

TABLE I
 ALIPHATIC ANIL DERIVATIVES OF GOSSYPOL

Compound (R in II)	Molecular Formula	M.P., °C.	Yield, %	Recrystal- lization Solvent	Analyses					
					Calc'd		Found		Found	
					C	H	N	C	H	N
CH ₃ CH ₂ —	C ₃₄ H ₄₀ N ₂ O ₆	251-255 (d)	72	Ethyl acetate	71.3	7.04	4.89	71.48	7.08	4.65, 4.71
CH ₃ (CH ₂) ₄ —	C ₄₀ H ₅₂ N ₂ O ₆	218-221 (d)	69	Benzene			4.27			4.41, 4.32
CH ₃ (CH ₂) ₉ —	C ₆₀ H ₇₂ N ₂ O ₆	164.5-165.5	64	Benzene			3.51			3.46, 3.54
CH ₃ (CH ₂) ₁₃ —	C ₈₈ H ₈₈ N ₂ O ₆	126.5-127	75	Isopropyl alcohol			3.08			3.02, 3.07
CH ₃ (CH ₂) ₁₅ —	C ₆₂ H ₉₆ N ₂ O ₆	116-116.5	50	Benzene			2.90			2.71, 2.85
CH ₃ (CH ₂) ₁₇ —	C ₆₆ H ₁₀₄ N ₂ O ₆	112.5-113	60	Ethanol	77.6	10.2	2.75	77.49	10.20	2.95
								77.59	10.40	2.95
C ₆ H ₅ CH ₂ —	C ₄₄ H ₄₄ N ₂ O ₆	241.5 (d)	72	Chloroform and benzene	75.84	6.37	4.02	75.90	6.34	3.83
								75.99	6.40	3.93

(with no decomposition) of the long chain amino-gossypols is a unique feature of these types.

Figure 1 shows the ultraviolet absorption spectra of didodecylaminogossypol and dianilinogossypol. It is noted that the broad band at about 370-410 m μ in the dodecyl derivative is shifted to longer wave lengths in the dianilino compound. This is to be expected in view of the greater conjugation of the latter compound. Dibenzylaminogossypol shows an ultraviolet absorption spectrum nearly identical with the didodecylaminogossypol in the region of the spectrum shown in Figure 1.

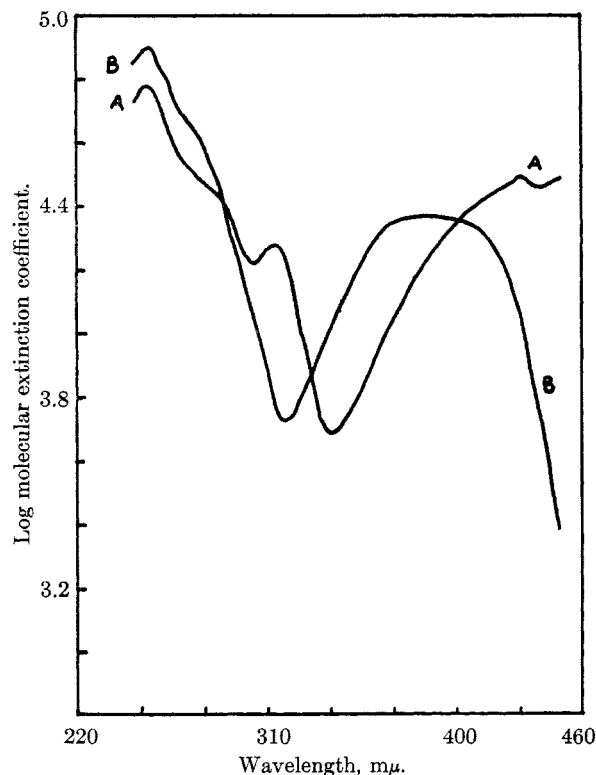


FIG. 1.—ULTRAVIOLET ABSORPTION SPECTRA IN CHLOROFORM. A, Dianilinogossypol; B, Didodecylaminogossypol.

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 EXPERIMENTAL⁵

Didodecylaminogossypol. A solution of 0.52 g. (0.001 mole) of pure gossypol⁶ in 45 ml. of isopropyl alcohol was heated to boiling and a solution of 0.37 g. (0.002 mole) of pure dodecylamine in 10 ml. of isopropyl alcohol was added. The mixture was boiled for one minute and allowed to stand at 5° overnight. The precipitated yellow crystalline solid was filtered off and dried to yield 0.81 g. of yellow, crystalline product corresponding to a 95% yield. The product melted at 170-171° and this melting range was not altered by additional crystallization.

Anal. Calc'd for C₆₄H₈₀N₂O₆: C, 76.0; H, 9.40; N, 3.29. Found: C, 76.0 and 75.9; H, 9.42 and 9.46; N, 3.21 and 3.26.

Crude gossypol acetic acid complex can also be used to form didodecylaminogossypol in fair yield. One gram (0.00173 mole) of the chocolate-brown complex⁶ in 70 ml. of isopropyl alcohol and 0.64 g. (0.00346 mole) of amine treated as before gave 0.84 g. (58%) of didodecylaminogossypol, m.p. 170-171°. One recrystallization from isopropyl alcohol was necessary to reach this melting point.

The compounds listed in Table I were prepared in general accordance with the above procedure except that recrystallization solvents varied as shown in the table.

(5) Microanalyses by Galbraith Microanalytical Laboratories of Knoxville, Tennessee.

(6) Supplied by Dr. F. H. Thurber.

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 Some New 2- and 3-Substituted
 Dibenzarsenolic Acids¹

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Recently, the preparation of several amino derivatives of dibenzarsenolic acid (arsafluorinic acid, 9-arsafluorenic acid) have been described.^{2,3} Thus,

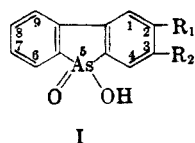
(1) Abstracted from the theses presented by Albert A. Carr and Thomas R. Hauser in partial fulfillment of the requirements for the Master of Science degree at Xavier University.

(2) Fietelson and Petrow, *J. Chem. Soc.*, 2279 (1951).

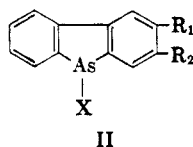
(3) Garascia and Mattei, *J. Am. Chem. Soc.*, 75, 4589 (1953).

3-aminodibenzarsenolic acid can be readily prepared by direct nitration of dibenzarsenolic acid itself followed by chemical or catalytic reduction. The synthesis of 1-amino and 2-amino dibenzarsenolic acids has been accomplished by ring closure of appropriately substituted biphenyl-2-arsonic acids. Up to the present, however, no derivatives of these interesting bodies have been reported involving replacement of the aminoid hydrogens or the diazotization of the primary amine groups. The present communication describes such an attempt.

The preparation of 2-aminodibenzarsenolic acid (I, $R_1 = \text{NH}_2$, $R_2 = \text{H}$) and 3-aminodibenzarsenolic acid (I, $R_1 = \text{H}$, $R_2 = \text{NH}_2$) was accomplished by methods already described,² but some remarks are in order. In the first place, both amines as prepared by us proved to be colorless compounds and not orange and pink respectively as previously reported. It is suggested that the colors described were due to the presence of polynitration products in the intermediates used. Secondly, the sequence of reactions leading to the 2-amino compound involved the nitration of 2-tosylaminobiphenyl, a reaction described by several workers,^{4,5} and one that gave us considerable trouble, being extremely difficult to control properly. Accordingly, we have given in the experimental section, an improved procedure for the reaction, giving 2-tosylamino-5-nitrobiphenyl in good yield and purity.



I



II

In addition to the synthesis of compounds described below, the reduction of dibenzarsenolic acid to dibenzarsenole (II; $R_1, R_2, X = \text{H}$) was attempted following the technique of Aeschlimann⁶ using metallic zinc and hydrochloric acid. This procedure and several variations of it failed to give the desired product, yielding only the partially reduced compound, 5-chlorodibenzarsenole (II; $R_1, R_2 = \text{H}$, $X = \text{Cl}$). Similarly, attempts to reduce 5-chlorodibenzarsenole with zinc and acid were also unsuccessful, though on one occasion, after contact with zinc and acid in ethanolic solution for two days, a good quantity of unidentified material was isolated melting at 262° and nearly insoluble in common organic solvents and dilute sodium hydroxide. Furthermore, attempts at direct bromination of both dibenzarsenolic acid and 5-chlorodibenzarsenole, employing various media, temperatures, times, and catalysts, gave no bromo compound, initial material being recovered in each case. This

resistance to direct halogenation is somewhat surprising in view of the very easy nitration of dibenzarsenolic acid.

EXPERIMENTAL

Note. Melting points were obtained with an aluminum block using a thermometer calibrated against compounds of known melting points. Arsenic analysis was accomplished by the method of Robertson.⁷

2-Tosylamino-5-nitrobiphenyl. Purified 2-tosylaminobiphenyl (20 g., 0.060 mole) and 80 ml. of glacial acetic acid were heated to reflux in a 3-necked flask. After permitting the temperature to drop five degrees, 3.16 ml. of fuming nitric acid (*sp. gr.* 1.5, 0.066 mole) dissolved in 6.5 ml. of glacial acetic acid was added drop-wise at such a rate that one-half was added during the first hour and a half. The temperature then was lowered to 95° and the rest of the nitrating mixture was added at the same rate. The total reaction time was three hours. The reaction mixture then was cooled to room temperature and the crystalline product was filtered and washed with cold glacial acetic acid. On recrystallization from a mixture of ethanol and benzene, the 5-nitro compound was obtained as a light-yellow product melting at 172° and weighing 20.2 g. (91.7%).

2-Acetaminodibenzarsenolic acid (I, $R_1 = \text{NHCOCH}_3$, $R_2 = \text{H}$). 2-Aminodibenzarsenolic acid (0.75 g., 0.0027 mole) and 4 ml. of acetic anhydride were stirred on a water bath at 75–80° for two hours. The supernatant liquid was decanted from some oily material and cooled to 0°. The crystalline substance separating was purified *via* the sodium salt. The yield was 0.64 g. (80.6%) of a white compound melting at 245°.

Anal. Calc'd for $\text{C}_{14}\text{H}_{12}\text{AsNO}_3$: As, 23.6. Found: As, 23.6.

2-Carbamylmethylaminodibenzarsenolic acid (I, $R_1 = \text{NHCH}_2\text{CONH}_2$, $R_2 = \text{H}$). One gram (0.0036 mole) of 2-aminodibenzarsenolic acid was mixed with 1.8 ml. of 2 N potassium hydroxide and 2.5 ml. of water. This solution was diluted with 8 ml. more of water and treated with 0.05 g. of potassium iodide and 0.8 g. (0.0108 mole) of chloroacetamide. The solution was stirred on a boiling water bath for 2.5 hours and then was cooled. Dilution with acetone gave a white product which was purified *via* the sodium salt. The compound decomposed instead of melting on heating and weighed 0.15 g. (12.5%).

Anal. Calc'd for $\text{C}_{14}\text{H}_{13}\text{AsN}_2\text{O}_3$: As, 22.5. Found: As, 22.2.

2-Chlorodibenzarsenolic acid (I, $R_1 = \text{Cl}$, $R_2 = \text{H}$). 2-Aminodibenzarsenolic acid (3 g., 0.0108 mole) was placed in 20 ml. of water and enough 6 N sodium hydroxide was added to just dissolve the compound. To this solution was added slightly more than an equivalent quantity of sodium nitrite dissolved in 3 ml. of water. The mixture was cooled to 0° and dropped into 10 ml. of 12 N hydrochloric acid also at 0°. This cold diazonium solution then was added dropwise to an equimolar amount of copper^I chloride suspended in 50 ml. of concentrated hydrochloric acid. When the addition was complete, the temperature was elevated to 60–70° to remove nitrogen and the resulting solid was filtered and purified by means of the sodium salt to give 0.8 g. (27%) of product. The compound decomposed without melting at temperatures in excess of 300°.

Anal. Calc'd for $\text{C}_{12}\text{H}_8\text{AsClO}_2$: As, 25.5. Found: As, 25.4.

2,5-Dichlorodibenzarsenole (II, $R_2 = \text{H}$; $R_1, X = \text{Cl}$). To a suspension of 0.7 g. (0.0023 mole) of 2-chlorodibenzarsenolic acid in 7 ml. of warm chloroform was added phosphorus trichloride, dropwise, until the arsenic acid dissolved (about 1–2 ml.). The reaction mixture was filtered warm and kept in the ice chest overnight. The resulting crystals were purified by recrystallization from chloroform or

(4) Bell, *J. Chem. Soc.*, 2770 (1928).

(5) Ray and Barrick, *J. Am. Chem. Soc.*, **70**, 1492 (1948).

(6) Aeschlimann, Lees, McLeland, and Nicklin, *J. Chem. Soc.*, 127, 66 (1925).

(7) Robertson, *J. Am. Chem. Soc.*, **43**, 182 (1921).

through the sodium salt. The crystalline material melted at 135–136° and weighed 0.18 g. (26.8%).

Anal. Calc'd for $C_{12}H_7AsCl_2$: As, 25.2. Found: As, 25.1.

3-Bromodibenzarsenolic acid (I, $R_1 = H$, $R_2 = Br$). This compound was prepared from 3-aminodibenzarsenolic acid using a procedure similar to that described above for the preparation of the 2-chloro derivative. The diazonium solution in this case was added to a suspension of copper^I bromide in concentrated hydrobromic acid. The crude product was purified by dissolution in sodium carbonate solution, and, after charcoaling the solution, was reprecipitated by the addition of excess hydrochloric acid. The compound melted at 314–315° and was obtained in 54% yield. Titration in ethanolic solution with standard alkali using Thymolphthalein as an indicator gave neutral equivalents of 341 and 337, the theoretical value being 339.

Anal. Calc'd for $C_{12}H_6AsBrO_2$: As, 22.1. Found: As, 22.0.

3-Bromo-5-chlorodibenzarsenole (II, $R_1 = H$, $R_2 = Br$, $X = Cl$). 3-Bromodibenzarsenolic acid (2 g.) together with 10 g. of amalgamated zinc and 100 ml. of benzene were placed in a 3-necked flask equipped with stirrer, water condenser, and dropping-funnel. Concentrated hydrochloric acid (about 50 ml.) was added slowly over a period of four to five hours until the solid had almost completely dissolved in the benzene layer, gentle warming with a water-bath being applied all the while. The benzene layer was partially evaporated to give the crystalline product in long needles weighing 0.8 g. (40%) and melting at 176°. The compound was not analyzed for arsenic.

3-Chlorodibenzarsenolic acid (I, $R_1 = H$, $R_2 = Cl$). This compound was prepared from 3-aminodibenzarsenolic acid using the procedure indicated above for the 2-chloro compound. The product was obtained in 44% yield and melted at 313–314°.

Anal. Calc'd for $C_{12}H_6AsClO_2$: As, 25.5. Found: As, 25.6.

3,5-Dichlorodibenzarsenole (II, $R_2 = H$; $R_1, X = Cl$). Finely divided 3-chlorodibenzarsenolic acid (0.2 g.) was suspended in 5 ml. of glacial acetic acid. The mixture was warmed to 80° on a water-bath and phosphorus trichloride (1 ml.) was added dropwise until a clear solution was effected. The solution then was heated for an additional 15 minutes on the water-bath and was kept in the ice chest overnight. The crystalline material was filtered and dried. The yellow compound was recrystallized from glacial acetic acid and weighed 0.1 g. (50%) and melted at 154–155°. In a similar manner, using chloroform as a reaction solvent and recrystallization medium, phosphorus tribromide converts 3-chlorodibenzarsenolic acid to *3-chloro-5-bromodibenzarsenole* (II, $R_1 = H$, $R_2 = Cl$, $X = Br$) in 43% yield, melting at 153°. No elemental analysis was made on these compounds.

3-Cyanodibenzarsenolic acid (I, $R_1 = H$, $R_2 = CN$). 3-Aminodibenzarsenolic acid (3 g., 0.011 mole) was diazotized at 0–5° with 1.2 g. (0.012 mole) of sodium nitrite in dilute hydrochloric acid medium. The cold diazonium solution was added dropwise to a mixture of 3.16 g. (0.034 mole) of copper^I cyanide, 1.47 g. (0.030 mole) of sodium cyanide, and 50 ml. of water held at 60–70°. The mixture then was heated on a boiling water-bath for 20 minutes and the insoluble portion was isolated by filtration. Purification was effected by dissolution in sodium carbonate, charcoaling, and reprecipitation with hydrochloric acid. A product was obtained weighing 1.2 g. (38.7%), remaining unmelted at 360° with some decomposition.

Anal. Calc'd for $C_{13}H_5AsNO_2$: As, 26.3. Found: As, 25.9.

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Organosilanes Containing Aralkyl Groups

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Rochow's¹ tables note the physical properties of tetrabenzyl silane and a group of organosilanes containing the benzyl group in combination with a variety of short-chained alkyl groups. Recently, Maienthal, *et al.*² reported the preparation of diphenyldibenzylsilane and phenyltribenzylsilane. The use of triphenylbenzylsilane has been mentioned³ but its method of preparation was not described. The compound was prepared in this laboratory⁴ by the interaction of benzylmagnesium chloride and triphenylchlorosilane. Earlier,⁵ it was prepared by the reaction of phenyllithium with benzyltriethoxysilane, the latter being made by the interaction of benzylmagnesium chloride and chlorotriethoxysilane.

We had prepared the two compounds reported by Maienthal, *et al.* and had also made several other organosilanes containing one or more benzyl, *beta*-phenylethyl, or *gamma*-phenylpropyl radicals in a variety of combinations. Our sample of diphenyldiphenylsilane was found to have the same melting point as that of Maienthal and co-workers. However, our sample of phenyltribenzylsilane melted at 41–42.5° while that reported in the literature² melted at 130°. A second experiment in this laboratory confirmed the m.p. to be 41–42.5°. After recrystallization, the melting points of our samples became 59–60°. However, no change in the infrared spectra could be detected, thus indicating the two different melting materials to be isomeric.^{6b} The yield of tribenzylphenylsilane was improved over the 59% of viscous liquid reported by Maienthal, *et al.*² and a 56% yield obtained in our first experiment. The two experiments giving low yields were carried out by the reaction of three equivalents of benzylmagnesium chloride and one equivalent of phenyltrichlorosilane during a 4–8 hour heating period without any solvent. By re-

(1) Rochow, *An Introduction to the Chemistry of the Silicones*, 2nd edition, John Wiley and Sons, New York, N. Y., 1951, pp. 171–172.

(2) Maienthal, Hellmann, Haber, Hymo, Carpenter, and Carr, *J. Am. Chem. Soc.*, **76**, 6392 (1954).

(3) Gilman and Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951).

(4) Miller, Doctoral Dissertation, Iowa State College, (1950).

(5) Melvin, Doctoral Dissertation, Iowa State College, 1954.

(6a) Through the kind cooperation of Drs. Hellmann and Haber, their compound was shown to be identical with tetrabenzylsilane by a mixture melting point in their laboratories and by infrared analyses of their compound and authentic tetrabenzylsilane in this laboratory. The tetrabenzylsilane may have resulted from high temperature disproportionation of the tribenzylphenylsilane.

(6b) See Smart, Gilman, and Otto, *J. Am. Chem. Soc.*, **77**, 5193 (1955) for a report on isomeric tetra-*o*-tolylsilanes.