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Harnessing Ionic Liquids for Rapid Alkylation: Efficient Access to Methyl 2-oxo-hexahydro-2H -cyclopenta[*b*]furan-3-carboxylate

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Abstract An efficient synthetic protocol for the alkylation of 2-chlorocyclopentanone with dimethyl malonate was developed using sodium hydride as the base and various ionic liquids as reaction media. This study evaluated three ionic liquids—[BMIM]PF_6, [BMIM]BF_4, and [EMIM]PF_6—and compared their performance directly to that of a conventional DCM solvent. Under optimized conditions (70 ℃, 6 h), the ionic liquids achieved significantly enhanced yields of dimethyl 2-(2-oxocyclopentyl) malonate: [BMIM]PF_6 provided a yield of 59%, [BMIM]BF_4 yielded 75%, and [EMIM]OTf reached 79%, in contrast to the 53% yield observed with the DCM system. The superior performance of the ionic liquids is attributed to their high polarity and unique solvation properties, which promote efficient deprotonation of dimethyl malonate and stabilize the reactive enolate intermediate, thereby lowering the activation barrier for the nucleophilic substitution step. These findings underscore the potential of ionic liquids as sustainable and efficient alternatives to traditional organic solvents, offering improved reaction kinetics and enhanced yields for carbon–carbon bond-forming reactions. The methodology presented herein contributes to the advancement of greener synthetic strategies in organic chemistry.

Keywords Ionic liquids, Alkylation, 2-Chlorocyclopentanone, Dimethyl malonate, Enolate formation, Nucleophilic substitution, Green chemistry, Sustainable synthesis

1. Introduction

Ionic liquids (ILs) have garnered substantial interest as alternative media in organic synthesis, attributed to their unique physicochemical properties, which include negligible vapor pressure, high thermal stability, and tunable solvation characteristics. [1] These distinctive features render ILs particularly appealing as green solvents in synthesis and catalysis. [2,3] Initially derived from molten salts, ILs have developed into a diverse class of room-temperature solvents that are suitable for a wide array of industrial and academic applications. [4] Their classification as hydrophilic or hydrophobic, along with their structural tunability, further extends their applicability in green chemistry. [5,6]

The versatility of ILs encompasses stereoselective and asymmetric synthesis. [7] Their negligible volatility and high chemical stability facilitate their use under demanding reaction conditions. [8] In the realm of organic synthesis, ILs have demonstrated effectiveness across numerous transformations, ranging from C–C bond formation to complex cyclization reactions. [9,10] This adaptability is attributable to the ability to tailor both the cation and anion, thus fine-tuning solvation characteristics and reactivity profiles. [11,12]

Quantitative structure–activity relationships have been utilized to predict the toxicity of ILs, emphasizing the necessity of designing task-specific ILs with favorable environmental and biological profiles. [13,14] Moreover, ILs have achieved notable success in catalysis, including applications involving both Brønsted and Lewis acid sites. [15,16] In chemical manufacturing and processing, they contribute to waste minimization, recyclability, and overall sustainability. [17,18]

A particularly advantageous aspect of ILs is their dual functionality, enabling them to serve as both solvent and catalyst, often eliminating the need for additional reagents. [19] For instance, efficient alkylation of enolate intermediates has been accomplished in ILs, frequently surpassing traditional solvent systems in terms of both selectivity and yield. [20,21] ILs are especially appropriate for reactions that require high ion stabilization, exemplified by the alkylation of 2-chlorocyclopentanone with active methylene compounds. [22]

Despite the well-documented advantages of ILs,

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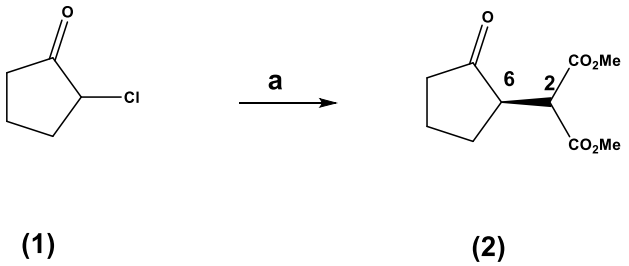
comprehensive side-by-side comparisons with conventional solvents remain limited, particularly for challenging transformations involving steric hindrance or competing side reactions. [23] Previous research by Makama [24] demonstrated that the alkylation of 2-chlorocyclopentanone with dimethyl malonate in ILs yielded diesters with favorable stereochemistry and clean spectral profiles, as verified by NMR, IR, and MS techniques.

In addition to traditional reactions, ILs are increasingly being utilized in biocatalysis, where their unique solvation environments can enhance enzyme stability and activity. [25] Concurrently, structurally similar deep eutectic solvents (DESs) have emerged as promising green alternatives, providing comparable physicochemical benefits at a lower cost. [26] ILs have also proven effective in microwave-assisted organic synthesis, which allows for rapid reaction acceleration under environmentally benign conditions. [27]

Consequently, ILs represent a compelling platform for innovation in synthetic chemistry. Their environmental compatibility, tunable properties, and catalytic potential render them ideal for integration into modern, sustainable methodologies. The present study evaluates the use of $[BMIM]PF_6$, $[BMIM]BF_4$, and $[EMIM]PF_6$ in the alkylation of 2-chlorocyclopentanone with dimethyl malonate, comparing their performance to that of traditional THF/DCM systems under identical reaction conditions. The objective is to benchmark IL-based processes not only by yield and selectivity but also by their broader environmental and mechanistic advantages.

2. Results and Discussion

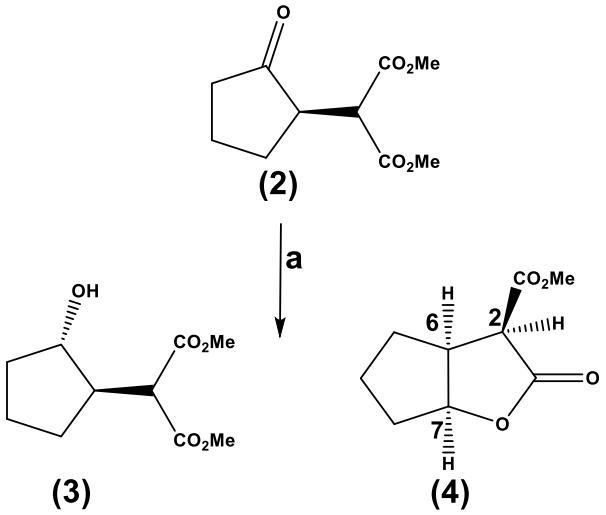


(a) dimethyl malonate, $[BMIM][BF_4]$, NaH, 75%

Scheme 1. $[BMIM][BF_4]$, Mediated Alkylation

It has been previously demonstrated that 2-chlorocyclopentanone **(1)** can be converted into dimethyl 2-(2-oxocyclopentyl) malonate **(2)**, resulting in the formation of the corresponding diester **(2)** with a yield of 53%. We reported earlier that the ¹H NMR spectrum provided substantial evidence supporting the proposed structure **(2)**, displaying a doublet centered at δ 3.84 ppm (J = 5.8 Hz), which corresponds to a methine proton associated with the diester. Furthermore, two singlets, each integrating for three protons, were identified at δ 3.78 ppm and δ 3.73 ppm, representing the methyl ester protons. A one-proton resonance at δ 2.97–2.88 ppm was assigned to the methine proton adjacent to the ketone. The presence of the ester groups and the ketone was further validated by the IR spectrum, which exhibited characteristic absorptions at 1738 cm^{-1} and 1749 cm^{-1}, respectively. Additionally, the mass spectrum corroborated these findings, revealing a molecular ion at m/z 214 (Scheme 1). [24]

Furthermore, we have established that the reduction of the ketone in **(2)**, accomplished using 1.2 equivalents of sodium borohydride at 0 ℃, yielded a mixture of two chromatographically separable products. The predominant compound, identified as **(3)**, resulted from the **reduction** of the ketone group and exhibited a distinct broad absorption in the IR spectrum at 3504 cm^{-1}, corresponding to the hydroxyl group. The ^1H NMR spectrum revealed a one-proton resonance at δ 3.96-3.91 ppm, attributed to the methine proton adjacent to the hydroxyl-bearing carbon, along with two three-proton singlets at δ 3.68 ppm and δ 3.67 ppm for the two methoxy groups. The C-2 proton resonated at δ 3.32 ppm with a coupling constant of 7.8 Hz, supporting the *cis* configuration of this predominant product at C-6 and C-2. The minor product, **(4)**, was determined to be the desired lactone, obtained with an overall yield of 26%. The IR spectrum exhibited a characteristic band at 1742 cm^{-1}, strongly indicating the presence of a γ-lactone, along with an absorption at 1733 cm^{-1} for the acyclic ester. The ^1H NMR spectrum displayed a triplet at δ 5.06 ppm attributed to the C-7 methine proton with a coupling constant of 5.3 Hz, and a singlet at δ 3.73 ppm associated with the methoxy ester protons. The *cis* configuration between C-2 and C-6 was further confirmed by a doublet at δ 3.68 ppm, indicative of the proton adjacent to the ester, exhibiting a characteristic *cis* coupling of 3.3 Hz. The molecular ion at *m/z* 184 for this compound was also consistent with structure **(4)** (see Scheme 2).



(a) ethanol, $NaBH_4$, 0 ℃, 30 min.

Scheme 2. Lactonization Mediated by Sodium Borohydride

In this report, we present a comparative analysis of the alkylation of 2-chlorocyclopentanone with dimethyl malonate under optimized conditions, utilizing sodium hydride as the base in conjunction with various ionic liquids. Specifically, we examined three ionic liquids—$[BMIM]PF_6$, $[BMIM]BF_4$,

and [[EMIM]OTf —and contrasted their performance with that of a conventional DCM. Under consistent reaction conditions (6 hours at 70–80 ℃), the ionic liquids demonstrated significantly higher yields of dimethyl 2-(2-oxocyclopentyl) malonate compared to the DCM system, as summarized in Table 1.

Table 1. Results of the Alkylation

Solvent	Isolated Yield (%)	Reaction Time (h)	Volatility	Inhalation Hazard	Carcinogenicity	Environmental Impact
[BMIM][PF_6]	59	6.0	Very low	Negligible	Not classified	Toxic to aquatic life
[BMIM][BF_4]	75	6.0	Very low	Negligible	Not classified	Toxic to aquatic life
[EMIM][OTf]	79	6.0	Very low	Negligible	Not classified	less toxic than PF_6^- ILs
DCM	53	6.0	High	Significant	Group 2B (IARC) – possible	VOC, ozone-depleting potential

The superior performance observed in ionic liquids can be primarily attributed to their unique solvation properties. These solvents possess high polarity and ionic strength, which facilitate the deprotonation of dimethyl malonate and stabilize the resultant enolate intermediate. This stabilization lowers the activation barrier for the nucleophilic substitution step, accelerating the reaction and minimizing side reactions. Our findings align with earlier reports indicating that ionic liquids enhance reaction kinetics in similar alkylation processes. Among the ionic liquids tested, [BMIM]PF_6 exhibited the highest yield, likely due to an optimal balance between viscosity and polarity, which enhances mass transfer and improves overall reaction efficiency. The performance of [BMIM]BF_4 and [EMIM]PF_6 was slightly lower but still significantly superior to that of DCM. Further supporting evidence for the improved efficiency was provided by spectroscopic analysis. The disappearance of the OH stretching vibration in the IR spectrum of the product confirmed the successful progression of the reaction, consistent with mechanistic expectations for nucleophilic substitution reactions in these media. [9]

The present study elucidates the enhanced efficacy of selected ionic liquids (ILs) in promoting the alkylation of 2-chlorocyclopentanone with dimethyl malonate; however, several limitations warrant consideration. Primarily, the investigation was confined to a limited selection of ILs—[BMIM]PF_6, [BMIM]BF_4, and [EMIM]PF_6—which, while representative of imidazolium-based systems, do not encompass the extensive diversity inherent to the broader ionic liquid families. Alternative classes, such as pyridinium, phosphonium, or cholinium-based ILs, may present significantly distinct reactivity profiles, environmental behavior, or scalability. Furthermore, although reaction yields and spectroscopic data were employed to substantiate the observed results, the study lacked comprehensive mechanistic investigations, including kinetic measurements, intermediate isolation, or computational modeling. Consequently, the precise mechanistic role of the ILs—particularly concerning their contributions to enolate stabilization or modulation of the transition state—remains speculative. These limitations underscore the necessity for expanded screening and in-depth mechanistic studies to thoroughly elucidate and optimize IL-mediated alkylation systems.

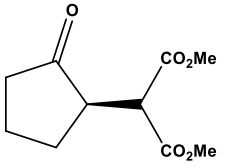
3. Experimental Techniques

Commercial reagents were procured from Thermo Scientific or VWR and were utilized either as received or subjected to purification prior to application, adhering to established protocols. Non-aqueous reagents were transferred under a nitrogen atmosphere utilizing a syringe. Organic solutions were concentrated under reduced pressure employing a Büchi rotary evaporator with a water bath, or they were evaporated using a sand bath. Thin-layer chromatography (TLC) was conducted on Merck aluminum-backed plates coated with 0.2 mm silica gel 60-F. Visualization of the developed chromatogram was achieved through UV fluorescence quenching at 254 nm.

Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were acquired on a Jeol JNM-ECZ spectrometer operating at 400 MHz for protons. Data for ^{1}H NMR are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant (Hz). Data for ^{13}C NMR spectra are presented in terms of chemical shift (ppm) relative to tetramethylsilane (TMS). Infrared (IR) spectra were recorded on a Bruker Alpha spectrometer utilizing direct attenuated total reflectance (ATR) methodology. All absorption frequencies are reported in units of cm^{-1}.

3.1. Experimental

Dimethyl 2-(2-oxocyclopentyl)malonate (2)



Method A

To a stirred solution of sodium hydride (158 mg, 6.58 mmol, 1.30 equivalents) in dichloromethane (10 mL) maintained at 0 ℃, dimethyl malonate (1.05 mg, 6.58 mmol, 1.3 equivalents) was added. The resulting solution was stirred for 30 minutes at ambient temperature. Subsequently, 2-chlorocyclopentanone **(1)** (600 mg, 5.06 mmol, 1 equivalent) was introduced, and the mixture was stirred at ambient

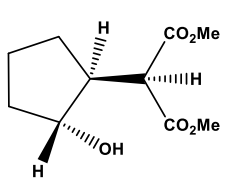
temperature for an additional 8 hours. Thin-layer chromatography (TLC) analysis at this stage indicated the formation of a new product. To the reaction mixture, saturated aqueous ammonium chloride solution (10 mL) was added, and the organic layer was extracted with diethyl ether (4 ×15 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (4 ×10 mL) and brine (4 ×10 mL), then dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, utilizing a gradient of solvents from hexane:ethyl acetate (5:1 to 100% ethyl acetate), yielding the title compound as a colorless oil (430 mg, 41% yield). The product was characterized using spectroscopic data: υmax (thin film/cm-1) 2961, 1749, 1738; δH (250 MHz, CDCl3) 3.84 (1H, d, *J* 5.8 Hz, C**H**(CO2CH3)2), 3.78 (3H, s, C**H**3), 3.73 (3H, s, C**H**3), 2.97-2.88 (1H, m, C**H**C=O), 2.56-1.99 (4H, m, C**H**2CH, C**H2**C=O), 2.00-1.81 (2H, m, C**H2CH2**C=O); δC (62.5 MHz, CDCl3) 216.2, 169.1, 168.6, 53.9, 51.6, 51.2, 41.2, 38.2, 23.8, 20.8; m/z (C.I) 215 (MH+, 100%), 214 (4%), 183 (11%), 155 (7%), 123 (3%); C10H15O5, requires 215.092, found: 215.0913.

Method B

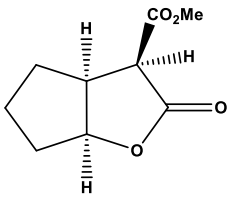
To a stirred solution of sodium hydride (158 mg, 6.58 mmol, 1.30 equivalents) in dichloromethane (10 mL) at 0 ℃, dimethyl malonate (1.05 mg, 6.58 mmol, 1.3 equivalents) was added. The resulting solution was stirred for 30 minutes at room temperature. Subsequently, 2-chlorocyclopentanone **(1)** (600 mg, 5.06 mmol, 1 equivalent) was introduced to the solution and the mixture was stirred at room temperature for an additional 8 hours. Thin-layer chromatography (TLC) analysis at this point indicated the formation of a new product. To the reaction mixture, saturated aqueous ammonium chloride solution (10 mL) was added, and the organic layer was extracted with diethyl ether (4 x 15 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (4 x 10 mL) and brine (4 x 10 mL), then dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, employing a gradient of solvents from hexane: ethyl acetate (5:1 to 100% ethyl acetate), yielding the title compound as a colorless oil (734 mg, 68% yield).

Dimethyl 2-2-hydroxycyclopentyl) malonate (3)

Methyl 2-oxo-hexahydro-2H-cyclopenta[*b*]furan-3-carboxylate (4)



(3)



(4)

To a stirred solution of dimethyl 2-(2-oxocyclopentyl) malonate (2) (80 mg, 0.37 mmol, 1.00 equiv) in ethanol (5 mL) contained within an Erlenmeyer flask, sodium borohydride (NaBH4) was added in small portions at room temperature (16.8 mg, 0.44 mmol, 1.20 equiv) over a period of 15 minutes. The reaction mixture was subsequently stirred for an additional 30 minutes and then transferred to water (5 mL). A 5% dilute solution of hydrochloric acid (4 drops) was introduced, and the organic layer was extracted with diethyl ether (2 x 10 mL), dried over magnesium sulfate (MgSO4), and concentrated under reduced pressure. Column chromatography on silica gel, eluting with a mixture of hexane and ether (3:1), yielded product **(3)** as a colorless oil (66 mg, 65% yield). The spectral data obtained included: υmax (thin film/cm-1) 3504, 2955, 2255, 1731; δH (250 MHz, CDCl3) 3.96-3.91 (1H, m, C**H**OH), 3.68 (3H, s, C**H**3), 3.67 (3H, s, C**H**3), 3.32 (1H, d, *J*7.8 Hz, C**H**(CO2Me)2), 2.33-2.28 (1H, m, C**H**), 1.88-1.83 (2H, m, C**H2**), 1.63-1.53 (3H, m, C**H2**), 1.28-1.25 (1H, m, C**H2**); δC (62.5 MHz, CDCl3) 169.2, 168.6, 76.2, 55.9, 51.5, 51.0, 46.8, 33.4, 28.3, 21.3;m/z (C.I) 216 (MH+, 9%), 159 (10%), 150 (4%), corresponding to C10H17O5, with a calculated mass of 216.0998 and a found mass of 216.0935. Further elution provided product **(4)** (18 mg, 26% yield), with the following spectral data: υmax (thin film/cm-1) 2957, 1742, 1733; δH (250 MHz, CDCl3) 5.06 (1H, t, *J* 5.3 Hz, C**H**O), 3.73 (3H, s, CO2C**H3**), 3.68 (1H, d, *J* 3.3 Hz, C**H**C=O), 3.14-3.10 (1H, m, C**H**CHC=O), 1.98-1.56 (6H, m, C**H**2); δC (62.5 MHz, CDCl3) 176.9, 168.5, 86.5, 54.8, 53.7, 43.5, 33.5, 32.9, 23.9;m/z (C.I) 185 (MH^+, 45%), 141 (51%), 134 (43%), 124 (67%), 101 (77%), 84 (54%) corresponding to $C_9H_{13}O_4$, with a calculated mass of 185.0814 and a found mass of 185.0806.

4. Conclusions

In conclusion, the successful alkylation of 2-chlorocyclopentanone with dimethyl malonate utilizing ionic liquids as reaction media underscores the notable efficiency and environmental potential of these innovative solvents. The significant enhancement in yield observed with [BMIM]BF_4 and [EMIM]OTf, in comparison to conventional dichloromethane (DCM), illustrates the distinctive solvation environment and polarity of ionic liquids, which promote enolate formation and stabilize critical reaction intermediates. In addition to their performance advantages, the low volatility and recyclability of ionic liquids provide substantial environmental benefits, aligning with the principles of green chemistry. This study not only demonstrates the feasibility of substituting hazardous organic solvents with ionic liquids but also reinforces their capacity as versatile platforms for advancing sustainable carbon–carbon bond-forming transformations. The findings contribute to the potential for broader adoption of ionic liquid-based methodologies in contemporary synthetic protocols.

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Author contributions: Bello Makama undertook the research, while Laurence M. Harwood provided initial supervision.

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Declarations:

Ethics approval and consent to participate: Not applicable.

Consent to publication: Not applicable.

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