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Norbornadiene–quadricyclane — an effective molecular system for the storage of solar energy

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ABSTRACT. The results of studies on intramolecular interconversions in systems of norbornadiene ⇄ quadricyclane and their derivatives are classified and discussed. The mechanisms of the forward photoreaction and reverse thermal process in relation to the nature of the substituents and carbocycles, type of sensitiser and catalyst, and properties of the medium are discussed in detail and classified. An analysis is made of the influence of these factors on the spectroscopic, kinetic, and thermodynamic properties of this system as an accumulator and converter of light energy. Methods of improving its chararacteristics — light absorption, the quantum yield of the photoreaction, and stability of the photoproduct — have been established.

The bibliography includes 188 references.

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I. Introduction

According to the calculation of specialists, with the most economical consumption of fuel, all of its forms used by man at the present time (coal, oil, natural gas, uranium) will be exhausted after 130 years.[1,2] This period is allotted to changing over to the use of alternative, ecologically clean energy sources — solar, wind, and oceanic energy.

The extent of utilisation of solar radiation is very considerable. Solar energy is used to operate high-temperature units that concentrate a stream of radiation by means of mirrors, where the accumulators of energy used are either physical heat-carriers or inorganic compounds that can undergo cyclic thermal decomposition–synthesis reactions (oxides, hydrates, sulphates, carbonates). Systems of a different type convert radiant energy into electrical, heat, or chemical reaction energy by means of photophysical or photochemical processes.[1,3,4]

At the present time the following methods of photochemical conversion of solar energy (SE) have been widely studied:

— the photocatalytic decomposition of water using metal-complex compounds as catalysts;[2,5]

— the development of "solar photoelectrolysers" based on photoelectron transfers, the photogalvanic effect, stabilisation of the products of photoelectron transfers in the electrical double layer at a phase boundary, etc.;[2,5–7]

— photosynthesis[2,7,8] — the most efficient biochemical method of storing solar energy.

A comparative analysis of the possibilities and prospects of these trends in the use of SE has been carried out in a number of monographs and reviews.[2,4,9–11] An aspect of the abiotic conversion of SE that has been less studied is its storage as strain energy in metastable photoisomers of organic compounds followed by its release in the form of heat energy.

In a number of review articles[12–16] devoted to a study of this aspect of solar energy conversion and an analysis has been carried out of the requirements to be met by a photochromic compound A, its photoform B, and the parameters of the process by which storage and conversion of solar energy occurs.

$$A \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} B + \Delta H. \qquad (1)$$

1. The initial compound A must absorb in the UV and visible region of the spectrum (from 400–600 nm) since more than 50% of the sun's light energy that reaches the earth is distributed over the region 300–700 nm (380–170 kJ per Einstein). The photoisomer B, on the other hand, should be colourless so as to avoid photoinitiation of the reverse reaction. Both components of reaction (1) should be nonluminescent compounds.

2. The energy level of the ground state of compound B formed in photoreaction (1) must lie sufficiently above the level of the ground state of A for the liberation of heat ΔH in the reverse reaction to be considerable (> 300 J g^{-1}), exceeding the heat stored in the solar warming ($\Delta T = 50$ °C) of water ($\Delta H = 209$ J g^{-1}), sand ($\Delta H = 42$ J g^{-1}) and salt hydrates ($\Delta H = 250$ J g^{-1}).

3. For prolonged conservation of energy stored by photoisomer B the activation barrier of the thermal transition B → A ($\Delta H^{\pm}$) must be sufficiently high — of the order of 85–105 kJ mol^{-1}.

4. The photochemical reaction A→B must have a high quantum yield, the transition B→A, which liberates stored energy, must be susceptible to catalytic acceleration or thermal initiation. High chemical yields and the absence of by-products are necessary for both processes.

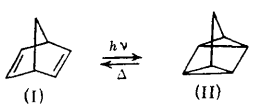
5. Compounds A and B must be sufficiently cheap, available, nontoxic, nonexplosive, incombustible, and chemically stable towards air and atmospheric moisture.

Some of these requirements can be expressed quantitatively in the form of Eqn. (2), which reflects the efficiency of a system that is capable of storing and converting SE.[17–19]

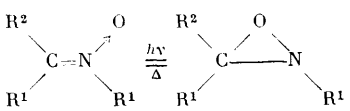
$$\eta_e = \frac{\Delta H \Phi}{E_{h\nu}} \cdot \frac{\int_0^{\lambda_{lim}} I_\lambda (\lambda/\lambda_{lim}) d\lambda}{\int_0^{\infty} I_\lambda d\lambda} \eta_{abs} 100, \quad (2)$$

where η_e is the efficiency of the photochrome; ΔH is the difference in enthalpy between the initial compound A and its photoform B; Φ is the quantum yield of photoreaction (1); $E_{h\nu}$ is the energy of the photons (per Einstein) of absorbed light (for λ_{max} of compound A); λ_{lim} is the long-wavelength limit of absorption of compound A; I_λ is the distribution of power of solar radiation by wavelength; η_{abs} is the coefficient of absorption (ratio of the number of photons absorbed by compound A to the total number of photons in the solar spectrum with $\lambda \leqslant \lambda_{lim}$. For a more precise determination of the efficiency of photochromes as SE accumulators it is necessary to take into account the energy capacity of the material W, i.e., the quantity of energy stored per gram of initial compound and the number of working cycles [reaction (1)] without appreciable decomposition of the compound. Quite a wide range of photochromic organic compounds have been studied up to the present time. Amongst the most important reactions of A ⇄ B are the following:

1) valence isomerisation, for example, that of norbornadiene–quadricyclane (3)[20] or nitrone–oxaziridine (4) systems:[21]



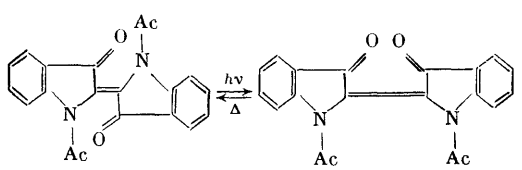
(I) (II) (3)



(III) (IV) (4)

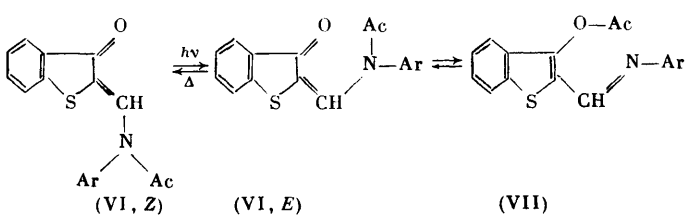
R¹, R² = H, Alk, Ar.

2) geometric (*Z*) ⇄ (*E*) isomerisation, for example, that of indigo derivatives:[22,23]



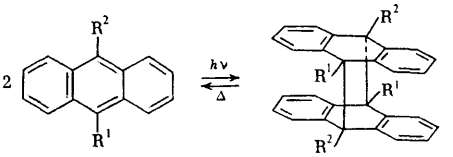
(V, *E*) (V, *Z*)

3) geometric isomerisation followed by intramolecular rearrangement, as in the case of *N*-acylated aminovinyl ketones of the type (VI):[24]



(VI, *Z*) (VI, *E*) (VII)

4) thermally reversible photodimerisation reactions, for example, those of anthracene derivatives:[19]



(VIII) (IX)

R¹, R² = H, Alk.

A summary of the results concerning these and other systems acting as accumulators of light energy appears in a monograph.[25] Table 1 indicates the parameters of some of the most efficient photochromic systems from which it is possible to determine whether they satisfy the requirements imposed on photochemical accumulators of SE.

Cyclic photodecomposition–thermal recombination reactions are also characteristic of certain inorganic systems that can also store light energy. The reaction of nitrosyl chloride can serve as an example:

$$NOCl \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} NO + {}^1/_2Cl_2.$$

Although nitrosyl chloride has optimal spectroscopic data (λ_{lim} = 600 nm) and the quantum yield Φ of the photoreaction is close to unity, it is necessary to separate the photoproducts NO and Cl_2 to prevent too rapid a reverse reaction occuring in parallel with the forward process.

The main advantage of organic photochromes over inorganic ones is the possibility of extensive variation of their molecular structure in order to improve their properties as accumulators and converters of SE, namely: increasing the long-wavelength limit λ_{lim} of the absorption spectrum, increasing the quantum yield Φ of the photoreaction A → B, increasing the exothermicity ΔH of the dark reaction, and the choice of an effective catalyst for the reaction B → A, which causes the liberation of heat.

Intensive investigations in recent years have shown that the most promising development in optimising all of the required parameters is the modification of systems that are characterised by photoinitiated valence isomerisation involving ($2\pi + 2\pi$) cycloaddition, primarily in relation to the readily available norbornadiene derivatives (I). Thus, the main advantage of the norbornadiene–quadricyclane system is the very high exothermicity of the thermally forbidden ($2\sigma + 2\sigma$)-cyclodecomposition of quadricyclane (II) (-110 kJ mol^{-1})[26] (see Table 1). The aim of the present review is to analyse the main approaches to improving the characteristics of this system and to bring them into possibly closer correspondence with the above-mentioned requirements.

II. Optimisation of the spectroscopic properties of the system norbornadiene–quadricyclane

The valence isomerisation of norbornadiene to quadricyclane (3) was first studied by Hammond et al.[20,27] The storage of energy in this photoreaction occurs through the formation of the metastable quadricyclane structure (II), which contains the highly strained cyclobutane and two cyclopropane rings. The following advantages of this photochromic system may be noted: 1) the forward reaction

Table 1. Parameters of certain photochromic systems that can store solar energy.

System	λ_{lim}, nm	Φ	ΔH, kJ mol^{-1}	Q, %	η_A	η_e, %	W, mW g^{-1}	Properties of form B	
								Thermal stability*	Photostability (Φ_{irr})
(I) ⇄ (II) (CuCl sensitiser) CuCl)	388	0.4	110(1200)	14	0.015	0.21	1.75	14 h (140 °C)	~0
(V, *E*) ⇄ (V, *Z*)	610	0.2	34(109)	3.5	0.27	0.95	300	200 s (25 °C)	0.1
(VI) ⇄ (VII) (Ar = Ph)	460	0.6	23(79)	6.2	0.09	0.56	230	20–30 days (25 °C)	0
Photosynthesis	700	0.1	467	26	0.36	8 **			

* Thermal stability — period of half-decomposition for the reaction $B \xrightarrow{\Delta} A$ at the temperature indicated.
** Theoretical value of efficiency; in real systems η_E approximately equals 0.1–0.3%.

can be sensitised and there are effective catalysts for the reverse reaction; 2) the reverse reaction has a high activation barrier (half-decomposition time of (II) is equal to 14 h at 140 °C);[27] 3) the starting products for the synthesis of norbornadiene (I) and its derivatives are amongst those produced by large-scale synthesis; 4) both forms (I) and (II) are liquids, which provides a number of production benefits.

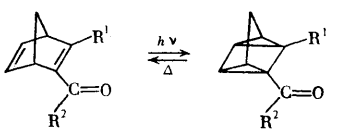
However, there are also considerable disadvantages in system (3). Thus, photochrome (I) has an absorption at too short a wavelength (about 300 nm),[28] in the absence of a sensitiser the quantum yield of the photoreaction is very small, and chemical modification of the structure of norbornadiene often results in irreversible secondary photoreactions.

Thus, in order to improve the properties of the photoconversion of norbornadiene–quadricyclane it is necessary, first of all, to shift the long-wavelength limit of absorption of norbornadiene to longer wavelength in the spectrum [improve λ_{lim} in Eqn. (2)] and at the same time increase the quantum yield of Φ of the photoisomerisation of (I) → (II).

In order to resolve this problem substituents with various chromophoric groups are introduced into the norbornadiene molecule. Three possible ways of "colouring" norbornadiene are known: 1) the introduction of electron-withdrawing substituents or an electron-donating and electron-withdrawing substituent into one of the double bonds of norbornadiene; 2) the introduction of electron-donating and electron-withdrawing substituents into the different double bonds of norbornadiene, resulting in the appearance of a charge-transfer band; 3) the formation of charge-transfer complexes of norbornadiene with transition metal compounds.

1. Norbornadienes containing substituents on one of its C=C double bonds

For the majority of known norbornadiene with simple electron-withdrawing groups (COOH, COOMe, CN, etc.) at the 2- and 3-positions, λ_{lim} does not exceed 365 nm.[29–35] 2-Aroyl-3-aryl-norbornadienes (X),[36] in which charge transfer occurs from the aryl group to the aroyl group thus increasing the efficiency of the photo-reaction for formation of quadricyclanes (XI), absorb at longer wavelength.

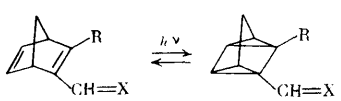


(X) (XI)

R¹, R² = Ar. (5)

Compounds (X) have λ_{max} = 320–370 nm (Table 2), which corresponds to λ_{lim} = 400 nm, while for the norbornadiene (X, *f*), λ_{lim} = 450 nm. Irradiation of norbornadienes (X) with light of wavelength 350 nm yields the corresponding quadricyclanes with high quantum yields (Φ = 0.3–0.6). Electron-donating groups in the aroyl residue assist both an increase in λ_{max} and the quantum yield Φ, while a nitro group, although increasing λ_{max}, sharply reduces the efficiency of photoisomerisation.

3-Phenylnorbornadiene-2-carbaldehyde and its imines (XII) have spectroscopic properties which are similar to compounds (X).[37]



(XII) (XIII)

R = Ar; X = O, NAr. (6)

The absorption maxima of (XII) are grouped in the region of 310–370 nm, the limit of the long-wavelength band reaching 420 nm (Table 2). However, in contrast to norbornadienes (X), the nature of the photoreaction of imines (XII) is determined by the type of solvent; in nonpolar aprotic solvents only isomerisation on the C=N bond occurs, while in proton-donating solvents quadricyclanes (XIII) are formed.

Table 2. Spectroscopic properties of norbornadienes and quantum yields of photoreactions (5)–(11).

Compound (X)	R¹	R²	λ_{max}, nm in MeCN	log ε	λ_{lim}, nm (ε=0)	λ_{irr}, nm	Φ
a	Ph	Ph	325	3.62	~400	350	0.30
b	C_6H_4Me-*p*	Ph	332	3.69		350	0.44
c	C_6H_4OMe-*p*	Ph	348	3.72		350	0.60
d	C_6H_4Cl-*p*	Ph	323	3.69		350	0.36
e	$C_6H_4NO_2$-*p*	Ph	341	4.00		350	0.09
f	C_6H_4OMe-*p*	$C_6H_4NO_2$-*p*	370	3.65	450	366	0.07
g	Ph	β-naphthyl	330	3.73	~400	350	0.32
h	C_6H_4OMe-*p*	C_6H_4Cl-*p*	353	3.74		366	0.50
i	$C_6H_3(OMe)_2$-3,4	C_6H_4Cl-*p*	364	3.73		366	0.41
j	OMe	C_6H_4Br-*p*	353	3.75		366	0.52
k	Me	C_6H_4Br-*p*	337	3.69		366	0.40

Compound (XII)	R	X	λ_{max}, nm in 2-propanol	log ε	λ_{lim}, nm (ε=0)	λ_{irr}, nm	Φ
a	Ph	O	318	4.1	400	313	0.4
b	Ph	NPh	343	4.1	430	365	0.15
c	Ph	NC_6H_4OMe-*p*	365	4.2	440	365	0.1

Compound (XIV)	R¹	R²	λ_{max}, nm in CH_2Cl_2	log ε	λ_{lim}, nm	ε	Φ (λ_{irr}=405 nm)
a	H	H	337	3.44	460	34	0.21
b	Me	H	342	3.50	460	42	0.21
c	Me	Me	345	3.55	460	52	0.22
d	OMe	H	410	3.03	460	480	0.22

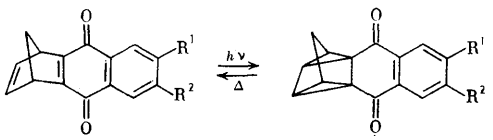
Compound (XVI)	R¹	R²	λ_{max}, nm in aqueous Na_2CO_3 solution	log ε	λ_{lim}, nm (ε=0)	Φ (λ_{irr}=313 nm)
a	H	H	290	3.11	365	0.59
b	Me	H	285	3.30	365	0.52
c	CH_2Ph	H	280	3.49	370	0.59
d	C_4H_9-*t*	H	280	3.40	370	0.54
e	Me	Me	275	3.11	335	0.45
f	$-(CH_2)_4-$		270	3.20	340	0.50
g	Ph	H	307	3.88	430	0.09
h	Ph	Me	270	3.42	360	0.31
i	$-C_6H_4-(CH_2)_2-$		292	3.86	415	0
j	Ph	Ph	270	3.74	405	0
k	CH_2COOH	H	285	3.34	365	0.57

Compound (XX)	λ_{max}, nm in ethanol	log ε	λ_{lim}, nm (ε=0)	Φ (λ_{irr}=334 nm)
a	315	3.83	~380	0.72
b	306	3.92		0.78
c	316	3.93		0.79

Compound (XXII)	λ_{max}, nm (in MeCN)	log ε	λ_{lim}, nm (ε=0)
a	364	3.80	~470
b	314	3.79	~400
c	328	3.64	

Compound (XXV)	R¹	R²	λ_{max}, nm in CH_2Cl_2	log ε	λ_{lim}, nm (ε=0)	Φ (λ_{irr}=546 nm)
a	H	H	495	4.29	580	0.5
b	Me	H	480	4.11	570	0.1
c	Me	Me	470	3.94	550	<0.01

Norbornadienes containing benzo- or naphtho-quinone residues [for example, (XIV)] absorb in the region of 340–410 nm (Table 2) and they have λ_{lim} = ~460 nm.[38,39] Methyl or methoxyl substituents in the quinone part of the molecule displace λ_{lim} to longer wavelengths with a constant quantum yield.

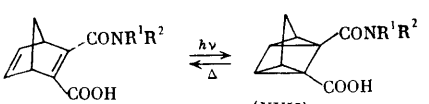


(XIV) (XV) (7)

R¹, R² = H, Me, OMe.

Irradiation of (XIV) with light with λ > 410 nm yields photoproducts (XV) in almost quantitative yield (Φ ~ 0.2). We should note that in earlier studies[40,41] the formation of quadricyclanes was not established.

Carbonyl substituents displace λ_{lim} appreciably to longer wavelengths.[41–45] The presence of carbamoyl and carboxyl groups at the 2- and 3- positions of the norbornadiene molecule makes it possible to carry out the photoisomerisation of (XVI) → (XVII) not only in organic solvents but also in weakly alkaline aqueous solutions.



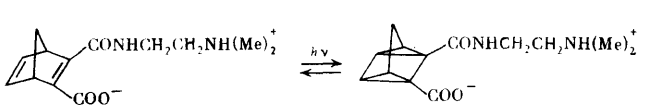
(XVI) (XVII) (8)

R¹, R² = H, Alk, Ar.

In the electronic spectra of compound (XVI) absorption bands occur at 280–340 nm (see Table 2) λ_{lim} ≈ 370–400 nm, while for norbornadiene (XVI, *i*), λ_{lim} = 430 nm. *N*-Alkylamides absorb at longer wavelength than *N,N*-dialkylamides, although they, in turn, are inferior to *N*-arylamides in this respect.

On irradiation of compounds (XVI) in aqueous Na_2CO_3 solutions, quadricyclanes (XVII) are formed with quantum yields of 0.1–0.6. By studying system (XVI) it is possible to establish an important principle of the photochemical behaviour of norbornadienes of this type, namely, displacement of λ_{lim} to longer wavelength in the spectrum results in a decrease in quantum yield Φ of photocyclisation.[45]

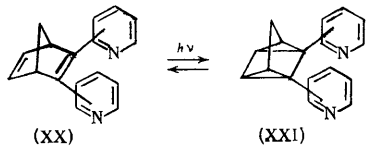
Further modification of carbamoyl-substituted norbornadienes led to the preparation of the first compound that was soluble in water.[46] For the bipolar ion (XVIII), λ_{lim} = 370 nm, but there was no information about the quantum yield of (XIX).[46]



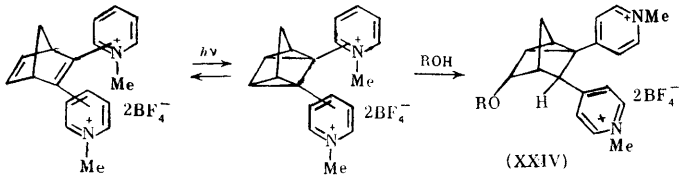
(XVIII) (XIX)

Norbornadienes containing heterocycles or heterocyclic cations as substituents are described in three studies.[47–49] The long-wavelength absorption of dipyridylnorbornadienes (XX) [47,48] reaches λ_{lim} ≈ 380 nm and irradiation with light of wavelength 334 nm results in

the formation of quadricyclanes (XXI) with high quantum yields (0.7–0.8).



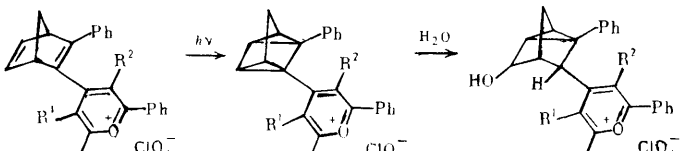
(9)



(10)

Quaternary salts of dipyridylnorbornadienes (XXII) have a considerably longer wavelength absorption up to $\lambda_{lim} \sim 470$ nm (see Table 2). However, when they are irradiated with light with $\lambda = 350$ nm, a photostationary state is established between the initial compounds and the photoreaction products in the ratio 12:88 (XXII, *b*) and 30:70 (XXII, *c*), which is apparently due to an absorption in the region of 350 nm that is present in the resulting quadricyclanes. In the presence of traces of water and methanol, norbornadiene (XXII *a*) under these conditions forms the adduct (XXIV).

Record values of λ_{lim} (from 550 to 580 nm) occur in norbornadienes (XXV) containing pyrylium cations at the 2-position[49] (see Table 2). Photoconversion of (XXV) to the corresponding quadricyclanes occurs rapidly and effectively even in diffuse light, but the reaction is very sensitive to traces of moisture, so the final products are adducts (XXVII).

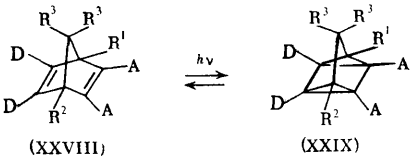


(11)

2. Norbornadienes with electron-donating and electron-withdrawing substituents on the different double bonds

The theoretical possibility of increasing λ_{lim} in a norbornadiene through a charge-transfer band that occurs by interaction of the electron-donating and electron-withdrawing substituents on the different double bonds was substantiated in two studies.[50,51] The geometric strain in the norbornadiene molecule leads to an interaction of the π-orbitals of the double bonds in the molecule through space, resulting in a considerable convergence of the energy levels of the frontier molecular orbitals.[52,53] This manifests itself spectroscopically in unsubstituted norbornadiene absorbing at longer wavelength than does a compound with two isolated C=C bonds.[28] The presence of electron-donating substituents on one of the two double bonds of norbornadiene and electron-withdrawing substituents on the other causes a further bathochromic shift of the long-wavelength absorption band.

Depending on the nature of the substituents D and A in (XXVIII) molecules, λ_{lim} can vary from 345 to 558 nm (Table 3), and the quantum yield of compounds (XXIX) remains high (0.26–0.96)



D = H, Me, Ar; A = CN, COOMe, CONHPh; R^1, R^2, R^3 = H, Me.

A bathochromic shift of the long-wavelength absorption band of norbornadienes (XXVIII) occurs[51,54,55] when the electron-donating and electron-withdrawing capacities of substituents D and A are increased [cf. compounds (XXVIII, *b*) and (XXVIII, *c*); (XXVIII, *d*) and (XXVIII, *f*); (XXVIII, *j*) and (XXVIII, *k*) in Table 3]. The most important characteristic of compounds (XXVIII) is that, in contrast to norbornadienes containing substituents on one of the double bonds, the increase in λ_{lim} is in many cases not accompanied by any significant decrease in quantum yield of the photoreaction (XVIII) → (XXIX). Quadricyclanes (XXIX) are formed quantitatively even in the presence of oxygen in solution. In the opinion of Hirao et al.,[54] norbornadiene (XXVIII, *k*), for which $\lambda_{lim} = 558$ nm, $\Phi = 0.75$, is the most suitable for storage of SE.

Table 3. Spectroscopic properties of donor-acceptor norbornadienes and quantum yields of the photoreaction (XXVIII) $\overset{h\nu}{\rightleftarrows}$ (XXIX).

Compound (XXVIII)	D	A	R^1	R^2	R^3	λ_{lim}, nm (in benzene)	Φ (λ_{irr} = 383 nm)
a	H	CN	H	H	H	345 *	0.59 **
b	Me	CN	Me	H	H	430 *	0.96 **
c	Ph	CN	H	H	Me	494 *	0.95 **
d	Me	CO_2Me	H	H	Me	441	0.66
e	Me, Ph	CO_2Me	H	H	Me	474	0.71
f	Me, C_6H_4OMe-*p*	CO_2Me	H	H	Me	526	0.26
g	C_6H_4OMe-*p*	CO_2Me	H	H	Me	554	0.08
h	Me, C_6H_4OMe-*p*	CONHPh	H	H	Me	528	0.28
i	C_6H_4OMe-*p*	CONHPh	H	H	Me	559	0.05
j	Ph	CO_2Me	Me	Me	H	487	0.56
k	Ph	COEt, CO_2Me	Me	Me	H	558	0.75

* in MeCN; ** $\lambda_{irr} = 313$ nm.

Photoconversions of the system (XXVIII) ⇄ (XXIX) can be carried out in poly(methyl methacrylate) films,[55] the magnitude of λ_{lim} and Φ remaining virtually unchanged, and the number of working cycles of (XXVIII) ⇄ (XXIX) without a change in extinction of the initial compound is 10^3. According to the results of Miki et al.,[65] with the same number of cycles the losses of working compound in solution can amount to 20%.

In order to increase the thermal stability of the quadricyclane structures, Hirao and Yamashita[56] proposed the introduction of stabilising acceptor groups (A = CF_3, CF_2Et, CHFEt) into the initial norbornadienes. However, the details of conducting the photoreaction have not been reported.

3. Complexes of norbornadiene with transition metal salts

A further method of increasing λ_{lim} is to use complexes of norbornadiene with different transition metals instead of the unsubstituted compound (I). In this case a new band appears in the electronic spectra of the resulting compounds at a longer wavelength than the absorption compound (I).[15] However, an efficient photoconversion of such systems to quadricyclane (II) only occurs for complexes of norbornadiene with univalent copper salts. The mechanism of such reactions is examined in Section III. We should merely note that λ_{lim} for complexes of norbornadiene with CuX (X = Cl, Br, I, OAc) is no greater than 360 nm. The main disadvantage of this method of inceasing λ_{lim} is the tendency of Cu(I) salts to undergo mild oxidation to bivalent copper salts, which no longer form complexes with norbornadiene.

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By comparing the above approaches to increasing λ_{lim}, the following conclusions can be drawn. The use of norbornadiene complexes with Cu(I) salts displaces λ_{lim} to 360 nm with a satisfactory quantum yield. The main problems of this method are the high sensitivity of the complexes of atmospheric moisture and the lack of scope for varying the structure.

In the case of norbornadienes that contain substituents on one of the two double bonds, λ_{lim} is shifted into the visible region as far as 400–470 nm (even to 580 nm in some cases). The main disadvantage of this method is the sharp decrease in quantum yield Φ of the photoreaction with an increase in λ_{lim}.

By using norbornadienes with electron-donating and electron-withdrawing substituents on the different double bonds it is possible to shift λ_{lim} to even longer wavelength (500–600 nm), and in this case it is possible at the same time to achieve high values of both λ_{lim} and Φ. This approach would appear to have the greatest potential, although, as before, there remain three disadvantages that are difficult to overcome: 1) the reduction in quantity of stored energy per gram of substance because of the increase in molecular weight of the substituted norbornadiene; 2) the relative complexity of the synthesis of such compounds; and 3) their high cost.

III. Methods of increasing the quantum yield of photoisomerisation of norbornadiene to quadricyclane

The photoconversion of unsubstituted norbornadiene to quadricyclane is characterised by quite a low quantum yield (Φ = 0.05),[28,55] but it can be increased substantially with the use of sensitisers. The following methods of sensitisation have been used: 1) formation of complexes between transition metal compounds and norbornadiene that are stable in the electronic ground state; and 2) interaction of a sensitiser (S) in an electronically excited state with norbornadiene (I), resulting in energy transfer and the formation of charge-transfer complexes or the addition-elimination of sensitiser.

In the first case the stable complex that is initially obtained undergoes photoexcitation

$$S + (I) \rightarrow [S\cdots(I)] \xrightarrow{h\nu} S + (II). \qquad (12)$$

The following requirements should be met by the transition metal compound S used as sensitiser:[57]

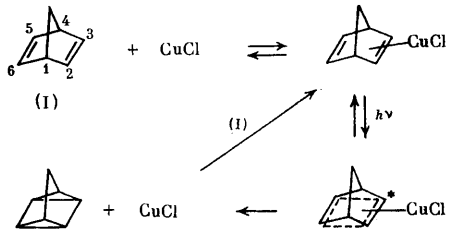
1) The transition metal in compound S must be in a low oxidation state and coordinated with a single norbornadiene molecule (the coordination of S with two norbornadiene molecules assists its dimerisation):

2) the [S···(I)] complex must absorb in the visible region:

3) S must not catalyse the reverse reaction (II) → (I);

4) S must not participate in secondary photochemical reactions.

Despite the fact that many transition metals are capable of forming complexes with norbornadiene,[15] only univalent copper compounds satisfy these requirements to a sufficient degree.[58–62] The photoisomerisation mechanism has been studied in the greatest detail in the case of the complex between norbornadiene and CuCl:



(13)

The initial components—norbornadiene (I) and CuCl—do not absorb in the region >300 nm, whereas the complex formed by them has an intense charge-transfer band with λ_{lim} = 350 nm. Photoexcitation of this complex by light with wavelength 313 nm results in the formation of quadricyclane as the sole product (Φ = 0.2–0.4, depending on the solvent). It is assumed that photoexcitation in the charge-transfer band of the [(I)...CuCl] complex causes the bonds between the C_2-C_3 and C_5-C_6 atoms in norbornadiene to become weaker and the bonds between the C_2-C_6 and C_3-C_5 atoms to become stronger. Subsequent relaxation of the excited state gives either norbornadiene again or quadricyclane. The latter does not form complexes with Cu(I) salts, so catalytic quantities of CuCl are sufficient for conversion of all of the norbornadiene to quadricyclane. The formation of quadricyclane when CuBr, CuI, CuOCOMe,[61,62] and also certain complex Cu(I) compounds are used occurs by a similar mechanism.[63,64] The quantum yields of the photoconversion (I) → (II) on irradiation of complexes of norbornadiene with $CuBr(Py)(PPh_3)$ and $Cu[HB(Pz)_3]$ (Py = pyridine, Pz = 1-pyrazolyl) with light at λ = 313 nm are 0.1–0.2 (in benzene) and (0.37–0.65) (in hexane) respectively, and $\lambda_{lim} \approx$ 370 nm.

The second possible way of sensitising the reaction (I) → (II) is by interaction of a sensitiser S with norbornadiene according to the mechanism

$$S + (I) \xrightarrow{h\nu} {}^*S + (I) \rightarrow S + (II). \qquad (14)$$

In the opinion of Juris et al.[57] this type of sensitiser must satisfy the following requirements: 1) not form complexes with norbornadiene in the ground state; 2) absorb in the visible region, with the lifetime of the excited state *S being sufficiently long for the bimolecular reaction (14) to occur; 3) not catalyse the reverse reaction (II) → (I); 4) not participate in secondary photochemical reactions. The latter two requirements match those represented in scheme (12).

Since the conversion of norbornadiene to quadricyclane occurs in a triplet state,[65,66] the greatest efficiency of photoreaction (I) → (II) is to be expected with triplet sensitisation, which consists of the following stages:[67]

$$S \xrightarrow{h\nu} {}^1S \rightarrow {}^3S + (I) \rightarrow S + {}^3(I) \rightarrow (II). \qquad (15)$$

At the first stage the sensitiser S undergoes photoexcitation to a

singlet state, at the second stage the intersystem crossing $^1S \rightarrow {}^3S$ occurs, at the third stage there is a triplet transfer of energy from ^3S to (I), and finally at the fourth stage (II) is formed from triplet-excited (I).

Such a transfer of energy is only favourable for sensitisers with a triplet state energy higher than in norbornadiene (i.e., $E_T > 293$ kJ). However, in this case, as can be seen from Fig. 1,[15] even a small value of the singlet-triplet splitting of such systems will correspond to $\lambda_{lim} \leqslant 400$ nm. The condition $E_T > 293$ kJ is met by a relatively small number of sensitisers,[20,27,68–72] the range of these being mainly limited to carbonyl compounds (Table 4). As expected, the highest values of Φ were found for acetophenone ($E_T = 309.6$ kJ, $\Phi = 0.91$) and benzophenone ($E_T = 289.5$ kJ, $\Phi = 0.45$,[66], 0.8 [69]), with λ_{lim} equal to 366 and 380 nm respectively.

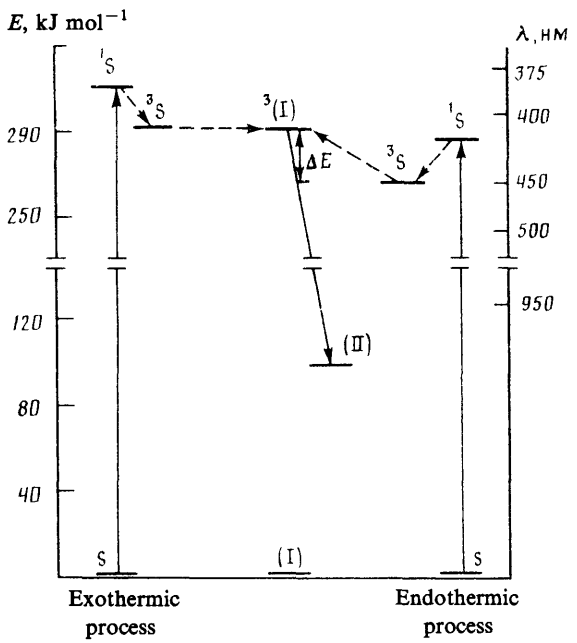
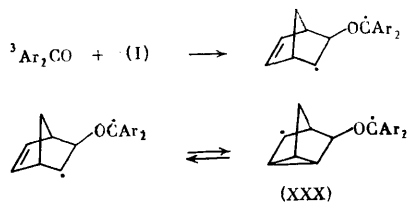


Figure 1. Energy levels of norbornadiene (I) and sensitiser (S).

For sensitisers with $E_T < 293$ kJ the transfer of energy from ^3S to norbornadiene is unfavourable (endothermic process in Fig. 1); nevertheless, efficiency sensitisation of reaction (I) → (II) even occurs in this case, which is due either to the formation of a [*S- - -(I)] complex in an excited state[15] or to the formation of covalent bonds between *S and (I).[73,74] Strong arguments in favour of the latter mechanism have only been established for substituted benzophenones. In fact, in a number of cases the value of Φ is not wholly determined by the magnitude of E_T (Table 4). With similar values of E_T the quantum yield is higher for benzophenones with electron-donating groups (compared to unsubstituted benzophenone) and less for benzophenones with electron-withdrawing groups. Arai et al.[74] conclude from kinetic data that in this case the following process competes with the energy transfer mechanism:



(16)

$$(XXX) \rightarrow (II) + Ar_2CO,$$
$$(XXX) \rightarrow (I) + Ar_2CO.$$

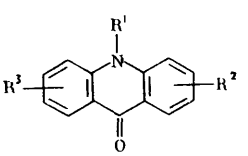
Table 4. Quantum yields of the sensitised photoreaction (I) ⇄ (II).

Sensitiser	E_T, kJ mol^{-1}	λ_{irr}, nm	$\Phi_{(I)\rightarrow(II)}$ (in CH_3CN)
Acetophenone	309.6	313	0.91
4,4'-Dimethoxybenzophenone	294.1	360	0.56
4,4'-Dimethylbenzophenone	290.0	360	0.59
4-Methylbenzophenone	289.5	360	0.50
Benzophenone	289.5	360	0.45
3-Benzoylpyridine	288.7	360	0.36
4-Methoxybenzophenone	288.7	360	0.53
4-Chlorobenzophenone	287.9	360	0.29
4,4'-Dichlorobenzophenone	286.2	360	0.29
4-Hydroxybenzophenone	285.8	360	0.42
2-Benzoylpyridine	282.0	360	0.35
4-Benzoylpyridine	281.2	360	0.40
4-Cyanobenzophenone	280.3	360	0.33
Triphenylene	278.2	360	0.02
Michler's ketone	259.4	360	0.04
4-Phenylbenzophenone	254.0	360	0.23
2-Naphthaldehyde	251.0	313	0.06
2-Acetonaphthone	246.9	313	0.05
Substituted acridinones			
(XXXI, a)	250	366	0.4 *
(XXXI, b)	260	366	0.75 *
(XXXI, c)	260	366	0.5 **
(XXXI, d)	239	366	0.7 ***
(XXXI, e)	240	366	0.4 *

*in DMF; **in toluene; ***in 1,4-dioxan.

However, the most common mechanism of sensitisation is the formation of [*S- - -(I)] complexes between the sensitiser (with $E_T < 293$ kJ) in an excited state and norbornadiene.[15,63]

The substituted acridunones (XXXI) acting by this type of mechanism absorb at longer wavelengths (λ_{lim} = 360–420 nm) than benzophenone[75] and have $\Phi(I)\rightarrow(II) = 0.4–0.7$ (see Table 4).



(XXXI)

a) R^1 = Me, R^2 = 3-NMe_2, R^3 = 6-NMe_2;
b) R^1 = Me, $R^2 = R^3$ = H;
c) R^1 = H, R^2 = 2-Br, R^3 = 7-Br;
d) R^1 = Me, R^2 = 2-Br, R^3 = 7-Br;
e) $R^1 = R^3$ = H, R^2 = 3,4-C_6H_4.

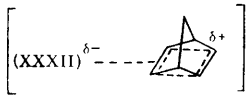
A general disadvantage of using carbonyl-containing compounds for sensitisation of the reaction (I) → (II) is the formation of products obtained by their photoaddition to norbornadiene or quadricyclane.[75–79] Moreover, they promote the polymerisation of norbornadiene, although this can be avoided by adding certain phenols such as 2,6-di-t-butyl-*p*-cresol to the solution.[70,72]

There are also reports on complex compounds of univalent copper that do not form complexes with norbornadiene in the ground state but effectively sensitise the reaction (I) → (II) [80,81] presumably by an endothermic route (Fig. 1) through the thermally activated transfer of energy from S to (I).[15,82] The value of λ_{lim} for $Cu[PPh_2Me]_3BH_4$, $Cu[PPh_3]_2BH_4$, Cu(prophos)BH_4 [prophos = 1,3-bis(diphenylphosphino)propane] is about 330 nm, while the Φ values in benzene at λ_{irr} = 313 nm are equal to 0.56, 0.76, and 0.88 respectively.

By incorporating groups that provide chromaticity into the molecule of the sensitiser Ph_3PCuXL (X = Cl, Br; L = 2,2′-dipyridyl, *o*-phenanthroline, phthalazine, pyridine) it is possible to conduct the reaction (I) → (II) on exposure to light of wavelength 313 nm and 366 nm.[41,83] The quantum yields in ethanol and THF constitute 0.03–0.13 (λ_{irr} = 313 nm) and 0.008–0.011 (λ_{irr} = 366 nm). The use of the compounds $[Cu(PPh_3)_2(dpk)]NO_3$, $[Cu_2I_2(PPh_3)_2(dpk)]$, and $Cu_4I_4(dpk)_3$] (dpk = di-2-pyridyl ketone)[84] as sensitisers results in λ_{lim} being shifted to 500–600 nm and with quantum yields in dichloromethane equal to 0.17, 0.25, and 0.36 respectively (λ_{irr} > 320 nm).

Certain sensitisers can form complexes with norbornadiene in both the ground state and an excited state.[85,86] On irradiation of norbornadiene with light with λ_{irr} > 270 nm in the presence of $Cu_2Br_2(AsPh_3)_3$ and $[CuCl(AsPh_3)]_4$, the quantum yield of the reaction in chloroform is 0.17 and 0.45 respectively, and the limiting value of Φ = 0.75 is reached with high concentrations of norbornadiene.[85] Sensitisation with the complexes $(Ph_2PCH_2CH_2.PPh_2)CuCl$, $(Ph_3P)_3CuX$ and $(MePh_2P)_3CuX$ (X = Cl, Br, I) makes it possible to reach the maximum quantum yield of $\Phi_{(I)\rightarrow(II)}$ = 1.0 in concentrated solution,[86] but dilution sharply reduces the quantum yield.

In a number of studies[57,62,87–89] there are reports on sensitisers containing other transition metals: $Ru(bipy)_3^{2+}$, $Ru(phen)_3^{2+}$, *cis*-$Ir(phen)_2Cl_2^+$, $Rh(phen)^{2+}{}_3$, where bipy = di-2-pyridyl, phen = 1,10-phenanthroline. However, in these cases $\Phi_{(I)\rightarrow(II)}$ does not exceed 0.006 (λ_{irr} = 366 nm). Only in the case of $Ir(bipy)_2.(bipy')^{3+}$ (XXXII) does the quantum yield amount to 0.72, which Grutsch and Kutal[89] relate to the formation of a charge-transfer complex in an excited state



By comparing the properties of the sensitisers described above it may be concluded that when compounds that form a ground state complex with norbornadiene are used, it is difficult to expect large values of λ_{lim} for the system [S- - -(I)], so that a considerable proportion of solar radiation cannot be utilised.

The action of triplet sensitisers such as acetophenone (with E_T > 293 kJ) is limited by the value λ_{lim} = 400 nm. It would appear that the development of sensitisers that have E_T < 293 kJ, absorb in the visible region, and are capable of forming charge-transfer complexes in the excited state with norbornadiene has the greatest future potential.

Although both processes (forward and reverse) for converting norbornadiene to quadricyclane are effected with kinetic control, surmounting the energy barrier of the counter reactions is achieved by different methods. The photochemical forward reaction is complemented by a dark thermal process whose efficiency is determined in many respects by the choice of catalyst.

IV. Catalysis of the thermal reaction quadricyclane → norbornadiene

A necessary condition for creating systems that store light energy is the kinetic stability of the product of the photoreaction. For the thermal conversion of quadricyclanes to norbornadiene, the high value of the energy barrier is dictated by the orbital restriction on the (2σ + 2σ)-cycloaddition reaction. The height of this barrier can be reduced when transition metal compounds and Lewis acids are used as catalysts and also by carrying out the conversion via radical cation intermediates.

Table 5. Catalytic activity of square-planar complex compounds in the isomerisation of quadricyclane to norbornadiene.

Ligand	Electronic structure of metal ion							
	d^5	d^6	d^7	d^8		d^9		d^{10}
	Mn(II)	Fe(II)	Co(II)	Ni(II)	Pt(II)	Cu(II)	Ag(II)	Zn(II)
Phthalocyanine	–	+	+	–	+	–	–	–
Tetraphenylporphyrin			+	+		–	–	–
			+	–		–		–
N,N′-Ethylenebis(salicylidenimine)								

Note. + = reaction goes to completion; – = no reaction.

1. Catalysis of unsaturated coordination transition metal complexes

The mechanism of catalysis of symmetry-forbidden electrocyclic reactions by transition metals was first analysed by Mango and Schachtschneider[90] and subsequently examined in more recent studies.[91–95] According to three studies[90,94,95] the role of the transition metal is that with a suitable orientation its *d* orbitals can form combined MOs with the delocalised σ-orbitals of the cyclobutane ring of quadricyclane and the π-MOs of the double bonds of norbornadiene. The change in symmetry of the frontier MOs resulting from this leads to a removal of the orbital restriction on the thermal reaction. According to another view of the role of the catalyst,[91] the transition metals make available their orbitals that are intermediate in energy between the HOMOs and LUMOs of the initial compounds and the reaction products, which results in a decrease in the energy of activation of the process, which remains forbidden.

The dependence of the catalytic activity of transition metal complexes on the extent of occupancy of the *d* shell and the geometric configuration was studied by Manassen.[96] It follows from the results given in Table 5 that metal complexes with a d^6–d^8

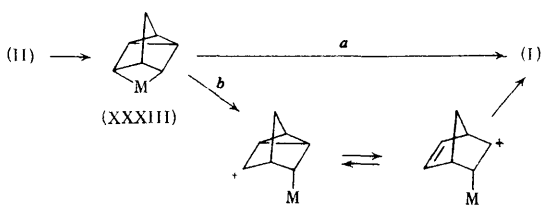
electronic shell in which there is either a vacant d_{zy} orbital or a higher populated p orbital that is similar in energy to an occupied d orbital are effective catalysts. In complex compounds of d^{10} elements [Cu(I), Ag(I)] all of the bonding orbitals are occupied by electrons and these complexes cannot catalyse a concerted opening of the cyclobutane ring.[93]

Another necessary condition for catalytic activity to occur in transition metal complexes is a square-planar structure of their molecules,[96] providing ease in additional coordination.

The available data on the opening of the cyclobutane residue catalysed by transition metal compounds are consistent with a multistage mechanism.[93,97,98] Depending on the properties of the central atom of the metal complexes, two main mechanisms for the multistage catalysed rearrangement of quadricyclane to norbornadiene can be distinguished:

1) an oxidative addition mechanism, which involves the insertion of a metal atom into the strained carbon–carbon bond to form the metallocyclobutane intermediate (XXXIII) followed by elimination of the catalyst[94,99,100] (route *a*);

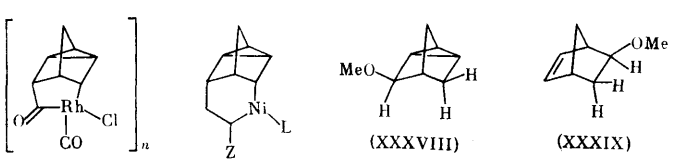
2) a mechanism through which carbocations (XXXIV) and (XXXV) are formed[97,101,102] (route *b*).



(17)

The ability of the catalyst to induce a particular reaction mechanism is determined by the magnitudes of the electron affinity and promotion energy (Table 6). While the first mechanism is typical for the initial members of the series—Ni(0), Pd(0), Pt(0), Rh(I)—the use of metal compounds with large values of these parameters—Pd(II), Pt(II), Cu(I), Ag(I), Zn(II), Hg(II)—leads to the formation of carbocation intermediates (XXXIV) and (XXXV). This is due to the fact that in the metallocycle (XXXIII) the metal atom is in a higher oxidation state and is quite a strong oxidising agent, resulting in heterolytic cleavage of the metal–carbon bond.

The choice between these two mechanisms can be made by analysing the reaction products. For the isomerisation of quadricyclane to norbornadiene catalysed by $[Rh(CO)_2Cl]_2$, complexes of the type (XXXVI) were isolated,[91] being formed by insertion of a carbonyl ligand into the metal–carbon bond of intermediate (XXXIII).



(XXXVI) (XXXVII) (XXXVIII) (XXXIX)

(I)

The formation of subsidiary nickel complexes (XXXVII) as intermediates in the reaction between quadricyclane and bis(acrylonitrilo)nickel has been postulated.[100] It should be noted that the organorhodium compounds (XXXVI) were only detected when rhodium dicarbonyl chloride dimer was used, which may be due to the specific properties of carbon monoxide as a ligand. In other cases the formation of metallocyclic intermediates was not established directly but followed from an analysis of the reaction products and the kinetic data. The formation of the derivatives of nortricyclane (XXXVIII) and norbornene (XXXIX) during isomerisation of quadricyclane by silver(I) and palladium(II) compounds in proton-donating solvents[104] is an argument in favour of reaction (17) occurring by route *b*. A similar dependence of the reaction products on the oxidising properties of the metal ion were found in the isomerisation of cubane catalysed by transition metal compounds.[105]

Table 6. Electron affinities and promotion energies of certain atoms or ions.

Electronic configuration	Atom or ion	Promotion energy, eV*	Electron affinity, eV
d^{10}	Ni(0)	1.72	1.2
d^{10}	Pd(0)	4.23	1.3
d^{10}	Pt(0)	3.28	2.4
d^8	Rh(I)	1.6	7.31
d^8	Ir(I)	2.4	7.95
d^8	Pd(II)	3.05	18.56
d^8	Pt(II)	3.39	19.42
d^{10}	Cu(I)	8.25	7.72
d^{10}	Ag(I)	9.94	7.59
d^{10}	Zn(II)	17.1	17.96
d^{10}	Hg(II)	12.28	18.75
d^{10}	Cd(II)	16.6	16.9

* Energy of transition beween the levels:

$$nd^{10} \rightarrow nd^9(n+1)p \text{ and } nd^8 \rightarrow nd^7(n+1)p.$$

The isomerisation of quadricyclane to norbornadiene catalysed by transition metal complexes was first reported in 1967.[106] It was shown that on treatment of a solution of quadricyclane with di-*m*-chloro-bis(norbornadiene)dirhodium in chloroform at −26 °C the time of half-conversion is 45 min [without a catalyst $\tau_{1/2}$ (140 °C) ≈ 14 h].[27] Other complexes of Rh(I) [90,104,106–109] and also Ni(0) [100,110] and Pd(0) [104,106,108,111] have similar properties.

The rate constants for isomerisation of quadricyclane in the presence of the norbornadiene complex [(I)RhCl], which were obtained by Cassar[99] do not depend on the concentration of norbornadiene and have values of 2.2 mol^{-1} s^{-1} and 1.8 mol^{-1} s^{-1} in chloroform and carbon tetrachloride respectively. However, it was shown previously[112] that this dimeric complex is decomposed by norbornadiene;

$$[(I)RhCl]_2 + 2(I) \rightleftarrows 2(I)_2RhCl. \quad (18)$$

This apparent contradiction was clarified by Taylor and Jennings.[109] From data on the position of equilibrium at different temperatures it follows that at 40 °C it is shifted quite considerably to the left, so there is no effect from norbornadiene. On lowering the temperature the equilibrium concentration of the monomeric complex $(I)_2RhCl$ increases, and because of its greater activity compared to the dimer, the rate of isomerisation increases by a factor of 1.7. The

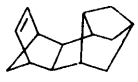
dependence of the equilibrium constant of (18) on temperature with a ratio of (I):$[(I)RhCl]_2$ = 4:1 is given below.

T, K	203	208	213	218	223	228	233
K	1.39	0.73	0.44	0.11	0.07	0.03	0.01

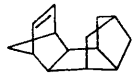
Replacement of a chloride ligand in $[(I)RhCl]_2$ by acetate results in a new equilibrium being established:

$$[(I)Rh(OAc)]_2 + (I) \rightleftarrows (I)_3Rh_2(OAc)_2. \quad (19)$$

Isomerisation of quadricyclane catalysed by the complexes $[(I)Rh(OAc)]_2$ and $(I)_3Rh_2(OAc)_2$ leads to the formation of the novel products (XL) and (XLI):[107]



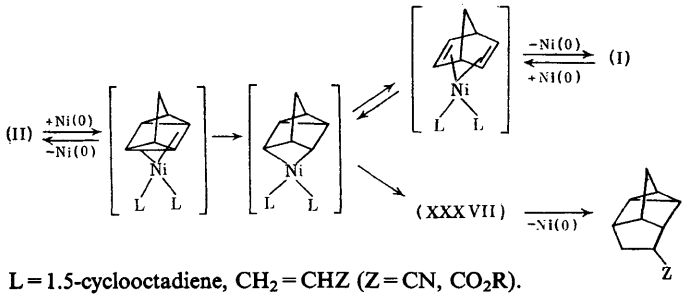
(XL)



(XLI)

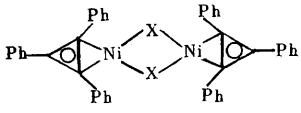
On the other hand, when carbonyl ($[Rh(CO_2)Cl]_2$) and norbornadiene complexes of univalent rhodium are used, norbornadiene is formed in quantitative yield.[104,113]

The formation of by-products (norbornadiene dimers, products of the insertion of ligands into the metal–carbon bond) occurs in the rearrangement of quadricyclane to norbornadiene catalysed by Ni(0) complexes:[100,114]



L = 1.5-cyclooctadiene, $CH_2=CHZ$ (Z = CN, CO_2R).

Derivatives of triphenylcyclopropenylnickel ($Ph_3C_3Ni(CO)X$, X = Cl, Br) (XLII) are active catalysts for the isomerisation of (II) → (I).[110] The initial rate of reaction depends on the concentration of catalyst and quadricyclane and comprises 2–4 (mol cat)$^{-1}$ s^{-1}. The data obtained indicate that the nickel complex (XLII) readily loses its carbonyl ligand and the reactive species is the square-planar dimeric complex (XLII).



(XLIII)

The ability of (XLIII) to form complexes with both quadricyclane and norbornadiene results in steady-state conditions being established.

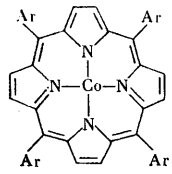
Replacement of the carbonyl in (XLII) by ligands that form stronger bonds with the metal atom [THF, $P(OPh)_3$, $PPhCl_2$, PPh_2Cl, $P(OPr\text{-}iso)_3$, $P(OMe)_3$, py, bipy] and an increase in the ratio of L:Ni in the molecule of the complex compound lead to a reduction in catalyst activity.

The relatively high activity of triphenylpropenylnickel complexes compared to other Ni(II) derivatives (also square-planar) may be due to the tendency of the cyclopropene ring to acquire a positive charge, and at the same time nickel becomes relatively negative. Thus, because of the unusual properties of the cyclopropene ligand, the Ni atom in $Ph_3C_3Ni(L)X$ will be sterically similar to Ni(II) and electronically similar to Ni(0).[110]

Because of the comparatively low value of the promotion energy of the palladium atom (4.23 eV) an oxidative addition mechanism can be proposed for the isomerisation of (I) → (II) catalysed by Pd(0) complexes. Analysis of the reaction products indicates the similarity of the intermediates formed by Rh(I) and Pd(0) complexes.[111]

Thus, only in rare cases do the above-mentioned process for the isomerisation of quadricyclane which are induced by Rh(I), Ni(0), and Pd(0) complexes result in the quantitative formation of norbornadiene. For the most part, by-products are formed.

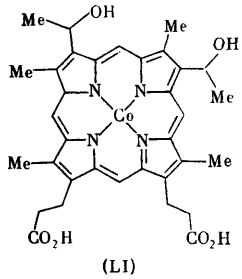
Some of the most widely studied and effective catalysts of the rearrangement of quadricyclanes to norbornadienes are the square-planar unsaturated coordination complexes of cobalt(II) with porphyrin (XLIV)–(LI), phthalocyanine (LII)–(LIV) and bis(azomethane) (LV, n = 2) ligands[51,96] (extending the methylene bridge in complexes (LV) by just one CH_2 group leads to deviation from a planar structure of the chelate centre and a loss of catalytic properties).



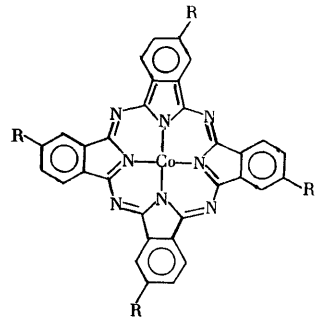
(XLIV)–(L)

(XLIV): Ar = Ph (Co-TPP),
(XLV): Ar = *p*-Me–C_6H_4 [Co-TPP(*p*-Me)],
(XLVI): Ar = *o*-Me–C_6H_4 [Co-TPP(*o*-Me)],
(XLVII): Ar = 2,4,6-$Me_3C_6H_2$ (Co-TMP),

(XLVIII): Ar = *p*-$C_5H_4\overset{+}{N}Me$ (Co-TMPy),
(XLIX): Ar = C_6H_4–SO_3H-*p* (Co-TPPS),
(L): Ar = C_6H_4–CO_2H (Co-TPPC).

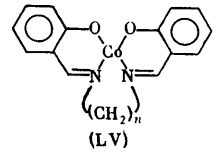


(LI)



(LII)–(LIV)

(LII): R = H (Co-Pc),
(LIII): R = SO_3H (Co-PcS_4),
(LIV): R = CO_2H (Co-PcC_4).



(LV)

The active catalytic site in these molecules occurs in the axial position (relative to the plane of the chelate CoN_4- or CoN_2O_2-centre); shielding of this reduces the efficiency of the catalyst:[115,116]

Co-TPP ~ Co-TPP(*p*-Me) > Co-TPP(*o*-Me) > Co-TMP.

In studies of the catalytic activity of Co(II) porphyrin and phthalocyanine complexes it was found that: 1) introduction of electron-withdrawing substituents into the ligand molecule increases the efficiency of the catalyst;[51,117] 2) the catalysts are effective in both aqueous solution and organic media (except for pyridine bases, which block the axial positions of the complexes);[96,118] 3) cobalt(II) porphyrin complexes in aqueous solution are more active than phthalocyanine complexes because of the ability of the latter to undergo aggregation.[118]

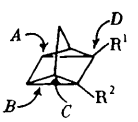
An increase in the hydrophobic properties of quadricyclanes—replacement of amide and carboxyl hydrogen atoms by alkyl or aryl groups—increases their reactivity, since the process that limits the rate of isomerisation in aqueous solution is approach of the quadricyclane to the hydrophobic environment of the active site of Co(II) porphyrin catalysts (Table 7).[118]

Table 7. Second-order rate constants for isomerisation of quadricyclanes (XVII).

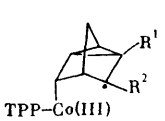
$CONR^1R^2$	k, $mol^{-1}\,s^{-1}$		Refs.
	Co-TPPC in $D_2O-Na_2CO_3$	Co-TPP in $CDCl_3$	
$CONH_2$	2.6	7.6	[116]
CONHMe	2.8		[118]
$CONHC_4H_9$-t	2.5		[116]
$CONMe_2$	3.9	4.5	
$CONCH_2CH_2CH_2CH_2$	6.9		[116]
CONHPh	6.7	6.4*	[118]
$CONHC_6H_4Cl$-*p*	7		[44]
$CONHC_6H_4Me$-*p*	6		[44]
$CONHC_6H_4OM$-*p*	7		[44]
$CONHCH_2Ph$	5.6		[116]
CONMePh	61.6	3.7	[116]
$CONHCH_2COOH$	2.0		[116]
COOMe	22.3	7.5	[116]
COOH	9.6		[116]

* in acetone-d_6.

It follows from the data given in Table 8 that an increase in steric hindrance to the approach of substrate and catalyst along direction *A* in (LVI) significantly reduces the rate of isomerisation. This direction of attack by cobalt(II) porphyrin catalysts is different from the direction of attack on quadricyclane by rhodium and nickel catalysts (routes *B* and *C*):[99,100]



(LVI)

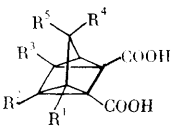


(LVII)

The ability of cobalt(II) porphyrin complexes to catalyse the isomerisation of quadricyclane is due to the presence of an unpaired electron in the d_{z^2} orbital of cobalt(II).[119] The existing literature data[120,121] are consistent with a radical mechanism for the process which involves the formation of the radical intermediates (LVII).

The advantage of cobalt catalysts is their quantitative conversion of quadricyclanes to norbornadienes in both organic solvents and water, but at the same time it should be borne in mind that there is a possibility of cobalt(II) being oxidised to cobalt(III), whose square pyramidal complexes, although more active,[122–124] are capable of inducing side reactions.

Table 8. Rate constants for isomerisation of substituted quadricyclanes (Co-TPPC, D_2O/Na_2CO_3)



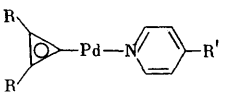
R^1	R^2	R^3	R^4	R^5	k, $mol^{-1}\,s^{-1}$
H	H	H	H	H	$1\cdot10$
Me	H	H	H	H	$4\cdot10$
H	Me	H	H	H	$7\cdot10^{-3}$
H	Me	Me	H	H	$<5\cdot10^{-3}$
H	H	H	Me	H	$2\cdot10$
H	H	H	H	Me	$1\cdot10^{-3}$
H	H	H	Me	Me	$9\cdot10^{-4}$

2. Carbocation mechanism of isomerisation

It was shown earlier that when transition metal complexes with a high electron affinity and promotion energy are used as catalysts, the reaction occurs via the formation of carbocation intermediates.

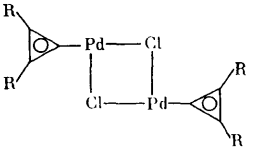
The ratio of isomerisation products of quadricyclane when the reaction is carried out in the presence of palladium dichloride and its complex compounds depends on the nature of the solvent used; in aprotic media only norbornadiene is formed,[104,111,126] while in proton-donating solvents (in methanol, for example) there is a mixture of products consisting of norbornadiene (40%), methanol adducts, and compounds of an undetermined structure.[104]

The Pd(II) cyclopropene derivatives (LVIII)–(LXI) are effective catalysts of the quadricyclane → norbornadiene process.[125]



(LVIII)–(LXIII)

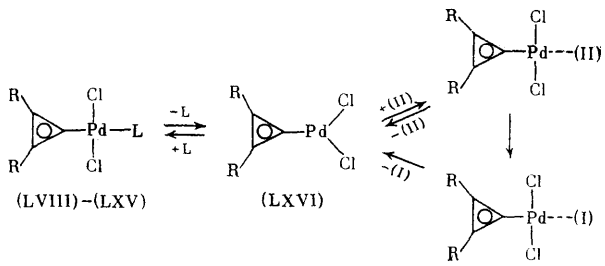
(LVIII): R = t-C_4H_9 R^1 = H; (LXI): R = iso-C_3H_7, R^1 = H;
(LIX): R = t-C_4H_9, R^1 = Me; (LXII): R = iso-C_3H_7, R^1 = Me;
(LX): R = t-C_4H_9, R^1 = CN; (LXIII): R = iso-C_3H_7, R^1 = CN.



(LXIV), (LXV)

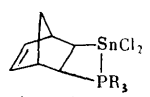
(LXIV): R = t-C_4H_9;
(LXV): R = iso-C_3H_7.

The catalytic activity of the complexes (LVIII)–(LX), (LXIV), and (LXV) is comparable to the activity of $[(I)RhCl]_2$, but in contrast to the latter they are not susceptible to oxidation. The active species in this case are unsaturated coordination complexes of the type (LXVI).



The efficiency of catalysts of this type depends on the tendency of the initial forms to dissociate—an increase of the electron-withdrawing properties of the ligands increases the catalytic activity. The dimeric complexes (LXIV) and (LXV) are more active than the monomeric (LVIII)–(LXIII) because of their higher dissociation constants.

The values of the ionisation potential and electron affinity of tin(II) (11 ± 5 and 14.6 eV respectively) provide an indication that Sn(II) ions are moderately good acceptors and poor donors of electrons. Hence it may be expected that metallocyclobutane complexes of the type (XXXIII, M = Sn) will be unstable. Only one form of complex between $SnCl_2$ and norbornadiene was detected using ^{119}Sn NMR.[126] The activation parameters for isomerisation of (II) → (I) catalysed by $SnCl_2$ are: $\Delta G^{\neq} = 94.05$ kJ mol^{-1}; $\Delta H^{\neq} = 58.10$ kJ mol^{-1}, $\Delta S^{\neq} = -120$ J deg^{-1} mol^{-1}. The less negative value of the entropy of activation compared to that for $PdCl_2$ (-230 J deg^{-1} mol^{-1}) may result from a reaction mechanism that is different from that represented by scheme (17). The bonding of $SnCl_2$ in the complexes with phosphine ligands $Me_3P{=}SnCl_2$ (LXVII) and $Ph_3P{=}SnCl_2$ (LXVIII) increases the catalytic activity of Sn(II) compounds—the half-conversion time of (II) → (I) in these cases is about 5 s (compared to 1 min for $SnCl_2$). Adducts (LXIX) or charge-transfer complexes may be reaction intermediates.[127]



The conversion of quadricyclane to norbornadiene accelerated by $HgCl_2$ that occurs in quantitative yield at 18–20 °C has also been reported.[128] The process mechanism involves chloromercuration of the substrate during a rapid initial stage in which 60% conversion is achieved [the Hg(II) compound acts as a catalyst]. Further conversion takes place slowly and is represented by zero-order kinetics.

The action of Ag(I) ions on quadricyclane and its derivatives has been reported in sufficient detail.[104,129–133] It was found[129] that the formation of norbornadiene, nortricyclane (XXXVIII), and norbornene (XXXIX) is accompanied by the reduction of Ag(I) ions, which is due to higher value of the ionisation potential of Ag(I) (7.57 eV)[101,129] compared to quadricyclane (7.40 eV).[134] Quadricyclanes with electron-withdrawing substituents have higher ionisation potentials, which inhibits the reduction of Ag(I).

The formation of carbocation species can occur not only via cyclic intermediates but also by direct addition of a catalyst ion to the substrate,[130] as in the case of catalysis by protic acids.[51,54,130,135,136]

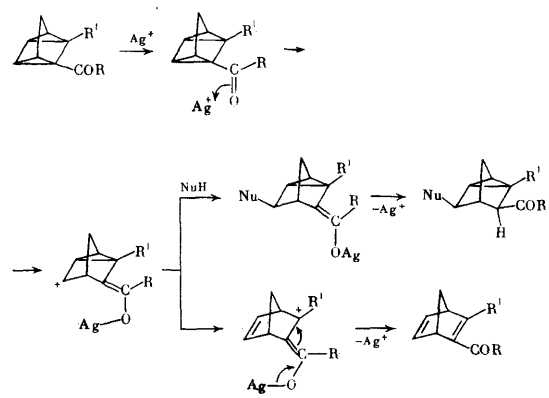
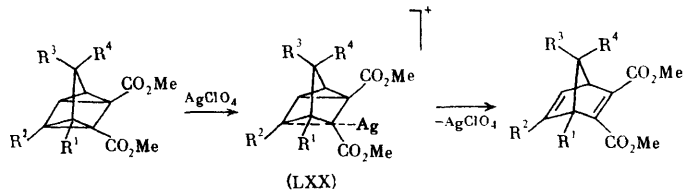


Table 9. Rate constants for isomerisation in reaction (20) catalysed by Ag(I).

R^1	R^2	R^3	R^4	$k^* \times 10^{-5}$, mol^{-1} s^{-1}, at: 25 °C	60 °C
H	H	H	H	1	30
Me	H	H	H	1	30
H	Me	H	H	$2.4 \cdot 10^3$	–
H	H	Me	H	1	40
H	H	H	Me	0	1
H	H	Me	Me	0	0.7

* Apparent initial second-order rate constants.

A different view is expressed in studies by Maruyama and Tamiaki.[131–133] It follows from the results given in Table 9 [131] that an increase in steric hindrance that makes *exo* attack by the catalyst on the 2-position of quadricyclane difficult results in a considerable slowing down of the reaction, since in this case attack by silver ions occurs along direction *D* (see above) to form the cation (LXX).



(20)

The reaction mechanism does not change when organic solvents are replaced by water.[132] The introduction of methyl substituents into the 6-position of quadricyclane-2,3-dicarboxylic acids and their esters considerably increases the rate of their isomerisation [through stabilisation of intermediate (LXX)] and it suppresses side reactions involving the addition of nucleophiles.

The rearrangement of 2,3-bis(trifluoromethyl)quadricyclane to the corresponding norbornadiene in the presence of a tungsten catalyst ($PhWCl_3-AlCl_3$) occurs with yields that are almost quantitative.[137]

3. Heterogeneous catalysis

The processes presented above involving valence isomerisation of quadricyclanes to the corresponding norbornadienes are carried out under conditions of homogeneous catalysis, which may have only limited practical application. In order to achieve a cyclic recurrence of the process of storage and release of light energy by the norbornadiene–quadricyclane system, it is necessary to fulfil at least two conditions—separation of the catalyst and the light-sensitive medium and to achieve a yield of virtually 100% for the thermal reaction. It follows from an analysis of the literature data that this is feasible under conditions of heterogeneous catalysis.[138] Transition metal complex compounds immobilised on various types of supports and also inorganic compounds were investigated as catalysts of this type.

While crystal hydrate chlorides of Sn(II) and Pd(II) are effective catalysts under conditions of homogeneous catalysis, only anhydrous salts of these metals are active during heterogeneous catalysis,[140] which is due to the blocking of the active sites on the surface of crystals of the catalyst by water molecules.

Anhydrous copper(II) sulphate has similar properties to those of anhydrous Sn(II) and Pd(II) chlorides,[140] while in the case of copper(II) halides a secondary redox process occurs, giving nortricyclane halides and univalent copper salts (with sufficiently high concentrations of CuX_2 this process predominates). The catalytic activity of copper salts results from the formation of charge-transfer complexes between quadricyclane and CuX_2 in which both rearrangement to norbornadiene and the reduction of Cu(II) to Cu(I) and addition of halogen to quadricyclane may occur.

Table 10. Classification of oxides according to their ability to accelerate the isomerisation of (XXIX, *j*).

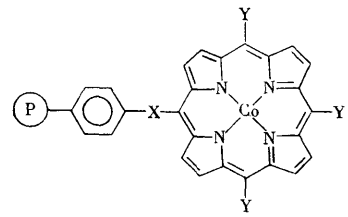
Group of catalysts	Time of reaction for the given group of catalysts	Oxide*
I	10 min	ReO_3 (24.7), MoO_3 (23.4), WO_3 (22.1), As_2O_5 (22.0), Sb_2O_5 (20.9), PtO_2 19.8, RuO_2 (19.8), TeO_2 (18.9), V_2O_5 (17.6), Nb_2O_5 (17.6)
II	24 h	Ta_2O_5 (16.5), SiO_2 (16.2), GeO_2 (16.2), SnO_2 (16.2), PbO_2 (16.2)
III	isomerisation has not occurred after 24 h	Rh_2O_3 (15.4), MnO_2 (13.5), TiO_2 (13.5), Sb_2O_3 (13.3), Bi_2O_3 (13.3), Tl_2O_3 (12.6), Fe_2O_3 (12.6), Ni_2O_3 (12.6), ZrO_2 (12.6), In_2O_3 (11.9), Co_3O_4 (11.4), Cr_2O_3 (11.2), Ga_2O_3 [11.2), HgO (9.5), AgO (9.5), CuO (9.5), CdO (8.5), ZnO (8.0), BaO (4.5)

* Electronegativity values of metals (χ_i) are given in brackets.

Inorganic oxides have the ability to accelerate effectively the isomerisation of quadricyclane to norbornadiene.[140–142] It was demonstrated that the catalytic activity of the latter varies in the same way as the electronegativity value of the metal[142] (Table 10). Such a correlation makes it possible to assume that the metal oxides act in the same manner as a proton, whose behaviour has been described by Hirao et al.,[54] namely, the first stage of catalysis is attack by the metal on the carbonyl oxygen atom. An increase in solvating power of the solvent reduces the activity of the catalyst, and a solvent such as pyridine completely suppresses it. The use of an oxide mixture increases the efficiency of the catalytic system (a mixture of TiO_2 and ZnO correspond approximately to SiO_2 in efficiency), which is due to the increase in acidic properties of such a mixture.[143,144]

Immobilised transition metal complexes also have the ability to catalyse the isomerisation of (II) → (I).[145–147] The catalysts of this type known at the present time are obtained either by the adsorption of transition metal compounds on various types of supports or by their complexation with polymer-bound ligands.

The properties of covalently bonded Co(II) complexes have been studied by different groups of chemists.[118,14]



(LXXI)–(LXXIX)

P = polymer support

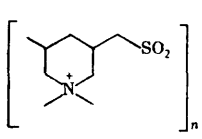
Compound	–X–	Y
(LXXI)	–NHCO–	CO_2Me
(LXXII)	$-NHSO_2-$	SO_2Me
(LXXIII)	$-CH_2NHCOC_6H_4-$	$C_6H_4CO_2H$-*p*
(LXXIV)	$-CH_2COC_6H_4-$	$C_6H_4CO_2H$-*p*
(LXXV)	$-COC_6H_4-$	$C_6H_4CO_2H$-*p*
(LXXVI)	$-CH_2-\overset{+}{N}(C_6H_4)-$	C_6H_4Me-*p*
(LXXVII)	$-CH_2-\overset{+}{N}Me_2-C_6H_4-$	4-C_5H_4N
(LXXVIII)	$-CH_2-\overset{+}{N}Me_2-C_6H_4-$	$C_6H_4NMe_2$-*p*
(LXXIX)	$-CH_2NHC_6H_4-$	$C_6H_4NH_2$-*p*

During the reaction the catalyst gradually loses its activity, which is due to the partial oxidation of Co(II) as well as its reaction with impurities. Treatment of the spent catalyst with reducing agents increases its activity. The rate of isomerisation of quadricyclane by such catalysts is virtually independent of the residue X, but the properties of the latter determine the stability of the catalyst under different conditions. Catalysts (LXXI)–(LXXIV) are hydrolysed in aqueous alkaline solution.

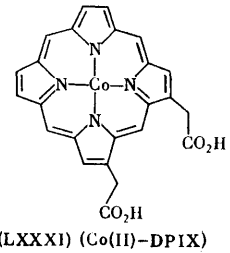
In addition to polymer-bound cobalt complexes, heterogeneous catalysts obtained by adsorption of complexes (XLIV)–(LV) on ion-exchange resins and inorganic materials have been studied.[118] In contrast to catalysts of the type (LXXI)–(LXXIX), Co(II) phthalocyanine and porphyrin complexes immobilised on carbon are less prone to a loss of activity during the process. Thus, for Co-TPPC (see IV.1) it is halved only after 10^4 cycles. Simple washing of the spent catalyst with boiling tetrahydrofuran completely restores the catalyst's efficiency.

Square-planar Co(II) complexes immobilised on aluminium oxide modified with polyaminosulphone (LXXX) are very promising

catalysts for the isomerisation of quadricyclanes. As in the case of cobalt porphyrins immobilised on carbon

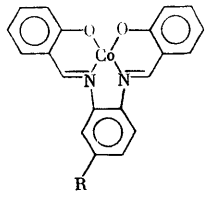


(LXXX) (PAS)



(LXXXI) (Co(II)-DPIX)

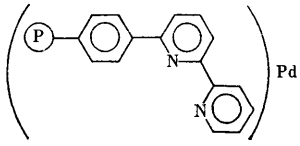
they are sufficiently effective, undergo slow deactivation, and are readily regenerated by heating under vacuum at 200 °C. However, the catalysts Co(II)-TPS/PAS/Al_2O_3 and Co(II)-DPIX/PAS/Al_2O_3 are not very active towards substituted quadricyclanes,[149] which is due to the steric repulsion between the equatorial ligands and the polysubstituted nortricyclane derivative (LVII). Complexes Co(II) such as (LV) (n = 2) and (LXXXII)–(LXXXV), with ligands that are more flexible than porphyrins, do not have these disadvantages.[150] In addition to activated carbon and alumina, poly(methacrylic acid), Florisil, magnesium silicate, and silica are also suitable as supports.



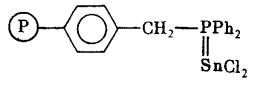
(LXXXII): R = H,
(LXXXIII): R = Me,
(LXXXIV): R = CO_2Me,
(LXXXV): R = CO_2H

(LXXXII)–(LXXXV)

The disadvantage noted for polymer-bound Co(II) porphyrin complexes are also typical for Pd(0), Pd(II), Sn(II) complexes fixed on polystyrene.



(LXXXVI)



(LXXXVII)

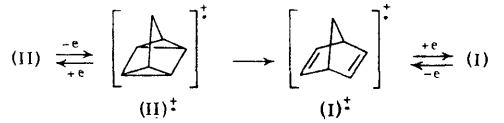
Thus, complex (LXXXVI) is deactivated during isomerisation as a result of oxidation and leaching of the metal.[127,128,152] Initially this catalyst is 30 times more active than palladium on carbon, but after two cycles their activities become equal.

Even less successful was the attempt to fix [Pd(MeCN)Cl_2] on a diphenylphosphine derivative of polystyrene. The activity of this type of catalyst proved to be much lower than for soluble [Pd(PPh_3)Cl_2] and it decreased even further on repeated introduction of this catalyst into the cycle.[152]

4. Radical cation mechanism for isomerisation

The barrier for many pericyclic reactions that occur via radical cation intermediates is known to be low in comparison with the barrier of similar reactions between neutral molecules.[153,154] When applied to the present problem of the catalysis of the isomerisation of quadricyclane, this method of lowering the activation barrier has the additional advantage of the ability of a radical cation of norbornadiene to oxidise quadricyclane and hence to the involvement of a redox chain mechanism.[155–160]

The generation of a radical cation of quadricyclane can be achieved, firstly, by oxidation of substrate with a photochemically generated oxidising agent,[161–165] secondly, by oxidising it with electronically excited sensitisers,[166,167] and finally, by electrochemical anodic oxidation of quadricyclane.[168] In each of these cases the $(II)^{+\cdot}$ radical cation is isomerised to the corresponding norbornadiene derivative $(I)^{+\cdot}$, which participates in the development of a redox chain reaction, so that the quantum yield (or yield based on current) of the reaction is greater than 1 (the isomerisation of quadricyclane to norbornadiene catalysed by dimethyldioxirane is also a chain process).[169]



Ikezawa and Kutal[161] showed that irradiation of n-type semiconductors (CdS, TiO_2, ZnO) in the presence of quadricyclane results in the formation of norbornadiene [$E^{Ox}_{1/2}(I)$ = 1.56, $E^{Ox}_{1/2}(II)$ = 0.91 V relative to a standard calomel electrode (SCE)].[162] The role of the oxidising agent in such systems is fulfilled by photogenerated holes that migrate to the surface of the semiconductor (Fig. 2*a*).

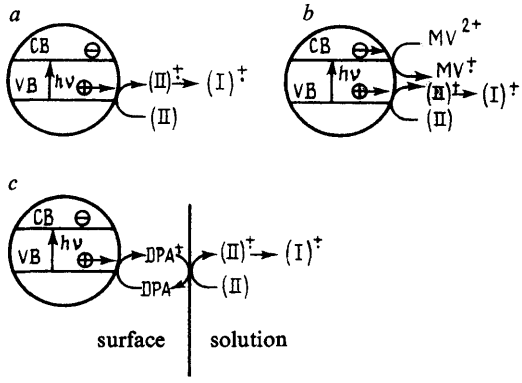


Figure 2. Schematic representation of the radical-cation mechanism of isomerisation of (II) → (I) on the surface of a semiconductor being irradiated. Adopted notation: CB = conductivity band; VB = valence band; MV^{2+} = methylviologen dication; DPA = diphenylamine.

The yield of norbornadiene is inversely proportional to the width of the forbidden band and varies in the series CdS > TiO_2 ⩾ ZnO. It can be increased by the addition of a methylviologen dication, which binds photogenerated electrons and thus prolongs the lifetime of the holes in the valence band (Fig. 2*b*). Addition of diphenylamine (DPA) ($E^{Ox}_{1/2}$ = 0.83 V), which acts as intermediate agent between the holes of the valence band and the quadricyclane molecules in solution (Fig. 2*c*) slightly increases the yield of norbornadiene. However, the ability of $DPA^{+\cdot}$ to dimerise to *N,N'*-diphenylbenzidine inhibits the cyclic processes [a more suitable intermediate agent may be tri-*p*-tolylamine ($E^{Ox}_{1/2}$ = 0.75 V)]. Although the attempts undertaken did lead to an increase in the yield of norbornadiene, the latter was still small (6–10%).

The results on the dependence of the rate of isomerisation of quadricyclane on the presence of oxygen in the system, obtained by Draper and de Mayo,[170] are different from those published by Kutal.[169] They found that when zinc was used, the rate of formation of norbornadiene increased in the presence of oxygen, which was due to the increase in lifetime of the photoinduced hole through bonding of an electron in a superoxide radical anion.[171] When CdS and TiO_2 were used the reverse effect occurred.[161,170,172,173] This may be due to predominating concurrent processes that involve the reduction of a radical cation by the superoxide anion, blocking of the surface of the semiconductor, and also the donation of an electron by chemisorbed oxygen to the photoinduced hole. The dark formation of norbornadiene (about 30%) in the presence of CdS was also detected.

Dichloronorbornadienepalladium molecules that are excited on exposure to radiation can act as oxidising agents. Irradiation of (I)$PdCl_2$ complexes in the presence of quadricyclane leads to isomerisation of the latter to norbornadiene with a yield exceeding 85%.[167,168,174] The quantum yield of the process is inversely proportional to the value of the half-wave oxidation of the strained hydrocarbon and for unsubstituted quadricyclane reaches a value of several hundred (Table 11), which is clear evidence in favour of a redox chain mechanism. For organic sensitisers the quantum yield is less than 1.[88,158,166,175–177]

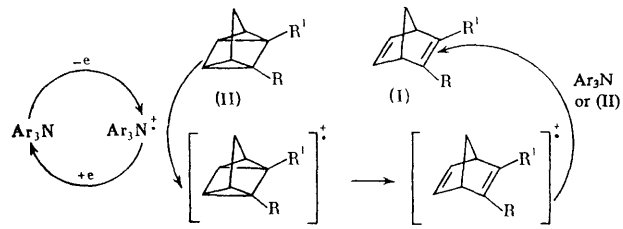
Table 11. Quantum yields of isomerisation of substituted quadricyclanes in the presence of (I)$PdCl_2$ (solvent—CH_2Cl_2, λ_{irr} = 405 nm).

Compound	$E^{Ox}_{1/2}$, V (vs. SCE)	Φ
Quadricyclane	0.91	230
2-Carbomethoxyquadricyclane	1.2	3.0
2,3-Dicarbomethoxyquadricyclane	1.64	0.06

Table 12. Electrochemical conversion of (II) → (I) (solvent—CH_2Cl_2).

Quantity of electricity passed through solution, $F \times 10^5$	Quantity of (II) before electrolysis, mol × 10^3	Quantity of (I) obtained mol × 10^3	Yield based on current	Quantity of (I) + (II) after electrolysis
2.1	0.97	0.16	7.6	1.02(±1.8%)
2.1	0.97	0.14	6.7	0.94(±0.7%)
0.89	0.42	0.056	6.3	–
4.1	1.52	0.45	11	1.83(±1.5%)

In the isomerisation processes examined above a preliminary stage—derivation of the active form of the catalyst—is required. A more convenient method is the direct generation of $(II)^+$ by anodic oxidation. The results obtained by Kutal et al.[168] (Table 12) show that: 1) electrolysis is quite suitable for obtaining norbornadiene; 2) the reaction is a catalytic process; 3) the yield based on current increases with an increase in concentration of quadricyclane; and 4) the conversion is sufficiently selective. A drawback of this method is contamination of the anode with a polymer film, which inhibits further reaction. This can be remedied with the use of an intermediate agent such as triarylamine, which is first oxidised at the anode and then reacts with quadricyclane.[178,179]



Better results were obtained for unsubstituted quadricyclane in the presence of tri-*p*-bromophenylammonium hexachloroantimonate ($E^{Ox}_{1/2}$ = 1.05 V). The introduction of substituents into the quadricyclane molecule and the use of the salts $(p\text{-}C_6H_4Br)_3.N^+GaCl_4^-$ and Ph_3PMeX^- (X = $SbCl_6$, $GaCl_4$) increases the isomerisation time considerably and reduces the yield of product.[180]

5. Comparative properties of catalysts

It may be concluded from an analysis of the literature data on the efficiency of catalysts for the isomerisation of quadricyclane to norbornadiene that those with the greatest potential are square-plane complexes of bivalent cobalt. Their activity under conditions of both homogeneous and heterogeneous catalysis is usually comparable to the activity of compounds of other transition metals and in a number of cases substantially exceeds it. Moreover, when Co(II) catalysts are used, side reactions are absent in virtually all cases, in contrast to catalysis with cobalt(III) compounds. Amongst the disadvantages of catalysts of this type it is necessary to include the ease with which the oxidative process Co(II) → Co(III) takes place and the reduced efficiency of Co(II) towards quadricyclanes that are substituted with electron-withdrawing groups. These disadvantages do not occur in the carboxyl derivatives (LXXXV) on inorganic supports (activated carbon, alumina). An undoubted advantage of catalysts (LXXXV) is the possibility of regenerating them by relatively simple methods.

Metal oxides have very promising catalytic properties, but as yet no data exists on the possibility of carrying out cyclic processes with them.

Electrochemical oxidation of quadricyclanes is a fairly convenient method of accelerating the isomerisation of quadricyclanes to the corresponding norbornadienes. In the opinion of Gassman et al.,[178,179] some of these systems are feasible for use in real cases. Nevertheless, we should note that the conditions for the quantitative derivation of norbornadienes with this method have so far not been found.

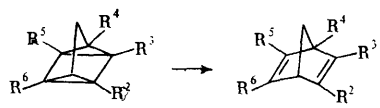
V. Exothermicity of the thermal reaction

As was mentioned in Section II, the exothermicity of the isomerisation of quadricyclane to norbornadiene satisfies the requirements imposed on photochemical materials that can store solar energy—it amounts to ~10^3 kJ kg^{-1}. The introduction of

substituents, while improving the spectroscopic properties of norbornadiene, results in an increase in molecular weight and hence causes a worsening of the energy parameters of the system.

The amount of energy accumulated by the photochemical isomerisation of norbornadienes to the corresponding quadricyclanes is determined both indirectly (from the difference between the heats of hydrogenation[181–183] and combustion[184] of both isomers) and by direct methods (by different scanning calorimetry[185] through measuring the enthalpy of isomerisation of quadricyclanes by homogeneous and heterogeneous catalysts[26,44,118,150] and by photocalorimeter). Photocalorimetry involves the measurement of energy absorbed by the system when the photoreaction is conducted directly in a calorimeter.[186] The results obtained are given in Table 13.

Table 13. Heats of isomerisation of the process



R^2	R^3	R^4	R^5	R^6	ΔH, kJ mol^{-1}	Refs.
H	H	H	H	H	96*	
H	H	H	CONHPh	CO_2H	59±4	[44, 118]
H	H	H	$CONHC_6H_4Cl$-*p*	CO_2H	60±4	[44]
H	H	H	$CONHC_6H_4Me$-*p*	CO_2H	60±5	[44]
H	H	H	$CONHC_6H_4OMe$-*p*	CO_2H	59±4	[44]
H	H	H	CONHMe	CO_2H	52±4	[44]
H	H	H	CO_2Me	CO_2Me	105.4±14.6	[186]
H	H	H	CO_2Me	CO_2Me	77.1±1	[185]
H	H	H	CN	CN	92.0±9.6	[186]
Me	Me	Me	CN	CN	88.0±8.0	[151, 186]
Me	Me	H	CO_2Me	CO_2Me	80	[51]
Me	Me	H	CN	CN	88	[51]
Me	Me	H	CN	CN	92	[51]

*Average value given. The values obtained by different methods are (in kJ mol^{-1}): 100,[181] 91.42,[182] 91.63,[183] 41.64,[184] 88.7 ± 0.8,[185] 110 ± 1, 113 ± 1,[26] 92 ± 4,[185] 59 ± 4,[186] 81 ± 1.[118]

The experimentally determined values of the heats of isomerisation of quadricyclane (ΔH) are virtually independent of the method used, except in two cases.[184,186] The low value of ΔH = 59 ± 4 kJ mol^{-1} obtained by calorimetry is attributed to an interaction of norbornadiene and quadricyclane with the sensitiser (acetophenone).

A comparison of the exothermicities of the rearrangements of substituted quadricyclanes shows that the introduction of methyl, cyano, and carboxymethyl groups has hardly any effect on the value of ΔH, whereas carboxyl and carboxamide groups reduce it by ~20 kJ mol^{-1}.

VI. Conclusion

The practical value of the system norbornadiene (I) ⇄ quadricyclane (II), if it is characterised by high values of λ_{lim} and Φ, is obvious. Information is available[51] on engineering studies carried out in Japan aimed at developing small-scale experimental systems operating on norbornadiene to heat buildings, garden houses, and greenhouses and to generate electrical energy.

However, in progressing towards the large-scale utilisation of heat energy liberated by the catalytic conversion of quadricyclane to norbornadiene there are certain difficulties, in particular those of an economic nature. The operating scheme of a system for absorbing solar energy followed by the production of low-pressure steam[12,13,187] is depicted in Fig. 3. Norbornadiene stored in tank *1* is transmitted by pump *2* at a pressure slightly above atmospheric through a planar collector *3* (possibly with an immobilised sensitiser). The quadricyclane obtained by the photoreaction is stored in tank *4*, from which it can pass at a required pressure (pump *5*) into heat-exchanger *6*. The latter is necessary only if the reverse reaction (II) → (I) is carried out thermally (for example, on heating quadricyclane to 140 °C). The heat liberated is used to obtain low-pressure steam (or hot water) in reactor-boiler *7*, which is supplied with immobilised catalyst *8* in order to carry out the conversion of (II) → (I).

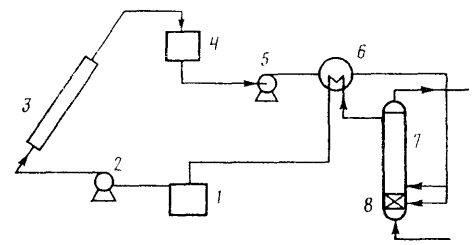


Figure 3. Operating scheme of a system for absorbing solar energy and the production of low-pressure steam (hot water): *1*, *4*, storage tanks; *2*, *5*, pumps; *3*, collector; *6*, heat-exchanger; *7*, reactor-boiler; *8*, immobilised catalyst.

Table 14. Cost of the unit shown in Fig. 3 with output of 100 kW (at 1981 prices).[187]

Equipment	Dimensions	Cost, in dollars
Collector *3*	Area 116000 m^2, depth 2 cm	2320000
Storage tanks *1* and *4*	120 m^3 each	60000
Heat-exchanger *6*	length 102 m	2500
Reactor-boiler *7*	27 tubes each of length 4.7 m	15000
Pumps *2* and *7*	—	4000
	Total	2410000

The norbornadiene used in such a system must be stable so that a large number of cycles of (I) ⇄ (II) can be achieved. 1440 cycles is considered to be the optimum number (corresponding to 99.99%

regeneration of norbornadiene per cycle and a total degree of discoloration of the initial material of 25%), and the cost of norbornadiene should not exceed 0.003 dollars per gram according to 1979 estimates.[188] We should note that in the light of the results of Yoshida et al.,[51,55] the required degree of cyclic recurrence does not seem impracticable nor does the reduction in price of the production of substituted norbornadienes (Table 14).

Taking into account the fact that the cost of steam obtained on such a system is substantially higher (by a factor of about 50) than the cost of steam produced by alternative methods, the main direction of efforts at the present time remains the development of less powerful small-scale units.

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