M. Szwarc, *J. Chem. Soc.*, 3944 (1960).

(20) H. Weingarten, *J. Org. Chem.*, **26**, 730 (1961).

(21) The apparent deviation of the ferric chloride and aluminum chloride systems may be due to the relative insolubility of these reagents, permitting reaction to take place on the surface of undissolved catalyst or on the surface of colloidal aggregates thus changing the steric requirements.

(22) D. R. Angood and G. H. Williams, *Chem. Revs.*, **57**, 172 (1957).

(23) J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

(24) Ref. 9, p. 158.

this was added a solution of 0.003 mole of chlorine in 10 ml. *o*-dichlorobenzene. A third solution of 0.1 to 0.3 g. of catalyst (aluminum bromide or gallium chloride) in 5 ml. of cold *o*-dichlorobenzene was added rapidly with stirring. A 5-ml. aliquot was then removed, washed with water, dried over magnesium sulfate, filtered, and used directly for gas chromatographic analysis.

Chlorination method D. Chlorine was bubbled through a solution of 0.01 mole of biphenyl or monochlorobiphenyl and 0.1 g. of catalyst ($SnCl_4$, antimony pentachloride, ferric chloride, or aluminum chloride) in 12 ml. of benzene at a rate which maintained the temperature at 40 ± 1°. Two-milliliter aliquots were taken at 5, 10 and 15 min. The aliquots were washed with water, dried over magnesium sulfate, filtered and most of the solvent removed. The concentrate was used directly for gas chromatographic analysis.

Analytical procedure.[25] The analyses were performed on a Barber-Colman Model 20 gas chromatograph equipped with a 200-ft. apiezon "L" capillary column and an argon ionization detector. Although areas were found generally to be proportional to mole percent any deviation from linearity was corrected for by use of calibrated standard samples.

ST. LOUIS, MO.

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(25) Details of the analytical procedure for biphenyl, the three monochlorobiphenyls and the twelve dichlorobiphenyls are reported elsewhere, H. Weingarten *et al.*, *Anal. Chim. Acta, in press.*

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, REED COLLEGE]

The Nature of Lagidze's Hydrocarbons. III.[1] The 217° Hydrocarbon Produced by Dehydrogenation of 5,5,10,10-Tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1,*a*]indene

J. E. H. HANCOCK AND D. L. PAVIA

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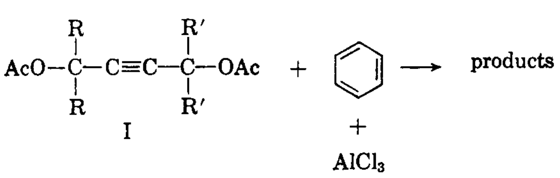
Dehydrogenation of IIa over palladium-on-charcoal at 300–350° yields III.

Previous studies[1-4] in this field have been concerned with the structures of hydrocarbons formed by the following general sequence:



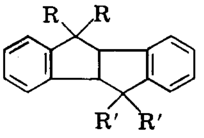
$$AcO-\overset{R}{\underset{R}{C}}-C\equiv C-\overset{R'}{\underset{R'}{C}}-OAc \;+\; C_6H_6 \;\longrightarrow\; \text{products}$$

I

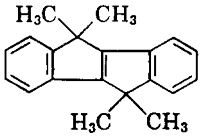
+ $AlCl_3$

Ia. R = R' = H
Ib. R = R' = CH_3
Ic. R=CH_3; R'R' = $(CH_2)_5$

Recently Lagidze has carried out[4] many different condensations of this type, using both different acetylenic diacetates, and also some substituted benzenes; as a result of this work it would appear that there are in general two types of products—diacetate Ia produces 2-phenylnaphthalene, and all other diacetates apparently give rise to substituted tetrahydroindenoindenes (II).



II



III

IIa. R = R' = CH_3
IIb. R = CH_3; R'R' = $(CH_2)_5$

We have studied the mechanisms of these reactions, and it was hoped that Part III of this series would consist of a detailed discussion of the mechanism of formation of 2-phenylnaphthalene; however, no clear-cut evidence in favor of our hypothesis of ring-expansion of indenes[1] has as yet been accumulated, since experiments with these substances have so far only yielded polymeric materials.

It is the purpose of this paper to report on the dehydrogenation of IIa, m.p. 84°. Lagidze has stated[4a] that treatment of IIa with palladium-on-charcoal catalyst at 300° in a carbon dioxide atmosphere gave a hydrocarbon, m.p. 216–217°; he has further claimed that *dehydrogenation of IIb yields the same hydrocarbon.* This interesting report has caused us to examine the dehydrogenation of IIa, but we find it difficult to reconcile our results with the preceding italicized statement, for all the evidence herein presented points to the conclusion that the 217° hydrocarbon has the constitution III. Thus no methane was detected (mass spectrometer) during the dehydrogenation, the infrared absorption

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(1) Part II, J. E. H. Hancock and D. R. Scheuchenpflug, *J. Am. Chem. Soc.*, **80**, 3621 (1958); the title of the series has been changed, since Lagidze's original proposals[2] involving cyclobutadiene-like structures have been withdrawn.[3]

(2) R. M. Lagidze and A. D. Petrov, *Doklady Akad. Nauk, S.S.S.R.*, **83**, 235 (1952).

(3) R. M. Lagidze, N. R. Loladze, and A. D. Petrov, *Soobshchenya Akad. Nauk, Gruzin. S.S.R.*, **19**, 279 (1957); G. Maier, *Chem. Ber.*, **90**, 2949 (1957); J. E. H. Hancock and H. W. Taber, *Tetrahedron*, **3**, 132 (1958); S. W. Fenton *et al.*, *J. Org. Chem.*, **23**, 994 (1958).

(4) *Cf.*, *inter alia*, (a) R. M. Lagidze and Sh. D. Kuprava, *Doklady Akad. Nauk, S.S.S.R.* **110**, 795 (1956); (b) R. M. Lagidze, N. K. Iremadze, and Sh. D. Kuprava, *Doklady Akad. Nauk, S.S.S.R.*, **121**, 470 (1958); (c) R. M. Lagidze *et al.*, *Soobshchenya Akad. Nauk, Gruzin. S.S.R.*, **25**, 19 (1960).