PHOTOCHEMISTRY OF LINEARLY CONJUGATED CYCLOHEXADIENONES IN SOLUTION[1]

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ABSTRACT

Objects of study: The cyclohexa-2,4-dienones I, II and III.
Special methods of examination: Low temperature spectroscopy and *Mauser diagrams*.
Main results of investigation: *Cyclo/seco* isomerization of a $\pi^{\star}$,n-excited reactant to a transient dienylketene, able to recyclize and/or to add a protic nucleophile, furnishes derivatives of a substituted hexadienoic acid in high yield. Alternatively, a cyclohexa-2,4-dienone/bicyclo-|3.1.0|hex-2-enone rearrangement of a $\pi^{\star}$,π-excited reactant may take place. Whether the latter reaction occurs (as with III under special conditions) or not (as with I and II under any conditions investigated) is a question of the spatial symmetry of the lowest excited state. The light-induced ring opening of the linearly conjugated cyclohexadienone XX represents the key reaction of a three-stage synthesis of dimethylcrocetin starting from 2,6-dimethylphenol and 1,4-dibromobut-2-ene.

In spite of a characterization of a recent[3] total synthesis of vitamin D_3, where special emphasis was laid on having succeeded without the use of photochemical methods, natural product synthesis is tending towards the invention of strategies including light induced reactions as important key steps[4]. Times are over, where one felt almost obliged to confess to a weakness for photochemical reactions, and where the larger part of the chemical community thought of electronically excited molecules as queer species, rather to be considered from an energetic point of view as 'states' than from a structural standpoint as 'compounds'.

The story to be told here commences with observations caused by mere curiosity about the behaviour of linearly conjugated cyclohexadienones towards absorbed light. They were made at the Whiffen Laboratory of Imperial College in London[5] and were made at a time when the cross-conjugated cyclohexadienones had just revealed many of their photochemical secrets. This report will be closed with an account of a synthetic application of a light induced reaction which has been thoroughly studied in our laboratory (previously at Braunschweig and now at Frankfurt). Compounds I, II and III will serve as the most active representatives of their structural family, while compound IV will be referred to only occasionally (see *Chart 1*).

Chart 1

Chart 2

There is no understanding of any photochemical reaction without knowing the electron configuration and spin multiplicity of the reactant in its excited state(s). Very often the reactive excited state of a molecule from which photochemical reaction occurs differs from its initially excited state reached by absorption (see *Chart 2*). Information about the excited state(s) of a reactant involved in a photochemical process may be obtained indirectly by kinetic and structural analysis of the product; where possible, even better data may be acquired by analysis of the transient(s), and, more directly, by interpretation of the observed electronic absorption and emission spectra.

ELECTRONIC SPECTRA OF CYCLOHEXA-2,4-DIENONES[6]

According to the approximate notation introduced by Kasha[7], electronically excited states are classified in terms of one-electron transitions indicating the orbitals from and to which the electron is transferred. If certain requirements are fulfilled, there are two bands in the electronic absorption spectra of cyclohexa-2,4-dienones between 250 and 400 nm to be observed, which point to a participation of $\pi^\star,n-$ and $\pi^\star,\pi$-excited states. The precise location

of the two bands on the wavelength scale and the relative ordering of ground state, $\pi^\star$,n- and $\pi^\star$,π-excited states depend on chromophore substitution, nature of the solvent used, and temperature at which the spectrum has been taken.

Figure 1. Electronic absorption spectra of II (———), III (······), and IV (–––––) in *n*-heptane at room temperature.

Figure 1 shows the absorption spectra of II, III and IV at room temperature in *n*-heptane. As a consequence of methyl substitution at the dienone chromophore, a red shift of the $\pi^\star$,π band occurs causing overlap with and blurring of the vibrational structure of the $\pi^\star$,n band. These effects are the stronger the higher the number of methyl substituents is. *Figures 2, 3* and *4* indicate a red shift of the $\pi^\star$,π band and a blue shift of the $\pi^\star$,n band for I, II and III, respectively, brought about by changing solvent from methyl-cyclohexane to ethanol and then to 2,2,2-trifluoroethanol. In passing I should mention that there are strong similarities between changes of the absorption profiles caused by increasing the polarity of the solvent and those effected by decreasing the temperature at which the spectra were taken, from room temperature to $-189°C$.

After the foregoing discussion one cannot help asking two questions. First, does a variation of the wavelength of the exciting light have control—quantitatively and/or qualitatively—over product formation? Secondly, is the photochemistry of cyclohexa-2,4-dienones influenced by changing the solvent?

If the initially excited states were at the same time the reactive excited states, then a wavelength influence would seem compulsory. If, on the other

Figure 3. Electronic absorption spectra of II in methylcyclohexane (———), ethanol (———), and 2,2,2-trifluoroethanol (········) at room temperature.

Figure 2. Electronic absorption spectra of I in methylcyclohexane (———), ethanol (———), and 2,2,2-trifluoroethanol (········) at room temperature.

Figure 4. Electronic absorption spectra of III in methylcyclohexane (———), ethanol (-----), and 2,2,2-trifluoroethanol (······) at room temperature.

hand, the ordering of the initially excited states were to be parallelled by the ordering of the reactive excited states, solvent effects might be dramatic for the photochemical outcome—at least in those cases where perturbation effects by interaction between solute molecules and neighbouring solvent molecules would actually reverse the order of $\pi^\star,n$ and $\pi^\star,\pi$ reactive states.

So far multiplicity of the reactive excited state has not been brought up. Emission spectra, as a source of information about the spin state, cannot be used here since all the investigated linearly conjugated cyclohexadienones do not emit light either at room temperature or at $-189°C$. This means we have to rely on more indirect observations to be discussed later.

LOW TEMPERATURE TECHNIQUES IN PHOTOCHEMISTRY

Frequently the excited state(s) of a reactant is (are) not the only transient(s) in a light induced reaction. The product of a primary photochemical process may escape discovery even in its electronic ground state if its lifetime is so short that detectable concentrations cannot be produced: it either reacts to form a secondary product, or reverts to the unchanged reactant[8]. In both cases it is necessary to be aware of the kinetically unstable intermediate to avoid misconstructions with regard to mechanism. Porter[9] and Pimentel[10], together with their respective co-workers, proposed what is now called *the matrix isolation method*[11]. *Figures 5*(a) and *5*(b) give an idea of the equipment

289

Source of monochromatic
light

Blank

Cell

Monochromator

Detector

Irradiation lamp

Figure 5(a). Schematic representation of equipment for low temperature irradiation and electronic absorption spectroscopy[12]: phase of irradiation.

Source of monochromatic
light

Blank

Cell

Monochromator

Detector

Irradiation lamp

Figure 5(b). Schematic representation of equipment for low temperature irradiation and electronic absorption spectroscopy[12]: phase of spectral monitoring.

Figure 6. Cutaway view of low temperature i.r. cell.

for low temperature photolysis and electron spectroscopy[12], *Figure 6* shows the low temperature i.r. cell; both are used in routine procedures in our laboratory[2, 13]. It should be mentioned that quite a few groups are active now in low temperature photochemistry. Special reference must be made to the important accomplishments in this field of E. Fischer and his colleagues[14] and of O. L. Chapman and his group[15]. The use of low temperature techniques caused a breakthrough in the photochemistry of linearly conjugated cyclohexadienones. We do not intend to report here about the development historically but rather prefer to make use of three typical examples in the order of their increasing complexity.

AN ACCOUNT OF 6,6-DIMETHYLCYCLOHEXA-2,4-DIENONE

6,6-Dimethylcyclohexa-2,4-dienone (I), on irradiation in the presence of a protic nucleophile, gives the corresponding carboxylic acid derivative V in exceedingly high yield[5, 16]. Its constitution and steric relation around the

291

V: λ_{max}: 240 nm (24 500)

Chart 3

disubstituted double bond follow from the details of *Chart 3*. Before it was recognized that the u.v. data of the two stereoisomers (V and VI; X = NH—C$_6$H$_{11}$) are of no diagnostic value for individual identification, the photoproduct was erroneously thought to be represented by VI[5].

According to the linear diagram of extinction differences (*Figure 7*), both wavelengths 365 and 313 nm effect what Mauser[17] has designated *a spectroscopically simple photoreaction*. This characterization excludes, for instance,

Chart 4

292

Figure 7. Linear diagram of extinction differences for the irradiation of I in ether in the presence of cyclohexylamine at room temperature with 313 ($\cdots\cdots$) or 365 nm light (xxxxx).

that any spectroscopically detectable transient takes part[18]. Participation of a dienylketene as a kinetically unstable intermediate, nevertheless, had already been proposed in the first publication on the photochemistry of linearly conjugated cyclohexadienones[5] (*Chart 4*). It would justify the formation of the isolated carboxylic acid derivative, as well as the observation

293

that seemingly no photochemical reaction occurs, if no protic nucleophile is present.

Evidence for a thermoreversible photoisomerization of I to the corresponding dienylketene was obtained by low temperature u.v., i.r. and n.m.r. spectroscopy. On irradiation of a methylcyclohexane/isopentane (4:1) solution of I at −189°C with 365 nm light a reaction takes place which can easily be monitored electron spectroscopically[19]. *Figure 8* represents the absorption spectra of the solution at the low temperature before irradiation and after the reaction has been completed. *Figure 9* indicates that on intermediate warming up to room temperature, the original state of the sample is restored.

Figure 8. Electronic absorption spectra of the *cyclo/seco* isomers I (————) and V (-----) in methylcyclohexane/isopentane (1:4) at −189°C.

The half-life of the photoproduct is almost twelve minutes at −15·4°C. That the compound actually is a ketene which thermally recyclizes to the cyclohexadienone follows from an i.r. study[19] of a chloroform solution at −63°C (*Figure 10*). On irradiation of I with light of wavelengths >340 nm, an intense ketene band at 2120 cm^{-1} is formed, while at the same time, the dienone absorption disappears. A n.m.r. spectroscopic examination[19] (*Figure 11*) of the structural change caused by treatment of I in deuterochloroform at about −60°C with light of a medium pressure mercury lamp (from which the wavelengths <340 nm had been filtered) supports the conclusions already drawn. The reactant[23], with a complex multiplet for four vinyl protons and one singlet only for the protons of two isochronous

Figure 9. Electronic spectroscopic evidence of periodic cycle of isomerization: I → V → I → V in methylcyclohexane/isopentane (1:4) at −70°C. A: solution of I using the low temperature cell of *Figure 7* in loc. cit. ref. 13c; B: after irradiation with 365 nm light using the irradiation apparatus of *Figure 8* in loc. cit. ref. 13c; C: after intermediate warming up to room temperature and recooling to −70°C; D: after repetition of treatment under B.

methyl groups, affords a photoproduct with a complex multiplet for three vinyl protons, a doublet for the proton of an aldoketene group, and two singlets for the protons of two anisochronous methyl groups. Here again the initial spectrum reappears on warming the irradiated sample.

There is no doubt of the constitution of the dienylketene or of Z orientation around the central double bond of the conjugated system. Its stereochemistry agrees with that of the corresponding carboxylic acid derivative and follows from an application of the 'principle of least structural change' to the photochemical ring opening (see *Chart 4*). The linear diagram of extinction differences (*Figure 12*), proper to the n.m.r. investigation just discussed, excludes a secondary photoisomerization of a primary photoproduct.

The quantum yield for the transformation of I to V, independent of the wavelength used (365 or 313 nm), amounts to 0.6 at room temperature. Since recyclization and 1,2 addition of HX compete for the transient (see *Chart 4*), the quantum yield ought to be controlled by the concentration

295

Figure 10. Infra-red spectroscopic evidence of periodic cycle of isomerization: I → V → I in chloroform at −63°C. A: solution of I using the low temperature cell of *Figure 6*; B: after irradiation with light of wavelengths >340 nm; C: after intermediate warming up to room temperature and recooling to −63°C.

Figure 11. N.m.r. spectra of the *cyclo/seco* isomers I (A) and V (B) in deuterochloroform at about −60°C.

Figure 12. Linear diagram of extinction differences for the irradiation of I in dichloromethane at $-60°C$ (isosbestic point at 294.5 nm, $\varepsilon = 3950$).

and nucleophilic strength of HX. This actually is so: a relatively weak nucleophile like ethanol must be present at very high concentrations to guarantee limiting conditions while for cyclohexylamine, a small excess relative to the dienone is already sufficient to trap the intermediate completely. Piperylene proves to be inactive as a common quencher[24] of ketone triplets.

MORE INFORMATION FROM 6-PHENYL-6-METHYLCYCLOHEXA-2,4-DIENONE[25]

An important difference between I and 6-phenyl-6-methylcyclohexa-2,4-dienone (II) is that the former is symmetric while the latter is not. The foregoing study of the photochemistry of I has shown that the reactant is related to VII and the transient is connected with V (see *Chart 4*). The photochemistry of II is expected to be more complex (*Chart 5*). By light induced *cyclo/seco* isomerization, II should be linked with both the Z,E dienylketene VIII and the Z,Z dienylketene IX; addition of a nucleophile

Chart 5

would transform VIII to X and IX to XI, provided no isomerization occurs at the transient and/or the product stage, and provided the addition would take place again at the 1,2 position of the dienylketenes, respectively. As far as the stereochemistry of the structural changes is concerned, II is therefore a better informant than I.

To ensure correct assignment of the product, all four *N*-cyclohexylamides X, XI, XII and XIII (X = NH—C$_6$H$_{11}$) (see *Chart 5*) have been synthesized in a constitutionally as well as stereochemically unambiguous manner[26]. Before tackling the product problem we should take a glance at the transient. In analogy to I, low temperature photolysis affords thermoreversible ring opening of II as established by low temperature spectroscopy (*Figures 13 to 15*)[13d]. The half-life of the transient has increased now to 95 minutes at −15.4°C.

The composition of the product obtained by irradiation of an ethanol solution of II depends on the wavelength used. 365 nm light effects *a spectroscopically simple reaction (Figure 16)*; the corresponding u.v. spectra intersect at an isosbestic point, and the related diagram of extinction differences is linear. The reaction with 313 nm light is characterized by absorption curves without an isosbestic point and by a non-linear diagram of extinction differences—that is the photoreaction *spectroscopically* is *not at all simple*. That the complexity is due to the additional occurrence of *one* spectroscopically recognizable reaction step follows from the linear diagram of

Figure 14. Electronic spectroscopic evidence of periodic cycle of iso-merization: II → VIII/IX → II → VIII/IX in methylcyclohexane/iso-pentane (1:4). A: solution of II at room temperature; B: at −189°C; C: after irradiation with 365 nm light; D: after intermediate warming up to room temperature; E: after recooling to −189°C; F: after irradiation with 365 nm light.

Figure 13. Electronic absorption spectra of the *cyclo/seco* isomers II (————): at room temperature, (------): at −189°C and VIII/IX (·······): at −189°C in methylcyclohexane/iso-pentane (1:4).

Figure 15. Infra-red spectroscopic evidence of periodic cycle of isomerization: II → VIII/IX → II in chloroform at −65°C. A: solution of II; B: after irradiation with light of wavelengths > 340 nm; C: after intermediate warming up to room temperature and recooling to −65°C.

Figure 16. Irradiation of II in ethanol at room temperature with 365 nm light. A: electronic absorption spectra intersecting at an isosbestic point (306 nm); B: linear diagram of extinction differences.

300

Figure 17. Irradiation of II in ethanol at room temperature with 313 nm light. A: electronic absorption spectra non-intersecting at an isosbestic point; B: linear diagram of quotients of extinction differences; C: non-linear diagram of extinction differences.

Figure 18. Linear diagram of extinction differences for the irradiation of II in ethanol at room temperature consecutively with 365 (————) and 313 nm light (————).

quotients of extinction differences (*Figure 17*). Consecutive irradiation with 365 and 313 nm light suggests a secondary change of a primary product (*Figure 18*). On irradiation with 365 nm light, X and XI are produced in comparable quantities whereas after prolonged treatment with 313 nm light only XI can be isolated (*Chart 6*).

The complex product is preceded by a binary transient. The low temperature n.m.r. spectrum (*Figure 19*) shows signals for two stereoisomeric dienyl-ketenes and the linear diagram of extinction differences (*Figure 20*) excludes

Chart 6

Figure 19. N.m.r. spectra of the *cyclo/seco* isomers II and VIII/IX. A: solution of II in deutero-chloroform at room temperature; B: after irradiation with light of wavelengths > 340 nm at about −60°C; C: after irradiation of a solution of II in deuterochloroform/deuterobenzene (3:1) at about −60°C with light of wavelengths > 340 nm; D: after warming up to room temperature.

303

Figure 20. Linear diagram of extinction differences for irradiation of II in dichloromethane at −60°C.

a secondary photoisomerization at the transient stage. *Chart 7* presents a summary of the case under discussion: it implies that the protic nucleophile not only determines what sort of derivative of 6-phenylhepta-3,5-dienoic acid is formed, but also influences its quantum yield and the relative proportion of its two stereoisomers. Under limiting conditions—different for any individual cyclohexa-2,4-dienone and protic nucleophile, respectively— the quantum yield at 25°C in the present example amounts to 0.55[27] while X and XI are formed in a ratio of 0.56 independently of the wavelength (365 or 313 nm) used[13d].

By the way, the light induced transformation of a linearly conjugated cyclohexadienone to a derivative of a carboxylic acid passes through a short lived transient besides the dienylketene. The characteristic absorption of the dienylketenes VIII and IX (*Figure 13*) is not to be seen if a methylcyclohexane/isopentane solution of II in the presence of cyclohexylamine is irradiated with the appropriate light at −189°C; a new absorption with a maximum at 465 nm arises instead[28]. On warming, it disappears while the *N*-cyclohexyl amides X and XI (X = NH—C_6H_{11}) are formed. If on the *other hand the above solution is flash photolysed at* −150°C, *oscillographic*

304

Chart 7

traces of the dienylketenes and of the extra transient are easily distinguished. Spectrophotometric point by point scanning shows an absorption maximum for the new species at about 460 nm[29]. The additional transient ranks between the dienylketenes and the amides. It may be formulated as the respective enols (*Chart 8*) and considered to be the kinetically controlled adduct that finally rearranges to the thermodynamically controlled product (*Chart 9*)

The photochemical *cyclo/seco* isomerization of II is stereoselective, but

Chart 8

not as much here as in other examples[30], and not as extreme as has been generally assumed to be the case by other workers[33] in the field. To use stereochemistry as a probe for exploring structurally the energy profile of a reaction is not without pitfalls, but we would still like to know how the photoreactive excited cyclohexa-2,4-dienone goes over to the dienylketenes. Is there any bifunctional intermediate or 'a range of molecular conformations which operationally behaves as a true intermediate'[34, 37] between them?

305

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          ┌~~~~~~~~~~~~~~~~→ Reactant ◄──────────┐
          │                   ↕│ hν             │
          │          Initially excited cyclohexa-2,4-dienone
          │                   ↕                 │
          └~Photoreactive excited cyclohexa-2,4-dienone
                              ↕                 │
                       ('Biradical')────────────┤
                              ↓                 │
                       Dienylketene  ───────────┘
                              ⇅
                  Kinetically controlled adduct
                              ↓
             Thermodynamically controlled adduct
                      ≡ Final product
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Chart 9

Unfortunately we do not have available any result of a 'practical experiment', or of a 'theoretical experiment', either.

So we can merely speculate! On the one hand orbital overlap arguments suggest stereoselective ring opening for each of the two non-planar conformers [see loc. cit. ref. 35(a)]. On the other hand, according to our experience[13e, 35b], $\pi^\star$,n-excited carbonyl compounds, having at least one adjacent carbon atom with four ligands, intermediately afforded bifunctional species. The latter more or less lose their configurational integrity, leading to product formation which is either only partially or not at all stereoselective. But where do we know the participation of a $\pi^\star$,n-excited cyclohexa-2,4-dienone from? 6-Acetoxy-2,4,6-trimethylcyclohexa-2,4-dienone (III) will give the answer.

THREE ROUTES FROM VARIOUS ELECTRONIC STATES OF 6-ACETOXY-2,4,6-TRIMETHYLCYCLOHEXA-2,4-DIENONE[31]

Independently of the wavelength (365 or 313 nm) of the light used, irradiation of III in methanol solution furnishes three isomeric methyl esters (*Chart 10*). Two of them (XIV and XV) are stereoisomeric 1,2-adducts, the third ester (XVI) has the constitution of a 1,6-adduct. They are formed in a *spectroscopically simple photoreaction* (*Figure 21*) in yields of 93, 2 and 5 per cent respectively. *Figures 22* and *23* present low temperature spectroscopic evidence for the thermoreversible ketene production[13a]. The half-life of this transient in an aprotic solvent is comparatively short (< 1 min at $-75°$C). A protic nucleophile has to be present in relatively high concentration in order to prevent a waste of light quanta by return to III. The limiting value of quantum yield ($\Phi_{\mathrm{III}}^{\mathrm{III}} = 0.42$)[36] is only reached here by a 3000-fold excess of cyclohexylamine relative to the dienone, and cannot be obtained at all in neat methanol.

The picture changes dramatically if the photochemical reaction is carried out in trifluoroethanol or on silica gel in place of methanol. The related diagrams of extinction differences and of quotients of extinction differences for 365 nm light at room temperature are non-linear and linear, respectively

Chart 10

Figure 21. Irradiation of III in methanol at room temperature. A: electronic absorption spectra for the reaction caused by 313 nm light (isosbestic point at 267 nm); B: linear diagram of extinction differences for irradiation with 313 or 365 nm light, respectively.

307

Figure 22. Electronic absorption spectra of the *cyclo* isomer III (–––––) and its corresponding *seco*-isomeric transient (······) in methylcyclohexane/isopentane (1:4) at −189°C.

(*Figure 24*). This suggests that the total reaction consists of *two* partial steps recognizable by u.v. spectroscopy.

Product isolation followed by gas–liquid chromatography and product identification managed by spectroscopic and chemical methods lead to the

Chart 11

Figure 23. Infra-red spectroscopic evidence of a periodic cycle of *cyclo/seco/cyclo* isomerization in Nujol at − 156°C. A : suspension of III : B : after irradiation with light of wavelengths > 340 nm : C : after intermediate warming up and recooling.

details of *Chart 11*, which are the same for 313 nm light. No trace of an ester is formed now! Light induced isomerization of III to XVII[37] precedes the *spectroscopically simple photorearrangement* (*Figure 25*) of XVII to XVIII[38], which can be reverted[39] by 254 nm light. *Chart 12* puts emphasis on the peculiar part played by the system 6-acetoxy-2,4,6-trimethylcyclo-hexa-2,4-dienone in 2,2,2-trifluoroethanol. With rising methyl substitution at the dienone chromophore, the $\pi^\star,\pi$ state goes down in energy. With growing polarity of the solvent and with its increasing ability to take possession of the lone pair electrons at the oxygen atom of the dienone

Figure 24. Irradiation of III in 2,2,2-trifluoroethanol at room temperature with 365 nm light. A: electronic absorption spectra; B: non-linear diagram of extinction differences; C: linear diagram of quotients of extinction differences.

Increase of chromophore substitution	Nucleophile / Dienone	CH$_3$OH or C$_2$H$_5$OH	CF$_3$CH$_2$OH
	I	1 Ester adduct	1 Ester adduct
	II	2 Ester adducts	2 Ester adducts
	III	3 Ester adducts	2 Isomeric ketones

Increase of acidity

Chart 12

310

Figure 25. Photoisomerization of XVII to XVIII in 2,2,2-trifluoroethanol at room temperature with 365 nm light. A: electronic absorption spectra (isosbestic point at 227 nm, $\varepsilon = 6\,000$); B: linear diagram of extinction differences.

Figure 26. Schematic representation of the two stereochemical modes of a $[\sigma_a^2 + \pi_a^2]$-cyclo-addition of a $\pi^\star,\pi$ excited cyclohexa-2,4-dienone.

311

involved in $\pi^\star$,n excitation, the $\pi^\star$,π state will be stabilized and the $\pi^\star$,n state will be destabilized, respectively.

On reflection, the argument proposed by H. Hart[37a]—that irrespective of of the initially excited state reached by absorption, the photorearrangement of III to XVII passes the $\pi^\star$,π photoreactive state—gains weight. The reaction might be viewed as an intramolecular $[\sigma_a^2 + \pi_a^2]$ cycloaddition (*Figure 26*) analogous to the photoisomerizations of 9,11-dehydroergo-sterol[40] and of 9,11-dehydrolumisterol[41] (*Chart 13*), where $\pi^\star$,n-excitation,

Chart 13

III   **XIX**

Chart 14

of course, is absent. By exclusion, therefore, the light induced *cyclo/seco* isomerization of a linearly conjugated cyclohexadienone to a dienylketene transient goes through the $\pi^\star$,n photoreactive state, provided a ring opening of the vibrationally excited electronic ground state of the reactant can be excluded. Fortunately enough, on warming slightly above room temperature, III smoothly rearranges to XIX via [3.3] sigmatropic shift (*Chart 14*).

SYNTHETIC APPLICATION OF THE PHOTOCHEMICAL RING OPENING OF LINEARLY CONJUGATED CYCLOHEXADIENONES

The insight into the reactivity of electronically excited cyclohexa-2,4-dienones gained by the foregoing discussion challenges the organic chemist to apply this synthetic potential. By ring cleavage of a linearly conjugated cyclohexadienone derived from a phenolic precursor, a phenyl ring is eventually split, thereby affording a chain with several functional groups.

Some years ago D. H. R. Barton and the present author[42] adumbrated a

simple synthesis of crocetin and of derivatives of this diapocarotenoid, respectively, in which the new method of light induced *cyclo/seco* isomerization plays the leading role. Preselection of the key photochemical transformation, in combination with the structural characteristics of the symmetric target molecule, practically predestines the synthetic route (*Chart 15*). Two molecules of 2,6-dimethylphenol not only supply twelve out of sixteen carbon atoms of the final chain, but also provide two pairs of methyl branches each growing out from the chain in 1,5 position. The phenolic nature of the starting material permits two molecules to be connected by a still missing link of a four carbon chain thereby producing the critical structure sensitive to light.

Chart 15

Chart 16

313

GERHARD QUINKERT

This goal can be accomplished by C-alkylation of the phenolate with 1,4-dibromobut-2-ene (*Chart 16*). The corresponding product obtained in fair yield, on irradiation in methanol almost quantitatively affords a mixture of stereoisomeric dimethyltetrahydrocrocetins, which on dehydrogenation by means of dichloro-dicyano-*p*-benzoquinone leads to a mixture from which the naturally occurring dimethylcrocetin can be isolated. The synthetic product proves to be identical with an authentic sample of this food colourant[43] in all examined respects (compare u.v. spectra of *Figure 27*).

Figure 27. Electronic absorption spectra of dimethylcrocetin in *n*-hexane at room temperature. A: synthetic product; B: authentic sample.

ACKNOWLEDGEMENTS

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