

## Cytotoxic Compounds. Part 22.<sup>1</sup> Reaction of 2,2'-Iminodiethanol with Some Chloronitrobenzenes

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Conditions have been established for the reaction of 2,2'-iminodiethanol with 2,3-, 2,4-, and 2,5-dichloronitrobenzene to give, as major products, the 2-(bis-2-hydroxyethylamino)-compounds: 3,4-dichloronitrobenzene and 4-chloro-3-nitrobenzoic acid gave the 4-(bis-2-hydroxyethylamino)-compounds. Minor products were the corresponding 2-hydroxyethylamino-compounds and the amino- or azo-compounds formed by reduction of the nitro-group.

Conversion of the bis-2-hydroxyethylamino-compounds into the bis-2-chloroethylamino-derivatives, followed by catalytic hydrogenation of the nitro-group and reaction of the resultant primary amines with aryl chloroformates, led to mustard carbamates of potential interest as anti-tumour agents.

AROMATIC nitrogen mustards (ring-substituted *NN*-bis-2-chloroethylanilines) are prepared from the corresponding diols, which are usually made by bishydroxyethylation of the ring-substituted aniline, a reaction which is impracticable when the basic character of the amine is diminished by the presence of an *o*- or *p*-nitro-group. Thus it was not possible to prepare the diols (1) and (5) by reaction of ethylene oxide with 4-chloro-2-nitroaniline or with 2-chloro-4-nitroaniline, respectively.<sup>1</sup> In principle, however, these diols should be accessible by nucleophilic aromatic substitution.

<sup>1</sup> Part 21, A. J. Abela Medici, L. N. Owen, and C. Sflomos, *J.C.S. Perkin I*, 1977, 2258.

<sup>2</sup> K. F. Waldkötter, *Rev. Trav. chim.*, 1939, **58**, 132.

<sup>3</sup> J. Degutis and V. Bieksa, *Liet. T.S.R. Akad. Darbai, Ser. B*, 1965, **42**(3), 71; O. Barauskaite, V. Bieksa, and J. Degutis, *Liet. T.S.R. Mokslu Akad. Darbai, Ser. B*, 1971, **66**(3), 139.

Waldkötter<sup>2</sup> prepared *NN*-bis-2-hydroxyethyl-2,4-dinitroaniline by treatment of 1-chloro-2,4-dinitrobenzene with 2,2'-iminodiethanol, and a similar reaction has been carried out on some 4-bromo-3-nitrobenzenesulphonamides,<sup>3</sup> but 2-chloronitrobenzene gave only a mixture of *N*-(2-aminophenyl)morpholine, 2,2'-dichloroazobenzene, 2-chloroaniline, and 2-nitrophenol, whilst the sole product obtained from 4-chloronitrobenzene was 4,4'-dichloroazobenzene.<sup>4</sup> Only tars, with reduction and hydrolysis products, were obtained by heating various dichloronitrobenzenes with iminodiethanol at 175 °C in the presence or absence of sodium carbonate.<sup>5</sup>

Notwithstanding the unpromising nature of these

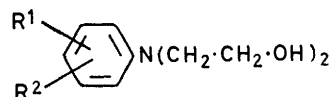
<sup>4</sup> M. Meltner, L. Greenstein, G. Gross, and M. Cohen, *J. Amer. Chem. Soc.*, 1937, **59**, 2660.

<sup>5</sup> C. B. Kremer and A. Bendich, *J. Amer. Chem. Soc.*, 1940, **62**, 1279.

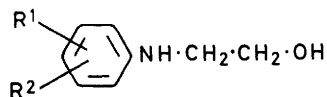
reports, the reaction was considered to be worthy of further study, under milder conditions, as a potential source of *NN*-bis-2-hydroxyethylanilines containing one nitro-group and one other function as additional ring-substituents. Such products, after sequential conversion into the mustards, reduction of the nitro-group, and reaction of the resultant primary amines with an aryl chloroformate, would lead to certain hitherto inaccessible mustard carbamates of potential interest as

was present in the iminodiethanol was ruled out by g.l.c. analysis of the reagent, and it therefore appears that loss of a 2-hydroxyethyl group, either from iminodiethanol or from the *NN*-bis-2-hydroxyethylamine, must be occurring as a minor side-reaction.

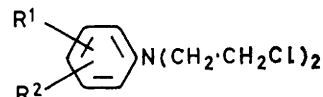
Reaction of iminodiethanol with 4-chloro-3-nitrobenzoic acid also proceeded satisfactorily; the crude product was difficult to purify because of its low solubility, and it was therefore esterified to give the methyl



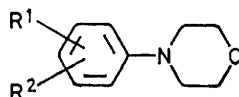
R1	R2
(1) 4-Cl	2-NO <sub>2</sub>
(2) 6-Cl	2-NO <sub>2</sub>
(3) 5-Cl	2-NO <sub>2</sub>
(4) 3-Cl	4-NO <sub>2</sub>
(5) 2-Cl	4-NO <sub>2</sub>
(6) 4-CO <sub>2</sub> Me	2-NO <sub>2</sub>



R1	R2
(7) 4-Cl	2-NO <sub>2</sub>
(8) 6-Cl	2-NO <sub>2</sub>
(9) 5-Cl	2-NO <sub>2</sub>
(10) 2-Cl	4-NO <sub>2</sub>



R1	R2
(12) 4-Cl	2-NH·CO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> Cl (o)
(13) 6-Cl	2-NH·CO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> Cl (o)
(14) 2-Cl	4-NH·CO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> Cl (o)
(15) 4-CO <sub>2</sub> Me	2-NH·CO <sub>2</sub> Ph



(11)

anti-tumour agents.<sup>1</sup> This approach proved to be fruitful.

Treatment of 2,5-dichloronitrobenzene with iminodiethanol at 110 °C gave the required 5-chloro-2-(bis-2-hydroxyethylamino)nitrobenzene (1) as the main product (54%); small amounts of 2,2',5,5'-tetrachloroazobenzene (4%) and the 2-hydroxyethylamino-compound (7) (2%) were also isolated. Under similar conditions, 2,3-dichloronitrobenzene gave the diol (2) (49%), 2,3-dichloroaniline (3%), and the 2-hydroxyethylamino-compound (8) (4%). 2,4-Dichloronitrobenzene gave the diol (3) (74%), the isomeric diol (4) (6%), and the 2-hydroxyethylamino-compound (9) (2%); it is known<sup>6,7</sup> that the 2-position is much more reactive than the 4-position in 2,4-dichloronitrobenzene, and there is only one previous record of the isolation of a minor amount of 4-substituted product, the nucleophile then being ammonia.<sup>8</sup> The relatively low reactivity of the 4-position towards reaction with iminodiethanol was also evident when 3,4-dichloronitrobenzene was used, a much longer reaction time being necessary to obtain the diol (5) in good yield (61%), the by-products being 3,3',4,4'-tetrachloroazobenzene (9%) and the 2-hydroxyethylamino-compound (10) (2%).

The origin of the monohydroxy-compounds (7)–(10) is obscure. The possibility that some 2-aminoethanol

ester (6). In contrast, 4-chloro-3-nitroanisole gave only 2-chloro-5-methoxyaniline and 2,2'-dichloro-5,5'-dimethoxyazobenzene, the activating effect of the *o*-nitro-group on the reactivity of the halide towards nucleophilic displacement being completely overshadowed by the deactivation caused by the *p*-methoxy-group.

By reaction with phosphoryl chloride the diols (1)–(6) were converted into the corresponding bis-2-chloroethylamino-compounds, small amounts of the *N*-aryl-morpholines (11) also being formed. Catalytic hydrogenation of the nitro-mustards derived from the diols (1), (2), (5), and (6), followed by reaction of the crude amino-mustards with phenyl or 2-chlorophenyl chloroformate, gave the mustard carbamates (12)–(15).

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were recorded for solutions in deuteriochloroform (Varian T-60 instrument); signals due to hydroxy- or amino-protons were identified by deuterium exchange; resonances for aromatic protons are omitted, though the integrals were in accord with those of other quoted resonances. I.r. spectra were recorded for routine structural confirmations but are not reported here. Kieselgel GF<sub>254</sub> (Merck) was used for t.l.c. Petroleum refers to the fraction of b.p. 40–60 °C.

<sup>7</sup> C. B. Kremer and A. Bendich, *J. Amer. Chem. Soc.*, 1939, **61**, 2658.

<sup>6</sup> A. F. Holleman, W. J. De Mooy, and J. Ter Weel, *Rec. Trav. chim.*, 1915, **35**, 1; J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1.

<sup>8</sup> H. J. den Hertog and C. Jouwersma, *Rec. Trav. chim.*, 1953, **72**, 44.

*Reactions with 2,2'-Iminodiethanol.*—(a) A mixture of 2,5-dichloronitrobenzene (5 g) and iminodiethanol (10 ml) was stirred at 110 °C (oil-bath) for 3 h, then allowed to cool, and partitioned between water and dichloromethane. The organic layer was washed with water, then dried, and concentrated to an oil, which was separated by t.l.c. (ether) into the following fractions (in order of increasing  $R_F$ ): (i) 2-(bis-2-hydroxyethylamino)-5-chloronitrobenzene (1) (3.6 g), an oil,  $\tau$  6.33 (4 H, t, O-CH<sub>2</sub>), 6.67 (4 H, t, N-CH<sub>2</sub>), 7.1br (2 H, OH) (Found: C, 45.8; H, 5.0; Cl, 13.6; N, 10.7. C<sub>10</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>4</sub> requires C, 46.1; H, 5.0; Cl, 13.6; N, 10.75%); (ii) 2,2',5,5'-tetrachloroazobenzene (118 mg), m.p. 188 °C (from benzene) (lit.,<sup>9</sup> 189 °C); and (iii) 5-chloro-2-(2-hydroxyethylamino)nitrobenzene (7) (86 mg), orange needles (from dichloromethane-petroleum), m.p. and mixed m.p. 106–108 °C (lit.,<sup>7</sup> 107.5 °C),  $\tau$  1.67br (1 H, NH), 6.00 (2 H, t, O-CH<sub>2</sub>), 6.43 (2 H, t, N-CH<sub>2</sub>), and 8.3 br (1 H, OH).

(b) Similar treatment of 2,3-dichloronitrobenzene (5 g) with 2,2'-iminodiethanol (10 ml) for 5 h at 115 °C gave the following fractions (t.l.c. in dichloromethane): (i) 2-(bis-2-hydroxyethylamino)-3-chloronitrobenzene (2) (3.35 g), yellow needles (from aqueous ethanol), m.p. 70–71 °C,  $\tau$  6.35 (4 H, t, O-CH<sub>2</sub>), 6.70 (4 H, t, N-CH<sub>2</sub>), and 7.5br (2 H, OH) (Found: C, 46.15; H, 4.9; Cl, 13.8; N, 10.8%); (ii) 3-chloro-2-(2-hydroxyethylamino)nitrobenzene (8) (0.21 g), an oil (lit.,<sup>7</sup> oil),  $\tau$  3.2br (1 H, NH), 6.3 (4 H, m, CH<sub>2</sub>), and 7.7br (1 H, OH); (iii) 2,3-dichloroaniline (0.16 g) [*N*-acetyl derivative, m.p. 159 °C (from water) (lit.,<sup>10</sup> 156–157 °C)]; and (iv) unchanged 2,3-dichloronitrobenzene (1.3 g).

(c) Reaction of 2,4-dichloronitrobenzene (5 g) with iminodiethanol (10 ml) for 2 h at 108 °C gave (t.l.c. in ether) (i) 4-(bis-2-hydroxyethylamino)-2-chloronitrobenzene (4) (0.38 g), yellow needles (from aqueous ethanol), m.p. 78–79 °C,  $\tau$  6.05 (4 H, t, O-CH<sub>2</sub>), 6.30 (4 H, t, N-CH<sub>2</sub>), and 7.1br (2 H, OH) (Found: C, 46.2; H, 5.1; Cl, 13.3; N, 10.7%); (ii) 2-(bis-2-hydroxyethylamino)-4-chloronitrobenzene (3) (5.1 g), an orange oil,  $\tau$  6.35 (4 H, m, O-CH<sub>2</sub>), 6.63 (4 H, m, N-CH<sub>2</sub>), and 7.0br (2 H, OH) (Found: C, 46.0; H, 5.1; Cl, 13.2; N, 10.7%); and (iii) 4-chloro-2-(2-hydroxyethylamino)nitrobenzene (9) (0.12 g), m.p. 116–117 °C (from petroleum) (lit.,<sup>7</sup> 116 °C),  $\tau$  1.7br (1 H, NH), 6.03 (2 H, t, O-CH<sub>2</sub>), 6.50 (2 H, t, N-CH<sub>2</sub>), and 7.4br (1 H, OH).

(d) 3,4-Dichloronitrobenzene (5 g) and iminodiethanol (10 ml) were heated together for 24 h at 118 °C. The product, isolated as previously described, was a black oil, which, when dissolved in dichloromethane and set aside, deposited orange crystals (0.23 g) (m.p. 150–154 °C) of the azo-compound described below. The filtrate was concentrated and the residue subjected to t.l.c. (ethyl acetate) to give (i) 4-(bis-2-hydroxyethylamino)-3-chloronitrobenzene (5) (4.15 g), an orange oil,  $\tau$  6.30 (8 H, sext, CH<sub>2</sub>) and 7.4br (2 H, OH) (Found: C, 46.0; H, 5.2; Cl, 13.8; N, 10.6%); (ii) 3-chloro-4-(2-hydroxyethylamino)nitrobenzene (10) (0.13 g), m.p. 115–117 °C (from ether-petroleum) (lit.,<sup>7</sup> 120 °C); and (iii) 3,3',4,4'-tetrachloroazobenzene (0.15 g), m.p. 152–154 °C (from ether) (lit.,<sup>11</sup> 158 °C) (Found: C, 44.6; H, 2.1; Cl, 44.6; N, 9.0. Calc. for C<sub>12</sub>H<sub>6</sub>Cl<sub>4</sub>N<sub>2</sub>: C, 45.0; H, 1.9; Cl, 44.3; N, 8.75%).

(e) A mixture of 4-chloro-3-nitrobenzoic acid (25 g) and 2,2'-iminodiethanol (50 ml) was heated at 105 °C for 5 h,

then worked up to give an oil which was dissolved in methanol (350 ml) containing sulphuric acid (80 ml). This solution was boiled under reflux for 20 h, then neutralised with aqueous sodium hydrogen carbonate, concentrated, and extracted with ethyl acetate to give methyl 4-(bis-2-hydroxyethylamino)-3-nitrobenzoate (6) (11.7 g), an oil, purified by t.l.c. (ethyl acetate),  $\tau$  6.03 (3 H, s, CO<sub>2</sub>Me), 6.25 (4 H, t, O-CH<sub>2</sub>), 6.44 (4 H, t, N-CH<sub>2</sub>), and 7.0br (2 H, OH) (Found: C, 51.0; H, 5.8; N, 9.7. C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub> requires C, 50.7; H, 5.7; N, 9.85%).

(f) 4-Chloro-3-nitroanisole (5 g) and iminodiethanol (10 ml) were mixed and heated at 116 °C for 77 h. A solution of the washed and dried product in dichloromethane deposited orange crystals (1.92 g) of 2,2'-dichloro-5,5'-dimethoxyazobenzene, m.p. 175–176 °C (from dichloromethane) (lit.,<sup>11</sup> 172 °C). The filtrate was concentrated and purified by t.l.c. (dichloromethane) to give 2-chloro-5-methoxyaniline (1.3 g),  $\tau$  6.0br (2 H, NH<sub>2</sub>) and 6.29 (3 H, s, OMe), characterised as the *N*-acetyl derivative, m.p. 102 °C (from water) (lit.,<sup>12</sup> 99 °C).

*Ring-substituted (Bis-2-chloroethylamino)nitrobenzenes.*—(a) Phosphoryl chloride (3 ml) in benzene (4 ml) was added to a solution of 5-chloro-2-(bis-2-hydroxyethylamino)nitrobenzene (1.6 g) in benzene (6 ml). The mixture was boiled under reflux for 4 h, then cooled, stirred with aqueous sodium hydrogen carbonate, and extracted with dichloromethane to give an oil. T.l.c. (dichloromethane) gave (i) 2-(bis-2-chloroethylamino)-5-chloronitrobenzene (1.6 g), an orange oil,  $\tau$  6.45 (8 H, s, CH<sub>2</sub>) (Found: C, 40.3; H, 3.8; Cl 36.0; N, 9.45. C<sub>10</sub>H<sub>11</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>2</sub> requires C, 40.4; H, 3.7; Cl, 35.7; N, 9.4%); and (ii) *N*-(4-chloro-2-nitrophenyl)morpholine (55 mg), orange needles, m.p. 45–46 °C (from carbon tetrachloride-petroleum) Found: C, 49.35; H, 4.35; Cl, 14.6; N, 11.75. C<sub>10</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>3</sub> requires C, 49.5; H, 4.6; Cl, 14.6; N, 11.5%).

(b) Similar treatment of 2-(bis-2-hydroxyethylamino)-3-chloronitrobenzene (1.5 g) gave (i) 2-(bis-2-chloroethylamino)-3-chloronitrobenzene (0.9 g), an oil,  $\tau$  6.47 (8 H, s, CH<sub>2</sub>) (Found: C, 41.0; H, 3.7; Cl, 35.7; N, 9.1%); and (ii) *N*-(2-chloro-6-nitrophenyl)morpholine (0.26 g), yellow needles, m.p. 97 °C (from carbon tetrachloride-petroleum) (Found: C, 49.5; H, 4.7; N, 11.5%). Separation of these two products was difficult because the difference in  $R_F$  was small.

(c) 2-(Bis-2-hydroxyethylamino)-4-chloronitrobenzene (1.5 g) gave (i) 2-(bis-2-chloroethylamino)-4-chloronitrobenzene (1.3 g), an oil,  $\tau$  6.44 (8 H, s, CH<sub>2</sub>) (Found: C, 40.4; H, 3.7; Cl, 35.5; N, 9.5%); and (ii) *N*-(5-chloro-2-nitrophenyl)morpholine (87 mg), orange needles, m.p. 70–71 °C (from carbon tetrachloride-petroleum),  $\tau$  6.14 (4 H, t, O-CH<sub>2</sub>) and 6.92 (4 H, t, N-CH<sub>2</sub>) (Found: C, 49.7; H, 4.3; Cl, 14.8; N, 11.4%).

(d) 4-(Bis-2-hydroxyethylamino)-2-chloronitrobenzene (0.46 g) gave (i) 4-(bis-2-chloroethylamino)-2-chloronitrobenzene (93 mg), yellow needles, m.p. 115 °C (from carbon tetrachloride),  $\tau$  6.40 (8 H, s, CH<sub>2</sub>) (Found: C, 40.6; H, 3.8; N, 9.2%); and (ii) *N*-(3-chloro-4-nitrophenyl)morpholine (44 mg), yellow needles, m.p. 124–125 °C (from carbon tetrachloride-petroleum) (Found: C, 49.5; H, 4.7; Cl, 14.7; N, 11.5%).

(e) 4-(Bis-2-hydroxyethylamino)-3-chloronitrobenzene (1.5 g) gave (i) 4-(bis-2-chloroethylamino)-3-chloronitrobenzene (1.3 g), an oil,  $\tau$  6.30 (8 H, q, CH<sub>2</sub>) (Found: C, 40.6;

<sup>9</sup> T. de Crauw, *Rec. Trav. chim.*, 1931, **50**, 753.

<sup>10</sup> F. Beilstein and A. Kurbatow, *Annalen*, 1879, **196**, 214.

<sup>11</sup> J. F. Corbett and P. F. Holt, *J. Chem. Soc.*, 1963, 2385.

<sup>12</sup> J. A. Cummins and M. L. Tomlinson, *J. Chem. Soc.*, 1955, 3475.

H, 3.7; Cl, 35.7; N, 9.5%); and (ii) N-(2-chloro-4-nitrophenyl)morpholine (60 mg), yellow plates, m.p. 130 °C (from carbon tetrachloride-petroleum),  $\tau$  6.06 (4 H, t, O·CH<sub>2</sub>) and 6.76 (4 H, t, N·CH<sub>2</sub>) (Found: C, 49.2; H, 4.4; Cl, 14.5; N, 11.6%).

(f) Methyl 4-(bis-2-hydroxyethylamino)-3-nitrobenzoate (11.0 g) gave methyl 4-(bis-2-chloroethylamino)-3-nitrobenzoate (9.8 g), an oil,  $\tau$  6.05 (3 H, s, CO<sub>2</sub>Me) and 6.35 (8 H, s, CH<sub>2</sub>) (Found: C, 44.9; H, 4.3; Cl, 22.2; N, 8.7. C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub> requires C, 44.9; H, 4.4; Cl, 22.1; N, 8.7%).

2-Chlorophenyl N-[2-(Bis-2-chloroethylamino)-5-chlorophenyl]carbamate (12).—A solution of 2-(bis-2-chloroethylamino)-5-chloronitrobenzene (1.35 g) in methanol (250 ml), containing 10% palladium-charcoal (0.15 g), was shaken in hydrogen until the calculated amount of gas had been absorbed. The solution was then filtered into 50% hydrogen chloride in methanol (30 ml), and the mixture was evaporated to give a solid hydrochloride which rapidly became brown. It was therefore treated, in benzene (25 ml) and pyridine (0.7 g), with 2-chlorophenyl chloroformate<sup>13</sup> (0.7 g), and after being boiled under reflux for 12 h the solution was cooled and washed with 10% hydrochloric acid and with water, then dried and evaporated to give the carbamate (0.7 g), m.p. 98 °C (from ether-petroleum),  $\tau$  1.11br (1 H, NH) and 6.58 (8 H, q, CH<sub>2</sub>) (Found: C, 48.2; H, 3.9; Cl, 33.5; N, 6.6. C<sub>17</sub>H<sub>16</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub> requires C, 48.4; H, 3.8; Cl, 33.6; N, 6.6%).

2-Chlorophenyl N-[2-(Bis-2-chloroethylamino)-3-chlorophenyl]carbamate (13).—By a similar procedure, hydrogenation of 2-(bis-2-chloroethylamino)-3-chloronitrobenzene

(0.5 g) gave a crude hydrochloride, which on reaction with 2-chlorophenyl chloroformate (275 mg) in benzene (10 ml) and pyridine (1 ml) afforded the carbamate (200 mg), m.p. 103–105 °C (from ether-petroleum),  $\tau$  0.70br (1 H, NH) and 6.10 (8 H, s, CH<sub>2</sub>) (Found: C, 48.3; H, 3.9; Cl, 33.8; N, 6.7%).

2-Chlorophenyl N-[4-(Bis-2-chloroethylamino)-3-chlorophenyl]carbamate (14).—Hydrogenation of 4-(bis-2-chloroethylamino)-3-chloronitrobenzene under the same conditions gave a crude hydrochloride, which afforded the carbamate, m.p. 28–32 °C (from ether-petroleum),  $\tau$  2.0–3.0 (8 H, m, aromatic and NH) and 6.48 (8 H, s, CH<sub>2</sub>) (Found: C, 48.3; H, 4.2; Cl, 32.9; N, 6.5%).

Phenyl N-[2-(Bis-2-chloroethylamino)-5-methoxycarbonylphenyl]carbamate (15).—Prepared in a similar way from methyl 4-(bis-2-chloroethylamino)-3-nitrobenzoate (4.0 g), the crude hydrochloride reacted with phenyl chloroformate (3 ml) in pyridine (6 ml) and benzene (50 ml) (4 h under reflux) to give the carbamate (1.8 g), m.p. 111–113 °C (from ether),  $\tau$  1.27 (1 H, s, NH), 6.08 (3 H, s, CO<sub>2</sub>Me), and 6.52 (8 H, m, CH<sub>2</sub>) (Found: C, 55.3; H, 4.9; N, 6.55. C<sub>19</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub> requires C, 55.5; H, 4.9; N, 6.8%).

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<sup>13</sup> R. E. Oesper, W. Broker, and W. A. Cook, *J. Amer. Chem. Soc.*, 1925, **47**, 2609.