

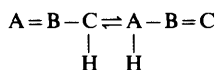
# Light-induced Tautomerism of $\beta$ -Dicarbonyl Compounds

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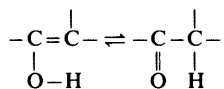
## 1 Scope

The idea of tautomerism was introduced by Laar in 1885.<sup>1</sup> The dual reactivity of  $\beta$ -dicarbonyls is believed to be due to uncertainty in the position of one double bond, caused by the intramolecular oscillation of a hydrogen atom within the framework of the three-centre unsaturated system:



This state of the molecule has been defined as 'tautomeric'.

By the turn of the century it was generally accepted that the properties of  $\beta$ -dicarbonyl compounds could be related to the tautomeric equilibrium:



This was the earliest in a long series of examples that were to prove the versatility and generality of the phenomenon. Later, the concept of tautomerism was extended to comprise all types of rapidly and reversibly equilibrated transformations (see, for examples, *refs.* 2 and 3).

Since these early days the tautomeric equilibria in solutions of  $\beta$ -dicarbonyl compounds have been the subject of continuous interest. Various aspects of this subject have received extensive treatment in several review articles.<sup>4-6</sup>

The group of  $\beta$ -dicarbonyls comprises compounds such as (a), (b), and (c).

<sup>1</sup> C. Laar, *Chem. Ber.*, 1885, **18**, 648.

<sup>2</sup> M. I. Kabachnik, *Zh. Vses. Khim. Ova.*, 1962, **7**, 263.

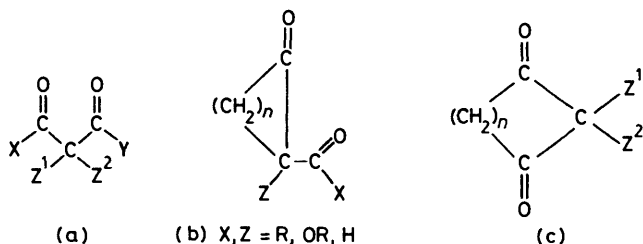
<sup>3</sup> C. K. Ingold, 'Structure and Mechanism in Organic Chemistry', Cornell University Press, Ithaca, New York, 1953, Chapter 11.

<sup>4</sup> S. Forsen and M. Nilson, in 'The Chemistry of the Carbonyl Group', Vol. II, ed. J. Zabicky, Interscience, New York, N.Y., 1970, pp. 157-240.

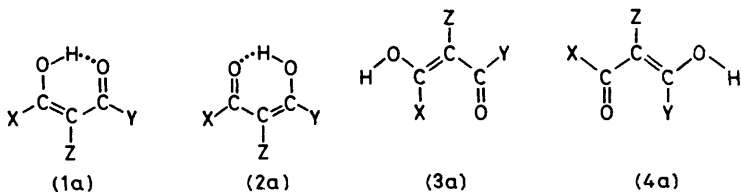
<sup>5</sup> O. Ya. Neiland, Ya. P. Stradyn, E. A. Silin'ysh, D. A. Balode, S. P. Vatore, V. P. Kadysh, S. V. Kalinin, V. E. Kampar, I. B. Mazheina, and L. F. Taure, 'Stroenie i Tautomernie Perevrashcheniya  $\beta$ -Dikarbonylnykh Soedinenii' (Structure and Tautomeric Conversions of  $\beta$ -Dicarbonyl Compounds), Zinatne, Riga, 1979.

<sup>6</sup> V. I. Minkin, L. P. Olekhovich, and Y. A. Zhdanov, *Acc. Chem. Res.*, 1981, **14**, 210.

*Light-induced Tautomerism of  $\beta$ -Dicarbonyl Compounds*



Open-chain  $\beta$ -dicarbonyl compounds [type (a)] with at least one hydrogen atom at  $\alpha$ -position ( $Z^1 = \text{H}$ ) can, in principle, exist in the following forms: keto form (a), chelated enols (1a), (2a), and non-chelated enols (3a), (4a).



The free energies of the keto and enol forms differ only slightly and the tautomeric equilibrium constants are fairly easy to determine. The influence of the structural features on the keto–enol equilibrium cannot be traced in a unique manner since the effects on the keto and enol forms are difficult to disentangle and solvent effects are often marked. However, it seems that the electron-withdrawing substituents at the  $\alpha$ -carbon atom tend to increase the stability of the enol form. If present at all, the trans–enol forms constitute less than about 3% of the tautomers.

The most striking feature of all studies in this field is that they are exclusively directed to the ground-state properties of the  $\beta$ -dicarbonyl compounds. A limited number of widely scattered and isolated data on the photochemistry of the compounds under consideration is now available. As shown in Figure 1, the characteristic phototransformations include  $\alpha$ -cleavage, decarbonylation, 1,3-shift, and conformational changes.

Prolonged irradiation of benzoylacetalddehyde yields acetophenone and  $\text{CO}$ .<sup>7</sup> Non-enolizable  $\beta$ -diketones undergo 1,3-shift and decarbonylation. 2,2-Dimethylcyclohexane-1,3-diones undergo 1,3-shift upon irradiation in benzene (Scheme 1).<sup>8</sup>

<sup>7</sup> R. A. Finnegan and A. W. Hagen, *Tetrahedron Lett.*, 1963, 365.

<sup>8</sup> H. Nozaki, Z. Yamaguti, T. Okada, R. Noyori, and M. Kawanisi, *Tetrahedron*, 1967, 23, 3993.

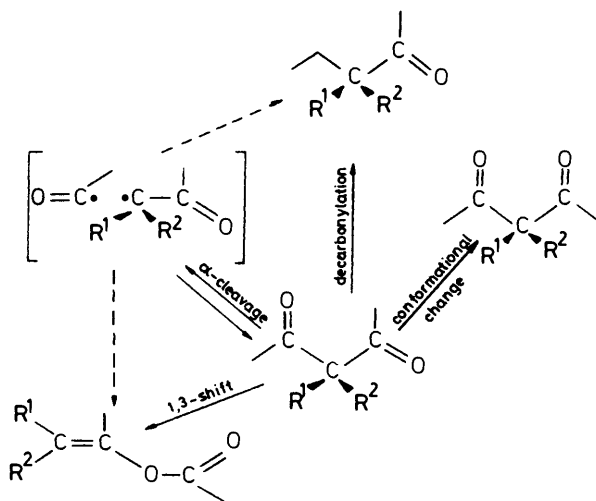
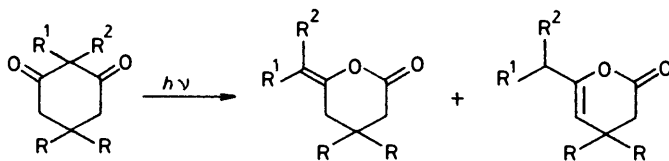


Figure 1 Photoreactions of  $\beta$ -dicarbonyl compounds



Scheme 1

Propyl bromide enhances the reaction rate, indicating a heavy atom acceleration of the intersystem crossing to the reactive triplet state. Nozaki and co-workers<sup>9</sup> have studied several bicyclic non-enolizable  $\beta$ -diketones. They found that 1,3-shift products were formed with extremely high yields. An  $n\pi^*$  triplet state is assumed to be responsible for these reactions.

Gorodetsky *et al.*<sup>10-12</sup> have studied the photochemistry of different types of cyclic, steroidal, and acyclic enol benzoates and acetates. Irradiation causes an intramolecular 1,3-shift. A simple example is provided by the conversion of vinyl benzoate into benzoyl acetaldehyde in 6% conversion in benzene solution.<sup>7</sup> Irradiation in transparent solvents produces decarbonylation with formation of acetophenone (Scheme 2).

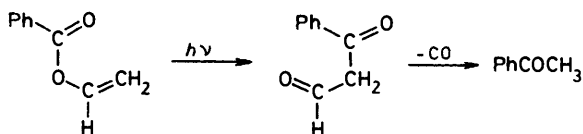
<sup>9</sup> H. Kato, N. Miyamoto, M. Kawanisi, and H. Nozaki, *Tetrahedron*, 1970, **26**, 2975

<sup>10</sup> M. Feldkimmel-Gorodetsky and Y. Mazur, *Tetrahedron Lett.*, 1963, 369.

<sup>11</sup> M. Gorodetsky and Y. Mazur, *Tetrahedron*, 1966, **22**, 360.

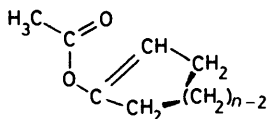
<sup>12</sup> A. Yogev, M. Gorodetsky, and Y. Mazur, *J. Am. Chem. Soc.*, 1964, **86**, 5208.

Light-induced Tautomerism of  $\beta$ -Dicarbonyl Compounds



Scheme 2

Exceptions to this behaviour are observed with compounds such as (5) which additionally form products of  $\alpha$ -cleavage, followed by hydrogen abstraction or dimerization.



(5)

According to Houk<sup>13</sup> the photochemical reactions of non-enolizable  $\beta$ -diketones and enol esters, can be rationalized on the basis of biradical intermediates, formed by  $\alpha$ -cleavage from  $n\pi^*$ -excited states. Unlike the  $\beta$ ,  $\gamma$ -unsaturated ketone and aldehydes, the  $\alpha$ -cleavage of  $\beta$ -diketones seems to involve triplet states in many cases. Two basic types of 1,3-shift for non-enolizable  $\beta$ -dicarbonyls may be envisioned: concerted reactions or intermediate formation of radical pairs. Berson and Salem<sup>14</sup> have suggested that the transition state of orbital symmetry forbidden reactions should be stabilized with respect to radical pairs or biradicals involved in stepwise mechanisms.

From a phenomenological point of view, light-induced tautomerism has to be associated with the large area of intramolecular proton transfer in electronically excited molecules. In 1931 Weber<sup>15</sup> showed the link between the fluorescent intensity of some fluorescent species and the acidity of the media. Förster<sup>16-18</sup> suggested that such a dependence is probably due to the differences in electron distribution for the fluorescent molecules depending on their electronic states. Weller<sup>19-21</sup> was first to show experimentally that the pH values of several organic compounds possessing an acidic hydrogen atom are closely related to their electronic states.

The concept of photo-induced hydrogen migration was originally put forward in order to explain the photochemical behaviour of salicylic acid and some related

<sup>13</sup> K. N. Houk, *Chem. Rev.*, 1976, **76**, 1.

<sup>14</sup> J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, 1972, **94**, 8917.

<sup>15</sup> K. Weber, *Z. Phys. Chem.*, 1931, **B 15**, 18.

<sup>16</sup> T. Förster, *Naturwissenschaften*, 1949, **36**, 186.

<sup>17</sup> T. Förster, *Z. Elektrochem.*, 1950, **54**, 42.

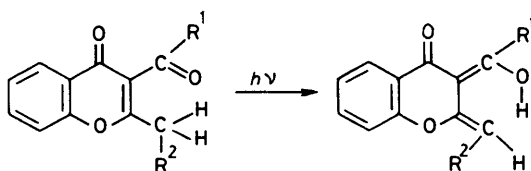
<sup>18</sup> T. Förster, *Z. Elektrochem.*, 1950, **54**, 531.

<sup>19</sup> A. Weller, *Z. Elektrochem.*, 1952, **56**, 662.

<sup>20</sup> A. Weller, *Z. Phys. Chem.*, N. F., 1955, **3**, 238.

<sup>21</sup> A. Weller, *Z. Phys. Chem.*, N. F., 1958, **15**, 438.

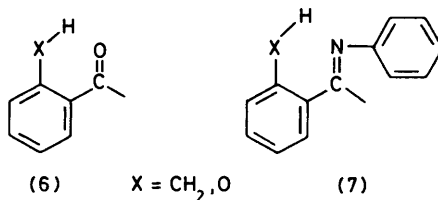
compounds.<sup>22,23</sup> Cohen, Hirschberg, and Schmidt<sup>24</sup> showed that the photochromic properties of salicylidene anilines are due to intramolecular proton transfer in an excited state. Later, Wettermark<sup>25</sup> found experimental evidence of photo-induced intramolecular hydrogen migration for some substituted acetophenones. During the last few years interest has been growing in the field of light-induced enolization and related transformations.<sup>26-29</sup> Photoenolization is a very general phenomenon that occurs with a wide variety of substrates. The first present-day study in this area was carried out by Huffman *et al.*,<sup>30</sup> with some chromone derivatives as an example. They showed that irradiation produces dienol species (Scheme 3):



Scheme 3

The process could be reversed by a non-photochemical dark reaction. Several important topics of this field have been reviewed.<sup>31</sup>

Thus far, where compounds show intramolecular excited state proton transfer this is known to be related to the presence of molecular fragments of the type (6) and (7) in which hydrogen transfer takes place in the 6-centre system in the direction of the existing hydrogen bond (Scheme 4).



<sup>22</sup> A. Weller, *Z. Elektrochem.*, 1956, **60**, 1144.

<sup>23</sup> A. Weller, *Naturwissenschaften*, 1955, **42**, 175.

<sup>24</sup> M. D. Cohen, Y. Hirschberg, and G. M. J. Schmidt, 'Hydrogen Bonding', Symposium in Ljubliana, Pergamon, New York, 1959, p. 293.

<sup>25</sup> G. Wettermark, *Photochem. Photobiol.*, 1965, **4**, 621.

<sup>26</sup> D. I. Schuster and M. D. Goldstein, *Mol. Photochem.*, 1976, **7**, 209.

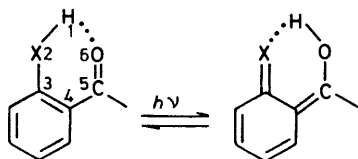
<sup>27</sup> J. A. Barltrop and J. Wills, *Tetrahedron Lett.*, 1968, 4987.

<sup>28</sup> A. Pawda, A. Au, and W. Owens, *J. Org. Chem.*, 1978, **43**, 303.

<sup>29</sup> E. Hadjoudis, *Mol. Cryst. Liq. Cryst.*, 1971, **13**, 233.

<sup>30</sup> K. R. Huffman, M. Loy, and E. F. Ullman, *J. Am. Chem. Soc.*, 1965, **87**, 5417.

<sup>31</sup> P. Sammes, *Tetrahedron*, 1976, **32**, 405.

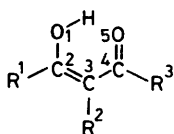


Scheme 4

## 2 Spectra

Until the advent of n.m.r. spectroscopy, ultraviolet and infrared spectroscopies were the most useful techniques for the study of tautomeric molecules and even now they are still invaluable as diagnostic tools. Among the many applications are structure determinations,<sup>32-36</sup> kinetic measurements,<sup>37,38</sup> determinations of equilibrium constants,<sup>39-42</sup> mechanistic studies<sup>43-45</sup> and analysis of isomer mixtures.<sup>46</sup> The present brief discussion will be restricted to the advancement in this area, related to the effect of ultraviolet and visible light on tautomeric equilibria.

The strong absorption in the 250–300 nm region of the u.v.-spectra of enolizable  $\beta$ -dicarbonyl compounds is due to the  $\beta$ -hydroxyvinyl carbonyl system (8).



(8)

Theoretical PPP<sup>47</sup> and CNDO/S<sup>48</sup> studies on this molecular fragment indicate that the high-intensity band should be assigned to a  $\pi \rightarrow \pi^*$  transition in the CO conjugated ethylene system. Numerical calculations<sup>49</sup> predict, however, two  $n \rightarrow \pi^*$  transitions in the visible or near-ultraviolet region. The position of the high-intensity band is virtually independent of the type of aliphatic substituents

<sup>32</sup> S. J. Rhoads, J. C. Gilbert, A. W. Decora, T. R. Garland, R. J. Spangler, and M. J. Urbigkit, *Tetrahedron*, 1963, **19**, 1626.

<sup>33</sup> S. Forsen, F. Merenyi, and M. Nilson, *Acta Chem. Scand.*, 1967, **21**, 620.

<sup>34</sup> S. Forsen, F. Merenyi, and M. Nilson, *Acta Chem. Scand.*, 1964, **18**, 1208.

<sup>35</sup> P. Courtot, J. Le Saint, and N. Platzter, *Bull. Soc. Chim. Fr.*, 1969, 3281.

<sup>36</sup> Y. Hoppilliard, G. Bouchoux, and P. Jaudon, *Nouv. J. Chim.*, 1982, **6**, 43.

<sup>37</sup> H. Baba and T. Takemura, *Tetrahedron*, 1968, **24**, 4779.

<sup>38</sup> T. Takemura and H. Baba, *Tetrahedron*, 1968, **24**, 5311.

<sup>39</sup> A. Yogev and Y. Mazur, *J. Org. Chem.*, 1967, **32**, 2162.

<sup>40</sup> J. Billmann, S. Soyka, and Ph. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2034.

<sup>41</sup> J. Burdett and M. Rogers, *J. Am. Chem. Soc.*, 1964, **86**, 2105.

<sup>42</sup> J. Burdett and M. Rogers, *J. Phys. Chem.*, 1966, **70**, 939.

<sup>43</sup> J. S. Chickos, D. W. Larsen, and L. E. Legler, *J. Am. Chem. Soc.*, 1972, **94**, 4266.

<sup>44</sup> J. S. Splitter and M. Calvin, *J. Am. Chem. Soc.*, 1979, **101**, 7329.

<sup>45</sup> J. H. Clark, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1326.

<sup>46</sup> C. A. Erastov, C. N. Ignatieva, and Z. G. Gabulin, *Izv. Acad. Nauk SSSR, Ser. Khim.*, 1969, 1620.

<sup>47</sup> F. Fratev, P. Markov, and R. Vasileva, *Izv. Otd. Khim. Nauk, BAN*, 1974, **7**, 737.

<sup>48</sup> P. Markov and F. Fratev, *C. R. Acad. Bulg. Sci.*, 1975, **28**, 771.

<sup>49</sup> W. Hug, J. Kuhn, K. J. Seibold, H. Labhart, and C. Wagniere, *Helv. Chim. Acta*, 1971, **54**, 1451.

$R^1$ ,  $R^2$ , and  $R^3$ . Somewhat more noticeable is the influence of the benzyl radical ( $R^1 = \text{PhCH}_2$ ), resulting in a bathochromic shift of the absorption maximum. The introduction of alkyl substituents at the  $\alpha$ -carbon atom produces similar spectral changes. Aromatic substituents in 2- and 4-positions of the  $\beta$ -hydroxy-carbonyl system give rise to a new absorption band in the 250–260 nm range, assignable to the aryl group of the ketonic form.

At higher concentrations of the enol tautomer ( $10^{-3} \text{ mol l}^{-1}$ ) a low-intensity absorption band can be found in the 290–410 nm region. The exact position of the band depends strongly on the structural peculiarities of the  $\beta$ -dicarbonyl compound. The accumulated data<sup>50</sup> show that the 240–270 nm excitation is ineffective in giving rise to luminescence. Conversely, excitation in the long-wave band range produces emission lines. The excitation and emission spectral maxima for some  $\beta$ -dicarbonyl compounds are presented in Table 1.

**Table 1** Luminescence spectral data for  $R^1 - \text{CO} - \text{CH}_2 - \text{CO} - R^2$  in cyclohexane solutions,  $C = 1 \times 10^{-2} \text{ mol l}^{-1}$

Compound		max (nm)	
$R^1$	$R^2$	excitation	emission
Me	OEt	300	390
Ph	OEt	350	440
Me	$\text{OC}_6\text{H}_4$	310, 340	370
Me	$\text{OCH}_2\text{CH:CHPh}$	252, 327	308, 375
Ph	Ph	380	520
Ph	Me	400	510
Me	Me	—	—

The long-wave absorption ( $A_N$ ) of concentrated solutions of  $\beta$ -dicarbonyls is due to the formation of molecular associates,

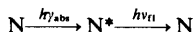


where M is a monomeric enol molecule and N is molecular associate. From the linear dependence<sup>50</sup>

$$A_N = (\epsilon_N K_N)^{-1/n} (A_N^{n-1})^{-1/n} + 1/\epsilon_N$$

one can find the association constant  $K_N$  and molar absorptivity  $\epsilon_N$  of the dimer molecules (N). The numerical value of  $K_N$  for  $\text{MeCOCH}_2\text{CO}_2\text{CH}_2\text{CH:CHPh}$  (Table 1) is  $8.39 \times 10^4$ . This corresponds to a free energy change of  $\Delta G = -6.6 \text{ kcal mol}^{-1}$ . The assumption of the existence of dimeric species is in agreement with the results of n.m.r. studies on similar molecular systems.<sup>51,52</sup>

Since the long-wave absorption band coincides with the respective excitation band, the process



is likely to occur. In this sense, the emission observed is to be unequivocally related to the presence of dimeric associates. It should be noted that long-wave luminescence, due to dimeric associates, has been reported elsewhere.<sup>53</sup>

<sup>50</sup> P. Nikolov, F. Fratev, I. Petkov, and P. Markov, *Chem. Phys. Lett.*, 1981, **83**, 170.

<sup>51</sup> M. T. Rogers and J. L. Burdett, *Can. J. Chem.*, 1965, **43**, 1516.

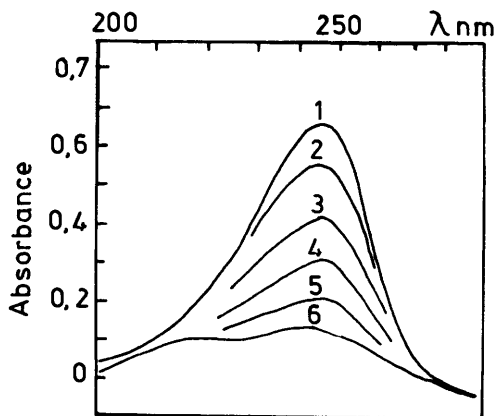
<sup>52</sup> C. Giessner-Prettre, *C. R. Acad. Sci. (Paris)*, 1960, **250**, 2547.

<sup>53</sup> K. C. Ingham and M. A. El-Bayoumi, *J. Am. Chem. Soc.*, 1974, **96**, 1674.

### 3 Reversible Photochemistry

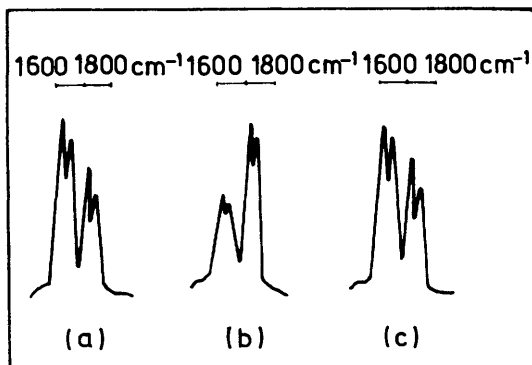
**A. Enolizable  $\beta$ -Dicarbonyl Compounds.**—Studies up to 1971 had demonstrated the influence of ultraviolet light on the prototropic equilibria of  $\beta$ -dicarbonyl compounds.<sup>54,55</sup>

Figure 2 shows the change in intensity of the 246 nm absorption band in the u.v.-spectrum of ethyl acetoacetate after successive irradiation of its heptane solution.



**Figure 2** *U.v. spectra of ethyl acetoacetate in cyclohexane (ca.  $1.5 \times 10^{-3} \text{ mol l}^{-1}$ ) measured at different times after the start of u.v. (254 nm) irradiation*

Ultraviolet light also causes changes in the i.r.-spectral characteristics. The respective absorption bands in the 6 region found for the ethyl acetoacetate before (curve a), immediately after 8 h of u.v. irradiation (curve b), and 16 h after the end of irradiation (curve c) are presented in Figure 3.



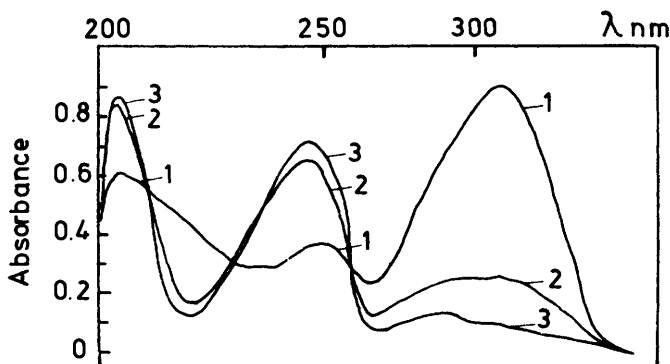
**Figure 3** *I.r. spectra of a cyclohexane solution of ethyl acetoacetate ( $0.95 \times 10^{-2} \text{ mol l}^{-1}$ ) (a) before irradiation, (b) after 8 h exposition to 254 nm u.v. irradiation, (c) 16 h after the end of irradiation*

<sup>54</sup> P. Markov, L. Shishkova, and Z. Zdravkova, *Tetrahedron Lett.*, 1972, **39**, 4017.

<sup>55</sup> P. Markov, L. Shishkova, and A. Radushev, *Tetrahedron*, 1973, **29**, 3203.



Absorptions due to the enolic form at  $1640$  and  $1660\text{ cm}^{-1}$  decrease, with a parallel absorption increase at  $1718$  and  $1742\text{ cm}^{-1}$ , related to the ketonic form. Similar spectral changes have been obtained with structural analogues of the reference compound. The enol forms of benzoylacetone, dibenzoylmethane and other similar compound are sensitive towards sunlight.<sup>57</sup> The spectral changes in the u.v.-spectrum of dibenzoylmethane after successive exposures of the solution are shown in Figure 4.



**Figure 4** U.v. absorption spectrum of dibenzoylmethane in heptane (ca.  $0.25 \times 10^{-4}\text{ mol l}^{-1}$ ) curve 1, before exposure to sunlight; curve 2, after a 60 min exposure; curve 3, after a 120 min exposure

The spectral changes caused by ultraviolet irradiation are reversible, *i.e.* the original solution spectra are restored in the dark.

Available spectral data (for example *refs.* 59—61) for  $\beta$ -dicarbonyl compounds reveal that the observed spectral changes are due to a shift of the keto–enol equilibrium towards the keto form. Kinetic studies of photoketonization together with quantum yields have been described.<sup>56,58</sup> In the region of high optical densities ( $c^\circ = 1 \times 10^{-4}\text{ mol l}^{-1}$ ), the photoinduced transformation follows zeroth-order kinetics. At lower concentrations of the enolic form ( $c^\circ = 0.5 \times 10^{-4}\text{ mol l}^{-1}$ ) the process is described by the function

$$\ln c_0^\circ - \ln c_t^\circ = kt$$

which is a solution of the rate equation for first-order kinetics. Under high-intensity pulsed-laser irradiation, a hyperbolic relationship between transmittance ( $T$ ) and time of irradiation ( $t$ ) was found.<sup>62</sup> In this case the rate of photoketonization is given by

<sup>56</sup> I. Petkov and P. Markov, *Rev. Roum. Chim.*, 1982, 27, 847.

<sup>57</sup> P. Markov and I. Petkov, *Tetrahedron*, 1977, 33, 1013.

<sup>58</sup> P. Markov, I. Petkov, and D. Jeglova, *J. Photochem.*, 1978, 8, 277.

<sup>59</sup> R. A. Morton, A. Hassan, and T. C. Calloway, *J. Chem. Soc.*, 1934, 883.

<sup>60</sup> R. Rasmussen and R. Brattain, *J. Am. Chem. Soc.*, 1949, 71, 1075.

<sup>61</sup> L. J. Bellamy, 'Infrared Spectra of Molecules', Moscow, 1957, p. 221.

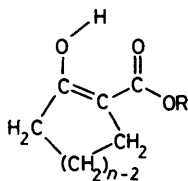
<sup>62</sup> W. Majewski, W. Skubizak, T. Kotowski, S. Dinev, P. Markov, and I. Petkov, *Mol. Photochem*, 1979, 9, 463.

### Light-induced Tautomerism of $\beta$ -Dicarbonyl Compounds

$$\frac{dc}{dt} = -\frac{lg e}{sl} \cdot \frac{b}{at^2 + bt}$$

where  $a, b$  are constants,  $l$  is optical length, and  $t$  is time of irradiation.

A considerable body of evidence shows that the type of the substituents  $R^1$ ,  $R^2$ , and  $R^3$  has no marked effect on the photoketonization rate in its first (zeroth-order kinetics) and second (first-order kinetics) stages. In some cases, however, the  $k_0$  and  $k_1$  values are particularly dependent on some structural features of the enolizable species. The presence of a ring system such as (9) reduces considerably the rate of photoconversion.<sup>63</sup> A similar effect is produced by the replacement of enolic hydrogen with deuterium.<sup>56</sup>



Veierov *et al.*<sup>64</sup> have tested the photoisomerization kinetics for the enol form by flash photolysis. In their view these species undergo facile photoisomerization to the corresponding non-chelated short-lived forms. The photoprocess obeys the first-order reaction law.

The relevant energies associated with the hydrogen migration within the framework of the three-centre unsaturated system of the enol form vary with the structure peculiarities from 5 to 8 kcal mol<sup>-1</sup>.<sup>65</sup> Quantum yield measurements show that the photoinduced hydrogen transfer seems to occur with a nearly constant quantum yield. The variation of the  $\beta$ -ketoester structure produces minor differences in the  $\Phi$ -values. The oscillator strength for the  $S_1 \leftarrow S_0$  transition in the C=O conjugated system seems to be related to the respective rate constants and quantum yields.

A logical extension of the studies in the area under consideration has been recently made by Getoff *et al.*<sup>66</sup> They were the first to report on triplet-sensitized prototropy of ethyl acetoacetate in solution. The ketonization of this  $\beta$ -dicarbonyl compound was found to be sensitized by benzene, toluene, and *p*-xylene, used as energy donors. The quenching of the donor fluorescence was studied and the Stern-Volmer constants were determined. On the assumption that sensitized ketonization takes place subsequent to energy transfer from the donor triplet state, the donor triplet quantum yield has been calculated. The lowest excited state of

<sup>63</sup> P. Markov and E. Radeva, *J. Photochem.*, 1975, 4, 179.

<sup>64</sup> D. Veierov, T. Bercovici, E. Fischer, Y. Mazur, and A. Yogev, *J. Am. Chem. Soc.*, 1977, 99, 2723.

<sup>65</sup> P. Markov, unpublished data.

<sup>66</sup> G. Kittel, G. Köhler, and N. Getoff, *J. Phys. Chem.*, 1979, 83, 2174.

ethyl acetoacetate in its enolic form is of  $\pi\pi^*$  nature and it is not observed by absorption spectroscopy in dilute solutions. CNDO/S calculations<sup>48</sup> gave 3.382 eV, corresponding to 365 nm for its vertical energy. According to Getoff *et al.*, the  $^3n\pi^*$  and  $\pi\pi^*$ -states have to be expected at energies below 3 eV (410 nm). In such a case benzene and its derivatives should be efficient triplet energy donors for ethyl acetoacetate, since their relaxed triplet energy is higher than 3.4 eV.<sup>67</sup>

In 1973 Courtot and Le Saint<sup>68</sup> showed that the ultraviolet irradiation causes interconversions between chelated enolic species of diaroylacetic acids. More recently Courtot *et al.* have studied in detail the photochemical properties of triacylmethane<sup>69</sup> and some nitrogen-containing analogues.<sup>70</sup> It is concluded that  $Z \rightarrow E$  isomerization takes place directly by rotation around the olefinic double bond of the enolic chelate system after cleavage of the intramolecular hydrogen bond. In this case the intermediate formation of ketonic species as a result of photoinduced hydrogen transfer cannot be ruled out.

Until recently no information concerning the possible influence of  $\gamma$ -irradiation on tautomeric equilibria was available. Getoff and Fratev<sup>71</sup> have shown that  $^{60}\text{Co}$ -irradiation causes a decrease in the concentration of the enol form of ethyl acetoacetate in solution, yielding the keto form.

As already mentioned, the thermodynamic ratio between the two tautomeric forms is completely restored in the dark. The rate of re-enolization (dark reaction) depends on several factors, including the presence of specific catalysts and the duration of the irradiation.<sup>72</sup> The experimental data in the case of base-catalysed re-enolization satisfy the function

$$\ln \frac{C^\infty - C^0}{C^\infty - C} = kt$$

$C^0$  and  $C^\infty$  denote the initial and the equilibrated concentrations of the enol form and  $C$  is the concentration  $t$  seconds after starting the kinetic run. A plot of  $\ln \frac{C^\infty - C^0}{C^\infty - C}$  vs.  $t$  at different concentrations of the catalyst (n-amylamine) is presented in Figure 5.

The rate of the reverse process gradually increases as a result of repeatedly performed photoketonization, when tertiary amine is used as a catalyst (Figure 6).

The initial  $k$  value is 15-times smaller than that obtained after six prototropic interconversions (photoketonization–enolization). The accelerating effect of ultraviolet irradiation occurs only in the case when tertiary amine is used as a catalyst.

<sup>67</sup> J. B. Birks, 'Photophysics of Aromatic Molecules', Wiley-Interscience, London, 1970.

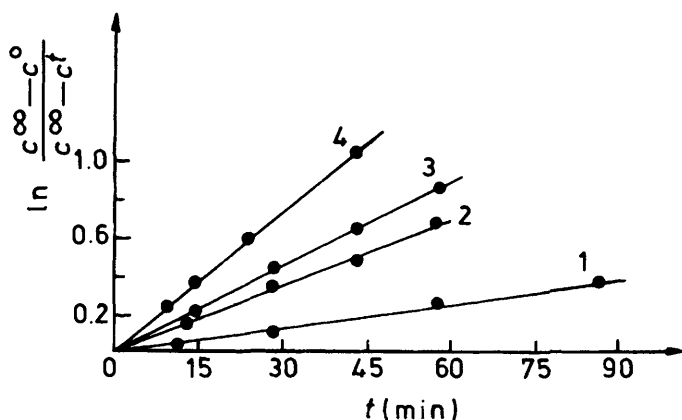
<sup>68</sup> P. Courtot and J. Le Saint, *Tetrahedron Lett.*, 1973, 33.

<sup>69</sup> B. Couchouron, J. Le Saint, and P. Courtot, *Bull. Soc. Chim. Fr.*, 1981, II, 381.

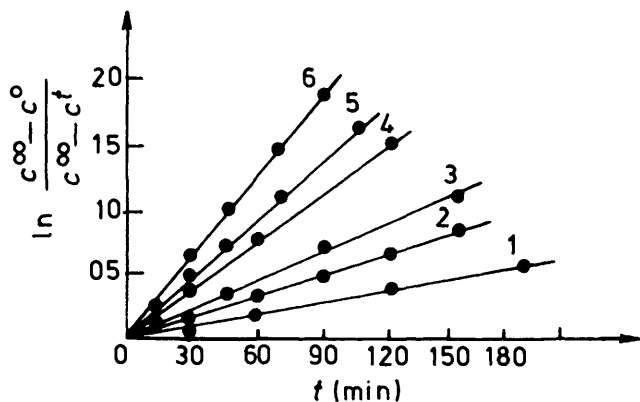
<sup>70</sup> R. Pichon, J. Le Saint, and P. Courtot, *Tetrahedron*, 1981, **37**, 1517.

<sup>71</sup> N. Getoff and F. Fratev, *Z. Phys. Chem.*, N. F., 1977, **104**, 131.

<sup>72</sup> P. Markov, *J. Photochem.*, 1976–77, **6**, 91.



**Figure 5** Plot of  $\ln[(C^\infty - C^0)/(C^\infty - C^1)]$  vs.  $t$  at different concentrations ( $C_b$ ) of the catalyst (*n*-amylamine): 1,  $0.08 \times 10^{-7}$ ; 2,  $0.32 \times 10^{-7}$ ; 3,  $1.30 \times 10^{-7}$ ; 4,  $5.00 \times 10^{-7}$ .  $C^0 = 0.2 \times 10^{-4} \text{ mol l}^{-1}$ ,  $\lambda_{\text{max}} = 246 \text{ nm}$

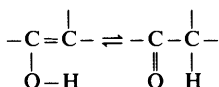


**Figure 6** Plot of  $\ln[(C^\infty - C^0)/(C^\infty - C^1)]$  vs.  $t$  after successive 20 min irradiations. Basic catalyst, triethylamine ( $C_b = 0.5 \times 10^{-7} \text{ mol l}^{-1}$ )

*Theoretical Considerations.* In the theoretical analysis of tautomeric interconversions an energy value can be assigned to each tautomeric form. Since in a molecule of many atoms there are several geometrical variables and the energy depends on all of them, the total energy of the respective tautomer can be represented as a hypersurface over the multi-dimensional space of the internal co-ordinates. The tautomerism of  $\beta$ -dicarbonyl compounds corresponds to the paths of minimum energy of these hypersurfaces, while stable conformations and transition states are represented by minima and saddle points, respectively.

During the last few years, energy surfaces for the interaction between small molecules or ions have become available by *ab initio* LCAO MO calculations. The most extensive of these studies<sup>73-77</sup> claim to have an accuracy of a few kcal mol<sup>-1</sup> relative to the energy minimum over the most important parts of the surface. For large molecules such as  $\beta$ -dicarbonyls, however, the orthodox approach is not practicable. The calculation of the energy surface becomes possible if the number of geometrical variables is reduced on the basis of a well-founded model for the transition state.<sup>78,79</sup> In the common case, the principle of least motion<sup>80</sup> and orbital symmetry conservation rules<sup>81</sup> have to be considered.

The main assumption in the case of proton transfer within the framework of the three-centre unsaturated system



of a tautomeric molecule is that the nature of the potential surface depends exclusively on the internal co-ordinate of the migrating particle. The most probable path of the system during the tautomeric interconversion can be represented by a line on the surface that follows the lowest possible energy contours between the

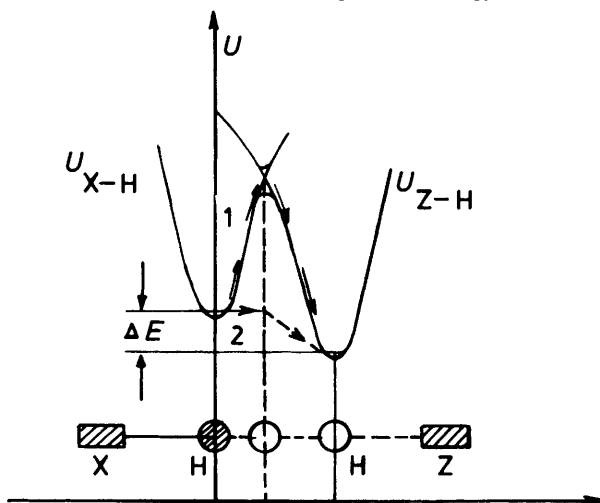


Figure 7 Energy diagram for proton-transfer reaction

<sup>73</sup> G. H. F. Diercksen, *Theor. Chim. Acta.*, 1971, **21**, 335.

<sup>74</sup> G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.*, 1970, **5**, 570.

<sup>75</sup> H. Popkie, H. Kistenmacher, and E. Clementi, *J. Chem. Phys.*, 1973, **59**, 1325.

<sup>76</sup> E. Clementi and H. Popkie, *J. Chem. Phys.*, 1972, **57**, 1077.

<sup>77</sup> O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, 1976, **64**, 1351.

<sup>78</sup> M. Simonetta, *Fortschr. Chem. Forsch.*, 1973, **42**, 2.

<sup>79</sup> M. J. S. Dewar, *Chem. Br.*, 1975, **11**, 97.

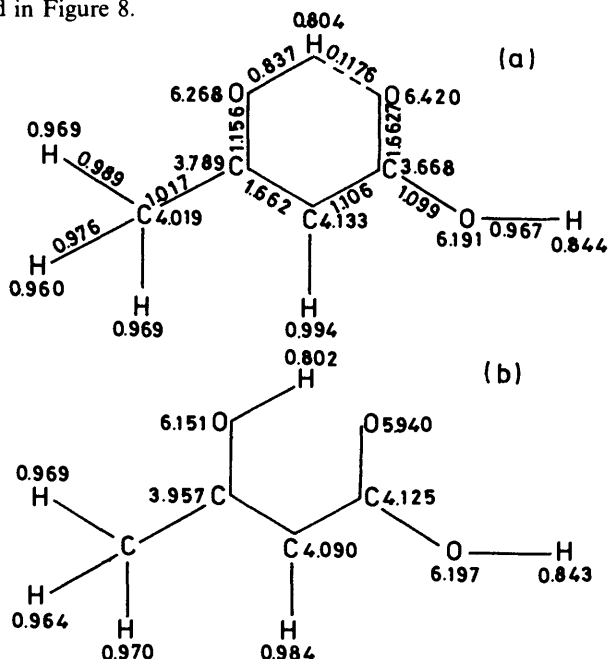
<sup>80</sup> L. Salem, *Acc. Chem. Res.*, 1971, **4**, 322.

<sup>81</sup> J. W. McIver, *Acc. Chem. Res.*, 1974, **7**, 72.

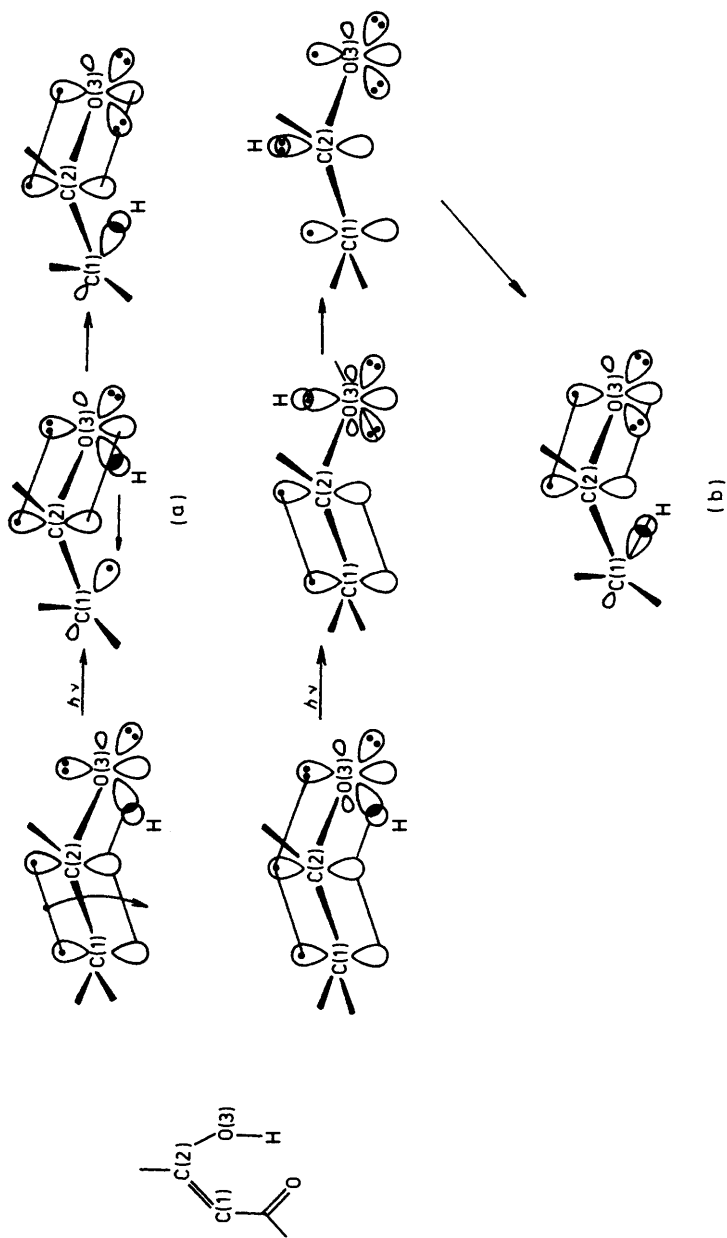
initial and the final state, so that a two-dimensional diagram like Figure 7 represents a section of the energy surface.

The two curves represent the potential energies of the two separate tautomers X-H and Z-H as a function of the position of the hydrogen atom, migrating between two centres X and Z. The reaction co-ordinate has a simple significance, namely, the distance of the proton from either X or Z. The energy of the transition state is given by the point of intersection between two potential energy curves.

Some insight into the type of transition involved and the direction of the main internal co-ordinates may be obtained from the kinetic features of the photoinduced tautomerism and from the theoretical data on the two tautomers. As already mentioned, the photoactivated prototropic change follows zero (at high optical densities) and first (at low optical densities) order reaction law. Consequently, the photoinduced ketonization, taking place under suitable experimental conditions (inert aprotic solvent and absence of catalyst), is to be ascribed to intramolecular hydrogen atom migration. There are arguments showing that the process does not go along the hydrogen bond of the chelated form. The photoexcitation of the enol tautomer produces important changes in the electron density distribution of the  $\beta$ -hydroxyvinyl carbonyl system. Calculated CNDO/S values of the total charge density of each atom and the respective bond indices of the planar enol form in the ground and the first excited state are presented in Figure 8.



**Figure 8** Electron density distribution in (a) the ground state and (b) the excited state of ethyl acetoacetate

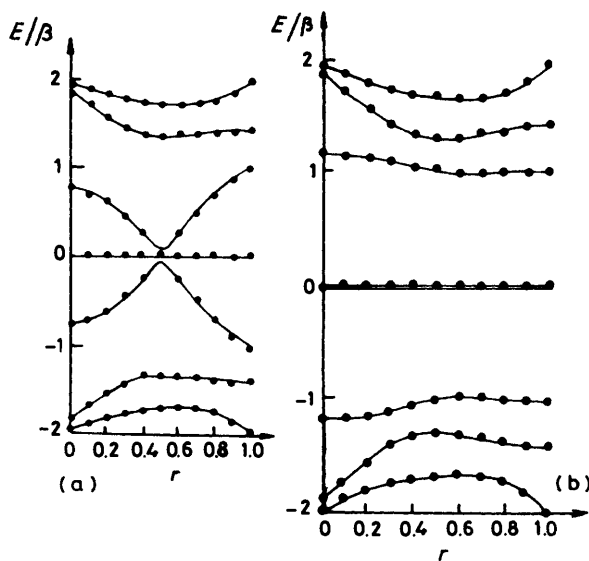


**Figure 9** Possible reaction pathways for the photoinduced intramolecular hydrogen transfer: (a) through-space transfer (b) through-bond transfer

The population analysis shows the presence of a positively charged oxygen atom ( $\Delta q = +0.060$ ) indicating that in the excited state there is no intramolecular hydrogen bond in the *cis*-enolic species. Evidently, migration of a positively charged hydrogen to the carbonyl oxygen is improbable.

There are two possible reaction pathways for the photoinduced intramolecular hydrogen transfer, under aprotic conditions, leading to the keto form. These pathways are: (i) Through-space transfer (Figure 9a) which involves a change in the hybridization scheme of the C<sup>1</sup>-atom as a result of twisting the carbon-carbon double bond. (ii) Through-bond transfer (Figure 9b) involving a 'jump' of a proton to the  $\pi$ -orbital of the neighbouring oxygen atom and subsequent localization of the hydrogen atom at the C<sup>1</sup>-atom with a prior or subsequent change in the hybridization of this carbon atom so as to attain the final keto form.

In order to distinguish between the two pathways, the orbital symmetry conservation rules (OSCR) have been applied.<sup>82</sup> The parameter  $r$  was used to represent the rupture ( $r = 0$ ) or formation ( $r = 1$ ) of bonds during the photoketonization process. The results from the tests of these two reaction paths are illustrated by Figures 10a and b.



**Figure 10** Correlation diagrams for ethyl acetoacetate: (a) through-bond transfer (b) through-space transfer

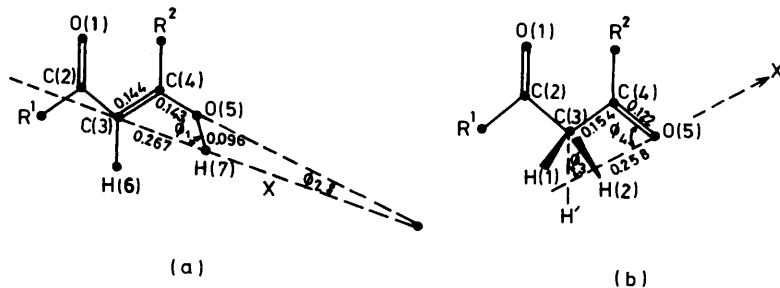
It is seen that ketonization is orbitally allowed in the ground state and the first excited state by the through-space mechanism and forbidden by the through-bond variant.

<sup>82</sup> G. St. Nikolov and P. Markov, *Annuaire de l'Université de Sofia Faculté de Chimie*, 1977-78, **72**, 109.



An important consequence of this finding is that the change in  $C^1$ -atom hybridization is possible only if the OH group is out of the plane of conjugation in the enol tautomer. It is known that the barriers to internal rotation about  $C-O$  bonds are in the range of 8–10 kcal mol<sup>-1</sup>. The twisting of the ethylenic double bond depends on the bond order. PPP-calculations<sup>47</sup> show that the singlet state bond orders  $C^2-C^3$  and  $C^3-C^4$  have nearly the same magnitude. Since twisting of the ethylenic quasi-double bond is an important mode to lose quanta,<sup>83</sup> this path should be preferred. Experimental evidence for the twisting mechanism could be the photoisomerization of the enol form. As already mentioned, spectroscopic data concerning such a process have been recently published by Veierov *et al.*<sup>64</sup> It may be thus concluded that the orbital restriction on overlapping between the  $2p$ -orbital of the  $C^3$ -atom and the  $1s$ -orbital of the hydrogen atom is possibly lifted as a result of twisting about the  $C^2-C^3$  bond in the excited state of the enol tautomer.

A model of the transition state of the photoprocess, based on the above-mentioned assumptions, is presented in Figure 11.



**Figure 11** Assumed ( $C^3=C^4$ ,  $C^4-O^5$ ,  $O^5-H^7$ ) and calculated ( $C^3-H^7$ ) bond distances in the unchelated sickle form of the enol. Both carbon and oxygen are assumed to be  $sp^2$  hybridized. Calculated:  $\phi_1 = 68.84^\circ$ ,  $\phi_2 = 8.84^\circ$ .  $X$  denotes the reaction co-ordinate. (b) Assumed ( $C^3-C^4$ ,  $C^4=O^5$ ,  $C^3-H^7$ ) and calculated ( $O^5-H^7$ ) distances in the keto form.  $H^1$  and  $H^2$  are above and below the molecular plane and  $H'$  is their projection on this plane  $\phi_3 = 66.56^\circ$ ,  $\phi_4 = 47.55^\circ$

It can be seen that the formation of a transition state with the shape of a distorted trapezium is assumed. The reaction co-ordinate is taken along the direction between the OH hydrogen atom and  $C^3$ -carbon atom. As the reaction co-ordinate is invariant to rotation about the  $C^2-C^3$  bond the choice of the configuration does not affect the final results.

It seems likely that the photoinduced hydrogen shift within the framework of the model presented, consists of an intramolecular radiationless H-migration. The idea that photochemical reactions are radiationless relaxation processes has emerged from earlier concepts concerning non-radiative transitions.<sup>84-86</sup> During the last

<sup>83</sup> A. Devaquet, *J. Am. Chem. Soc.*, 1972, **94**, 5160.

<sup>84</sup> R. M. Langer, *Phys. Rev.*, 1929, **34**, 92.

<sup>85</sup> O. K. Rice, *Phys. Rev.*, 1929, **34**, 1451.

<sup>86</sup> N. Rosen, *J. Chem. Phys.*, 1933, **1**, 319.

few years this approach has successfully been applied in the field of photochemical hydrogen abstraction processes, particularly in the cases of excited ketones.<sup>87,88</sup> The basic problem is whether these reactions should be treated as radiationless transitions or as hydrogen atom transfer over a potential energy barrier.<sup>89-93</sup> That and some similar problems can be solved, at least in principle, on the basis of general theoretical considerations (see, for instance, *refs.* 94 and 95). Such theories can be extended to interpret photochemical reactions with the ultimate aim of finding structure-reactivity relationships in the electronically excited states. However, the complex nature of this approach, as well as the necessity to introduce physical and mathematical approximations connected with the application of the theory, reduces its efficiency considerably.

It is reasonable to presume on the other hand that in the case of hydrogen migration there will be an important digression from the classical behaviour of a moving particle. The wave associated with the motion of the hydrogen atom has a wavelength in the  $10^{-8}$ – $10^{-9}$  cm range. Since the barriers on the pathways of chemical reactions have a total width of a few Ångström units, one can expect the tunnel effect to be of some importance. This was suggested at an early date by a number of authors.<sup>96-99</sup> More recently, experimental evidence has been forthcoming and there has been renewed interest in the part played by the tunnel effect in the transfer of protons or hydrogen atoms and in other phenomena. According to Kasha, tunnelling arises since the construction of the potential energy surfaces implies a separation of the electronic and vibrational motions. In this sense the tunnel-effect theory considers hydrogen transfer reactions with electronically excited carbonyl compounds as radiationless transitions.<sup>100-102</sup> Its application to the photoketonization of  $\beta$ -dicarbonyl compounds has been discussed elsewhere.<sup>103</sup> In order to assess the relative contributions of both tunnelling and over-the-barrier processes for photoketonization the Gamow factor<sup>104</sup> can be compared to the Boltzmann one. For enol-keto interconversion (ethyl acetoacetate) the energy barrier is  $3.5 \text{ kcal mol}^{-1}$  and the Gamow factor is significantly higher. Consequently, the contribution of the over-the-barrier process can be neglected. From an experimental point of view, the quantum tunnelling is

<sup>87</sup> J. C. Scaiano, *J. Photochem.*, 1973-74, **2**, 81.

<sup>88</sup> S. G. Cohen, A. Parola, and G. H. Parsons, jun., *Chem. Rev.*, 1973, **73**, 141.

<sup>89</sup> W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, 1975, **8**, 41.

<sup>90</sup> S. J. Formosinho, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1313.

<sup>91</sup> A. Haller, *Mol. Photochem.*, 1969, **1**, 257.

<sup>92</sup> R. C. Dougherty, *J. Am. Chem. Soc.*, 1971, **93**, 7137.

<sup>93</sup> C. M. Previtali and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1667.

<sup>94</sup> J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, 1969, **7**, 149.

<sup>95</sup> S. A. Rice, *Adv. Chem. Phys.*, 1971, **21**, 153.

<sup>96</sup> S. Roginsky and L. Rosenkewitsch, *Z. Phys. Chem.*, 1930, **B10**, 47.

<sup>97</sup> E. Wigner, *Z. Phys. Chem.*, 1932, **B19**, 203.

<sup>98</sup> R. P. Bell, *Proc. R. Soc. London, Ser. A*, 1933, **139**, 466.

<sup>99</sup> S. G. Christov, *Ann. Univ. Sofia, Fac. Phys. Math.*, 1945-46, **42**, 69.

<sup>100</sup> S. J. Formosinho, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 608.

<sup>101</sup> S. J. Formosinho, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 1978.

<sup>102</sup> S. J. Formosinho, *Mol. Photochem.*, 1977, **8**, 459.

<sup>103</sup> G. St. Nikolov and P. Markov, *J. Photochem.*, 1981, **16**, 93.

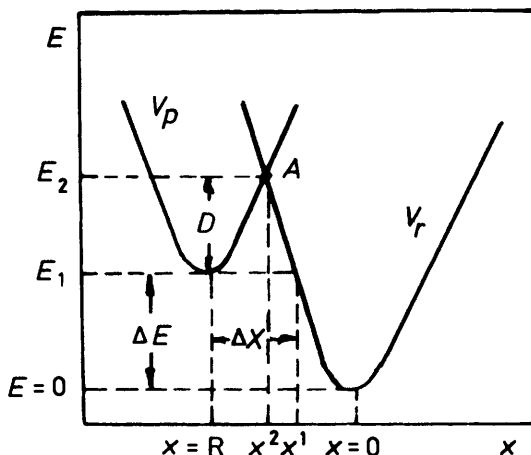
<sup>104</sup> G. Gamow, *Z. Phys.*, 1928, **51**, 204.

well founded by the significant isotope effect of the process under consideration.<sup>56</sup>

The rate of photoconversion, enol  $\rightarrow$  ketone, is given by<sup>102</sup>

$$k_r = k_0 \exp \left[ -\frac{1}{\hbar} (2\mu D)^{1/2} \Delta x \right]$$

The quantities presented in the equation are illustrated in Figure 12.



**Figure 12** Illustration of the quantities involved in the description of the crossing of the two potential energy curves:  $V_p$ , for the products;  $V_r$ , for the reactants;  $X$ , the reaction co-ordinate;  $R$ , the displacement of the two parabolas

For intramolecular processes the transmission factor  $k_0$  is taken to be  $10^{-13} \text{s}^{-1}$ . Potential energy curves  $V_r$  and  $V_p$  are estimated for harmonic oscillators O–H and C–H. As can be seen, the rate of photoketonization is strongly dependent on the barrier width ( $\Delta x$ ),  $\Delta x$  along with the barrier height ( $D$ ) being a function of the displacement of the potential energy curves ( $R$ ) and the energy gap ( $\Delta E$ ).

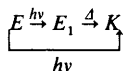
$$\Delta E = E_{e1} - E_{\text{O-H}} + E_{\text{C-H}}$$

As  $\Delta x$  decreases with increasing  $\Delta E$ , it becomes evident why excitation of the enolic species enables formation of the keto tautomer. The contribution of O–H and C=O oscillators along the direction of the bond to be formed (C–H), depends on the presumed geometry of the transition state (Figure 11). From this point of view the good agreement between the calculated<sup>103</sup> and experimentally found<sup>56,58</sup> characteristics of the photoinduced tautomerism lends support, to a certain extent, to the basic assumptions concerning its mechanism.

In spite of the marked reproducibility of the experimental data assuming a singlet state of the reacting species, the nature of the reactive excited state is still controversial. Generally speaking the higher singlet reactivity is entirely accounted for by a higher electronic energy value, which produces smaller energy barriers and

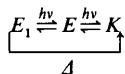
barrier widths. Since the difference  $E^S - E^T$  is probably constant and not too large, the possibility of a triplet precursor formed as a result of intersystem crossing ( $S_1 \rightarrow T_1$ ) cannot, however, be avoided. The lifetimes of the first excited singlets for the enol forms are very small (approximately  $2 \times 10^{-9}$  s). Consequently, the internal conversion leading to the population of the first excited triplet must occur in a very short time interval at a very high rate. The internal conversion rate constant  $k_{isc}$  is known<sup>105</sup> to be in order of  $10^{-7}$ — $10^{-11}$  s<sup>-1</sup> which is sufficiently high compared with the lifetime of the first excited singlet. According to El-Sayed<sup>106</sup> carbonyl compounds, such as those considered here, undergo efficient intersystem crossing. That is why it seems reasonable that photoketonization can proceed from the triplet state of the excited enol as well. Strong evidence of a triplet-sensitized ketonization of ethyl acetoacetate was recently obtained by Getoff *et al.*<sup>66</sup>

There is, however, yet another possibility: the primary photoproduct can be a short-lived rotamer (presumably *trans*) of the enol form which undergoes fast thermal conversion into the keto form. Since the tautomerism of  $\beta$ -dicarbonyls is also a thermal reaction such an idea is considered as promising. It was first explained in *ref.* 47. Later, Veierov *et al.*<sup>64</sup> proposed the mechanism



where  $E$  is chelated enol,  $E_1$  is non-chelated enol, and  $K$  is the keto form. There is, however, no experimental evidence for the process  $E_1 \rightarrow K$ .

In order to get a further insight into the link between the processes of photoisomerization and phototautomerism, the photochemical behaviour of some cyclic  $\beta$ -ketoesters was studied (see *ref.* 63). In spite of any possibility for a photoisomerization *via* rotation about the  $C^2-C^3$  bond, the keto-enol equilibrium was observed to be shifted to the keto form when solutions of these compounds were irradiated. It becomes evident that the phototautomerization occurs independently:



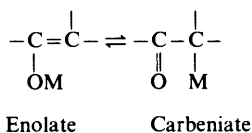
It is also clear, however, that other rotational or vibrational motions lifting the orbital restriction for hydrogen migration are indeed possible. Recently an independent mechanism for the formation of photoisomerization and phototautomerization products was proposed by Courtot *et al.*<sup>69</sup> for the case of  $\beta$ -tricarbonyl compounds.

**Metal Derivatives of  $\beta$ -Dicarbonyl Compounds.**—*Some Remarks on the Concept of Metallo-tropy.* The preparation of alkali-metal derivatives of  $\beta$ -dicarbonyl

<sup>105</sup> N. J. Turro, 'Molecular Photochemistry', Benjamin, New York, 1965.

<sup>106</sup> M. A. El-Sayed, *J. Chem. Phys.*, 1963, **38**, 2834.

compounds was described by Wislicenus<sup>107</sup> as early as 1877. After this pioneer work, interest in the structure and reactivity of the metal salts of  $\beta$ -dicarbonyls has been steadily increasing. Michael<sup>108</sup> has demonstrated their dual reactivity towards alkyl halides, *i.e.* the formation of both *O*- and *C*-alkyl derivatives of ethyl acetoacetate. The logical explanation of such a phenomenon was the assumption of the existence of a metallotropic (prototropic-like) equilibrium:



Regardless of the efforts in this field, however, no direct experimental evidence in favour of such an equilibrium has ever been found. It was for this reason that in the late fifties the 'non-existence' of a metallotropic equilibrium in solutions of metal derivatives of the  $\beta$ -dicarbonyl compounds was postulated.

In his fundamental work 'Theoretical Backgrounds of Organic Chemistry' (Leipzig, 1952) Hückel noted: 'The numerous efforts for argumentation of this idea theoretically or experimentally undoubtedly has showed its inacceptability. The notation tautomerism is inapplicable to the case of metal derivatives of keto-enols...' (Chapter 5.8.1.). In his book 'Theoretical Problems of Organic Chemistry' (Moscow, 1956), Reutov remarks: 'There is no example of a structure type isomerism in the case of metal derivatives of keto-enols depending on the position of the metal atom' (Chapter X). An attempt to elucidate the dual reactivity not involving the idea of metallotropy was made in 1948 by Nesmeyanov and associates.<sup>109</sup> For the first time they drew attention to the importance of the 'shift of the reaction centre' during the reaction. In fact, the metallotropic tautomerism was found to be irrelevant. Since the type of migrating species is in principle not critical, the lack of a logical background for such a conclusion becomes apparent.

From a general point of view, two extremes of the situation may be considered. If the potential function representing the enolate-carbeniate transformation is of a double-minimum type with a barrier high above the ground state of the normal modes for the skeletal vibrations in the metallotropic forms, it would be reasonable to treat the metallotropic conversion as an ordinary chemical reaction. If the potential barrier is, however, comparable with the ground state vibration energies, quantum-mechanical tunnelling is likely to occur. On the other hand, if the potential barrier is of a single-minimum type, there will be no different metallotropic forms. In this case, it would be somewhat inadequate to speak about a metallotropic equilibrium or interconversion. From this point of view the unsuccessful attempt to prove experimentally the metallotropy of alkali-metal derivatives of  $\beta$ -dicarbonyls should be attributed to the very low energy barrier between the two tautomeric forms, relative to the high electropositivity of the metal atom.

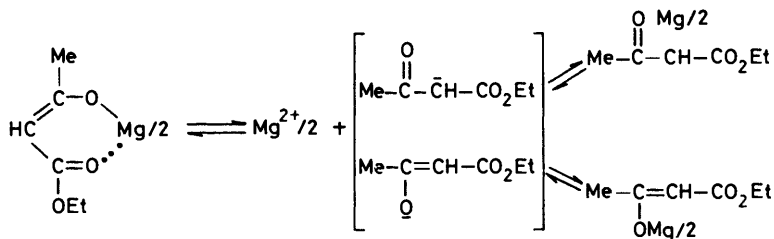
<sup>107</sup> J. Wislicenus, *Annalen*, 1877, **186**, 161.

<sup>108</sup> A. Michael, *J. Prakt. Chem.*, 1887, **37**, 473.

<sup>109</sup> A. N. Nesmeyanov, V. A. Sazonova, and E. B. Lander, *DAN (SSSR)*, 1948, **63**, 395.

## Light-induced Tautomerism of $\beta$ -Dicarbonyl Compounds

Spectroscopic proof for the existence of a metallotropic equilibrium in magnesium ethyl acetoacetate solutions was first reported in 1964<sup>110</sup> (Scheme 5).



Scheme 5

The quantitative description of the metallotropic process has been given in the paper.<sup>111</sup> It was later shown that calcium and copper derivatives of ethyl acetoacetate also possess such a property.<sup>112</sup> The latest studies in this field<sup>113</sup> extend the area of known metallotropic transformations to the nickel and cobalt derivatives of ethyl acetoacetate and the ethyl ester of benzoylactic acid.

Since 1964 there have been a number of very extensive studies on reversible metallotropic-type rearrangements (for example, *refs.* 114, 115). Metallotropic equilibria in solutions of mercury derivatives of  $\beta$ -dicarbonyl compounds have been thoroughly studied.<sup>116-120</sup> The estimated free-energy change in these cases is about  $10 \text{ kcal mol}^{-1}$ . The activation energy is found to be  $9 \text{ kcal mol}^{-1}$ . It is supposed on this basis that a metallotropic process proceeds as an intramolecular reaction. The geometrical parameters of the various metallotropic forms have been determined using *X*-ray diffraction.<sup>121</sup> Subsequently, Nakamoto and co-workers<sup>122</sup> have confirmed that the frequencies above  $1600 \text{ cm}^{-1}$  in the carbonyl region of i.r. spectra of metal derivatives of  $\beta$ -dicarbonyl compounds are due to the presence of the respective carbeniate form.

A number of interesting studies on the structure and reactivity of metal derivatives of keto-enol systems has been performed by Gaudemar and

<sup>110</sup> P. Markov, C. Ivanov, and M. Arnaudov, *Chem. Ber.*, 1964, **97**, 2987.

<sup>111</sup> B. Jordanov, C. Ivanov, M. Arnaudov, and P. Markov, *Chem. Ber.*, 1966, **99**, 1518.

<sup>112</sup> C. Ivanov, M. Arnaudov, P. Markov, and L. Shishkova, *Izv. Otd. Khim. Nauk BAN*, 1980, **13**, 198.

<sup>113</sup> I. Petkov, K. Roumyan, C. Ivanov, and P. Markov, 'Annuaire de l'Université de Sofia, Faculté de Chimie', in press.

<sup>114</sup> M. Kirilov and G. Petrov, *Ber.*, 1967, **100**, 3139.

<sup>115</sup> A. B. Bogatski, T. K. Tchumatchenko, A. E. Kojuchina, and M. B. Grenadirova, *J. Gen. Chem. (Russ.)*, 1972, **42**, 403.

<sup>116</sup> K. Flatau and H. Musso, *Angew. Chem.*, 1970, **82**, 390.

<sup>117</sup> F. Bonati and G. Minghetti, *J. Organomet. Chem.*, 1970, **22**, 5.

<sup>118</sup> R. Allmann, K. Flatau, and H. Musso, *Chem. Ber.*, 1972, **105**, 3067.

<sup>119</sup> R. H. Fisch, *J. Am. Chem. Soc.*, 1974, **96**, 6664.

<sup>120</sup> R. H. Fisch, R. E. Lundin, and W. E. Hadden, *Tetrahedron Lett.*, 1972, 921.

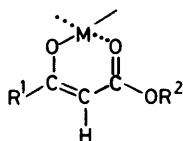
<sup>121</sup> R. Allmann and H. Musso, *Ber.*, 1973, **106**, 3001.

<sup>122</sup> G. Behnke and K. Nakamoto, *Inorg. Chem.*, 1967, **6**, 433, 490.

associates.<sup>123-125</sup> On the basis of i.r. and n.m.r. data, they have found evidence for the presence of carbeniate-, enolate- and chelate-type species in solutions of Reformatsky reagents. Their results provide support that the ratio between the different forms depends strongly on the solvation ability of the solvent used.

Various examples of reversible migration of an element included in an organic group in tautomeric systems have been studied by Lutzenko *et al.* (see for example *refs.* 126—128).

*Photoinduced Metalotropic Interconversions.* The influence of ultraviolet light on some metal derivatives of  $\beta$ -dicarbonyl compounds (10) in non-polar aprotic solvents was first described in *refs.* 129,130. Contrary to known examples where



(10) M = Cu, Ca, Mg, Co, Ni;

R<sup>1</sup> = Me, Ph; R<sup>2</sup> = various aliphatic radicals

their photoreductive destruction takes place in polar media,<sup>131-133</sup> it was found that under these conditions the changes caused by ultraviolet irradiation are fully reversible.

In some cases, a significant spectral change occurs in the course of time after dissolving the metal salt. The observed alterations in the u.v. spectrum of copper ethyl acetoacetate are presented in Figure 13.

<sup>123</sup> M. Gaudemar, *Bull. Soc. Chim. Fr.*, 1966, 3113.

<sup>124</sup> M. Gaudemar and M. Martin, *C. R. Acad. Sci. (Paris)*, 1968, **267C**, 1053.

<sup>125</sup> M. Bellassoued, F. Dardereze, F. Gaudemar-Bardone, M. Gaudemar, and N. Goasdoone, *Tetrahedron*, 1976, **32**, 2713.

<sup>126</sup> I. F. Lutzenko, Yu. T. Baukov, O. V. Dudukina, and E. N. Karamoarova, *J. Organomet. Chem.*, 1968, **11**, 35.

<sup>127</sup> I. F. Lutzenko, Yu. I. Baukov, I. Yu. Belavin, and A. N. Tworgov, *J. Organomet. Chem.*, 1968, **14**, 229.

<sup>128</sup> I. F. Lutzenko, Yu. I. Baukov, and I. Yu. Belavin, *J. Organomet. Chem.*, 1970, **24**, 359.

<sup>129</sup> P. Markov, I. Petkov, and C. Ivanov, *C. R. Acad. Sci. (Paris)*, 1978, **286C**, 505.

<sup>130</sup> P. Markov, I. Petkov, and C. Ivanov, *J. Organomet. Chem.*, 1979, **173**, 211.

<sup>131</sup> N. Filipescu and H. Way, *Inorg. Chem.*, 1969, **8**, 1863.

<sup>132</sup> H. D. Gafney and R. Lintvedt, *Inorg. Chem.*, 1970, **9**, 1728.

<sup>133</sup> H. D. Gafney and R. Lintvedt, *J. Am. Chem. Soc.*, 1970, **92**, 6996.

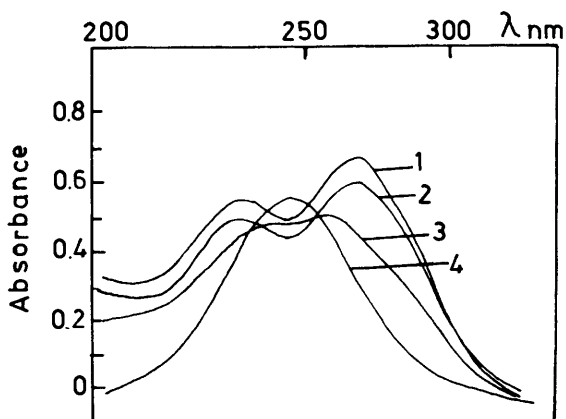


Figure 13 *U.v. spectra of copper ethyl acetoacetate in heptane (ca.  $0.5 \times 10^{-4} \text{ mol l}^{-1}$ ) measured at different times after solution (1)0, (2)1, (3)7, (4)20 h*

The ultraviolet irradiation of the stabilized (constant u.v. spectral characteristics with time) heptane solutions produces profound spectral changes (Figures 14—15).

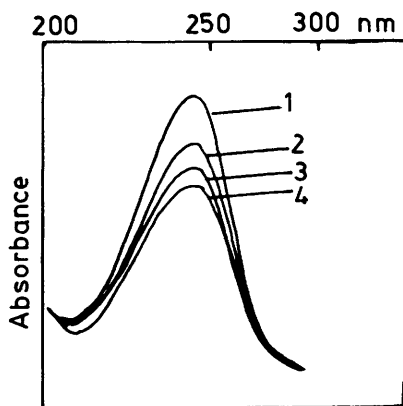
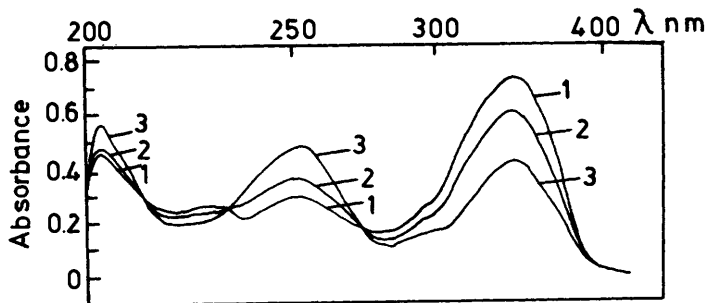


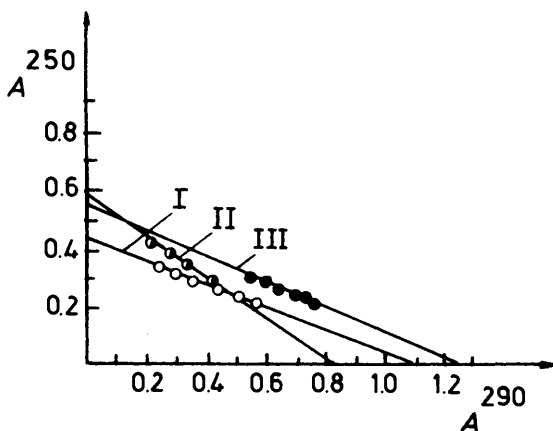
Figure 14 *U.v. spectra of copper ethyl acetoacetate in heptane (ca.  $0.5 \times 10^{-4} \text{ mol l}^{-1}$ ) at different times after the start of the u.v. (254 nm) irradiation*





**Figure 15** U.v. spectra of  $\text{Cu}(p\text{-ClC}_6\text{H}_4\text{COCH}_2\text{CO}_2\text{Et})_2$  in heptane (ca.  $0.5 \times 10^{-4} \text{ mol l}^{-1}$ ) at different times after the start of the u.v. irradiation (313 nm)

The linear dependences between 290 and 250 nm peaks of some metal derivatives ( $\text{R}^1 = \text{Ph}$ ), measured after different durations of ultraviolet irradiation, are given in Figure 16.



**Figure 16** Dependence between the absorbances  $A_{250}$  and  $A_{290}$  of compounds I, II, and III measured at different times after the start of u.v. irradiation (313 nm). Initial concentrations  $0.5 \times 10^{-4} \text{ mol l}^{-1}$ . (I),  $\text{Cu}(m\text{-MeC}_6\text{H}_4\text{COCH}_2\text{CO}_2\text{Et})_2$ ; (II),  $\text{Cu}(p\text{-ClC}_6\text{H}_4\text{COCH}_2\text{CO}_2\text{Et})_2$ ; (III),  $\text{Cu}(p\text{-MeC}_6\text{H}_4\text{COCH}_2\text{CO}_2\text{Et})_2$

Efforts to obtain a theoretical interpretation of the u.v.-spectra of some metal chelates of  $\beta$ -dicarbonyl compounds have been made by Basu and Chatterji.<sup>134</sup> According to Belford *et al.*<sup>135</sup> the 254 nm absorption band in the u.v. spectrum of copper ethyl acetoacetate is due to a  $\pi \rightarrow \pi^*$  transition in the CO-conjugated system of the chelate form. Substantially different results—two bands at 239 and

<sup>134</sup> S. Basu and K. K. Chatterji, *J. Phys. Chem.*, 1958, **209**, 360.

<sup>135</sup> R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, 1956, **2**, 11.

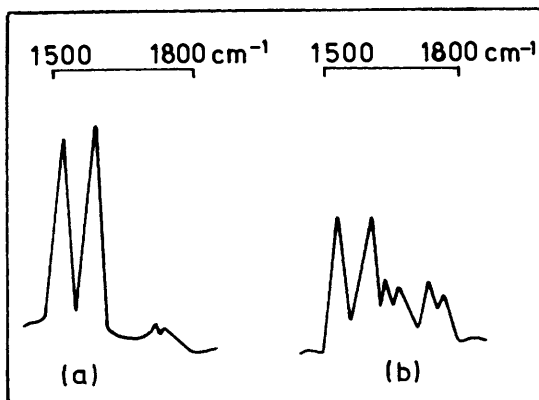
### Light-induced Tautomerism of $\beta$ -Dicarbonyl Compounds

269 nm—have been reported by Sen and Thankarajan.<sup>136</sup> Previously the Pariser–Parr–Pople scheme<sup>47</sup> and CNDO/S method<sup>48</sup> were used to study the ground- and excited-state properties of the enol form of acetoacetic acid. The energy of the  $\pi \rightarrow \pi^*$  transition, calculated for the chelate form is 5.00 eV (248 nm). On the other hand it has been shown experimentally<sup>64</sup> that the open (non-chelated) form absorbs at 228 nm.

Consequently, it may be concluded that monochromatic (254 nm) irradiation of metal salts solutions of ethyl acetoacetate ( $R^1$ -aliphatic radical) shifts the metallotropic equilibrium



to the carbeniate form. This conclusion gains support also from the available i.r. spectral data (Figure 17).



**Figure 17** *I.r. spectra of  $0.5 \times 10^{-3} \text{ mol l}^{-1}$  heptane solution of copper ethyl acetoacetate (a) before irradiation (b) after 120 min irradiation*

The strong i.r. absorption near  $1530$  and  $1600 \text{ cm}^{-1}$ , attributed to the chelate complex, decreases in intensity during irradiation while the intensity of the  $1720$  and  $1740$  absorption bands (carbeniate form) increases. Accordingly, new maxima appear at  $1640$  and  $1660 \text{ cm}^{-1}$  (enolate).

In the case of metallo-derivatives of benzoylactic acid ethyl ester ( $R^1 = C_6H_5$ ), the diminishing intensity in the  $280$ – $310 \text{ nm}$  region is accompanied by the appearance and enhancement of a new absorption band at  $245$ – $255 \text{ nm}$  (Figure 14). The presence of isobestic points in the successive u.v. spectra of irradiated solutions and the linear relationship found between the absorbances of two forms (Figure 17) undoubtedly show the existence of a photometalotropic interconversion producing predominantly the carbeniate form.

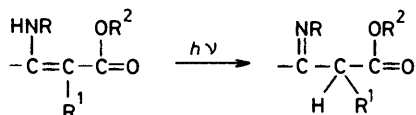
<sup>136</sup> D. N. Sen and N. Thankarajan, *Indian J. Chem.*, 1968, 6, 746.

The kinetics of the photometalotropic process depends on the type of the metal included.<sup>113</sup> The quantum yields vary from 0.017 to 0.029.

As it was pointed out, spectrophotometric assays of the solutions after irradiation show a gradual restoration of the chelate concentration. This reversibility implies that no destructive photoprocesses ensue under the chosen experimental conditions.

It is as yet difficult to rationalize the effect of u.v. light on the metalotropic equilibria. The available experimental data are insufficient to allow the discussion of the possible involvement of electronically excited states of the metal chelate in the process of photoactivated metalotropy. As far as this transformation is effected as a thermal reaction, it seems probable that an open enolate form is the resulting species. This assumption implies that the rate of the photoactivated process must depend on the stability of the respective metal chelate. However, the dependence of the rate of photoactivated metalotropy on some structural peculiarities of the ligand system and on the nature of the metal cannot be clearly traced. A correlation exists between the values of the rate constants and the respective quantum yields.<sup>130</sup> The substitution of electron-releasing atoms or groups at the *para*-position in benzene ring tends to increase the oscillator strength due to the lengthening of the conjugate system.

**Other Tautomeric Compounds.**—The nitrogen-containing analogues of ethyl acetoacetate, the ethyl ester of 3-aminocrotonic acid and its *N*-substituted derivatives, are photosensitive compounds. The alteration found<sup>137</sup> in the i.r. and u.v. spectra show that the irradiation gives rise to a photoinduced hydrogen transfer from the nitrogen to the carbon atom (Scheme 6):



Scheme 6

More recently,<sup>138</sup> supporting evidence for photoinitiated hydrazine–hydrazone isomerization, as shown in Scheme 7, has also been obtained.



Scheme 7

<sup>137</sup> P. Markov, I. Petkov, and M. Arnaudov, *Mol. Photochem.*, 1979, 9, 295.

<sup>138</sup> I. Petkov and P. Markov, to be published.

#### **4 Conclusion**

Three obvious areas for further development in the field of photoinduced tautomerism of  $\beta$ -dicarbonyl compounds can be outlined: *Mechanistic Aspects*. Further efforts in tracing the path of the migrating particle may show more clearly the roles of excitation, solvents, and catalysts. *Synthetic Aspects*. The thermal chemistry of  $\beta$ -dicarbonyls has been an active field of research for a very long time. Such studies have covered several areas of synthetic applications. It can be foreseen that their photochemical variants will be used in new synthetic pathways. *Biochemical Aspects*. Photoinduced tautomerism is an interesting phenomenon since it may play an important role in photochemical processes of biological significance.