related to $n_{AS} \rightarrow \sigma^*$ transitions. The maximum of the similar band in the spectra of trialkylphosphines is found below 200 nm due to the higher IP of the phosphorus unshared electron pair.

EXPERIMENTAL

The UV spectra were obtained on a Specord UV-VIS spectrophotometer. The solvents were initially purified and dried. The solution concentrations were from $2\cdot10^{-2}$ to $5\cdot10^{-3}$ mole/liter. The arsines and arsine selenides were synthesized according to the procedures of Zingaro and Merijanian [9].

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2-[4-BIS(2-CHLOROETHYL)AMINOPHENYL]INDANE-1,3-DIONE AND ITS DEHYDRODIMER

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UDC 542.91:547.665:542.953:547.584:547.586.2

The reaction of the phthalic anhydrides with phenylacetic acids in acetic anhydride and triethylamine was used for the synthesis of 2-[4-bis(2-chloroethyl)-aminophenyl]indane-1,3-dione (II). The oxidation of (II) by ferric chloride or DDQ gave the corresponding dehydrodimer (IV).

In a study of the chemistry and physicochemical properties of *p*-amino-substituted 2-phenylindane-1,3-diones and the corresponding dimers [1-3], the need arose for the synthesis of their analogs having functional groups bound to the nitrogen atom. One of these interesting intermediates with high activity in nucleophilic substitution reactions, permitting the synthesis of various derivatives, is *p*-bis(2-chloroethyl)aminophenylindane-1,3-dione (II). The corresponding dehydrodimer (IV) and analogs, obtained by the nucleophilic substitution of the chlorine atoms, potentially have the capacity to decompose reversibly to give free radicals, which is reflected in thermo-, photo-, and mechanochromism [2, 3].

The synthesis of this compound by the reported methods for the preparation of 2-arylindane-1,3-diones such as the Dieckmann–Shapiro condensation [1] or isomerization of the products of the Perkin–Gabriel condensation [4], is impossible since sodium methylate is used in these methods, leading to substitution of the atom in the alkylating reagent with the 2-chloroethyl fragment.

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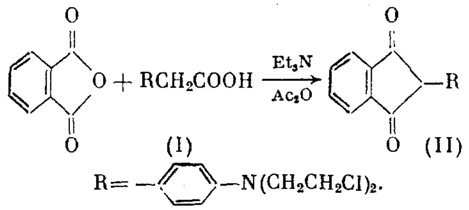
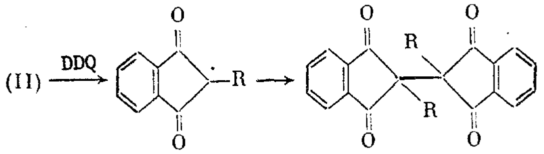
Dione (II) may be synthesized only by the condensation of the phthalic anhydride with 4-bis(2-chloroethylamino)phenylacetic acid (I) in acetic anhydride in the presence of triethylamine, which is a weaker nucleophile than sodium methylate.



(I) (II)

The low yield of (II) (20%) is apparently a consequence of quaternization of triethylamine by (I) and (II). Dione (II) exists in the keto form in the crystalline state as indicated by strong IR bands at 1710 and 1745 cm^{-1} belonging to the antisymmetric and symmetric stretching vibrations of the carbonyl groups. The diketone structure of indanedione (II) is attributed to the lack of additional electron-withdrawing groups in the indane system [1] and the reduced basicity of the nitrogen atom due to the effect of the 2-chloroethyl substituent.

Dimer (IV) was prepared by one of the mildest oxidation methods, not employing a basic medium, namely, the oxidative dehydrogenation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in methanol [5].

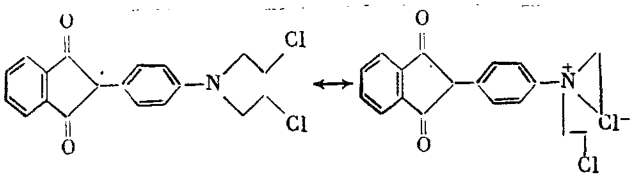


(III) (IV)

Dimer (IV) was also obtained upon maintenance of an ethanolic solution of (II) for one month. However the oxidation of (II) by ferric chloride in aqueous ethanol proved to be the most convenient method for the synthesis of (IV). The structures of (II) and (IV) were supported by IR and PMR spectroscopy and elemental analysis.

Dimers similar to (IV) with, for example, R = p-$Me_2NC_6H_4$, exist in organic solvents in thermodynamic equilibrium with the corresponding radicals (III), which are stabilized by the captodative effect of carbonyl and p-dimethylamine groups and detected by EPR and electronic absorption spectroscopy [3].

Dimer (IV) does not decompose into radicals upon heating to 100°C, which is attributed to the lower electron-donor effect of the nitrogen atom. Resonance structure (V) apparently makes a significant contribution to the ground state of radical (III) and, thereby, destabilizes this radical.



(III) (V)

EXPERIMENTAL

The IR spectra were taken on a Specord 75 IR spectrophotometer in KBr pellets. The PMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz in $CDCl_3$ with TMS as the internal standard.

2-[4-Bis(2-chloroethyl)aminophenyl]indane-1,3-dione (II). A sample of 27.6 g (0.1 mole) p-bis(2-chloroethyl)aminophenylacetic acid and 14.8 g (0.1 mole) phthalic anhydride were dissolved in 61.2 g (0.6 mole) acetic anhydride upon heating on a steam bath. Then, 30.3 g (0.3 mole) triethylamine was added and heated with stirring for 50 min. The reaction mixture was poured onto 400 g ice and 200 ml concentrated hydrochloric acid. The oil obtained was separated and treated with 40 ml concentrated hydrochloric acid upon heating. The solution was filtered and the filtrate was neutralized by the addition of saturated aq. Na_2CO_3 to pH 5. The precipitate was filtered off and subjected to chromatography on a silica gel column with chloroform as the eluent. The yield of (II) was 7.57 g (21%), mp 88-90°C, R_f 0.90 on silufol with 2:1 benzene-ethyl acetate as the eluent. Found: C, 62.35; H, 4.77%. Calculated for $C_{19}H_{17}O_2Cl_2$: C, 62.99; H, 4.73%. PMR spectrum (δ, ppm): 3.61 t (NCH_2, $J = 7$

Hz), 3.69 t (CH_2Cl, $J = 7$ Hz), 4.18 s (H^2), 6.67 d (H^3 and H^5, $J_0 = 8$ Hz), 7.06 d (H^2 and H^6, $J_o = 8$ Hz), 7.91 d.d (H^5,H^6, $J_o = 6$, $J_m = 3$ Hz), 8.07 d.d (H^4 and H^7, $J_o = 6$, $J_m = 3$ Hz). IR spectrum (ν, cm^{-1}): 1710, 1745 (C=O).

2,2′-Bis{[4-bis(2-chloroethyl)aminophenyl]indane-1,3-dione} (IV). *a.* A sample of 0.114 g (0.5 mmole) DDQ was added to 0.362 g (1 mmole) (II) in 10 ml methanol. The mixture was stirred for 24 h at ~20°C. The precipitate was filtered off and washed with ethanol. The yield of (IV) was 28%. The product was recrystallized from 1:1 chloroform-ethanol, mp 185-187°C (dec.).

b. A sample of 0.724 g (0.002 mole) (II) was dissolved upon heating in 50 ml ethanol and a solution of 1.08 g (0.004 mole) $FeCl_3 \cdot 6H_2O$ in 15 ml water was added. The precipitate was filtered off. The yield of (IV) was 0.6 g (83%). Found: C, 63.50; H, 4.73%. Calculated for $C_{38}H_{32}N_2O_4Cl_4$: C, 63.13; H, 4.46%. PMR spectrum (δ, ppm): 3.61 t (NCH_2, $J = 8$ Hz), 3.72 t (CH_2Cl_2, $J = 8$ Hz), 6.55 d (H^3 and H^5, $J_o = 9$ Hz), 7.08 d (H^2 and H^6, $J_o = 9$ Hz), 7.73 d.d (H^5 and H^6, $J_o = 6$, $J_m = 3$ Hz), 7.86 d.d. (H^4 and H^7, $J_o = 6$, $J_m = 3$ Hz). IR spectrum (ν, cm^{-1}): 1705, 1733 (C=O).

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THE STRUCTURE AND A NEW METHOD FOR THE SYNTHESIS OF THE DIMER OF 2,2-DIPHENYL-1,3,2-BENZOXAZAPHOSPHOLE

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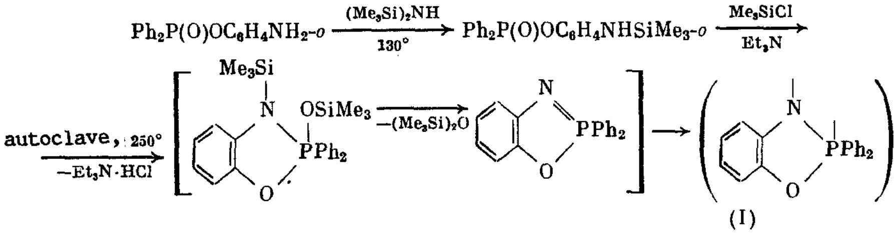
UDC 542.91:541.63:548.737:547.1'118

X-ray diffraction structural analysis established the structure of the dimer of 2,2-diphenyl-1,3,2-benzoxazaphosphole with a pentacoordinated phosphorus atom. A new method is proposed for the preparation of this dimer.

In the present communication, results are given for the x-ray diffraction structural analysis of the dimer of 2,2-diphenyl-1,3,2-benzoxazaphosphole (I) with a pentacoordinated phosphorus atom. A new synthesis of this dimer is also reported. Among the dimeric 2,2-disubstituted 1,3,2-benzoxazaphosphole, only the structure of the dimer of 2,2-diethyl-1,3,2-benzoxazaphosphole (II) has been studied [1, 2]. In contrast to the methods reported for the synthesis of (I) [3, 4], phosphorane (I) was obtained in our laboratory from the *o*-aminophenyl ester of diphenylphosphonic acid.



(I)

Institute of Physiologically Active Compounds, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 945-947, April, 1990. Original article submitted July 3, 1989.