15 minutes while cooling in ice. Then 1.8 g. of *p*-quinone dibenzenesulfonimide was added all at once. The mixture was allowed to warm up to room temperature and stirred for 1.25 hours, then permitted to stand for several hours. It was poured into excess of hydrochloric acid and ice and the precipitate collected by filtration. The crude green product was digested with 5% aqueous sodium hydroxide, the solution filtered and the filtrate acidified with hydrochloric acid. The gray-white material was recrystallized from glacial acetic acid, m.p. 246-247° (dec.). The alkali-insoluble material proved to be undissolved product and was recrystallized from glacial acetic acid (Darco). The total yield was 0.8 g. (30.5%). The melting point of the mixture of this product with that formed by method A showed no depression. The infrared spectra of the products prepared by methods A and B were identical.

2-[9-(10-Bromoanthryl)]-*p*-phenylenedibenzenesulfonamide.—A mixture of 0.56 g. of 2-(9-anthryl)-*p*-phenylene-1,4-dibenzenesulfonamide, 0.16 g. of bromine, and 5 ml. of glacial acetic acid was warmed on a steam-bath for 2 hours. The product was then collected by filtration and weighed 0.4 g. (63%). It was recrystallized from glacial acetic acid; light-yellow crystals, m.p. 234-235° (cor.) (dec.).

Anal. Calcd. for $C_{32}H_{23}BrN_2O_4S_2$: C, 59.72; H, 3.60. Found: C, 59.47; H, 3.75.

This same compound was formed on bromination of samples of 2-(9-anthryl)-*p*-phenylenedibenzenesulfonamide produced either by methods A or B.

2-(9-Anthryl)-*p*-phenylenedimethanesulfonamide.—A mixture of 1.25 g. of *p*-quinone dimethanesulfonimide and 1.0 g. of anthracene in 7 ml. of acetic acid was heated under gentle reflux for 2 hours. On cooling a white solid separated. The yield was 2.0 g. (95%). It was recrystallized by adding water to a hot acetone solution until incipient cloudiness, m.p. 239-240° (cor.) (dec.).

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2$: C, 59.98; H, 4.58; N, 6.36. Found: C, 59.93; H, 4.74; N, 6.64.

Triptycene-2,5-dibenzenesulfonamide.—A solution of 21 g. of 2,5-triptaquinone[2] and 80 g. of hydroxylamine hydrochloride in 1900 ml. of ethanol was boiled for 2 hours. The product, formed by pouring the reaction mixture into water, did not appear to be pure.

A mixture of 2 g. of this product with 5.5 g. of hydroxylamine hydrochloride in 25 ml. of water was brought to the neutral point with 10% aqueous sodium hydroxide (about 30 ml.). Ethanol was added until complete solution was effected and the mixture then heated on a steam-bath for 1 hour. Ethanol was evaporated off until crystallization started, the mixture was cooled, and water added. The product weighed 1.7 g. After purification from glacial acetic acid it melted at 243° (cor.) (dec.).

The dioxime was reduced according to the directions of Bartlett.[2] The diamine dihydrochloride begins to darken above 224-229° (cor.) and then gradually decomposes. According to Bartlett the diamine dihydrochloride gradually decomposes above 210°.

A suspension of 0.5 g. of the diamine dihydrochloride in 15-20 ml. of 10% aqueous sodium hydroxide was treated with 0.5 g. of benzenesulfonyl chloride and the mixture stirred and allowed to stand for an hour before heating on a steam-bath for 1 hour. After cooling, it was acidified with hydrochloric acid and filtered. The white precipitate was purified by crystallization from glacial acetic acid, m.p. 298° (dec.).

Anal. Calcd. for $C_{32}H_{24}N_2O_4S_2$: C, 68.06; H, 4.28. Found: C, 67.96; H, 4.46.

Triptycene-1,4-dimethanesulfonamide.—To 0.5 g. of triptycene-1,4-diamine dihydrochloride in 15 ml. of pyridine was added 1.0 g. of methanesulfonyl chloride and the mixture allowed to stand overnight. It was then poured into ice and hydrochloric acid, and the product collected on a filter. After recrystallization from a 1:1 acetone-water mixture, the compound was pure; it gradually decomposed above 360°. The yield was 0.5 g. (70%). The compound was quite hygroscopic.

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2$: C, 59.98; H, 4.58. Found: C, 59.80; H, 4.60.

Reaction of Bicyclohexenyl with *p*-Quinone Dibenzenesulfonimide.—A mixture of 1 g. of *p*-quinone dibenzenesulfonimide and 0.4 g. of bicyclohexenyl in 7 ml. of *n*-butyl alcohol (or glacial acetic acid) was refluxed for eight hours. On cooling, the product, weighing 0.5 g., separated. After recrystallization from glacial acetic acid, it melted at 251-252.5° (cor.) (dec.) and proved to be *p*-phenylenedibenzenesulfonamide.

Reaction of 1,3-Diphenylisobenzofuran with *p*-Quinone Dibenzenesulfonimide.—A mixture of 0.5 g. of diphenylisobenzofuran and 0.7 g. of *p*-quinone dibenzenesulfonimide in 15 ml. of ethanol was heated under reflux for 5 hours. Complete solution gradually occurred. On cooling, a white crystalline product separated. The yield was 0.5 g. (94%). It was recrystallized from ethanol, m.p. 145° (cor.). The product proved to be *o*-dibenzoylbenzene, which did not depress the melting point of an authentic sample. Apparently an oxidation reaction had occurred rather than a Diels-Alder reaction.

URBANA, ILL. RECEIVED AUGUST 2, 1950

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[2] P. D. Bartlett, THIS JOURNAL, **64**, 2649 (1942).

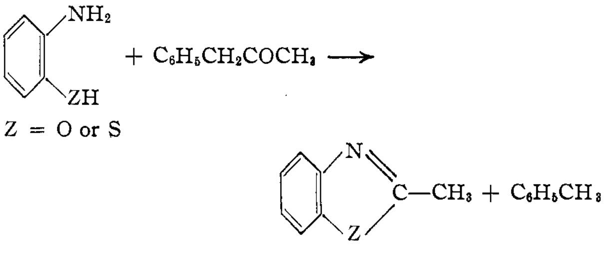
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF ST. JOHN'S UNIVERSITY]

Reaction of Benzyl Methyl Ketone with *o*-Aminophenol, *o*-Aminobenzenethiol and 1,8-Naphthalenediamine

BY FRANK J. KREYSA, VINCENT F. MATURI, JOHN J. FINN, JOHN J. McCLARNON AND FLORA LOMBARDO

Direct heating of *o*-aminophenol, *o*-aminobenzenethiol and 1,8-naphthalenediamine with benzyl methyl ketone results in the formation of toluene and aromatic heterocyclic rings, *i.e.*, 2-methylbenzoxazole, 2-methylbenzothiazole and 2-methylperimidine, respectively.

The formation of benzimidazoles, presumably *via* intermediate benzimidazolines, when *o*-phenylenediamine or its monoalkyl derivatives are heated with ketones[1] suggests that similar formation of oxazole, thiazole and perimidine derivatives should occur from *o*-aminophenol, *o*-aminobenzenethiol and 1,8-naphthalenediamine, respectively. These derivatives have been found to be formed when the above substances were heated with benzyl methyl ketone, *e. g.*



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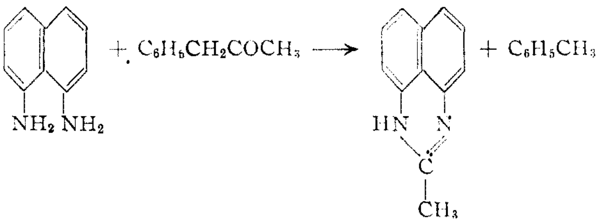
[1] Elderfield, Kreysa, Dunn and Humphreys, THIS JOURNAL, **70**, 40 (1948); Elderfield and Kreysa, *ibid.*, **70**, 44 (1948).



Toluene was identified as one of the products of the reactions.

Experimental[2]

Reaction of *o*-Aminophenol with Benzyl Methyl Ketone.—A mixture of 11 g. (0.1 mole) of *o*-aminophenol and 27 g. (0.2 mole) of benzyl methyl ketone was heated for 6 hours in a flask equipped with an inside thermometer and a condenser set downward for distillation. The temperature of the mixture was rapidly raised so that approximately 200° was reached in the first hour; then heating was continued at a slower rate until 250° was reached at the end of 6 hours.

The slightly yellow distillate (10 g.) which collected in the ice-cooled receiver consisted of two layers. The lower layer (1-2 g.) was found to be water which had formed in the course of the reaction. The entire distillate was then taken up in 25 ml. of ether and dried over anhydrous sodium sulfate. The filtered ether solution was fractioned and the fraction boiling at 110-111° (3 g.) was identified as toluene by oxidation to benzoic acid with potassium permanganate.

The dark brown viscous residue in the reaction flask was further distilled under reduced pressure and the fraction coming over at 135-145° at 114 mm. (10 g.) was crude 2-methylbenzoxazole in 70% yield.

The picrate prepared from this crude material melted at 117-118° and was identified by mixed m.p. with an authentic sample.[3]

Condensation of Benzyl Methyl Ketone with *o*-Aminobenzenethiol.—Nine grams (0.072 mole) of *o*-aminobenzenethiol[4] was mixed with 15 g. (0.11 mole) of benzyl methyl ketone in a flask fitted with an inside thermometer and a condenser set for distillation. The temperature was slowly raised until approximately 250° was reached at the end of 6 hours. The amount of volatile distillate obtained under these conditions was so small that it was not further investigated.

The residue in the reaction flask, subjected to distillation *in vacuo*, yielded 5 g. of a fraction boiling at 120-123° at 20 mm. The picrate prepared from this fraction melted at 153-154° and was identified as 2-methylbenzothiazole picrate by mixed m.p. with an authentic sample.[5]

Condensation of Benzyl Methyl Ketone with 1,8-Naphthalenediamine.—A mixture of 4.74 g. (0.03 mole) of 1,8-diaminonaphthalene[6] and 5 g. (0.047 mole, 20% excess) of benzyl methyl ketone was heated in a small distilling apparatus equipped with a capillary gas inlet tube extending to the bottom, and a receiver cooled by Dry Ice. Nitrogen streaming through this capillary furnished agitation and protected the amine from oxidation. The mixture was heated as before so that a temperature of approximately 315° was obtained at the end of 6 hours.

The distillate (about 2 ml.) collected in the frozen state was first thawed at room temperature into a liquid mixture with two layers; it was then taken up in ether, dried with anhydrous sodium sulfate and fractionated. The fraction boiling at 110-111° (0.5 g.) was identified as toluene by oxidation to benzoic acid with potassium permanganate.

The brown resinous residue in the distilling flask was soluble in alcohol, chloroform, acetone and dioxane. A portion dissolved in hot dioxane was precipitated by pouring into an equal volume of chloroform. The resulting green solid precipitate melted at 210-214° and was identified as 2-methylperimidine[7] by two mixed melting point determinations; *i.e.*, the free perimidine and its oxalate[8] (m.p. 230-232°) with authentic samples.

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(2) All melting points are corrected.

(3) Ladenburg, *Ber.*, **9**, 1524 (1876); Phillips, *J. Soc. Chem. Ind.*, **56**, 474T (1937); Wagner, *J. Org. Chem.*, **5**, 139 (1940).

(4) Hofmann, *Ber.*, **13**, 1230-1231 (1880); *ibid.*, **30**, 2260 (1887); Gardner, British Patent 558,877 (1944).

(5) Ochiai and Nisizawa, *J. Pharm. Soc. Japan*, **60**, 132-140 (1940) [*C. A.*, **34**, 5082 (1940)].

(6) Wagner, *J. Org. Chem.*, **5**, 136 (1940); Leonard and Hyson, THIS JOURNAL, **71**, 1961 (1949). In our preparation we modified the procedure of Wagner: The 1,8 dinitronaphthalene was extensively purified by several recrystallizations and finally a suspension reduced in ethanol with palladium or platinum oxide catalyst in a Parr hydrogenator The reduction took place in a few minutes and the yield was nearly quantitative.

(7) Sachs, *Ber.*, **39**, 3027 (1906).

(8) Sachs, *Ann.*, **365**, 90 (1909).

BROOKLYN 6, N. Y RECEIVED AUGUST 7, 1950

[CONTRIBUTION FROM THE RAYON TECHNICAL DIVISION, E. I. DU PONT DE NEMOURS & CO.]

Reaction of Perfluoroalkyl Chlorides with Silicon

BY E. F. IZARD AND STEPHANIE L. KWOLEK

An attempt has been made to prepare perfluoroalkyl silicon halides by the direct thermal addition of perfluoroalky chlorides to silicon and silicon copper alloy at various temperatures. Below 400°, in which temperature range alkyl halides react, no reaction takes place with the perfluoro compounds. At higher temperatures, 500-1000°, an exothermic reaction takes place but is not addition to silicon to form perfluoro silicon chlorides but appears to be a complete transfer of halogen from carbon to silicon. The volatile reaction products appear to be silicon halides and carbon has been identified in the silicon bed. The smoothness of the reaction suggests that it may be possible to develop the reaction into an analytical method for removing fluorine and other halogens from carbon in volatile fluoro carbons.

Introduction

Recent chemical literature has abundant references to the preparation of various alkyl silicon chlorides and their derivatives which are intermediates in the formation of the alkyl silicones from which the various silicone resins are derived. In recent books Post[1] and Rochow[2] have reviewed the literature of recent years. In general there are two methods for the preparation of these silicone intermediates. An alkyl halide may be converted to a Grignard reagent and this reagent reacted with a silicon compound such as tetraethyl silicate or silicon tetrachloride and the intermediates thus formed converted into alkyl silicon derivatives and ultimately to silicone resins.

The other route is the direct reaction of an alkyl halide with silicon, usually in the form of a silicon-copper alloy. In this case the alkyl halide adds directly to the silicon and the primary reaction product is dialkyl dichlorosilane. By disproportionation this compound may be converted

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(1) H. W. Post, "Silicones and Other Organic Silicon Compounds," Reinhold Publishing Corp., New York, N. Y., 1949.

(2) Eugene G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley & Sons, Inc., New York, N. Y., 1946.