

# Photochemical isomerization of 2-(*N*-phenylamino)-2-phenyl-1,3-indandione

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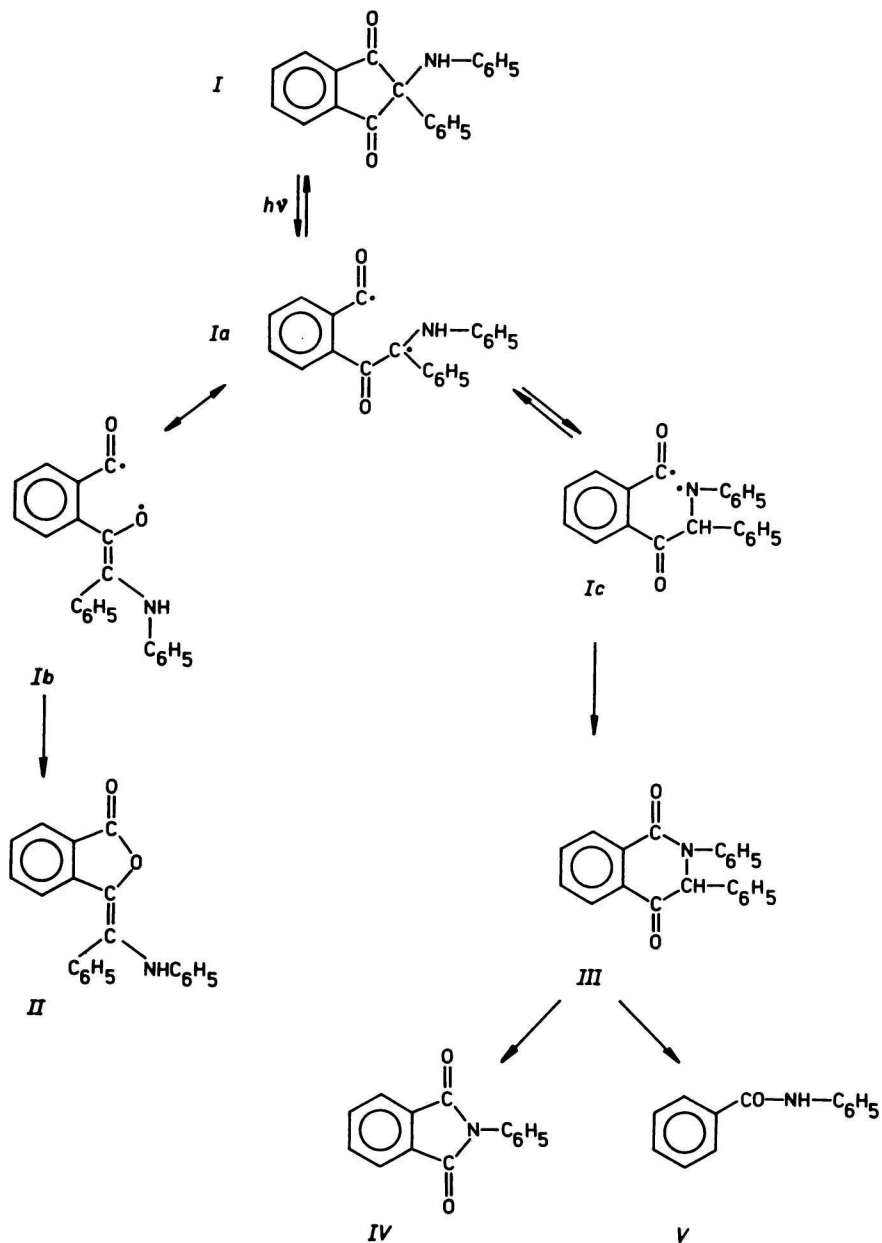
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Photochemical isomerization of 2-(*N*-phenylamino)-2-phenyl-1,3-indandione was studied at two different wavelengths  $\lambda_{\text{exc}} > 360$  nm and  $\lambda_{\text{exc}} = 254$  nm. In both cases the same products 3-[(*N*-phenylamino)phenylmethylene]phthalide, *N*-phenylphthalimide, *N*-phenylbenzamide, and 1,4-dioxo-2,3-diphenyl-1,2,3,4-tetrahydroisoquinoline were formed, however in a different percentage proportion in each case. After light has been absorbed,  $\alpha$ -cleavage takes place, followed by formation of the above compounds. The emission spectra of the starting compound recorded in methanol and in hexane revealed minimal dependence of fluorescence maximum on solvent polarity.

Фотохимическая изомеризация 2-(*N*-фениламино)-2-фенил-1,3-индандиона была изучена при двух различных длинах волн  $\lambda_{\text{exc}} > 360$  нм и  $\lambda_{\text{exc}} = 254$  нм. В обоих случаях образовывались одинаковые продукты: 3-[(*N*-фениламино)фенилметиле]фталид, *N*-фенилфталимид, *N*-фенилбензамид и 1,4-диоксо-2,3-дифенил-1,2,3,4-тетрагидроизохинолин, но в разном процентном отношении в каждом случае. После поглощения света имеет место  $\alpha$ -расщепление, сопровождаемое образованием вышеназванных соединений. Эмиссионные спектры исходного соединения, записанные в метаноле и гексане, отражали минимальную зависимость положения максимума флуоресценции от полярности растворителя.

Preceding papers on photochemical transformations of variously substituted 1,3-indandiones dealt with derivatives substituted at the position 2 by alkyls, alkylaryls or aryls [1—4]. The present work is devoted to 2-(*N*-phenylamino)-2-phenyl-1,3-indandione (*I*) and is aimed at studying the influence of the phenylamino group on photochemical behaviour of —CO—CR—CO— moiety. From the photochemical point of view, due to the presence of a phenylamino group, compound *I* represents a more complicated system than any of those examined previously.

The electronic absorption spectrum of the compound under study exhibits no identifiable maximum in the near UV region. The spectrum in this region is



Scheme 1

unexceptional and apart from a shoulder at  $\lambda = 240$  nm possesses a strong absorption at  $\lambda = 220$  nm, corresponding to  $\pi, \pi^*$  transitions. Thus, the spectrum is very much like the spectrum of 2-phenyl-1,3-indandione the lowest  $n, \pi^*$  singlet state of which appears at  $\lambda = 340$  nm. These facts indicate no formation of intramolecular CT complex observed for 2-(4-*N,N*-dimethylaminophenyl)-1,3-indandione [5]. Similar conclusions can also be drawn from the fluorescence spectrum of *I*. The fluorescence maximum was observed at  $\lambda = 412$  nm and, as well as quantum yields of fluorescence, showed a very slight dependence on solvent polarity. The spectrum is practically identical with the emission spectrum of 2-phenyl-1,3-indandione [6, 7].

On the basis of energy differences of singlet-triplet splitting of  $n, \pi^*$  and  $\pi, \pi^*$  states and the absorption and emission spectra of *I*, one can conclude that the lowest triplet state of this compound is an  $n, \pi^*$  triplet. Similarly to 2-phenyl-1,3-indandione [3], this state is responsible for the photochemical behaviour of this derivative.

After photolysis of *I* in benzene at  $\lambda_{\text{exc}} > 360$  nm four products have been identified: *N*-phenylphthalimide (*IV*), *N*-phenylbenzamide (*V*), presumably 1,4-dioxo-2,3-diphenyl-1,2,3,4-tetrahydroisoquinoline (*III*), and 3-[(*N*-phenylamino)phenylmethylene]phthalide (*II*). Formation of these compounds can be interpreted in the following way: Absorption of the light brings about  $\alpha$ -cleavage of the C—C bond (Scheme 1). Isomerization of the intermediate biradical *Ia* yields either biradical *Ib* or biradical *Ic*. Combination of biradical *Ib* gives phthalide *II*. Combination of biradical *Ic* leads to the isoquinoline derivative *III*, which, however, was not isolated in a pure state due to its instability. *Wanag et al.* [8] also reports instability of 1,4-dioxo-2,3-diphenyl-1,2,3,4-tetrahydroisoquinoline but, apart from *N*-phenylphthalimide, decomposition products were not firmly identified. In order to confirm the presence of the isoquinoline derivative *III* in the mixture of products formed on irradiation of *I*, compound *III* was synthesized by a different route [8]. We have found that the compound is thermally unstable and it decomposes readily, and instead, compound *IV* (formed by extrusion of phenylcarbene from *III*) was isolated from the reaction mixture. However, we failed to trap phenylcarbene. Compound *III* prepared according to the procedure of *Wanag et al.* [8] possessed the correct elemental analyses for C, H, and N. However a mass spectrum of this compound showed a molecular ion  $M^+$  with  $M_r = 223$ , i.e. 90 ( $\sim C_7H_6$ ) less than the value expected for structure *III*. A fragment  $m/z = 90$  was completely absent. Furthermore IR and  $^1H$  NMR spectra suggested the presence of a mixture of compounds. Therefore, we presume that during photolysis the isoquinoline derivative also undergoes further transformations. We assume that compound *III* gives rise to *IV* and *V* together with additional unisolated products; e.g. 3-(*N*-phenylamino)phthalide.

Photochemical reaction of *I* at  $\lambda_{\text{exc}} = 254$  nm in benzene under conditions of sensitized photolysis affords the same products as a reaction performed at  $\lambda > 360$  nm. This confirms the assumption that all the above compounds are formed from the same lowest excited state. Of course, the percentage proportion of each compound at  $\lambda_{\text{exc}} > 360$  nm is not the same as at  $\lambda_{\text{exc}} = 254$  nm (see Experimental), which can also be attributed to the work-up procedure. It was found that photochemical transformation of *I* in a mixture of  $\text{CCl}_4$  and methanol ( $\phi_r = 2:1$ ) was unsuccessful yielding only a mixture of oily substances. Presumably these compounds arose from some combination of the radicals generated on photochemical transformation of *I* with radicals generated from  $\text{CCl}_4$  and methanol.

## Experimental

UV spectra were recorded on a UV, VIS, NIR, PE450 instrument. Fluorescence spectra were measured on a fluorescence spectrometer Perkin—Elmer LS 5 in hexane (anal. grade) and in methanol at  $\lambda_{\text{exc}} = 366$  nm. IR spectra were taken on a spectrometer PE 180 in chloroform.  $^1\text{H}$  NMR spectra were recorded on a Tesla BS 487 spectrometer with 80 MHz working frequency in deuterated chloroform. Mass spectra were measured on a MS-902S instrument (A.E.J.-Kratos, Manchester) at 70 eV energy of electrons and at ionization current of 100  $\mu\text{A}$ . Only peaks with relative intensities higher than or equal to 4 % were taken into account.

### *2-(N-phenylamino)-2-phenyl-1,3-indandione (I)* (Modified procedure [9])

To a solution of 7.6 g (0.03 mol) of 2-chloro- or 8.9 g (0.03 mol) of 2-bromo-2-phenyl-1,3-indandione in 300  $\text{cm}^3$  of diethyl ether is added 3.6  $\text{cm}^3$  (0.04 mol) of freshly distilled aniline. The mixture is left to stand at room temperature for 4 days. After removal of the ether the crude product is crystallized from ethanol. Yield = 6.5 g (70 %) of yellow crystalline compound, m.p. = 214—215  $^{\circ}\text{C}$ , being in accord with Ref. [10]. UV spectrum (hexane):  $\lambda_{\text{max}} = 242$  nm,  $\log(\epsilon/(\text{m}^2 \text{mol}^{-1})) = 4.5$ .

### *1,4-Dioxo-2,3-diphenyl-1,2,3,4-tetrahydroisoquinoline (III)*

In 6  $\text{cm}^3$  of hot dry methanol is dissolved 1.0 g (0.003 mol) of *I*. Five drops of 5 % sodium methoxide solution in methanol is added into the boiling mixture and reflux is continued for additional 15 min, while a yellow colour of the solution turns to red. After cooling a compound with m.p. = 120—125  $^{\circ}\text{C}$  (decomp.) crystallizes. Ref. [8] reports m.p. = 156  $^{\circ}\text{C}$  *in vacuo*.

For  $\text{C}_{21}\text{H}_{15}\text{NO}_2$  ( $M_r = 313$ )  $w_i(\text{calc.})$ : 80.50 % C, 4.50 % N, 4.79 % H;  $w_i(\text{found})$ : 79.80 % C, 4.41 % N, 4.76 % H. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{O})$  1650,  $\nu(\text{C}-\text{N})$  1310.

$^1\text{H}$  NMR spectrum,  $\delta/\text{ppm}$ : 6.50—7.50 (m, 15H, ar). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 223 (30), 197 (10), 180 (15), 105 (40), 93 (100). By the next day the filtrate will have afforded a pale yellow crystalline compound, 300 mg (30 %), m.p. = 201—204°C in accord with Ref. [8]. The structure of *N*-phenylphthalimide is attributed to this compound. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{O})$  1725,  $\nu(\text{C}=\text{N})$  1350.  $^1\text{H}$  NMR spectrum,  $\delta/\text{ppm}$ : 6.50—7.50 (m, 9H, ar). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 223 (100), 179 (79), 104 (20), 76 (76).

*Photoisomerization of 2-(N-phenylamino)-2-phenyl-1,3-indandione (I)*  
at  $\lambda_{\text{exc}} > 360 \text{ nm}$

A solution of 1.0 g of *I* in 420 cm<sup>3</sup> of benzene (spectrophotometric grade) ( $c = 8 \times 10^{-3} \text{ mol dm}^{-3}$ ) was irradiated in a photochemical reactor with a 400 W high-pressure mercury lamp for 6 h. Prior to irradiation, oxygen was removed from the solution by bubbling nitrogen through it during 20 min. The course of the reaction was monitored spectrophotometrically. After the irradiation was terminated, the solvent was stripped off *in vacuo* and the residue was chromatographed on silica gel. A mixture of benzene—petroleum ether ( $\phi_r = 5:2$ ) was used as eluant.

From the first band, unchanged starting compound (*I*) (60 %) was isolated. The second band contained a compound to which the structure of *N*-phenylphthalimide (*IV*) (m.p. = 203—204°C) was assigned after comparison of data obtained with the data given in Ref. [8] and with the data known from the synthesis of *IV* described above. The third band consisted of the substance the IR and  $^1\text{H}$  NMR spectra of which are similar to compound *III* prepared above. The compound failed to be purified as it decomposed during crystallization. The fourth band was composed of *N*-phenylbenzamide (*V*) (5 %). The structure was assigned on the basis of m.p. = 113—115°C, IR,  $^1\text{H}$  NMR, and mass spectra. All the spectra are in accord with Ref. [8]. 3-[(*N*-Phenylamino)phenylmethylene]phthalide (*II*) (15 %), m.p. = 259—260°C, was found in the fifth band.

For  $\text{C}_{21}\text{H}_{15}\text{NO}_2$  ( $M_r = 313$ )  $w_i(\text{calc.})$ : 80.50 % C, 4.79 % H, 4.50 % N;  $w_i(\text{found})$ : 79.89 % C, 4.70 % H, 4.39 % N. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{C})$  1695,  $\nu(\text{C}=\text{N})$  1260,  $\nu(\text{CO}-\text{O}-\text{C})$  1225,  $\nu(\text{N}-\text{H})$  3260.  $^1\text{H}$  NMR spectrum,  $\delta/\text{ppm}$ : 6.00—8.50 (m, 14H, ar). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 313 (24), 180 (100), 165 (10), 104 (10), 77 (45), 51 (15).  $^1\text{H}$  NMR and IR spectra do not allow to settle which one of two possible isomers has been formed.

*Photoisomerization of 2-(N-phenylamino)-2-phenyl-1,3-indandione (I)*  
at  $\lambda_{\text{exc}} = 254 \text{ nm}$

A solution of 700 mg of *I* in 300 cm<sup>3</sup> of benzene (spectrophotometric grade) was irradiated in a photochemical reactor with a low-pressure mercury lamp for 14 h. The reaction mixture was stirred during irradiation. The course of the reaction was monitored by UV spectroscopy and TLC. After the reaction was complete, the solvent was removed *in vacuo* and the residue was subjected to column chromatography on silica gel. A mixture of benzene—petroleum ether ( $\phi_r = 5:2$ ) was used as eluant.

Compounds *I*—*V* were isolated from the individual bands eluted successively in the following order: 1. *I* (45 %), 2. *IV* (5 %), 3. *III* (4 %), 4. *V* (15 %), 5. *II*. Other compounds isolated from additional bands represented decomposition products showing no carbonyl absorption in IR spectra.

## References

1. Rigaudy, J. and Derible, P., *Bull. Soc. Chim. Fr.* 10, 3047 (1965).
2. Rigaudy, J. and Derible, P., *Bull. Soc. Chim. Fr.* 10, 3055 (1965).
3. Gáplovský, A., Donovalová, J., and Hrnčiar, P., *Collect. Czechoslov. Chem. Commun.* 49, 1569 (1984).
4. Hrnčiar, P., Gáplovský, A., Drgoncová, V., and Donovalová, J., *Chem. Papers* 40, 649 (1986).
5. Zalukaev, L. P., Vorobyeva, R. P., Oleynikova, T. A., and Shmyrev, Kh. N., *Zh. Prikl. Spektrosk.* 19, 750 (1973).
6. Zechner, J., Getoff, N., Timtcheva, J., Fratev, F., and Minchev, S., *Z. Naturforsch.* 38a, 1337 (1983).
7. Zechner, J., Grabner, G., Köhler, G., Getoff, N., Timtcheva, J., Fratev, F., and Minchev, S., *J. Photochem.* 23, 61 (1983).
8. Wanag, G. and Walbe, B., *Ber.* 71, 1448 (1938).
9. Nathanson, F., *Ber.* 26b, 2579 (1893).
10. Ozol, E., Ozol, J., Aren, A., and Wanag, G., *Zh. Org. Khim.* 4, 88 (1968).

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