sodium methoxide produced the diketone; neither the oxide I or the stereoisomeric *cis*-benzalacetophenone oxide[6] could be isolated from either of the reaction mixtures. It will be noted that the conversion of the *threo* chlorohydrin IIIb to *cis*-benzalacetophenone oxide would require the phenyl and benzoyl groups to be eclipsed; the dehydrochlorination of IIIb to yield the diketone IV involves the energetically favorable staggered orientation of the benzoyl and phenyl groups.

The fluorohydrin which was formed by the reaction of the oxide I with boron trifluoride in ether[7] was found to undergo the same reactions as the chlorohydrin IIIb. The fluorohydrin, m.p. 113–114°, has therefore, been assigned the *threo* configuration V.

EXPERIMENTAL

Preparation of the chlorohydrins. A solution of 1.0 g. (0.0045 mole) of *trans*-benzalacetophenone oxide in 25 ml. of anhydrous ether, cooled in an ice-bath, was saturated with hydrogen chloride. The mixture was allowed to stand in an ice-bath for 75 minutes, and then was washed with cold water, dried over magnesium sulfate, and concentrated under reduced pressure. The residual yellow oil crystallized from ether-petroleum ether mixture. Recrystallization from hexane afforded the *threo* chlorohydrin IIIb as white prisms, m.p. 70–72°, yield 0.51 g. (43%). An additional recrystallization sharpened the melting point of the product to 71–72°. The infrared spectrum[8] of the product has bands at 3510 cm.$^{-1}$ (O—H), 1695 cm.$^{-1}$ (conjugated C=O) and 1115 cm.$^{-1}$ (C—O of a secondary alcohol).

The *erythro* chlorohydrin IIIa was prepared according to the procedure of Widman,[1] a reaction time of 75 minutes being employed. The product crystallized from hexane as white prisms, m.p. 105–107° (lit.[1] 106–107°), yield 44%. The infrared spectrum[8] of the product resembles closely the spectrum of the *threo* isomer in all regions of the spectrum; diagnostic bands are found at 3510 cm.$^{-1}$ (O—H), 1690 cm.$^{-1}$ (conjugated C=O) and 1115 cm.$^{-1}$ (C—O of a secondary alcohol).

Reactions with alcoholic sodium acetate. Solutions of 0.5 mmole of the compounds tested at 82 mg. (1.0 mmole) of sodium acetate in 10 ml. of 95% ethanol were refluxed for the appropriate times, diluted with water, and cooled. After any *trans*-benzalacetophenone oxide (identified by a mixture melting point with an authentic sample) present had been removed the solutions were treated with 100 mg. (0.55 mmole) of *o*-phenylenediamine dihydrochloride, boiled for 30 minutes, and cooled. Any 2-benzyl-3-phenylquinoxaline (identified by a mixture melting point with an authentic sample)[1] present was collected on a filter and recrystallized from aqueous ethanol if necessary. The results are summarized in Table I.

TABLE I

REACTIONS OF THE HALOHYDRINS WITH ALCOHOLIC SODIUM ACETATE

Compound	Reaction time, Min.	Yield of oxide I, %	Yield of the quinoxaline of IV, %
IIIa	35	—	10
	180	32	26
IIIb	35	—	61
V	35	—	54
I	35	91	—
	180	92	—

Reactions with alcoholic sodium methoxide. Cold solutions of the compounds to be tested in 10 ml. of absolute ethanol were treated with one equivalent of sodium methoxide as described by Wasserman and Aubrey.[4] A 0.5-mmole sample of the *erythro* chlorohydrin IIIa (m.p. 105–107°) produced *trans*-benzalacetophenone oxide (72% yield), the reaction time being of 20 minutes. Samples (1.0 mmole) of the *threo* chlorohydrin IIIb (m.p. 71–72°) and the *threo* fluorohydrin V were allowed to react for periods of both 20 minutes and 60 minutes. In no case could either of the benzalacetophenone oxides be isolated. After a 60 minute reaction period the fluorohydrin V produced 2-benzyl-3-phenylquinoxaline (28% yield) accompanied by the unchanged fluorohydrin (18% recovery). The analogous reaction with the chlorohydrin IIIb produced 2-benzyl-3-phenylquinoxaline (27%).

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[6] The preparation of this compound has been described by H. H. Wasserman and N. E. Aubrey [*J. Am. Chem. Soc.*, **77**, 590 (1955)].

[7] H. O. House, *J. Am. Chem. Soc.*, **78**, 2298 (1956).

[8] Determined in carbon tetrachloride solution with a Baird double beam infrared recording spectrophotometer, model B, equipped with a sodium chloride prism.

Some *m*-Biphenylyl-Substituted Silicon Compounds

HENRY GILMAN AND GLEN LICHTENWALTER

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In connection with the investigation of monomeric organosilicon compounds having special thermal properties, a number of *m*-biphenylyl-substituted silicon compounds has been prepared. A similar group of *p*-biphenylyl-substituted compounds has recently been synthesized[1] by condensing chlorosilanes and *p*-chlorobiphenyl with sodium in ether by a method similar to that used by Schumb and co-workers[2] in the preparation of tetraphenylsilane.

In our preparation of the *m*-biphenylyl-substituted compounds, chlorosilanes were reacted with *m*-biphenylyllithium which was prepared from the interaction of *m*-bromobiphenyl with lithium wire in ether. The preparation of *m*-biphenylyllithium was patterned after the preparation of *o*-biphenylyllithium.[3]

The totally aromatic compounds listed in Table II were all crystalline solids with the exception of phenyl-tri-*m*-biphenylylsilane which formed a supercooled liquid. Attempts to crystallize this glass-like material from common solvents were unsuccessful, although an apparently amorphous powder with

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[1] L. Spialter, D. C. Priest, and C. W. Harris, *J. Am. Chem. Soc.*, **77**, 6227 (1955).

[2] W. C. Schumb, J. Ackerman, and C. M. Saffer, *J. Am. Chem. Soc.*, **60**, 2486 (1938).

[3] H. Gilman and K. Oita, *J. Org. Chem.*, **20**, 862 (1955).

no distinct melting point was obtained using *n*-butanol. Further attempted crystallizations from *n*-butanol yielded a solid which reverted to a glass between 50° and 60°. This glass did not become fluid until heated to about 100°.

The *m*-biphenylyl derivatives containing aliphatic groups were highly viscous oils with the exception of those containing trimethylsilyl groups which were quite fluid and considerably lower-boiling. *m,m'-bis*-Trimethylsilylbiphenyl was prepared by the reaction of *m,m'*-dilithiobiphenyl with trimethylchlorosilane.

The melting points of the various *m*-biphenylyl-substituted and *p*-biphenylyl-substituted phenyl silanes are given in Table I.

TABLE I

MELTING POINTS OF *m*-BIPHENYLYL-SUBSTITUTED AND *p*-BIPHENYLYL-SUBSTITUTED PHENYL SILANES

Compound	M.p., °C. *x* = *m*	 *x* = *p*
(1) $(x\text{-}C_6H_5C_6H_4)_4Si$	137–137.5	283–285
(2) $(x\text{-}C_6H_5C_6H_4)_3SiC_6H_5$	Amorphous	Dimorphic 155–155.5 172.5–174
(3) $(x\text{-}C_6H_5C_6H_4)_2Si(C_6H_5)_2$	134–134.5	169–170
(4) $x\text{-}C_6H_5C_6H_4Si(C_6H_5)_3$	128–129	158.5–159

It is of particular interest to note that the abnormally high melting point of (1) in the *p*-series is not observed in the *m*-series.

Because the melting points of the *m*-biphenylyl-substituted series were very similar, mixture melting points of all combinations of (1), (3), and (4) were taken, and a significant depression was noted in each case. These mixture melting point ranges were as follows: (1) and (3), 118–125°; (1) and (4), 110–124°; (3) and (4), 112–123°.

EXPERIMENTAL[4]

m-Biphenylyllithium. To a stirred suspension of 1.37 g. (0.197 g. atom) of finely-cut lithium wire in 50 ml. of anhydrous ether was added over a 30-minute period 20 g. (0.086 mole) of *m*-bromobiphenyl in 300 ml. of ether. Addition was accompanied by a spontaneous reflux and the formation of a deep-red coloration of the solution. After complete addition the reaction mixture was refluxed for three hours. Yields of 75–80% were indicated by a single acid titration.

The following reaction for the preparation of tetra-*m*-biphenylylsilane is described in detail, and this general procedure was used for the preparation of the other compounds listed in Table II. In the case of the oils listed, a distillation under reduced pressure was carried out using a modified Vigreux column in an electrically heated air-oven.

Tetra-m-biphenylylsilane. To a stirred solution of 200 ml. (0.05 mole) of *m*-biphenylyllithium was added rapidly 1.7 g. (0.01 mole) of silicon tetrachloride in 30 ml. of ether. Vigorous refluxing accompanied the addition as well as the

TABLE II

PHYSICAL CONSTANTS AND RELATED DATA FOR *m*-BIPHENYLYL-SUBSTITUTED SILICON COMPOUNDS

Compound	Yield, %	B.p. °C.	 Mm.	M.p., °C.	n_D^{20}	d_{20}^{20}	MR[a] Calc'd	 Expt'l	Silicon Calc'd	 Found	Recrys. Solvent	Chlorosilane, Mole	$m\text{-}C_6H_5\text{-}C_6H_4Li$, Mole
$(m\text{-}C_6H_5C_6H_4)_4Si$	45			137–137.5					4.38	4.37	Benzene–ethyl acetate	0.01	0.05
$(m\text{-}C_6H_5C_6H_4)_3SiC_6H_5$	68	285–295	0.001	[e]					4.96	4.68, 4.76	[e]	.0172	.0643
$(m\text{-}C_6H_5C_6H_4)_2Si(C_6H_5)_2$	56			134.5–135					5.74	5.87	Ethyl acetate	.018	.036
$(m\text{-}C_6H_5C_6H_4)Si(C_6H_5)_3$	62			128–129					6.82	6.98, 7.02	Ethyl acetate	.036	.0257
$(m\text{-}C_6H_5C_6H_4)_3Si\text{-}n\text{-}C_{18}H_{37}$	65	300–310	.0005		1.5948	1.030	241.6	243.0	3.79	3.86		.0141	.053
$(m\text{-}C_6H_5C_6H_4)_3Si\text{-}n\text{-}C_{12}H_{25}$	78	310–315	.01		[b]	[b]			4.28	4.37		.0121	.0453
$m\text{-}C_6H_5C_6H_4Si(CH_3)_3$	75	170–172	20		1.5684	0.990	74.5	75.0				.043	.0477
$(m\text{-}C_6H_5C_6H_4)_3Si\text{-}O\text{-}Si(C_6H_4\text{-}C_6H_5)_3$	50			219.5–220					5.67	5.67, 5.67[d]	Benzene	.0082[f]	.0687
$m,m'\text{-}(CH_3)_3SiC_6H_4C_6H_4Si(CH_3)_3$	72	103–104	.005		1.5480	0.950	99.8	98.2	18.8	18.2, 18.5[c]		.071	.032

[a] The values used for the calculated MR are those of Warrick, *J. Am. Chem. Soc.*, **68,** 2455 (1946). [b] Because of its very high viscosity, neither the refractive index nor the density could be measured accurately. [c] Analysis for silicon in *m,m'*-trimethylsilylbiphenyl was by the Parr Bomb technique, Parr Bomb Manual No. 121. [d] A semimicro technique similar to that described by Miller, Doctoral Dissertation, Iowa State College, 1950, was used. [e] Compound is amorphous (see introduction). [f] Hexachlorodisiloxane was used in this reaction.

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[4] All reactions were carried out under a dry, nitrogen atmosphere using oven-dried glassware. All melting points are uncorrected.

[5] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47,** 2002 (1925).

formation of a heavy precipitate. After refluxing in ether for 24 hours, benzene was added, and solvent was distilled until the reaction temperature was about 50°. After refluxing at this temperature for three hours, Color Test I[6] was negative. The reaction mixture was hydrolyzed with water, and the organic layer was separated and dried over sodium sulfate. Removal of solvent yielded 6.4 g. (45.3%) of crystals, m.p. 133.5–137°. Two recrystallizations from a benzene-ethyl acetate mixture gave white needles, m.p. 137–137.5°.

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Synthesis of 2,5-Diaminoethylbenzene and Some Hazards Involved Therein

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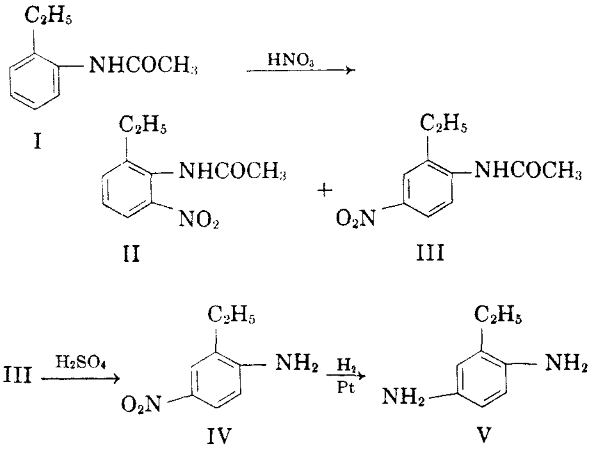
For the preparation of a sizable quantity of 2,5-diaminoethylbenzene, heretofore uncharacterized, the following scheme appeared practicable:



Hansch[1] has reported that the nitration of I (100 g.) gives a mixture of II and III from which, after hydrolysis, the free amines can be separated by tedious steam distillation (40 liters of distillate). 2-Amino-3-nitroethylbenzene (17.6 g.) appears in the distillate with a small quantity of IV from which it is purified by chromatography and the 5-isomer (IV) appears (26.5 g.) in the residue contaminated with some tar. In our attempts to scale up this preparation, certain hazards were encountered and improvements in the purification of the 5-isomer were achieved.

When 250 g. of I was nitrated according to the procedure of Hansch, by dropwise addition of fuming nitric acid to an acetic acid solution of I, at 50–55°, the reaction got out of control and the solution erupted out of the flask spewing acid out in all directions. The size of the charge was reduced to 100 g. of I and although more than a dozen successful runs were made, the reaction got out of control in one experiment even though the temperature was being carefully regulated. The reaction should be run with good stirring and the dropwise addition of the 150 ml. of fuming nitric should take about 0.5 hour and should be only fast enough to keep the temperature in the desired range without appreciable external cooling. Suitable isolation and shielding of the reaction system should, of course, be employed.

After sulfuric acid hydrolysis of the nitrated mixture, the dark red solution was decanted from a black tar and the solution was allowed to cool, whereupon a brown solid separated. This precipitate was separated, air-dried, extracted with ether, and suspended in sodium bicarbonate solution. The precipitate then was filtered and found to be essentially pure 2-amino-5-nitroethylbenzene.

Since our isolation procedure gave pure IV and the previous work indicated almost as much isomeric 2-amino-3-nitroethylbenzene might be present, the decanted tar secured above was investigated in an attempt to isolate the 2,3-isomer. The tar was transferred to a distilling flask and an *in vacuo* distillation attempted. After a few drops of distillate had been secured, the tar erupted, thrusting the thermometer out of the flask and filling the room with copious dense brown fumes. No further investigation was made of the tar.

Platinum oxide-catalyzed reduction of an ethanol solution of IV gave 2,5-diaminoethylbenzene, the only diaminoethylbenzene which has not been previously characterized.

EXPERIMENTAL

Nitration of 2-acetylaminoethylbenzene (I). A solution of 100 g. of I in 180 ml. of glacial acetic acid and 40 ml. of fuming nitric acid (*d.* 1.50) in a three-necked flask containing an unsealed stirrer, dropping-funnel, and thermometer was warmed to 50° with stirring. There then was added 150 ml. of fuming nitric acid, dropwise, at such a rate that the temperature was kept at 50–55° while the flask was occasionally cooled with a shallow ice-water bath. The rate of addition cannot be too slow, otherwise the temperature falls and too much unreacted nitric acid accumulates. On the other hand, too rapid addition also leads to difficulties, already described above. The addition should take about 0.5 hour. After the addition of all the nitric acid, the mixture was kept at 50–55° for 1.5 hours and then poured into 1 l. of ice-water. After 1 hour, the precipitate was filtered off, suspended in a sodium bicarbonate solution, and stirred for 15 minutes. The bicarbonate suspension was filtered and the precipitate was air-dried, leaving 72 g. (56.5 percent) of mixed acetylaminonitroethylbenzenes.

2-Amino-5-nitroethylbenzene (IV). A mixture of 100 g. of the crude nitrated product described above, 80 ml. of con-

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(1) C. Hansch, *J. Org. Chem.*, 20, 1026 (1955).