posed of 25 g. (0.10 mol.) of sodium sulfide nonahydrate, 8 g. (0.1 mol.) of sodium bicarbonate, 60 ml. of water, and 40 ml. of methanol. When one half of this mixture had been added, another 2.4 g. (0.028 mol.) of sodium bicarbonate was added to the reaction mixture in one lot. The addition of the sulfide-bicarbonate solution was carried out over a 1.5 hr. period. After that, the reaction was refluxed for an additional 0.5 hr. and allowed to cool. A rust-colored material precipitated from the dark solution. It weighed 1.4 g. (20%). Recrystallization from 40% aqueous ethanol gave material of m.p. 119–120°. Another recrystallization from 50% aqueous ethanol gave matted, orange needles melting at 118.5–119°. A mixed m.p. with an authentic sample of 3-amino-5-nitroanisole (Lit. m.p. 118°)[8] was not depressed.

Anal. Calcd. for $C_7H_8N_2O_3$: C, 50.00; H, 4.84; N, 16.66. Found: C, 49.75; H, 4.79; N, 16.95.

Another crop of crystalline material weighing 2.1 g. was obtained from the original reaction solution. This substance melted at 100–115° after a recrystallization from water containing a small amount of ethanol. Further recrystallizations from other solvents did not change this m.p. The material appeared to be a mixture of two or more compounds, one of which is probably the aminonitroanisole. It was not purified further.

3,5-Dinitroanisole. To a hot solution of 10 g. (0.047 mol.) of 1,3,5-trinitrobenzene in 150 ml. of methanol, was added a slurry of 12.8 g. (0.15 mol.) of sodium bicarbonate in a mixture of 60 ml. of water and 40 ml. of methanol. The red mixture was refluxed and stirred for 2.5 hr. and allowed to cool over a period of several hours. The tan crystals which precipitated were filtered and dried in a desiccator. Recrystallization from 200 ml. of hot methanol gave 5.5 g. (60%) of nearly colorless product, m.p. 104–106°. This melting point was not depressed by admixture with an authentic sample of 3,5-dinitroanisole (Lit. m.p. 105°).[3] Additional crystalline fractions were obtained from the mother liquors indicating a higher yield of product. These fractions, however, were not brought to a constant melting point.

When the reaction was run with potassium bicarbonate a more easily purified product melting at 104–106° was obtained in 86% yield, while sodium carbonate (0.15 mol. under the same conditions as described above) gave the product in 70% yield.

Attempted reactions with sodium acetate, dibasic sodium phosphate dodecahydrate, sodium iodide, ammonium carbonate, and carbon dioxide. A mixture of 0.05 mol. of 1,3,5-trinitrobenzene, 0.15 mol. of the requisite salt, and 250 ml. of 76% aqueous methanol was refluxed for 3 hr. In all cases, at least 70% of the trinitrobenzene was easily recovered by cooling the reaction mixture and washing the pale yellow crystals with water and cold methanol. The identity of starting material was shown by mixed m.p.'s.

In the case of the carbon dioxide experiment, this gas was bubbled through a boiling 76% aqueous methanol solution of trinitrobenzene for 3 hr. The recovery of the starting material was quantitative.

Behavior of 1,3,5-trinitrobenzene with strong alkali. To a hot solution of 10 g. (0.05 mol.) of 1,3,5-trinitrobenzene in 150 ml. of methanol was added 6 g. (0.15 mol.) of sodium hydroxide dissolved in a mixture of 60 ml. of water and 40 ml. of methanol. The dark red solution was stirred under reflux for 3 hr. No crystalline product was obtained from the black, amorphous reaction product.

Behavior of 1,3,5-trinitrobenzene with sodium bicarbonate in the presence of potassium iodide. To a hot solution of 10 g. (0.05 mol.) of 1,3,5-trinitrobenzene in 150 ml. of methanol was added a slurry of 12.8 g. (0.15 mol.) of sodium bicarbonate and 16.6 g. (0.1 mol.) of potassium iodide in a mixture of 60 ml. of water and 40 ml. of methanol. The red mixture was stirred under reflux for 2.5 hr., and cooled. A crystalline material precipitated which was filtered and recrystallized from 100 ml. of methanol. The crystals weighed 3.7 g. and melted at 104–106°. A mixed m.p. with an authentic sample of 3,5-dinitroanisole was not depressed. The original reaction solution was evaporated to about one-half volume whereupon another 1.6 g. of crude crystals was obtained. Two recrystallizations from ethanol gave a compound melting at 120–122°, which by mixed m.p. was shown to be unreacted 1,3,5-trinitrobenzene. The mother liquor was concentrated further to a small, dark, aqueous solution, which was extracted with ether several times. Evaporation of the ether gave a negligible amount of solid which was recrystallized from ethanol and melted at 120–122°. A mixed m.p. with 1,3,5-trinitrobenzene was not depressed. The yield of 3,5-dinitroanisole calculated on recovered TNB was 47%.

Attempted reaction of m-dinitrobenzene with sodium carbonate. To a solution of 4 g. (0.024 mol.) of *m*-dinitrobenzene in 75 ml. of methanol was added a suspension of 8 g. of sodium carbonate (0.075 mol.) in a mixture of 30 ml. of water and 20 ml. of methanol. No color change occurred. The mixture was stirred under reflux for 2.5 hr. and cooled in ice. The precipitated crystals were filtered and recrystallized from aqueous ethanol giving 4 g. of crystals melting at 89–90°. This m.p. remained undepressed by admixture with authentic *m*-dinitrobenzene.

Attempted reaction of 3,5-dinitroaniline with sodium bicarbonate. A 1 g. (0.005 mol.) sample of 3,5-dinitroaniline (m.p. 161–162°)[9] was dissolved in 15 ml. of not methanol. A slurry of 1.3 g. (0.015 mol.) of sodium bicarbonate in a mixture of 6 ml. of water and 7 ml. of methanol was added, and the reaction was refluxed for 3 hr. On cooling, yellow crystals precipitated. These were filtered and air-dried, giving 0.9 g. of material melting at 159–161°. A mixed m.p. with 3,5-dinitroaniline was not depressed.

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(8) J. J. Blanksma, *Rec. trav. chim.*, **24**, 40 (1905).

(9) Prepared by the method of J. J. Blanksma and G. Verberg, *Rec. trav. chim.*, **53**, 988 (1934).

Synthesis of 2,4,5-Trichloro-Cl^{36}-phenol

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2,4,5-Trichlorophenol is a versatile compound in agricultural pest control, appearing in many products either as such, or as an integral part of some other chemical molecule. Our investigations required the use of the chlorine-36 labeled compound; since it was not available, its synthesis was undertaken.

Because we had a quantity of the compound[1] 1,2,4,5 - tetrachloro - *1-Cl^{36}* - benzene, the obvious

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(1) R. W. Meikle, *J. Org. Chem.*, **24**, 277 (1959).

pathway to 2,4,5-trichloro-Cl^{36}-phenol was through hydrolysis.[2]

EXPERIMENTAL

2,4,5-Trichloro-Cl^{36}-phenol. The compound[1] 1,2,4,5-tetrachloro-*1*-Cl^{36}-benzene (84.8 mg., 0.39 mmol., specific activity 20.8 μc./mmol.) and 2 ml. of 5*M* sodium hydroxide in methanol[3] were sealed in a Pyrex test tube (1.4 × 14 cm.). The atmosphere in the tube was dry nitrogen. The tube was put in a Parr high-pressure bomb together with sufficient methanol to equalize the pressure within the tube. The bomb was heated without shaking for a total of 5 hr.[4,5] and then cooled as rapidly as possible under tap water. Fifty min. was required for the temperature of the bomb to reach the operating temperature of 160°.

As soon as the bomb was cool, the tube was removed. Sodium chloride was visible as a precipitate in the bottom of the tube. The contents were quantitatively transferred to a steam distillation apparatus (commonly used for Kjeldahl nitrogen determinations) and any unreacted starting material or such by-products as trichloroanisole, or both, were removed by steam distillation. None of these compounds were found in the first 30 ml. of distillate. The reaction mixture was then acidified with dilute sulfuric acid and again steam distilled until 60 ml. of distillate had been collected. The 2,4,5-trichloro-Cl^{36}-phenol sublimed very rapidly. The distillate was extracted with methylene chloride, and the extracts were dried over a minimal amount of anhydrous magnesium sulfate.

The 2,4,5-trichloro-Cl^{36}-phenol was isolated by evaporating the solvent through a column of glass tubing 0.6 × 84 cm.[7] The yield of product was 69 mg. (89%); the specific activity was 15.6 μc./mmol. The m.p. of the product was 66° (for unlabeled compound, lit.[2] 66°). The infrared absorption spectrum of the compound was identical with that of unlabeled 2,4,5-trichlorophenol, and a mixed m.p. with an authentic specimen thereof showed no depression in melting point.

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(2) W. S. W. Harrison, A. T. Peters, and F. M. Rowe, *J. Chem. Soc.*, 235 (1943).

(3) 1.1*M* Potassium hydroxide in Carbitol was also investigated as a hydrolyst, but this system was not nearly so efficient as the methanolic sodium hydroxide in the conversion.

(4) During the course of preliminary work it was found that the effect of reaction time on the yield of product was quite marked: as the time of reaction increased beyond the optimum of 5 hr., the yield decreased. This showed that the product was being subjected to hydrolysis or methanolysis, or both, resulting in the formation of polyphenols and some or all of their methyl esters. However, the method of isolation was such that these by-products could not have been detected, and no attempt was made to isolate them.

(5) Trichloroanisole is to be expected as a by-product in the methanolic sodium hydroxide hydrolysis of 1,2,4,5-tetrachlorobenzene. Holleman[6] found the anisole derivative, but he used a higher temperature (180° instead of 160°) and a longer time (12 hr. instead of 5 hr.). No trichloroanisole was detected when the shorter reaction time and lower temperature were used.

(6) A. F. Holleman, *Rec. trav. chim.*, **39**, 736 (1920).

(7) It was found in preliminary work that the use of a 1.4 × 20-cm. Vigreux column resulted in a loss of 5-6 mg. of product.

Aryl and Aryl-alkyl Isocyanosilanes[1]

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Alkylisocyanosilanes have been prepared by Eaborn[2] and by McBride and Beachell.[3] While the present work was in progress, the first arylisocyanosilane, triphenylisocyanosilane, was reported by Bithner and co-workers.[4] The structure of these compounds has been the subject of some controversy. The "iso" structure was favored by Eaborn and by McBride and Beachell. Infrared studies have been made by Bithner and co-workers who suggest that the trialkyl compounds are temperature-dependent equilibrium mixtures of the normal and isocyanide forms. Linton and Nixon[5] studied isotopic shifts in the CN-stretching frequency of the trimethyl compound and concluded that this compound is the normal rather than the isocyanide. The Raman spectra of the trimethyl compound permitted no definite differentiation.[6]

This paper reports the preparation of diphenyldiisocyanosilane, dimethylphenylisocyanosilane, and the recently described triphenylisocyanosilane. The molar refractions of the first two compounds (dimethylphenylisocyanosilane is a liquid and diphenyldiisocyanosilane a low-melting solid with a strong tendency to supercool) are much closer to the calculated values for isocyanides than for normal cyanides.

The aryl and aryl-alkyl isocyanosilanes, like the alkyl compounds, are, with the exception of the triphenyl compound, extremely susceptible to hydrolysis and react violently with water. Triphenylisocyanosilane did not hydrolyze appreciably on standing in air for 0.5 hr. The great reactivity of the compounds is also shown by the reaction of diphenyldiisocyanosilane with the phenyl Grignard at the temperature of refluxing ethyl ether. Tetraphenylsilane was obtained in 80% yield. With diphenyldibromosilane and the phenyl Grignard under the same conditions, no tetraphenylsilane was obtained.

A new isothiocyanate, dimethylphenylsiliconisothiocyanate, and a new bromide, methylphenyldibromosilane, are described.

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(1) Florida Agricultural Experiment Stations Journal Series, No. 909.

(2) C. Eaborn, *J. Chem. Soc.*, 2757 (1949); 3077 (1950).

(3) J. J. McBride, Jr., and H. C. Beachell, *J. Am. Chem. Soc.*, **74**, 5427 (1952).

(4) T. A. Bithner, W. H. Knoth, R. V. Lindsey, Jr., and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 4151 (1958).

(5) H. R. Linton and E. R. Nixon, *J. Chem. Phys.*, **28**, 990 (1958).

(6) J. Goubeau and J. Rehying, *Z. anorg. u. allgem. Chem.*, **294**, 92 (1958).