Topics in Current Chemistry

103

P. Margaretha

Preparative Organic Photochemistry

Preparative Organic Photochemistry

By P. Margaretha

Editor: J.-M. Lehn

With 9 Figures

Springer-Verlag
Berlin Heidelberg New York 1982

Professor Dr. Paul Margaretha
Institut für Organische Chemie und Biochemie,
Universität Hamburg, Martin-Luther-King-Platz 6,
D-2000 Hamburg 13, FRG

This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for "Topics in Current Chemistry" in English.

103 Topics in Current Chemistry

Fortschritte der Chemischen Forschung

Managing Editor: F. L. Boschke

Preface

It is now more than 13 years ago that the second edition of A. Schön-
berg's "Preparative Organic Photochemistry" appeared, a work representing
a thorough compilation of photochemical reactions of preparative concern
to the organic chemist.

Research in organic photochemistry over this period has not only produced
a vast accumulation of factual knowledge, but the understanding of *how*
these reactions proceed has also dramatically increased. The high rate of
development in synthetic applications of photochemical reactions has — at
least in part — only become possible due to this theoretical and mechanistic
know-how. Organic photochemistry is today a multidisciplinary field itself.

It is not the purpose of this book to be a supplement to the earlier
work bearing the same title. The intent is to demonstrate the usefulness of
organic photochemical reactions as powerful tools in organic synthesis. In
contrast to the preceding monograph, an exhaustive compilation of all pre-
parative applications of photochemical reactions has become virtually im-
possible in this vigorously expanding field. I have therefore tried to select
the (subjectively) most representative examples of synthetic utile reactions
with a strong preference for more recent publications and reviews. In this
context the literature was covered up to June 1981.

Hamburg, November 1981   P. Margaretha

A. Schönberg

Preparative Organic Photochemistry

In cooperation with G. O. Schenck,
O. A. Neumüller

2nd completely revised edition of "Präparative
Organische Photochemie". 1968. 4 figures,
51 tables. XXIV, 608 pages
ISBN 3-540-04325-X

From the reviews of the German edition:
"A monograph dealing with a rarely treated
subject matter. It is a comprehensive, well-
balanced discussion of the reactions and tech-
niques which are of importance to the prepara-
tive organic photochemist."   *The Chemist*

"The author is well known for the contribu-
tions to this subject which have originated from
his laboratories at the University of Cairo
during the past fifteen years. ...The aim has
been to assemble in a systematic manner those
reactions which have at present, or may be
expected to have in the future, preparative
value. The result is a well documented and
critically selected compilation of reactions,
written specifically for the organic chemist,
with detailed experimental procedures for each
type of synthesis described."
Journal of the American Chemical Society

"The printing and general layout are excellent,
making the book easy to read and to use for
reference. Some will doubtless wish for an
English translation..."   *Nature*

Springer-Verlag
Berlin
Heidelberg
New York

Reactivity and Structure

Concepts in Organic Chemistry
Editors: K. Hafner, J.-M. Lehn, C. W. Rees,
P. v. R. Schleyer, B. M. Trost, R. Zahradnik

Table of Contents

1 Introduction

1.1 Photochemistry

Chemical reactions can be differentiated fundamentally by describing the electronic configuration of the reactive species itself. On the one side there are species with unoccupied antibonding orbitals (ground-state molecules, radical cations), on the other side we deal with species with occupied antibonding orbitals (radical anions, excited molecules). While radical cations and radical anions are usually generated by electron transfer from or to the ground state molecule, the excited species is formed by promotion of an electron from a bonding or a nonbonding orbital to an antibonding orbital (Fig. 1).
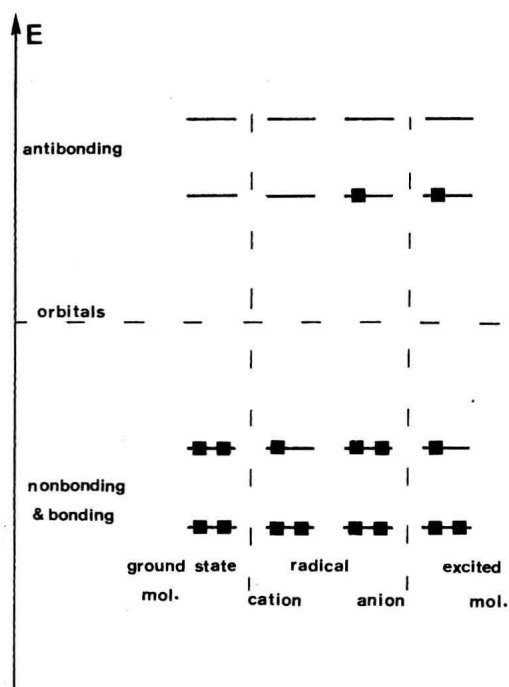
Fig. 1. Electronic configuration of intermediates obtained by electron transfer or by excitation

Excitation of organic molecules is usually achieved with visible or ultra-violet light ($\lambda = 750–200$ nm) corresponding to a difference in energies between the excited state of a molecule and its ground state of about 40–145 kcal/mole. As the excited state is created directly by absorption of a light quantum ground state reactions from higher vibrational levels, e.g. bond breaking, are avoided although the amount of energy would be largely sufficient for such a process to occur. The excited molecule posesses the intrinsic tendency of either liberating this excess energy or of undergoing chemical reactions. Photochemistry therefore deals with chemical changes undergone by such excited molecules while the purely physical processes of setting this excess energy free give back the molecule in its ground state.

Radiation chemistry has to do with the effects of more energetic radiation ($\lambda < 150$ nm) and although related to photochemistry, is traditionally dealt with separately.

Photochemistry as topic is covered in several introductory textbooks [101–107]. The annual literature is surveyed in a specialist periodical report [108]. Two series of monographs have to do with selected chapters from organic photochemistry [109] or photochemistry in general [110]. A series on molecular rearrangements also covers photochemical reactions [111].

1.2 Generation of Excited Molecules

The excited states of a molecule are characterized by their multiplicity (usually singlet or triplet states) and by the difference in energy between the excited state itself and the ground state (Fig. 2).

While in the thermal or electrochemical activation of a molecule the energy is transfered in a continuous way, photochemical activation is inso-far unique as it occurs by absorption of a photon of well defined energy. Although there are chemical ways of generating excited states [112], under normal conditions a molecule can only be excited by absorption of light of the wavelength corresponding to the energy difference between the excited state and the ground state. This is known as Planck's law (1.1).

$$E_n - E_0 = h\nu_n = \frac{hc}{\lambda_n} \tag{1.1}$$

where h is Planck's constant, ν is the frequency at which absorption occurs and c is the speed of light. The position of the absorption band is more often expressed by the wavelength λ in nanometers (1 nm $= 10^{-9}$ m). The

E

antibonding

orbitals

bonding

S_0 S_1 S_2 T_1 T_2
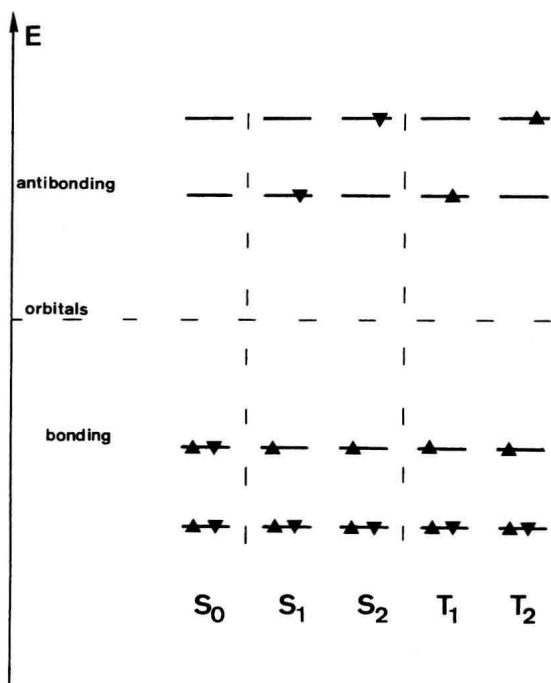
Fig. 2. Electronic configuration of the first two excited singlet and triplet states

conversion of energy (kcal/mole) to the wavelength λ (nm) is given by the following expression (1.2).

$$\Delta E \text{ (kcal/mole)} = \frac{2.86 \times 10^4}{\lambda \text{ (nm)}} \tag{1.2}$$

Continuous energy transfer implies, that A giving B at a temperature T_1 (or potential E_1) and giving C at a temperature T_2 (or potential E_2), that B will also convert to C under these "higher energy" conditions. This is so for all thermal or electrochemical reactions. In photochemical reactions A gives B (an excited state) with light of wavelength λ_1 and C (a higher excited state [113, 114]) with light of shorter wavelength λ_2; but now B will *not* give C with λ_2 as this wavelength does not correspond to the difference in energies between the excited states B and C (Fig. 3).

Before irradiating a compound one has therefore to know its absorption spectrum. A typical absorption spectrum is shown in Fig. 4, affording the following information:
a) the energy(ies) of the excited state(s) can be deduced from the wavelength where the absorption curve ends towards longer wavelengths
b) the degree of allowedness of a transition is reflected by the intensity of the band.
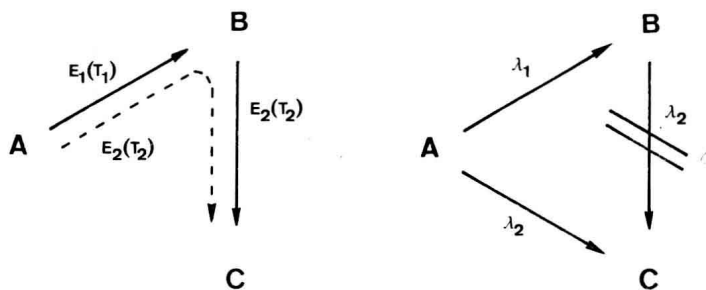
Fig. 3. Continuous energy transfer versus discontinuous energy transfer

This intensity is expressed by the molar absorption coefficient ε which can be calculated from the (measured) absorbance A, ($A = \log I_0/I$) via the well known equation of Lambert & Beer (1.3), wherein c is the concentration (mole/l) and d is the optical path length of the cell (in cm).

$$A = \varepsilon \cdot c \cdot d \tag{1.3}$$
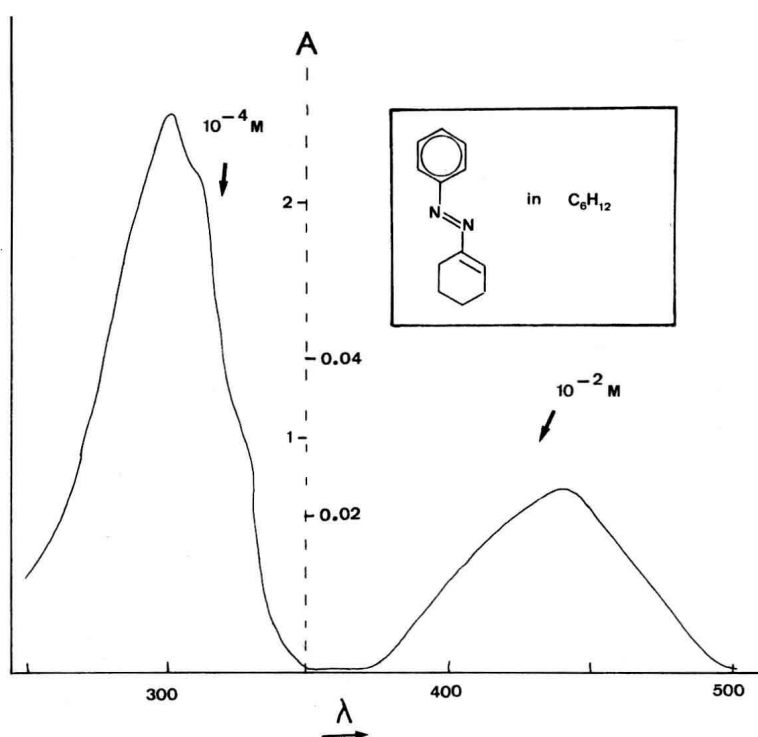
Fig. 4. UV.-absorption spectrum of phenylazocyclohexene in cyclohexane as solvent

While for thermal reactions one usually does not correlate the energy input with the amount of product formed, electrochemists and photo-chemists are certainly more "energy-minded". The first ones use the current yield to define the amount of product formed per electrons consumed. The latter ones use the so called quantum yield Φ which is defined as the ratio of number of molecules undergoing a particular process from an excited state over moles of photons absorbed by the system, or in other words, the ratio of the rate constant for the process defined over the sum of all rate constants for all possible processes from this excited state (1.4). Thus, if for every photon absorbed, a molecule undergoes only one chemical process, the quantum yield for this process is unity; if other processes compete it will be less than unity.

$$\Phi_x = \frac{k_x}{k_a + k_b + \dots + k_x} \tag{1.4}$$

For the conversion of the molecule AB to the Product P the quantum yield Φ for the formation of P corresponds to the number of molecules P formed over the number of light quanta absorbed by AB. For such a reaction one should not correlate quantum yield and chemical yield. In (1.5) an example of a reaction is given where the quantum yield of product formation is very low although the chemical y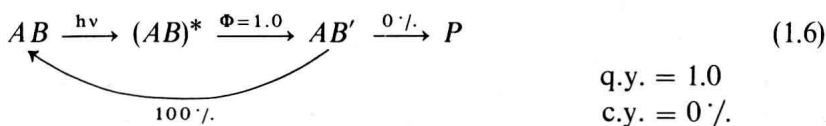ield is high. In (1.6) the chemical yield is zero although the photochemical step itself is highly efficient. In this latter case the thermolabile intermediate AB' can obviously be trapped before reconverting to starting material, or the formation of P can be favoured by running the reaction at low temperature.

$$AB \xrightarrow{h\nu} (AB)^* \xrightarrow{\Phi = 0.01} P \tag{1.5}$$

$\Phi = 0.99$

q.y. = 0.01
c.y. = 100 %.

$$AB \xrightarrow{h\nu} (AB)^* \xrightarrow{\Phi = 1.0} AB' \xrightarrow{0\%} P \tag{1.6}$$

100 %.

q.y. = 1.0
c.y. = 0 %.

1.3 Excited Molecules — Physical Processes

By absorption of light a molecule is promoted to a higher electronic state. The monomolecular physical processes for the dissipation of the excess energy are outlined in Fig. 5 in a so called Jablonski diagramm. In principle one has to differentiate between radiative and non-radiative deactivation on the one side and on the other side one has to consider if the multiplicity of the system is conserved or not. Radiative deactivation, i.e. deactivation accompanied by emission of light, is termed
fluorescence if the transition occurs with spin conservation and
phosphorescence, if spin inversion occurs.
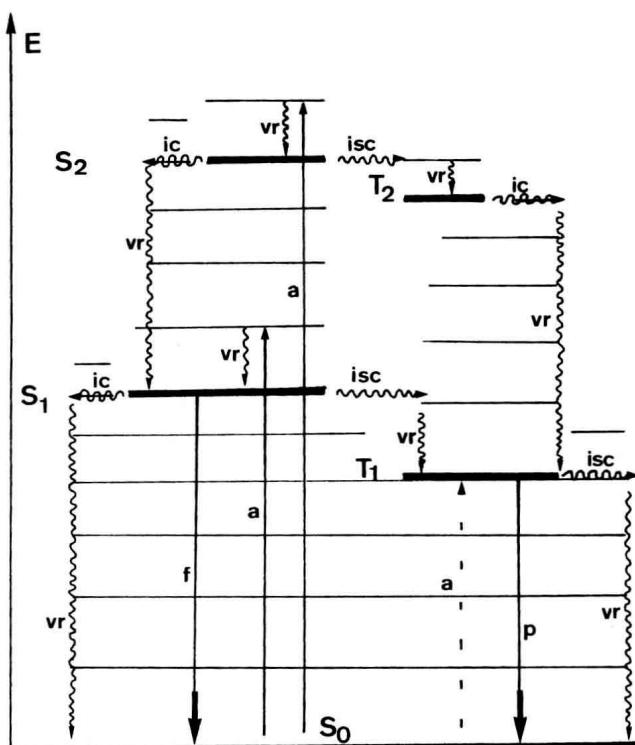
Fig. 5. Jablonski diagram
a) absorption   *vr*) vibrational relaxation

                                        ic) internal conversion *
                        non radiative
                                        isc) intersystem crossing **
    deactivation
                        radiative   *f*) fluorescence *
                                        p) phosphorescence **
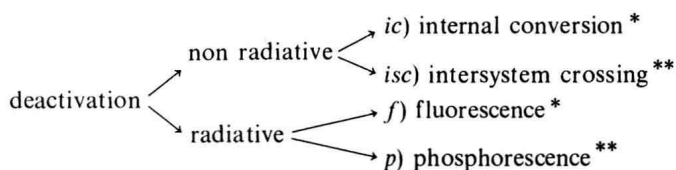
* $\Delta S = 0$ ** $\Delta S \neq 0$

The radiationless transition between two states of same spin is called *internal conversion*, the one occuring with inversion of spin being termed *intersystem crossing*. In both processes the excess energy is liberated as heat. All these transitions between different electronic states are customarily preceded by vibrational relaxation, i.e. the deactivation from a higher vibronic level to the v_0-level of the same electronic state (Fig. 5).

As shown in Fig. 6, there is a correlation between absorption spectrum and emission spectrum. Taking into consideration the Franck-Condon principle, which states that there is no motion of the atoms during an electronic transition, one has to differentiate between the two following possibilities:
in the one the geometry of the excited state is similar to the one of the ground state (same interatomic distances),
in the other one the geometries are different (usually the distances between the atoms become larger in the excited state).

In the first case the so called 0—0 transition will be the most probable one, both for absorption and emission, and therefore the most intense
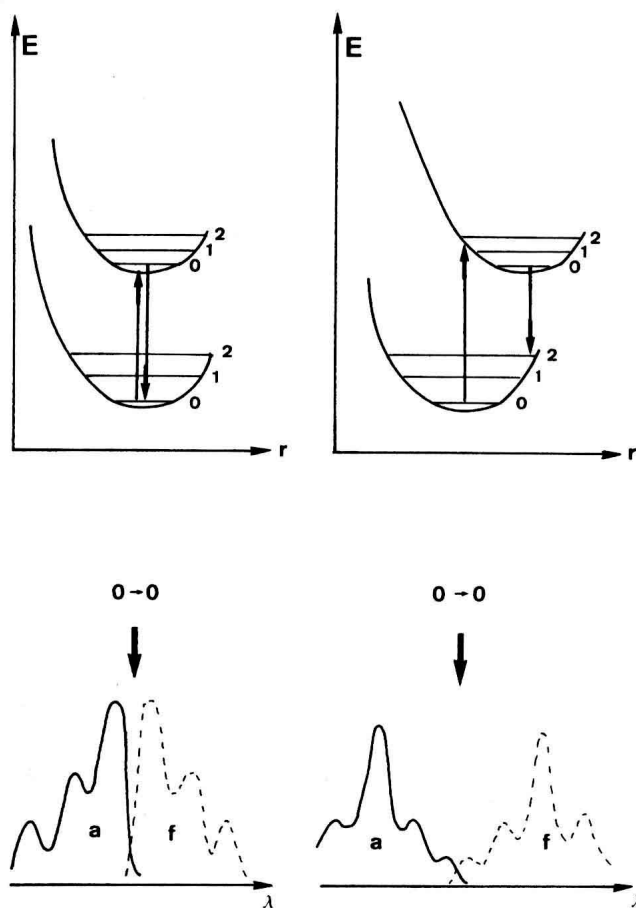
Fig. 6. Correlation between absorption and emission (fluorescence) spectrum