

Research Note

PREPARATION OF (CHLOROCARBONYL) PHENYLKETENE AND ITS CYCLOADDITION REACTION WITH BENZALDEHYDE[‡]

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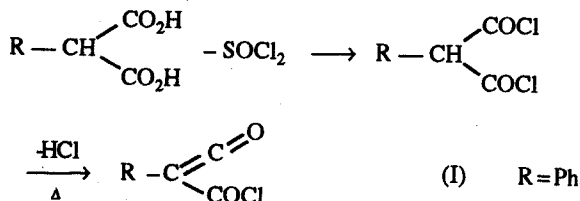
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Abstract

Meldrum's acid, 2,5-diphenyl-1,3-dioxane-4,6-dione, was produced by [2+2] cycloadditions of the (chlorocarbonyl)phenylketene with benzaldehyde. Acid hydrolysis of the meldrum's acid regenerated benzaldehyde and also yielded phenylacetic acid as the final product.

(Chlorocarbonyl)phenylketene (I) was prepared by the dehydrohalogenation [1] of phenylmalonyl chloride. This ketene was formed during the distillation of the corresponding acid chloride [2]. It is a yellow-coloured liquid which boils at 182° C, is very stable, does not dimerize upon heating and can be stored for long periods of time even at room temperature. The compound was solidified upon cooling 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 and the mixture was stirred for 72 h at ambient temperature. Rather unexpectedly, the dehydrohalogenation occurred spontaneously during the distillation process to yield the ketene.



Keywords: (Chlorocarbonyl)phenylketene; Cycloaddition; Meldrum's acid; 2,5-diphenyl-1,3-dioxane-4,6-dione; Phenylacetic acid

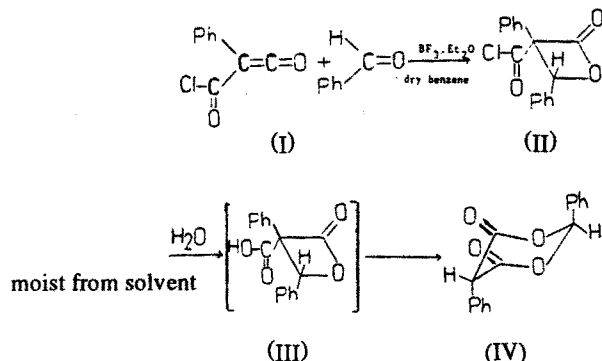
The acidic proton could be lost along with the chlorine atom very readily at elevated temperatures even without using a base such as triethylamine which is commonly used as a dehydrohalogenation reagent of acid halides [3,4]. The ketene band appeared at the infrared spectrum at about 2137.4 cm⁻¹. The proton NMR spectrum of the ketene revealed a multiplet centered at about δ : 7.4 ppm. The carbon-13 nuclear magnetic resonance spectrum of (I) was as follows: the sp² hybridized carbon atom resonance was found at low field position at δ : 64.2 and at δ 167.1 ppm, and sp hybridized carbon atom ketene at δ 170.4 ppm, phenyl ring carbons at δ 124.1 (C), 126.5 (CH), 127.5 (CH), 129.6 (CH).

Generally, the condensation of ketenes with carbonyl compounds [5] in the presence of catalysts, such as boron trifluoride etherate [6] or zinc halide etherate, gives 2-oxetanones, this complex probably undergoes exchange with the aldehyde, resulting in activation of the carbonyl group to cycloaddition. It is pertinent to note that this cycloaddition occurs even in the absence of Lewis acid catalysts. The title ketene (I) appears to undergo [2+2] cycloaddition with benzaldehyde very readily under very mild experimental conditions [4, 7].

The addition of equimolar quantities of (I) and benzaldehyde at ambient temperature under a nitrogen atmosphere afforded a 1:1 cycloadduct in 68% yield,

[‡] This paper is dedicated to Chemical Engineer Alireza Afzalipour the founder of Shahid Bahonar University.

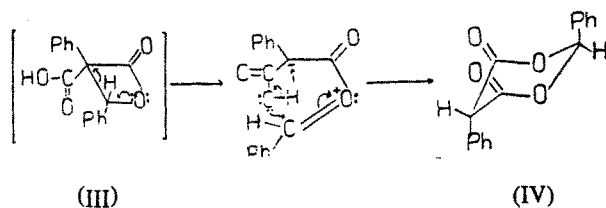
in a few minutes. Spectral data and elemental analysis did not show the presence of β -lactonic acid chloride (II). Furthermore, no evidence was adduced for the presence of a carboxyl group (III).



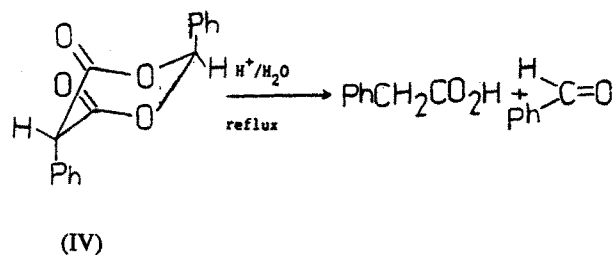
Apparently the product of the [2+2] cycloaddition reaction, namely 3,4-diphenyl-3-chlorocarbonyl-2-oxetanone (II), was hydrolyzed during work up to yield 3,4-diphenyl-3-carboxy-2-oxetanone (α , β -diphenyl- β -propiolactone- α -carboxylic acid III). Meldrum's acid, 2,5-diphenyl-1,3-dioxane-4,6-dione (IV) was derived from the corresponding carboxy-2-oxetanone (III) very readily [8,9,10] as evidenced by the infrared and nuclear magnetic resonance spectroscopies data.

The infrared spectrum for the compound IV revealed the carbonyl band at 1810.5 and 1761.4 cm^{-1} . The ^1H NMR spectrum of IV revealed four singlets at δ : 7.46 and 7.26 ppm for the two phenyl protons, and at δ : 6.58 and 5.01 ppm for the two methine protons. ^{13}C NMR and mass spectra are consistent with the structure.

Persuasive evidence exists that β -lactonic acid, which was formed by the hydrolysis of acid chloride as intermediate, rearranges to meldrum's acid (IV). A plausible mechanism is as follows:



Further characterization and elucidation of the adduct was accomplished by acid hydrolysis in boiling water. The reaction produces equal amounts of phenylacetic acid and benzaldehyde, which were identified by comparison with authentic samples.



Experimental Section

Materials

All reagents were obtained commercially (Merck); benzaldehyde was distilled prior to use; thionyl chloride and phenylmalonic acid were used as purchased, benzene was dried over sodium and distilled prior to use. Infrared spectra were obtained on a Mattson 1000 series FT-IR instrument (Unicam Limited). The proton NMR and ^{13}C NMR spectra were recorded on JEOL, JNM-EX 90 MHz FT nuclear magnetic resonance spectrometer employing tetramethylsilane as the internal standard. Mass spectra were determined on a Shimadzu GC/MS Q 2000 A spectrometer.

Elemental analyses were performed by NIOC Research Lab. Tehran. Melting points were obtained by Gallenkamp apparatus (England) and are uncorrected.

Preparation of (Chlorocarbonyl)phenylketene

In a 250-ml round-bottomed flask was placed 50 mmole (9.0g) of phenylmalonic acid and 200 mmole (23.8 g) of thionyl chloride. The reaction mixture was stirred for 72 h. Excess thionyl chloride was removed and (chlorocarbonyl)phenylketene was distilled at 182°C. The yield is 6.78 g (75% yield). IR: (neat) 2137.4 cm^{-1} ; ^1H NMR (CDCl_3) with TMS as a reference) δ : 7.4 ^{13}C NMR δ : 170.4, 167.1, 129.6, 127.5, 126.5, 124.0, 64.2 ppm. Mass spectrum, parent peak m/z at 180(m), 182 (M+2), 145 (M-Cl), 117, 89, 51, 39.

Anal. Calcd. for $\text{C}_9\text{H}_5\text{ClO}_2$: C, 59.8; H, 2.7; Cl, 19.6. Found: C, 59.9; H, 2.8; Cl, 19.6.

Typical Procedure for (Chlorocarbonyl)phenylketene Cycloaddition with Benzaldehyde

A 20 mmol (3.61 g) solution of freshly distilled I in 10 ml of benzene was added dropwise to a stirred solution of 20 mmole (2.12 g) benzaldehyde in 10 ml benzene containing a few drops of boron trifluoride etherate at room temperature under a nitrogen atmosphere. When the addition was complete, 1 h, the stirring was continued until the ketene band had been

consumed as evidenced by the disappearance of the ketene band in the IR at 2137.4 cm^{-1} . The solvent was decanted, the solid was washed with cold benzene several times and recrystallized from benzene to give 3.65 g of IV; m.p. 146°C (decomposed); IR (KBr), 1810.5 (unsymmetrical C=O), 1761.4 (symmetrical C=O) and 1242.1 cm^{-1} (C-O); ^1H NMR (CDCl_3 with TMS as a reference) δ : ppm 7.46 (s, 5H), 7.26 (s, 5H), 6.58 (s, 1H) and 5.01 (s, 1H) respectively; ^{13}C NMR (DMSO with TMS as a reference) δ : 165.8, 130.7, 129.3, 129.0, 128.8, 128.0, 126.7, 96.0, 31.0 ppm. Mass spectrum, parent peak, m/z 268, found m/z: 190 (3.6% loss of benzene), 162 (3.5% loss of benzaldehyde), 118 (100% base peak $\text{phCH}=\text{C}=\text{O}$), 105 (11.3% $\text{ph-C}^+=\text{O}$), 90 (50.8% phC^+H), 89 (23.6% ph^+C).

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_4$; C, 71.4; H, 4.5. Found: C, 71.6; H, 4.5.

Acknowledgements

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