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REDUCTION OF AROMATIC NITRO COMPOUNDS WITH PHOSPHINE

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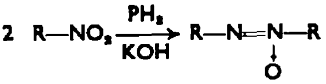
Abstract—The reduction of 1- and 2-nitronaphthalene and of some mono- and dinitro-biphenyls with phosphine was carried out under the conditions described by Buckler.[1] Reduction of 1-nitronaphthalene did not yield any crystalline product while reduction of 2-nitronaphthalene yielded benzo[f]naphtho[2,1-c]cinnoline-N-oxide together with 2,2′-azoxynaphthalene. The mononitrobiphenyls and 4,4′-dinitrobiphenyl were readily reduced to azoxy compounds, while reduction of 2,2′-dinitrobiphenyl gave benzo[c]cinnoline-N,N′-dioxide.

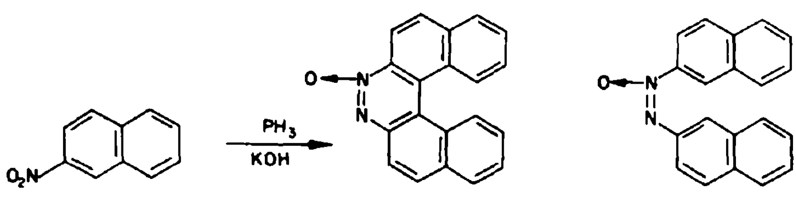
Buckler[1] reported that azoxybenzene is formed in high yield when phosphine is passed through a nearly saturated solution of nitrobenzene in aqueous ethanol containing four molar equivalents of potassium hydroxide. He thought this reaction to be general, since examination of other nitro compounds showed only azoxy compounds to be formed in all cases.



$$2\ \mathrm{R{-}NO_2} \xrightarrow[\mathrm{KOH}]{\mathrm{PH_3}} \mathrm{R{-}N{=}}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{N}}\mathrm{{-}R}$$

In a previous communication[2] we described the reduction of 6-nitroquinoline with phosphine yielding an oxygen-free compound together with a pyridazine diquinoline-oxide.* Having found one exception to Bucklers generalization we were anxious to investigate whether in certain instances other than azoxy compounds could be obtained. We therefore tried to reduce 1-nitronaphthalene with phosphine under the circumstances mentioned above and obtained a dark brown reduction product from which no crystalline compound could be isolated.

Reduction of 2-nitronaphthalene, however, yielded benzo[f]naphtho[2,1-c]cinnoline N-oxide together with a small amount of 2,2′-azoxynaphthalene.



2-nitronaphthalene   benzo[f]naphtho[2,1-c]cinnoline-N-oxide   2,2′-azoxynaphthalene

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* In the communication mentioned this substance was erroneously called 6,6′-azoxyquinoline. A discussion with Dr. W. V. Farrar of Manchester University, however, induced us to have a mass spectrum taken. The mol. wt. proved to be 298 which is in accordance with pyridazino[4,3-f: 5,6-f′]-diquinoline-3-oxide (6,6′-azoxybiquinolyl-5,5′).

[1] S. A. Buckler, L. Doll, F. K. Lind and M. Epstein, *J. Org. Chem.* **27**, 794 (1962).

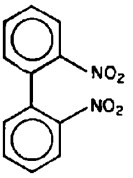
[2] A. C. Bellaart, *Rec. Trav. Chim.* **83**, 718 (1964).

2,2′-Azoxynaphthalene was obtained as small pale-yellow needles, m.p. 162·5–163·5° (Cumming[3]: 164°); on exposure to UV light, preferably in alcoholic solution it is converted into a red compound, m.p. 162·5–163·5° (Cumming[3]: 162°). A mixture of the red and yellow compound melted at 162·5–163·5 (Cumming[3]: 157–159°). Moreover, we observed on very careful and slow heating that the yellow compound melts to a yellow liquid which subsequently changes colour to red; this takes place within a temperature interval of about 0·3°. So far we have not succeeded in reconverting the red substance into the yellow form.

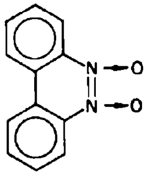
The IR spectra of the two compounds (measured from 4000–650 cm^{-1} with the KBr pellet technique) are identical in every detail that can be noticed by visual inspection. The UV spectra (190–450 nm in 96% EtOH solution) are also identical; they show a complex band with peak positions near 262, 277, 287 and 348 nm. From these two experiments it is again clear that the two compounds are not *cis-trans* isomers but, if anything, two conformations of *cis*-2,2′-azoxynaphthalene. This is supported by the fact that the red compound shows a weak but distinct absorption band near 506 nm which is completely absent in the spectrum of the yellow compound; this extra band appears independent of the method of preparation (either by UV irradiation or by heating at the m.p.).

Finally we reduced 2,2′-azoxynaphthalene and benzo[f]naphtho[2,1-c]cinnoline-N-oxide according to the method of Meisenheimer[4] and obtained 2,2′-azonaphthalene and benzo[f]naphtho[2,1-c]cinnoline respectively.

Reduction of 2-nitrobiphenyl, 3-nitrobiphenyl, 4-nitrobiphenyl and 4,4′-dinitrobiphenyl with phosphine in alkaline aqueous ethanol gave the corresponding azoxy compounds, while reduction of 2,2′-dinitrobiphenyl produced benzo[c]cinnoline-N,N′-dioxide in very good yield.



2,2′-dinitrobiphenyl



benzo[c]cinnoline-N,N′-dioxyde

This investigation shows that reduction of aromatic nitro compounds with phosphine in alkaline aqueous alcoholic medium does not always lead to azoxy compounds. Generally the products are easily obtainable in a pure state; reactions carried out via this method often give higher yields than alternative methods.

EXPERIMENTAL

(With the collaboration of G. J. van den Dungen)

Microanalyses were carried out in the Microanalytical Department of the Laboratory of Organic Chemistry, Technological University, Eindhoven by P. L. M. van den Bosch. M.ps were determined in a Buchi m.p. apparatus (designed by Tottoli) and are uncorrected.

2-*Nitronaphthalene*. This compound was prepared from 2-aminonaphthalene in accordance with the method described by Meisenheimer.[4] The yield was about 30%, m.p. 78–79°.

[3] W. M. Cumming and G. S. Ferrier, *J. Chem. Soc.* **125**, 1109 (1924).

[4] J. Meisenheimer and K. Witte, *Ber. Dtsch. Chem. Ges.* **36**, 4153 (1903).

2,2′-Azoxynaphthalene and benzo[f]*naphtho*[2,1-c]*cinnoline*-N-*oxide*. Phosphine (50 ml/min) was passed through a stirred solution of 2-nitronaphthalene (5·19 g = 0·03 gmol) and KOH (6·7 g = 0·12 gmol) in 230 ml of 80% aqueous EtOH at 20–25° for 8 hr.

The precipitate formed (3·8 g) consisted of 2,2′-azoxynaphthalene and benzo[f]naphtho[2,1-c]-cinnoline-N-oxide, which were separated by repeated extraction in the dark with cold ether (freed from peroxide), in which the latter compound is nearly insoluble.

The collected, ethereal extracts were evaporated and the residue crystallized from glacial acetic acid without exposure to light, yield: 0·7 g of small, pale-yellow needles, m.p. 162·5–163·5° (Cumming[3]: 164°). Mass spectrometric analysis proved the mol. wt. to be 298 which is correct for 2,2′-azoxynaphthalene. (Found: C, 80·8; H, 4·6; N, 9·4. Calc. for $C_{20}H_{14}N_2O$ (298·35): C, 80·52; H, 4·73; N, 9·39%.) Exposure to direct sunlight converted the yellow compound in alcoholic solution into a red isomeride, m.p. 162·5–163·5° (Cumming[3]: 162°; Lefort[5]: 160–161°). The mixed m.p. of the original compound with the red isomeride was 162·5–163·5° (Cumming[3]: 157–159°).

The fraction of the precipitate insoluble in ether was crystallized from glacial acetic acid, yielding 2·3 g of yellow needles, m.p. 247–248°(dec) (Meisenheimer[4]: 247–248° (dec)). Mass spectrometric analysis proved the mol. wt. to be 296 which is right for benzo[f]naphtho[2,1-c]cinnoline-N-oxide. (Found: C, 80·8; H, 4·0; N, 9·3. Calc. for $C_{20}H_{12}N_2O$ (296·33): C, 81·06; H, 4·08; N, 9·45%.)

2,2′-Azonaphthalene. 2.2′-Azoxynaphthalene (100 mg) was reduced in alkaline aqueous EtOH with Zn dust according to the method of Meisenheimer.[4] The yield was 80 mg of orange leaflets (from benzene), m.p. 208–209°. (Meisenheimer[4]: 208°; Kuhn[6]: 208–209°). The mol. wt. was found to be 282 by mass spectrometric analysis.

Benzo[f]*naphtho*[2,1-c]*cinnoline*. Benzo[f]naphtho[2,1-c]cinnoline-N-oxide (1·0 g) was reduced in alkaline aqueous EtOH with Zn dust according to the method of Meisenheimer,[4] yielding 0·8 g of pale-yellow needles, m.p. 269·5–270·5°, which was not depressed by admixture with a sample of benzo[f]naphtho[2,1-c]cinnoline prepared by Went. (Meisenheimer[4]: 267–268°; Holt[7]: 270°). The mol. wt. was found to be 280 by mass spectrometric analysis.

2,2′-Diphenyl-azoxybenzene. Phosphine (50 ml/min) was passed through a stirred solution of 2-nitro-biphenyl (19·9 g = 0·1 moles) and KOH (22·4 g = 0·4 moles) in 2 l of 80% aqueous EtOH at 30–35° for 18 hr.

The precipitate formed (3·5 g) was recrystallized from EtOH to furnish 3·3 g of light-yellow leaflets, m.p. 157·5–158·5°, which was not depressed by admixture with a sample of 2,2′-diphenyl-azoxybenzene prepared according to Friebel.[8] (Friebel:[8] 157–158°; Wenkert:[9] 160–163°) Mass spectrometric analysis proved the mol. wt. to be 350 which is in accordance with the formula mentioned below. (Found: C, 82·4; H, 5·2; N, 7·9 Calc. for $C_{24}H_{18}N_2O$ (350·42): C, 82·26; H 5·18; N, 7·99%.) By evaporation of the original reaction solution 13·5 g of starting material was recovered.

3,3′-Diphenyl-azoxybenzene. Phosphine (50 ml/min) was passed through a stirred solution of 3-nitro-biphenyl (19·9 g = 0·1 moles) and KOH (22·4 g = 0·4 moles) in 2 l of 80% aqueous EtOH at 30–35° for 9 hr.

The precipitate formed (12·5 g) was recrystallized from EtOH and furnished 11·0 g of yellow needles, m.p. 111–111·5°. Mass spectrometric analysis proved the mol. wt. to be 350 which is correct for 3,3′-diphenyl-azoxybenzene. (Found: C, 82·5; H, 5·3; N, 8·1. Calc. for $C_{24}H_{18}N_2O$ (350·42): C, 82·26; H, 5·18; N, 7·99%.)

4,4′-Diphenyl-azoxybenzene. Phosphine (50 ml/min) was passed through a stirred solution of 4-nitro-biphenyl (19·9 g = 0·1 moles) and KOH (22·4 g = 0·4 moles) in 2 l of 80% aqueous EtOH at 30–35° for 18 hr.

The precipitate formed (16·6 g) was recrystallized from glacial acetic acid and yielded 16·0 g of light yellow leaflets, m.p. 212·5–213°, which was not depressed by admixture with a sample of 4,4′-diphenyl-azoxybenzene prepared according to Zimmermann[10] (Zimmermann[10]: 205°; Bell:[11]

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[5] D. Lefort, C. Four and A. Pourchez, *Bull. Soc. Chim. Fr.* 2381 (1961).

[6] R. Kuhn and P. Goldfinger, *Liebigs Ann.* **470**, 190 (1929).

[7] P. F. Holt and C. W. Went, *J. Chem. Soc.* 4099 (1963).

[8] G. Friebel and B. Rassow, *J. Prakt. Chem.* [2] **63**, 458 (1901).

[9] E. Wenkert and B. F. Barnett, *J. Amer. Chem. Soc.* **82**, 4671 (1960).

[10] J. Zimmermann, *Ber. Dtsch. Chem. Ges.* **13**, 1960 (1880).

[11] F. Bell, J. Kenyon and P. H. Robinson, *J. Chem. Soc.* 1245 (1926).

212°; Vorländer[12]: 215–216°). The mol. wt. was found to be 350 by mass spectrometric analysis. (Found: C, 82·3; H, 5·2; N, 8·3. Calc. for $C_{24}H_{18}N_2O$ (350·42): C, 82·26; H, 5·18; N, 7·99%.) Starting material recovered 0·5 g.

4,4'-Bis-[4-nitrophenyl]-azoxybenzene. Phosphine (50 ml/min) was passed through a stirred solution of 4,4'-dinitro-biphenyl (17·08 g = 0·07 moles) and KOH (15·68 g = 0·28 moles) in 2 l of 80% EtOH at 30–35° for 9 hr.

The precipitate formed (14·2 g) was washed twice with alcohol and ether and recrystallized from aniline. The crystals obtained were thoroughly washed with alcohol and ether and analysed, yield: 13·1 g of ocrous crystals decomposing at 280–282°. IR spectra of this compound and of 4,4'-bis-[4-nitrophenyl]-azoxybenzene prepared according to the method of Wald[13] are identical. Mass-spectrometric analysis proved the mol. wt. to be 440, which is in accordance with the formula mentioned below. (Found: C, 65·4; H, 3·9; N, 12·7. Calc. for $C_{24}H_{16}N_4O_5$ (440·42): C, 65·45; H, 3·66; N, 12·72%.)

Benzo[c]*cinnoline*-N,N'-*dioxide.* Phosphine (50 ml/min) was passed through a stirred solution of 2,2'-dinitrobiphenyl (19·52 g = 0·08 moles) and KOH (17·92 g = 0·32 moles) in 2 l of 80% EtOH at 30–35° for 18 hr.

The precipitate formed (13·5 g) was recrystallized from EtOH yielding 12·5 g of nearly colourless crystals, m.p. 234–236° (dec) which was not depressed by admixture with a sample of benzo[c]-cinnoline-N,N'-dioxide prepared according to (Täuber[14]). The mol. wt. was found to be 212 by mass spectrometric analysis. (Found: C, 67·6; H, 3·9; N, 13·0. Calc. for $C_{12}H_8N_2O_2$ (212·21): C, 67·92; H, 3·80; N, 13·20%.) Starting material recovered: 1 g.

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[12] D. Vorländer, *Ber. Dtsch. Chem. Ges.* **66**, 1666 (1933).

[13] H. Wald, *Ber. Dtsch. Chem. Ges.* **10**, 137 (1877).

[14] E. Täuber, *Ber. Dtsch. Chem. Ges.* **24**, 3083 (1891).