

TABLE I  
 PHYSICAL CONSTANTS OF THE NITROALCOHOLS

Name of compound	B. p., °C., and pressure	Mm.	Sp. gr., $d_{4}^{20}$	Refr. ind., $n_D^{20}$	Formula	% Nitrogen	
						Calcd.	Found <sup>b</sup>
3-Methyl-3-nitro-2-hexanol	97	5	1.0512	1.4522	C <sub>7</sub> H <sub>15</sub> O <sub>2</sub> N	52.17 <sup>a,c</sup>	50.47
3-Methyl-3-nitro-4-nonanol	99-101	1.5	0.9835	1.4540	C <sub>10</sub> H <sub>21</sub> O <sub>2</sub> N	59.11 <sup>a</sup>	58.73
3-Methyl-3-nitro-4-octanol	90-94	2.5	.9734	1.4568	C <sub>9</sub> H <sub>19</sub> O <sub>2</sub> N	57.14 <sup>a</sup>	56.92
1-Nitro-2-octanol <sup>d</sup>	120	2	...	1.4500	C <sub>8</sub> H <sub>17</sub> O <sub>2</sub> N	8.00	7.81
2-Nitro-3-nonanol	110	1.5	.9937	1.4508	C <sub>9</sub> H <sub>19</sub> O <sub>2</sub> N	7.42	6.93
2-Methyl-2-nitro-3-nonanol	109	1	.9854	1.4525	C <sub>10</sub> H <sub>21</sub> O <sub>2</sub> N	6.90	6.82
4-Nitro-5-hendecanol	135	2	.9550	1.4550	C <sub>11</sub> H <sub>23</sub> O <sub>2</sub> N	6.47	6.40
3-Methyl-3-nitro-4-decanol	128	1.3	.9477	1.4578	C <sub>11</sub> H <sub>23</sub> O <sub>2</sub> N	60.83 <sup>a</sup>	60.67
1-Nitro-2-nonanol	120-121	1	.9838	1.4508	C <sub>9</sub> H <sub>19</sub> O <sub>2</sub> N	7.42	7.33
2-Nitro-3-decanol	125	2	.9761	1.4506	C <sub>10</sub> H <sub>21</sub> O <sub>2</sub> N	6.90	6.61
3-Nitro-4-hendecanol	128	2	.9636	1.4509	C <sub>11</sub> H <sub>23</sub> O <sub>2</sub> N	6.47	6.29
2-Methyl-2-nitro-3-decanol	124-125	1.2	.9784	1.4533	C <sub>11</sub> H <sub>23</sub> O <sub>2</sub> N	6.47	6.30
4-Nitro-5-dodecanol	130	1.2	.9666	1.4522	C <sub>12</sub> H <sub>25</sub> O <sub>2</sub> N	6.06	5.73
3-Methyl-3-nitro-4-hendecanol	111	1.5	.9521	1.4569	C <sub>12</sub> H <sub>25</sub> O <sub>2</sub> N	62.28 <sup>a</sup>	62.44
2-Nitro-3-hendecanol	128	1.8	.9640	1.4513	C <sub>11</sub> H <sub>23</sub> O <sub>2</sub> N	6.47	6.20
3-Nitro-4-dodecanol	138-140	2.2	.9622	1.4517	C <sub>12</sub> H <sub>25</sub> O <sub>2</sub> N	6.06	5.97
2-Methyl-2-nitro-3-hendecanol	125	3	.9240	1.4524	C <sub>12</sub> H <sub>25</sub> O <sub>2</sub> N	6.06	5.83
1-Nitro-2-hendecanol	140	2	.9587	1.4548	C <sub>11</sub> H <sub>23</sub> O <sub>2</sub> N	6.47	6.23
2-Nitro-3-tridecanol	153-155	2	.9496	1.4618	C <sub>13</sub> H <sub>27</sub> O <sub>2</sub> N	5.72	5.30
3-Nitro-4-tetradecanol	150-155	1.5	.9480	1.4638	C <sub>14</sub> H <sub>29</sub> O <sub>2</sub> N	5.41	5.02

<sup>a</sup> % Carbon (not nitrogen), by "Wet Method," Pollard and Forsee, *Ind. Eng. Chem., Anal. Ed.*, **7**, 77 (1935). <sup>b</sup> "Kjeldahl," Harte, *ibid.*, **7**, 432 (1935). <sup>c</sup> Low carbon analysis is due to the presence of 1-nitrobutane in the nitropentanes. <sup>d</sup> Not a new compound (2).

the nitroparaffin and aldehyde followed by dilution and hydrolysis with dilute acetic acid, and (c) by the mixing of a dilute solution of the sodium salt of the nitroparaffin with an aqueous suspension of the sodium bisulfite addition product of

the aldehyde and subsequent heating of the mixture.

2. Some of the physical constants of these nitroalcohols have been measured.

LAFAYETTE, INDIANA

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## Arsine Oxides of Naphthalene and Biphenyl<sup>1</sup>

BY G. O. DOAK, HARRY EAGLE AND H. G. STEINMAN

Arsine oxides, derived from naphthalene and biphenyl, have been prepared by us in order that their treponemicidal activity might be investigated.

Reduction of  $\alpha$ -naphthylarsonic acid with sulfur dioxide and potassium iodide yielded an arsine oxide identical with that obtained by Michaelis,<sup>2</sup> and by Blicke and Smith<sup>3</sup> by other methods.

The  $\beta$ -naphthylarsonic acid, used by Michaelis to prepare the corresponding oxide, was shown by Brown<sup>4</sup> to be a mixture of  $\alpha$ - and  $\beta$ -naphthyl-

arsonic acids.  $\beta$ -Naphthylarsonic acid, prepared by Brown's method, yielded an arsine oxide on reduction which did not melt below 360°.

Saunders, Hamilton and Sweet<sup>5</sup> have described the preparation of a number of nitro-naphthylarsonic acids. We have discovered that the more convenient Scheller-Bart reaction<sup>6</sup> is equally applicable for the preparation of these compounds. Some of these nitronaphthylarsonic acids were reduced catalytically to the corresponding amino compounds by the use of Raney nickel. The yields were comparable to those ob-

(1) Paper V in the series entitled "The Preparation of Phenyl-arsenoxides."

(2) Michaelis, *Ann.*, **320**, 271 (1902).

(3) Blicke and Smith, *THIS JOURNAL*, **51**, 3479 (1929).

(4) Brown, *Trans. Kansas Acad. Sci.*, **42**, 209 (1939).

(5) (a) Saunders and Hamilton, *THIS JOURNAL*, **54**, 636 (1932); (b) Sweet and Hamilton, *ibid.*, **56**, 2408 (1934).

(6) Scheller, French Patent 824,028, *Chem. Zentr.*, **98**, II, 229 (1927); Doak, *THIS JOURNAL*, **62**, 167 (1940).

tained by Saunders and Hamilton,<sup>5a</sup> who used ferrous hydroxide.

The substance described by Adler and Adler<sup>7</sup> as 1-hydroxy-4-naphthylarsonic acid may be 1-hydroxy-2-naphthylarsonic acid according to Brown and Hamilton.<sup>8</sup> Although Brown<sup>9</sup> was unable to synthesize the former compound by the customary methods, and we were unable to prepare it from 4-amino-1-naphthol by the Scheller-Bart procedure, it was finally obtained, in small yield, by a series of reactions which leave no doubt as to its identity.

The only biphenylarsine oxides prepared previously are those described by Worrall<sup>10</sup> and by Oneto and Way.<sup>11</sup> We have obtained three new biphenylarsine oxides.

In an attempt to find a procedure for the synthesis of 4-amino-4'-arsonobiphenyl, simpler than that published by Bauer and Adams,<sup>12</sup> we employed the Bart reaction and diazotized only one amino group of benzidine by following Tauber's directions.<sup>13</sup> Instead of the desired product, a small amount of 4,4'-diarsonobiphenyl, formed from some tetrazotized benzidine, and a large quantity of an unidentified substance were obtained. 4-Amino-4'-arsonobiphenyl was produced finally by another synthesis, and converted into the acetamido and carboxy derivatives; all three products yielded arsine oxides on reduction.

Although an attempt to obtain 3-amino-4-hydroxy-4'-arsonobiphenyl by a process which involved diazotization of 3-nitrobenzidine<sup>14</sup> was unsuccessful, several interesting new compounds were isolated.

### Experimental Part

**4-Nitro-1-naphthyl Benzoate.**—This substance was obtained in 40% yield by the Schotten-Baumann reaction, and in 92% yield by the procedure of Hazlet.<sup>15</sup> It crystallized from acetone in pale yellow needles; m. p. 176° (cor.).

*Anal.* Calcd. for C<sub>17</sub>H<sub>11</sub>O<sub>4</sub>N: N, 4.78. Found: N, 4.9.

**4-Amino-1-naphthyl Benzoate Hydrochloride.**—The above nitro compound, suspended in acetone, was reduced catalytically employing Raney catalyst. After filtration, the addition of hydrochloric acid to the filtrate precipitated

the amine hydrochloride. Recrystallization from alcohol-acetone mixture gave needles; m. p. 258–263° (cor.) with decomposition. The yield was 89%.

**4-Hydroxy-1-naphthylarsonic Acid.**—Although the customary Bart reaction with the above amine hydrochloride failed to give an arsonic acid, the desired compound was obtained in a 2.5% yield with the Scheller-Bart reaction. It crystallized from water as needles which did not melt below 360°. The acid gave a deep green color with ferric chloride solution, and coupled with benzenediazonium chloride to give a bright red dye.

**6-Carboxy-2-naphthylarsonic Acid.**—The Sandmeyer reaction, employing nickelous cyanide, was applied to 6-amino-2-naphthylarsonic acid, and the resulting nitrile isolated through the magnesium salt. Hydrolysis with alkali followed by acidification gave the desired acid.

**6-Carbamyl-2-naphthylarsine Oxide.**—A suspension of the preceding compound in chloroform was treated with phosphorus trichloride and pentachloride and the mixture poured into ammonium hydroxide. The arsine oxide separated as an amorphous precipitate, insoluble in all common solvents.

**Reaction Product of Diazotized Benzidine and Sodium Arsenite.**—A solution of diazotized benzidine, prepared according to Tauber,<sup>13</sup> was added to a solution of sodium arsenite containing a little cupric sulfate. A copious brown precipitate formed immediately. After standing several days the mixture was filtered. The filtrate yielded 3.4% of 4,4'-diarsonobiphenyl after acidification. The brown precipitate, which constituted most of the reaction product, could not be positively identified.

**4-Amino-4'-arsonobiphenyl.**—4-Amino-4'-nitrobiphenyl by the Scheller-Bart reaction gave 4-nitro-4'-arsonobiphenyl, which gave the desired amine by catalytic reduction employing Raney catalyst.

**4-Carbamyl-4'-arsenosobiphenyl.**—The Sandmeyer reaction, employing nickelous cyanide, was applied to the above amine, and the resulting nitrile hydrolyzed in solution without isolation. The resulting 4-carboxy-4'-arsonobiphenyl was converted to 4-carbamyl-4'-arsenosobiphenyl in the usual manner.

**3-Nitro-4-amino-4'-arsonobiphenyl and 3-Nitro-4,4'-diarsonobiphenyl.**—The Bart reaction when applied to 3-nitrobenzidine gave a mixture of the above compounds. This mixture was dissolved in ammonium hydroxide, cooled, treated with magnesia mixture, and filtered after standing for one hour. The precipitate was triturated with dilute hydrochloric acid, again dissolved in ammonium hydroxide and the process repeated. In this manner, a pure sample of 3-nitro-4,4'-diarsonobiphenyl was obtained. On boiling the filtrate from the first separation, the magnesium salt of 3-nitro-4-amino-4'-arsonobiphenyl precipitated, which was similarly purified. We have found it to be a general rule that diarsonic acids give insoluble magnesium salts in the cold, whereas the magnesium salts of monoarsonic acids usually precipitate only on heating.

**3-Nitro-4-hydroxy-4'-arsonobiphenyl.**—3-Nitro-4-amino-4'-arsonobiphenyl was boiled in a 25% potassium hydroxide solution for several hours. The impure acid, which separated upon acidification, was purified by dissolving in sodium bicarbonate solution, followed by treatment with Darco and then again acidifying. Reduction of the nitro

(7) Adler and Adler, *Ber.*, **41**, 931 (1908); German Patent 205,775, *Chem. Zentr.*, **80**, I, 881 (1909).

(8) Brown and Hamilton, *This Journal*, **56**, 151 (1934).

(9) Brown, Thesis, University of Nebraska, 1933.

(10) Worrall, *This Journal*, **52**, 664 (1930).

(11) Oneto and Way, *ibid.*, **63**, 3068 (1941).

(12) Bauer and Adams, *ibid.*, **46**, 1925 (1924).

(13) Tauber, *Ber.*, **27**, 2627 (1894).

(14) Le Fèvre and Turner, *J. Chem. Soc.*, 245 (1928).

(15) Hazlet, *This Journal*, **59**, 287 (1937).

TABLE I  
ARSONIC ACIDS AND ARSINE OXIDES DERIVED FROM NAPHTHALENE AND BIPHENYL

Compound, R = Arsono	Description	Yield, %	Formula	As analyses, %		N analyses, %	
				Calcd.	Found	Calcd.	Found
6-R-2-naphthoic acid	White powder	22	C <sub>11</sub> H <sub>9</sub> O <sub>5</sub> As	25.3	25.5		
4-R-1-naphthol	White needles	2.5	C <sub>10</sub> H <sub>9</sub> O <sub>4</sub> As	27.9	27.9		
3-Nitro-4,4'-di-R-biphenyl <sup>a</sup>	Yellow powder	19.4	C <sub>12</sub> H <sub>11</sub> O <sub>8</sub> NAs	33.5	33.6	3.1	3.3
3-Nitro-4-amino-4'-R-biphenyl	Brown powder	14.9	C <sub>12</sub> H <sub>11</sub> O <sub>6</sub> N <sub>2</sub> As	22.2	22.3	8.3	8.0
3-Nitro-4-hydroxy-4'-R-biphenyl	Red powder	75	C <sub>12</sub> H <sub>10</sub> O <sub>6</sub> NAs	22.1	22.0	4.1	4.3
4-Nitro-4'-R-biphenyl	Pale yellow needles	34	C <sub>12</sub> H <sub>10</sub> O <sub>6</sub> NAs	23.2	22.9	4.3	4.4
4-Amino-4'-R-biphenyl	White needles	80	C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> NAs	25.6	25.4	4.8	4.8
4-Acetamido-4'-R-biphenyl	White needles	100	C <sub>14</sub> H <sub>14</sub> O <sub>4</sub> NAs	22.4	22.6	4.2	4.1
4-Carboxy-4'-R-biphenyl	White powder	14	C <sub>12</sub> H <sub>11</sub> O <sub>6</sub> As	23.3	23.4		
4,4'-Di-R-biphenyl	White prisms	3.4	C <sub>12</sub> H <sub>12</sub> O <sub>8</sub> As <sub>2</sub>	37.3	36.9		
R = Arsenoso							
2-R-naphthalene	White powder	90	C <sub>10</sub> H <sub>7</sub> OAs	34.2	34.0		
4-Acetamido-1-R-naphthalene <sup>b</sup>	White needles	71	C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> NAs	27.2	27.2	<sup>c</sup>	
2-Acetamido-1-R-naphthalene <sup>d</sup>	White powder	65	C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> NAs	27.2	27.3	<sup>c</sup>	
6-R-2-naphthamide	White powder	91	C <sub>11</sub> H <sub>9</sub> O <sub>2</sub> NAs	28.7	28.3	5.4	5.4
4-Carbamyl-4'-R-biphenyl <sup>e</sup>	White powder	85	C <sub>18</sub> H <sub>10</sub> O <sub>2</sub> NAs	26.1	26.0	4.9	4.7
4-Amino-4'-R-biphenyl <sup>f</sup>	White powder	100	C <sub>12</sub> H <sub>10</sub> ONAs·2H <sub>2</sub> O	25.4	25.3	4.8	4.8
4-Acetamido-4'-R-biphenyl <sup>g</sup>	White powder	100	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub> NAs·H <sub>2</sub> O	23.4	23.5	4.4	4.4

<sup>a</sup> M. p. 249.5–250.5° (all melting points are corrected). <sup>b</sup> M. p. 272°. <sup>c</sup> We have been unable to obtain satisfactory nitrogen analyses on many naphthalenearsonic acids and arsine oxides containing nitrogen attached directly to the ring. Kjeldahl determinations were entirely unsatisfactory. Using the Dumas procedure, even with the addition of potassium chlorate, the results were erratic and we were never able to obtain the theoretical value. <sup>d</sup> M. p. 256.5°. <sup>e</sup> M. p. 271–273°. <sup>f</sup> M. p. 221–222°. <sup>g</sup> M. p. 297.5–298.5°.

group with ferrous hydroxide, or catalytically, using Raney catalyst, was unsatisfactory.

Table I lists the new compounds, or compounds prepared by a new procedure. Except as noted in the text, the arsine oxides were prepared by sulfur dioxide reduction of the corresponding arsonic acids in the usual manner. They were insoluble in water and the usual organic solvents. 4-Arsono-1-naphthol was recrystallized from hot water. The remaining crys-

talline compounds were crystallized from alcohol.

### Summary

Several new arsonic acids derived from naphthalene and biphenyl have been prepared, and more convenient methods have been described for the preparation of other known compounds. The arsonic acids have been reduced to the corresponding arsine oxides.

BALTIMORE, MD.

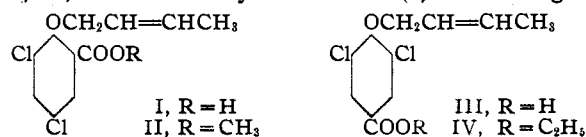
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

## The Rearrangement of 4-Crotyloxy-3,5-dichlorobenzoic Acid

BY D. S. TARBELL AND J. W. WILSON<sup>1</sup>

In a previous paper<sup>2</sup> it was shown that O-crotyl-3,5-dichlorosalicylic acid (I) rearranges



smoothly at 125° with loss of carbon dioxide to give 2,4-dichloro-6-( $\alpha$ -methylpropenyl)-phenol. This reaction therefore goes with inversion

(attachment of the  $\gamma$ -carbon atom) just as the ordinary Claisen rearrangement does. The present paper reports a study of a similar compound, 4-crotyloxy-3,5-dichlorobenzoic acid (III), in which the substituted allyl group migrates to the para position.

The crotyl ether of ethyl 3,5-dichloro-4-hydroxybenzoate (IV) was obtained using aqueous sodium hydroxide-acetone as the reaction medium. Saponification of the ester yielded 4-crotyloxy-3,5-dichlorobenzoic acid (III), which was

(1) Sherman Clarke Fellow, 1941–1942.

(2) Tarbell and Wilson, *THIS JOURNAL*, **64**, 607 (1942).