distilled to dryness under a vacuum. The residue was dissolved in 1500 cc. of water and treated with 50 g. of Norite at the boiling point. The filtrate was carefully acidified with glacial acetic acid. The 2-mercaptopyridine formed in bright yellow crystals which were collected, after chilling to 5°, and washed with 2 liters of ice water. The dry product weighed about 400 g. and melted at 121–124°. A further 67–77 g. (m. p. 125–128°) was obtained by extraction of the filtrate and washings by chloroform, removing the latter by distillation and crystallizing the residue from benzene. The total yield was 461–483 g. (83–87%).

COMMUNICATION NO. 1014 FROM
KODAK RESEARCH LABORATORIES
ROCHESTER 4, NEW YORK
RECEIVED OCTOBER 27, 1945

NEW COMPOUNDS

Derivatives of Mesitylene

Methyl 3,5-Dinitromesitoate.—Two grams of methyl mesitoate was added dropwise to an ice-cold mixture of 25 ml. of concentrated sulfuric acid and 25 ml. of fuming nitric acid at such a rate that the temperature did not rise above 10°. It was necessary to cool and stir continuously. The solution was kept cold for fifteen minutes and poured on cracked ice. The dinitro ester was recrystallized from methanol: yield 2.3 g. (m. p. 136–138.5°). The pure compound melted at 138.5–139.5°.

Anal. Calcd. for $C_{11}H_{12}O_6N_2$: N, 10.4. Found: N, 10.6.

α,α-Diphenylacetomesitylene. A. From the Acetone Derivative of Mesitylglycolic Acid.—A solution of 50 g. of the acetone derivative of mesitylglycolic acid[1] in 100 ml. of ether was added slowly to a solution of phenylmagnesium bromide containing approximately four times the theoretical amount of active reagent. The mixture was heated overnight under reflux and decomposed in the usual way. The product, presumably 1,1-diphenyl-2-mesitylethylene glycol, was an oil boiling at 190° (4 mm.). A 5-g. portion of the oil was heated under reflux for one hour with a mixture of 65 ml. of glacial acetic acid and 15 ml. of hydrochloric acid. When the mixture was poured on ice the α,α-diphenylacetomesitylene separated as a solid. It was recrystallized from ethanol; m. p. 152–153°; yield 4.5 g.

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.70; H, 7.04.

B. *From Diphenylacetyl Chloride.*—Twenty-seven grams of anhydrous aluminum chloride was added portionwise over a period of twenty minutes to a mixture of 29.5 g. of diphenylacetyl chloride, 15.1 g. of mesitylene and 200 ml. of carbon disulfide. The mixture was kept in an ice-bath and was stirred continuously throughout the period of addition and for seventy minutes afterward. By pouring the reaction mixture on ice the α,α-diphenylacetomesitylene was precipitated as a solid melting at 148–150°; yield 83%. It was purified by repeated recrystallization from ethanol; m. p. 152–153°.

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.50; H, 7.20.

Mesityl *p*-Phenylphenyl Ketone.—A solution of 9 g. of *p*-phenylbenzoyl chloride in 75 ml. of carbon disulfide was added slowly to a mixture of 5.5 g. of mesitylene, 6.5 g. of anhydrous aluminum chloride and 20 ml. of carbon disulfide. After the addition was completed the reaction mixture was stirred at room temperature for two hours. A portion of the solvent was evaporated and the residual mixture was poured into a mixture of ice and concentrated hydrochloric acid. The ketone, after one recrystallization from ethanol, melted at 108–110°; yield 80% of the theoretical. The melting point of the pure compound was 111–112°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.75; H, 6.77.

3,5-Dinitromesityl 4-Methyl-3-nitrophenyl Ketone.—Two grams of *p*-toluylmesitylene was dissolved in 8 ml. of concentrated nitric acid, and the mixture heated at 45° for ten minutes. The trinitro derivative, precipitated by pouring the reaction mixture on cracked ice, was recrystallized from 95% ethanol; m. p. 168–169°.

Anal. Calcd. for $C_{17}H_{15}N_3O_7$: C, 54.71; H, 4.02; N, 11.26. Found: C, 54.33; H, 4.09; N, 11.14.

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[1] Fuson and Rachlin, THIS JOURNAL, **64**, 1567 (1942).

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RECEIVED NOVEMBER 2, 1945

Di-*o*-tolylglycolic Acid

A solution of the binary mixture, Mg–MgI_2,[1] was made from 6 g. of magnesium, 30.6 g. of iodine, 120 ml. of ether and 240 ml. of benzene. To this reagent was added a solution of 20 g. of *o*-toluyl chloride in 20 ml. of ether. The mixture was heated under reflux, with stirring, for eighteen hours and treated with an ice cold solution of 20 ml. of water in 200 ml. of acetic acid. The organic layer was washed successively with 5% sodium thiosulfate solution, 10% potassium bicarbonate solution and water. After the solution had been dried the solvent was evaporated. The residual oil was mixed with a solution of 35 g. of hydrated copper sulfate in 25 ml. of water and 20 ml. of pyridine. The mixture was heated under reflux, with stirring, for four hours. The yellow *o*-tolil was distilled at 140–170° (2 mm.). It solidified and was recrystallized from ethanol; m. p. 92–94° (cor.)[2]; yield 34%.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.98; H, 6.25.

o-Tolil was found to undergo the benzilic acid rearrangement. To a solution of 10 g. of *o*-tolil in 200 ml. of ether was added a solution of 5 g. of sodium ethoxide in 40 ml. of 95% ethanol. The container was stoppered tightly and allowed to stand for twenty-four hours. The solution was extracted with 200 ml. of water. Acidification of the aqueous solution precipitated 7 g. of the **di-*o*-tolylglycolic acid.** It was recrystallized from benzene; m. p. 162–163°; yield 65%. It gave a purple color with concentrated sulfuric acid.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29; neut. equiv., 256. Found: C, 74.85; H, 6.49; neut. equiv., 251.

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(1) Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

(2) Since this work was done, *o*-tolil has been described by Kharasch, Nudenberg and Simons [THIS JOURNAL, **65**, 495 (1943)].

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A. I. RACHLIN
RECEIVED NOVEMBER 23, 1945

X-[N-(β-Acetamidoethyl)-N-methyl]-aminoazobenzene

Aniline (0.98 ml., 0.0108 mole) was dissolved in a mixture of 2.50 ml. (0.030 mole) of concentrated hydrochloric acid and about 8 ml. of water. The temperature was brought to 0° by adding ice, and the solution was diazotized at 0–5° by adding in the usual manner a solution of 0.77 g. (0.0108 mole) of 97% sodium nitrite in 1.5 ml. of water.

After the solution had been kept at 0° for ten minutes, excess nitrous acid was removed by the addition of ammonium sulfamate. The volume at this point had increased to 25–30 ml. because of occasional additions of ice. N-(2-N-Methylanilinoethyl)-acetamide[1] (2.07 g., 0.0108 mole) was added and the mixture was stirred for one hour at 0–5°, after which 1.25 g. of sodium acetate trihydrate was added, and stirring was continued two hours. After the mixture had stood an additional two hours at 0–5° a duplicate portion of sodium acetate in a little water was added, the mixture was stirred a few minutes, then left overnight in the refrigerator. After the slurry had stood at room temperature for one hour the precipitate was filtered off, washed with water and recrystallized from ethanol. The yield was 2.76 g. (86.5%) of orange-red parallelograms exhibiting occasional twinned forms with bifurcated ends: m. p. 177.5–178° (cor.). A solution of the substance in 0.1 *N* hydrochloric acid showed an absorption maximum in the visible spectrum at about 520 mμ.[2]

Anal. Calcd. for $C_{17}H_{20}N_4O$: N, 18.91. Found:[3] N, 18.79.

Attempts to remove the acetyl group by refluxing with 6 *N* hydrochloric acid resulted in deep seated changes in the molecule,[4] whereas heating with 5 *N* aqueous alcoholic alkali for seven hours gave only slight evidence of deacetylation.

In view of results repeatedly recorded for couplings involving N,N-disubstituted anilines having free *p*-positions, it is highly probable that the phenylazo group of this compound is in the *p*-position.

CHEMICAL SECTION, DRUG DIVISION
U. S. FOOD AND DRUG ADMINISTRATION
FEDERAL SECURITY AGENCY LLEWELLYN H. WELSH
WASHINGTON 25, D. C.

RECEIVED AUGUST 31, 1945

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(1) J. von Braun, *et al.*, *Ber.*, **70B**, 979 (1937).

(2) Determination by Rachel N. Sclar, Cosmetic Division, U. S. Food and Drug Administration.

(3) By Thomas H. Harris, Food Division, U. S. Food and Drug Administration.

(4) Rowe and Dangerfield, *J. Soc. Dyers Colourists*, **52**, 48 (1936), and Hodgson and Foster, *J. Chem. Soc.*, 755 (1941), have reported on the decomposition of certain azo compounds by mineral acids.

COMMUNICATIONS TO THE EDITOR

DIETHYLSILANEDIOL

Sir:

Although organosilanediols have been known for forty years[1,2] no dialkylsilanediol has been reported. The non-isolation of this type compound was generally attributed to rapidity of intermolecular condensation.[3] Hydrolysis studies on diethyldichlorosilane have previously failed to give the diol.[4]

By careful control of conditions during the hydrolysis and the working up of the product we have prepared diethylsilanediol in good yield from diethyldichlorosilane. Best results were obtained with dilute alkali or saturated sodium bicarbonate solution. However, concentrated sodium chloride solution may also be used. A solution of 30 g. of diethyldichlorosilane in 500 cc. of dry ether was added during five minutes with stirring to the theoretical amount of 1.5 *N* alkali at 0°. Immediate separation of the ether layer and ether extraction of the water layer were followed by drying over 25 g. of potassium carbonate for a short time. The ether solution of the product was then concentrated *in vacuo* to 250 cc. Addition of 250 cc. of pentane followed by cooling gave 15 g., 65% yield, of diethylsilanediol, a white crystalline solid, m. p. 96° before and after recrystallization and boiling with decomposition at about 140°.

Anal. Calcd. for $C_4H_{12}SiO_2$: Si, 23.34; C, 39.97; H, 10.07. Found: Si, 23.12; C, 39.91; H, 10.10.

Diethylsilanediol can be stored in ordinary corked bottles. Even exposure to a laboratory atmosphere for long periods of time gives no change. At room temperature it is soluble in water and in oxygen-containing organic solvents, and is sparingly soluble in chlorinated hydrocarbons. The compound is easily recrystallized from ether–pentane, acetone–pentane, chloroform and carbon tetrachloride.

Treatment of diethylsilanediol with thionyl chloride and quinoline gave diethyldichlorosilane. Refluxing with benzene and iodine gave the theoretical amount of water. More extensive data on the preparation and properties of dialkylsilanediols will be reported shortly.

We thank R. N. Walter of this Laboratory for the analyses reported in this Communication.

DEPARTMENT OF CHEMISTRY P. A. DIGIORGIO
THE PENNSYLVANIA STATE COLLEGE L. H. SOMMER
STATE COLLEGE, PENNA. F. C. WHITMORE

RECEIVED JANUARY 10, 1946

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(1) For references to diphenylsilanediol see Burkhard, THIS JOURNAL, **67**, 2173 (1945).

(2) For the preparation of the phenylethyl, benzylethyl, benzylphenyl and dibenzyl compounds see Robison and Kipping, *J. Chem. Soc.*, **101**, 2148 (1912); Robison and Kipping, *ibid.*, **101**, 2156 (1912).

(3) See for example Krause and Grosse, "Die Chemie der Metallorganischem Verbindungen," Borntraeger Geb., Berlin, 1937, p. 284; Rochow, *Chem. Eng. News*, **23**, 614 (1945).

(4) Martin and Kipping, *J. Chem. Soc.*, **95**, 313 (1909); Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941).

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o-NITROBENZOYL CHLORIDE AND HAZARD INVOLVED IN ITS DISTILLATION

Sir:

N. C. Cook and F. C. Whitmore have called attention (*Ind. Eng. Chem., News Ed.*, **23**, 2394 (1945)) to the treacherous distillation behavior