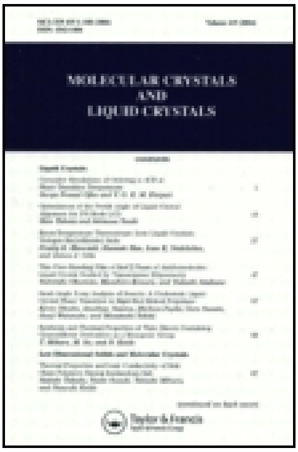

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PHOTOINITIATED REARRANGEMENTS OF 3-PHENYLNORBORNADIENE WITH CONJUGATED SUBSTITUENTS IN 2-POSITION

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Abstract A series of novel 3-phenylnorbornadienes with conjugated substituents in 2- position (carbaldimine, carbaldoxime, amide, aroylvinyl and heterocyclic groups) have been synthesized. All the compounds obtained absorb in the 310-420 nm spectral region and under UV-Vis-irradiation form corresponding quadricyclanes with quantum yields in the range of 0.1-0.7. The back reaction proceeds almost quantitative yield under homogeneous and heterogeneous catalysis or on heating.

INTRODUCTION

Photoinduced isomerization of substituted bicyclo[2.2.1]hepta-2,5-dienes (norbornadienes) into corresponding tetracyclo[3.2.0.0.^{2,7}.0^{4,6}]heptanes (quadricyclanes) represents one of the most perspective abiotic systems of solar energy storage.[1-3] Unsubstituted norbornadiene has, however, well known drawbacks: 1) it does not absorb in the region where Sun light radiance achieves its maximum and 2) quantum yield of the photoisomerization is very small - 0.05. [4,5] In order to improve photochemical characteristics of the norbornadiene - quadricyclane system the absorption edge (λ_e <300 nm for norbornadiene) and quantum yield of the photoreaction must be increased.

The usual way for this consists in attachment to one or both double bonds of a norbornadiene molecule the substituents expanding the system of conjugated bonds. In the present work we report on the synthesis of a series of novel photochromic norbornadienes 1 in which their double bonds are conjugated to various electron releasing (D) and electron withdrawing (A) substituents.[6-12]

EXPERIMENTAL

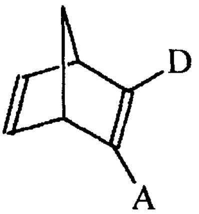
UV/ Vis absorption spectra were measured with a Specord M-40 spectrophotometer. IR spectra were recorded on a Specord IR-75 instrument. ^{1}H NMR spectra were recorded using Varian Unity 300 (300 MHz) spectrometer.

Irradiation of solutions of all the compounds was carried out by filtered light of a high-pressure mercury lamp DRSh (250 W) using a set of glass filters, Aberchrome 540 was used as an actinometer.

Compounds 2 - 6 were prepared by a procedure to that previously described.[6,7,9,10,12,13]

RESULTS AND DISCUSSION

Table1 contains the data on spectral and photochemical properties of the derivatives of norbornadiene:



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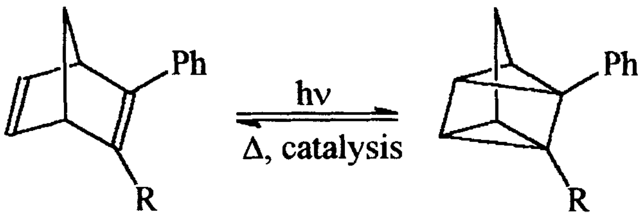


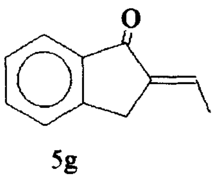
2-6 7-11

2 R= CH=NOR; R=H (a), CH_3 (b);

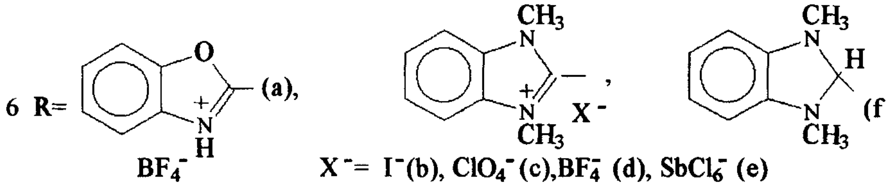
3 R= CONHAr; Ar=C_6H_5 (a), $C_6H_4CH_3$-p (b), $C_6H_4CH_3$-o (c), $C_6H_4OCH_3$-p(d), $C_6H_4COCH_3$-p (e), C_6H_4COOEt-p (f), $C_6H_4NO_2$-m (g), α-$C_{10}H_7$ (h), β-$C_{10}H_7$ (i)

4 R= CH=NAr; Ar=C_6H_5 (a), C_6H_4-n-C_4H_9-p (c) $C_6H_4OCH_3$-p (d), $C_6H_4OC_8H_{17}$-p (e), $C_6H_4N(CH_3)_2$-p (f), C_6H_4Cl-p (g), C_6H_4OH-p (h)

5 R= CH=CHCOAr; Ar=C_6H_5 (a), $C_6H_4CH_3$-p (b), C_6H_4Cl-p (c), C_6H_4Br-p (d), $C_6H_4NO_2$-m (e), C_6H_4-C_6H_5-p (f),



5g



X$^-$= I$^-$(b), ClO$_4^-$(c), BF$_4^-$ (d), SbCl$_6^-$ (e)

TABLE 1 Absorption spectra of norbornadienes and quantum yields of the (2-6) → (7-11) photoisomerization (2-propanol)

Comp.	λ_{max}(2-6), nm ($\varepsilon\cdot10^{-3}$)	λ_{edge} (2-6), nm	λ_{edge} (7-11), nm	$\Phi_{(2-6)\rightarrow(7-11)}$
2 a	310 (13.6)	360	310	0.19
b	313 (14.8)	370	330	0.16
3 a	280 (0.9)	375	295	0.53
b	285 (7.8)	380	295	0.46
c	280 (7.6)	380	295	0.49
d	290 (7.6)	400	310	0.15
e	295 (12.8)	380	370	-
f	310 (7.4)	380	310	0.71
g	305 (8.7)	390	300	0.66
h	295 (2.8)	380	-	-
i	300 (10.0)	380	320	0.22
4 a	343 (16.6)	425	350	0.15
b	350 (18.2)	455	390	-

d	365 (16.8)	440	360	0.12
e	363 (23.7)	465	360	-
f	405 (20.0)	525	-	-
g	350 (19.8)	450	-	-
h	362 (9.1)	455	325	-
5 a	377 (16.9)	470	415	0.10
b	375 (16.3)	470	410	0.12
c	380 (17.2)	475	420	0 .15
d	381 (17.1)	475	420	0.16
e	389 (15.5)	500	420	0.25
f	390 (18.9)	500	440	0.08
6 a	420 (18.5)	550	-	-
b	320 (9.6)	400	350	0.44
c	320 (10.8)	400	350	0 .42
d	320 (10.3)	410	365	0.45
e	318 (12.0)	400	360	0.41
f	310 (8.5)	380	340	0.02

3-Phenyl-2-phenylaminocarbonylnorbornadiene **3** and the oxime **2** absorb at the short waves. The oximes **2** form corresponding quadricyclanes **7** under UV- irradiation of their solutions. This back reaction proceeds spontaneously at room temperature in the absence of catalysts.

In the contrast to this, the quadricyclanes **8** obtained by photoisomerization of the amides **3** are very stable. The back reaction occurs only in the presense of heterogeneous catalysts (MoO_3) ($k_{20} = 5\ 10^{-3} - 10^{-3}\ c^{-1}$). The structure of the photoproducts was elucidated by means of UV and ^1H NMR spectral data. These compounds are characterized by absorption at λ_{max} 250 nm and λ_c 295 nm (Figure 1). ^{1}H NMR spectra contain resonance signals of only quadricyclane protons.

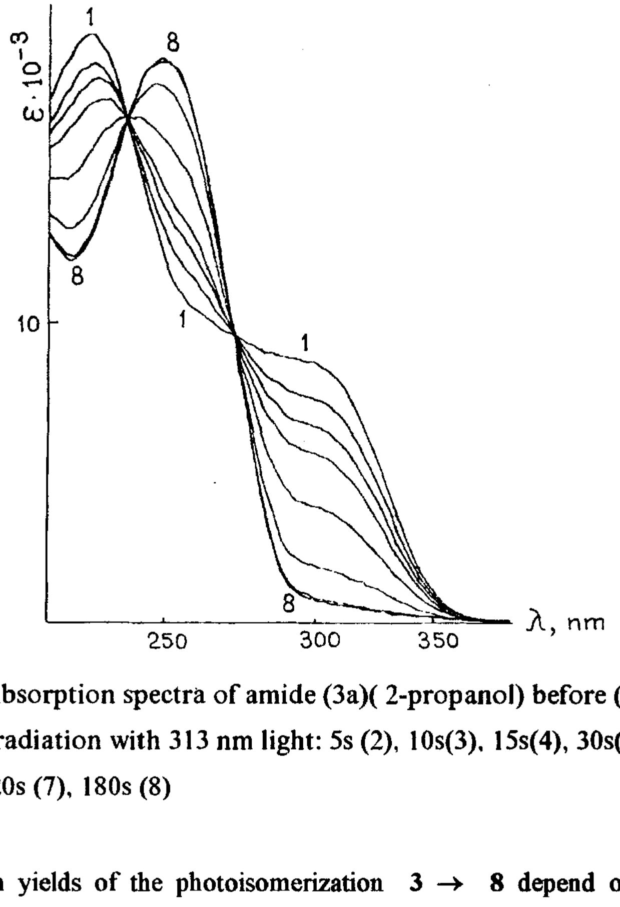


FIGURE 1 Absorption spectra of amide (3a)(2-propanol) before (1) and after irradiation with 313 nm light: 5s (2), 10s(3), 15s(4), 30s(5),60s(6), 120s (7), 180s (8)

Quantum yields of the photoisomerization **3 → 8** depend on the nature of substituents in the amide fragment of the norbornadiene. They increase for the compounds with electron withdrawing substituents and decrease for those containing electron releasing groups in the phenyl ring as compared with unsubstituted N-phenyl-3-phenylnorbornadiene-2-carboxamide 3a (Table 1). Lengthening of the conjugated chain in imines **4** results in essential increase in λ_{max} and λ_c values (Table 1). As for the amides **3**, - electron withdrawing substituents in the phenyl group increase the values of Φ and λ_{max}.

Of all the studied compounds, aroylvinilnorbornadienes **5** possess the most suitable spectral characteristics. At the same time for the unsubstituted 2-phenyl-3-(2-benzoylvinyl)norbornadiene 5a (λ_{max} 377 nm, λ_c 450 nm) the quantum efficiency of the photocyclization reaction rather low(Φ= 0.1). Substituents the in phenyl group of compounds 5 have a little influence on the position of λ_{max} (Table 1) but significantly affect the values of the quantum yields. Thus an electron releasing methyl substituent decreases Φ, whereas introduction of electron withdrawing substituents (Cl, Br, NO_2) increase Φ up to the value of 0.25. This phenomenon is associated with a mesomeric interaction between the electron releasing (Ph) and electron withdrawing (CH=CHCOAr) groups attached to the double bond of a norbornadiene.

To confirm this conclusion we synthesized and studied the compounds 6 bearing electron withdrawing heterocyclic cation groups in 2-position of norbornadiene. Benzoxazolyl derivative 6a possesing the strongest electron drawing substituent exhibits irreversible photoisomerization into quadricyclane 11a. Electron releasing NCH_3-Group in heterocyclic fragment (6b-e) makes this process reversible. The back reactions take place when heating the solutions: for the compound (6b) in acetonitrile solution
k_{70} 6 10^{-4} c^{-1}, $t_{1/2}$ ~ 20 min.

CONCLUSIONS

1. Novel norbornadienes containing chromophores improving spectral characteristics of unsubstituted norbornadiene (absorption edge and quantum yield) have been synthesized.
2. Corresponding quadricyclanes are readily formed under irradiation of solutions of 2,3-disubstituted norbornadienes. Quantum yields achieve the value of 0.6 - 0.7.
3. The back reaction is almost quantitative yields and proceeds under homogeneous (CF_3COOH) or heterogeneous (MoO_3) catalysis or on heating toluene solutions at 70 - 80°C ($t_{1/2}$ 20 -40 min).

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