Tetrahedron Vol. 49, No. 47, pp. 10897-10902, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Photorearrangement and Electron Transfer Photooxidation of 1-Acetoxy-1,2-diphenylcyclopropane

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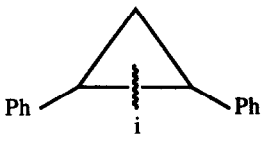
(*Received in UK* 5 *August* 1993; *accepted* 17 *September* 1993)

Abstract: Direct irradiation of the title compound **4** in hexane led to 1,3-diphenyl-1,4-pentanedione (**5**) in 75 % yield. This is explained through carbonyl-oxygen bond cleavage (process iii), to afford a cyclopropyloxy radical (I) which rearranges to a β-carbonyl radical (II) prior to in cage recombination. In methanol, the solvent addition product **6** was obtained as byproduct. It formation is rationalized by means of the symmetrical cationic intermediate IV, on the basis of deuterium incorporation to C(1) and C(3) in MeOD. Photosensitization by acetone resulted exclusively in *trans* to *cis* isomerization, via the diradical III (process i). Finally electron transfer activation by means of cerium(IV) ammonium nitrate (CAN) or excited triphenylpyrylium tetrafluoroborate (TPT) gave rise to chalcone (**7**) or the β-functionalized ketones **8** or **9**. These products must arise from a common cationic precursor (V), after cleavage of the central carbon-carbon bond (process i) in the radical cation $4^{+\cdot}$. From the preparative point of view, the obtention of diketone **5** in 75 % yield by photolysis of **4** in hexane is exploitable, since it constitutes a synthetic equivalent of the addition of acyl anions or acyl radicals to enones.

INTRODUCTION

It has been established that the photochemistry of 1,2-diarylcyclopropanes (**1**)[1-5] and benzyl esters (**2**)[6-8] is dominated by primary cleavage of the carbon-carbon (i) or the acyloxy-carbon (ii) bonds, respectively. In this context, it appeared interesting to examine the photochemical behaviour of 1-acetoxy-1,2-diphenylcyclopropane (**4**), whose structure combines in the same molecule the abovementioned moieties (**1** and **2**) with a cyclopropyl ester. The latter might direct the photoreactivity towards carbonyl-oxygen bond breaking (iii), as it has been reported for the analogous enol esters (**3**),[9-12] providing direct entry to a cyclopropyloxy radical (I). Species of this type are known to rearrange to β-carbonyl radicals (II),[13-16] whose intermolecular trapping constitutes a useful carbon-carbon bond formation reaction of considerable synthetic interest.[17-20] A feasible intramolecular counterpart would be in cage recombination of II with the acetyl radical to afford a 1,4-diketone (**5**), a process which would be analogous to the 1,3-acyl migration of enol esters (photo-Fries rearrangement).[11,12] This appeared to be an attracting possibility, in view of the applicability of 1,4-dicarbonyl compounds as precursors for the synthesis of five-membered heterocycles.[21-23]



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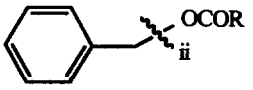

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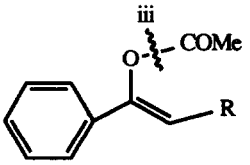

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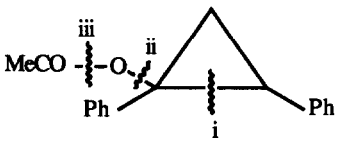
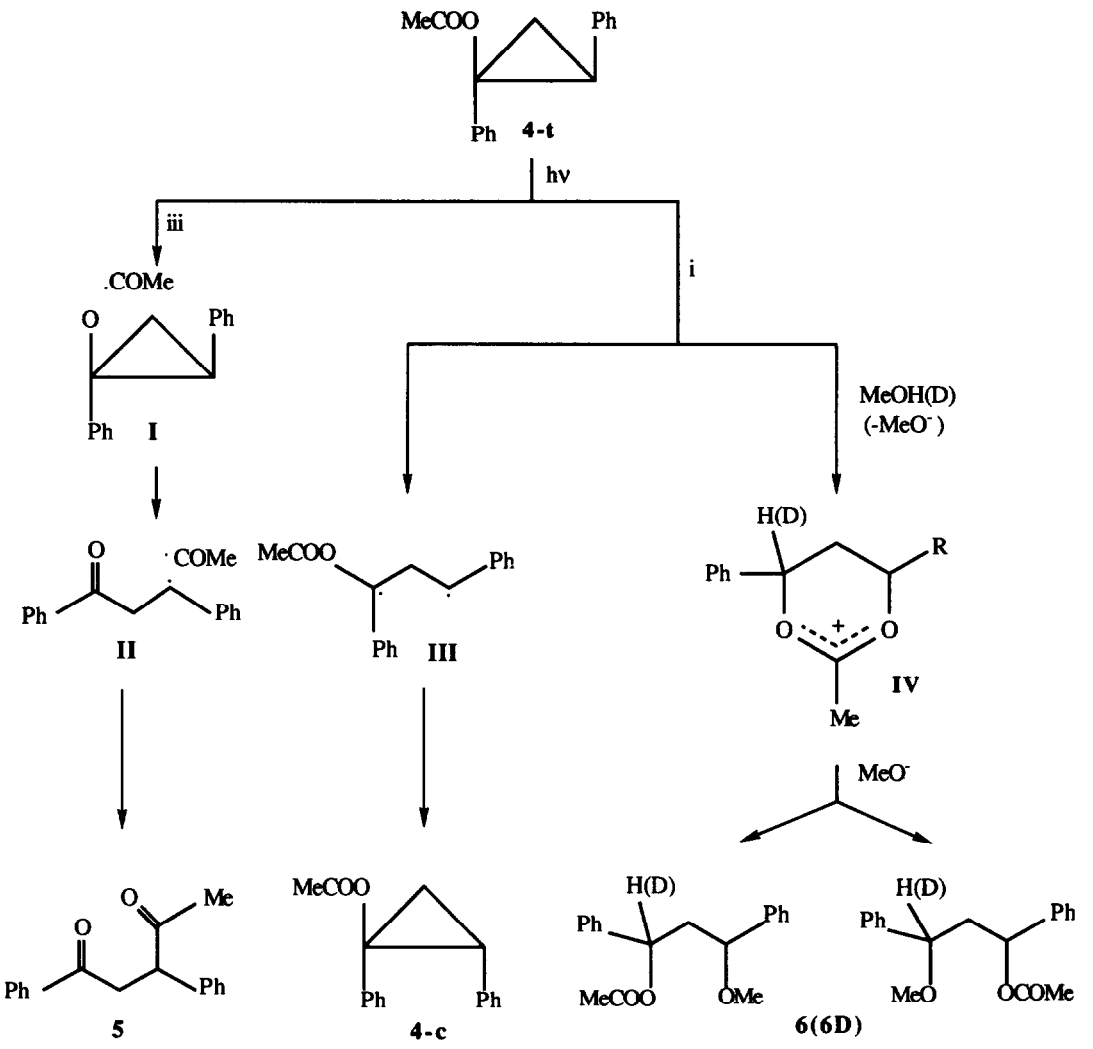


4

Another aspect of interest in the reactivity of **4** was its behaviour under electron transfer (ET) oxidation conditions. Cyclopropanes with aryl substituents at the positions 1 and 2 are known to undergo ET-induced cleavage of the central carbon-carbon bond (process i).[24-27] The resulting 1,3-radical cations rearrange subsequently to propenes (retro-di-π-methane reaction)[28,29] or, in the presence of oxygen, are trapped to afford 1,2-dioxolanes.[30,31] These results suggested the possible interconversion between **4** and the corresponding enol ester **3** (R = CH_2Ph), whose ET-photooxygenation has been the matter of current interest in this laboratory.[10] As a consequence, the projected study on the direct photolysis of the cyclopropyl derivative **4** was extended to include the reactivity of its radical cation $4^{+\cdot}$, generated either by photosensitization with triphenylpyrylium tetrafluoroborate (TPT)[32] or by chemical oxidation with cerium(IV) ammonium nitrate (CAN).[33]

RESULTS AND DISCUSSION

The required substrate **4** (*trans/cis* stereoisomeric ratio ca. 3:1) was prepared by condensation of chalcone with hydrazine, followed by treatment of the obtained dihydropyrazole with lead tetraacetate and thermal denitrogenation of the resulting acetoxypyrazoline.[34-36] Irradiation of **4** through quartz in hexane, using a medium pressure mercury lamp as light source, led to 1,3-diphenyl-1,4-pentanedione (**5**)[37] as major product (75 %). Besides, some starting substrate (14 %) was recovered. When the photolysis was carried out in methanol, under identical conditions, the diketone **5** (60 %), was also obtained; however, an additional photoproduct was in this case 1-acetoxy-3-methoxy-1,3-diphenylpropane (**6**, 8 %).[38,39] The amount of unchanged **4** in this experiment was 15 %. By contrast, the acetone-photosensitized irradiation of **4**, using pyrex filter, resulted exclusively in *trans* to *cis* isomerization (photoequilibrium ratio 1:1). A plausible rationalization of the above results is provided in scheme 1. The formation of diketone **5** upon direct irradiation in hexane showed that carbonyl-oxygen bond cleavage (process iii) is actually the preferred pathway from the excited singlet state. Rearrangement of cyclopropyloxy radical I to β-carbonyl radical II[13-20] prior to in cage recombination would account for the formation of the obtained photoproduct. The clean *trans/cis* isomerization observed upon photosensitization with acetone indicated that carbon-carbon bond cleavage, to give the 1,3-diradical III (process i), is the only reaction mode characteristic of the triplet state. Finally, the photochemical addition of methanol can be best explained through the stabilized cationic intermediate IV.

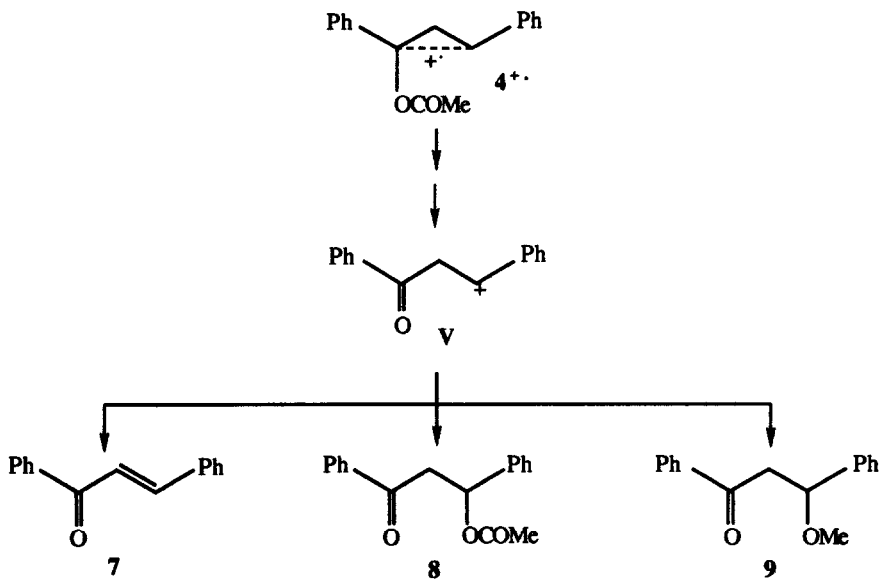


Scheme 1

The addition of protic solvents such as alcohols or amines to excited 1,2-diarylcyclopropanes has been reported earlier.[1-4] These experimental results have been justified through a mechanistic pathway proceeding *via* initial formation of polarized complexes (exciplexes) between the 1,2-diarylcyclopropanes and the protic solvents; their conversion into the final addition products would occur by either proton transfer or carbon-heteroatom bond formation. With this background, it appeared interesting to perform the irradiation of **4** in monodeuterated methanol (MeOD). As it had been previously found with related substrates, the solvent addition product exhibited extensive deuterium incorporation; however, an interesting feature was in our case that the label of **6D** was statistically distributed between C(1) and C(3). Such conclusion was clearly drawn from the MS analysis of the product,[39] where the peaks with m/z 121 ($PhCHOMe^+$) and 122 ($PhCDOMe^+$) showed similar intensities (100 and 97 %, respectively). This strongly supported the involvement of a symmetrical cationic

species (IV), arising from protonation (deuteration) of the excited cyclopropane **4** with assistance of the acetoxy group. Nucleophilic attack of methanol to this species at the positions 1 or 3 would account for the observed pattern of isotopic labelling.

The reactivity of 1-acetoxy-1,3-diphenylcyclopropane (**4**) under ET-oxidation conditions was also examined. Generation of the radical cation $4^{+\cdot}$ was achieved by two alternative methods: a) photosensitization with triphenylpyrylium tetrafluoroborate (TPT) and b) chemical oxidation with cerium(IV) ammonium nitrate (CAN). Irradiation ($\lambda > 300$ nm) of **4** with TPT in methylene chloride led to a complex mixture containing chalcone (**7**, 35 %) and 3-acetoxy-1,3-diphenylpropan-1-one (**8**, 28 %). Likewise, treatment of **4** with CAN in methanol afforded **7** (15 %), **8** (5 %) and 3-methoxy-1,3-diphenylpropan-1-one (**9**, 30 %),[41] together with a considerable amount of unreacted starting material (45 %). These results are rationalized in scheme 2.



Scheme 2

Cleavage of the central carbon-carbon bond would give rise to a 1,3-radical cation whose further oxidation to a β-carbonyl carbocation (V), followed by deprotonation or nucleophilic trapping by acetic acid or methanol, might explain formation of the isolated products.

In summary, direct irradiation of 1-acetoxy-1,2-diphenylcyclopropane (**4**) produces homolysis of the acetyl-oxygen bond (process iii), to give the 1,4-dicarbonyl compound **5**. In methanol, heterolytic carbon-carbon bond cleavage (process i) leading to the solvent addition product **6** is observed. Triplet sensitized photolysis (acetone) produces *trans-cis* isomerization. Finally, electron transfer activation gives rise to enones (**7**) or β-functionalized ketones (**8**, **9**). From the preparative point of view, the obtention of diketone **5** in 75 % yield by photolysis of **4** in hexane is exploitable, since it constitutes a synthetic equivalent of the addition of acyl anions or acyl radicals to enones (in fact, the cyclopropane **4** is prepared from chalcone in high yield by condensation with hydrazine and subsequent treatment with lead tetraacetate in the same pot).

ACKNOWLEDGEMENTS

Financial support by the Spanish DGICYT (Grant No. PB88-0494) is gratefully acknowledged.

EXPERIMENTAL

Direct photolysis of 1-acetoxy-1,2-diphenylcyclopropane

Solutions of **4** (*trans/cis* stereoisomeric ratio ca. 3:1) in hexane, methanol or methanol-O-d (10^{-2} M) were placed in quartz test-tubes and irradiated for 2 h with a 125 W medium pressure mercury lamp located inside a quartz immersion well. The reaction was monitorized by GC (Hewlett-Packard 5890 fitted with a 25 m capillary column of crosslinked 5 % phenylmethylsilicone) as well as GC/MS (Hewlett-Packard 5988 A spectrometer) and GC/FTIR (Hewlett-Packard 5965 A instrument). The structures of photoproducts were established by comparison of their spectral properties with those of authentic samples.[37-41]

Sensitized photolysis of 1-acetoxy-1,2-diphenylcyclopropane

A solution of **4** (30 mg, *trans/cis* stereoisomeric ratio ca. 3:1) in acetone (10 ml) was irradiated in pyrex tubes for 3 h, using the irradiation system described above. *Trans-cis* isomerization was the only process observed. The reaction was also performed in CH_2Cl_2 (10 ml), using TPT (80 mg) as photosensitizer. Analysis of the photomixtures was done in the usual way (GC/MS and GC/FTIR).

Oxidation with cerium(IV) ammonium nitrate (CAN)

To a solution of **4** (50 mg, *trans/cis* stereoisomeric ratio ca. 3:1) in methanol (25 ml) was added CAN (200 mg) under magnetic stirring at room temperature. The mixture was allowed to react for 5 h and then analysed as in the photolysis experiments.

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39. MS of **6**: m/z (%); 284 (1), 252 (2), 224 (15), 223 (5), 210 (5), 121 (100), 105 (21), 104 (15), 77(23). MS of **6D**: m/z (%); 285 (1), 253 (2), 225 (10), 224 (3), 211 (15), 122 (97), 121 (100), 105 (64), 104 (33), 77 (22).
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