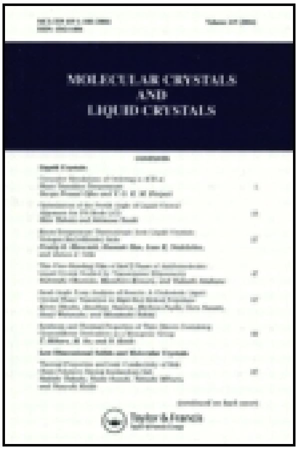

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Photochromic Behaviour of 2,3-Substituted Norbornadiehes

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PHOTOCHROMIC BEHAVIOUR OF 2,3-SUBSTITUTED NORBORNADIENES

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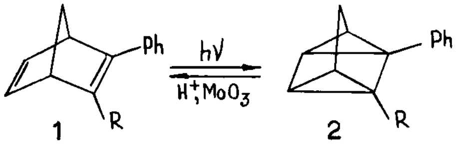
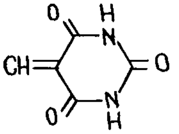
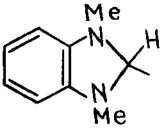
Abstract A series of novel 2,3-substituted norbornadienes has been prepared. Under UV- and Vis-irradiation in isopropanol and acetonitrile compounds undergo (2+2) valence isomerization into the corresponding quadricyclanes, the back interconversion being catalysed by CF_3COOH or MoO_3.

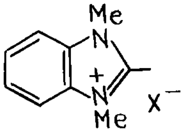
Norbornadiene-quadricyclane rearrangements represent the most promising molecular system for the solar energy storage[1-3]. Since unsubstituted norbornadiene does not absorption in the visible region of the Sun light spectrum appropriate substituents should be attached to the double bonds to sensitize the intramolecular cycloaddition reaction (1) to the Sun light. For this purpose some novel norbornadienes containong chromophores improving spectral characteristics of the $1 \rightleftharpoons 2$ photochromic system have been synthesized.



R = CHO (a), CH=NAr (b), CH=NNHAr (c), CONHAr (d), CH=CHCOAr (e), COCH=CHPh (f), $CH{=}C(CN)_2$ (g), CH=C(CN)COOEt (h), $CH{=}C(COOEt)_2$ (i),


(j),


(k),


(l)

Compound 1a was prepared by use of Diels-Alder reaction between cyclopentadiene and corresponding acetylene[4]. Norbornadienes 1b,c,e,g-l have been synthesized by coupling 1a with various compounds containing active methylene or amine groups[5]. Norbornadienes 1d,f were obtained from chloroanhydride of 3-phenylnorbornadiene-2-carboxylic acid and 3-phenyl-2-acetylnorbornadiene.

The long-wave absorption bands of norbornadienes 1 are batochromically shifted to 370-420 nm as compared to 230 nm (shoulder) in the absorption maximum of unsubstituted norbornadiene, the absorption edge (λ_e) of 1j being expanded to 520 nm.

TABLE 1 UV spectra in isopropanol and quantum yields of the photocycloaddition of norbornadienes 1.

Compound	λ_{max} of 1, nm ($\varepsilon \cdot 10^{-3}/mol^{-1}dm^{3}cm^{-1}$)	λ_e^a of 1, nm	Φ^b	λ_e^a of 2, nm
a	318 (9.6)	400	0.40	330
b(Ar=Ph)	343 (16.6)	425	0.15	350
c(Ar=Ph)	373 (30.6)	455	0.05	370
d(Ar=Ph)	280 (9.0)	375	0.53	295
e(Ar=Ph)	377 (16.9)	470	0.10	415
g	382 (21.5)	480	0.74	330
j	420 (5.0)	520	0.12	350

[a] Absorption edge (ε=0). [b] Aberchrome 540 was used as an actinometer.

Quadricyclanes 2 were readily formed (Fig.1) by irradiation of isopropanol or acetonitrile solutions of norbornadienes 1 with filtered light of high pressure lamp DRSH (250 W). Irradiation of the following wave-lengths has been applied: 313 nm for 1a,k,l, 365 nm for 1b-i and 436 nm for 1j. The structure of photochemically obtained products was elucidated by use of ^{1}H NMR spectral data.

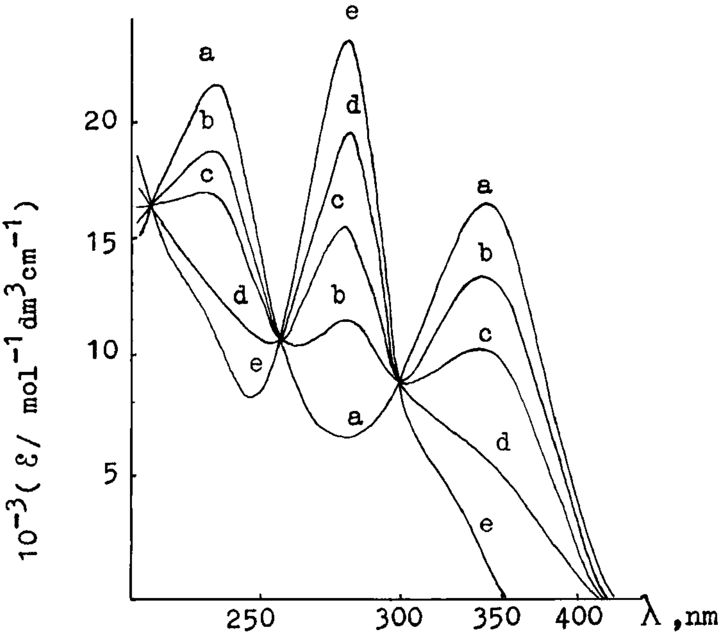


FIGURE 1 Electronic absorption spectra of compound 1b in isopropanol before (a) and after irradiation with 365 nm filtered light: 20 s (b), 40 s (c), 60 s (d), 120 s (e).

The reverse reaction of carbonylcontaining quadricyclanes 2 occurs almost instantaneously when trifluoroacetic acid is add to toluene solution of 2 at room temperature (10^{-3}mol/dm^3 of acid and $5 \cdot 10^{-5}$mol/dm^3 of 2). The heterogeneous catalyst MoO$_3$[6] can also be used (shaking of 2 ml of toluene $5 \cdot 10^{-5}$ mol/dm^3 solution with 0.2-0.5 mg of MoO$_3$ during 10-20 minutes). In the latter case the cycle $1 \rightleftharpoons 2$ can be repeated many times.

REFERENCES

1. V.A.Bren, A.D.Dubonosov, V.I.Minkin and V.A.Chernoivanov, Uspekhi Khimii (Rus.), 60, 913 (1991).
2. C.Kutal, Sci. Pap. Inst. Phys. Chem. Res. (Jpn.), 78, 186 (1984).

3. Z. Yoshida, J. Photochem., 29, 27(1985).
4. V.A.Chernoivanov, A.D.Dubonosov, V.I.Minkin and V.A.Bren Z. org. khimii (Rus.), 25, 443(1989).
5. V.A.Chernoivanov, A.D.Dubonosov, V.A.Bren, V.I.Minkin, S.V.Galichev and A.N.Suslov Z. org. khimii (Rus.), 28, 1647(1992).
6. K. Hirao, A. Yamashita and O. Yonemitsu Tetrahedron Lett., 29, 4109(1988).