4,7-DIPHENYL-2-(P-DIMETHYLAMINOPHENYL)-1,3-INDANEDIONE AND ITS DEHYDRODIMER

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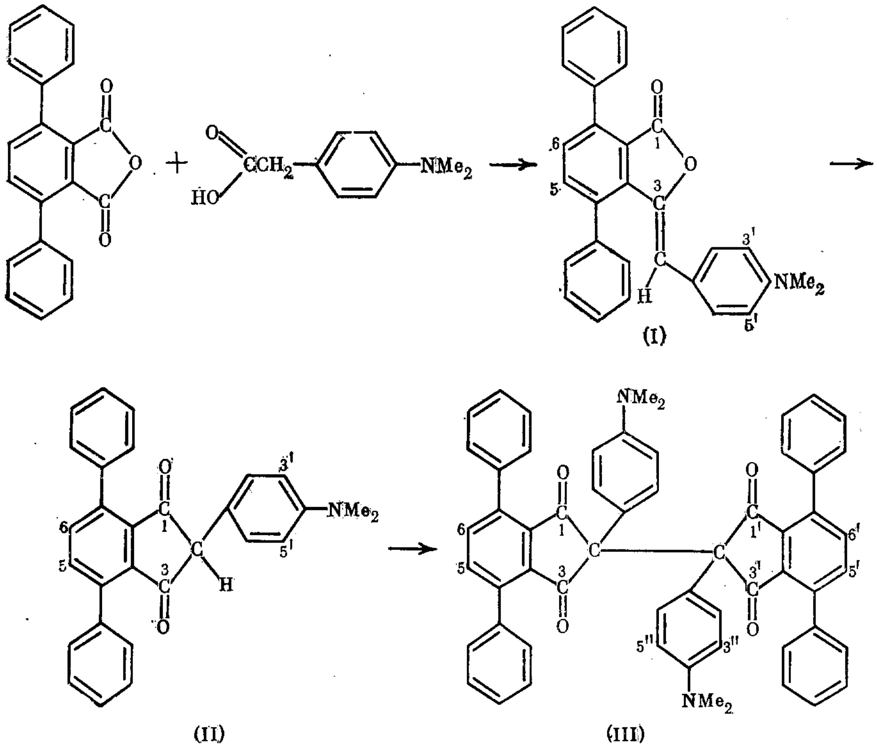
Continuing their study of compounds reversibly forming indanedionyl radicals [1], the authors had the intention of synthesizing a dehydrodimer having bulky substituents in positions ortho to the carbonyl groups. A study of the influence of the ortho-effect on the equilibrium constant of dimer—radical and also on the rate constant of recombination of these radicals would aid understanding of the mechanism for stabilization of radicals. Most interesting from the point of view of synthesis was the introduction of two phenyl groups at the 4- and 7-positions.

An intermediate product in the synthesis of 4,7-diphenyl-2-(p-dimethylaminophenyl)-1,3-indanedione (II) is 4,7-diphenyl-3-(p-dimethylaminobenzylidene)phthalide (I), obtained according to the method of Perkin—Gabriel [2].



The reaction for formation of phthalide (I) proceeds regioselectively with the formation of one isomer. In [3] it was shown that under similar conditions phthalic anhydride condenses with phenylacetic acid to give only the (Z)-isomer. In order to establish the structure of phthalide (I), a comparison of its electronic spectra with the spectra of (Z)- and (E)-3-benzylidenephthalide (Fig. 1) was undertaken. In the spectrum of phthalide (I) (Fig. 1, curve 1) there is an absorption band at 262 nm (log ε 4.57) corresponding to the absorption of a p-terphenyl fragment (p-terphenyl, λ_{max} (EtOH) 279 nm, log ε 4.48 [4]), and a broad intense absorption band in the visible region with maximum at 427 nm (log ε 4.34) caused by charge-transfer from the dimethylamino group to the carbonyl. In order to approach comparable systems, the spectrum of phthalide (I) was recorded after the addition of hydrochloric acid (see Fig. 1, curve 2) under conditions where there is an absence of charge-trans-

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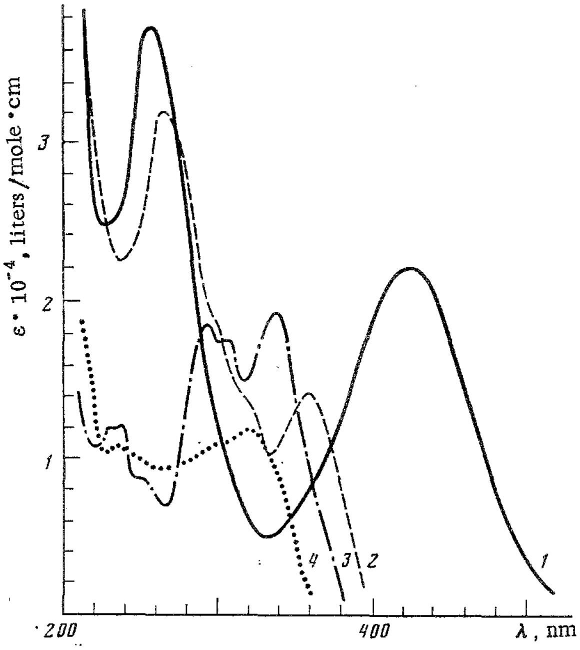

Fig. 1. Electronic absorption spectra: 1) phthalide (I) in ethanol; 2) phthalide (I) (ethanol + 0.5 M HCl); 3) (Z)-3-benzylidenephthalide; 4) (E)-3-benzylidenephthalide (spectra 3 and 4) are taken from [3]).

fer from the amino group to the carbonyl. The spectrum obtained of the hydrochloride salt of phthalide (I) is closer to the spectrum of (Z)-3-benzylidenephthalide (Fig. 1, curve 3). Examination of Stuart—Briegleb molecular models showed that the (E)-isomer of phthalide (I) cannot exist if there are very large steric hindrance effects. This, on condensation of 3,6-diphenylphthalic anhydride with p-dimethylaminophenylacetic acid only the (Z)-isomer is formed, this being caused by spatial interactions in the phthalide being formed.

Phthalide (I) in a solution of sodium methoxide rearranges to the indanedione (II) with quantitative yield. The light-yellow compound (II) in the solid state is in the diketo form; this is corroborated by the presence in the IR spectrum of carbonyl group absorptions at 1707 and 1747 cm^{-1}. A similar absorption of carbonyl groups at 1708 and 1737 cm^{-1} is observed in the spectrum of the yellow derivative 2-(p-dimethylaminophenyl)-1,3-indanedione (IV), the analog of indanedione (II) not containing phenyl substituents in the phthaloyl fragment [5].

The electronic absorption spectrum of the anion of compound (II), recorded in a system of 95% EtOH and 25% aqueous NH_3(10:1), is similar to the spectrum of the anion of compound (IV) recorded under these same conditions [λ_{max}, nm (log ε)]: (II)- 310 (4.30), 373 (3.94), 490 (3.11); (IV) – 292 (4.50), 346 (4.24), 490 (3.22).

Solutions of dimer (III) possesses thermochromism, changing on heating to a green color caused by the reversible decomposition to free radicals, detected in EPR spectra (Fig. 2a). The electronic absorption spectrum of the 4,7-diphenyl-2-(p-dimethylaminophenyl)-1,3-indanedionyl radical (V) in the visible region is virtually indistinguishable from the spectrum of the 2-(p-dimethylaminophenyl)-1,3-indanedionyl radical (VI) [6] (see Fig. 2b).

EXPERIMENTAL

PMR spectra were obtained on a Bruker WM-360 instrument in $CDCl_3$ with TMS as internal standard; IR spectra were obtained on a Specord 75-IR spectrometer using KBr pellets, and electronic absorption spectra on a Specord UV-VIS spectrometer.

4,7-Diphenyl-3-(p-dimethylaminobenzylidene)phthalide (I). A carefully ground mixture of 9.6 g (0.032 mole) 3,6-diphenylphthalic anhydride, 7.2 g (0.04 mole) p-dimethylaminophenylacetic acid [7], and 0.14 g anhydrous sodium acetate was heated to 250-270°C for 2.5 h. The melt was recrystallized from acetic acid. 7.06 g (53%) reddish-brown crystals were obtained, mp 172-173°C. Found, %: C 82.47; H 5.53. $C_{29}H_{23}NO_2$. Calculated, %: C 83.45; H 5.56. IR spectrum (ν, cm^{-1}): 1769 (C=O), 1600, 1590, 1520 (aromatic C=C), 1560 (C=C). PMR spectrum (δ, ppm): 2.93 s (CH_3), 5.75 s (CH=C), 6.59 d ($H^{3'}$ and $H^{5'}$, J_0 = 8 Hz), 7.3-7.6 M (aromatic H), 7.78 s (H^5 and H^6).

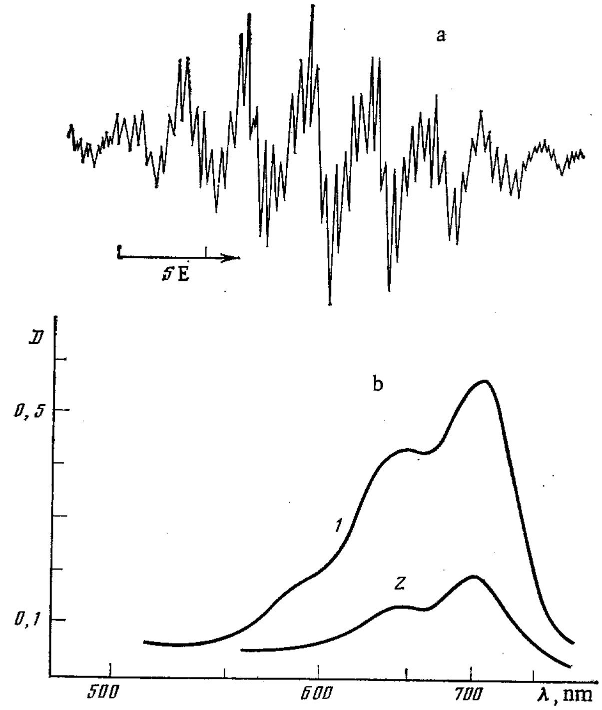

Fig. 2. a) EPR spectrum of radical (V) in benzene at 75°C, amplitude of modulation 0.3 E; b) electronic absorption spectra of radicals in benzene at 79.6°C (length of cell 3.1 cm): 1) (VI); 2) (V). Concentrations of the dimers are $1.69\cdot10^{-3}$ and $1.67\cdot10^{-3}$ M, respectively.

<u>4,7-Diphenyl-2-(p-dimethylaminophenyl)-1,3-indanedione (II).</u> 2.09 g (5 mmole) phthalide (I) was boiled for 1 h in a solution of 0.35 g (0.013 mole) sodium in 30 ml absolute methanol; after filtering, 100 ml water was added, and the mixture was neutralized with concentrated HCl to pH 6. The precipitate was filtered off and dried in air; 2 g (96%) was obtained. After recrystallization from a benzene–heptane (1:1) mixture, the yield was 1.25 g (60%), mp 150-152°C (with decomp.). Found, %: C 83.03; H 5.87. $C_{29}H_{23}CO_2$. Calculated, %: C 83.45; H 5.56. IR spectrum (ν, cm^{-1}): 1707, 1747, (C=O), 1521, 1613 (aromatic C=C). PMR spectrum (δ, ppm): 2.89 s (CH_3), 4.18 s (H^2), 6.68 d ($H^{3'}$ and $H^{5'}$, J_0 = 8 Hz), 7.06 d ($H^{2'}$ and $H^{6'}$, J = 8 Hz), 7.4-7.6 m (aromatic H), 7.76 s (H^5 and H^6).

<u>2,2-Bis[4,7-diphenyl-2-(p-dimethylaminophenyl)-1,3-indanedione] (III).</u> To a solution of 0.15 g (6.5 mmole) sodium in 25 ml methanol was added 1.04 g (2.5 mmole) indanedione (II), then 0.62 g (2.5 mmole) iodine in 5 ml methanol. The mixture was agitated for 2 h, and the precipitate was filtered off and washed with alcohol. Water was added to the mother liquor, and the additional precipitate formed was filtered off and washed with alcohol. Yield 0.66 g (64%), decomposed at 208-210°C (chloroform–alcohol). Found, %: C 83.70; H 5.30. $C_{58}H_{44}N_2O_4$. Calculated, %: C 83.62; H 5.33. IR spectrum (ν, cm^{-1}): 1707, 1740 (C=O), 1520, 1607 (aromatic C=C). PMR spectrum (δ, ppm): 2.93 s (CH_3), 6.62 d ($H^{3'}$ and $H^{5'}$, J_0 = 8 Hz), 7.06 d ($H^{2''}$ and $H^{6''}$, J_0 = 8 Hz), 7.35 s (aromatic H), 7.42 s (H^5 and H^6).

CONCLUSIONS

4,7-Diphenyl-2-(p-dimethylaminophenyl)-1,3-indanedione is obtained by the Perkin–Gabriel reaction, with subsequent oxidation to the dehydrodimer.

LITERATURE CITED

1. L. M. Pisarenko, V. I. Nikulin, A. B. Gagarina, V. A. Roginskii, and N. M. Émanuél', Dokl. Akad. Nauk SSSR, <u>279</u>, 641 (1984).
2. O. K. Popova and N. I. Kopteva, Izv. Vyssh. Uchebn. Zaved., Ser. Khim. i Khim. Tekhnol., <u>25</u>, No. 12, 1454 (1982).
3. J. Berti, Gazz. Chim. Ital., <u>86</u>, 655 (1956).

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*Analysis was conducted according to [8], as the usual method of combustion gave low results for determination of carbon.

4. J. Derkash and F. Langer, Monatsch., 86, 924 (1955).
5. O. Ya. Neiland and M. Ya. Tsirule, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 65 (1963).
6. I. V. Khudyakov, L. M. Pisarenko, A. B. Gagarina, V. A. Kuz'min, and N. M. Émanuél', Dokl. Akad. Nauk SSSR, 222, 1390 (1975).
7. B. W. Ladislaw and H. Viertler, J. Chem. Soc., B, 5, 576 (1968).
8. N. É. Gel'man and Z. M. Anashina, Zhur. Anal. Khim., 24, 1722 (1969).

SYNTHESIS AND EQUILIBRIUM OF STEREOISOMERS OF 5-PHENYL-5-THIO(SELENO)-2-PHENYL(ETHOXY)-1,3,5-DIOXAPHOSPHORINANES

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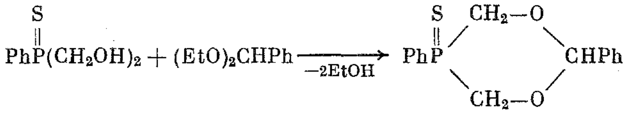
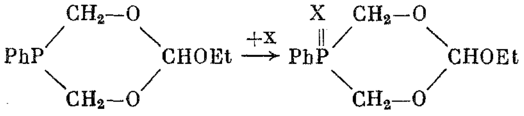
During the transition from 1-phenyl-phosphorinanes and their derivatives [1-3] to 5-phenyl-1,3,5-dioxaphosphorinanes and their derivatives [4, 5], the equilibrium of their conformers and stereoisomers shifts toward the form with the axial orientation of the phenyl group on the P atom. It seems to be expedient to investigate an influence of substituents in the acetal fragment on the equilibrium of 5-phenyl-1,3,5-dioxaphosphorinanes in the case of P(III) and P(IV). It has been shown in [6] that the replacement of CHR by BPh shifts the equilibrium of phosphines toward the Ph_a form and phosphine sulfides toward the Ph_e form. This indicates the difference in interactions of the phosphino- and thiophosphorylic group. It has been discovered in [7] that introduction of the ethoxy group in the 2-position of 5-phenyl-1,3,5-dioxaphosphorinane shifts the equilibrium towards the Ph_e form. In the present work we determined the influence of the substituent in the 2-position on the equilibrium of 5-phenyl-5-thio(seleno)-1,3,5-dioxaphosphorinanes.

2,5-Diphenyl-5-thio-1,3,5-dioxaphosphorinane was easily obtained by interaction of bis(hydroxymethyl)phenylphosphine sulfide with $PhCH(OEt)_2$ by removal of volatile components under vacuum. In the ^{31}P NMR spectrum of the reaction mixture, the signal of the starting diol disappears and a strong signal of a product with a chemical shift (ChS) at 9 ppm appears. Signals of other stereoisomers were absent



(I)

Stereoisomeric sulfides and selenides of 5-phenyl-2-ethoxy-1,3,5-dioxaphosphorinane were obtained by addition of sulfur and selenium to a compound with P(III). The latter constitutes a mixture of two stereoisomers, changing one into another under the reaction conditions [7], and gives mixtures of stereoisomers of sulfides and selenides. Chromatography on silica gel allowed us to isolate individual stereoisomers of sulfides with ChS in their ^{31}P NMR spectrum 10 and 14 ppm (II) and (III) and individual stereoisomers of selenides with ChS 3 and 1 ppm (IV) and (V)



(II)—(V)

X = S (II)and(III); X = Se (IV)and(V).

The structure of stereoisomers was established by NMR spectroscopy. The parameters of the spectra are shown in Table 1.

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