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Synthesis and Photoinitiated Isomerizations of 3-(4-Nitrophenyl)- and 3-(4-Aminophenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde and -2-carboxylic acid Derivatives*

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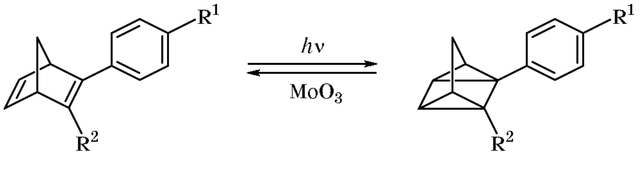
Abstract—3-(4-Nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde and its derivatives at the formyl group were synthesized. By reduction of the nitro group the corresponding 3-(4-aminophenyl)-substituted compounds were obtained, as well as 4,4′-bis(bicyclo[2.2.1]hepta-2,5-dien-2-yl)azobenzenes. Irradiation of the resulting norbornadiene derivatives in the region of their absorption maxima resulted in valence isomerization with formation of the corresponding quadricyclanes. The reverse transformations are promoted by molybdenum(VI) oxide as heterogeneous catalyst. 4,4′-Bis(bicyclo[2.2.1]hepta-2,5-dien-2-yl)azobenzenes undergo reversible (on heating) photochemical *E*/*Z* isomerization at the N=N bond.

Photochemical valence isomerization of substituted norbornadienes into corresponding quadricyclanes (Scheme 1) attracts interests from the viewpoints of both its possible application for accumulation of solar energy [1–4] and study of energy transfer mechanisms in organic molecules [5, 6].

Scheme 1.



Ia–Ie, IIa, IIb **IIIa–IIIe, IVa, IVb**

I, **III**, $R^1 = NO_2$; R^2 = CHO (**a**), 1,3-dioxolan-2-yl (**b**), CH=CHCOPh (**c**), $CH=C(CN)_2$ (**d**), $COOCH_3$ (**e**); **II**, **IV**, $R^1 = NH_2$; R^2 = $CH=C(CN)_2$ (**a**), $COOCH_3$ (**b**).

The efficiency of this process increases when the long-wave boundary (λ_b) of absorption of initial norbornadienes shifts to the red region. In continuation of studies on the effect of substituent at the double bond of norbornadiene on the λ_b value and photoisomerization quantum yield φ we synthesized 3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde and its derivatives **Ia**–**Id**, methyl 3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**Ie**), 3-(4-aminophenyl)-2-dicyanovinylbicyclo[2.2.1]-hepta-2,5-diene (**IIa**), and methyl 3-(4-aminophenyl)-bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**IIb**) (Table 1). The *Z*/*E* photoisomerization shown in Scheme 2 was studied with 4,4′-bis(3-formylbicyclo-[2.2.1]hepta-2,5-dien-2-yl)azobenzene (**Va**) and 4,4′-bis[3-(2-cyano-2-ethoxycarbonylvinyl)bicyclo-[2.2.1]hepta-2,5-dien-2-yl)azobenzene (**Vb**).

Compounds **Ia** and **Ie** were synthesized by the Diels–Alder reaction of cyclopentadiene with the corresponding substituted acetylenes [1, 3]. Norbornadiene derivatives **Ib**–**Id** were prepared from aldehyde **Ia** and ethylene glycol, acetophenone, and malononitrile, respectively. The reduction of nitrophenyl-substituted compounds **Id** and **Ie** with iron(II) sulfate in aqueous ammonia gave 4-aminophenyl derivatives **IIa** and **IIb**. Bis-norbornadiene **Va** was obtained by reduction of aldehyde **Ia** with zinc in alkaline medium; treatment of **Va** with ethyl cyanoacetate afforded bis-norbornadiene derivative **Vb**. The structure of products **I**, **II**, and **V** was confirmed by the electron absorption, IR, and ^1H NMR spectra. The electron absorption spectrum of methyl ester **IIb** is well consistent with the data reported in [1, 3]. The presence of an electron-donor substituent ($R^1 = NH_2$)

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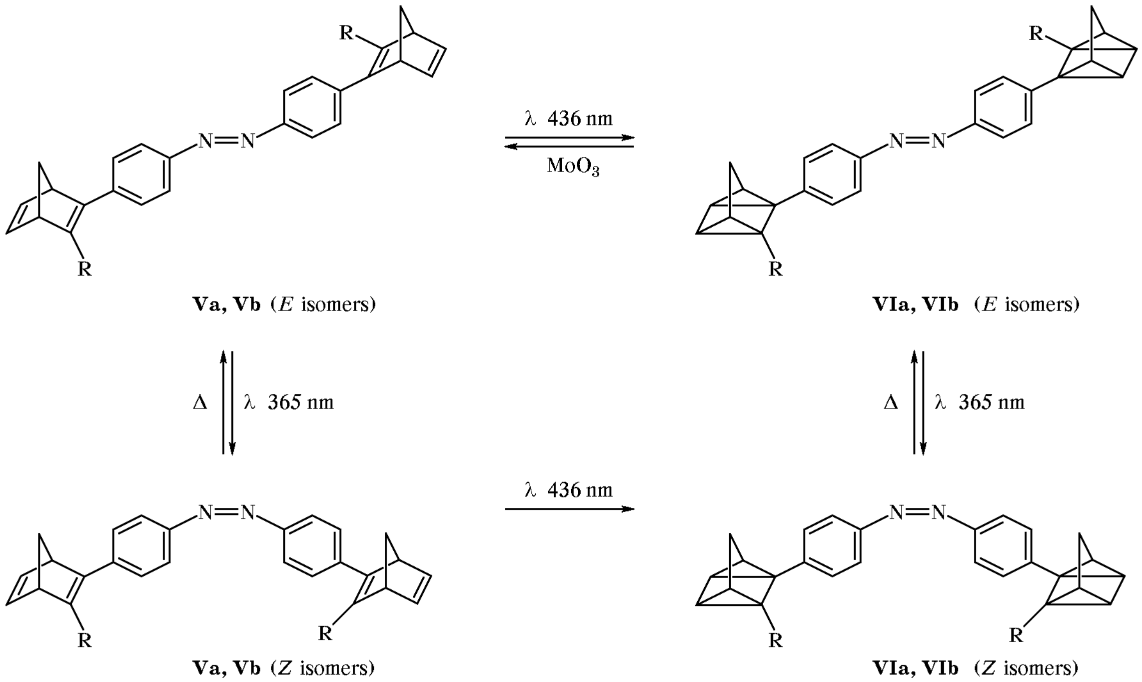
Scheme 2.



V, **VI**, R = CHO (**a**), $CH{=}C(CN)COOC_2H_5$ (**b**).

in the phenyl ring leads to a red shift of the long-wave absorption boundary (λ_b = 445 nm) and increases the quantum yield of quadricyclane formation (φ = 0.2). Electron-acceptor substituent ($R^1 = NO_2$) affects the long-wave absorption boundary to a lesser extent (λ_b = 415 nm), while the quantum yield φ decreases to 0.01. The spectral and photochemical parameters of 3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde and its derivatives (Table 2) conform to the above relations only partially.

Aldehyde **Ia** and its derivatives **Ib**–**Id** absorb in the region 310–390 nm, and λ_b successively increases from 420 nm for initial aldehyde **Ia** to 480 nm for dicyanomethylene derivative **Id**. As with bicyclo-[2.2.1]hepta-2,5-diene-2-carboxylic acid derivatives **Ie** and **IIb**, the presence of electron-donor amino group in the phenyl substituent of **IIa** gives rise to a considerable red shift of λ_b (to 620 nm). Irradiation of compounds **I** and **II** in the region of their long-wave absorption maxima using a DRSh-250 mercury lamp (filtered light; λ_{irr} = 365 nm for **Ia**, **Ib**, **Ie**, and **III**; λ_{irr} = 436 nm for **Ic**, **Id**, and **V**) changes their electron absorption spectra which become typical of quadricyclane structures [1, 3, 4] (see figure). However, the quantum yields φ did not always change in parallel to λ_b (Table 2). 2-(2-Benzoylvinyl)-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (**Ic**) and 2-dicyanovinyl-3-(4-nitrophenil)bicyclo[2.2.1]hepta-2,5-diene (**Id**) are characterized by anomalously high quantum yields (φ = 0.6 and 0.75, respectively) for compounds containing an electron-acceptor group in the phenyl ring at the double bond. Moreover, despite the presence of electron-donor amino group ($R^1 = NH_2$), the quantum yield for photoisomerization of 2-(4-aminophenyl)-3-dicyanovinylbicyclo[2.2.1]-hepta-2,5-diene (**IIa**), is as low as 0.1 (λ_b = 620 nm). By analogy with [2], these data may be explained by the through-space interaction between π orbitals of the unsubstituted double bond in **Ic** and **Id** and the other C=C bond bearing two electron-acceptor substituents. In the ground state this interaction is weak, but it becomes significant in the excited state. As a result, the quantum yield of the reaction increases.

Azobenzene derivatives **Va** and **Vb** are characterized by λ_b values of 500 and 560 nm, respectively (Table 2). These compounds give rise to two types of photochemical processes: *E*/*Z*-isomerization at the N=N bond and valence isomerization into the corresponding quadricyclanes. Irradiation of compounds **Va** and **Vb** in weakly polar solvents (e.g., in toluene) for 3–5 min (λ_{irr} = 365 nm) induces fast *E*/*Z* isomerization which is accompanied by reduction of the molar absorption coefficient at the long-wave maximum and by a small blue shift (5 nm) which is

Table 1. Yields, melting points, and elemental analyses of norbornadiene derivatives **I**, **II**, and **V**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Ia	60	78	69.82	4.55	5.93	$C_{14}H_{11}NO_3$	69.70	4.60	5.81
Ib	51	130	67.41	5.28	5.02	$C_{16}H_{15}NO_4$	67.36	5.30	4.91
Ic	30	145	76.88	4.94	4.15	$C_{22}H_{17}NO_3$	76.95	4.99	4.08
Id	70	127	70.70	3.93	14.47	$C_{17}H_{11}N_3O_2$	70.58	3.83	14.53
Ie	42	52–53	66.56	4.76	5.20	$C_{15}H_{13}NO_4$	66.41	4.83	5.16
IIa	25	145–146	78.81	5.01	16.18	$C_{17}H_{13}N_3$	78.74	5.05	16.21
IIb	30	105	74.87	6.17	5.92	$C_{15}H_{15}NO_2$	74.67	6.27	5.81
Va	91	175	80.26	5.19	6.77	$C_{28}H_{22}N_2O_2$	80.36	5.30	6.70
Vb	57	215	75.35	5.17	9.30	$C_{38}H_{32}N_4O_4$	75.31	5.30	9.21

typical of such processes [7]. This transformation is reversible, and the initial *E* isomers are formed on heating. Irradiation of compound **Va** at λ = 405 nm or of **Vb** at λ = 436 nm leads to formation of quadricyclanes **VIa** and **VIb**, respectively; however, the quantum yields of these transformations are low: $\varphi \approx 0.025$. The electron absorption spectrum of **VIb** (λ_{max} = 340 nm) is well simulated by the spectrum of 4,4′-dimethylazobenzene (λ_{max} = 335 nm) [7]. Quadricyclanes **VIa** and **VIb** undergo *E*/*Z* isomerization at the N=N bond on irradiation at λ = 313 nm.

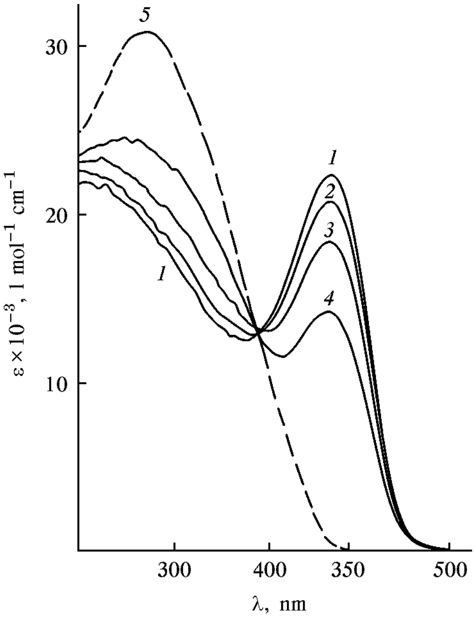
All photochemically generated quadricyclanes (**III**, **IV**, and **VI**) are stable at room temperature; their reverse transformation into initial bicyclo[2.2.1]hepta-2,5-dienes was effected by the procedure described in [3, 8] using molybdenum(VI) oxide as heterogeneous catalyst. The rate constant of the reverse reaction was 10^{-2} to 10^{-3} s^{-1} at 21°C.

EXPERIMENTAL

The electron absorption spectra were measured on a Specord M-40 spectrophotometer. Solutions of norbornadiene derivatives in 2-propanol were irradiated with a DRSh-250 mercury lamp using a set of light filters. The IR spectra were recorded from mulls in mineral oil on a Specord 75IR instrument, and the ^{1}H NMR spectra were obtained on a Varian Unity 300 spectrometer (300 MHz) in $CDCl_3$.

3-(4-Nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde (Ia). 3-(4-Nitrophenyl)-2-propynal, 7.3 g, was dissolved in 50 ml of toluene, and 8 g of cyclopentadiene was added to the solution. The mixture was refluxed for 4 h, and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography on aluminum oxide using toluene as eluent and was then recrystallized from octane. Yield 6 g (60%). Light-yellow crystals. IR spectrum, ν, cm^{-1}: 1647, 1594, 1580, 1500, 1340. ^{1}H NMR spectrum, δ, ppm: 2.10–2.20 m (2H, C^7H_2), 3.96 m (1H, 4-H), 4.24 m (1H, 1-H), 6.94 m (2H, 5-6, 6-H), 7.56–8.27 m (4H, C_6H_4), 9.85 m (1H, CHO).

2-[3-(4-Nitrophenyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]-1,3-dioxolane (Ib). Aldehyde **Ia**, 1 g, was dissolved in 10 ml of benzene, and 0.26 ml of ethylene glycol and a few crystals of *p*-toluenesulfonic acid



Electron absorption spectra of 2-(2-benzoylvinyl)-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (**Ic**) in 2-propanol (*1*) before irradiation, (*2*) after 0.5-min irradiation, (*3*) after 2-min irradiation, (*4*), after 5-min irradiation, and (*5*) after 15-min irradiation; λ_{irr} = 436 nm.

Table 2. Spectral parameters of norbornadiene derivatives **I**, **II**, and **V** and quadricyclanes **III**, **IV**, and **VI**

Comp. no.	λ_{max},[a] nm ($\varepsilon \times 10^{-3}$)	λ_b, nm (**I**, **II**, **V**)	Quantum yield φ	λ_b, nm (**III**, **IV**, **VI**)
Ia	310 (4.5)	420	0.12	390
Ib	328 (13.1)	435	0.05	410
Ic	387 (22.6)	470	0.60	400
Id	386 (29.8)	480	0.75	340
Ie	322 (15.3)	415	0.01	380
IIa	505 (36.2)	620	0.1	380
IIb	353 (20.7)	445	0.20	330
Va	381 (16.4)	500	0.025	490
Vb	417 (21.0)	560	0.023	500

[a] In 2-propanol.

were added. The mixture was refluxed for 2.5 h in a flask equipped with a Dean–Stark trap. The solution was cooled, treated with an aqueous solution of sodium carbonate, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography on aluminum oxide using toluene as eluent. The product was recrystallized from methanol. Yield 0.6 g (51%). Pale yellow crystals. IR spectrum, ν, cm^{-1}: 1633, 1585, 1513, 1340. ^{1}H NMR spectrum, δ, ppm: 2.06–2.16 m (2H, C^{7}H$_2$), 3.86–4.18 m [6H, 4-H, 1-H, O(CH$_2$)$_2$O], 5.54 m (1H, OCHO), 6.90–7.00 m (2H, 5-H, 6-H), 7.60–8.25 m (4H, C$_6$H$_4$).

2-(2-Benzoylvinyl)-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (Ic) was synthesized by the procedure reported in [9] from aldehyde **Ia** and acetophenone. The product was purified by chromatography on aluminum oxide using toluene as eluent. Yellow powder. IR spectrum, ν, cm^{-1}: 1647, 1593, 1567, 1513, 1340. ^{1}H NMR spectrum, δ, ppm: 2.18–2.28 m (2H, C^{7}H$_2$), 4.09 m (1H, 4-H), 4.38 m (1H, 1-H), 7.03–7.08 m (2H, 5-H, 6-H), 7.53–8.32 m (11H, C$_6$H$_5$, C$_6$H$_4$, 2CH=).

2-Dicyanovinyl-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (Id). Aldehyde **Ia**, 2 g, was dissolved in 20 ml of methanol on heating, 0.6 g of malononitrile was added, and the mixture was made slightly alkaline (pH 8–9) by adding 10 ml of aqueous sodium carbonate. The mixture was stirred for 0.5 h on heating and for 0.5 h without heating. The product was isolated as an orange powder (1.7 g) which was recrystallized from methanol. Orange needles. IR spectrum, ν, cm^{-1}: 2220, 1600, 1560, 1520, 1340. ^{1}H NMR spectrum, δ, ppm: 2.32–2.46 m (2H, C^{7}H$_2$), 4.24 m (1H, 4-H), 4.77 m (1H, 1-H), 7.09 m (2H, 5-H, 6-H), 7.80–8.37 m (4H, C$_6$H$_4$).

Methyl 3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (Ie). Methyl 3-(4-nitrophenyl)-2-propynoate, 1.8 g, was dissolved in 40 ml of toluene, and 1.7 g of cyclopentadiene was added. The mixture was refluxed for 4 h, and the solvent was removed under reduced pressure. The residue was purified by chromatography on aluminum oxide using toluene–hexane (3 : 1) as eluent. The eluate was evaporated to obtain 1 g (42%) of product **Ie** which was recrystallized from heavy petroleum ether. Pale yellow crystals. IR spectrum, ν, cm^{-1}: 1713, 1593, 1513, 1340. ^{1}H NMR spectrum, δ, ppm: 2.13–2.29 m (2H, C^{7}H$_2$), 3.68 m (3H, OCH$_3$), 3.85 m (1H, 4-H), 4.09 m (1H, 1-H), 6.95–7.01 m (2H, 5-H, 6-H), 7.63–8.20 m (4H, C$_6$H$_4$).

Methyl 3-(4-aminophenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (IIb). A mixture of 0.87 g of ether **Ie** and 6.9 g of iron(II) sulfate in 87 ml of concentrated aqueous ammonia was heated for 2 h on a water bath. The product was extracted into toluene, the extract was dried over anhydrous calcium chloride and evaporated, and the residue was purified by chromatography on aluminum oxide using chloroform as eluent. The product was recrystallized from methanol. Yield 0.2 g (30%). Yellow powder. IR spectrum, ν, cm^{-1}: 3440, 3353, 1688, 1633, 1607, 1580, 1505. ^{1}H NMR spectrum, δ, ppm: 2.00–2.16 m (2H, C^{7}H$_2$), 3.69 m (3H, OCH$_3$), 3.85–4.02 m (4H, 4-H, 1-H, NH$_2$), 6.65 m (2H, 5-H, 6-H), 7.63–8.20 m (4H, C$_6$H$_4$).

3-(4-Aminophenyl)-2-dicyanovinylbicyclo[2.2.1]hepta-2,5-diene (IIa) was synthesized as described above for ester **IIb**. Violet crystals. IR spectrum, ν, cm^{-1}: 3451, 3347, 2193, 1623, 1593, 1511. ^{1}H NMR spectrum, δ, ppm: 2.20 m (2H, C^{7}H$_2$), 3.95 m (1H, 4-H), 4.10 m (2H, NH$_2$), 4.68 m (1H, 1-H), 6.69–7.51 m (7H, C$_6$H$_4$, 5-H, 6-H, CH=).

4,4′-Bis(3-formylbicyclo[2.2.1]hepta-2,5-dien-2-yl)azobenzene (Va). Aldehyde **Ia**, 0.5 g, was dissolved in 20 ml of 2-propanol on heating, and 0.5 ml of a 30% solution of sodium hydroxide was added. Zinc powder, 2 g, was slowly added in portions with stirring, and the mixture was heated for 0.5 h while stirring. The unreacted zinc was filtered off, and the filtrate was cooled. The precipitate (~0.4 g) was purified by chromatography on aluminum oxide with toluene as eluent and was recrystallized from 2-propanol. Yield 91%. Orange crystals. IR spectrum, ν, cm^{-1}: 1651, 1593, 1560. ^{1}H NMR spectrum, δ, ppm: 2.19–2.28 m (4H, C^{7}H$_2$, C$^{7'}$H$_2$), 4.00–4.22 m (4H, 1-H, 4-H, 1′-H, 4′-H), 6.95 m (4H, 5-H, 6-H, 5′-H, 6′-H), 7.55–8.42 m (8H, $2C_6H_4$), 9.91 m (2H, 2CHO).

4,4′-Bis[3-(2-cyano-2-ethoxycarbonylvinyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]azobenzene (Vb). Compound **Va**, 0.3 g, was dissolved in 40 ml of 2-propanol, 0.2 ml of ethyl cyanoacetate and a few drops of aqueous sodium carbonate were added, and the mixture was stirred for 2 h under slight heating. It was then left to stand for 5 h at room temperature, and 0.25 g of the product was isolated, which was recrystallized from 2-propanol. Dark red needles. IR spectrum, ν, cm^{-1}: 2220, 1724, 1580. ^1H NMR spectrum, δ, ppm: 1.33 m (6H, $2CH_3$), 2.26–3.31 m (4H, $2C^7H_2$), 4.00–4.87 m (4H, 1-H, 4-H, 1′-H, 4′-H), 4.30 m (4H, $2CH_2$), 6.88–7.02 m (4H, 5-H, 6-H, 5′-H, 6′-H), 7.40–8.40 m (10H, $2C_6H_4$, 2CH=).

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