

SHORT
COMMUNICATIONS

[2+2]-Photodimerization of 3-Arylindenones

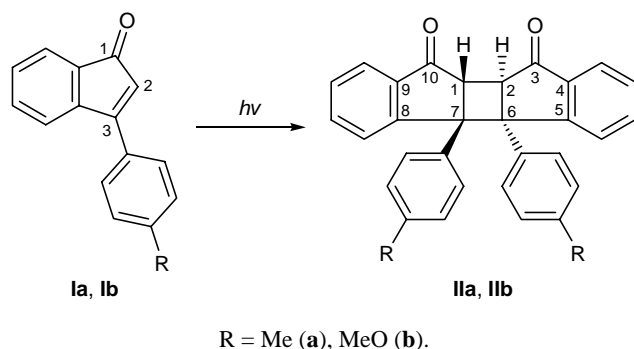
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We recently reported on a new synthesis of 3-arylindenones via intramolecular cyclization of 1,3-diarylpropynones in liquid superacids [1]. It was also noted that 3-arylindenones are quite sensitive to temperature, UV irradiation, and nucleophilic reagents [1]. The present communication describes a new [2+2]-dimerization of 3-arylindenones **Ia** and **Ib** to *syn,trans*-adducts **IIa** and **IIb**, which occurs extremely readily on exposure to daylight.



Solutions of compounds **Ia** and **Ib** (0.25 mmol) in diethyl ether (50 ml) were exposed to daylight over a period of 3 days at room temperature. Removal of the solvent, followed by recrystallization of the residue from methanol, gave dimeric products **IIa** and **IIb** in 67 and 72% yield, respectively. During the exposure, intensely yellow–orange solutions of **Ia** and **Ib** gradually turned colorless. When solutions of 3-arylindenones **Ia** and **Ib** in diethyl ether were kept in the dark, other conditions being equal, unreacted initial compounds were quantitatively recovered.

The structure of dimer **IIb** was determined by X-ray analysis (see figure). We failed to obtain crystals of **IIa** suitable for X-ray diffraction study. However, compound **IIa** was assigned the same configuration as that found for **IIb**, taking into account similarity of their

¹³C NMR spectra. The ¹³C NMR spectra of **IIa** and **IIb** contain signals at δ_c 59.90 and 59.61 ppm, respectively, which are typical of the C⁶ and C⁷ atoms in the cyclobutane ring; the C¹ and C² signals appear in the same spectral range, δ_c 50.48 (**IIa**) and 50.66 ppm (**IIb**). For comparison, the signals from C¹ and C² in the spectrum of analogous [2+2]-photodimerization product obtained from 3-acetoxyindenone [2] appear at δ_c 51.40 ppm; like **IIa** and **IIb**, this product has *syn,trans* configuration of the four-membered ring.

Apart from 3-acetoxyindenone [2], analogous [2+2]-photodimerization was reported for 2-phenylindenone [3] and 3-benzylthioindenone [4]; however, in the two latter cases fine structure of the dimers was not determined.

The formation of adducts **IIa** and **IIb** may be rationalized in terms of general relations holding in photochemical cycloaddition of enones to alkenes. Interaction between the enone system in the triplet excited state and strongly polarized double C²=C³ bond in the indenone molecule in the ground state gives rise to four-membered ring according to the *syn*-dimerization pattern [5]. The *trans*-junction of initial 3-arylindenone molecules **Ia** and **Ib** is likely to result from an additional stabilizing π – π interaction in the transition state between π -systems of the 3-aryl substituent in one indenone molecule and benzene fragment of the indenone system in the other molecule.

The revealed [2+2]-photodimerization of 3-arylindenones can be regarded as a new and efficient method of synthesis of polycyclic adducts **II** which are isomeric to natural biologically active truxene derivatives [6].

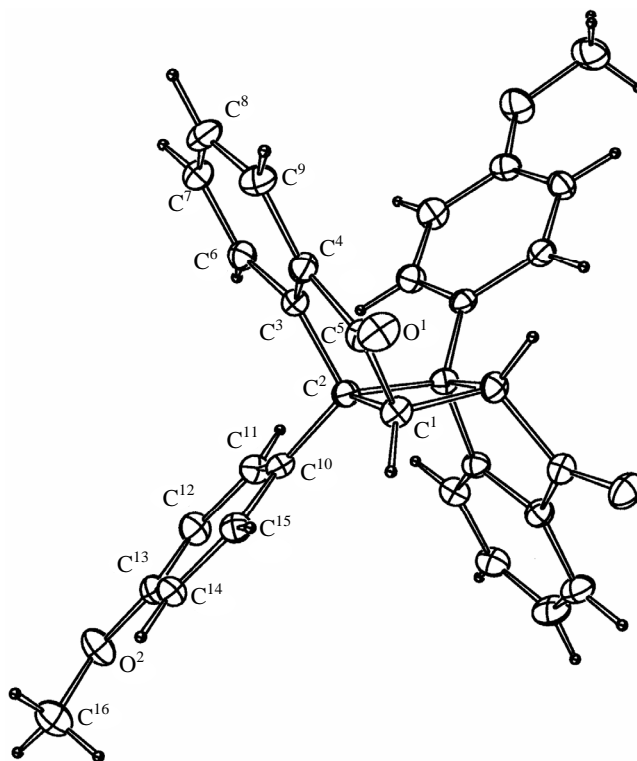
The synthesis and properties of 3-(4-methylphenyl)indenone (**Ia**) and 3-(4-methoxyphenyl)indenone (**Ib**) were reported in [1].

(1*S*,2*S*,6*R*,7*R*)-6,7-Bis(4-methylphenyl)dibenzo[4,5:8,9]tricyclo[5.3.0.0^{2,6}]decane-3,10-dione (IIa). mp 133–135°C (decomp.). ¹H NMR spectrum, δ , ppm: 2.25 s (6H, 2Me), 3.60 s (2H, 1-H, 2-H), 7.02 d (4H, H_{arom} , $J = 8.0$ Hz), 7.17 d (4H, H_{arom} , $J = 8.0$ Hz), 7.28–7.42 m (6H, H_{arom}), 7.76–7.79 m (2H, H_{arom}). ¹³C NMR spectrum, δ_{C} , ppm: 20.89 (Me), 50.48 (C¹, C²), 59.90 (C⁶, C⁷), 124.36, 127.12, 128.34, 129.08, 129.43, 134.11, 136.69, 136.85, 136.90, 155.55, 202.97 (C³, C¹⁰). Mass spectrum, m/z (I_{rel} , %): 440 (42) [M]⁺, 423 (81), 349 (100), 220 (23). Found, %: C 86.83; H 5.50. C₃₂H₂₄O₂. Calculated, %: C 87.25; H 5.49.

(1*S*,2*S*,6*R*,7*R*)-6,7-Bis(4-methoxyphenyl)dibenzo[4,5:8,9]tricyclo[5.3.0.0^{2,6}]decane-3,10-dione (IIb). mp 178–180°C (decomp.). ¹H NMR spectrum, δ , ppm: 3.57 s (2H, 1-H, 2-H), 3.72 s (6H, MeO), 6.74 d (4H, H_{arom} , $J = 8.8$ Hz), 7.17 d (4H, H_{arom} , $J = 8.8$ Hz), 7.29–7.37 m (6H, H_{arom}), 7.76–7.80 m (2H, H_{arom}). ¹³C NMR spectrum, δ_{C} , ppm: 50.66 (C¹, C²), 55.18 (MeO), 59.61 (C⁶, C⁷), 113.70, 124.39, 128.34, 128.38, 129.36, 131.77, 134.11, 136.89, 155.61, 158.47, 202.94 (C³, C¹⁰). Mass spectrum, m/z (I_{rel} , %): 472 (28) [M]⁺, 454 (45), 364 (100), 236 (48). Found, %: C 79.99; H 5.30. C₃₂H₂₄O₄. Calculated, %: C 81.34; H 5.12.

Principal crystallographic parameters of compound **IIb**: C₃₃H₂₈O₅ (**IIb**+MeOH; a half of the molecule is crystallographically independent); M 504.59; monoclinic crystals with the following unit cell parameters (at 173 K): $a = 12.9243(2)$, $b = 28.4039(8)$, $c = 9.0628(2)$ Å; $\beta = 125.885(5)^\circ$; $V = 2695.5(1)$ Å³; $d_{\text{calc}} = 1.24$ g/cm³; $Z = 4$ (for crystallographically independent fragment); space group $C12/c1$. Total of 7230 reflections were measured ($\theta_{\text{max}} = 30.01^\circ$); final divergence factors $R_f = 0.062$ (from 1679 independent reflections with $F(hkl) > 4.0\sigma(F)$ and $wR(F^2) = 0.088$ (from all reflections). The complete set of crystallographic data is available from the authors.

The ¹H and ¹³C NMR spectra were recorded from solutions in CDCl₃ on a Bruker Avance-300 spectrometer (300 MHz for ¹H and 75 MHz for ¹³C) using the solvent signals as reference (CHCl₃, residual protons, δ 7.25 ppm; CDCl₃, δ_{C} 77.0 ppm). The mass spectra (electron impact, 70 eV) were measured on a TSQ 700 Finnigan MAT instrument. Single crystals of compound **IIb** were obtained by slow evaporation of its dilute solution in methanol over a period of several days at room temperature; the X-ray diffraction data



Structure of the molecule of (1*S*,2*S*,6*R*,7*R*)-6,7-bis(4-methoxyphenyl)dibenzo[4,5:8,9]tricyclo[5.3.0.0^{2,6}]decane-3,10-dione (**IIb**) according to the X-ray diffraction data.

were acquired on a KappaCCD diffractometer [$\mu(\text{MoK}\alpha)$ 0.083 mm⁻¹, graphite monochromator, ϕ scanning].

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