[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

Electrical Effects in the Biphenyl and Naphthalene Systems. The Influence of Alkyl Groups Attached to Silicon on Desilylation Reactions

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Quantitative evidence is presented for the operation of a conjugative effect between the rings of biphenyl during electrophilic substitution. Evidence for the operation of an important inductive effect in this system also is presented. The rates of desilylation of α- and β-trimethylsilylnaphthalene indicate the α-position of naphthalene to be at least four times as reactive as the beta toward electrophilic attack. These data correlate well with those obtained from carbinyl chloride solvolysis. The rates of desilylation of phenyltrimethylsilane, dimethylethylphenylsilane, triethylphenylsilane and triisopropylphenylsilane were found to decrease in the order $Me_3Si- > Me_2EtSi- > Et_3Si- >> (i\text{-}Pr)_3Si-$. A steric effect is thus clearly indicated in such cleavage reactions.

Biphenyls.—There has been a great deal of interest for a number of years in the electrical effects which are operative in the biphenyl system.[1-4] In 1928, Le Fevre and Turner[5] concluded that the two biphenyl rings function independently of one another. This conclusion was based primarily on the observation that electrophilic substitution occurs almost invariably *ortho-para* in the unsubstituted ring of a biphenyl containing a *m*-directing group. Recent work by Berliner[6-8] and co-workers has done much to clear up these early misconceptions.

It is now definitely established that the two biphenyl rings are *not* isolated electrically one from the other; however transmission of electrical effects between the rings is considerably damped. From data on the hydrolysis of certain biphenyl esters, it was estimated that electrical effects are transmitted through this system at approximately one-quarter the efficiency of transmission through a single benzene ring.[7] Because of this damping effect it is difficult at times[8] to decide whether electrical effects are transmitted *via* an inductive or a conjugative (resonance) type process. Apparently in the ground state there is little, if any, significant conjugation between the two rings.[9]

It was thought that a study of the rate of removal of the trimethylsilyl group (desilylation) from various positions in the biphenyl ring would be a convenient method for determining directly and quantitatively the electrical effects operative at these positions.[10] In this same connection we have studied the rates of desilylation of 4-trimethylsilylbiphenyl, 2′- and 4′-methyl-4-trimethylsilylbiphenyl and 2′- and 4′-chloro-4-trimethylsilylbiphenyl. The results are presented in Table I.

The reactions employed to synthesize the isomeric methyl- and chlorotrimethylsilylbiphenyls are

Sequence A (4-chloro-4′-trimethylsilylbiphenyl)

$$\text{4-nitrobiphenyl} \xrightarrow[\text{HOAC}]{Br_2} \text{4-nitro-4'-bromobiphenyl}$$

$$\xrightarrow[HCl]{SnCl_2} \text{4-amino-4'-bromobiphenyl} \xrightarrow[\text{2, } Cu_2Cl_2]{\text{1, } NaNO_2\text{–}HCl}$$

$$\text{4,4'-bromochlorobiphenyl} \xrightarrow[\text{2, } Me_3SiCl]{\text{1, } n\text{-BuLi}} \text{product}$$

Sequence B (4-methyl-4′-trimethylsilylbiphenyl)

$$p\text{-toluidine} \xrightarrow[\text{2, } C_6H_6\text{–NaOH}]{\text{1, } NaNO_2\text{–}HCl} \text{4-methylbiphenyl} \xrightarrow{Br_2}$$

$$\text{4-bromo-4'-methylbiphenyl} \xrightarrow[\text{2, } Me_3SiCl]{\text{1, } n\text{-BuLi}} \text{product}$$

Sequence C (2-chloro-4′-trimethylsilylbiphenyl)

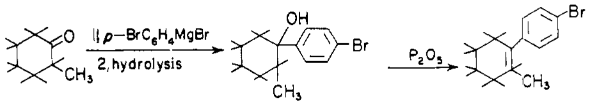
$$\text{2-nitrobiphenyl} \xrightarrow{Br_2;\ FeCl_3} \text{2-nitro-4'-bromobiphenyl}$$

$$\xrightarrow{H_2(Pt)} \text{2-amino-4'-bromobiphenyl} \xrightarrow[\text{2, } HgCl_2]{\text{1, } NaNO_2\text{–}HCl}$$

$$\text{diazonium-mercuric chloride complex} \xrightarrow[\Delta]{NH_4Cl}$$

$$\text{2-chloro-4-'-bromobiphenyl} \xrightarrow[\text{2, } Me_3SiCl]{\text{1, } n\text{-BuLi}} \text{product}$$

Sequence D (2-methyl-4′-trimethylsilylbiphenyl)



$$\xrightarrow[\text{1, } Br_2]{\text{2, }\Delta\text{, vacuum}} \text{4-bromo-2-methylbiphenyl} \xrightarrow[\text{2, } Me_3SiCl]{\text{1, } Na(Et_2O)} \text{product}$$

In sequence A, an alternate procedure for the synthesis of 4,4′-bromochlorobiphenyl was found satisfactory also. This involved the direct chlorination of 4-bromobiphenyl with sulfuryl chloride in the presence of sulfur chloride and aluminum chloride. A mixture of nitrobenzene and tetrachloroethane was employed as solvent.

$$\text{4-Bromobiphenyl} \xrightarrow[S_2Cl_2;\ AlCl_3]{SO_2Cl_2;} \text{4,4'-bromochlorobiphenyl}$$

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(1) D. Vorlander, *Ber.*, **58**, 1893 (1925).

(2) F. Bell, J. Kenyon and P. H. Robinson, *J. Chem. Soc.*, 1242 (1926).

(3) H. A. Scarborough and W. A. Waters, *ibid.*, 557 (1926).

(4) W. S. M. Grieve and D. H. Hey, *ibid.*, 2245 (1932).

(5) R. J. W. Le Fevre and E. E. Turner, *ibid.*, 245 (1928).

(6) E. Berliner and E. A. Blommers, THIS JOURNAL, **73**, 2479 (1951).

(7) E. Berliner and L. H. Liu, *ibid.*, **75**, 2417 (1953).

(8) E. Berliner, B. Newman and T. M. Liaboff, *ibid.*, **77**, 478 (1955).

(9) V. P. Kreiter, W. A. Bonner and R. H. Eastman, *ibid.*, **76**, 5770 (1954).

(10) We have since learned from Professor Eaborn (private communication) that he has undertaken a similar study. As a consequence we are curtailing this portion of our investigation.

TABLE I

RATE CONSTANTS AND HALF-LIVES FOR THE CLEAVAGE OF 4-TRIMETHYLSILYLBIPHENYLS IN GLACIAL ACETIC ACID (0.62 MOLAR IN HYDROGEN CHLORIDE AND 2.05 MOLAR IN WATER AT 25°)[a]

4-Trimethylsilylbiphenyl substituent	Rate const. × 10^3, min.$^{-1}$	Average	Half-life min. (av.)	P.R.-R.F.[b]
H	2.74, 2.76, 2.83	2.77	249	3.2
4′-CH_3	4.81, 4.73	4.77	145	5.5
4′-Cl	1.38, 1.44	1.40	495	1.6
2′-CH_3	6.40, 6.52	6.46	107	7.5
2′-Cl	0.68, 0.64	0.66	1050	0.77

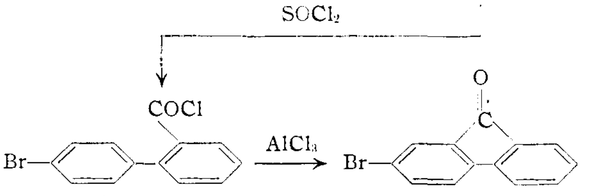
[a] The average rate constant for trimethylsilylbenzene in this medium was 8.6×10^{-4} min.$^{-1}$ which corresponds to a half-life of 805 min. [b] Based on trimethylsilylbenzene having a value of 1.0.

When nitrobenzene alone was used, the yield was lowered. The reaction failed entirely when only tetrachloroethane was employed.

In sequence C it was deemed advisable to establish the structure of 2-amino-4′-bromobiphenyl with certainty. This amine was reported previously (see ref. 25) but had not been well characterized. The structure proof was accomplished by deamination (88% yield) to the well known 4-bromobiphenyl.

In sequence D the structure of 4-bromo-2′-methylbiphenyl was determined by permanganate oxidation to the acid, followed by ring closure of the acid chloride to the known 2-bromofluorenone.

$$\text{4-bromo-2}'\text{-methylbiphenyl} \xrightarrow{KMnO_4} \text{4-bromo-2}'\text{-carboxybiphenyl}$$



Naphthalenes.—In a recent publication it was shown that the electrical effects[11,12] operative at the α- and β-positions of the naphthalene nucleus could be evaluated by studying the rates of hydrolysis of α- and β-naphthylmonomethylcarbinyl chlorides in 80% aqueous acetone. The dimethylcarbinyl chlorides, which had found widespread utility in such studies,[13] gave anomalous results in the naphthalene system, presumably because of steric interferences with the *peri* hydrogen.[11] It was of interest to determine whether similar anomalies would be found in desilylation reactions. For this purpose α- and β-trimethylsilylnaphthalenes were synthesized and their rates of acid cleavage determined. The results are given in Table II.

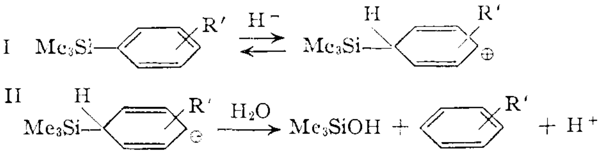
Mixed Trialkylphenylsilanes.—Considerable effort has been put forth in determining the rates of cleavage of the trimethylsilyl group from various aromatic nuclei. However, no one has studied the effect of varying the alkyl groups attached to silicon on the rate of this cleavage. In 1953, the following mechanism was proposed for the acid-catalyzed cleavage of the trimethylsilyl group[14]

TABLE II

RATE CONSTANTS AND HALF-LIVES FOR THE CLEAVAGE OF α- AND β-TRIMETHYLSILYLNAPHTHALENES IN GLACIAL ACETIC ACID (2.490 MOLAR IN HYDROGEN CHLORIDE AND 3.2 MOLAR IN WATER AT 25°)

Compound	*k* × 10^3, min.$^{-1}$	Average	Half-life min. (av.)	P.R.-R.F.[a]
$Me_3SiC_6H_5$	4.03, 3.90	3.96	176	1
1-$Me_3SiC_{10}H_7$	56.1, 57.0	56.6	12.3	14.3
2-$Ne_3SiC_{10}H_7$	12.8, 12.8	12.8	54.1	3.2

[a] The relative rates listed by Okamoto and Brown[11] for these compounds were 1, 23 and 9, respectively. Berliner and Shieh[12] report 1, 17 and 7.



III $2Me_3SiOH \longrightarrow (Me_3Si)_2O + H_2O$

Step II in this sequence was proposed as the rate-determining step, although the evidence for this decision is not unambiguous. Whether step I or II is rate determining it would seem that an increase in the size of the alkyl groups attached to silicon should decrease the rate of acid cleavage. In order to obtain quantitative information in this regard the rates of cleavage of trimethylphenyl-, dimethylethylphenyl-, triethylphenyl- and triisopropylphenylsilane under comparable conditions were determined. The results are given in Table III.

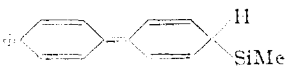
TABLE III

RATE CONSTANTS AND HALF-LIVES FOR THE CLEAVAGE OF VARIOUS TRIALKYLPHENYLSILANES IN GLACIAL ACETIC ACID (1.2 MOLAR IN *p*-TOLUENESULFONIC ACID AND 4.0 MOLAR IN WATER)

Compound	*k* × 10^4, min.$^{-1}$	Average	Half-live min. (av.)	P.R.R.F.
$Me_3SiC_6H_5$	1.25, 1.26	1.26	5500	1
$Me_2EtSiC_6H_5$	1.18, 1.20	1.19	5830	0.94
$Et_3SiC_6H_5$	0.611, 0.607	0.609	11,400	0.48
$(i\text{-}Pr)_3SiC_6H_5$	0.08	0.08	9 × 10^4	0.06

Discussion

Biphenyls.—It is apparent from Table I that 4-trimethylsilylbiphenyl is cleaved by acid three times faster than is phenyltrimethylsilane under comparable conditions. This clearly indicates that there are conjugative effects operative between the two biphenyl rings in the formation of the protonated intermediate, and is an excellent example of a situation where the phenyl ring is acting as an electron supplier.



These results are also quite consistent with the observation that biphenyl is more reactive toward

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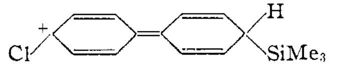
(11) Y. Okamoto and H. C. Brown, THIS JOURNAL, **79**, 1903 (1957).

(12) See also E. Berliner and N. Shieh, *ibid.*, **79**, 3849 (1957).

(13) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957); H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957); Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957).

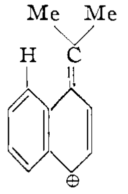
(14) C. Eaborn, *J. Chem. Soc.*, 3148 (1953).

electrophilic substitution than is benzene itself.[15,16] It is interesting to note that the 4′-chlorophenyl group still acts as an electron supplier since the chloro compound is cleaved approximately 1.6 times faster than the unsubstituted phenyl. Apparently the inductive effect of the *p*-chlorine is not sufficient to over-ride the conjugative effects of the phenyl ring.



The inductive effect of the halogen finally over-rides the conjugative effects in the 2′-chloro compound which cleaves slower than either 4′-chloro-4-trimethylsilylbiphenyl or phenyltrimethylsilane. Further evidence for the importance of inductive effects can be seen from the results of the cleavage of the 2′- and 4′-methyl (the former cleaves faster.) If there were any appreciable steric inhibition to resonance in the 2′-methyl compound it would be predicted that the 4′-methyl would cleave more rapidly, which obviously it does not. Hence steric inhibition to resonance does not seem of prime importance in the methyl system, and, by analogy, the same should be true in the case of the 2′- and 4′-chloro compounds.

Naphthalenes.—It is well known that the α-position in naphthalene is more reactive than the beta toward electrophilic substitution.[17] Okamoto and Brown[11] found, however, that both the α- and β-naphthyldimethylcarbinyl chlorides hydrolyze at approximately the same rate in aqueous acetone. They rationalized this as caused by steric hindrance to coplanarity in the case of the α-carbonium ion.



That this was a reasonable explanation is shown by their results with the α- and β-naphthylmonomethylcarbinyl chlorides. In the latter case relative rates of 1.00, 23.0 and 9.0 were obtained for the solvolysis of phenyl-, α-naphthyl and β-naphthylmonomethylcarbinyl chlorides.[11] These results are in reasonably close agreement with our values of 1.00, 14.3 and 3.2 obtained from the desilylation reactions. Since no undue complications were encountered by steric effects in the α-position it must be concluded that again desilylations seem more reliable than dimethylcarbinyl chloride solvolysis in simulating conditions encountered during electrophilic aromatic substitution.

Mixed Trialkylphenylsilanes.—It is obvious from Table III that the rate of cleavage of the trialkylsilyl group becomes slower with increasing size of the alkyl groups. This would be predicted by the Eaborn mechanism (see Introduction) regardless of the rate-determining step. It would seem logical that both the proton attack in step I and the attack by water in step II would be slowed down the bulkier the alkyl groups attached to the silicon atoms. This becomes more obvious when one realizes that the attacking species in step I is probably hydronium ion rather than a simple proton.

Rate Determinations.—The rates shown in Tables I, II and III were all obtained by volume expansion methods through the use of dilatometers. The techniques employed in such determination have been described in detail in earlier papers of this series.[18]

Experimental

4-Nitro-4′-bromobiphenyl.—A solution of 4-nitrobiphenyl in glacial acetic acid was treated with bromine, as reported by Le Fevre and Turner.[19] The yield of tan needles, melting at 170–172°, was 53%.

4-Amino-4′-bromobiphenyl.—The procedure described is an adaptation of one outlined by Le Fevre and Turner.[19] A mixture of 19.3 g. (0.069 mole) of 4-nitro-4′-bromobiphenyl, 90 ml. of glacial acetic acid, 80 ml. of concd. hydrochloric acid and 72 g. (0.383 mole) of stannous chloride was heated under reflux for 1.5 hours. During this time the nitro compound dissolved and crystals of the amine stannichloride complex separated. The crystalline slurry was cooled and the complex filtered off and washed with acetic acid and water. The crystals were then added to a solution of 35 g. of potassium hydroxide in 200 ml. of water and the slurry heated on the steam-bath for 15 minutes. The mix was then cooled and the amine filtered off and washed with water. After drying in the air, the light tan crystals had a melting point of 141–142° (reported[20] 142–143°) and were pure enough for conversion to the chloride. The yield was 16 g. (94%).

4-Chloro-4′-bromobiphenyl; Diazo Method.—A suspension of 16 g. (0.065 mole) of 4-amino-4′-bromobiphenyl in 300 ml. of water and 50 ml. of concd. hydrochloric acid was stirred in a 1-liter beaker surrounded with ice and salt while a solution of 5.5 g. (0.08 mole) (slight excess) of sodium nitrite in 30 ml. of water was added slowly below the surface. The addition took 10 minutes and the temperature was kept below 5°. The yellow suspension of diazonium salt was stirred for an additional half-hour to ensure complete reaction. In the meantime, a solution of cuprous chloride in 75 ml. of concentrated hydrochloric acid was prepared as described in reference 20 from 18.25 g. of copper sulfate pentahydrate, 4.7 g. of sodium chloride, 3.9 g. of sodium bisulfite and 2.4 g. of sodium hydroxide.

The diazonium suspension was added all at once to the cuprous chloride solution which had been cooled to 5° in a 2-liter beaker. Nitrogen evolution was brisk and froth filled the beaker. After 2 hours the mix was allowed to reach room temperature and then warmed slightly to complete the decomposition of the diazonium salt. The yellow precipitate was collected and washed with water. The crude product, m.p. 140–143°, weighed 15.6 g. (89%). Attempts at recrystallization were attended with very large losses so the material was distilled through a short path still at 1–2 mm. The solid distillate was recrystallized from acetone to give light tan needles, m.p. 153–154°. The yield of pure material was 7 g. (40%). The m.p. has been reported[5,21] as 147° and 157–158°, respectively.

4-Chloro-4′-bromobiphenyl; Chlorination Method.—This method is an adaptation of one employed by Silberrad[22] for the chlorination of benzene and toluene. A solution of 23.3 g. (0.1 mole) of *p*-bromobiphenyl in 30 ml. of tetrachloroethane and 10 ml. of nitrobenzene was treated with 0.5 g.

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(15) K. Lauer, *Ber.*, **69**, 2618 (1936); K. Lauer and R. Oda, *ibid.*, **69**, 978 (1936).

(16) B. Menschutkin, *J. Russ. Phys. Chem. Soc.*, **45**, 1710 (1913).

(17) L. F. Fieser, "Theory of the Structure and Reactions of Aromatic Compounds," Chapter 3 in "Organic Chemistry," Vol. I, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943.

(18) R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **76**, 6353 (1954); R. A. Benkeser, R. A. Hickner and D. I. Hoke, *ibid.*, **80**, 2279 (1958).

(19) R. J. W. Le Fevre and E. E. Turner, *J. Chem. Soc.*, 2041 (1926).

(20) "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 170.

(21) F. R. Shaw and E. E. Turner, *J. Chem. Soc.*, 285 (1932).

(22) O. Silberrad, *ibid.*, **27**, 2677 (1925).

of anhydrous aluminum chloride. After heating to 70°, a mixture of 1.3 g. of sulfur chloride and 13.5 g. (0.1 mole) of sulfuryl chloride was added dropwise over a 15-minute period, with efficient stirring. The mix was heated an additional 15 minutes and then allowed to cool and stand overnight. The crystals which had separated were collected and washed with acetone. The mother liquors were steam distilled to remove nitrobenzene and tetrachloroethane. Treatment of the residue with acetone afforded more of the desired product. The total yield of material, m.p. 154–155°, was 12 g. (45%). When nitrobenzene alone was used as a solvent only a 26% yield was obtained, but the reaction did not appear to proceed in the total absence of nitrobenzene due to the insolubility of the catalyst in tetrachloroethane. A mixed m.p. determination with material prepared by the diazonium procedure was undepressed.

4-Chloro-4'-trimethylsilylbiphenyl.—To a solution of *n*-butyllithium prepared from 2 g. (0.286 g. atom) of lithium wire and 16.1 g. (0.118 mole) of *n*-butyl bromide in 75 ml. of ether, was added a solution of 20 g. (0.075 mole) of 4-chloro-4'-bromobiphenyl in 150 ml. of dry benzene. The addition was made at 10° over a period of 15 minutes. After stirring an additional hour, a solution of 8.5 g. (0.079 mole) of chlorotrimethylsilane in 24 ml. of benzene was added dropwise while the temperature was maintained below 30°. The mixture was then allowed to stir for another five hours at room temperature. After pouring onto water, the ether layer was separated, dried over magnesium sulfate, and evaporated to dryness on a steam-plate. The solid residue was recrystallized from 95% ethanol to give 14 g. (72%) of white needles, m.p. 114–115°.

Anal. Calcd. for $C_{15}H_{17}ClSi$: Si, 10.75. Found: Si, 10.50.

4-Trimethylsilylbiphenyl.—To a solution of *n*-butyllithium prepared from 1.7 g. (0.24 g. atom) of lithium wire and 13.7 g. (0.1 mole) of *n*-butyl bromide, in 75 ml. of ether, was added a solution of 15 g. (0.064 mole) of 4-bromobiphenyl in 75 ml. of ether. The addition took 15 minutes. After stirring at room temperature for one hour, a solution of 7.0 g. (0.064 mole) of chlorotrimethylsilane in 20 ml. of ether was added dropwise, while the temperature was maintained at 25°. The resulting mixture was stirred at room temperature for an additional 2 hours. After working up in the usual manner, there was obtained 9.5 g. (65%) of a viscous oil, boiling at 160–161° (6 mm.), which soon solidified, m.p. 49–50°.[23]

4-Methylbiphenyl was prepared from *p*-toluidine and benzene in a Gomberg reaction essentially as described by Gomberg and Pernert.[24] The yield of material (m.p. 43–45°) suitable for further work was 18%.

4-Methyl-4'-bromobiphenyl.—The procedure was that of Gomberg and Pernert.[24] The yield of product melting at 129–131° was 45%; m.p. reported 133°.

4-Methyl-4'-trimethylsilylbiphenyl.—To a solution of *n*-butyllithium, in 100 ml. of ether, prepared from 2 g. (0.286 g. atom) of lithium wire and 16.1 g. (0.118 mole) of *n*-butyl bromide, was added a benzene solution of 20 g. (0.081 mole) of 4-methyl-4'-bromobiphenyl. The addition took 10 minutes and the temperature was kept at 15°. After stirring for half an hour, a solution of 8.5 g. (0.079 mole) of chlorotrimethylsilane in ether was added dropwise while the temperature was maintained at 25°. After stirring at room temperature for 2 hours the reaction mixture was poured onto water and worked up in the usual manner to afford 18.1 g. of crude product which solidified on standing. Recrystallization from 90% ethanol afforded 12.5 g. (64%) of white needles, m.p. 66–67°.

Anal. Calcd. for $C_{16}H_{20}Si$: Si, 12.17. Found: Si, 11.93.

2-Nitro-4'-bromobiphenyl.—This procedure is a modification of that employed by Le Fevre and Turner.[19] A heterogeneous mixture of 90 g. (0.45 mole) of 2-nitrobiphenyl, 4 g. of ferric chloride and 100 ml. of water was placed in a 3-necked flask fitted with a stirrer, reflux condenser and dropping funnel. The mix was well stirred and kept at 35–40° while 96 g. (0.6 mole) of bromine was added dropwise. After stirring at 35–40° for 2 hours, the mix was allowed to stand overnight at room temperature. The next morning, stirring was started again and the two-phase mixture was heated on a steam-bath for 4 hours. The excess bromine was then allowed to escape by removing the condenser. The product was taken up in ether and washed with sodium carbonate solution. After drying over magnesium sulfate, the ether was distilled off and the residue fractionated. The fraction boiling at 195–200° (4 mm.) solidified when triturated with ethanol. The crystals were collected and washed with ethanol to afford 50 g. (40%) of product melting at 63–65°, m.p. reported[19] 65°.

2-Amino-4'-bromobiphenyl Hydrochloride.—A solution of 35 g. (0.126 mole) of nitro compound in 100 ml. of glacial acetic acid was reduced in a Parr hydrogenator at 60 lb. pressure in the presence of 100 mg. of platinum oxide catalyst. The theoretical amount of hydrogen was taken up in 5 hours. The catalyst was filtered off and 15 ml. of concd. hydrochloric acid added to the filtrate. Addition of a large quantity of ether then precipitated the hydrochloride which was collected after 3 hours and washed with ether. The yield of white crystals was 26.5 g. (76%), m.p. 215–217°. Recrystallization from dilute hydrochloric acid afforded white needles,[25] m.p. 220–222°.

Calcd. for $C_{12}H_{11}NBrCl$: neut. equiv., 284. Found: neut. equiv., 278.

Deamination of 2-Amino-4'-bromobiphenyl.—A solution of 1 g. of 2-amino-4'-bromobiphenyl in 25 ml. of glacial acetic acid and 20 ml. of 50% hypophosphorous acid was treated with a slight excess of solid sodium nitrite. After a few moments nitrogen was evolved, the solution became warm and crystals began to separate. After standing one hour the crystals were collected and washed with 50% acetic acid. They were identified as 4-bromobiphenyl, m.p. and mixed m.p. with authentic material 88–90°. The filtrate deposited a second crop of this material on dilution with water. The total yield of 4-bromobiphenyl was 720 mg. (88%).

4-Bromo-2'-biphenyldiazonium Chloride Mercurichloride Complex.—A solution of 11.36 g. (0.046 mole) of 2-amino-4'-bromobiphenyl hydrochloride in 30 ml. of concd. hydrochloric acid and 600 ml. of warm water was cooled to 5°. The hydrochloride separated as a fine precipitate to which 3.2 g. (0.046 mole) of sodium nitrite in 40 ml. of water was added slowly with good stirring. The salt dissolved and the solution turned yellow. After a small quantity of insoluble material was filtered off, a solution of 12.5 g. (0.046 mole) of mercuric chloride and 24 g. of calcium chloride in 100 ml. of water was added in a thin stream to the cold, well stirred, solution of the diazonium salt. The curdy, yellow precipitate was collected, washed with water and dried in the air. The yield was 22.6 g. (100%). This salt showed no evidence of decomposition on standing at room temperature for a week.

2-Chloro-4'-bromobiphenyl.—An intimate mixture of 22.6 g. of mercuric chloride complex and 50 g. of ammonium chloride was placed in a 500-ml. round-bottom flask fitted with a reflux condenser and immersed in an oil-bath. The temperature was raised slowly to 130° whence decomposition set in and spread smoothly throughout the mass. After it was heated for 2.5 hours (the temperature was raised to 150° during this time), the mass was cooled, dissolved in water and the product extracted with ether. After drying and treating with Darco G-60, the ether was removed to leave an oil which solidified on scratching. Recrystallization from aqueous ethanol gave 8 g. (75%) of white crystals melting at 49–50°.

2-Chloro-4'-trimethylsilylbiphenyl.—This preparation was conducted in the same way as that for the isomeric 4-chloro compound described above. After distilling off the solvent, however, the product was left as an oil which could not be induced to crystallize. Distillation through a Todd wire spiral column afforded a 65% yield of a colorless oil, b.p. 167–169° at 6 mm., $n^{20}D$ 1.5732.

Anal. Calcd. for $C_{15}H_{17}SiCl$: Si, 10.75. Found: Si, 10.48.

1-Methyl-2-(*p*-bromophenyl)-cyclohexene.—To a solution of *p*-bromophenylmagnesium bromide, prepared from 123.6 g. (0.525 mole) of *p*-dibromobenzene and 12.6 g. (0.525 g. atom) of magnesium, was added 56 g. (0.5 mole) of 2-methylcyclohexanone dropwise with good agitation. After working up in the usual manner, the crude carbinol was warmed with 35 g. of phosphorus pentoxide for dehydration. The mix was thrown into water and the organic

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(23) H. A. Clark, *et al.*, THIS JOURNAL, **73**, 3798 (1951), reported m.p. 50–51° and b.p. 131° (1 mm.).

(24) M. Gomberg and J. C. Pernert, *ibid.*, **48**, 1372 (1926).

(25) D. H. Hey, *et al.*, *J. Chem. Soc.*, 2892 (1951).

phase extracted with ether. After drying over magnesium sulfate, the ether was removed and the residue distilled to afford 78 g. (62%) of product boiling at 155–160° (8 mm.).

Anal. Calcd. for $C_{13}H_{15}Br$: C, 62.1; H, 5.97. Found: C, 62.3; H, 5.82.

2-Methyl-4′-bromobiphenyl.—Dehydrogenation of the olefin described above was accomplished by a method developed by v. Braun, *et al.*,[26] for similar compounds.

To a solution of 50 g. (0.2 mole) of 1-methyl-2-(*p*-bromophenyl)-cyclohexene in 500 ml. of chloroform, kept at 0°, was added 32 g. (0.2 mole) of bromine dropwise. After the addition, the chloroform was distilled off and the residue heated at a bath temperature of 170–180° and at the full vacuum of the oil-pump. Hydrogen and hydrogen bromide were evolved and the substituted biphenyl distilled over. After washing with carbonate and drying over magnesium sulfate the oil was distilled to give 30 g. (63%) of the desired product boiling at 303–306°.[27]

Oxidation of a small quantity of this material with neutral permanganate gave an acid which was cyclized *via* the acid chloride and aluminum chloride to 2-bromofluorenone, m.p. 148–149°.[27]

An attempt at dehydrogenating the olefin with chloranil led to only a very low yield of the biphenyl.

2-Methyl-4′-trimethylsilylbiphenyl.—A mixture of 22 g. (0.089 mole) of 2-methyl-4′-bromobiphenyl and 10.8 g. (0.1 mole) of chlorotrimethylsilane was added dropwise to 5 g. (0.22 g. atom) of sodium sand in 100 ml. of ether. After most of the bromide had been added, the solution began to reflux and the sodium turned dark blue. Refluxing continued spontaneously for 40 minutes. After this, heat was applied and the mixture was refluxed for an additional 3 hours. Working up in the usual manner gave 11 g. (52%) of silane boiling at 295°, which gave a negative Beilstein test for halogen.

Anal. Calcd. for $C_{16}H_{20}Si$: C, 80.0; H, 8.35; Si, 11.66. Found: C, 79.85; H, 8.71; Si, 11.50.

Isolation of Cleavage Products.—A solution of 10 g. (0.044 mole) of 4-trimethylsilylbiphenyl in 150 ml. of the cleaving medium was allowed to stand at room temperature for a week. After pouring into an excess of water, the mixture was extracted thoroughly with ether. After drying over magnesium sulfate, the ether was removed and the residue distilled. There was obtained 2.8 g. (73%) of hexamethylethyldisiloxane, b.p. 98°, $n^{20}_{\rm D}$ 1.3776, and 4.5 g. (66%) of biphenyl, b.p. 253–256°, m.p. 70°.

Trimethyl-1-naphthylsilane was prepared by the method described by Gilman and co-workers[28]; b.p. 115–116° (1 mm.), $n^{20}_{\rm D}$ 1.5806, d^{20}_4 0.981; $MR_{\rm D}$ (calcd.) 67.40, $MR_{\rm D}$ (found) 67.60.

Trimethyl-2-naphthylsilane was prepared from 2-naphthyllithium and trimethylchlorosilane; b.p. 93–95° (0.5 mm.), $n^{20}_{\rm D}$ 1.5613, d^{20}_4 0.968; $MR_{\rm D}$ (calcd.) 67.40, $MR_{\rm D}$ (found) 67.08.

Anal. Calcd. for $C_{13}H_{16}Si$: Si, 14.02. Found: Si, 13.63.

Dimethylethylphenylsilane.—Over a period of 4 hours 150 ml. of anhydrous ether containing phenylmagnesium bromide (from 19.5 g. (0.8 g. atom) of magnesium and 73.5 ml. (0.7 mole) of bromobenzene) was added to 103 g. (0.8 mole) of dimethyldichlorosilane. This mixture was heated to reflux during this addition. The ether was then distilled off and the residue refluxed overnight. Approximately 0.9 mole of ethereal ethylmagnesium bromide was added, and the solution again was refluxed overnight.

The product was hydrolyzed with water and worked up in the usual fashion. It was distilled through a Todd continuous wire spiral column and 19 g. of a middle cut was collected for the kinetic work; b.p. 195°, $n^{20}_{\rm D}$ 1.4938, d^{20}, 0.878; $MR_{\rm D}$ (calcd.) 54.73, $MR_{\rm D}$ (found) 54.47. The compound was reported previously,[29] and these constants given: $n^{20}_{\rm D}$ 1.4928, d^{20}_4 0.877.

Anal. Calcd. for $C_{10}H_{16}Si$: C, 73.09; H, 9.28. Found: C, 73.10, 73.08; H, 9.89, 9.98.

Triethylphenylsilane was prepared from ethylmagnesium bromide and phenyltrichlorosilane in the usual manner. The sample used for the kinetic studies had b.p. 73° (1 mm.), $n^{20}_{\rm D}$ 1.5025, d^{20}_4 0.893; $MR_{\rm D}$ (calcd.) 63.96, $MR_{\rm D}$ (found) 63.63. The compound was reported previously[29] with the constants $n^{20}_{\rm D}$ 1.5024, d^{20}_4 0.891.

Triisopropylphenylsilane was prepared from phenyltrichlorosilane and isopropyllithium. The sample used for kinetic studies had b.p. 95° (4 mm.), $n^{20}_{\rm D}$ 1.5104, d^{20}_4 0.904. The reported[30] constants were $n^{20}_{\rm D}$ 1.5105, d^{20}_4 0.905.

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[26] J. V. Braun, G. Irmisch and J. Nelles, *Ber.*, **66B**, 1471 (1933).

[27] M. Gomberg and J. Pernert, THIS JOURNAL, **48**, 1372 (1926), report a b.p. of 303–305° for 2-methyl-4′-bromobiphenyl prepared by a diazo coupling method. They converted this material to 2-bromofluorenone, m.p. 149°.

[28] H. Gilman, R. A. Benkeser and G. E. Dunn, THIS JOURNAL, **72**, 1689 (1950).

[29] A. Bygden, Uppsala Dissertation, Sweden, 1916; *C. A.*, **14**, 1974 (1920).

[30] H. Gilman and R. N. Clark, THIS JOURNAL, **69**, 1499 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Stereochemistry of the Conversion of Organic Chlorides to Acids by Carbonation of the Grignard Reagents[1]

BY HARLAN L. GOERING AND FRED H. MCCARRON[2]

RECEIVED NOVEMBER 4, 1957

The stereochemistry of the conversion of (a) optically active 3,3-dimethylcyclohexyl chloride, (b) *cis*-(Ia) and *trans*-3-methylcyclohexyl chloride (Ib) and (c) *cis*-(IIIa) and *trans*-5-methyl-2-cyclohexenyl chloride (IIIb) to acids by carbonation of the Grignard reagents has been examined. Under the mildest conditions that the chlorides could be converted to the Grignard reagents (refluxing ether) no stereospecificity was observed with any of these three cyclic systems. The optically active system gave completely racemic acid and in the other two systems, epimers gave products having the same configurational composition. The 3-methylcyclohexanecarboxylic acid derived from the 3-methylcyclohexyl chlorides contained 26% of the *trans* isomer and the acid derived from the 5-methyl-2-cyclohexenyl chlorides contained 68% of the *trans* isomer.

There is considerable evidence that the two-step conversions of alkyl halides to various products *via* the Grignard reagents are non-stereospecific, *i.e.*, enantiomeric and epimeric halides give the same product. It has been found in several cases that optically active halides in which the halogen atom

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[2] Shell Oil Co. Fellow 1955–1956.