

33% ethyl alcohol raised the decomposition point to 197°; colorless, flat pointed needles. *Anal.* Calcd. for  $C_8H_9O_3N_5$ : C, 43.05; H, 4.06; N, 31.38. Found: C, 42.96; H, 4.21; N, 31.50.

**Method B.**—From 0.5 g. of methylnitrosoguanidine and 0.45 g. of benzhydrazide in 10 ml. of 50% ethyl alcohol, there was recovered 0.6 g. of compound (90%), decomposing at 197.5°. A mixed melting point with the compound made by the above procedure was the same.

**1-(4-Nitrobenzamido)-3-nitroguanidine. Method A.**—The same procedure was employed as in the preparation of 1-benzenesulfonamido-3-nitroguanidine except that 3.71 g. of *p*-nitrobenzoyl chloride was used. The yield was 1.5 g. (28%). One recrystallization from 375 ml. of 76% ethyl alcohol gave a product identical with that prepared by the following method.

**Method B.**—From the reaction of 0.01 molar quantities of methylnitrosoguanidine and *p*-nitrobenzhydrazide in 140 ml. of 70% ethyl alcohol, there was recovered after three days at room temperature 2.15 g. (80%) of a compound decomposing at 193°. Recrystallization from 75% ethyl alcohol gave small, pale yellow needles decomposing at 195.5–196.5°. *Anal.* Calcd. for  $C_8H_8O_3N_5$ : N, 31.34. Found: N, 31.62.

**Ethyl N-Nitroguanidocarbamate.**—To a slurry of 3.94 g. of methylnitrosoguanidine in 10 ml. of water and 5 ml. of ethyl alcohol was added 2.10 g. of ethyl hydrazinocarbonate. There was an immediate and rapid evolution of gas. After the mixture had remained several days at 0°, the white solid was removed by filtration and washed with three 5-ml. portions of cold water. The yield was 4.0 g. After two recrystallizations from a minimum volume of water, the melting point was 203–203.5° (dec.). This compound does not form a hydrazone with benzaldehyde. *Anal.* Calcd. for  $C_4H_9O_4N_3$ : C, 25.13; H, 4.74; hydrazino N, 14.66. Found: C, 24.62; H, 4.63; hydrazino N by the Jamieson method, 14.66.

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### Cetyl Chloro- and Iodoacetates

**Cetyl Chloroacetate.**—Into a 500-ml. flask were placed 48.4 g. (0.20 mole) of cetyl alcohol and 30.0 g. (20.0 ml., 0.26 mole) of chloroacetyl chloride. The reactants were heated gently with a free flame under reflux for two hours. The reaction mixture was then distilled under reduced pressure, the product collected at 218–220° (10 mm.), which crystallized on cooling to a white wax-like solid m. p. 31°. The yield amounted to 45 g. (70%).

*Anal.* Calcd. for  $C_{18}H_{36}O_2Cl$ : Cl, 11.12. Found: Cl, 11.08.

**Cetyl Iodoacetate.**—A solution of 6.38 g. (0.020 mole) of cetyl chloroacetate in 25 ml. of acetone<sup>1</sup> was mixed with a solution of 4.00 g. (0.027 mole) of sodium iodide in 25 ml. of acetone. The mixture was refluxed one hour and the reaction mixture poured into 300 ml. of ice-cold water. The crude product filtered off and crystallized from alcohol (12 ml./g.) by cooling in ice-salt freezing mixture gave a white crystalline product, 7.5 g. (92%), m. p. 28°. For analysis a further recrystallization from alcohol gave product m. p. 28.5°.<sup>2</sup>

*Anal.* Calcd. for  $C_{18}H_{36}O_2I$ : I, 30.94. Found: I, 30.60.

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(1) Finkelstein, *Ber.*, **43**, 1538 (1910).

(2) Product decomposed on distillation at 4 mm.

### 1,1,1-Trichloro-2,2-bis-(3-carboxy-4-hydroxy-5-nitrophenyl)-ethane and its Dehydrohalogenation Product

**1,1,1-Trichloro-2,2-bis-(3-carboxy-4-hydroxy-5-nitrophenyl)-ethane.**—Fifty grams (0.123 mole) of 1,1,1-trichloro-2,2-bis-(3-carboxy-4-hydroxyphenyl)-ethane,<sup>1</sup> prepared by the condensation of chloral and salicylic acid with sulfuric acid, and 300 ml. of glacial acetic acid, were heated to reflux while concentrated nitric acid was added slowly. After 15 ml. of nitric acid had been added, the solid material had dissolved. A total of 50 ml. of nitric acid was added over a one-hour period at the reflux temperature. The reaction mixture was allowed to stand overnight at room temperature. The precipitated yellow crystals were filtered off to give 43 g. (70%) of the dinitro derivative, m. p. 241–243°. Recrystallization did not raise the melting point.

Assignment of the 5-position to the nitro groups entering the ring is based on the well-known orienting influence of the substituents already present in the ring and on the observed positions of nitration of other related types.<sup>2,3</sup>

*Anal.* Calcd. for  $C_{14}H_5Cl_3N_2O_{10}$ : Cl, 21.5; N, 5.66. Found: Cl, 21.6 and 21.3; N, 5.79.

**1,1-Dichloro-2,2-bis-(3-carboxy-4-hydroxy-5-nitrophenyl)-ethylene.**—Five and one half grams (0.011 mole) of 1,1,1-trichloro-2,2-bis-(3-carboxy-4-hydroxy-5-nitrophenyl)-ethane was added to a solution of 20 g. of potassium hydroxide in 750 ml. of water. The mixture was heated to boiling for a few minutes and then acidified with hydrochloric acid. The precipitated solid was separated and recrystallized from a mixture of nitrobenzene and petroleum ether. Four grams (78%) of the yellow crystals of the dehydrohalogenated product, melting at 235–237°, was obtained.

*Anal.* Calcd. for  $C_{14}H_5Cl_2N_2O_{10}$ : Cl, 15.5. Found: Cl, 15.5, 15.7.

(1) Calvet and Mejuto, *J. Chem. Soc.*, 554 (1936).

(2) Shirley, Goreau and Eiseman, *THIS JOURNAL*, **71**, 3173 (1949).

(3) Forrest, Stephenson and Waters, *J. Chem. Soc.*, 335 (1946).

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### Some Bis-(aryloxy)-methanes

The new compounds were prepared by the reaction of dichloromethane with the sodium salt of the phenol.<sup>1,2</sup> The yields, based on single experiments, are not necessarily the best that could be obtained. The properties and analyses of the compounds prepared are summarized in Table I. These compounds have been tested against the two-spotted spider mite and Mexican bean beetle.<sup>3</sup> The general method of preparation is illustrated by a specific example.

**Bis-(2-allyl-4,6-dichlorophenoxy)-methane.**—A mixture of 154 g. (0.76 mole) of 2-allyl-4,6-dichlorophenol, 36 g. (0.42 mole) of dichloromethane, 35 g. (0.85 mole) of 97% NaOH, and 200 ml. of methanol were placed in a  $KA_2S$  bomb, having a volume of 2 l. and a working capacity of 1.2 l., and heated to 130–140° for 12 hours with a pressure of 100–200 p.s.i.g. The contents were then cooled to room temperature and the material was dumped into a beaker. The bomb was washed out with two 500-ml. portions of distilled water and then with 500 ml. of chlorobenzene. The reaction mixture and washings were placed together and separated in a separatory funnel. The oil layer was then washed twice with 250-ml. portions of water. The aqueous layers were combined and titrated for chlorides to determine the conversion, which was 94%. The oil

(1) Moyle, U. S. Patent 2,330,234, September 28, 1943.

(2) Britton, Monroe and Hand, U. S. Patent 2,493,711, January 8, 1950.

(3) Kenaga and Hummer, *J. Econ. Entomol.*, **42**, 998 (1949).

TABLE I  
 SUBSTITUTED BIS-(ARYLOXY)-METHANES, (R)<sub>2</sub>CH<sub>2</sub>

R	Yield, %	<i>n</i> <sup>20</sup> <sub>D</sub>	M. p., °C.	B. p.		Formula	Carbon, %		Hydrogen, %		Chlorine, %	
				°C.	mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found
1 <i>o</i> -Allylphenoxy	67.1	1.5580		180-181	1	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	81.49	81.63	7.14	7.14		
2 2-Allyl-4-chlorophenoxy	29.6	1.5769		202-203	2.8	C <sub>10</sub> H <sub>9</sub> ClO <sub>2</sub>					20.3	20.5
3 2-Allyl-6-chlorophenoxy	52.6	1.5695		200-202	4.1	C <sub>10</sub> H <sub>9</sub> ClO <sub>2</sub>					20.30	20.29
4 2-Allyl-6-cyclohexylphenoxy	25.6	1.5567		241-242	2.7	C <sub>16</sub> H <sub>16</sub> O <sub>2</sub>	83.70	83.40	9.00	9.02		
5 2-Allyl-4,6-dichlorophenoxy	63.8		51-52	212-215	2.6	C <sub>10</sub> H <sub>8</sub> Cl <sub>2</sub> O <sub>2</sub>					33.9	33.43
6 2-Allyl-4-methoxyphenoxy	31	1.5612		193-195	1.3	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub>	74.09	74.09	7.11	7.20		
7 2-Allyl- <i>p</i> -toloxy	88.8	1.5528		220-224	5.9	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	81.8	82.25	7.85	8.27		
8 <i>p</i> - <i>n</i> -Butoxyphenoxy	58.7		68-70	189-191	1.3	C <sub>11</sub> H <sub>16</sub> O <sub>4</sub>	73.2	73.42	8.2	8.44		
9 2- <i>s</i> -Butyl-4-chlorophenoxy	72.5	1.5477		199-201	2.7	C <sub>11</sub> H <sub>12</sub> ClO <sub>2</sub>					18.60	18.60
10 4- <i>s</i> -Butyl-2-chlorophenoxy	78.1	1.5471		218-219	3.6	C <sub>11</sub> H <sub>12</sub> ClO <sub>2</sub>					18.60	18.47
11 <i>o</i> - <i>s</i> -Butylphenoxy <sup>a</sup>	43.3	1.5314		165-166	2.7	C <sub>11</sub> H <sub>16</sub> O <sub>2</sub>	80.72	80.58	9.03	9.08		
12 4-Chloro- <i>o</i> -toloxy <sup>a,d</sup>	46.5		146-146.5			C <sub>10</sub> H <sub>10</sub> ClO <sub>2</sub>					23.86	23.83
13 6-Chloro- <i>o</i> -toloxy	53.4	1.5664		165-168	2.3	C <sub>10</sub> H <sub>10</sub> ClO <sub>2</sub>					23.86	23.87
14 2,6-Dimethoxyphenoxy <sup>a</sup>	37.2		133-135			C <sub>11</sub> H <sub>10</sub> O <sub>4</sub>	63.74	63.45	6.29	6.28		
15 <i>p</i> -Methoxyphenoxy <sup>a</sup>	55.5		47-50			C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	69.21	69.15	6.19	6.21		
16 Pentachlorophenoxy <sup>b,d</sup>	42.6		261-262			C <sub>11</sub> H <sub>2</sub> Cl <sub>10</sub> O <sub>2</sub>					65.09	64.96
17 2,3,4,6-Tetrachlorophenoxy <sup>c,d</sup>	29.8		160.5-161.5			C <sub>11</sub> H <sub>4</sub> Cl <sub>4</sub> O <sub>2</sub>					59.61	59.84
18 2,4,5-Trichlorophenoxy <sup>a</sup>	51.3		124-126			C <sub>11</sub> H <sub>5</sub> Cl <sub>3</sub> O <sub>2</sub>					52.04	52.17

<sup>a</sup> Recrystallized from ethanol. <sup>b</sup> Recrystallized from chlorobenzene. <sup>c</sup> Recrystallized from 60-100° petroleum ether. <sup>d</sup> These compounds were not distilled.

layer was distilled to remove the chlorobenzene and finally the product, 101 g., was distilled at 212-215° (2.6 mm.), m. p. 51-52°, 63.8% yield.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub>: Cl, 33.9. Found: Cl, 33.43.

(4) Wilson Baker, *J. Chem. Soc.*, 1765 (1931).

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#### Tris-(*m*-trifluoromethylphenyl)-fluorosilane and Tetra-*kis*-(*m*-trifluoromethylphenyl)-silane

Silicone tetrafluoride, generated by the addition of 100 ml. of concd. sulfuric acid to a mixture of 30 g. of sodium silicofluoride and 10 g. of silicon dioxide, was bubbled slowly into a solution of *m*-trifluoromethylphenylmagnesium bromide prepared from 112.0 g. (0.5 mole) of *m*-bromobenzotrifluoride<sup>1</sup> and 12.1 g. of magnesium in 250 ml. of anhydrous ether. The reaction mixture was allowed to stand at room temperature and with stirring for two days. The reaction mixture was hydrolyzed and additional quantities of ether were used to extract the desired products from the partially gelatinous aqueous phase. The ethereal extract after drying was distilled and after removal of the ether the residue was fractionated in a 1-foot column.

Tris-(*m*-trifluoromethylphenyl)-fluorosilane was isolated as the fraction boiling at 168-174° (1-2 mm.), *n*<sup>20</sup><sub>D</sub> 1.4859, *d*<sup>20</sup> 1.4008; *M*<sub>R</sub><sub>D</sub> calcd. 97.68, found 98.84. The yield was 18.8 g. or 23.4%.

*Anal.*<sup>2</sup> Calcd. for C<sub>21</sub>H<sub>12</sub>F<sub>10</sub>Si: C, 52.28; H, 2.50. Found: C, 52.88; H, 2.48.

From the high boiling fractions of several preparations of tris-(*m*-trifluoromethylphenyl)-fluorosilane there was obtained on fractionation the tetraarylsilane, b. p. 197-200° (2-3 mm.). Several crystallizations from methanol

(1) We acknowledge with thanks the generous gift of benzotrifluoride from the Hooker Chemical Co.

(2) Microanalyses by the Micro-Analytical Laboratory, University of Pittsburgh.

gave the pure tetrakis-(*m*-trifluoromethylphenyl)-silane melting at 102-103°.

*Anal.*<sup>2</sup> Calcd. for C<sub>28</sub>H<sub>16</sub>F<sub>12</sub>Si: C, 55.26; H, 2.65; mol. wt., 608. Found: C, 55.22; H, 2.57; mol. wt. (Rast method), 571, 572.

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#### 4-Benzyloxyacetophenone and -phenylmethylcarbinol

A vigorously agitated mixture of 59 g. (0.43 mole) of 4-hydroxyacetophenone,<sup>1</sup> 56.9 g. (0.45 mole) of benzyl chloride, 150 g. of anhydrous potassium carbonate and 350 cc. of methyl ethyl ketone was refluxed for 12 hours. Water (750 cc.) was added and the product extracted with ether. The solution was washed with alkali and water, dried and concentrated. The oily residue crystallized spontaneously. After trituration with petroleum ether, the 4-benzyloxyacetophenone was recrystallized from isopropyl alcohol. It melted at 96-97°; yield 63 g. (64.3%).

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>: C, 80.6; H, 6.2. Found: C, 80.3; H, 6.1.

In an efficient column, 9.3 g. of 4-benzyloxyacetophenone was reduced with 8.5 g. of aluminum isopropoxide and 150 cc. of isopropyl alcohol in the usual manner, replacing the isopropyl alcohol from time to time. The reaction product was treated with an aqueous solution of 15 g. of potassium hydroxide and the precipitate extracted with ether. 4-Benzyloxyphenylmethylcarbinol boiled at 195-200° at 16 mm. and solidified spontaneously. It was recrystallized from a mixture (1:1) of benzene and petroleum ether and melted at 79-80°; yield, 3.5 g. (37.6%).

*Anal.* Calcd. for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>: C, 78.9; H, 7.0. Found: C, 78.9; H, 7.0.

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(1) Noller and Adams, *This Journal*, **46**, 1892 (1924).