Preparation of 4,4′,5,5′,-Tetranitro-1,1′-binaphthyl

Louis A. Jones[1] **and Charles T. Joyner**
Department of Chemistry, North Carolina State University, Raleigh, N.C. 27607

The synthesis and proof of structure of 4,4′,5,5′-tetranitro-1,1′-binaphthyl is described.

Previous communications from this laboratory have described the nitration products of acenaphthene and the subsequent conversion to diaminonaphthalic anhydrides or derivatives thereof *(10, 11)*. As an extension of these studies, the nitration of binaphthyl (Compound 1) was examined since it differed from acenaphthene in that the 8-position of the naphthalene moiety was available for substitution, whereas the corresponding position in acenaphthene was not. Lossen reported in 1867 that the direct nitration of compound 1 with fuming nitric acid resulted in a product whose empirical formula was $C_{20}H_{10}(NO_2)_4$ although no structural assignment was reported *(15)*. Mild nitration of compound 1 has been reported to yield the 4,4′-dinitro derivative (Compound 2) *(19)*. In view of the paucity of information concerning this nitration, we became interested in determining the products obtained under a variety of nitrating conditions and, in particular, attempting to prepare 4,4′,5,5′-tetranitro-1,1′-binaphthyl (Compound 3), since this could be converted to a tetraamino compound capable of forming ladder polymers with the appropriate acids or anhydrides *(3)*. Although unsymmetrical tetranitrobinaphthyl compounds have been prepared by the Ullman reaction with dinitrohalonaphthalenes *(17)*, Compound 3 has not been previously reported.

To prepare the necessary dinitronaphthalene derivative for Ullman coupling, 1-bromo-5-nitronaphthalene (Compound 4) was nitrated under vigorous conditions and yielded two products. Liquid chromatographic separation and analysis showed the mixture to be 80% of the desired 1-bromo-4,5-dinitronaphthalene (Compound 5) and surprisingly, 1,5-dinitronaphthalene (Compound 6). Only one other unusual displacement of this type has been reported *(12)*. The nmr of compound 5 indicated that the shielding effect of the bromine and the nitro group are essentially equal since protons 2 and 3 had the same chemical shifts and appeared as a single 2H peak at δ 8.2. Alternatively, nitration of 1-bromo-4-nitronaphthalene (Compound 7) produced the desired Compound 5 in high yields *(8)* with no noticeable replacement side products and the ir and nmr of Compound 5 produced by the two methods were identical.

Rogavik et al. reported that when 1,8-dinitronaphthalene was heated with phthalic anhydride in acetic acid and iron, a phthaloperinone was formed *(18)*. Examination of Dreiding models showed the formation of such a compound could occur only when the nitro groups are in the 3,4- or 4,5-positions. However, the directive properties of the nitro group and the naphthalene moiety suggest that 3,4-substitution would be most unlikely *(7, 10, 16)*. Thus when Compound 5 from both sources was treated with phthalic anhydride and iron in acetic acid, the 3-bromo [12*H*-benz[4,5]isoindolo[2,1*a*]perimidin-12-one] (Compound 8) was formed in good yield, offering further support for the 4,5-dinitro derivative 5.

When Compound 5 was heated with activated copper *(21)* to 180°C under nitrogen, complete decomposition occurred while the use of refluxing solvents such as nitrobenzene, ethylene glycol, and butyl cellosolve for long periods of time resulted in the recovery of unreacted Compound 5. The literature contains a few examples of the use of highly polar aprotic solvents to obtain fair yields of coupled benzene products via the Ullman reaction *(1, 13)*. However, when Compound 5 was refluxed for 24 hr with activated copper *(21)* in distilled *N,N*-dimethylformamide (DMF), filtered, and the mixture then quenched with water, a red precipitate was obtained. Elemental analysis indicated an empirical formula of $C_{12}H_{11}N_3O_4$ while the mass spectrum showed a molecular ion of 261. The nmr contained a singlet in the aliphatic region at δ 3.0 which integrated to six protons, and the data are consistent with 1-*N,N*-dimethylamino-4,5-dinitronaphthalene (Compound 9) which was obtained in 89% yield. It is interesting to note, however, that when 1-bromonaphthalene is refluxed with Cu(I) in DMF, it is not the *N,N*-dimethylamino derivative that is produced but rather the reduced product naphthalene *(2)*. It is apparent that two different mechanisms are operating but insufficient data are available to postulate a mechanism for either reaction. The use of other solvents such as dimethylsulfoxide, dimethylacetamide, and *N*-methylpyrrolidin-2-one, resulted in the production of 1,8-dinitronaphthalene (Compound 10) suggesting that acidic α-hydrogens are required for this reduction although the reaction in DMF is anomalous. Similar replacement results were obtained

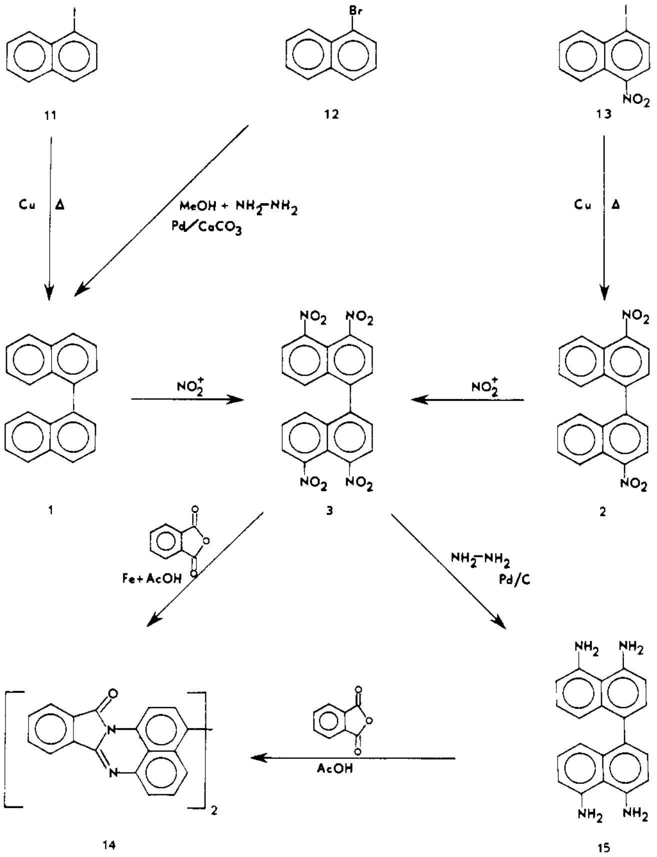

Figure 1. Preparation of 4,4′,5,5′-tetranitro-1,1′-binaphthyl and derivatives

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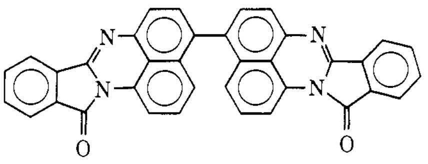
[1] *To whom correspondence should be addressed.*

when Compound 7 was used with the above corresponding solvents.

Several alternative synthetic routes were then studied to effect the preparation of Compound 3. Compound 1 was prepared by either Ullman-type coupling *(6, 17)* of 1-iodonaphthalene (Compound 11) or the Busch reaction *(5)* of 1-bromonaphthalene (Compound 12). The reaction of Compound 1 with a mixture of acetic acid-nitric acid gave a compound which was identical to that prepared in fair yield from 1-iodo-4-nitronaphthalene (Compound 13) and copper powder under standard Ullman conditions (Figure 1). When Compound 1 was treated with a mixture of nitric acid and sulfuric acid at room temperature and then refluxed, there was obtained a 53% yield of a compound whose elemental and mass spectral analysis ($M/e = 434$) corresponded to $C_{20}H_{10}(NO_2)_4$ or Compound 3. The nmr spectrum of Compound 3 exhibited two multiplets at δ 7.6–8.1 and δ 8.3–8.7 which integrated to 6:4 protons. The area of the latter multiplet can be attributed to the 3,3′,6,6′ protons while the former arises from the 2,2′,7,7′,8,8′ protons. Similar yields of the same product were obtained using acetyl nitrate *(4)* or nitronium tetrafluoroborate *(14)* as the nitrating agents on Compound 2, but direct nitration of Compound 1 was superior method.

Although it was assumed on the basis of physical evidence that the product thus obtained was the desired Compound 3, chemical support was sought for confirmation. Thus, when Compound 3 was treated with phthalic anhydride and iron in acetic acid (vide supra) the analogous bisphthaloperinone binaphthyl compound, 3,3′bi[12-benz(4,5)-isoindolo(2,1-*a*)perimidin-12-one] was obtained. One of the three possible geometric isomers is shown.



Compound 14

Elemental analysis supported the empirical formula of $C_{36}H_{18}N_4O_2$ and the mass spectrum showed a molecular ion of 538. The nmr contained a complex aromatic proton pattern and no nitro group absorption was present in the ir spectrum although the carbonyl group stretching frequency (1690 cm^{-1}) was observed. Further, when Compound 3 was reduced and the resulting tetraamine (Compound 15) reacted with phthalic anhydride, Compound 14 was produced. The spectral analysis of Compound 15 indicated a molecular ion of 314 and N-H absorption in both the nmr and ir spectra, further supporting assigned structure of Compound 14.

Experimental

Melting points were determined on a Thomas Hoover capillary melting point apparatus, and elemental analyses were performed on a Perkin-Elmer Model 240 analyzer or by Galbraith Laboratory, Inc., Knoxville, Tenn. The nmr spectra were run on a Varian HA 100 NMR Spectrometer with tetramethylsilane as an internal standard, and ir spectra were obtained from either a Perkin-Elmer 521 or 257 spectrometer. An AEI Model MS12 produced the mass spectra.

The following were obtained from commercial sources: 1,1′-binaphthyl (Compound 1) 1-iodonaphthalene (Compound 11), 1-bromonaphthalene (Compound 12), nitronium tetrafluoroborate, palladium on calcium carbonate, and palladium black. Bakerflex silica gel 1B was used for the tlc work, and deuterated solvents were supplied by Stohler Isotopes.

The activated copper powder was prepared as described by Vogel *(21)*. 4,4′-Dinitro-1,1′-binaphthyl was synthesized from 1,1-binaphthyl and 1-iodo-4-nitronaphthalene *(19)* and 1,5-dinitrophthalene was prepared according to the method of Friedlander *(8)*.

4,4′,5,5′-Tetranitro-1,1′-binaphthyl (Compound 3). *Method A.* To a slurry of Compound 1 (10.0 grams) in glacial acetic acid (50 ml) and sulfuric acid (50 ml) were added 30 ml of 90% nitric acid (sp gr 1.5) in small portions with vigorous stirring keeping the temperature below 30°C. When addition was complete, the reaction was refluxed for 24 hr and then cooled to 0°C. The precipitate was collected, and two recrystallizations from glacial acetic acid gave 9.0 grams (53%) of Compound 3 as light cream-colored needles, mp 320–330°C dec; ir (nujol) 1535 cm^{-1} (NO_2); mass spectrum *m/e* 434 (molecular ion); nmr (DMSO-d_6) δ 7.6–8.1 (6H multiplet, aromatic), and δ 8.3–8.7 (4H multiplet, aromatic).

Anal. Calcd $C_{20}H_{10}N_4O_8$: C, 55.31; H, 2.32; N, 12.90. Found: C, 55.17; H, 2.32; N, 12.74.

Method B. Two grams of Compound 2 were refluxed for 28 hr in a solution of acetic acid (50 ml), sulfuric acid (10 ml), and 90% nitric acid (25 ml). The reaction mixture was cooled and 1.8 grams (50%) of Compound 3 were collected and recrystallized from acetic acid. The ir and nmr spectra of this compound were identical to those of the material prepared by direct nitration of Compound 1.

Method C. Five grams of Compound 1 were added with rapid stirring to NO_2BF_4 (5.0 grams) in freshly distilled tetrahydrothiophene-1,1-dioxide (50 ml). The reaction mixture was heated to 80°C for 1 hr, poured into water (50 ml), the precipitate collected and recrystallized from acetic acid to yield 3.9 grams·(45%) of product, which had the same ir and nmr spectra as that prepared by Method A.

Method D. A suspension of Compound 1 (2.0 grams) in acetic anhydride (10 ml) was added slowly to a solution of acetyl nitrate *(4)* in acetic anhydride at −20°C. After 10 min of stirring, the temperature was raised to 20°C and maintained for 10 min. Finally, the temperature was raised to 80°C for 2 hr during which time dark brown fumes were evolved. The reaction mixture was cooled, added to water (200 ml), and the precipitate filtered and recrystallized from acetic acid to yield 1.8 grams (50%) of Compound 3. Ir and nmr spectra showed this compound to be identical to that prepared by Method A.

1-Bromo-5-nitronaphthalene (Compound 4). Over a 5-hr period, bromine (85 grams) was added to a rapidly stirred melt of 1-nitronaphthalene *(20)* (173 grams) at 80°C. When all of the bromine had been added, the temperature was raised to 100°C and stirring was continued for 2 hr to expel excess bromine and HBr. The reaction product was recrystallized from ethanol to yield 213 grams (85%) of Compound 4 as orange-yellow needles: mp 122.0–123.0°C [lit. *(20)* mp 123°C] ir (nujol 1535, 1350 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 7.3–8.5 (multiplet, aromatic).

1-Bromo-4,5-dinitronaphthalene (Compound 5). *Method A.* To a slurry of Compound 4 (252 grams) in 1500 ml of acetic acid and 150 ml of sulfuric acid, 150 ml of nitric acid (90%) were added dropwise with rapid stirring. Then the reaction mixture was heated to 80°C for 30 min, 250 ml of nitric acid (90%) were added, and the mixture was refluxed for 22 hr. Cooling slowly to 20°C precipitated the product as very pale yellow-white needles. A second crop was precipitated by adding the filtrate to water (3 liters). Both crops were combined and recrystallized from acetic acid to yield 240 grams of cream-colored needles: mp 156–158°C. Qualitative tlc developed in ether–hexane (2:1 v/v) showed two compounds present.

One gram of the mixture was chromatographed on Florisil (250 grams) and eluted with ether–hexane (3:1 v/v). The first fraction was identified as Compound 6 by mixed melting point and comparison of its ir and nmr spectra with those of an authentic sample. A total of 0.19 grams was recovered: mp 218°C. The second fraction yielded a total of 0.78 grams of Compound 5. The reaction yield based on the amount of Compound 4 produced was 65%: mp 176.0°C [lit. *(20)* mp 174°C]; ir (nujol) 1535, 1350 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 7.8–8.0 (1H triplet, aromatic), δ 8.5–8.7 (1H doublet, aromatic), δ 8.2 (2H singlet, aromatic), and δ 8.3–8.4 (1H doublet, aromatic).

1,5-Dinitronaphthalene (Compound 6). Twenty-five ml of 90% nitric acid were slowly added to a suspension of 1-nitronaphthalene *(20)* (20.0 grams) in acetic acid (100 ml) and sulfuric acid (50 ml). After the addition, the mixture was refluxed for 5 hr and then cooled to 10°C. The precipitated product was recrystallized from acid to yield 23.0 grams (91%) of Compound 6 as pale yellow-white needles: mp 219.5°C [lit. *(8)* mp 219°C]; ir (nujol) 1350, 1520 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 7.6–7.8 (2H triplet, aromatic), δ 8.1–8.3 (2H doublet, aromatic) and δ 8.6–8.8 (2 H doublet, aromatic).

1-Bromo-4-nitronaphthalene (Compound 7). To a solution of Compound 12 (20.7 grams) in 70 ml of acetic acid was added 50 ml of nitric acid (sp gr 1.42) at a moderate rate with rapid stirring. After refluxing for 2 hr the reaction solution was cooled to 0°C and the first crop of crystals collected. The filtrate was then added to 500 ml of water and a second crop of precipitate was recovered. Both crops were recrystallized from ethanol to yield a total of 20.5 grams (81.4%) of Compound 7 as light yellow needles: mp 86.5–87.0°C [lit. *(9)* mp 87°C]; ir (nujol) 1530, 1345 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 7.6–8.6 (multiplet, aromatic).

3-Bromo[12H - benz[4,5]isoindolo[2,1-a]perimidin-12-one] (Compound 8). Phthalic anhydride (1.5 grams), powdered iron (3.4 grams), Compound 5 (3.0 grams), and acetic acid (50 ml) were refluxed for 4 hr and the reaction mixture filtered while hot. As the filtrate cooled, a red-brown precipitate formed, which was collected and recrystallized from acetic acid to yield 2.9 grams (75%) of Compound 8 as maroon needles: mp 243.5–245.5°C; ir (nujol) 1690 cm^{-1} C=O); nmr (DMSO-d_6) δ 7.1–8.1 (complex of multiplets, aromatic).

Anal. Calcd $C_{18}H_9N_2OBr$: C, 61.89; H, 2.60; N, 8.02. Found: C, 61.75; H, 2.61; N, 7.91.

1-N,N-Dimethylamino-4,5-dinitronaphthalene (Compound 9). Ten grams of Compound 5 and activated copper (10 grams) were reacted in refluxing distilled DMF (30 ml) for 24 hr. The reaction mixture was then poured into 100 ml of cold water and the precipitate collected and extracted (Soxhlet) with methanol. The extract was reduced to 50 ml and cooled to 0°C to precipitate 9.0 grams (89%) of the product as red-brown needles: mp 175.0–175.5°C [lit. *(20)* mp 176°C]; ir (nujol) 1560 cm^{-1} (C—N); mass spectrum *m/e* 261 (molecular ion); nmr ($CDCl_3$) δ 3.6 (6H singlet, methyl), δ 7.0–7.7 (2H multiplet, aromatic) δ 8.1–8.5 (3H multiplet, aromatic).

Anal. Calcd $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.08. Found: C, 55.07; H, 4.26; N, 16.12.

1,8-Dinitronaphthalene (Compound 10). Ten grams of (Compound 5) and activated copper (10 grams) were reacted in DMAC (50 ml) at reflux for 48 hr. The reaction mixture was then filtered to remove the unreacted copper and the filtrate added to water to precipitate the product. After recrystallizing from methanol, 6.6 grams (84%) of Compound 10 were obtained as light tan crystals: mp 170.0–171.5°C [lit. *(8)* mp 172°C]; ir (nujol) 1350, 1520 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 7.7–7.9 (2H doublet, aromatic) and δ 8.2–8.4 (4H multiplet, aromatic).

Anal. Calcd $C_{10}H_6N_2O_4$: C, 55.05; H, 2.77; N, 12.85. Found: C, 55.00; H, 2.78; N, 12.88.

The above compound was also obtained in good yields when *N*-methylpyrrolidin-2-one or diethylformamide were substituted for DMAC.

3,3 - Bi[12H-benz[4,5]isoindolo[2,1-a]perimidin-12-one] (Compound 14). Phthalic anhydride (15 grams), powdered iron (3.4 grams), Compound 3 (4.3 grams) and acetic acid (50 ml) were refluxed for 4 hr and the reaction mixture filtered while hot. As the filtrate cooled, a red-brown precipitate formed, which was collected and recrystallized from acetic acid to yield 3.6 grams (67%) of Compound 7 as dark ruby crystals: mp 380–400°C dec; δ 7.6–7.8 (4H multiplet, aromatic), δ 7.6–7.8 (4H multiplet, aromatic), and δ 8.3–8.5 (4H multiplet, aromatic).

Anal. Calcd $C_{36}H_{18}N_4O_2$: C, 80.29; H, 3.37; N, 10.40. Found: C, 80.15; H, 3.30; N, 10.45.

4,4′,5,5′-Tetraamino-1,1′-binaphthyl (Compound 15). *Method A.* Pulverized Compound 3 was mixed with palladium black (0.5 gram) in absolute alcohol (25 ml) and hydrazine hydrate was added dropwise over a period of 5 min, after which the reaction mixture was refluxed for 2 hr. After cooling, 250 ml of absolute ethanol was added and after the catalyst was removed by filtration, the volume was then reduced to 50 ml, the precipitate filtered and dried, yielding 0.5 gram (35%) of Compound 14 as a dark green amorphous solid: mp 200–230°C dec; ir (KBr) 3400, 3200 cm^{-1}, broad (NH_2); mass spectrum *m/e* 314 (molecular ion); nmr (DMSO-d_6) 53.7–4.1 (8H broad singlet, amine) and δ 8.3–8.7 (10H multiplet, aromatic).

Anal. Calcd $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.22; H, 6.14; N, 17.50.

Method B. A suspension of powdered Compound 3 in 40 ml of 0.5*m* sodium hydroxide solution and sodium bisulfite (3.0 grams) was refluxed for 15 min. After cooling, the mixture was filtered and the resulting black solid was recrystallized from nitrobenzene yielding 0.5 gram (35%) of Compound 15, identified by comparison of the ir and nmr spectra of the product of Method A.

Literature Cited

(1) Asquith, R. S., Lord, W. M., Peters, A. T., Wallace, F., *J. Amer. Chem. Soc.*, **74**, 5782 (1952).
(2) Bacon, R. G. R., Hill, H. A. O., *J. Chem. Soc.*, **1964**, p 1112.
(3) Bell, V. L., *Polym. Lett.*, **5**, 941 (1967).
(4) Bordwell, F. G., Garbisch, B. W., *J. Org. Chem.*, **28**, 1765 (1963).
(5) Busch, M., Weber, W., *J. Prakt. Chem.*, **146**, 1 (1936).
(6) Chudozilov, L., *Chem. Listy*, **19**, 187 (1925).
(7) Ferguson, L., *Chem. Rev.*, **50**, 47 (1952).
(8) Friedlander, P., *Chem. Ber.*, **32**, 3528 (1899).
(9) Hodgson, H., Hathaway, D., *J. Chem. Soc.*, **1944**, p 385.
(10) Jones, L. A., Joyner, C. T., Kim, W. K., Kyff, R. A., *Can. J. Chem.*, **48**, 3132 (1970).
(11) Jones, L. A., Kim, H. K., Watson, R., *J. Chem. Soc.*, **1971**, p 3891.
(12) Kerkhof, J., *Rec. Trav. Chim.*, **51**, 739 (1932).
(13) Kornblum, N., Kendall, D. L., *J. Amer. Chem. Soc.*, **74**, 5782 (1952).
(14) Kuhn, S. J., Olah, G. A., *ibid.*, **83**, 4564 (1961).
(15) Lossen, F., *Ann. Chem. Pharm.*, **144**, 71 (1867).

(16) Norman, R., Taylor, R., "Electrophilic Substitution in Benzeneoid Compounds," American Elsevier, New York, N.Y., 1965, p 61.
(17) Rindl, M., *J. Chem. Soc.*, **1913**, p 1911.
(18) Rogovik, V., Laurischen, V., Tikhonov, V., *Kim. Geterotsikl. Soedin.*, **1969**, p 1099; *CA*, **72**, 111425Y (1970).
(19) Schoepfle, C. S., *J. Amer. Chem. Soc.*, **45**, 1566 (1923).
(20) Ullman, F., Consonno, F., *Chem. Ber.*, **35**, 2802 (1902).
(21) Vogel, A. I., "Practical Organic Chemistry," Wiley, New York, N.Y., 1966, p 192.

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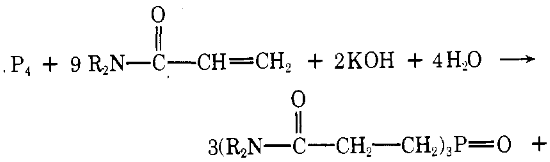
Synthesis of Tris(*N*,*N*-dimethyl-2-carbamoylethyl)phosphine Oxide

D. J. Daigle,[1] T. L. Vigo, and L. H. Chance
Southern Regional Research Laboratory,[2] New Orleans, La. 70119

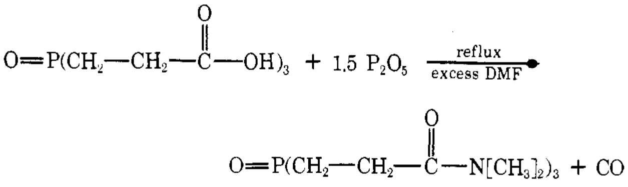
Tris(*N*,*N*-dimethyl-2-carbamoylethyl)phosphine oxide was prepared by reacting phosphorus pentoxide with tris(2-carboxyethyl)phosphine oxide in excess *N*,*N*-dimethylformamide. The compound was very hygroscopic and could only be recrystallized from a cold DMF–ethyl acetate–petroleum ether mixture.

Preparation of tris(*N*,*N*-dialkyl - 2 - carbamoylethyl)-phosphine oxides have been reported in the patent literature but their physical properties, yields, and general characteristics of identification have not been described (*5*). These compounds were prepared by the following reaction (*3*):



$$P_4 + 9\,R_2N{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2 + 2KOH + 4H_2O \longrightarrow 3(R_2N{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2)_3P{=}O + K_2HPO_3$$

The authors have prepared one of these compounds, tris(*N*,*N*-dimethyl-2-carbamoylethyl)phosphine oxide in quantitative yield by the Schindlbauer reaction, as shown by the following equation (*6*):



$$O{=}P(CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH)_3 + 1.5\ P_2O_5 \xrightarrow[\text{excess DMF}]{\text{reflux}} O{=}P(CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}N[CH_3]_2)_3 + CO$$

(Because carbon monoxide is a side product, this reaction should be performed under a well-ventilated hood.)

The crude material isolated was hygroscopic. Because of this latter property and its solubility (soluble in polar solvents and insoluble in nonpolar solvents), the compound was difficult to purify. Initial purification involved dissolving the dark brown crystals in ethanol and adding petroleum ether until a dark brown oil separated. The clear solution was decanted from the impure dark oil and evaporated to give light yellow crystals. Recrystallization was achieved by dissolving the yellow crystals in a minimum amount of *N*,*N*-dimethylformamide and adding a 2:1 by volume mixture of petroleum ether–ethyl acetate. The cloudy solution was refrigerated. The white needles were isolated the next day by filtering the solution under an argon atmosphere.

An ir spectrum of a chloroform solution of the compound showed the carbonyl absorption band at 5.93 μ (Vs) and the P=O absorption band at 8.6 μ (m). The proton nmr spectrum (Varian A-60A spectrometer) of a deuteriochloroform solution at 60 MHz showed a multiplet centered at δ 2.5 and two singlets, one at δ 3.03, the other at δ 3.13. The ratio of the multiplet to the methyl groups singlets was 3:2. The chemical shift between the methyl groups was due to their different environments in the planar structure (*1*, *2*).

Experimental

Tris(N,N-dimethyl-2-carbamoylethyl)phosphine oxide (I). Tris-(2-carboxyethyl)phosphine oxide (8.6 grams, 0.0323 mole) (*4*) was refluxed with phosphorus pentoxide (7.2 grams, 0.05 mole) in 125 ml of *N*,*N*-dimethylformamide for 15 hr under a well-ventilated hood. The resulting solution was cooled and the *N*,*N*-dimethylformamide (DMF–petroleum ether–ethyl acetate). *Anal:* Calcd for vacuum to give an oil which slowly crystallized. These dark crystals were dissolved in ethanol and enough petroleum ether added to separate a dark brown oil. The clear solution, after decantation and evaporation under vacuum, yielded 8.5 grams (76%). Mp 100–102°C (DMF–petroleum ether–ethyl acetate). Anal. Calcd for $C_{15}H_{30}O_4N_3P$: C, 51.85; H, 8.70; N, 12.09; P, 8.91. Found: C, 51.61; H, 8.81; N, 11.89; P, 8.84.

Literature Cited

(1) Gutowsky, H. S., Holm, C. H., *J. Chem. Phys.*, **25**, 1228 (1956).
(2) Phillips, W. D., *ibid.*, **23**, 1363 (1955).
(3) Rauhut, M. M., Bernhermer, R., Semsel, A. M., *J. Org. Chem.*, **28**, 478 (1963).
(4) Rauhut, M. M., Hechenbleikner, I., Currier, H. A., Schaefer, F. C., Wystrack, V. P., *J. Amer. Chem. Soc.*, **81**, 1103 (1959).
(5) Rauhut, M. M., Semsel, A. M., U.S. Patent 3,067,251 (to American Cyanamid Co., December 4, 1962).
(6) Schindlbauer, H., *Monatshefte Chem.*, **99**, 1799 (1968).

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[1] To whom correspondence should be addressed.

[2] One of the laboratories of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture.