droxide to a red purple color (pH 6.5–7.0) and brought to a final volume of 20 cc. Inasmuch as the average activity of the gallium as received was 18 millicuries (mc.) this yielded a solution containing approximately 1 mc./cc. which was used in physiological studies. By plotting a decay curve of samples prepared as described above, we have obtained a curve, log activity *vs.* time, for 15 half lives of Ga^{72}. No significant deviation from the straight line of a half life of 14.3 hours was observed, indicating no significant amounts of long life contaminants.

No attempt has been made to isolate the citrate of Ga^{72} since this would entail lengthy procedures and provide opportunities for serious radiation exposures. The citrate solutions containing Ga^{72} as described above contained considerable quantities of other ions, (Cl, NO_3, Na). The citrate ions in this solution serve to stabilize the mixture, preventing the precipitation of gallium hydroxide at pH 7–8, as would result if the citrate were not present. In a series of toxicological studies with stable gallium using a mixture containing the above mentioned ions plus citric acid or a solution containing only purified gallium citrate we have observed no difference in the effects or toxic properties when a comparison is made on an mg. Ga/kg. basis.

The penetrating β-γ spectrum of Ga^{72} (2.5 mev. γ, 3.1 mev. β) makes necessary the utmost effort for protection of personnel and especially for those carrying out chemical manipulations. The handling of the ampoules and all containers requires the use of suitable tongs. All glass apparatus, cylinders, beakers, etc., were placed in lead pots having a 25-mm. wall thickness. The chemical operations were carried on behind a wall of lead blocks 5 cm. in thickness. It has been found that when the above precautions were observed, a total body radiation of less than 20 milliroentgens (mr.) was received by personnel carrying out the chemical manipulations. Exposure to the hands was 20 to 40 mr., usually within a space of thirty minutes. Personnel injecting solutions of 0.5 mc./cc. activity in quantities up to 10 mc. per injection received less than 20 mr. total body radiation and less than 40 mr. on the hands, when using lead shielded syringes.[6] Therefore, it is recommended that personnel doing the chemical manipulations not carry out other studies or injections. No more than one unit of Ga^{72} (10–30 mc.) should be processed by one group in a single 24-hour period.

Studies using Ga^{72} must be carried out far removed from photographic storage and processing facilities since the hard gamma will penetrate the usual shielding, even that adequate for X-ray.

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[6] Dudley, Bronson and Taylor, *Science*, **110**, 16 (1949).

NAVAL MEDICAL RESEARCH INSTITUTE
NATIONAL NAVAL MEDICAL CENTER
BETHESDA, MARYLAND H. C. DUDLEY

RECEIVED MARCH 3, 1950

Certain 4,4′-Dinitrodiphenyl Sulfides and Sulfones

Bis-(2-methoxy-4-nitrophenyl) Sulfide.—An alcoholic solution of 8 g. (0.0345 mole) of 2-bromo-5-nitroanisole (m. p. 104°)[1] and the potassium ethyl xanthate prepared from 1.96 g. of potassium hydroxide and 2.66 g. of carbon disulfide was refluxed for a total of ninety-six hours. At intervals during this refluxing the mixture was filtered to remove the product. At one point an additional 2 g. of the nitrobromoanisole was added making a total of 10 g. A total of 5.1 g. (70.2%) of bright yellow sulfide (recrystallized from acetic acid) was obtained, m. p. 204–205°.

Anal. Calcd. for $C_{14}H_{12}O_6N_2S$: S, 9.54. Found: S, 9.61.

Bis-(2-methoxy-4-nitrophenyl) Sulfone.—Oxidation of the above sulfide (3.0 g.) was performed with chromic anhydride in acetic acid at reflux. Pouring onto ice and recrystallization from glacial acetic acid afforded 2.4 g. (75%) of fine white crystals melting at 231–232°.

Anal. Calcd. for $C_{14}H_{12}O_8N_2S$: S, 8.70. Found: S, 8.26, 8.39.

2-Iodo-2′-methoxy-4,4′-dinitrodiphenyl Sulfide.—An alcohol solution of 4.62 g. (0.025 mole) of 2-methoxy-4-nitrothiophenol (prepared from 2-bromo-5-nitroanisole by the methods of Price and Stacey)[2] 8.45 g. (0.025 mole) of 2-iodo-4-nitrobromobenzene and 2.6 g. (0.02 mole) of suspended potassium carbonate was heated under reflux for about five hours. After isolation in the usual way and recrystallization there was obtained 2.9 g. (33.6%) of light-brown microcrystalline powder melting at 191–192°.

Anal. Calcd. for $C_{13}H_9O_5N_2IS$: S, 7.42. Found: S, 6.67.

Oxidation of the above sulfide to **2-iodo-2′-methoxy-4,4′-dinitrodiphenyl sulfone** was carried out in the customary manner with chromic anhydride in acetic acid. From 2.9 g. of the sulfide there was obtained 3.0 g. (96.5%) of recrystallized light pink colored sulfone melting at 270–271°.

Anal. Calcd. for $C_{13}H_9O_7N_2IS$: S, 6.89. Found: S, 6.82.

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[1] Hanford and Adams, THIS JOURNAL, **57**, 1592 (1935), found m. p. 104°.

[2] Price and Stacey, *ibid.*, **68**, 498 (1946).

LEHIGH UNIVERSITY J. F. FEEMAN
BETHLEHEM, PENNSYLVANIA E. D. AMSTUTZ

RECEIVED MARCH 20, 1950

Triphenyl-*o*-methoxymethylphenyltin

Incidental to studies concerning water-soluble organotin compounds, triphenyl-*o*-methoxymethylphenyltin was prepared from the Grignard reagent which was obtained (1) directly from the organic halide, and (2) by means of a halogen–metal interconversion reaction.

Triphenyl-*o*-methoxymethylphenyltin.—To *o*-methoxymethylphenylmagnesium bromide prepared by refluxing for six hours 1.95 g. (0.080 gram atom) of magnesium and 15.1 g. (0.075 mole) of *o*-bromobenzyl methyl ether in 150 cc. of ether and 60 cc. of benzene, was added 20.0 g. (0.0518 mole) of triphenyltin chloride. From the mixture, after stirring for several hours, followed by hydrolysis with aqueous ammonium chloride, there was obtained, after two crystallizations from benzene–ethanol, 8.5 g. or a 35% yield of triphenyl-*o*-methoxymethylphenyltin melting at 93–95°. Another recrystallization from the same solvent, subsequent to vacuum drying, raised the melting point to 94.5–95.5°.

Anal. Calcd. for $C_{26}H_{24}OSn$: Sn, 25.22. Found: Sn, 25.88 and 25.90.

Since direct formation of the Grignard reagent was slow, it was also prepared by means of the halogen–metal interconversion reaction. To 15.1 g. (0.0752 mole) of *o*-bromobenzyl methyl ether in 50 cc. of ether, was added 0.0752 mole of *n*-butyllithium in 145 cc. of ether. After the mixture was stirred for twenty-five minutes, 0.085 mole of anhydrous magnesium bromide in 75 cc. of ether was added. By the procedure outlined above, after the addition of 19.0 g. (0.0493 mole) of triphenyltin chloride, there was obtained 8.8 g. or a 38% yield of triphenyl-*o*-methoxymethylphenyltin melting at 94–95.5°.

CHEMICAL LABORATORY
IOWA STATE COLLEGE HENRY GILMAN
AMES, IOWA CLYDE E. ARNTZEN

RECEIVED MARCH 6, 1950

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m-Phenyl-phenylacetic Acid

m-Acetylbiphenyl[1] (3.2 g.) with 1 g. of sulfur and 10 ml. of morpholine was refluxed for seven hours. The mixture was poured into 30 ml. of methanol and water was added until the product precipitated as a gummy

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[1] Huber, Renoll, Rossow and Mowry, THIS JOURNAL, **68**, 1109 (1946).

solid. This was separated and hydrolyzed by boiling for seven hours with 30 ml. of 70% ethanol and 10 ml. of 45% potassium hydroxide. The product was cooled, neutralized with hydrochloric acid and treated with Darco. The acid was obtained by acidification. It was recrystallized from acetic acid; yield 1.5 g.; recrystallized from ether, m. p. 135–137°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7. Found: C, 79.2; H, 5.6.

This completes a series of these acids since the *o*- and *p*-phenyl isomers have been described.[2,3]

I am grateful to Dr. David T. Mowry of the Monsanto Chemical Co. who provided the *m*-acetylbiphenyl.

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(2) von Braun and Manz, *Ann.*, **468**, 258 (1929).

(3) Schwenk and Papa, *J. Org. Chem.*, **11**, 798 (1946).

JEFFERSON MEDICAL COLLEGE
PHILADELPHIA, PENNA. D. L. TURNER

RECEIVED MARCH 17, 1950

5-Nitroquinoxaline

A solution of 5.0 g. (0.019 mole) of glyoxal sodium bisulfite and 2.5 g. (0.016 mole) of 1,2-diamino-3-nitrobenzene[1] in 30 ml. of water was heated at 90° for one hour. The dark red solution was filtered, cooled to 10° and made basic with 10 ml. of 30% potassium hydroxide solution. The yellow precipitate was filtered by suction, rinsed with cold water and dissolved in 25 ml. of warm (50°) 95% ethanol. The ethanol solution was treated with charcoal and filter-aid, and filtered into 75 ml. of warm water. After cooling, 2.0 g. (70% yield) of matted yellow needles came down, m. p. 93–94°.

For analysis the material was sublimed at 100° (1 mm.), recrystallized from ethanol–water and again sublimed to give yellow-white needles, m. p. 96–97°.

5-Nitroquinoxaline was insoluble in water and 10% hydrochloric acid, soluble in cold ethanol, soluble with decomposition in warm alkali solution.

Anal. Calcd. for $C_8H_5N_3O_2$: N, 24.0. Found: N, 23.9.

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(1) Borsche and Rantscheff, *Ann.*, **379**, 163 (1910).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MIAMI
CORAL GABLES, FLORIDA HARRY P. SCHULTZ

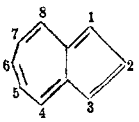
RECEIVED FEBRUARY 9, 1950

COMMUNICATIONS TO THE EDITOR

ELECTROPHILIC SUBSTITUTION OF AZULENE

Sir:

Since the elucidation of the azulene structure there has been considerable interest in the existence and properties of non-benzoid aromatic hydrocarbons. Although several different hypothetical structures (*i.e.*, pentalene and heptalene) have been proposed, azulene is the only known compound of this type and has, therefore, been the subject of numerous theoretical considerations. As previous chemical experiments[1] had shown only the strongly unsaturated character of the molecule, it seemed of importance in our study of azulene to investigate its behavior with aromatic substitution reagents.



Approximate quantum mechanical calculations according to Brown[2] of polarization energies and π-electron densities indicated that electrophilic substitution would take place in the 1-position. In the course of work in progress azulene has been allowed to react with certain electrophilic reagents. The results of one of these experiments support the prediction of Brown and current studies are designed to characterize the products and establish the position or positions of substitution in the other cases.

A minute amount of 1-methylazulene (λ_{max} in mμ at 240, log ϵ 4.28; 279, log ϵ 4.61; 338, log ϵ 3.62; 346, log ϵ 3.68; 364, log ϵ 3.50; 607, 658 and 732)[3] was obtained from the reaction of azulene with methyl chloride or iodide below room temperature and in the presence of aluminum chloride.

Azulene reacted readily with acetic anhydride in the presence of aluminum chloride. The principal product (62%), which is probably a diacetylazulene, was isolated as bright red needles, m. p. 189–190° (Calcd. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7. Found: C, 78.9; H, 5.6; λ_{max} in mμ at 240, log ϵ 4.51; 289, log ϵ 4.69; 308, log ϵ 4.49; 382, log ϵ 4.00; 498, log ϵ 2.85).

Reaction of azulene with copper nitrate and acetic anhydride at room temperature yielded red needles (51%), m. p. 98–99° (λ_{max} in mμ at 219, log ϵ 4.32; 269, log ϵ 4.23; 309, log ϵ 4.32; 382, log ϵ 4.03; 532, log ϵ 2.77; 572, log ϵ 2.69). The analysis most nearly corresponded to that calculated for a mononitroazulene (Calcd. for $C_{10}H_7O_2N$: C, 69.36; H, 4.08. Found: C, 68.71; H, 4.11).

Treatment of a solution of azulene in ethanol and aqueous sodium acetate with an aqueous solution of mercuric chloride resulted in an imme-

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(1) For a recent review article see A. J. Haagen-Smit, "Fortschritte der Chemie organischer Naturstoffe," Vol. V, Julius Springer, Wien, 1948, pp. 40–71.

(2) R. D. Brown, *Trans. Faraday Soc.*, **44**, 984 (1948).

(3) The absorption spectra for the various mono- and the known dialkylazulenes are characteristic; *cf.* Pl. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **30**, 910 (1947); **31**, 804 (1948); T. Wagner-Jauregg, H. Arnold, F. Hüter and J. Schmidt, *Ber.*, **74B**, 1522 (1941).