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NEW FACILE SYNTHESIS OF 2-ARYLOXY-4H-IMIDAZOLIN-4-ONES VIA BASE CATALYTIC REACTIONS OF PHENOLS WITH FUNCTIONALIZED CARBODIIMIDES

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Abstract: The carbodiimides 2, obtained from aza-Wittig reactions of vinyliminophosphorane 1 with aromatic isocyanates, reacted with phenols in presence of catalytic potassium carbonate at $50 \sim 60^{\circ}$ C to gave 5 in satisfactory yields.

The synthetic versatility of functionalized carbodiimides has increasingly become apparent because of their rich chemistry¹⁻³. Recently, aza-Wittig reactions of functionalized iminophosphoranes with isocyanates were applied to produce carbodiimides able to undergo a plethora of heterocyclization reactions^{4,5}. In case of the stable functionalized carbodiimides, subsequent treatment with various nucleophiles generated heterocycles such as quinazolines⁶, imidazolinones⁷, pteridinones⁸, fused pyrimidines⁹⁻¹² and aplysinopsin-type alkaloids of marine

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origin¹³⁻¹⁶.However, phenols were not used as nucleophiles to prepare aryloxy substituted heterocycles previously, probably due to their very weak nucleophilicity. Here we wish to report a new facile synthesis of 2-aryloxy-4H-imidazolin-4-ones 5 via base catalytic reactions of phenols with functionalized carbodiimides 2.

The easily accessible vinyliminophosphorane 1 reacted with aromatic isocyanates to give carbodiimides 2, which were allowed to react with phenols at 50~60°C. In the absence of any base, the reaction did not take place and the carbodiimide 2 was recovered unchanged. It was reported that phenols reacted with carbodiimides in need of high temperature (160°C) to form O,N,N'-isoureas or N,N,N'-ureas depending on the acidity of phenols¹. However, the carbodiimides 2 are unstable or will cyclize to isoquinolines at high temperature¹⁷. With regard to the stronger nucleaphilicity of phenoxides to phenols, we carried out the reaction of carbodiimides 2 with phenols in presence of catalytic solid potassium carbonate at 50~60°C. The reaction took place smoothly and the imidazolinones 5 were obtained in satisfactory yields. The formation of 5 can be rationalized in terms of an initial nucleophilic addition of phenoxides to the carbodiimides 2 to give 3, 3 are converted to the gualidene intermediates 4 which cyclize to give 5.



Table 1.Preparation of 2-Aryloxy-4H-imidazolin-4-ones			
Compounds	R	Ar	Yield(%)*
5a	Ph	NO2-	73
5b	Ph	NO ₂	67
5c	Ph	ci	80
5d	Ph	сн ₃	81
5e	Ph	CH3	72
5f	Ph	CH ₃	68
5g	Ph		76
5h	Ph	Ph	82
5i	Ph		trace
5j	Ph	COOEt	trace
5k	ci	ci<	78

*isolated yields based on vinyliminophosphorane 1.

The yields were satisfactory with most of the phenols used, however when more acidic and steric 2,4-dinitro-6-methylphenol or 2-ethoxylcarbonylphenol were used, no product was obtained due to their weak nucleaphilicity and steric hindrance. See Table 3. To our knowledge, this is the first reported example of the base catalytic reaction of phenol with carbodiimide. With regard to the mild condition and the satisfactory yield, this process supplies an efficient synthesis of 2-aryloxy-4Himidazolin-4-ones which were not easily accessible by other methods.

In summary, we demonstrate here that the tandem carbodiimide-mediated annulation affords a new general high-yield entry to a variety of 2-aryloxy-4Himidazolin-4-ones. Due to the easy access of the starting materials, and due to the simplicity of the experimental procedure and extremely mild conditions, we think that the synthetic approach discussed here in many cases compares favorably with other existing methods.

EXPERIMENTAL

Melting points were uncorrected. MS were measured on a HP5988A spectrometer. IR were recorded on a Shimadzu IR-408 infrared spectrometer. NMR were taken on a Varian XL-200 spectrometer. Vinyliminophosphorane 1 was prepared by the literature report^[17].

General procedure for the preparation of 2-aryloxy-4H-imidazolin-4-ones 5:

To a solution of vinyliminophosphorane 1 (2.26g,5mmol) in dry methylene dichloride (15ml) was added aromatic isocyanate (5mmol) under nitrogen at room temperature. After the reaction mixture was stirred for 2 hours, the solvent was removed off under reduced pressure and ether/petroleum ether (1:2,20ml) was added to precipitate triphenylphosphine oxide. Filtered, the solvent was removed to give carbodiimide 2. To the solution of 2 in CH₃CN (15ml) was added a phenol ArOH (5mmol) and catalytic solid K₂CO₃ (0.034g). The mixture was stirred for 5~8hr at 50~60°C and filtered, the filtrate was condensed and the residual was recrystallized from methylene dichloride/petroleum ether or purified by a short silica gel column to give imidazolinones 5.

¹HNMR,IR and MS data for some compounds of 5:

5b:yield 67%,light yellow crystals, m.p.108~110°C, ¹HNMR(CDCl₃,200MHz) δ 7.20(s,1H,=CH),7.22~8.59(m,14H,Ar-H); IR(cm⁻¹),1731,1648,1410,1352; MS(m/z), 385(M⁺,98%),241(99%),195(32%),166(63%),116(100%).

5c: yield 80%,light yellow crystals, m.p.177~178°C, ¹HNMR(CDCl₃,200MHz) δ 7.14(s,1H,=CH),7.25~7.97(m,14H,Ar-H); IR(cm⁻¹),1725,1656,1408; MS(m/z), 374 (M⁺,100%),230(83%),167(39%),111(98%).

5f: yield 68%,light yellow crystals, m.p.135~136°C, ¹HNMR(CDCl₃,200MHz) δ 2.28(s,3H,CH₃),7.10(s,1H,=CH),7.18~7.99(m,14H,Ar-H); IR(cm⁻¹),1728,1654,1402; MS(m/z), 354 (M⁺,78%),233(42%),144(32%),91(100%).

5g: yield 76%,light yellow crystals, m.p.113~114°C, ¹HNMR(CDCl₃,200MHz) δ 2.25(s,6H,2CH₃),7.10(s,1H,=CH),7.25~7.93(m,13H,Ar-H);IR(cm⁻¹),1727,1655,1404; MS(m/z), 368(M⁺,92%),221(86%),105(100%).

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