CHEMISTRY

Academician of the Academy of Sciences of the Latvian SSR G. Ya. VANAG, E. Yu. GUDRINIECE,

1962

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician of the Academy of Sciences of the Latvian SSR G. Ya. VANAG,
E. Yu. GUDRINIECE,
I. A. MEIROVICH

2-PHENYLPERINAPHTHINDANDIONE-1,3 AND SOME OF ITS DERIVATIVES

2-Phenylperinaphthindandione-1,3 (I) and its bromo derivative (II, X = Br) were first synthesized in 1912 (^{1}). It was then studied by Kölli and Rosenwald (^{2}), and more recently by collaborators of Cairo University (^{3}). To obtain I, naphthalic anhydride is fused with phenylacetic acid in the presence of sodium acetate at temperatures above 230°. Since naphthalic acid already passes into the anhydride at 140–150° (^{4}), for the synthesis of I we successfully used naphthalic acid instead of its anhydride and obtained I in 85.6% yield. The I obtained in this way (not recrystallized) proved sufficiently pure for further experiments. Naphthalic acid itself is obtained by oxidation of acenaphthene with potassium dichromate in glacial acetic acid with 30-hour boiling (^{5}), or even by oxidation under elevated pressure (^{6}). We succeeded in improving the method for preparing naphthalic acid and considerably shortening the oxidation time.

$$C_{10}H_6(COOH)_2 \xrightarrow[\text{240-280}^\circ]{C_6H_5\cdot CH_2\cdot COOH,\ CH_3\cdot COONa} (I) \longrightarrow (II)$$

$$(II)\ X = \mathrm{Br},\ \mathrm{Cl}$$

2-Phenylperinaphthindandione-1,3 (I), analogously to 2-phenylindandione-1,3 (^{7}), is readily brominated and chlorinated with formation of II. Chlorination was carried out both with gaseous chlorine and with sulfuryl chloride (^{8}). Bromo- and chloroperinaphthindandiones (II) are white crystalline substances, soluble in organic solvents; the chloro derivative is stable in air, while the bromo derivative slowly decomposes and turns yellow; alkalis split off the halogen with formation of the initial I. The same occurs on boiling with dilute sulfuric or hydrochloric acids.

It was not possible to obtain the iodo derivative (II, X = J) by direct iodination of 2-phenylperinaphthindandione-1,3. We then attempted to obtain it by an exchange reaction from the bromo derivative (II, X = Br) and NaJ in various solvents (glacial acetic acid, benzene, etc.) and under various conditions. In every case one and the same substance was obtained, whose composition proved very constant and corresponded to the empirical formula $C_{38}H_{22}O_4J_3$ or $C_{38}H_{24}O_4J_3$, i.e., as if 2 molecules of 2-iodo-2-phenylperinaphthindandione-1,3 were complexly bound with one iodine atom, or 2 molecules of 2-phenylperinaphthindandione-1,3 were complexly bound with 3 iodine atoms. The substance consists of black lustrous crystals (needles); above 160° it decomposes with liberation of iodine. It dissolves well in dioxane and chloroform with a reddish-brown coloration, and poorly in benzene. On heating with alcohol it gives back I. On heating with hydrochloric acid, iodine vapors are evolved and I remains. On standing in air the complex compound does not change, in contrast to what has been noted for the complex compounds of 2-nitroindandione-1,3 with iodine (^{9,10}). The true structure of the complex compound obtained has not yet been elucidated.

For indandione-1,3 and its 2-monosubstituted derivatives, ready nitration in position 2 is characteristic. Not only 2-nitroindandione-1,3 itself has been well studied

(II), but also 2-nitro-2-arylindandiones-1,3 (12–15); 2-nitroperinaphthindandione-1,3 has also been obtained (16). It proved that I is also readily nitrated, with formation of the hitherto undescribed 2-nitro-2-phenylperinaphthindandione-1,3 (III). Nitration with concentrated nitric acid (d_{20° 1.36) proceeds equally well both in glacial acetic acid and in dichloroethane (17, 18). III consists of white crystals with m.p. 185–186°; from glacial acetic acid it crystallizes in plates, from benzene—in needles. It dissolves with difficulty in alkalis, only on boiling.

It is known that 2-nitro-2-substituted indandiones-1,3, under the action of alkalis, are cleaved to phthalic acid and the corresponding nitro derivative (19–22). But only one C—C bond of the five-membered ring may be cleaved, and then a derivative of α-nitroacetophenone-*o*-carboxylic acid is obtained (23). It turned out that an analogous cleavage occurs with 2-nitro-2-phenylperinaphthindandione-1,3. Under the action of sodium alcoholate on it, one C—C bond is cleaved and the corresponding ester of 8-(α-nitrophenylacetyl)-naphthalene-1-carboxylic acid (IV) is formed; on boiling III with 10% NaOH, cleavage to naphthalic acid and phenylnitromethane occurs.

$$\text{(III)} \xrightarrow{\text{RONa}} \text{(IV)} \qquad (R = \mathrm{CH_3}, \mathrm{C_2H_5})$$

$$\text{(III)} \xrightarrow{\text{NaOH}} \text{naphthalic acid} + \mathrm{C_6H_5CH_2NO_2}$$

Experimental Part

Naphthalic acid. In a three-necked liter flask equipped with a mechanical stirrer and a reflux condenser, 31 g (0.206 mole) of technical acenaphthene and 66 g (0.402 mole) of anhydrous sodium acetate are dissolved, with heating, in 250 ml of acetic acid (98%); 110 g (0.375 mole) of potassium dichromate is gradually added over the course of an hour, and the mixture is boiled for a further 4 hours. The contents of the flask are diluted with 1 liter of hot water and filtered. The precipitate is washed again with hot water and dissolved in 800 ml of 5% NaOH. By acidifying the filtrate with hydrochloric or sulfuric acid, 35.6 g (82%) of naphthalic acid is isolated. Sublimation gives the anhydride with m.p. 273°. According to the literature (5), 100 g of acenaphthene, 1200 ml of glacial acetic acid, and 600 g of potassium dichromate are boiled for 30 hours and 125 g (89%) of naphthalic acid is obtained; m.p. of the anhydride 273–274° (from conc. nitric acid).

2-Phenylperinaphthindandione-1,3 (I). A thoroughly ground mixture of 16.5 g (0.05 mole) of naphthalic acid, 20.4 g (0.16 mole) of phenylacetic acid, and 6 g (0.073 mole) of anhydrous sodium acetate is heated in a retort or in a flask with a low side-arm tube on a sand bath for 2 hours at 240–280°. The contents of the flask are extracted with dilute ammonia (~2.5%) and finally with hot water. The combined filtrate is acidified to pH 6 with concentrated hydrochloric acid, and 17.7 g (85.6%) of 2-phenylperinaphthindandione-1,3 is obtained. Orange needles (from benzene), m.p. 215°. According to the literature (3), I was synthesized from naphthalic anhydride and phenylacetic acid in 48% yield, m.p. 214–216° (from alcohol).

2-Bromo-2-phenylperinaphthindandione-1,3 (II, X = Br). In a three-necked flask, to a suspension of 6.8 g (0.025 mole) of 2-phenylperinaphthindandione-1,3 in 50 ml of acetic acid (97%), heated to 50°, 4.8 g (0.03 mole) of bromine is added, and stirring is continued until the evolution of hydrogen bromide ceases (4–5 hours). The precipitate is separated and washed;

acetic acid. Dilution of the filtrate with water gives an additional amount of II (X = Br). Total yield 6.8 g (79%). After crystallization from acetic acid or benzene, 6.5 g (75.5%) of colorless needles were obtained, m.p. 197–198° (literature data: 198°).

Found, %: Br 23.41; 22.01. $C_{19}H_{11}O_2Br$. Calculated, %: Br 22.79

2-Chloro-2-phenylperinaphthindanedione-1,3 (II, X = Cl).
a) To 2.72 g (0.01 mole) of 2-phenylperinaphthindanedione-1,3 in ether are added 4.05 g (0.03 mole) of sulfuryl chloride in 20 ml of ether, and the mixture is boiled for 1 h. On the following day the ether is distilled off, the residue is washed with ether and crystallized from benzene. Yield 1.9 g (61.8%); colorless needles, m.p. 220°.

b) Chlorine is passed for 10 min through a suspension of 1.36 g (0.005 mole) of 2-phenylperinaphthindanedione-1,3 in acetic acid (98%), and after an hour the precipitate is separated. Dilution of the filtrate with water gives an additional amount of substance. Total yield 1.18 g (76.6%). It dissolves readily in benzene and acetone, less readily in chloroform, and with difficulty in alcohol and ether. After crystallization from benzene, 0.88 g (57.2%) of colorless needles were obtained, m.p. 219–220°.

Found, %: Cl 10.98 (a); 11.51 (b). $C_{19}H_{11}O_2Cl$. Calculated, %: Cl 11.57

Complex of 2-phenylperinaphthindanedione-1,3 with iodine. To a solution of 1.8 g (0.005 mole) of 2-bromo-2-phenylperinaphthindanedione-1,3 in benzene are added 0.9 g (0.006 mole) of sodium iodide, dissolved in a minimal amount of glacial acetic acid; the mixture is boiled for 7 h and the hot solution is filtered. Yield 1.55 g (76%) of black lustrous crystals. After crystallization from chloroform or glacial acetic acid, 1.25 g (61%) of small black needles were obtained, m.p. 160° (decomp.). Soluble in dioxane and chloroform, sparingly soluble in benzene.

Found, % (for freshly prepared): C 49.80; H 2.79; I 41.65
(after 70 days in air): C 49.50; H 2.82; I 40.80
$C_{38}H_{22}O_4I_3$. Calculated, %: C 49.40; H 2.38; I 41.27
$C_{38}H_{24}O_4I_3$. C 49.29; H 2.59; I 41.19

2-Nitro-2-phenylperinaphthindanedione-1,3 (III).
a) To a suspension of 2.72 g (0.01 mole) of 2-phenylperinaphthindanedione-1,3 in 40 ml of 1,2-dichloroethane are added 1.9 ml (0.032 mole) of nitric acid (d_{20}1.36), diluted with 10 ml of dichloroethane, and the mixture is shaken vigorously. A precipitate falls out within 10–15 min. After several hours it is separated. Yield 2.15 g (67.8%). After crystallization from acetic acid, 1.6 g (50.7%) of white lustrous plates were obtained, m.p. 185–186°.

b) To a solution of 2.72 g (0.01 mole) of 2-phenylperinaphthindanedione-1,3 in acetic acid at 50° are added 1.4 ml (0.023 mole) of nitric acid (d_{20}1.36); the mixture is shaken vigorously for 15 sec and, while continuing the shaking, cooled with ice water. After an hour the crystals that have separated are isolated. Yield 2.2 g (69.3%), m.p. 185° (from acetic acid).

Found, %: N 4.23 (a); 4.27 (b). $C_{19}H_{11}O_4N$. Calculated, %: N 4.41

Cleavage. 11 g of 2-nitro-2-phenylperinaphthindanedione-1,3 are dissolved on heating in 600 ml of 10% NaOH. The solution is diluted with water, acidified with dilute sulfuric acid, and steam-distilled. The distillate is extracted with ether, dried with anhydrous Na_2SO_4, and distilled in vacuo, collecting the phenylnitromethane fraction at 104–108° (6 mm).

Found, %: N 10.6. $C_7H_7O_2N$. Calculated, %: N 10.22

Methyl ester of 8-(α-nitrophenylacetyl)naphthalene-1-carboxylic acid (IV $R = CH_3$). 3.2 g of 2-nitro-2-phenylperinaphthindanedione-1,3 are dissolved with vigorous stirring in 50 ml of 3% sodium methylate; the brown solution formed is acidified with dilute sulfuric acid and diluted with water. A yellow···

flocculent precipitate, yield 2.51 g (72%). After crystallization from alcohol, 2.1 g (60.1%) of yellow crystals were obtained, m.p. 145–147°.

Found, %: N 3.88.
$C_{20}H_{15}O_5N$. Calculated, %: N 4.01.

Ethyl ester of 8-(α-nitrophenylacetyl)-naphthoic-1 acid (IV, $R = C_2H_5$). Analogously to the preceding, from 3.2 g of 2-nitro-2-phenylperinaphthindan-1,3-dione and 50 ml of 3% sodium ethylate, 2.19 g (60.3%) of yellow crystals were obtained, m.p. 128°.

Found, %: N 3.72.
$C_{21}H_{17}O_5N$. Calculated, %: N 3.85.

Riga Polytechnic Institute

Received
18 XI 1961

REFERENCES

1. M. Cesaris, *Gazz.*, **42**, 11, 453 (1912).
2. C. F. Koelsch, R. H. Rosenwald, *J. Am. Chem. Soc.*, **59**, 2166 (1937).
3. O. M. Ali, W. I. Awad, A. M. Islam, *J. Org. Chem.*, **23**, 1624 (1958).
4. A. Behr, W. A. van Dorp, *Ann.*, **172**, 266 (1874).
5. C. Graebe, E. Gfeller, *Ber.*, **25**, 652 (1892).
6. Y. Ishikawa, Y. Ito, K. Negoro, H. Hiyama, *Chem. Abstr.*, 9357 (1961).
7. F. Nathanson, *Ber.*, **26**, 2576 (1893).
8. E. Gudriniece, G. Vanags, A. Kurzemnieks, E. Grants, *Izv. Vyssh. ucheb. zav., khim.*, **3**, 119 (1960).
9. G. Vanags, M. Lipman, *Izv. AN LatvSSR*, No. 9, 35 (1949).
10. G. Vanags, M. Lipman, *DAN*, **68**, 693 (1949).
11. G. Vanags, *Nitroindandione*, Riga, 1954.
12. G. Wanag, *Ber.*, **69**, 1066 (1936).
13. L. Zalukaev, E. Vanag, *ZhOKh*, **26**, 607, 2639 (1956).
14. L. Zalukaev, E. Vanag, *ZhOKh*, **27**, 3278 (1957).
15. L. Zalukaev, E. Vanag, *Izv. AN LatvSSR*, No. 3, 109 (1956).
16. E. Gudriniece, E. Dreimanis, G. Vanag, *ZhOKh*, **26**, 272 (1956).

17. L. Zalukaev, *Izv. AN LatvSSR*, No. 3, 101 (1954).

18. E. Gudriniece, G. Vanag, Scientific Notes of the Riga Polytechnic Institute, **2**, Chemical Faculty, **7**, 2 (1959).

19. I. Keimatsu, *Zbl.*, **1**, 2745 (1934).

20. G. Y. Vanag, V. I. Palatpiere, M. A. Matskanova, *ZhOKh*, **19**, 1535 (1949).

21. L. P. Zalukaev, *Izv. AN LatvSSR*, No. 4, 85 (1953); No. 3, 85 (1954).

22. E. Vanag, in the collection *Cyclic β-diketones*, Riga, 1961, p. 127.

23. L. Zalukaev, *Izv. AN LatvSSR*, No. 11, 129 (1952).

Note: Figure translations are in progress. See original paper for figures.