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Rearrangements of Biradicals With Migration of an Alkyl Group or Hydrogen

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Studies published during the last decade on the rearrangement of biradicals are reviewed. In contrast to monoradicals for which reliably established examples of rearrangements with 1,2-migration of an alkyl group or hydrogen are unknown, such rearrangements have been observed with biradicals. Data on the types of rearrangements of biradicals with 1,2-migration of an alkyl group and 1,2-, 1,4-, and 1,5-migrations of hydrogen from carbon to carbon or from carbon to oxygen are reviewed. The available data on the mechanisms of the rearrangements are discussed.
The bibliography includes 65 references.

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I. INTRODUCTION

The study of the rearrangements of organic radicals constitutes a comparatively new branch of chemistry, The results obtained in this field have been described in a number of reviews[1-4]. As far as we are aware, no single review has been specially devoted to the rearrangements of biradicals. Nevertheless such somewhat exotic compounds can yield unique results[5]. Indeed, the study of the rearrangements of biradicals yielded results of fundamental importance both for synthetic organic chemistry and particularly for the understanding of the chemical properties of biradicals and for their comparison with those of monoradicals. We believe that the most interesting and newest feature in this field is the observation of rearrangements of biradicals with 1,2-migration of an alkyl group and hydrogen. Such rearrangements are unknown in the chemistry of monoradicals, although 1,2-migrations of hydrogen or the methyl group have been postulated in many investigations. However, the reactions usually described in such reports can be given an alternative interpretation which does not involve the above rearrangements[1-4,6,7]. Unusual types of rearrangements were described for the first time for biradicals generated photochemically but subsequently they were also noted in biradicals obtained by thermal and other procedures. Thus the ability of biradicals to undergo a rearrangement is probably a general property.

The field of rearrangements is still very new and a significant proportion of the known examples have been described only in "Letters to the Editor" and in brief communications. There are very few experimental data concerning the mechanisms of the observed reactions. Nevertheless the ability of biradicals to undergo rearrangements unknown in the chemistry of monoradicals must apparently be regarded as established.

In contrast to the rearrangements in monoradicals, which proceed according to the formal mechanism[4]

$$\underset{(I)}{\dot{A}-(B)_n-\overset{X}{\overset{|}{C}}} \xrightarrow{\text{rearrang.}} \underset{(II)}{A-(B)_n-\dot{\overset{X}{\overset{|}{C}}}} , \qquad (1)$$

where the migrating species (X = phenyl, halogen, hydrogen, etc.) forms a bond with the atom having an unpaired electron and therefore radical (I) isomerises to radical (II), which is usually more stable, the rearrangements of biradicals proceed in many cases in such a way that all the electrons in the product may be paired, for example in accordance with the following formal mechanism:

$$\cdot O-\overset{CH_3}{\overset{|}{\underset{R}{\underset{|}{C}}}}-CR'=CR''-O\cdot \xrightarrow{\text{rearrang.}} O=\overset{CH_3}{\overset{|}{\underset{R}{\underset{|}{C}}}}-CR'-\underset{R''}{\underset{|}{C}}=O . \qquad (2)$$

It has been suggested in some studies that the formation of compounds of this kind constitutes one of the driving forces of the rearrangement of biradicals.

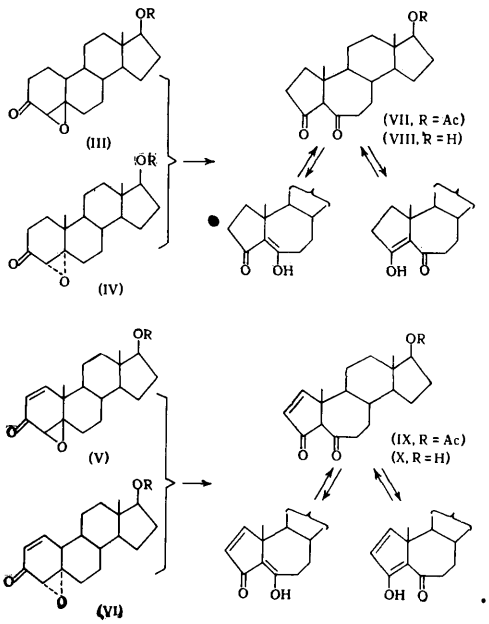
II. REARRANGEMENTS WITH 1,2-MIGRATION OF AN ALKYL GROUP

Rearrangements with 1,2-migration of an alkyl group have been observed in biradicals generated photochemically in systems with both $n-\pi^*$-excitation ($\alpha\beta$-epoxyketones) and with $\pi-\pi^*$-excitation (arylethylenes), thermally by the decomposition of the peroxides of substituted lactones, and also by the addition of triplet methylene to olefins.

a. Photochemical Rearrangement of $\alpha\beta$-Epoxyketones

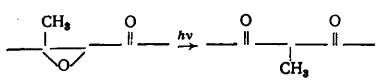
A photochemical rearrangement with 1,2-migration of an alkyl group was first described in 1962 for steroid epoxyketones[6]. Thus saturated and unsaturated diastereomeric 4,5-epoxy-3-oxosteroids (III)–(VI) isomerise in

high yields to compounds (VII)—(X) respectively on irradiation with ultraviolet light regardless of the configuration of the epoxy-ring in the molecule (see Scheme 3).



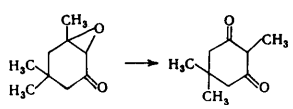
(3)

Soon a similar rearrangement was established in simpler examples: 3,4-epoxy-4-methyl-2-pentanone, isophorone oxide, and the stereoisomeric pulegone oxides[8]. In all cases products of isomerisation with 1,2-migration were accompanied by other compounds which can be described by the following formal scheme in the simplest instance:



(4)

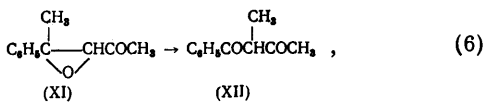
The reaction mechanism was not discussed in these first studies. However, the unusual sequence of groups in terms of their capacity for migration was pointed out[8], namely it was found that the methyl group migrates more readily in these systems than does the phenyl group. Thus isophorone oxide undergoes photochemical isomerisation, with 1,2-migration of the methyl group, to 2,5,5-trimethylcyclohexa-1,3-dione:



(5)

On the other hand, on prolonged irradiation with ultraviolet light, 2,3-epoxy-5,5-dimethyl-3-phenylcyclohexanone, which is an analogue of isophorone oxide, did not yield the isomerisation product 5,5-dimethyl-2-phenylcyclohexa-1,3-dione with 1,2-migration of the phenyl group. A similar difference between the capacities for migration of the methyl and phenyl groups was subsequently observed in a number of other instances[9]. This increase of capacity for migration, $C_6H_5 \ll CH_3$, conflicts with the rules observed in the rearrangements of radicals[3,4]. A molecular orbital calculation showed a decrease of the ease of 1,2-migration from carbon to carbon in the series carbonium ion > free radical > carbanion, the energy barrier being higher for the migration of an alkyl group than for the migration of an aryl group[10].

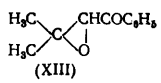
Zimmerman et al.[9] were the first to express the view in 1964 that the photochemical conversion of $\alpha\beta$-epoxyketones into β-diketones involves a rearrangement of the biradicals with 1,2-migration of an alkyl group. According to their data[9], 3,4-epoxy-4-phenyl-2-pentanone (XI) isomerises photochemically with 1,2-migration of the methyl group, forming 3-benzoyl-2-butanone (XII) as the main product (yield 25%):



(6)

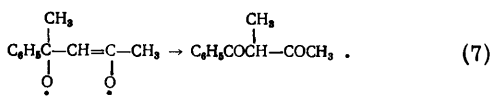
(XI) (XII)

while the isomeric compound



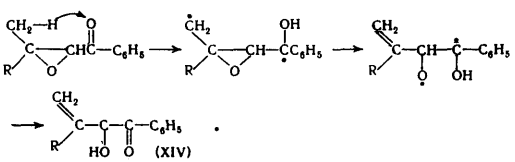
(XIII)

does not isomerise with 1,2-migration of the methyl group. The author suggested that in both cases there is $n-\pi^*$ excitation of the carbonyl group but in compound (XI) there is a greater localisation of the excited electron (π^*) in the carbonyl group and hence a greater probability of β-elimination with homolytic dissociation of the epoxy-ring at the C_α—O bond with the ultimate formation of a biradical, which isomerises:



(7)

In compound (XIII) the excited electron is delocalised over both the phenyl and carbonyl groups and is less accessible. 1,5- and 1,4-migration of hydrogen with formation of compound (XIV) then takes place intramolecularly†:



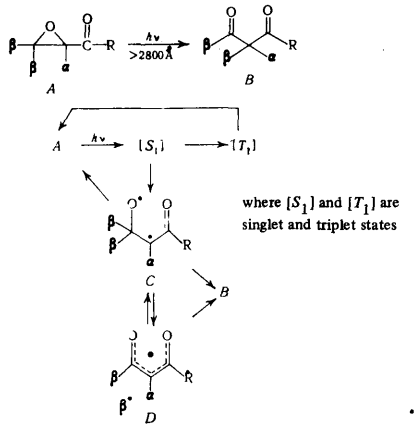
(8)

(XIV)

The homolytic mechanism of the photochemical rearrangement of $\alpha\beta$-epoxyketones to β-diketones is now widely recognised[11,12]. Zimmerman et al.[9] did not put forward any views concerning the mechanism of the methyl migration stage itself. This problem was discussed by other workers[11,12]. Markos and Reusch[11] considered the general case of the rearrangement of the $\alpha\beta$-epoxyketone *A* to the β-diketone *B* and described the mechanism of this rearrangement in terms of Scheme 9. Since the rearrangement of epoxyketones is not sensitive to the presence of oxygen or to a change in the nature of the solvent and since the addition of known triplet state quenching agents (piperylene and 2,5-dimethylhexa-2,4-diene) does not affect the rate or mode of the rearrangement, one may conclude that the intermediate biradical species *C* is formed preferentially from the singlet state $[S_1]$. The low quantum yield of this rearrangement, for example 0.03 for the conversion of 3,4-epoxy-4-methyl-2-pentanone into 3-methylpenta-2,4-dione, indicates either a low efficiency of the $[S_1] \rightarrow C$ transition or the competitive formation of the oxiran ring from *C*, which is unfavourable for the isomerisation. The authors believe that the

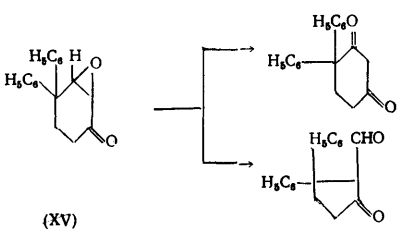
† For the formulation in terms of the symbols employed by the authors, see the Scheme in Ref. 9.

migrating group is of a radical type and that the migration can proceed either via a fragmentation (two-stage) mechanism with formation of a radical pair *D* in a solvent cage or via a synchronous (single-stage) mechanism with a transition state close to *D*. By experimental study of a number of rearrangements, the authors obtained evidence in support of both the intermediate formation of a radical pair and of the synchronous mechanism:



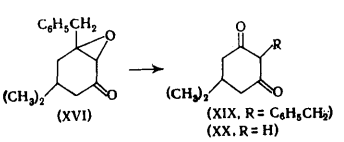
(9)

The above view concerning the rearrangement led the authors to the hypothesis that a particularly high capacity for migration should be observed for the benzyl and diphenylmethyl groups as β-substituents. This was confirmed by studying the rearrangement of 2,3-epoxy-4,4-diphenylcyclohexanone (XV) and 3-benzyl-2,3-epoxy-5,5-dimethylcyclohexanone (XVI). Thus irradiation of a solution of (XV) in ether for 3.5 h led to 50% conversion of the initial compound and the formation of a high yield of a mixture of (XVII) (1,2-migration of hydrogen in the intermediate biradical) and (XVIII) (1,2-migration of the alkyl-substituted diphenylmethyl group) in proportions of 1 : 4:



(10)

Irradiation of (XVI) yields the rearranged compound (XIX) as the main product (20%), but the reaction is accompanied by the formation of a significant amount of decomposition products [(XX), dibenzyl, and other products].

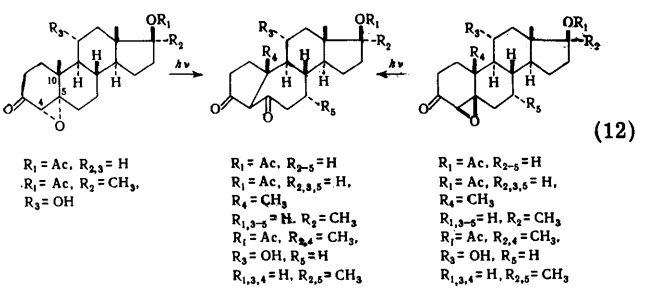


(11)

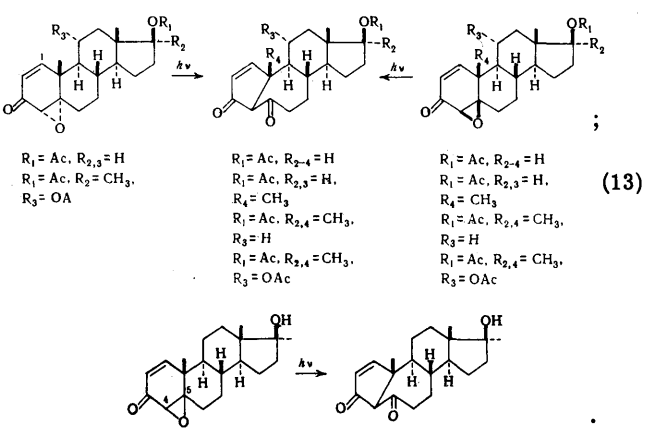
The formation of at least some fragmentation products is attributed to the conversion of *C* (Scheme 9) into the radical pair *D* and the liberation of the comparatively stable benzyl radical from the cage. By comparing their own results with data already available[8,9,12], the authors obtained the following sequence of groups in terms of their capacity for migration: diphenylmethyl and benzyl > hydrogen > methylene > methyl ≫ phenyl. The authors believe that the position of hydrogen in this series is evidence against the mechanism with fragmentation and formation of radical pairs, since a hydrogen atom is usually harder to form than an alkyl radical. Thus the migration capacity series of the groups is best explained by the synchronous mechanism of their migration in the biradical.

A team of investigators[12] who studied the photochemical conversion of a wide variety of steroid epoxyketones into β-diketones believe that this is a widely used and elegant method of synthesising β-diketones (see the references in the paper of Werli et al.[12] to other papers and reports by the authors).

These workers studied the conversion of epoxyketones with a saturated chromophoric keto-group (Scheme 12) into β-diketones on illumination with the unfiltered light of a mercury lamp ($n-\pi^*$-excitation). Unsaturated Δ^1-epoxyketones rearrange to β-diketones only on illumination with monochromatic light at λ = 253.7 ($\pi-\pi^*$ excitation) (Scheme 13).



(12)



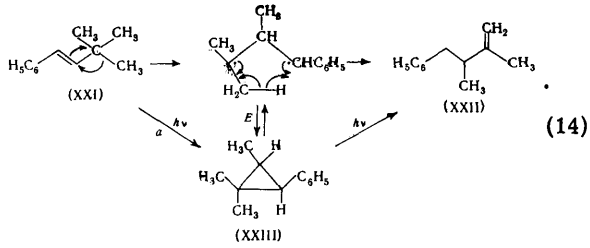
(13)

Werli et al.[12] noted that, although the rearrangement of saturated epoxyketones via Scheme 12, which involves the $n-\pi^*$ excitation, differs from the rearrangement of unsaturated epoxyketones which are unaffected by the $n-\pi^*$ excitation, selective $\pi-\pi^*$ excitation leads to an analogous rearrangement to β-diketones via Scheme 13.

The authors prefer the synchronous mechanism of the migration of an alkyl group in the biradical and note that the migrating group can be an alkyl group or hydrogen but not phenyl.

b. Photochemical Rearrangement of 3,3-Dimethyl-1-phenylbutene

The photochemical rearrangement of 3,3-dimethyl-1-phenylbutene (XXI) to 2,3-dimethyl-4-phenylbutene (XXII) via Scheme 14 was investigated[13]:



(14)

The authors noted[13] that they were first to observe the light-induced 1,2-migration of the methyl group in a hydrocarbon. The importance of this example of a rearrangement is that, whereas the $n-\pi^*$ excitation of epoxyketones can lead to the development of both heterolytic and homolytic processes[14,15], the comparatively low amount of the "ionic" character of the $\pi-\pi^*$ singlet or triplet states of alkyl- and aryl-substituted propenes is to a large extent responsible for the possibility of a homolytic process. In this case synchronous migration of the methyl group and cyclisation with formation of compound (XXIII) (pathway *a*) is possible. Indeed the *cis*- and *trans*-isomers of (XXIII) are readily converted into compound (XXII) by a photochemical reaction. The mechanism involving the formation of a common transition species, probably of type *E*, is also not ruled out. This hypothesis concerning the rearrangement entails the assumption of 1,4-migration of hydrogen in the transition state *E*. The possibility of such migration of the hydrogen atom in the related $n-\pi^*$- and $\pi-\pi^*$-states has been assumed in a number of investigations (see Section III of the present review).

c. Interaction of Tritium-labelled Methylene with *trans*-But-2-ene

The reaction of the photolytically generated methylene with *trans*-but-2-ene in the gas phase leads to the formation of various compounds containing five carbon atoms, among them a number of pentenes and 1,2-dimethylcyclopropane[6]. At higher pressures pentenes are also detected, which cannot be explained by the reaction with singlet methylene[17]. The formation of *cis*-pent-2-ene, 2-methylbut-1-ene, and 3-methylbut-1-ene is therefore attributed to the reaction with triplet methylene. It has been suggested that the first reaction step is the addition of methylene to the double bond according to the following scheme:

$$CH_2{:} + CH_3CH{=}CH{-}CH_3 \rightarrow CH_3\underset{\cdot}{C}H{-}\underset{\cdot}{C}HCH_3 \quad (15)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2$$

followed by a rearrangement of the biradical.

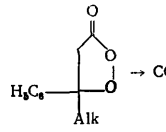
In order to investigate the mechanism of this rearrangement, the interaction of tritium-labelled methylene with *trans*-but-2-ene was studied[16]. In this case the biradical formed via Scheme 15 has the structure $CH_3-HCT-\underset{\cdot}{C}H\underset{\cdot}{C}HCH_3$ and the different modes of rearrangement should lead to different locations of tritium in the reaction products. The authors investigated the structures of two products important for the determination of the rearrangement mechanism: 3-methylbut-1-ene and *cis*-pent-2-ene. 1,2-Migration of the methyl group in the triplet biradical should lead to the formation of $(CH_3)_2CHCH{=}CHT$ and *cis*-$CH_3CHTCH{=}CHCH_3$, while $CH_3\underset{|}{C}H{=}CH_2$ might have been formed by 1,4-migration of hydrogen. The authors also examined the possible structures of the product generated by other reaction mechanisms (the closure of the three-membered ring and its subsequent opening at other bonds, the abstraction of hydrogen from but-2-ene by methylene, and subsequent recombination of the radicals). It was found that 3-methylbut-1-ene contained tritium in the alkyl and olefinic parts of the molecule, which indicates the operation of more than one mechanism in its formation. The presence of tritium-containing moieties in the olefinic part of the molecule suggests that the 1,2-migration of methyl plays an important role in the formation of 3-methylbut-1-ene. The authors believe that the formation of a double bond in this case provides an additional driving force for the rearrangement in the 1,3-biradical. Under the conditions investigated, *cis*-pent-2-ene did not contain tritium in the olefinic part of the molecule. This can be accounted for both by the mechanism involving 1,2-migration of the methyl group and by the hypothesis of the recombination of radicals. According to the authors, the fact that 3-methylbut-1-ene is not formed in the presence of oxygen and the product is propene constitutes additional evidence for the formation of the biradical. The propene obtained in the reaction of triplet CHT with *cis*- and *trans*-but-2-enes has the structure $CH_3CH{=}CHT$, which is consistent with the product expected via Scheme 16:

$$CH_3\underset{\cdot}{C}HCH_3 + O_2 \rightarrow CH_3{-}\underset{\cdot}{C}H\underset{\cdot}{C}HCH_3 \rightarrow CH_3CH{=}CHT + \text{oxidation products.} \quad (16)$$
$$\quad CHT \qquad\qquad\quad CHT\ \ O_2$$

d. Rearrangement with 1,2-Migration of an Alkyl Group in Biradicals Generated by the Thermolysis of Organic Compounds

A series of publications appeared very recently[18-21] on the 1,2-migration of alkyl groups in biradicals which were not generated photochemically but by the thermolysis of β-alkyl-β-phenyl-β-peroxypropiolactones[18-20] and also 4,4,6,6-tetramethyl-1-oxaspiro[2,3]hexan-5-one[21].

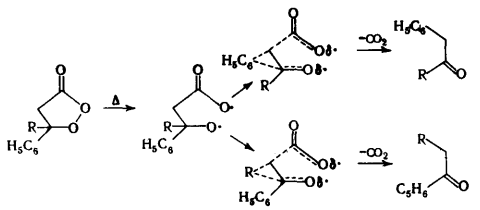
It has been shown[18] that CO_2 is evolved and ketones are formed with 1,2-migration of the alkyl or phenyl group in the thermolysis of β-alkyl-β-phenyl-β-peroxypropiolactones:



$$\rightarrow CO_2 + C_6H_5COCH_2Alk + C_6H_5CH_2COAlk\ . \quad (17)$$

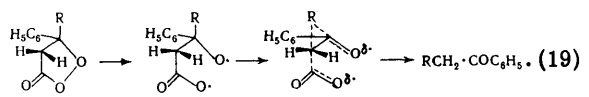
Comparison of a number of examples showed that the substituents can be arranged in the following sequence in terms of decreasing capacity for migration: isopropyl > benzyl > ethyl > methyl > phenyl. The authors drew attention to the fact that there are no instances in the literature of the preferred migration of the alkyl group compared with the phenyl group in thermally generated radicals. On the other hand, such

preference was observed in the 1,2-migration of a substituent in the photolysis of $\alpha\beta$-epoxyketones. The study of the kinetics of the thermal decomposition of β-alkyl-β-phenyl-β-peroxypropiolactones showed that the reaction is described by equations for first-order kinetics and the activation parameters are independent of the nature of the β-alkyl group. The authors put forward the following mechanism for this reaction:



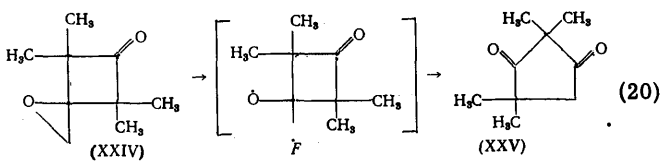
(18)

In subsequent studies[19,20] stereochemical investigations confirmed the hypothesis of the formation of non-classical bridge-type radicals. In particular, it was shown[20] in 1971 that the thermolysis of the optically active peroxide where R = $CH(CH_3)CH_2C_6H_5$ yields the optically active ketone $RCH_2COC_6H_5$ with complete retention of the configuration of the migrating group. The authors represent the stereochemical mechanism of this rearrangement as follows:



(19)

The thermolysis of 4,4,6,6-tetramethyl-1-oxaspiro-[2,3]hexan-5-one (XXIV) was carried out in a quartz tube at 650°C; the main reaction product was 2,2,4,4-tetramethylcyclopentane-1,3-dione (XXV):

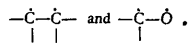


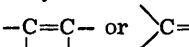
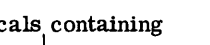
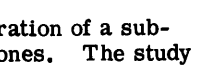
(20)

The authors suggest[21] that the reaction proceeds via the homolytic opening of the oxiran ring with formation of the biradical F the rearrangement of which with 1,2-migration of the alkyl group leads to the formation of the diketone (XXV).

III. REARRANGEMENTS WITH MIGRATION OF HYDROGEN

The migration of hydrogen was studied in biradicals with different relative positions of the radical centres: (a) $\alpha\beta$-homobiradicals and $\alpha\beta$-heterobiradicals with radical centres at adjacent atoms; these are biradicals incorporating the groups



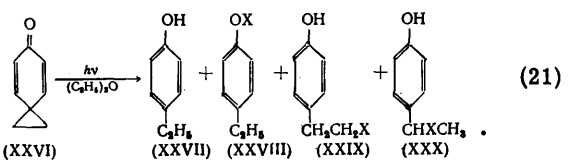
They are formed in the photolysis of the double bonds  or ; (b) $\alpha\gamma$-homobiradicals containing radical centres in the 1,3-positions: ; biradicals of this type are usually formed in the photolysis of compounds incorporating the cyclopropane ring; (c) $\alpha\omega$-heterobiradicals incorporating, for example, the group ; such biradicals are formed in the photochemical decomposition of *endo*-peroxides.

We shall examine the available data in the following sequence: instances of 1,2-migration of hydrogen first and then examples of migration from the fourth and fifth carbon atoms to a radical centre at a carbon or oxygen atom.

1. MIGRATION OF HYDROGEN FROM CARBON TO CARBON

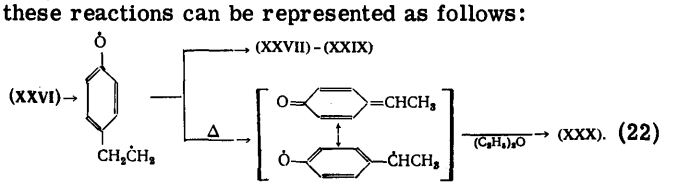
a. 1,2-Migration of Hydrogen

The photolysis of the spirodienone (XXVI) in ether[22] yields a series of *para*-substituted ethylphenols (XXVII)–(XXX), two of which [(XXIX) and (XXX)] contain the residue of an ether molecule $CH_3\dot{C}HOCH_2CH_3$ (X) in the α- and β-positions of the alkyl group:



(21)

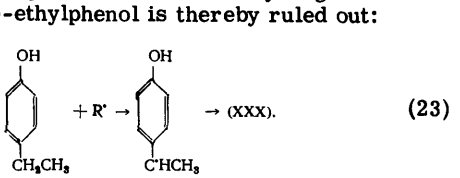
The overall yield of products (XXVII) and (XXVIII) is 15–25%. The phenols (XXIX) and (XXX) are formed in the proportion 37 : 63. The radical mechanism of the reaction is confirmed by the fact, when illumination is switched off, the reaction ceases and when the light is switched on again the reaction proceeds at the previous rate. This confirms the nature of the products, incorporating the ether residue, formed after the abstraction of hydrogen from the ether molecule. The mechanism of these reactions can be represented as follows:



(22)

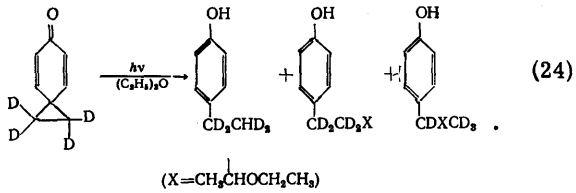
The authors believe that the intermediate quinonoid structure stabilises the transition state corresponding to the rearranged radical as a result of pairing all the electrons. The structure of the products isolated was demonstrated both by identification with compounds obtained by a specific synthesis and by ^1H NMR and mass spectrometry.

The same reaction was investigated in various solvents[23] (toluene, acetonitrile, t-butyl alcohol, and benzene). In all the solvents except toluene only polymers were obtained. It was shown that the products (XXIX) and (XXX) are not formed by the thermal process (100° and 200°C). The authors note that the proportions of these substances are independent of the initial concentration of compound (XXVI). This is evidence of a common intermediate species which leads to both substances; the formation of compound (XXX) as a result of a secondary reaction involving the abstraction of hydrogen from the α-position of *p*-ethylphenol is thereby ruled out:



(23)

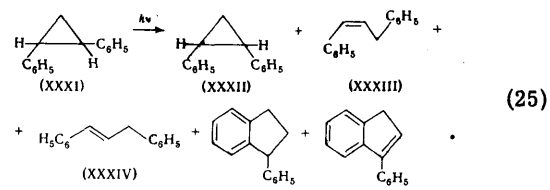
The study of the deuteriated analogue (XXVI) yielded convincing evidence for the rearrangement in the biradical[24]:



(24)

The distribution of deuterium in the reaction products was investigated by ^{1}H NMR and mass spectrometric methods. The authors showed that at least 95% of deuterium is retained in the products after the reaction. The distribution of deuterium in the products agrees almost exactly with predictions on the assumption of a biradical mechanism involving 1,2-migration of hydrogen (deuterium) rather than a series of intermolecular reactions with abstraction of hydrogen. The ratio (XXX)/(XXIX) not only does not increase but actually decreases on photolysis of (XXVI) in the presence of (XXVII), which confirms the intramolecular mechanism of the 1,2-migration of hydrogen.

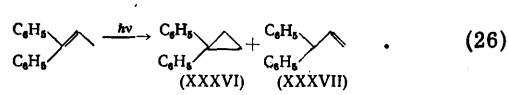
The hypothesis of the 1,2-migration of hydrogen in the biradicals has been put forward in a number of studies[25-27] to account for the mechanism of the formation of the individual products in reactions involving the opening or formation of the cyclopropane ring. Irradiation of *trans*-1,2-diphenylcyclopropane in benzene solution[25] yields a series of products with the following structures:



(25)

The authors believe that these substances are formed via the biradical C_6H_5 C_6H_5 (XXXV). The formation of compounds (XXXIII) and (XXXIV) from (XXXV) requires the hypothesis of 1,2-migration of hydrogen. The structure of compound (XXXIII) was demonstrated by its reduction to 1,3-diphenylpropane and by examining the mass and ^{1}H NMR spectra. In addition, an independent synthesis of compound (XXXIII) was achieved. Irradiation of (XXXIV) yields, apart from other products, compounds (XXXI) and (XXXII), which also requires the assumption of 1,2-migration of hydrogen in the biradical.

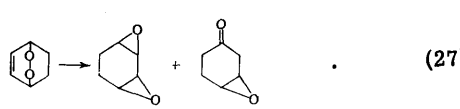
A similar example was quoted in another investigation[26]:



(26)

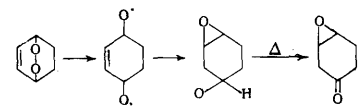
The formation of compound (XXXVI) can be explained by 1,2-migration of hydrogen and that of compound (XXXVII) by two 1,2-migrations or one 1,3-migration of hydrogen. However, in the above study a radical mechanism for the reaction was merely postulated without any evidence.

endo-Peroxides of the type of ascaridole yield diepoxides and ketoepoxides on photolysis (or thermolysis)[27]:



(27)

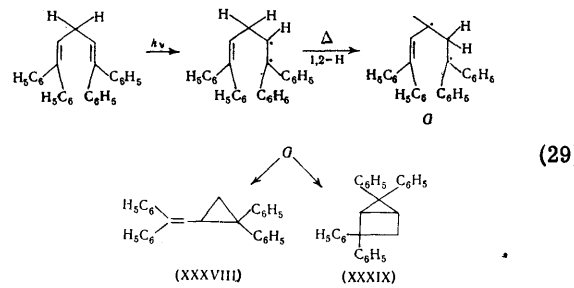
The formation of diepoxides is the normal reaction of compounds of this type. On the other hand, the authors explained the formation of ketoepoxides by a rearrangement in the intermediate biradical with 1,2-migration of hydrogen:



(28)

Since the diepoxides are stable under the chosen conditions, there is no reason to suppose that the formation of ketoepoxides is a result of secondary reactions of the diepoxides.

In one of their latest studies, Zimmerman and coworkers[28] considered the rearrangement of the biradicals formed as a result of the photolysis of 1,1,5,5-tetraphenylpenta-1,4-diene:



(29)

The conversion of the initial diene over a period of 24 h (in t-butyl alcohol solution) is 23%, the yields of compounds (XXXVIII) and (XXXIX) being 12 and 11% respectively.

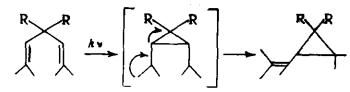
The structure of compound (XXXIX) was confirmed by hydrogenation to 1,1,3,3-tetraphenylcyclopentane. In addition the ^{1}H NMR spectra of (XXXVIII) and (XXXIX) were recorded and confirmed the above structure‡. The hypothesis of 1,2- or 1,5-migration of the hydrogen atom has been used to explain the formation of some of the products of the photolysis of various cyclo-octatrienes[39], but on the basis of the data put forward by the authors it is difficult to tell whether a rearrangement with migration of hydrogen or a stepwise isomerisation of the skeleton with the dissociation or migration of the double bond takes place.

A rearrangement of biradicals with 1,2-migration of hydrogen was noted in the photolysis of cycloalkanones (see Table 1).

b. 1,4- and 1,5-Migrations of Hydrogen

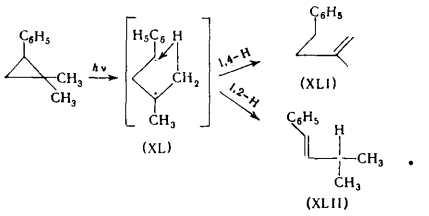
Rearrangements of biradicals with migration of hydrogen to centres in the molecule more remote than the adjacent atom are encountered much more frequently and have been investigated in a number of instances. The study of the opening and closure of the cyclopropane ring

‡ The photochemical rearrangements of cyclic and non-cyclic compounds containing the divinylmethane group, which leads to the formation of the cyclopropane ring in the molecule, for example via the mechanism



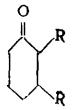
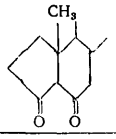
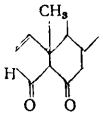
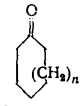
have been called the di-π-methane rearrangements[29-38].

also yielded examples of rearrangement with 1,4-migration of hydrogen in the biradical. 2,2-Dimethyl-1-phenylcyclopropane[40] was irradiated with ultraviolet light for 24 h in hexane solution. The authors postulated the formation of the biradical (XL), where 1,4- and 1,2-, migration of a hydrogen atom via the mechanism



(XL) (30)

Table 1.

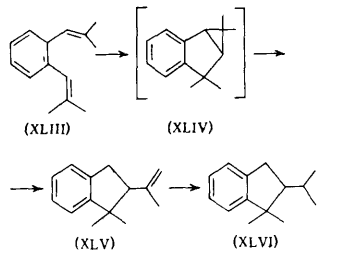
Initial ketone	Reaction conditions	Main products	References (type of migration)
 *cis*- and *trans*-isomers	u.v. (methanol + benzene)	RCH=CCH$_2$CH$_2$CH$_2$CHO (R) *cis*- and *trans*-isomers RCH$_2$CHCH$_2$CH$_2$CH$_2$COOCH$_3$ (R) RCH$_2$CHRCH$_2$CH$_2$CH=C=O	47, 48 (1,5-migration of hydrogen)
	u.v.		12 (1,4-migration of hydrogen)
 n=1,2,3	u.v. (λ=3130 Å)	 n=1,2,3	49 (1,2-migration of hydrogen)
	u.v. (λ=3130 Å)	CH$_3$CH=CHCH$_2$CH$_2$CH$_2$CHO *cis*- and *trans*-isomers CH$_2$=CHCH$_2$CH$_2$CHCHO (CH$_3$)	50 (1,5-migration of hydrogen)

is possible in principle. This results (in the given example) in the formation of 2-methyl-4-phenylbut-1-ene (XLI) with a yield exceeding 80%. On the other hand, the reaction involving 1,2-migration also plays an appreciable role in the case of 2,3-dimethyl-1-phenylcyclopropane. It is interesting to note that, when the isomerisation is carried out in benzene instead of hexane, the yield of the type (XLII) olefin is increased. This leads to the conclusion that benzene sensitises the 1,2-migration of hydrogen in the biradical.

These examples show that, other conditions being equal, the 1,4-migration of hydrogen in the biradical is preferred to 1,2-migration.

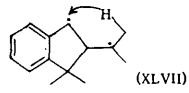
The same authors found[13] that 3,3-dimethyl-1-phenylbut-1-ene isomerises almost completely on photolysis in benzene with 1,4-migration of hydrogen in the intermediate biradical (see Scheme 14).

The authors suggested that the ultraviolet irradiation of *o*-di-isobutenylbenzene (XLIII) results in the formation of the cyclic compound (XLIV) with two ring closures, which is subsequently converted into compound (XLV) with opening of the cyclopropane ring[41]:



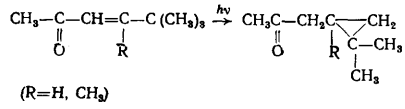
(31)

The structure of the product (XLV) was confirmed by ^{1}H NMR and also by its hydrogenation to (XLVI). The latter was also obtained by an independent procedure. It is suggested that the conversion of (XLIV) into (XLV) proceeds via the intermediate formation of the biradical (XLVII) and subsequent 1,4-migration of hydrogen.



It is noteworthy that in the studies mentioned above[13,40,41] the radical mechanism of the process was merely postulated and the problem of the intramolecular mechanism of hydrogen migration was not always specially considered.

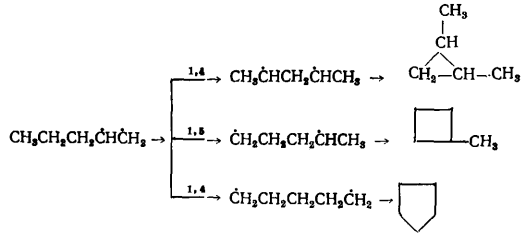
The photochemical conversion of 5,5-dimethyl-3-hex-2-enone into the isomeric ketone via the mechanism



(32)

has been described[42]. The structure of the products was confirmed by ^{1}H NMR and by independent synthesis. Although the authors in fact refrained from discussing the mechanism of the reactions (see Scheme 32), here too one can postulate 1,4-migration of hydrogen in the biradical with subsequent closure of a three-membered ring.

The formation of high yields of cyclic products (methylcyclobutene and dimethylcyclopropane) in the mercury-sensitised photolysis of pent-1-ene has been explained by a combination of 1,4- and 1,5-migration of hydrogen atoms[43]:

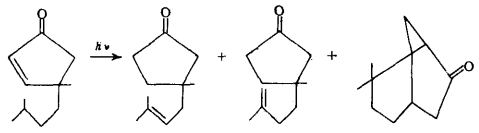


(33)

Cyclopentane is formed (Scheme 33) with greater difficulty (the radical centre moves from a secondary to a primary carbon atom) and therefore the yield of cyclopentane is low (1—2.5%). The yield of methylcyclobutane is 2.5 times greater than the yield of dimethylcyclopropane. Ethylcyclopropane was not found among the products identified, which the authors regard as evidence indicating that 1,2-migration of hydrogen does not occur.

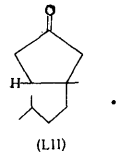
The isomerisation of the biradical with 1,2-, 1,4-, and 1,5-migration of hydrogen is possible in principle in this case, but the results show that 1,2-migration is relatively more difficult in the biradical, while migration to a more remote radical centre proceeds more readily.

Photolysis of 4-isopentyl-4-methylcyclopentenone (XLVIII) ($\lambda \simeq 3300$ Å) yields a mixture of three products (XLIX), (L), and (LI) (Scheme 34), which were isolated by gas–liquid chromatography and characterised by infrared spectroscopy and ^{1}H NMR.[44] In addition the structure was confirmed by a series of chemical reactions:



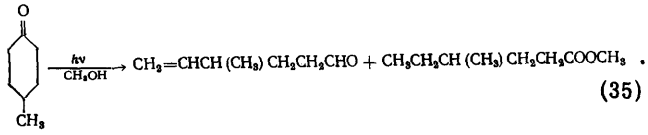
(34)

It is suggested that the formation of all the products can be explained by a sequence of rearrangements with migration of hydrogen via the intermediate biradical (LII) formed as a result of the 1,5-migration of hydrogen in the excited molecule of compound (XLVIII). However, the authors themselves refrained from a more concrete discussion of the mechanism of the formation of the reaction products:


(LII)

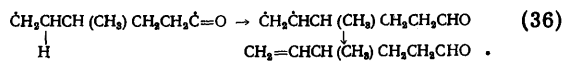
There are reviews[45,46] dealing with photochemical reactions of cycloalkanones. In particular, they deal also with reactions accompanied by rearrangements of biradicals with 1,4- or 1,5-migration of hydrogen atoms.

We shall consider in greater detail the last of a series of new studies[47-51] on the photolysis of cycloalkanones (Table 1), where the authors also devote some attention to the stereochemical aspect of the migration of hydrogen. When 4-methylcyclohexanone is irradiated in methanol solutions[51], products involving the dissociation of the 1,2-linkage are formed via the mechanism



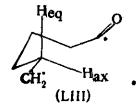
(35)

The formation of the aldehyde is explained by the 1,5-migration of hydrogen in the intermediate biradical:


(36)

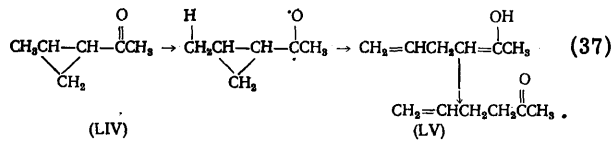
By carrying out the reaction with deuterated analogues, it was possible to establish that 1,5-migration does in fact occur; moreover, having discovered by ^{1}H NMR the configuration of the initial deuteroketones and the distribution of deuterium in the final products, the authors established that there is a preferential (to the extent of 2/3) migration of the hydrogen in the axial position in the initial ketone but 1/3 of the hydrogen in the equatorial position also migrates, i.e. the stereospecificity of the reaction is low.

The authors regard this result also as confirmation of the intermediate formation of the biradical (LIII) with free rotation of the groups:



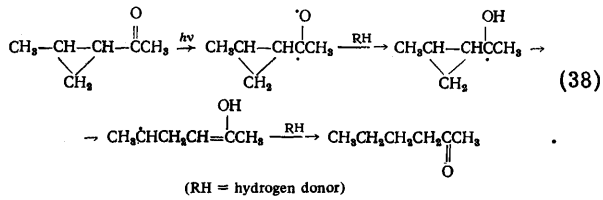
2. MIGRATION OF HYDROGEN FROM CARBON TO OXYGEN

The migration of hydrogen from carbon to oxygen was noted in the biradicals formed photochemically from conjugated cyclopropyl ketones with different structures[52,53]. For example, photolysis of the *cis*-isomer of compound (LIV) yields hex-1-en-5-one (LV) via the mechanism



(37)

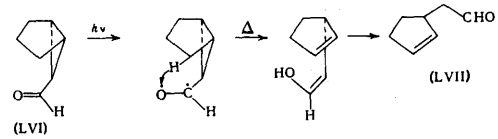
The structure of compound (LV) was established by comparing its ^{11}H NMR spectrum with that of an authentic specimen. The *trans*-isomer of compound (LIV) yields compound (LV) only after preliminary isomerisation to the *cis*-isomer (in pentane), whereas in isopropyl alcohol solution there is only abstraction of hydrogen from the solvent without isomerisation and with formation of aliphatic ketones via the mechanism



(38)

On the other hand, the *cis*-isomer gives rise to compound (LV) in yields up to 70% (determined by gas–liquid chromatography) even in isopropyl alcohol. According to the authors, this means that, when a rearrangement is possible, it proceeds faster than other parallel processes (for example, intermolecular abstraction of hydrogen from the solvent).

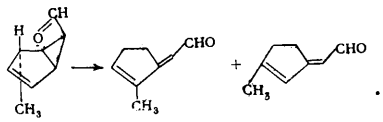
The isomerisation of the bicyclic *endo*-form of the aldehyde (LVI) also involves a rearrangement in the biradical to the extent of 30%:[54]



(39)

The fact that the *exo*-form of (LVI) does not give rise to (LVII) is evidence that the rearrangement proceeds without preliminary ring opening and confirms the necessity of forming a six-membered cyclic transition state which is most favourable for the rearrangement. A similar

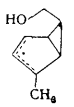
rearrangement was demonstrated also under thermal conditions (130° and 160°C in hexane) when the five-membered ring contains a double bond[55-57], for example:



(40)

(LVIII)

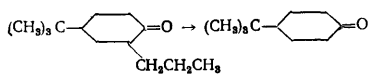
The aldehyde (LVIII) is formed preferentially. It is suggested that the rearrangement proceeds via the biradical (LIX).



(LIX)

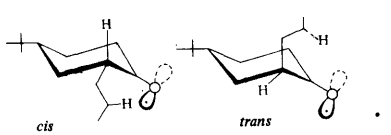
Judging from the previous investigation, this type of hydrogen migration is extremely probable, but Gilbert et al.[55] failed to quote any data which would make it possible to infer in greater detail the mechanism for the formation of the reaction products. In the photolysis of 2,3-epoxy-4,4-diphenylcyclohexanone it proved possible to compare the capacity of the hydrogen atoms and the diphenylmethyl group for migration in the biradical formed[11] (see Scheme 10).

Investigators who studied the photolytic cleavage of *cis*- and *trans*-4-t-butyl-2-propylcyclohexanones noted a significant role of stereochemical factors in the mechanism of the migration of hydrogen from the propyl group to oxygen[58,59]. The *cis*-isomer yields 4-t-butylcyclohexanone as the main product of the intramolecular hydrogen migration:



(41)

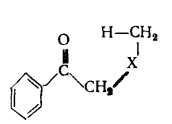
Under these conditions, the *trans*-isomer undergoes only epimerisation, yielding a ketone with the *cis*-configuration as the main product. The formula shows that conditions for the easy formation of a six-membered transition state for the intramolecular migration of hydrogen from carbon to oxygen are created only in the *cis*-conformation of cyclohexanones in the excited state:



cis *trans*

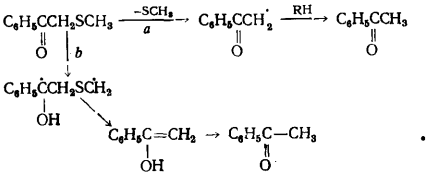
The addition of penta-1,3-diene does not affect the reaction of the *cis*-isomer. According to the authors, this shows that either the reaction proceeds via a singlet state or that cleavage of this type has a rate constant higher than 8×10^{10} s^{-1}.

A number of studies have been made on the photolysis of aliphatic-aromatic ketones with various heteroatoms X in the aliphatic chain:



The behaviour of such compounds depends significantly on the nature of X. Thus, when X = CH_2, O, S, or SO, a rearrangement with 1,5-migration of hydrogen in the triplet state proceeds to some extent, while for X = SO_2 only decomposition occurs.

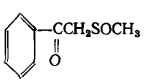
Acetophenone is formed in the photolysis of α-alkylthioacetophenone[60]. Two pathways leading to its formation can be postulated:



(42)

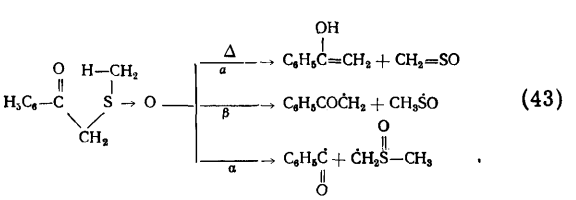
Pathway *a* involves β-elimination of the RS group with subsequent abstraction of hydrogen from a solvent molecule. Pathway *b* involves initial migration of hydrogen in the excited molecule with subsequent β-elimination in the biradical. When the photolysis was carried out in deuterated chloroform, the resulting acetophenone did not contain deuterium, which rules out pathway *a*. On the other hand, the photolysis of $C_6H_5COCH_2SCD_3$ yielded acetophenone with an appreciable deuterium content, which confirms pathway *b*. Separate experiments performed with a mixture of deuterated and non-deuterated starting materials showed that the formation of deuterated acetophenone in the corresponding yield cannot be accounted for by simple deuterium exchange or intermolecular deuterium transfer in the reaction.

Photolysis of the sulphoxide[61]



proceeds with formation of acetophenone, 1,2-dibenzoylethane (dimer), and $CH_3SO_2SCH_3$. The products were identified by gas–liquid chromatography using authentic specimens.

Various ways in which the reaction products can be formed are shown schematically in the original paper:



(43)

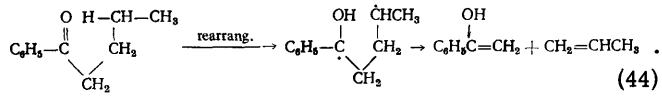
(α-cleavage, β-cleavage).

Judging from the reaction products, the α-decomposition pathway does not play a significant role. It was established that the relative yields of the final products depend significantly on the nature of the solvent. In methanol and acetonitrile the yield of acetophenone does not exceed 30%, while in isopropyl alcohol it reaches 80%, which is explained by the ease of abstraction of hydrogen from isopropyl alcohol. On the other hand, in benzene, which is a weak hydrogen donor, the yield of acetophenone is 67%. The authors believe[61] that in benzene solution acetophenone is most probably formed via pathway *a* (Scheme 43), which involves the initial 1,5-migration of hydrogen from carbon to oxygen and then β-cleavage of the biradical.

β-Decomposition (β pathway, Scheme 43) is preferred in polar solvents (alcohols, acetonitrile). Naturally, in this case the increased ease of hydrogen abstraction from the solvent (on passing from methyl to isopropyl alcohol) should imply an increase in the yield of acetophenone by facilitating the intermolecular hydrogen transfer. In the photolysis of valerophenone[62] the yield of acetophenone

increases significantly in the presence of polar solvents, but changes little when non-polar solvents are varied.

It is believed that more polar solvents accelerate β-decomposition after rearrangement with migration of hydrogen:



(44)

Table 2.

Solvent	C_6H_6	C_6H_{14}	$(CH_3)_3COH$	$(CH_3)_2CHOH$	C_6H_5OH	CH_3CN
Quantum yield of acetophenone	0.37	0.40	0.90	0.68	0.70	0.85

Table 2 shows that in this case the increase of the hydrogen-donating capacity of the solvent is hardly reflected in the yield of acetophenone, which makes it very likely that it is in fact formed as a result of the rearrangement.

It has been shown that the introduction of substituents into the ring of aliphatic aromatic ketones also affects the course of the reaction[63,64] (Table 3). The data in Table 3 show that it is so far difficult to note any consistent trend in the influence of substituents. Thus the introduction of the p-CH_3O group into the ketone (LX) increases the yield of acetophenone, while the introduction of the same substituent into the ketone (LXI) causes a sharp reduction of the yield.

Table 3.

Ketone (in benzene)	Quantum yield of aceto-phenone	Ketone (in benzene)	Quantum yield of aceto-phenone
$C_6H_5COCH_2OCH_3$ (LX)	0.57	$C_6H_5COCH_2OCH(CH_3)_2$	0.59
p-CH_3O—$C_6H_4COCH_2OCH_3$	0.72	$C_6H_5COCH_2CH_2CH_3$(LXI)	0.34
p-CF_3—$C_6H_4COCH_2OCH_3$	0.43	p-CH_3O—$C_6H_4COCH_2CH_2CH_3$	0.09
$C_6H_5COCH_2OCH_2CH_3$	0.38		

The authors suggest that the formation of acetophenone reflects a rearrangement with migration of hydrogen. However, one also cannot rule out at least partial formation of acetophenone by the mechanism involving intermolecular abstraction of hydrogen.

When sulphones of the type $RSO_2CH_2C(O)R'$ [R = $C_6H_5CH_2$ or $(CH_3)_3C$; R' = CH_3 or C_6H_5] are irradiated, hydrogen migration does not occur[65].

The results presented here show that certain features of the rearrangements in biradicals differ from those in monoradicals. Thus, while the possibility of the 1,2-migration of hydrogen in monoradicals remains controversial, the above results indicate the occurrence of such rearrangements in biradicals. It is noteworthy that, in contrast to monoradicals, biradicals with a specific structure probably have a greater ability to stabilise the transition state or the final biradical, which facilitates for example, 1,2-migration of hydrogen in biradicals.

Therefore one can hardly agree with certain investigators[22] who questioned the results obtained in the study of biradicals on the basis of the view expressed in a number of reviews that the probability of the 1,2-migration of hydrogen in the radical is low.

Thus the study of the reactions of biradicals reveals new types of possible rearrangements and their characteristic features.

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