

water, alcohol and ether to yield 9.4 g. (94%) of colorless needles melting at 212°. Recrystallization from alcohol did not raise the melting point. The amide is very soluble in acetone, but is insoluble in water, alcohol, ether and benzene.

Anal. Calcd. for $C_8H_8N_2O_4$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.16; H, 4.37; N, 14.07.

It is recommended that thionyl chloride be used for the conversion of 3-methoxy-2-nitrobenzoic acid to the acid chloride in place of phosphorus pentachloride which has been employed previously.⁶ An explosion occurred in our hands the second time we carried out this reaction with phosphorus pentachloride.

3-Methoxy-2-nitroaniline (II).—A suspension of 9.8 g. (0.05 mole) of I in 200 ml. of alkaline 0.5 *N* sodium hypochlorite solution⁷ was stirred for 3 hours at room temperature. A small amount of undissolved solid was removed, and the amber colored solution was heated. At 80° the solution became opaque, and soon thereafter yellow crystals separated. The reaction mixture was held at 80–90° for 30 minutes, and then overnight at room temperature. The precipitate was filtered off, washed with water, and dried to give 7.5 g. (89%) of bright yellow crystals, m.p. 124°. Recrystallization from benzene–ligroin gave bright yellow needles, m.p. 124–124.5°.

Anal. Calcd. for $C_7H_8N_2O_3$: C, 50.00; H, 4.80; N, 16.66. Found: C, 50.19; H, 4.88; N, 16.56.

Reverdin and Widmer⁸ have assigned the structure of II to a substance, m.p. 143°, which they obtained by hydrolysis of one of the products isolated from a mixture produced by the nitration of acetyl-*m*-anisidine. The small quantity of material they had isolated permitted no analyses. The structure of II was assigned to the hydrolysis product on the grounds that its melting point did not agree with that of any of the other possible isomers, all of which were known.

3-Methoxy-2-nitrodobenzene (III).—To a stirred suspension of 21 g. (0.125 mole) of II in 300 ml. of glacial acetic acid at 15° was added gradually an ice-cold mixture of 15 g. (0.18 mole) of potassium nitrite and 70 ml. of concd. sulfuric acid.⁹ The diazonium salt solution was poured into 650 g. of ice and water and the mixture was stirred for 30 minutes. Excess nitrous acid was destroyed by the addition of ammonium sulfamate. The clear solution was then treated with 30 g. of potassium iodide in 150 ml. of water. Gas was evolved and crystalline solid appeared. The mixture was then heated on the boiling water-bath for 1 hour. Free iodine was removed from the cooled solution by addition of sodium bisulfite. The product was filtered off, washed with cold water, and dried to yield 30.5 g. (88%) of reddish brown powder melting at 68–74°. Short-path vacuum distillation gave pale yellow crystals, m.p. 81°.

Anal. Calcd. for $C_7H_8NO_3$: C, 30.12; H, 2.17; I, 45.48. Found: C, 30.16; H, 2.61; I, 45.29.

3-Methoxy-2-nitrobenzoxitrile (IV).—A mixture of 2.7 g. (0.01 mole) of III and 0.9 g. (0.01 mole) of dry cuprous cyanide¹⁰ was heated in a flask immersed in an oil-bath at 180° for 2 hours. From the reaction mixture, 1.22 g. (70%) of tan solid, melting at 117–122°, was obtained by extraction with 25 ml. of boiling benzene and precipitation with 50 ml. of ligroin. Recrystallization from benzene and ligroin gave white needles, m.p. 122°.

Anal. Calcd. for $C_8H_8N_2O_3$: C, 53.93; H, 3.40; N, 15.73. Found: C, 54.14; H, 3.60; N, 15.63.

Hydrolysis of IV.—A mixture of 0.9 g. (0.005 mole) of IV, 2.0 g. of sodium hydroxide, 16 ml. of water and 4 ml. of alcohol was boiled under reflux for 1.5 hours. Ammonia was given off. After decolorization with charcoal, the hot solution was acidified with hydrochloric acid to give 1 g. (0.005 mole) of 3-methoxy-2-nitrobenzoic acid, m.p. 257° after one crystallization from alcohol.

BIOCHEMISTRY DIV., MEDICAL DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK

(6) M. Kotake, T. Sakan and S. Senoh, *THIS JOURNAL*, **73**, 1847 (1951).

(7) E. S. Wallis and J. F. Lane, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 281–282.

(8) F. Reverdin and K. Widmer, *Ber.*, **46**, 4073 (1913).

(9) C. Niemann and C. E. Redemann, *THIS JOURNAL*, **63**, 1550 (1941).

(10) H. J. Barber, *J. Chem. Soc.*, 79 (1943).

Diphenylcarbinylation of Methylbenzenes Using Sulfuric Acid¹

BY DONALD G. KUNDIGER AND ELWIN B. W. OVIST

RECEIVED NOVEMBER 14, 1953

Diphenylcarbinylation of aromatic nuclei using diphenylcarbinol and sulfuric acid has hitherto been restricted to phenols.² The reactivities of five methylbenzenes have now been tested using a modification of Shorigin's method of diphenylcarbinylation of phenols.² This modification succeeded with the methylbenzenes and failed with benzene and phenanthrene.

Shorigin² found that with excess diphenylcarbinol, two benzylhydril residues were introduced into the *p*-cresol nucleus. Into phenol three such groups were introduced; into *o*-cresol only one. We find that use of a tenfold excess of the hydrocarbon only gives monosubstitution products. Where both *ortho* and *para* substitution are possible, only the *para* substituted product is isolated. When the *para* position is blocked, diphenylcarbinylation occurs in the *ortho* position in about the same yield.

Our results may be compared with those of Hemilian³ who used phosphorus pentoxide and diphenylcarbinol in a refluxing toluene and xylene.

Experimental⁴

General Procedure.—Diphenylcarbinol (3.4 g.) and ten equivalents of the hydrocarbon were dissolved in 135 ml. of glacial acetic acid. To this solution 25 ml. of concentrated sulfuric acid was added dropwise with stirring and cooling. The mixture was allowed to stand, with occasional shaking, for 8 days at room temperature, then poured into ice-water and the sulfuric acid neutralized with 80 g. of sodium bicarbonate. The mixture was steam distilled to remove the unreacted hydrocarbon and acetic acid. The aqueous residue was extracted with ether, the ether evaporated, and the residue dried by distilling with benzene. The benzene solution was concentrated and passed through 20 g. of a one-to-one ratio of activated alumina (80 mesh)–Super-Cel column one to three times to remove colored impurities and unreacted diphenylcarbinol. The effluent and the benzene washings were evaporated to give 4 to 6 g. of colorless to light yellow sirup which crystallized on standing.

***p*-Diphenylcarbinyltoluene (I).**—The effluent, after the reaction with toluene, gave 4.7 g. of crude product containing solvent of crystallization, m.p. 60–63°. Two recrystallizations from ethanol gave 2.9 g. (61%) of I, m.p. 70.0–70.5° (reported m.p. 72°^{3d}).

1-Diphenylcarbiny-3,4-dimethylbenzene (II).—The effluent after the reaction with *o*-xylene gave 4.1 g. of crude product, m.p. 58–60°. Recrystallization from ethanol gave 3.78 g. (75%) of II, m.p. 67.5–68° (reported m.p. 68.5°^{3a}).

1-Diphenylcarbiny-2,5-dimethylbenzene (III).—After the reaction with *p*-xylene, the effluent gave 4.3 g. of crude product, m.p. 84–86°, which after recrystallization from ethanol gave 3.62 g. (72%) of III, m.p. 90.5–91.2° (reported m.p. 92°^{3b}).

1-Diphenylcarbiny-2,4-dimethylbenzene (IV).—After the reaction with *m*-xylene, the effluent gave 4.3 g. of crude product, m.p. 58–60°. Recrystallization from a Skelly B–ethanol–water mixture gave 3.4 g. (68%) of IV, m.p. 59–60°. Recrystallization from ethanol gave IV, m.p. 60.2–60.9° (reported m.p. 61.5°^{3c}).

Diphenylcarbiny-mesitylene (V).—After the reaction with mesitylene the product was chromatographed as a petroleum

(1) Abstracted from a portion of a Ph.D. thesis to be presented as partial fulfillment of the requirements of the degree Doctor of Philosophy in chemistry at Kansas State College.

(2) P. Shorigin, *Ber.*, **61B**, 2516 (1928). Triphenylcarbinylation of phenols along the same lines was reported by P. Shorigin, *ibid.*, **60B**, 2373 (1927).

(3) (a) W. Hemilian, *ibid.*, **19**, 3070 (1886); (b) **16**, 2360 (1883); (c) **19**, 3061 (1886); (d) **7**, 1209 (1874).

(4) All m.p.'s are uncorrected.

ether (b.p. 70°) solution. The effluent gave 6.2 g. of V, m.p. 115–119°, containing solvent of crystallization. Evacuation for 5 days gave 5.2 g. (99%) of V, a new compound, m.p. 119–120°. After recrystallization from ethanol the melting point remained at 119.0–119.5°. A second run gave the same results.

Anal. Calcd. for C₂₂H₂₂: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.72.

DEPARTMENT OF CHEMISTRY
KANSAS STATE COLLEGE
MANHATTAN, KANSAS

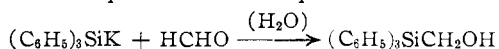
Reaction of Triphenylsilylpotassium with Formaldehyde

BY HENRY GILMAN AND T. C. WU

RECEIVED OCTOBER 3, 1953

It is generally known that an organometallic compound adds to the carbonyl group of an aldehyde or ketone to give the carbinol derivatives. Recently, however, it has been observed that when triphenylsilylpotassium is treated with benzophenone, followed by hydrolysis, the product obtained is a substituted alkoxy silane rather than the carbinol which one normally would expect.¹ In an ex-

(C₆H₅)₃SiK + C₆H₅COC₆H₅ $\xrightarrow{(H_2O)}$ (C₆H₅)₃SiOCH(C₆H₅)₂
tension of these studies to the addition reactions of triphenylsilylpotassium to a carbonyl group, we examined the reaction of triphenylsilylpotassium with formaldehyde. When a triphenylsilylpotassium suspension in ether was treated with formaldehyde for a period of one hour, a small amount of hydroxymethyltriphenylsilane was formed in addition to other products to be reported later.



In this reaction triphenylsilylpotassium reacts with formaldehyde in the same way as does triphenylmethylsodium. In the latter case β,β,β-triphenylethanol is formed.²

Experimental

A triphenylsilylpotassium suspension in ether was prepared by cleaving 0.01 mole of hexaphenyldisilane with sodium-potassium alloy, the excess of which was removed by the amalgamation procedure.³ Formaldehyde gas, generated by heating paraformaldehyde,⁴ was introduced over the surface of the stirred triphenylsilylpotassium suspension by a stream of dry nitrogen. It was observed that the brown color of the triphenylsilylpotassium suspension turned gray rapidly when the formaldehyde gas was introduced. After 1 hour the gray mixture gave a negative Color Test I.⁵ The reaction mixture was allowed to stand overnight. Ethanol was added to the reaction product and the mixture was heated and filtered hot. On standing, 0.3 g. of paraformaldehyde separated. This apparently came from the recombination of the formaldehyde. The ethanol was distilled from the mother liquor, and a mixture of water and ether was added to extract the residue. From the ethereal solution there was obtained a gummy residue. Two recrystallizations from petroleum ether (b.p. 60–70°) yielded 0.7 g. (12%) of colorless crystals melting at 116–118° (uncor.). This compound has the characteristic absorption band of a hydroxyl group, but not that of an Si–O bond,⁶ which would

have been expected if addition had occurred in the manner of addition of triphenylsilylpotassium to benzophenone.¹

Anal. Calcd. for C₁₉H₁₉OSi: C, 78.57; H, 6.24. Found: C, 78.67, 78.73; H, 6.31, 6.27.

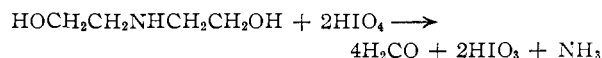
DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

On the Periodic Acid Oxidation of Diethanolamine

BY MANNING A. SMITH AND B. R. WILLEFORD, JR.

RECEIVED JANUARY 8, 1954

It has been reported by Nicolet and Shinn¹ that diethanolamine is oxidized by periodic acid to yield four moles of formic acid. The product to be expected from this reaction is formaldehyde as indicated by the equation



This work has been repeated in connection with another study,² and the consumption of two moles of periodic acid per mole of diethanolamine has been confirmed. The presence of formaldehyde in the reaction mixture has been established by the precipitation of its dimedon derivative. The error in the identification of the reaction product mentioned above has been carried over in the review of periodic acid oxidations by Jackson.³ Shupe⁴ has reported that "tests have failed to confirm the literature statement that diethanolamine yields 4 mols of formic acid," but apparently did not identify the product. The abstract of this paper⁵ contains conflicting statements concerning Shupe's work with diethanolamine, undoubtedly because of a typographical error. In view of this confusion in the literature, we feel that it is desirable to call attention to it here.

Experimental

Ten ml. of 0.1078 *M* periodic acid solution was added to 48.4 mg. (0.461 mmole) of diethanolamine. The reaction mixture was heated on a steam-bath for 2.5 hours. After cooling, solid sodium bicarbonate (0.1–0.5 g.) was added followed by an excess of standard arsenite solution and 2 ml. of 20% potassium iodide. The solution was allowed to stand for 10 minutes, and the excess arsenite was then titrated with standard iodine solution. This is the standard procedure for the determination of periodic acid described by Jackson.⁶ A consumption of 0.909 mmole of periodate by the diethanolamine was indicated. This gives a ratio of moles of periodate consumed per mole of diethanolamine of 0.909/0.461 or 1.98.

Another sample of diethanolamine (0.1059 g.) was treated with periodic acid according to the procedure of Reeves,⁷ and the formaldehyde formed was precipitated as its dimedon derivative. The white crystalline solid had a melting point of 191°. The melting point showed no depression on mixing with an authentic sample. The yield was 0.9930 g. This corresponds to 84% of the theoretical amount.

DEPARTMENT OF CHEMISTRY
BUCKNELL UNIVERSITY
LEWISBURG, PENNSYLVANIA

(1) H. Gilman and T. C. Wu, *THIS JOURNAL*, **75**, 2935 (1953).
(2) W. Schlenk and R. Ochs, *Ber.*, **49**, 608 (1916).
(3) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).
(4) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 188.
(5) H. Gilman and F. Schulze, *THIS JOURNAL*, **47**, 2002 (1925).
(6) The authors are grateful to Dr. V. A. Fassel and Mr. M. Margoshes for the infrared spectrum, and particularly to Clare W. Gerow for other assistance.

(1) B. H. Nicolet and L. A. Shinn, *THIS JOURNAL*, **61**, 1615 (1939).
(2) M. A. Smith and B. R. Willeford, Jr., *Anal. Chem.*, **26**, 751 (1954).
(3) E. L. Jackson, "Organic Reactions," Vol. II, Roger Adams, Editor, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 369.
(4) I. S. Shupe, *J. Assoc. Official Agr. Chem.*, **26**, 249 (1943).
(5) *C. A.*, **37**, 5552³ (1943).
(6) E. L. Jackson, ref. 3, p. 361.
(7) R. E. Reeves, *THIS JOURNAL*, **63**, 1476 (1941).