J. Org. Chem. 1984, 49, 3167–3170

Degenerate β-Aryl Rearrangements in Photochemically Generated Triarylvinyl Cations

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Received January 18, 1984

Irradiation of triphenyl- (**1a**), tri-*p*-tolyl- (**1b**), or tri-*p*-anisylvinyl bromide (**1c**) in methanol gave the vinyl ethers **4** and the phenanthrenes **5**. A study of [2-^{13}C]-labeled bromides showed that β-aryl rearrangement takes place in the photochemically generated vinyl cations **3***. Irradiation of triaryl[2-^{13}C]vinyl bromides **1*** in trifluoroethanol and analysis of the extent of scrambling from C-2 to C-1 in the trifluoroethyl vinyl ethers **8** showed 38%, 72%, and 92% rearrangement of the ^{13}C label for **1a***, **1b***, and **1c***, respectively. Similar irradiation of **1*** in methanol resulted in no rearrangement in **4**. The results are discussed in relation to the nature of the solvent, the stability of the triarylvinyl cations, and the migratory aptitudes of the aryl groups. The behavior of the photochemically and thermally generated ions was compared.

Introduction

It has been reported recently that vinyl cations are generated by photolysis of vinyl halides.[1-3] The photochemically generated vinyl cation undergoes rearrangement, elimination, and capture processes, i.e., reactions which are characteristic of the intermediates formed in solvolysis of vinylic derivatives.[4] The photochemical formation of vinyl cations differs mechanistically from thermal solvolyses. In the photolysis, a vinyl cation is formed by homolytic cleavage of the carbon–halogen bond in the excited molecule, followed by an internal electron transfer in the resulting radical pair.[5] In contrast, in solvolyses, a vinyl cation is formed directly by the heterolysis of the carbon–halogen bond. The cation from photolysis can also be generated in solvents of low polarity and under very mild conditions. The photochemical method is therefore complementary to the thermal method and enables the generation of ions which are difficult to obtain under solvolytic conditions. It is, therefore, of interest to investigate the generation and behavior of vinyl cations under photochemical conditions.

A comparison of the photochemically and solvolytically generated ions may give support to the intermediacy of these species under photochemical conditions, and point to the similarities and differences in the nature of the ions formed by the different routes. Two valuable comparisons have recently been reported. Lodder and co-workers[6] have shown that the photochemically generated trianisylvinyl cation has identical selectivity to capture by Br$^-$ or AcOH as the cation derived from the solvolysis of trianisylvinyl bromide, and Kitamura, Kobayashi and Taniguchi[5] have reported that several photochemically generated β-arylvinyl cations could rearrange to more stable vinyl cations as in the solvolytically generated ions.

Table I. Photolysis of Triarylvinyl Bromides in Methanol at 5 °C

RBr	irradiation time, h	yield, % (products)
1a	4	71 (**4a**); 18 (**5a**); 6 (**6a**)
1b	3	71 (**4b**); 19 (**5b**); 7 (**6b**)
1c	2	74 (**4c**); 22 (**5c**); trace (**6c**)

β-Aryl rearrangements across the double bond in triarylvinyl cations have been investigated extensively.[4,7] Lee[8] and Rappoport[9] have also made extensive studies of the degenerate β-aryl rearrangements in solvolytically generated triarylvinyl cations. These reactions have the advantage that the reactant and product ions are chemically identical so that the intrinsic driving force for the rearrangement itself is reflected by the ease of rearrangement of the different ions. In the present work, we have studied the photochemical formation and rearrangement of ^{13}C-labelled triphenyl-, tri-*p*-tolyl-, and tri-*p*-anisylvinyl cations. Two extreme solvents, the highly nucleophilic methanol and the poorly nucleophilic 2,2,2-trifluoroethanol (TFE) were used. The extents of rearrangement of the photochemically and thermally generated ions were then compared.

Results and Discussion

Photolysis of Triarylvinyl Bromides 1 in Methanol. Triphenylvinyl bromide (**1a**), tri-*p*-tolylvinyl bromide (**1b**), and tri-*p*-anisylvinyl bromide (**1c**) were irradiated at 5 °C in a 9:1 mixture of methanol and methylene chloride in the presence of a small amount of pyridine through a Pyrex

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(9) (a) Rappoport, Z.; Noy, E.; Houminer, Y. *J. Am. Chem. Soc.* **1976**, *98*, 2238–2244. (b) Houminer, Y.; Noy, E.; Rappoport, Z. *Ibid.* **1976**, *98*, 5632–5642.

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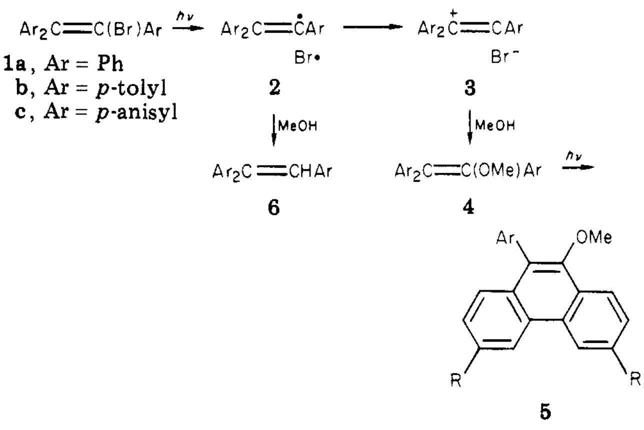
Scheme I



filter by the use of a 100-W high-pressure mercury lamp. The conversion was nearly complete and column chromatography on alumina gave three types of products: the vinyl ethers **4**, the 3,6-disubstituted-9-aryl-10-methoxyphenanthrenes **5** and a small amount of triarylethylenes **6**. The yields are given in Table I. Since irradiation of **4a** gave **5a**, we believe that the phenanthrenes are produced by further photoreaction of the vinyl ethers **4**, i.e., by a stilbene-like photocyclization.[10] Compounds **6** are probably formed from the radicals **2** by hydrogen abstraction from the solvent. The formation of the methanol incorporated products **4** shows that nucleophilic trapping of a photochemically generated triarylvinyl cation **3** takes place (Scheme I). This course of reaction is supported by the results of previous work.[11,12]

Compared with thermal solvolysis,[13] the results of Table I indicate the characteristics of photosolvolysis. Although the triarylvinyl cations **3** are stabilized by the α-aryl group, the solvolysis of triarylvinyl bromides in aqueous EtOH requires high temperatures (120–160 °C) and longer reaction times.[13] On the other hand, the photolysis gave high yields of the solvolysis products even when conducted below room temperature and for shorter reaction times. It therefore opens the way for the investigation of vinyl cations under mild conditions.

The photochemically generated ions **3** are capable of β-aryl rearrangement across the double bond. However, since the three aryl substituents are identical, this rearrangement is degenerate as the precursor and the product ions are identical. In order to study the extent of rearrangement the β-^{13}C-labelled triarylvinyl bromides were used.

Photolysis of Triaryl[2-^{13}-C]vinyl Bromides (1*) in Methanol and in Trifluoroethanol. (a) In MeOH. The triaryl[2-^{13}C]vinyl bromides **1a*–1c*** were irradiated in a 9:1 (v/v) mixture of methanol and methylene chloride containing pyridine. The main products, the vinyl ethers **4a*–4c*** were acid hydrolyzed to the ketones which were reduced by sodium borohydride to the 1,2,2-triarylethanols **7**. ^{13}C NMR showed that only [2-^{13}C]-**7** was formed. No scrambling of the label to C-1 was observed, even in the case of tri-*p*-anisyl[2-^{13}C]vinyl bromide (**1c***) which gives very extensive scrambling in the photolysis in TFE (see below).

Scheme II

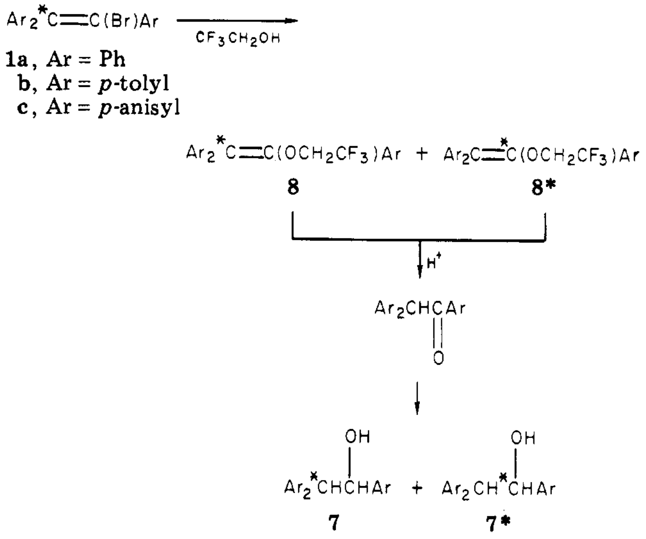


Table II. β-Aryl Rearrangements in the Photolysis of Triaryl[2-^{13}C]vinyl Bromides 1*

RBr	solvent/base	T, °C	% rearrangement from C-2 to C-1[a]	$k_{SOH}/k_{r(Ar)}$[b]
1a*	4:1 (v/v) TFE-CH_2Cl_2/2,6-lutidine	20	38 ± 2[c]	6.5
1b*		20	72 ± 2[d]	1.56
1c		20	92 ± 2[e]	0.35
1a*	9:1 (v/v) MeOH-CH_2Cl_2/pyridine	5	0 ± 3	>50
1b*		5	0 ± 3	>50
1c*		5	0 ± 3	>50

[a] 50% scrambling of the label from C-2 to C-1 amounts to 100% rearrangements. [b] Calculated by eq 1. [c] Calculated by the relative intensity ratio method[8c] with I_1^0/I_s, I_1/I_s, I_2^0/I_s, and I_2/I_s equalling 0.069, 0.73, 0.068, and 2.78, respectively. The most intense aromatic peak was used as internal reference standard, its integrated intensity being I_s, while I_1^0 and I_1 or I_2^0 and I_2 are the integrated intensities of the C-1 or C-2 absorptions, respectively, for the unlabeled 1,2,2-triphenylethanol and the labeled 1,2,2-triphenylethanol derived from the experiment. [d] I_1^0/I_s, I_1/I_s, I_2^0/I_s, and I_2/I_s equal 0.082, 1.23, 0.084, and 2.15, respectively, the most intense aromatic peak of 1,2,2-tri-*p*-tolylethanol being used as the internal reference standard. [e] I_1^0/I_s, I_1/I_s, I_2^0/I_s, and I_2/I_s equal 0.429, 7.83, 0.449 and 9.63, respectively, the methoxy absorption of 1,2,2-tri-*p*-anisylethanol being used as the internal reference standard. For an illustration of the calculations, see ref 8c.

(b) In TFE. Due to a combination of high polarity and low nucleophilicity,[14] trifluoroethanol (TFE) is a good solvent for observing 1,2-aryl rearrangements across the double bond since the vinyl cation may have sufficiently long lifetime to rearrange before a nucleophilic trapping by the solvent.

Irradiation of triaryl[2-^{13}C]vinyl bromides **1a*–1c*** in a mixed solvent of 4:1 (v/v) of TFE and methylene chloride was carried out in the presence of 2,6-lutidine through a Pyrex-filter with a high-pressure mercury lamp at room temperature. The main products were the vinyl ethers **8a–8a*–8c–8c*** and the phenanthrene derivatives **9**. Acid-catalyzed hydrolysis of **8–8*** mixtures to the ketone, followed by sodium borohydride reduction, gave a mixture of the 1,2,2-triarylethanols **7** and **7*** (Scheme II). The extent of scrambling of the label from C-2 to C-1 was

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[10] Stermitz, F. R. In "Organic Photochemistry"; Chapman, O. L., Ed.; Marcel Dekker: New York, 1966; Vol. 1, pp 248–282.

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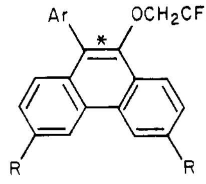

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determined from the intensity ratios of C-1 and C-2 in **7**–**7*** by ^{13}C spectroscopy.[8] Extensive scramblings were observed for all the substrates, indicating that 1,2-aryl rearrangements across the double bond take place in the photogenerated vinyl cations. The extent of scrambling (Table II) was found to increase in the order **1a*** < **1b*** < **1c***. This follows both the order of stability of the vinyl cations, i.e., tri-*p*-anisylvinyl (**3c**) > tri-*p*-tolylvinyl (**3b**) > triphenylvinyl (**3a**), and the order of migratory aptitudes of the aryl groups: anisyl > tolyl > phenyl.[15]

Comparison of Degenerate Rearrangements in Photosolvolysis and Thermal Solvolysis. The extents of degenerate rearrangements in triarylvinyl cations generated by photolysis of bromides **1*** are summarized in Table II. The reaction scheme which involves competition between 1,2-aryl rearrangement across the double bond (rate constant $k_{\mathrm{r(Ar)}}$ for a single aryl group) and nucleophilic trapping by the solvent (rate constant k_{SOH}) is given in Scheme III. (It should be noted that complete scrambling, i.e., formation of 50% **10**:50% **10′** amounts to 100% β-aryl rearrangement). Using the steady-state approximation for the ions **3*** and **3*′** eq 1 is obtained. The $k_{\mathrm{SOH}}/k_{\mathrm{r(Ar)}}$ ratios,

$$[\mathbf{10}]/[\mathbf{10'}] = 1 + (k_{\mathrm{SOH}}/2k_{\mathrm{r(Ar)}}) \qquad (1)$$

reflecting the combined effects of the stability of the vinyl cation, the migratory aptitude of the β-aryl group, and the nucleophilicity and ionization power of the solvent, are also given in Table II.

The effect of solvent is dramatically demonstrated by the differences in MeOH and in TFE. MeOH has a higher dielectric constant[16] but it is less ionizing than TFE.[17] However, the important difference is in the nucleophilicity values. Methanol is much more nucleophilic (i.e., has higher k_{SOH}) than TFE. Although the higher dielectric constant of MeOH may stabilize the bridged transition state more than TFE, its higher k_{SOH} results in an effective capture of the ion **3*** before any rearrangement takes place. In contrast, in TFE, k_{SOH} and $k_{\mathrm{r(Ar)}}$ compete and for ion **3c***, $k_{\mathrm{r(An)}} > k_{\mathrm{SOH}}$.

The effect of the aryl migrating group and the aryl substituents at the migration origin and migration terminus has previously been discussed.[4,7] A comparison of **3a***, **3b***, and **3c*** involves changes in all of these three groups. Since the inherent order of migratory aptitudes ($k_{\mathrm{r(Ar)}}$) is An > Tol > Ph, and the life time toward capture would be **3c** > **3b** > **3a**, i.e., k_{SOH}(**3c***) < k_{SOH}(**3b***) < k_{SOH}(**3a***), the net result in the order of $k_{\mathrm{SOH}}/k_{\mathrm{r(Ar)}}$ would be **3a*** > **3b*** > **3c***, as observed.

Scheme III

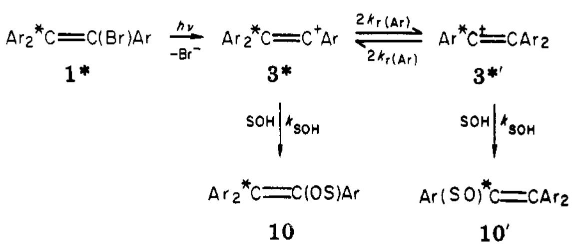

Table III. Analytical and ^1H NMR Data for the Photolysis Products

no.[a]	mp, °C[b]	^1H NMR solvent: δ[c]
4a	110–111	$CDCl_3$: 3.37 (s, MeO), 6.82–7.28 (m, Ar)
4b	115–116	CCl_4: 2.23, 2.29, 2.33 (3 s, 3 Me), 3.39 (s, MeO), 6.79–7.09 (m, Ar)
4c	114–116	$CDCl_3$: 3.46, 3.73, 3.77, 3.81 (4 s, 4 MeO), 6.37–7.15 (m, Ar)
5a	195–196[d]	$CDCl_3$: 3.59 (s, MeO), 7.49–8.75 (m, Ar)
5b	132–133	CCl_4: 2.33, 2.43, 2.48 (3 s, 3 Me), 3.42 (s, MeO), 6.78–8.20 (m, Ar)
5c	137–138	$CDCl_3$: 3.56, 3.91, 4.00, 4.04 (4 s, 4 (MeO), 6.60–8.06 (m, Ar)
9a	147–149	CCl_4: 3.85 (q, *J* = 8.4 Hz, CH_2), 7.01–8.98 (m, Ar)
9b	142–144	CCl_4: 2.37, 2.46, 2.51 (3 s, 3 Me), 3.63 (q, *J* = 8.5 Hz, CH_2), 6.91–8.02 (m, Ar)
9c	112–114	CCl_4: 3.74 (q, *J* = 8.4 Hz, CH_2), 3.86, 3.92, 3.96 (3 s, 3 MeO), 6.89–8.21 (m, Ar)

[a] Satisfactory elemental (C and H) analyses were obtained for all compounds. [b] Crystallized from EtOH. [c] The integration is consistent with the assignment. [d] Crystallized from EtOH–C_6H_6.

Unfortunately, only qualitative comparisons with the extents of the thermal solvolytic rearrangement are possible. First, data in TFE are available only for **1a*** and **1c***. Second, in the thermal solvolysis an extensive common ion rate depression makes the extent of rearrangement dependent on the extent of reaction.[8g] Third, and most important, due to the lower temperature used in the photolysis experiment, sufficient solubility was achieved only by the addition of methylene chloride as a cosolvent. Consequently, both the temperature and the solvent are different in the two types of experiments. Nevertheless, the qualitative order of the extent of the thermal rearrangement is identical with that in the photochemical work. In AcOH/AgOAc the $k_{\mathrm{SOH}}/k_{\mathrm{r(Ar)}}$ values are 25.4 (**3a***)[8a] > 10.8 (**3b***)[8f] > 6.0 (**3c***)[8c]. In buffered CF_3COOH the order is 3.16 (**3a***)[8c] > 0.30 (**3b***)[8f] > 0 (**3c***)[8c]. In TFE/2,6-lutidine $k_{\mathrm{SOH}}/k_{\mathrm{r(Ar)}}$ = 2.6 – 0.44 between 24 and 480 h for **3a***[8f] but >0.08 for **3c***.[9b] Qualitatively, the $k_{\mathrm{SOH}}/k_{\mathrm{r(Ar)}}$ values in Table II are larger, i.e., the extent of the degenerate β-aryl rearrangement in the photochemically generated ions is apparently lower than in the thermal solvolysis. Although the differences could be accommodated by introducing assumptions concerning temperature and solvent effects, we feel that this will not improve our understanding. In view of Lodder's identical selectivity of the photochemically and thermally generated ion,[6] we conclude, therefore, that the rearrangements in the photochemically and thermally generated ions follow semiquantitatively the same pattern.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were taken on Hitachi R-24B and R-60 spectrometers. The labeled vinyl bromides, triphenyl[2-^{13}C]vinyl bromide **1a***,[8b] tri-*p*-tolyl[2-^{13}C]vinyl bromide **1b***,[8f] and tri-*p*-anisyl[2-^{13}C]vinyl bromide **1c***,[8c] were prepared as already described in the literature. Similar methods were used to prepare the unlabeled bromides.

Photolysis of Triarylvinyl Bromides 1 in Methanol. Irradiation of the triarylvinyl bromide **1** (2.0 mmol) was carried out in methanol (90 mL) containing methylene chloride (10 mL) and pyridine (0.2 mL) at 5 °C under a nitrogen atmosphere by using

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[15] Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper & Row: New York, 1976; pp 284–286.

[16] The dielectric constants ε at 25 °C are: MeOH, 32.63 ("Handbook of Chemistry and Physics", 50th ed.; Weast, R. C., Ed.; 1969–1970, p E62); TFE, 26.14 (Mukherjee, L. M.; Grunwald, E. *J. Phys. Chem.* **1958**, *62*, 1311–1314).

[17] From a compilation of *Y* and *N* values which are based on *t*-BuCl, *Y* (MeOH) = −1.09, *N* (MeOH) = 0.01; *Y* (TFE) = 1.045, *N* (TFE) = −2.78 (Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674).

a Pyrex-filtered high-pressure mercury lamp (100 W). After irradiation the solvent was evaporated and the products were separated by column chromatography on alumina. The identified products were the vinyl ethers **4**, the phenanthrenes **5**, and small amounts of the known triarylethylenes **6a**,[18] **6b**,[19] and **6c**.[20] ^{1}H NMR chemical shifts for **4** and **5** are given in Table III. Irradiation of **4a** was carried out under the same conditions as described above without a Pyrex filter for 2 h. The sole product **5a** was obtained (conversion 45%).

Photolysis of Triaryl[2-^{13}C]vinyl Bromides 1* in TFE. Irradiation of triaryl[2-^{13}C]vinyl bromides **1*** (1.5 mmol, diluted with unlabelled vinyl bromide **1** to ca. 45% ^{13}C enrichment) was similarly carried out in a mixture of TFE (80 mL) and methylene chloride (20 mL) containing 2,6-lutidine (0.2 mL) at room temperature. For ^{13}C NMR analysis, the main products, i.e., the trifluoroethyl ethers **8** and **8*** were converted to triarylethanols **7** and **7*** in the following manner: after irradiation the solvent was removed, 5 mL of concentrated HCl and 50 mL of ethanol was added to the residue, and the solution was refluxed for 1 h. Extraction with ether gave the product mixture which was treated with sodium borohydride (120 mg) in ethanol (50 mL) without further purification to give the triarylethanols **7** and **7***. Column chromatography on silica gel gave both **7** and **7*** and the phenanthrenes **9**. The analytical and spectral data of compounds **9** are given in Table III. [2-^{13}C]-labelled triphenylethanol **7a**, mp 85–88 °C (aqueous ethanol) (lit.[8a] mp 88 °C), tri-*p*-tolylethanol **7b**, mp 93–96 °C (aqueous ethanol) (lit.[8f] 93–94 °C), and tri-*p*-anisylethanol **7c**, mp 110–111 °C (EtOH) (lit.[8c] mp 113–114 °C), were identical with the authentic samples.

Photolysis of Triaryl[2-^{13}C]vinyl Bromides 1* in MeOH. Irradiation of triaryl[2-^{13}C]vinyl bromides **1*** (diluted with unlabelled vinyl bromide **1** to ca. 45% enrichment, 1.5 mmol) was carried out in a mixture of methanol (90 mL) and methylene chloride (10 mL) containing pyridine (0.15 mL) at 5 °C under conditions similar to the photolysis of unlabelled **1** in methanol. Workup similar to that described above gave the main products, the vinyl ethers **4**. They were converted to the triarylethanol **7** and analyzed by ^{13}C NMR spectroscopy.

Registry No. 1a, 1607-57-4; **1b**, 66184-02-9; **1c**, 25354-46-5; **4a**, 62456-54-6; **4b**, 91083-68-0; **4c**, 91083-69-1; **5a**, 91083-70-4; **5b**, 91083-71-5; **5c**, 91083-72-6; **9a**, 91083-73-7; **9b**, 91083-74-8; **9c**, 91083-75-9.

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[19] Ando, T. *Yuki Gosei Kagaku Kyokaishi* **1959**, *17*, 339–334.

[20] Shelton, R. S.; Van Campen, M. G.; Meisner, D. F.; Parmerter, S. M.; Andrews, E. R.; Allen, R. E.; Wyckoff, K. K. *J. Am. Chem. Soc.* **1953**, *75*, 5491–5495.

Aspects of Tautomerism. 13. Alkaline Hydrolysis of γ-, δ-, and ε-Keto Esters and Their Desoxy Analogues. Geometrical Constraints on Keto Participation[1]

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Received December 20, 1983

The rates of alkaline hydrolysis of methyl β-benzoylpropionate (I), methyl γ-benzoylbutyrate (II) and methyl δ-benzoylvalerate (III) decrease in the order I > II > III. Keto participation is the predominant pathway in the case of γ-keto esters. Evidence has also been obtained for keto participation in the case of δ-keto esters, whereas no such evidence is available in the case of ε-keto esters studied.

Unexpected reactivity patterns are sometimes encountered when two or more functional groups are in close proximity. These effects cannot be accounted in terms of well-studied effects like steric, inductive, mesomeric, or field effects. A systematic study of the neighboring group effects as they pertain to carboxylic acids, their derivatives, and the keto group has been the subject of previous papers of this series.[1,2]

Rate enhancement of alkaline hydrolysis of esters by a suitably placed keto group has been recognized for almost 30 years.[3] However, a number of features of the keto participation have been analyzed only recently. One of the factors, sometimes the most important which has bearing on the extent of rate enhancement, is found to be the rate of initial attack of the base on the carbonyl group.[4] In this paper we attempt to define the geometrical constraints to keto participation in conformationally nonrigid systems.

The ring–chain tautomeric behavior of γ-keto acids and their derivatives is a frequently encountered phenomenon and also the one which has received detailed study. In contrast, information on the involvement of γ-keto and δ-keto function in the reactions of carboxylic acid and its derivatives is scanty. It is common knowledge that the formation of a five-membered ring tautomer or reaction product is generally preferred over a six-membered one when possibilities for the formation of either of them exists.[5] This generalization breaks down with carbohydrates. Factors like hydrogen bonding and conformational preferences tilt the stability order in favor of the six-membered rings. However, in the case of keto acid chlorides preference for five-membered ring formation is observed. While overhwelmingly a large number of γ-keto acids yields only pseudoacid chlorides, the situation regarding δ-keto acids is less clearcut.[6]

In the present investigation, we report two types of studies: (a) alkaline hydrolysis of methyl esters of β-benzoylpropionic acid (I), γ-benzoylbutyric acid (II), δ-benzoylvaleric acid (III) (Figure 1) and their desoxy analogues IV, V, and VI in 70% (v/v) acetone–water at three temperatures; (b) alkaline hydrolysis of methyl esters of meta- or para-substituted derivatives of I, II, and III and

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