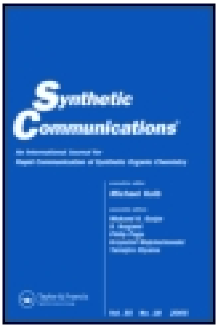

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A One Pot Synthesis of 5-Phenyl-1,3-Dioxane-4,6-Dione Derivatives

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To cite this article: K. Saidi , H. R. Shaterian & H. Sheibani (2000) A One Pot Synthesis of 5-Phenyl-1,3-Dioxane-4,6-Dione Derivatives, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:13, 2345-2351, DOI: 10.1080/00397910008086875

To link to this article: http://dx.doi.org/10.1080/00397910008086875

SYNTHETIC COMMUNICATIONS, 30(13), 2345–2351 (2000)

A ONE POT SYNTHESIS OF 5-PHENYL-1,3-DIOXANE-4,6-DIONE DERIVATIVES

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A general procedure for synthesis of 5-phenyl-1,3-dioxane-4,6-dione derivatives is described. The synthesis involves the cycloaddition of (α – chlorocarbonyl)phenyl ketene with carbonyl compounds to generate the corresponding substituted 2-oxetanone's which is readily transformed to the final products in one step. The 1,3-dioxane-4,6-dione is a rigid cyclic structure, and can undergo easy hydrolysis.

2,2-Dimethyl-1,3-dioxane-4,6-dione appears to be an attractive reagent in organic synthesis[1, 2, 3, 4, 5]. However, synthetic application of these acids have received little attention. The present investigation was undertaken to show the synthetic usefulness of 5-phenyl-1,3-dioxane-4,6-dione derivatives (IV a - k) readily accessible from (α-chlorocarbonyl)phenyl ketene (I) and carbonyl compounds in fair yield in a one step procedure.

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The procedure described here would appear to be applicable to the synthesis of (IV), which is a rigid cyclic structure, and can undergo easy hydrolysis to produce phenyl acetic acid and an aldehyde or a ketone.

(α-Chlorocarbonyl)phenyl ketene (I) was prepared by the dehydrohalogenation of phenylmalonyl chloride[6]. The ketene was formed during the distillation of the corresponding acid chloride, is a yellow liquid which boils at 182°C. It is stable, does not dimerize when heated and can be stored for long periods of time even at room temperature, the compound was solidified upon being cooled to 0°C. The preparation of this ketene is remarkable for its simplicity. Thus, two equimolar quantities of thionyl chloride were added to phenylmalonic acid in toluene over a 24 hour period under a slow stream of nitrogen. The dehydrohalogenation occurred spontaneously during the distillation process to yield the ketene.

The acidic proton could be lost along with chlorine atom very readily at an elevated temperature even without using a base such as triethylamine which is commonly used as a dehydrohalogenation reagent of acid halides. The ketene band appeared at the infrared spectrum at about 2137.4 cm^{-1}.

The title ketene (1) appears to undergo [2+2] cycloaddition with carbonyl compounds[7] such as propanal, butanal, 2-methyl propanal, benzaldehyde, cyclohexanecareoxaldehyde, crotonaldehyde propanone, 2-butanone, cyclopentanone, cyclohexanone and dibenzalacetone at very mild experimental conditions. The condensation of (I) with aldehydes in the presence or absence of a Lewis acid catalyst, such as boron trifluoride etherate or zinc halide gives 2-oxetanones (II). But, a catalyst is needed for the condensation of a ketene and ketones[8].

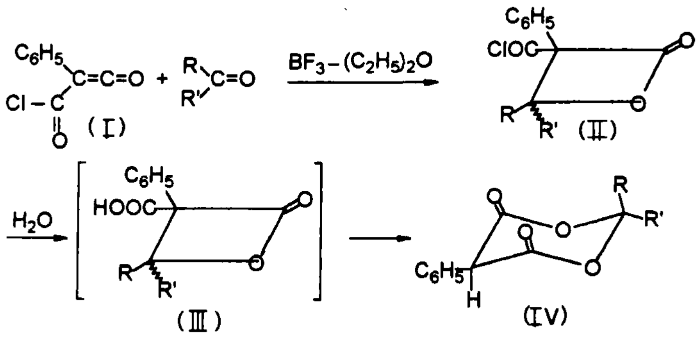
The addition of equimolar quantities of (I) and a carbonyl compound, such as propanal, at 0°C temperature under a nitrogen atmosphere afforded a 1:1 cycloadduct in fair yields.

Spectral data and elemental analysis did not show the presence of β-lactonic acid chloride (II), because the corresponding acid chloride was very susceptible to hydrolysis, and produced β-lactonic acid. Furthermore, no evidence was adduced for the presence of a carboxyl group (III).

Isolation of the β-lactonic acid which was formed by the hydrolysis of acid chloride was not possible due to spontaneous rearrangement[9] to the homologous 5-phenyl-1,3-dioxane-4,6-diones (IV a-k) as evidenced by the infrared and nuclear magnetic resonance spectroscopic data. This is likely due to the extreme stability of the six membered rings. The over all, one -pot conversion is outlined in scheme 1, and yield data are collected in table 1.

Compound (IVa) is a mixture of cis-trans isomer produced in this reaction with approximately equal amounts .The infrared spectrum of compound (IVa) revealed carbonyl

Scheme 1



bands at 1812.9 and 1750.0 cm^{-1}. The equatorial and axial hydrogens can be seen separately by ^{1}HNMR. The ^{1}HMMR spectrum of (IVa) in $CDCl_3$ indicated that the equatorial hydrogens are in a downfield shift compared to the axial hydrogens. The spectrum revealed two singlets at 7.4 and 7.2 ppm for the equatorial and axial phenyl hydrogens respectively.

Table 1. Yield Data for All Compounds

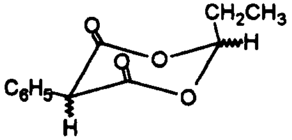
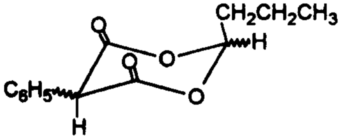
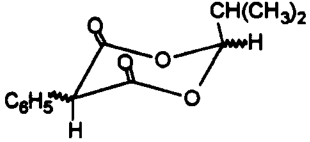
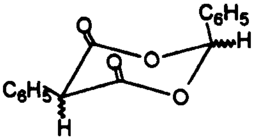
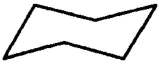
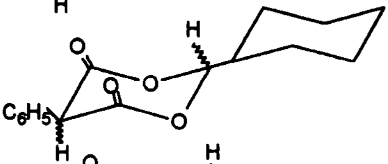
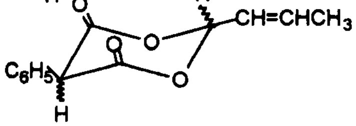
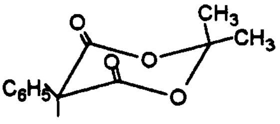
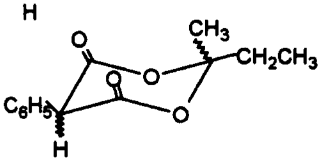
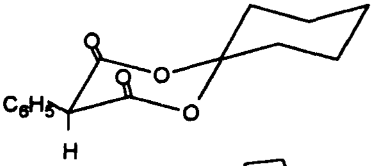
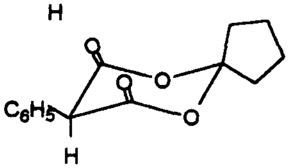
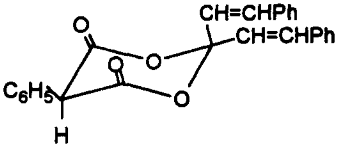
Entry	R	R'	Products	Yield[a] (%)
a	CH_3CH_2–	H		73
b	$CH_3CH_2CH_2$	H		62
c	$(CH_3)_2CH$	H		54
d	C_6H_5	H		68
e		H		64
f	$CH_3CH{=}CH$	H		52
g	CH_3	CH_3		32
h	CH_3	CH_3CH_2		39

Table 1. Continued

Entry	R	R'	Products	Yield[a] (%)
i	$-(CH_2)_5-$			25
j	$-(CH_2)_4-$			25
k	PhCH=CH	PhCH=CH		53

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[a] Yield of isolated products

The two triplets centered at 6.0 ppm and 5.6 ppm are due to the equatorial and axial hydrogens, indicating that these downfield shifts are due to being adjacent to the two oxygens. The hydrogen at C-5 adjacent to carbonyl groups gave two singlets at 5.0 and 4.8 ppm, a multiplet centered at 2.0 ppm was assigned to the methylene group, and two triplets at 1.2 and 1.0 ppm was due to methyl hydrogens. ^{13}CNMR, mass spectrum and elemental analysis were consistent with the proposed structure.

Further characterization and elucidation of the adducts was accomplished with acid hydrolysis in boiling water. The reaction produced an equal amount of phenylacetic acid and an aldehyde, or a ketone, which were identified by comparison with authentic samples.

Satisfactory IR, HNMR, ^{13}CNMR, mass spectra and elemental analysis were obtained for all the products.

2-ethyl-5-Phenyl-1,3-dioxane-4,6-dione (IV a). A 20 mmol (3.61 g) portion of I and 20 mmol (1.16 g) of propanal containing a few drops of $BF_3.Et_2O$ were reacted to give 3.2 g (72.7% yield); mp 167°C (decompose); IR (KBr), 1812.9 (unsymmetrical C=O); 1750.0 (symmetrical C=O) and 1244.6 cm^{-1} (C-O); ^{1}HNMR ($CDCl_3$ with TMS as a reference) δ:[7.4 (s), 7.2 (s), 5 H], [6.0 (t), 5.6 (t), 1 H], [5.0 (s), 4.8 (s), 1 H], 2.0 (m, 2 H), [1.2 (t), 1.0 (t), 3 H] ppm respectively; ^{13}CNMR δ: 165.2, 130.3, 130.1, 129.4, 129.0, 128.8, 126.8, 98.8, 98.5, 55.3, 54.8, 26.3, 16.8, 16.5 ppm. Mass spectrum, parent peak, m/z: 220 (32%, M^+), 119 (98%, $PhCH_2C{=}O$), 118 (100% base peak PhCH=C=O), 90 (61%, PhCH), 89 (31%, PhC).

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.70; H, 5.20.

Acknowledgment

The authors express appreciation to the Shahid Bahonar University of Kerman Faculty Research Committee for its support of this investigation.

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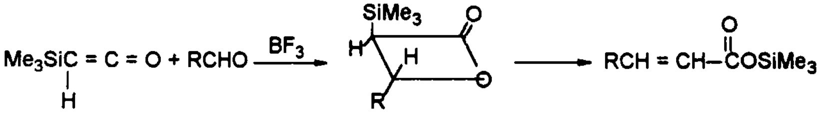
b) Cycloaddition of trimethylsilylketene with aldehydes in the presence of a catalytic amount of $BF_3.Et_2O$ was reported. The 2-oxetaneones formed were not stable and underwent a silicon migration from carbon to oxygen accomponied by a ring opening reaction.



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Received in Japan 7/12/99