[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SCIENTIFIC LABORATORY OF THE FORD MOTOR COMPANY]

Coupling Reactions of Xylylene Dihalides and Trimethylchlorosilane with Magnesium in Tetrahydrofuran

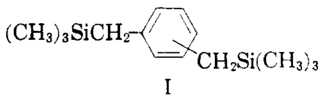
GLENN R. WILSON, GRETCHEN M. HUTZEL, AND ARTHUR G. SMITH

Received September 29, 1958

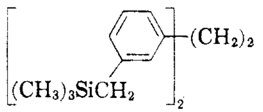
The preparation of three new organosilicon compounds—the *m*- and *p*-isomers of bis(trimethylsilyl)xylylene and 3,3'-bis(trimethylsilylmethyl)bibenzyl, from the coupling action of magnesium on the respective isomeric xylylene dihalides and trimethylchlorosilane in tetrahydrofuran, are reported.

The preparation of α,α'-disubstituted derivatives of xylene *via* the coupling of xylylene dihalides and other reactive organohalogen compounds with magnesium has received only scant attention in the chemical literature. Hersh,[1] in 1952 in a patent, described the preparation of bis-(trichlorosilyl)-*o*-xylylene (physical properties not given) by first treating *o*-xylylene dichloride with magnesium in ethyl ether followed by reaction with silicon tetrachloride. This would infer that a stable di-Grignard intermediate had been formed. Mann and Stewart,[2] in 1954, were unable to confirm Hersh's findings and isolated only poly-*o*-xylylene from the reaction of *o*-xylylene dichloride with magnesium. Attempts by these latter investigators[2] to couple *o*-xylylene dihalides with phenyldichlorophosphine by allowing them to react simultaneously with magnesium in ethyl ether likewise yielded only poly-*o*-xylylene and not the desired phenylphosphindoline. By converting the *o*- and *m*-xylylene dihalides to the respective chloromethylbenzyl ethers, Mann and Stewart[2] were able to convert only the *m*-substituted ether to a stable Grignard intermediate.

In the present instance, we wished to prepare the *m*- and *p*-isomers of bis(trimethylsilyl) xylylene (I) by an unequivocal route.



I



II

Chernyshev, *et al.*[3] had reported the synthesis of an intermediate, bis(methyldichlorosilyl)-xylylene, (from reacting benzene with chloromethylmethyldichlorosilane in the presence of aluminum chloride) that could be methylated to give bis(trimethylsilyl) xylylene; however, this intermediate was a mixture of isomers whose respective concentrations and separations were not disclosed.

As a starting point, we investigated the feasibility of coupling *p*-xylylene dihalides and trimethylchlorosilane with magnesium. None of the dihalides (dichloride, dibromide, and diiodide), reacted separately, or in the presence of large excesses of trimethylchlorosilane, with magnesium in solvents such as ethyl ether, di-*n*-butyl ether or *p*-dioxane to give the desired compound but instead yielded poly-*p*-xylylene. The reaction was quite sluggish and the magnesium became coated with the insoluble polymer.

We then investigated the reaction of *m*-xylylene dibromide with magnesium and changed the solvent to tetrahydrofuran. The reaction was quite vigorous and rapid and upon completion, trimethylchlorosilane was added. The product isolated from this reaction was a low-melting polymer (molecular weight 1850–1900), containing only traces of silicon and bromine, whose elemental analysis indicated that it was poly-*m*-xylylene (consisting of approximately 18 xylene units). Since no stable di-Grignard intermediate was formed, the experiment was repeated except that the *m*-xylylene dibromide was reacted with magnesium in the presence of trimethylchlorosilane. From this latter reaction we obtained the desired bis(trimethylsilyl)-*m*-xylylene. The yield was 32–33% whether a large excess or an equivalent quantity of trimethylchlorosilane was used. A second compound was also isolated and identified as 3,3'-bis(trimethylsilylmethyl)bibenzyl (II).

Using the same technique we were also able to prepare bis(trimethylsilyl)-*p*-xylylene from coupling *p*-xylylene dichloride with trimethylchlorosilane.

Both isomers were identified by their elemental analyses and the substitutions verified by their respective infrared absorption spectra (reproduced in Figs. 1 and 2). The meta isomer was a liquid and the para isomer a low melting (61–63°) solid.

These reactions clearly demonstrate the versatility of tetrahydrofuran, over other ethereal solvents, for conducting coupling reactions of the type illustrated. Although no stable di-Grignard intermediates of *m*- and *p*-xylylene dihalides could be prepared for subsequent reactions, the tetrahydrofuran enables one to force a coupling reaction in the desired direction to a much greater extent

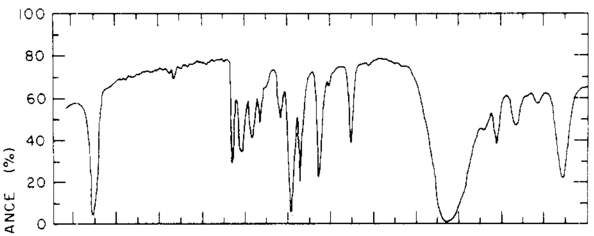
---

[1] J. M. Hersh, U. S. Patent **2,615,033** (1952).

[2] F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2826 (1954); F. G. Mann, I. T. Millar, and F. H. C. Stewart, *J. Chem. Soc.*, 2832 (1954).

[3] E. A. Chernyshev, M. E. Dolgaya and P. Egorov, *Zhur. Obshchei Khim.*, **27**, 2676 (1957).

Fig. 1. Bis(trimethylsilyl)-*p*-xylylene



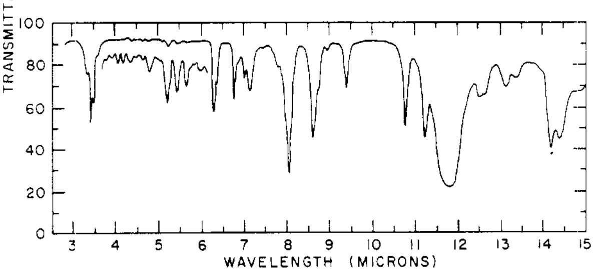


Fig. 2. Bis(trimethylsilyl)-*m*-xylylene

than was possible in the other ethereal solvents tried and thus provides a convenient and unequivocal route to the preparation of otherwise difficult-to-prepare α,α'-disubstituted xylenes.

EXPERIMENTAL

Starting materials: m-Xylylene dibromide. Eastman Kodak (Practical Grade). Recrystallized from ethanol, m.p. 76–77°. *p-Xylylene dichloride.* Eastman Kodak (White Label). *Trimethylchlorosilane.* Dow Corning. Redistilled through a 36-in. packed column and stored over Molecular Sieves, Type 4A. *Tetrahydrofuran.* Matheson, Coleman and Bell.

Further purification by distillation from lithium aluminum hydride and stored over calcium hydride. Traces of moisture or hydroxy compounds must be rigidly excluded due to reaction with the chlorosilane and subsequent reaction with the tetrahydrofuran.

Apparatus. All subsequent reactions were carried out in a 3-necked, round bottom flask equipped with a condenser, stirring assembly, addition funnel, and nitrogen inlet. All reactions were conducted under a dry nitrogen flush and protected from moisture.

Reaction of m-xylylene dibromide with magnesium in tetrahydrofuran followed by addition of trimethylchlorosilane. A solution of 61 g. (0.23 mole) of *m*-xylylene dibromide in 200 ml. of tetrahydrofuran was added to a stirred suspension of 11 g. (0.45 g.-atom) of magnesium chips (previously activated with iodine vapor) in 50 ml. of tetrahydrofuran. Reaction started immediately and the solution added at a rate sufficient to maintain gentle reflux. After stirring and refluxing for 2 hr., 50 g. (0.46 mole) of trimethylchlorosilane was added (little or no heat of reaction was noted) and the mixture stirred and refluxed for 3 hr. Upon cooling, 100 ml. of benzene was added, the mixture washed with water, the organic layer dried over Molecular Sieves, Type 4A, filtered, and distilled to remove solvents and low boiling materials.

The residue solidified upon cooling and extraction with acetone left an insoluble residue that melted at 65–75°. Attempts to crystallize the material from solvent mixtures were unsuccessful and yielded a viscous oil that solidified only after all traces of solvent were removed.

The elemental analysis and molecular weight agree with that calculated for poly-*m*-xylylene containing approximately 18 xylene units.

Anal. Calcd. for $C_{144}H_{146}$: C, 92.16; H, 7.84; mol. wt. 1877. Found: C, 91.41, 91.50; H, 8.02, 8.11; Si, trace; Br, trace; mol. wt., 1850, 1900.

The infrared spectrum of the polymer verified meta substitution and also exhibited weak bands at 8.05 and 11.80–11.90μ characteristic of Si—CH_3 and Si—C linkages, due probably to trimethylsilyl end groups.

Bis(trimethylsilyl)-m-xylylene. A. *Reaction of m-xylylene dibromide, in the presence of an excess of trimethylchlorosilane, with magnesium.* A mixture of 40 g. (0.15 mole) of *m*-xylylene dibromide and 130.3 g. (1.2 mole) of trimethylchlorosilane was reacted with 7.3 g. (0.3 g.-atom) of magnesium as described in the preceding experiment. After refluxing for 2 hr., the mixture was concentrated to remove unreacted trimethylchlorosilane and a portion of the solvent at which time the magnesium halide salts separated. The liquid portion was decanted from the salts and the latter washed with ethyl ether. The decanted liquid and washings were combined and distilled to remove solvents and the residue fractionated at reduced pressures. Five liquid fractions were collected of which fractions 3 and 4 constituted 11.9 g. (32% yield), b.p. 73–74° (0.6 mm.), n_D^{20} 1.4919 and 1.4920 respectively.

Anal. Calcd. for $C_{14}H_{26}Si_2$: C, 67.13; H, 10.46; Si, 22.40. Found: Fraction 3: C, 67.24; H, 10.20; Si, 22.60. Fraction 4: C, 67.13; H, 10.43; Si, 22.50.

The residue, a viscous, dark-colored oil, weighed 6.0 g.

B. *Reaction of m-xylylene dibromide, in the presence of an equivalent quantity of trimethylchlorosilane, with magnesium.* A solution of 52.1 g. (0.20 mole) of *m*-xylylene dibromide in 180 ml. of tetrahydrofuran was added to 9.6 g. (0.40 g.-atom) of magnesium chips suspended in a solution of 42.9 g. (0.40 mole) of trimethylchlorosilane and 200 ml. of tetrahydrofuran over a period of 2 hr. followed by refluxing for 19.5 hr.

Water, 200 ml., was added to the reaction mixture followed by 300 ml. of toluene. The organic layer was separated, dried, filtered; the solvents removed, and the residue fractionated. The fraction boiling at 66–66.5° (0.3 mm.) weighed 16.6 g. (33.7% yield), n_D^{20} 1.4919. The infrared absorption spectrum of this product was identical with that from (A).

Anal. Calcd. for $C_{14}H_{26}Si_2$: C, 67.13; H, 10.46; Si, 22.40. Found: C, 67.41, 67.48; H, 10.22, 10.29; Si, 22.85, 22.56.

Further distillation of the residue (17.0 g.) yielded 3.5 g. of liquid, b.p. 139–142° (0.65 mm.), n_D^{20} 1.5270, whose elemental analysis agreed with that calculated for 3,3'-bis(trimethylsilylmethyl)bibenzyl (II). The infrared absorption spectrum also supported the structure indicated by II.

Anal. Calcd. for $C_{22}H_{34}Si_2$: C, 74.51; H, 9.66; Si, 15.83. Found: C, 74.84; H, 9.20; Si, 16.04.

Bis(trimethylsilyl)-p-xylylene. A mixture of 35 g. (0.20 mole) of *p*-xylylene dichloride and 174 g. (1.6 mole) of trimethylchlorosilane in 200 ml. of tetrahydrofuran was added to 9.7 g. (0.40 g.-atom) of magnesium chips suspended in 50 ml. of tetrahydrofuran and reacted in the manner described in the preceding experiments.

The precipitated magnesium chloride was removed by centrifugation and the filtrate distilled to remove solvent and unreacted trimethylchlorosilane. The residue, partially crystalline upon cooling, was dissolved in hot ethanol, treated with charcoal, and filtered. Upon cooling, white needle-like crystals separated; however, these melted over a wide range and the crude product was distilled at reduced pressures. The fraction collected at 73–74° (0.3 mm.) melted at 61–63°.

Anal. Calcd. for $C_{14}H_{26}Si_2$: C, 67.13; H, 10.46; Si, 22.40. Found: C, 67.20, 67.06; H, 10.42, 10.30; Si, 22.14, 22.31.

Infrared spectra. The infrared spectra, reproduced in Figs. 1 and 2, were recorded on a Perkin-Elmer Infracord, Model 137. The spectrum of the *m*-isomer was taken from a film and a capillary (0.05 mm.) to resolve the 5–6μ region and the spectrum of the *p*-isomer was taken from a Nujol mull.

Acknowledgments. The preparation of these compounds was conducted under the sponsorship of the United States Air Force under Contract AF 33(600)-32448, monitored by Materials Laboratory, Director of Laboratory, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors also wish to express their gratitude to Dr. Harold Rosenberg for his helpful advice.

DEARBORN, MICH.

[RESEARCH DIVISION CONTRIBUTION NO. 275, JACKSON LABORATORY ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

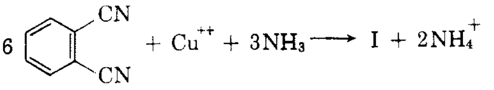
Chemistry of Copper Phthalocyanine Precursor

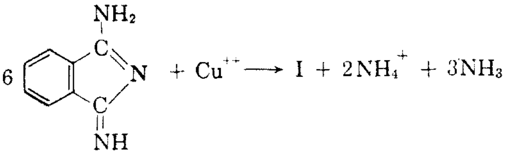
R. A. BROOKS, J. G. BURT, B. F. SKILES, AND M. S. WHELEN

Received October 1, 1958

The preparation and properties of a precursor of formula $C_{48}H_{25}N_{13}Cu$ which generates copper phthalocyanine upon reduction are discussed. A structure for the precursor is proposed.

Copper phthalocyanine precursor is the name given to a buff colored compound I of empirical formula $C_{48}H_{25}N_{13}Cu$ which generates copper phthalocyanine (II) upon reduction. I is formed by reaction under oxidizing conditions of phthalonitrile, ammonia and a cupric salt in dimethylformamide at about 90° or by reaction of 1-amino-3-iminoisoindolenine and a cupric salt under similar conditions. The yield by the phthalonitrile route is improved by the addition of a small amount of *N*-methylglucamine, the role of which has not been determined.





I is very soluble in dimethylformamide and in alcoholic solvents such as ethylene glycol monoethyl ether. It has limited solubility in benzene and is insoluble in aliphatic hydrocarbons. I is usually amorphous but can be crystallized from benzene. Stirring in a small amount of methyl alcohol also converts the amorphous material to a crystalline form[1] the x-ray diffraction pattern of which is reproduced in Fig. 1.

Unlike II, which is highly colored, I exhibits only very weak absorption in the visible region of the spectrum. The ultraviolet and infrared spectra are reproduced in Figs. 2 and 3, respectively.

When in crystalline form, I is quite stable and can be stored for long periods at room temperature. Its solutions decompose in a few days, especially in sunlight, to give copper phthalocyanine and other products of lower molecular weight.

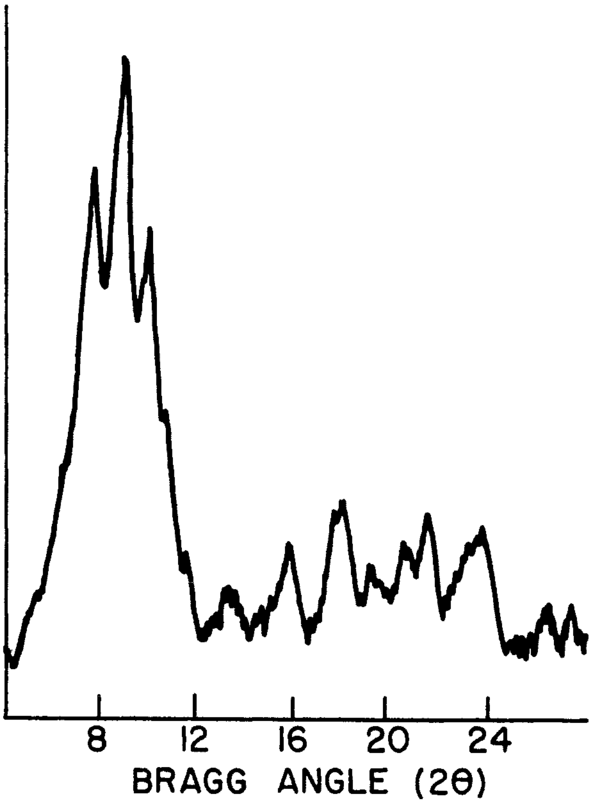


Fig. 1. X-ray diffraction pattern of copper phthalocyanine precursor

Reduction of I is easily effected with a large number of agents. The weight yield of II is 68%, the remaining weight being accounted for as ammonia and derivatives of phthalic acid. Hydrogenation over palladium indicates that reduction is a 2 electron process. Reduction with hot, alkaline glucose shows that 5 moles of ammonia are liberated. Pyrolysis of I at 180° gives about a 65% yield of II with liberation of 1 mole of ammonia and 2 moles of phthalonitrile. The slightly lowered

---

(1) M. S. Whelen, U.S. Patent 2,795,586, June 11, 1957; *Chem. Abstr.*, 51, 17184(1957).