COMPUTER SIMULATION OF INTRAMOLECULAR HYDROGEN TRANSFER TO CARBONYL OXYGEN BY A MONTE CARLO METHOD: PHOTOREACTIONS *VIA* REMOTE PROTON TRANSFER IN BENZOYLBENZOATES

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Abstract – The model based on the idea that the p_y-orbital of the carbonyl oxygen is responsible to receiving hydrogen was devised for simulation of intramolecular hydrogen transfer. A Monte Carlo method was applied to free rotation of a molecular chain performed by changing the dihedral angles, and a "hit" was defined as the case when the migrating hydrogen comes within the region defined as the p_y-orbital and satisfies all the geometrical requirements for abstraction. A set of parameters was employed for defining the region and the requirements; τ was defined as the angle formed between $O \cdots H$ vector and its projection on the mean plane of the carbonyl group ($-43° \leqq \tau \leqq +43°$), Δ as the $C=O \cdots H$ angle ($90 - 15° \leqq \Delta \leqq 90 + 15°$), θ as the $O \cdots H - C$ angle ($180 - 80° \leqq \theta \leqq 180 + 80°$), d as the distance from the center of the lobe of the p_y-orbital to hydrogen ($0 \leqq d \leqq 1.04$ Å). The minimum value for the distance between carbonyl oxygen (O_1) and the migrating hydrogen (H_i) and for that between non-bonded atoms except the pair of O_1 and H_i were assumed to be 0.52 Å and 1.54 Å, respectively. The application of this model to intramolecular β-, γ-, δ-, ϵ-, and ζ- hydrogen abstraction in ketones and η- and θ- proton transfer in oxoesters gave good results reflecting their photochemical behavior. The model was also used for prediction of photoreactivities of 2-(*N,N*-dibenzylamino)ethyl 2-, 3- and 4-benzoylbenzoate (**1a - c**).

INTRODUCTION

Photochemical reactions often provide new strategies for synthesis of organic compounds which can not be prepared easily by conventional methods.[1,2] Cyclobutanol formation in photochemistry of alkyl aryl ketones may be one of the typical examples.[2,3] Prediction of photo-reactivity of organic molecules is an important problem in photochemistry as well as in synthetic and industrial chemistry. The prediction may be achieved on the basis of the nature of the lowest excited state. The ketones having the lowest n, π^* excited state are far more reactive than those having the lowest, π, π^* excited state.[4-6] Geometrical consideration may be another approach for the reactivity. Intervention of biradical intermediates formed through intramolecular hydrogen abstraction by excited carbonyl oxygen is now well established in the photoreactions of the ketones.[4-6] The mode of the hydrogen abstraction is governed by stereoelectronic[7] or geometrical requirement[8]; the abstraction from the γ-carbon is much faster than that from any other position. The hydrogen abstraction *via* medium-sized cyclic transition states may be out of the geometrical requirement. However, several examples of formation of cyclic alcohols *via* ϵ-[9,10], ζ[11-15], η-[14-18], θ-[19-21], and ι- hydrogen migration[14] to carbonyl oxygen have

been reported by us and other groups. The possible hydrogen abstraction might be predicted by computer simulation. Winnic[22-24] estimated the possibility of remote hydrogen abstraction *via* large-membered cyclic transition states[25,26] by a Monte Carlo method[27] using lattice-based models. The localized orbital of hydrogen which migrates to carbonyl oxygen should overlap with the n-orbital of carbonyl oxygen. The model considering the size and the direction of the n-orbital empirically is simple, and might be more conveniently used for prediction of the intramolecular hydrogen migration in any ketone system. We report here the simple method of computer simulation, in which standard covalent bond lengths and angles are used and dihedral angles are determined on the basis of a Monte Carlo method for free rotation of a molecular chain containing a carbonyl group and abstractable hydrogen, and the application of the method for prediction of remote hydrogen migration in benzoylbenzoates.

MATERIALS AND METHODS

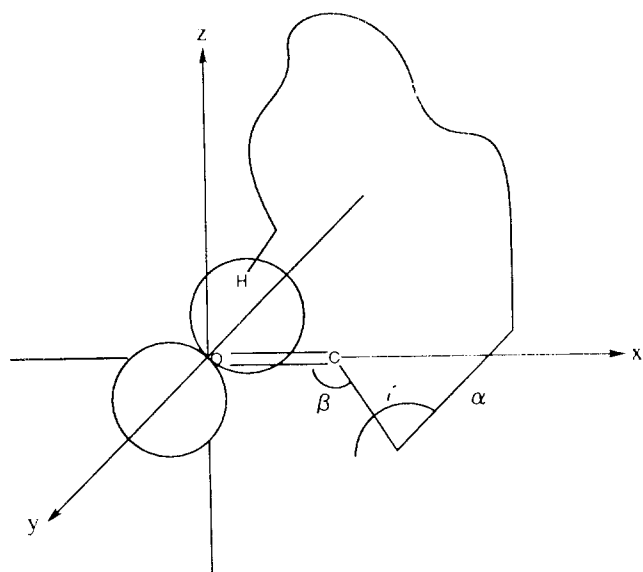*The Free Rotation Bonds Model.* In a ketone having a chain consisted in i-2 atoms, such as $O_1=C_2 - C_3 - C_4 \cdots C_{i-1} - H_i$, the

Figure 1. Model for intramolecular hydrogen transfer to carbonyl oxygen. Parameters α, β and γ represent the bond length, the bond angle, and the dihedral angle, respectively. The dihedral angles are determined by using random numbers (N) generated from a computer in order to simulate free rotation of bonds ($0 \leq N \leq 1$, $g=2 \times 3.1416 \times N$ radian)

positions of the atoms are defined by i-1 bond lengths (α), i-2 bond angles (β), and i-1 rotation (dihedral) angles (γ) (Fig. 1). The bond lengths and angles were assumed to be the standard values of the corresponding covalent bonds.[28] The carbonyl oxygen was placed on the origin of coordinates and the carbonyl carbon was placed on the x axis along the C=O distance, $+1.22$ Å. The y axis was defined as the axis including that of the p_y-orbital of oxygen. Then, the z axis was drawn so as to form a left-handed orthogonal system. The C_3 atom was placed on the x-y plane, (1.97, 1.33, 0), and the rotation angles at O_1 and C_2 were defined to be zero. The angle of rotation at C_3 is defined as the dihedral angle of O_1 $=C_2$ and C_3 - C_4, and at atom A_n as that of A_{n-2} A_{n-1} and A_n A_{n+1}. Dihedral angles were determined on the basis of random numbers (N_j) generated by a computer ($0 \leq N_j \leq 1$, $\gamma_j = 2 \times 3.1416 \times N_j$ rad). This ensures the free rotation of a molecule chain in a ketone. When a molecule has fixed configuration or conformation, such as *cis* and *trans*, the dihedral angle for the fixed portion was made to be constant.

The position of any atom A_j in the catenary bonds can be calculated from α_{j-1}, β_{j-2} and γ_j in terms of the position of the atoms A_{j-1} and A_{j-2} as

$$x'_j = \alpha_{j-1} \cos(\beta_{j-2}) \tag{1}$$

$$y'_j = \alpha_{j-1} \sin(\beta_{j-2}) \cos(\gamma_j) \tag{2}$$

$$z'_j = \alpha_{j-1} \sin(\beta_{j-2}) \sin(\gamma_j) \tag{3}$$

where the primed quantities indicate the specialized coordinate system used, i.e. taken about A_{j-1} as origin with the

x' axis drawing to contain the vector from A_{j-2} to A_{j-1}, the y' axis drawing to include the vector from A_{j-2} to A_{j-3} in the x'-y' plane and to get a positive value of the inner product of the vector from A_{j-2} to A_{j-3} and the unit vector on the y' axis, and the z' axis drawing to form a left-handed orthogonal system. The primed coordinates of A_j can be transformed into the original coordinates defined in the $O_1 = C_2$ - C_3 portion by a set of rotations followed by a linear translation of the axes. A rotation can be achieved by the following equations and calculation should be repeated j-3 times because the axis around C_2 are accordance with those around O_1. In every repetition x", y", z" obtained from the transformation using Eqs. (4) - (6) should be used as new x', y', z', respectively.

$$x''_j = x'_j \cos(\beta_k) - y'_j \sin(\beta_k) \tag{4}$$

$$y''_j = x'_j \cos(\gamma_{k+2}) \sin(\beta_k) + y'_j \cos(\gamma_{k+2})\cos(\beta_k) \\ - z'_j \sin(\gamma_{k+2}) \tag{5}$$

$$z''_j = x'_j \sin(\gamma_{k+2}) \sin(\beta_k) + y'_j \sin(\gamma_{k+2})\cos(\beta_k) \\ + z'_j \cos(\gamma_{k+2}) \tag{6}$$

Final linear transformation of the axes can be achieved as follow:

$$x_j = x_{j-1} + x''_j \tag{7}$$

$$y_j = y_{j-1} + y''_j \tag{8}$$

$$z_j = z_{j-1} + z''_j \tag{9}$$

The region where hydrogen can migrate to carbonyl oxygen is defined as in Fig. 2. A "hit" is defined as the case when the i-th hydrogen in the $O_1 = C_2 - C_3 - C_4 \cdots C_{i-1} - H_i$ system comes within the defined region and satisfies all the requirements shown in Fig. 2.

Spectroscopic methods. IR spectra were recorded with a JASCO A-3 spectrometer. ^{1}H-NMR spectra were determined with a JEOL FX90Q spectrometer using tetrarmethylsilane as an internal standard.
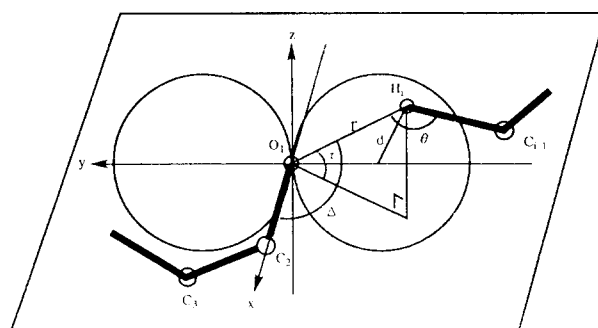

Figure 2. Geometric parameters for possible hydrogen transfer
$0 \leq d \leq 2.08/2$ Å
 $-43° \leq \tau \leq +43°$ (ideal value of τ is $0°$)
$90 - 15° \leq \Delta \leq 90 + 15°$ (ideal value of Δ is $90°$)
$180 - 80° \leq \theta \leq 180 + 80°$ (ideal value of θ is $180°$)
$2.08/4$ Å $\leq O_1$ H_i distance (r) O_1 $H_i \leq 2.08$ Å
Distance of non-bonded atoms except O_1 - $H_i \geq 1.54$ Å

Preparation of 2-(N,N-Dibenzylamino)ethyl-2-benzoylbenzoate (1a). Methyl *o*-benzoylbenzoate (5.01 g) and 2-*N,N*-dibenzylaminoethanol (4.95 g) were dissolved in 50 cm³ of toluene in a 100 cm³ round bottomed flask equipped with a magnetic stirrer and a reflux condenser. One lump of sodium was added and then the mixture was refluxed for 39 h. The mixture was cooled to the room temperature, washed with water and dried over sodium sulfate. After removal of the solvent, the residue was chromatographed on a silica gel column. Elution with benzene-ethyl acetate (30 : 1), vol/vol gave 1.96 g (22%) of **1a** : m.p. 94.5-95.5°C (from ethyl acetate-hexane); IR (KBr) 1670 and 1710 cm⁻¹; ¹H NMR (CDCl₃) δ 2.58 (2H, t, J = 6.2 Hz, CH₂N), 3.53 (4H, s, CH₂Ph), 4.12 (2H, t, J = 6.2 Hz, OCH₂), and 7.2-8.0 (19H, m, aromatic). Found: C 79.94, H 6.06, N 3.10 %. Calcd for C₃₀H₂₇O₃N: C 80.15, H 6.05, N 3.12 %.

Photolysis of 1a. A solution of **1a** (501 mg) in 50 cm³ of benzene was irradiated for 11 h with an Ushio 450 W high-pressure mercury lamp under nitrogen. After removal of the solvent, the residue was chromatographed on a silica gel column. Elution with benzene-ethyl acetate (30 : 1) , vol/vol gave 107 mg (21%) of 1,2-benzo-9-hydroxy-8,9-phenyl-7-oxa-4-aza-1-cyclononen-3-one (**2a**): m.p. 173-174.5°C (from benzene-hexane); IR (KBr) 1770 and 3550 cm⁻¹; ¹H NMR (CDCl₃) δ 1.27 (1H, s, OH), 2.59 (2H, m, CH₂N), 3.51 (2H, m, OCH₂), 3.69 (2H, ABq, J = 84.9 and 12.9 Hz, CH₂Ph), 4.79 (1H, s, CHPh), and 6.9-7.7 (19H, m, aromatic). Found: C 79.90, H 6.10, N 2.95 %. Calcd for C₃₀H₂₇O₃N: C 80.15, H 6.05, N 3.12 %.

RESULTS AND DISCUSSION

The intervention of a biradical intermediate is now well established in photoreactions *via* intramolecular hydrogen abstraction by carbonyl oxygen.[4-6] The same biradicals as those produced from possible direct hydrogen abstraction are formed *via* proton transfer to carbonyl oxygen from the charge-transfer states in photochemistry of ketones having an amino group.[29,30] The hydrogen migration regardless of whether as a hydrogen atom or a proton requires overlap of the n-orbital of the carbonyl oxygen and the s-orbital of migrating hydrogen. A simple model might be used for estimation of intramolecular hydrogen migration, in which the bond lengths (α) and the bond angles (β) are fixed, the dihedral angles(γ) are determined on the basis of a Monte Carlo method in order to achieve free rotation of a molecular chain (Fig. 1), and a "hit" is defined as the case when the migrating hydrogen comes within a defined region and satisfies all the requirements for abstraction. The region and the requirements must reflect the size of the n-orbital of carbonyl oxygen and the s-orbital of hydrogen and their effective overlap. The radii of the orbitals may be assumed to be van der Waars radii.

A set of parameters may define the geometrical relationship between the migrating hydrogen and carbonyl oxygen (Fig. 2). The parameter τ is defined as the angle formed between O $\cdots$ H vector and its projection on the mean plane of the carbonyl group, the parameter Δ as the C=O $\cdots$ H angle, and the parameter θ as the O $\cdots$ H - C angle. Since the hydrogen migration is expected to be most facile when hydrogen Hᵢ approaches the pᵧ-orbital of the carbonyl oxygen with maximum orbital overlap and there is agreement that the abstracting orbital is the non-bonding pᵧ-orbital which lies in the π-bond nodal plane,[31] the ideal values of these parameters, τ, Δ and θ are 0, 90, and 180°, respectively. The maximum permissible deviation in τ, Δ and θ from the ideal values must be estimated for computer simulation. Too small deviation makes a quite low number of "hit" in a great number of repetition and too larger deviation causes "hit" at any position. Since the crystalline environment limits the possible transition state geometries for hydrogen migration, the crystallographic data may provide a wealth of information on the geometric requirements for photochemical hydrogen abstraction. Scheffer has studied a variety of ketones that undergo intramolecular hydrogen transfer in their crystalline states and in two dozen examples in which x-ray crystal structures were obtained for reactive ketones, the value of τ ranged from 0 - 62°, with an average of 43° for 17 γ-hydrogen abstraction; of Δ, from 74 - 103°; and of θ, from 85 - 120°.[32] Since smaller deviation from ideal values should give better results for prediction, the range of the parameters were assumed as - 43° $\leq \tau \leq$ + 43°, 90 - 15° $\leq \Delta \leq$ 90 + 15°, and 180 - 80° $\leq \theta \leq$ 180 + 80° .

The remaining factor is the distance between the migrating hydrogen and carbonyl oxygen (r) and this distance determined from the x-ray crystal structure study is ranged from 2.3-3.1 Å.[25] This H - O distance has been considered to be the most important parameter for intramolecular hydrogen migration and the theoretically ideal value is $\leq$ 2.7 Å [32] (sum of the H and O van der Waals radii). However, the distance from the center of the lobe of the p-orbital to hydrogen should be more important because the hydrogen migration requires overlap of the n- and the s-orbital and the n-orbital is often assumed simply to be consisted of two balls. Then, the fourth parameter d, defined as the distance from the center of the p-orbital lobe to hydrogen, was introduced. Since the value of d should be smaller than a half of the sum of the H and O van der Waals radii, 2.7/2 was tentatively used as the value of d. Thus, all the parameters essential to the model assuming the pᵧ-orbital as the hydrogen receiving orbital were determined. In addition to the parameters there must be the limiting conditions for geometrical relationship between non-bonded atoms in a molecular chain because these atoms cannot approach too closely to each other. The value for the limitation must be larger than the distance of the C - C single bond (1.54 Å). Severe restriction may give a good result for the prediction of hydrogen migration but requires a great
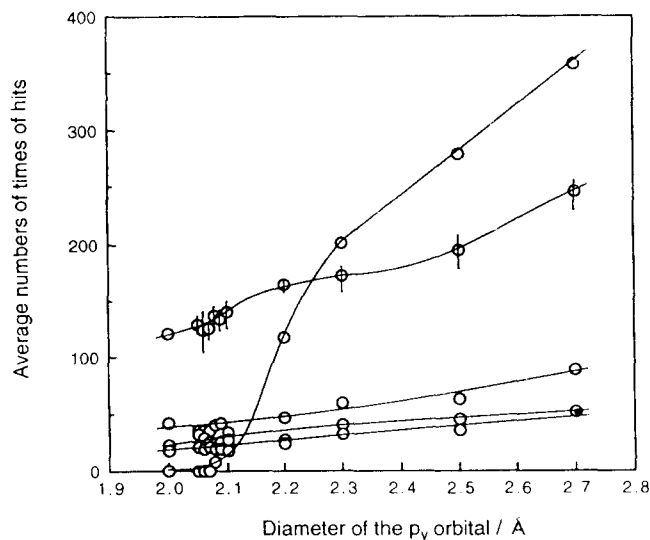
Figure 3. Effect of diameters of the P_y orbital lobe on probabilities of β-, γ-, δ-, ϵ-, and ζ-hydrogen abstraction in ketone system $O_1=C_2 - C_3 \cdots C_{i-1} - H_i$. The numbers of times of hit are average of three 10000 times reptition. The distribution of the numbers is shown in the case of γ-hydrogen abstraction

deal of repetition in calculation. Then, the minimum value for the distance between any non-bonded pair of atoms except the pair of the carbonyl oxygen and the migrating hydrogen was assumed to be 1.54 Å. Moreover, the hydrogen cannot approach too closely to the oxygen because of repulsive interaction between their nuclei. The limiting distance was assume to be a half of the p_y orbital radius.

The probabilities of occurrence of intramolecular hydrogen abstraction from β-, γ-, δ-, ϵ-, and ζ -carbons in ketone systems, $O_1=C_2 - C_3 \cdots C_{i-1} - H_i$, were estimated in order to verify the model. The number of the times of hit was the largest in hydrogen abstraction from the β-position. This is not accordance with experimental results because γ-hydrogen abstraction greatly predominates over other possible modes. Then, the distance d in the model was changed (Fig. 3). The number for β-
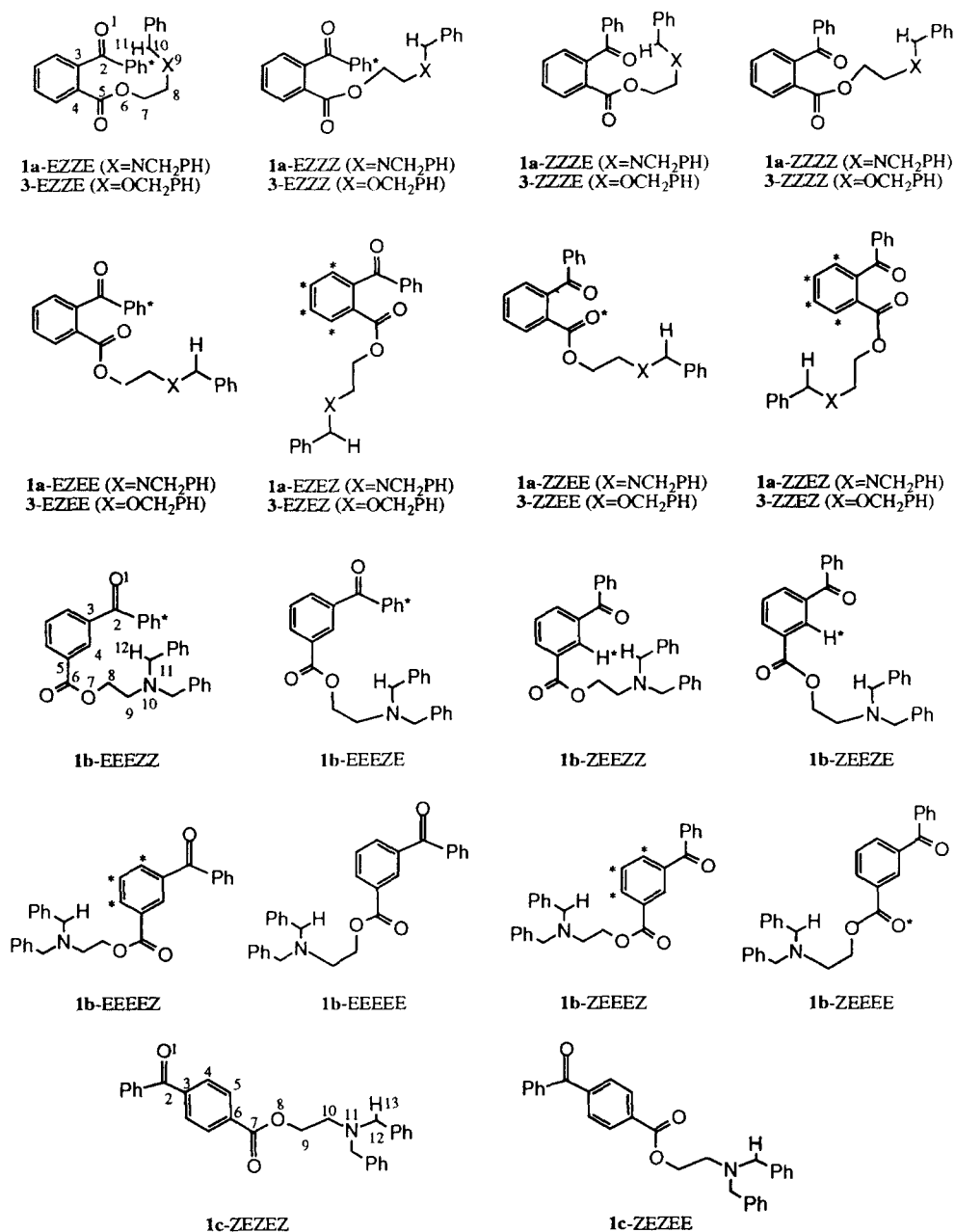
hydrogen abstraction decreased rapidly with a decrease of the d value and became zero at 2d = 2.07 though numbers for hydrogen abstractions from other positions decreased gradually. These results indicate that the distance is the quite important parameter especially in β-hydrogen abstraction. The d value was determined to be 2.08/2 because β-hydrogen abstraction[32-37] does not compete with γ-hydrogen abstraction in photochemistry of butyrophenone and valerophenone.[38] Times of hit at d = 2.08/2 are greater in γ- than β-hydrogen abstraction and decrease exponentially from γ- to ζ-hydrogen abstraction. This tendency is good accordance with the order of predominancy of hydrogen abstraction in the photochemistry of phenyl alkyl ketones. Hence, the model is expected to be used for prediction of occurrence of intramolecular hydrogen transfer in any carbonyl system though the numbers obtained as times of hit do not meet the relative quantum yields properly because the model does not contain any time-dependent factor, such as a lifetime.

Photocyclization to medium-sized cyclic alcohols *via* remote hydrogen transfer are rare event in photochemistry of carbonyl compounds.[11-21] All the migrating hydrogens are activated by a hetero atom or a special group, such as a phenyl or an allyl group. This indicates that remote hydrogen transfer occurs when a hydrogen locates in a suitable position and is activated. The model described above would provide information about the suitable position. Then, the model was applied to photoreactions of β- and γ-oxoesters *via* 1,9- and 1,10-proton shift, respectively. A long flexible molecular chain may allow approaching of the migrating hydrogen to ketone carbonyl oxygen from any direction. Steric effects by the benzoyl benzene ring must reduce the possibility of the migration of a remote hydrogen to the benzoyl carbonyl oxygen because the effects evidently obstruct the approach of a molecular chain through the space occupied by the benzene ring. The effects were taken into account in the calculation by the limitation on close approach of non-bonded atoms as described above. There must be a rotational barrier to interconver-

Table 1 . Probability of remote hydrogen transfer in oxoesters.

Compound	Yield of lactone	Mode[d]	Structure of conformer C - $C_{C=O}$ - O - C/degree	Times of hit[e]
PhCOCH$_2$COO(CH$_2$)$_2$N(CH$_2$Ph)$_2$	52[a]	1,9-shift	180	10
			0	9
PhCOCH$_2$COO(CH$_2$)$_2$OCH$_2$Ph	48[b]	1,9-shift	180	7
			0	10
PhCO(CH$_2$)$_2$COO(CH$_2$)$_2$N(CH$_2$Ph)$_2$	57[c]	1,10-shift	180	5
			0	7

[a]Ref. 13 and 15. [b]Ref. 14 [c]Ref. 18 [d]Mode of hydrogen shift [e]Average of three runs of 10000 times repetition; Steric effects by the benzene ring was taken into account in the calculation.

1a-EZZE (X=NCH$_2$PH)
3-EZZE (X=OCH$_2$PH)

1a-EZZZ (X=NCH$_2$PH)
3-EZZZ (X=OCH$_2$PH)

1a-ZZZE (X=NCH$_2$PH)
3-ZZZE (X=OCH$_2$PH)

1a-ZZZZ (X=NCH$_2$PH)
3-ZZZZ (X=OCH$_2$PH)

1a-EZEE (X=NCH$_2$PH)
3-EZEE (X=OCH$_2$PH)

1a-EZEZ (X=NCH$_2$PH)
3-EZEZ (X=OCH$_2$PH)

1a-ZZEE (X=NCH$_2$PH)
3-ZZEE (X=OCH$_2$PH)

1a-ZZEZ (X=NCH$_2$PH)
3-ZZEZ (X=OCH$_2$PH)

1b-EEEZZ

1b-EEEZE

1b-ZEEZZ

1b-ZEEZE

1b-EEEEZ

1b-EEEEE

1b-ZEEEZ

1b-ZEEEE

1c-ZEZEZ

1c-ZEZEE

Scheme 1

* Steric effect of the atom or atoms in the group was taken into caluculation

sion of conformers having E- and Z-conformation around the ester single C - O bond. Then, the calculation was performed assuming a fixed dihedral angle for the ester portion. The results summarized in Table 1 indicate that the remote hydrogen transfers are possible in all the oxoesters. These results are accordance with experimental results. The hydrogen transfer in the oxoesters might occur from both E- and Z-conformers.

Finally, the model was applied to new photoreactions; photoreactivities of 2-(N,N-dibenzylamino)ethyl 2- and 3-benzoylbenzoate (1a and b) were examined. The 2-benzoylbenzoate 1a may be expected to undergo photocyclization via 1,10-hydrogen transfer as O-homologue 2-(benzyloxy)ethyl 2-benzoylbenzoate (3) did.[20] However, photoreactivity of 1b is not so easy to predict because of its long flexible chain. The probabilities of remote hydrogen transfer in 1a, b, the corresponding 4-benzoyl derivative 1c, and 3 were simulated by the model. In these cases some dihedral angles must be fixed because of rings and conjugated systems. The benzoyl and ester carbonyl groups might be coplanar with the benzoate benzene ring and the ester function might be also coplanar with the ring.[22] Then, the estimation of the probabilities was performed for

eight conformers in the cases of **1a, b** and **3**, and two conformers in **1c**. The catenary bonds from carbonyl oxygen to migration hydrogen were regard as a molecular chain, and a fixed configuration or conformation about A_j - A_{j+1} - A_{j+2} - A_{j+3} (from O_1 - C_2 - C_3 - C_4 to C_{n-3} - $C_{(C=O)n-2}$ - O_{n-1} - C_n) was represented by the symbol Z or E (Scheme 1). The steric effect by atoms, marked with an asterisk in Scheme 1, was taken into account in calculation. The times of hit in all conformers of **1b** and **c** are null indicating no hydrogen transfer would occur in **1b** and **c**. These results are accordance with the fact that 2-(N,N-dimethylamino) ethyl 3-vareloylbenzoate and 4-benzoylbenzoate show no measurable internal charge transfer quenching.[39] In the cases of **1a** and **3** the average numbers of three runs of 10000 times repetition were 29 for the conformer **1a-ZZZE** and 15 for **3-ZZZE** though the numbers for other conformers were null. Therefore, **1a** is expected to undergo a photoreaction *via* 1,10 - hydrogen shift.

Irradiation of **1a** in benzene indeed gave **2a** in 21 % yield (Scheme 2). The IR spectrum of **2a** showed the characteristic peaks due to the hydroxyl and the lactone carbonyl groups at 3550 and 1770 cm^{-1}, respectively. Formation of **2a** can be reasonably explained in terms of photocyclization *via* 1,10-proton shift from the charge-transfer state. The proton shift probably occurs in the conformer **1a-ZZZE**
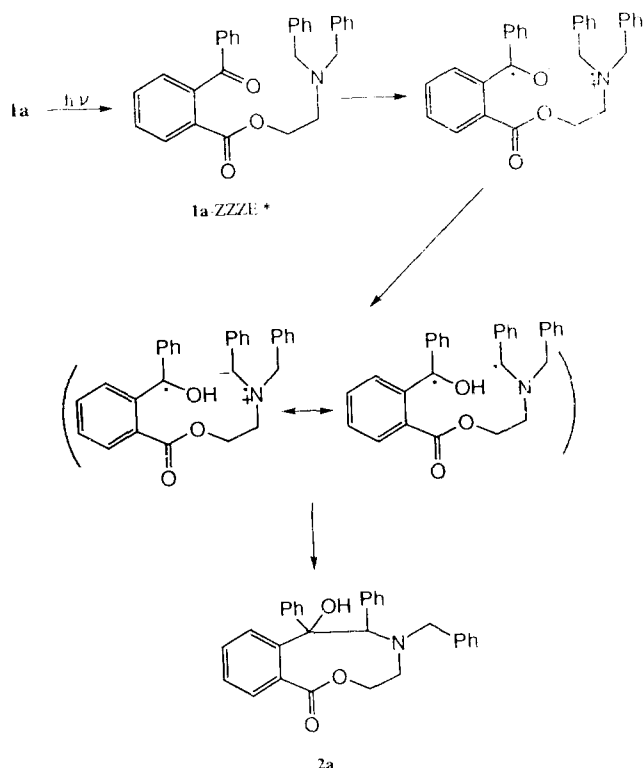
CONCLUSIONS

The model devised on the basis of the idea that the p_y-orbital of the carbonyl oxygen is responsible to receiving hydrogen could be used for estimation of probabilities of occurrence of intramolecular hydrogen abstraction from β-, γ-, δ-, ϵ-, and ζ-carbons in ketone systems, $O_1=C_2$ - $C_3 \cdots C_{i-1}$ - H_i, and proton transfer from η-and θ- carbon in β- and γ-oxoesters. Photoreactivities of 2-(N,N-dibenzylamino)ethyl 2-, 3- and 4-benzoylbenzoate (**1a-c**) *via* remote proton transfer could be successfully predicted by this model. The model is simple but can be used for prediction of photochemical behavior of carbonyl compounds.

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Scheme 2

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