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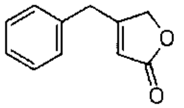
ACCENTUATION OF THE DI-π-METHANE REACTIVITY BY CENTRAL CARBON SUBSTITUTION IN THE 4-(PHENYLMETHYL)-2(5*H*)-FURANONE SYSTEM

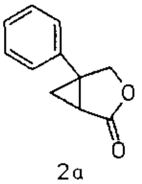
Osamu Muraoka,[*] Genzoh Tanabe,[#] and Takefumi Momose[##,*]
Faculty of Pharmaceutical Sciences, Kinki University[#]
Kowakae 3-4-1, Higashi-osaka, Osaka 577, Japan and
Faculty of Pharmaceutical Sciences, Toyama Medical and
Pharmaceutical University,[##] Sugitani 2630, Toyama 930-01, Japan

Abstract - The effect of 'central methane' substitution on the di-π-methane rearrangement in 4-(phenylmethyl)-2(5*H*)-furanones (1b-d) was investigated. Significant enhancement of efficiency in the reaction leading in high combined yields to two isomeric products (*endo*-2 and *exo*-2) was discussed in terms of both the substituent effects at the allylic methane carbon and the restrained feature of the ring-enrolled π-system.

There are three known versions of the di-π-methane rearrangement:[1] the divinyl methane variety, the arylvinylmethane type and the oxa-di-π-methane[1c,1d] variation. These differ in many aspects. The marked differences between the first two are as follows: the divinylmethane rearrangement requires the 'methane carbon' substitution while the arylvinyl type does not;[2] the arylvinylmethane singlet tends to react more slowly than does its divinyl counterpart, and substituent effects are reversed for these two cases.[2]

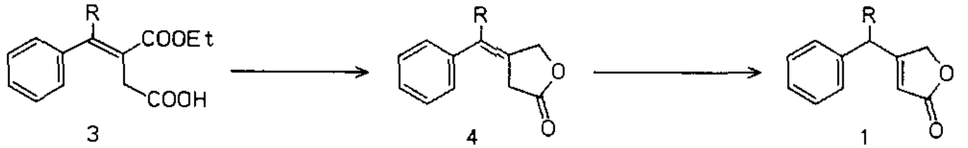
In a previous paper[3] dealing with photoreactivity of 4-(phenylmethyl)-2(5*H*)-furanone (1a), an arylvinylmethane example of the di-π-methane rearrangement, we obtained an expected photo-rearranged product (2a) in a poor yield (~ 23%). It was of considerable interest to study the photochemical behavior of the system with substituents on the central methano-carbon from a mechanistic standpoint in order to determine and understand the difference between these two versions of the di-π-methane rearrangement. Thus we synthesized some 'central methane'-substituted


1a


2a

4-(phenylmethyl)-2(5*H*)-furanones (**1b-d**), and investigated their photochemical reactivities and found significant enhancement of efficiency of the reaction under singletand acetone-photosensitized conditions.

The reactants (**1b-d**) were prepared as follows. The selective reduction of 1-ethyl 4-hydrogen succinates (**3b-d**)[4] with lithium aluminum hydride at 0°C, and subsequent acid-catalyzed lactonization of the resulting hydroxy acids gave 3-alkylidenedihydro-2(3*H*)-furanones (**4b-d**), which were isomerized into the desired 2(5*H*)-furanones (**1b-d**) in 62-82% yields by the action of tosic acid in dimethyl sulfoxide at 150°C.[5]



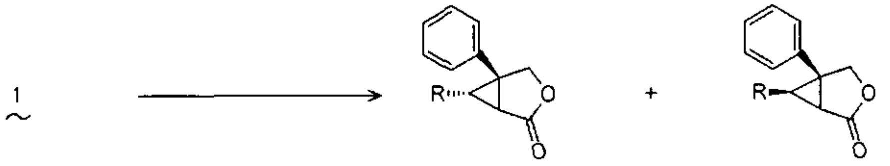
3
b:R=Ph
c:R=c-Hex (cyclohexyl)
d:R=Me

4
b:R=Ph
c:R=c-Hex
d:R=Me

1
b:R=Ph
c:R=c-Hex
d:R=Me

Direct irradiation[6] of (**1b-d**) in methanol through a Pyrex filter gave two isomeric photo-rearranged products, *endo*- and *exo*-6-substituted 5-phenyl-3-oxabicyclo[3.1.0]-hexan-2-ones (***endo*-2** and ***exo*-2**).[7,8] The configuration of the photo-products was determined on examination of the vicinal coupling constants across the cyclopropane ring in the ^{1}H-nmr spectra.[9] The acetone-sensitized irradiation of **1b-d** through a Pyrex filter also resulted in the formation of the same members of products as those obtained in the run carried out in methanol. The results of the irradiation are summarized in Table 1.

The efficiency of the rearrangement was greatly increased by the substitution on the central carbon. The substituent effect on central methane has mostly been examined



1
b:R=Ph
c:R=c-Hex
d:R=Me

endo-2
b:R=Ph
c:R=c-Hex
d:R=Me

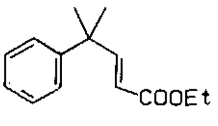
exo-2
b:R=Ph
c:R=c-Hex
d:R=Me

Table 1

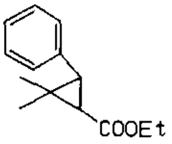
R	solvent	reaction time(hr)	*endo*-2	*exo*-2
			isolated yeild (%)	
Ph	acetone	4	70	15
	methanol	11	70	13
c-Hex	acetone	8	85	8
	methanol	11	74	19
Me[1]	acetone	6	90	trace
	methanol	11	70	7
H[2]	acetone	3	47 (recovered 7%)	
	methanol	12	39 (recovered 33%)	

1. The product distribution was determined by 500 MHz ^{1}H-nmr spectra.
2. The yields were optimized in the present study.

on disubstituted substrates.[2,10] Present findings reveal that the monosubstitution also exerts the effect in a similar fashion and enhances the efficiency of the di-π-methane rearrangement to a large extent irrespectively of substituent types. Most interestingly, triplet sensitization in an acetone solution led to highly efficient formation of the cyclopropane. Hammond[11] reported the photoirradiation of a 4,4-dimethylated 4-phenylbutenoate (5), an acyclic version of functionality similar to 1, where the di-π-methane reaction to yield 6 could only be effected upon direct irradiation, but not on acetone-photosensitized irradiation. Hixon[12] rationalized the non-occurrence of the di-π-methane reaction of the triplet excited state of 5 in terms of preferential dissipation of the triplet excitation energy by "free-rotor" effects (facile *E*-*Z* isomerization)[13] about the double bond. The efficiency of the rearrangement in the present study should be ascribed to both the substituent effects on the 'central methane' carbon in favor of its facile migration *via* radical fission and the inherent feature of the 2(5*H*)-furanone system where this alternative photo-process (*E*-*Z* isomerization) is precluded by incorporating the double bond in a furanone ring. In addition, the relatively consistent product ratios and increased efficiency of the reaction in the triplet-sensitized conditions are thought to indicate that the products resulted from the triplet state. The prolonged reaction periods observed in direct irradiations would be responsible for low efficiency of the intersystem crossing in methanol.



5



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