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RESEARCH ARTICLE

Three-Component Reaction Between Indan-1,2,3-trione 2-Oxime and Acetylenic Esters in the Presence of Triphenylphosphine

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Abstract: Reaction between indan-1,2,3-trione 2-oxime and electron-deficient acetylenic esters in the presence of triphenylphosphine leads to dialkyl 9-oxo-1,9-dihydro-2-oxa-1-aza-fluorene-3,4-dicarboxylate in good yields. This one-pot method is simple and effective under mild conditions.

Keywords: Indan-1,2,3-trione 2-Oxime, Acetylenic esters, Triphenylphosphine, dialkyl 9-oxo-1,9-dihydro-2-oxa-1-aza-fluorene-3,4-dicarboxylate, Wittig reaction

Introduction

The intramolecular Wittig reaction has become one of the favorites among the numerous methods of cycloalkene syntheses[1,2]. The importance of intramolecular Wittig reactions[1,2] in the synthesis of cycloalkenes and unsaturated heterocyclic compounds can hardly be overestimated. Three-component reaction between triphenylphosphine, acetylenic esters and an organic acidic compound has been reported to produce phosphorus which may further undergo intramolecular Wittig reaction to produce unsaturated hetro- or carbocyclic compounds in a one-pot proccess[3-6]. *N*-Heterocycles receive considerable attention in the literature as a consequence of their exciting biological properties and their role as pharmacophores[7]. In continues of our previous works on the reaction between phosphorus nucleophiles and acetylenic esters in the presence of organic acids[8-16]. We decided to investigate the reaction of OH-acidic compound such as indan-1,2,3-trione 2-oxime **1** with acetylenic esters in the presence of triphenylphosphine.

Experimental

All melting points are uncorrected. Elemental analyses were performed at the analytical laboratory of Science and Research Unit of the Islamic Azad University. Mass spectra were recorded on a Finnigan-MAT 8430 mass spectrometer operating at an ionisation potential of 70 eV.

IR spectra were recorded on a Shimadzu IR-470 spectrometer.^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-500 Avance spectrometer in solution in $CDCl_3$ using TMS as an internal standard. Indan-1,2,3-trione 2-oxime **1** was prepared by the literature method.[17] Others chemicals employed in this work were purchased from Merck and were used without further purification.

General procedure

*Synthesis of **3a-c***

A mixture of acetylenic ester **2** (2 mmol) in 2 mL dichloromethane at room temperature was added to a magnetically stirred solution of indan-1,2,3-trione 2-oxime **1** (2 mmol) and triphenylphosphine (2 mmol) in 10 mL dichloromethane. The reaction mixture was then allowed to stir for 24 h. The solvent was evaporated at reduced pressure and the residue was purified by silica gel column chromatography using hexane-ethyl acetate as eluent. The solvent was removed under reduced pressure to afford the product.

*Dimethyl 9-oxo-1,9-dihydro-2-oxa-1-aza-fluorene-3,4-dicarboxylate (**3a**)*

White powder, yield: 78%, m.p. 96–98 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 and 3.90 (6H, 2s, $2OCH_3$), 7.23-7.51 (4H, m, 4CH aromatic). 14.02 (1H, br s, NH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 51.85 and 52.96 ($2OCH_3$); 111.05, 119.70, 121.33, 122.17, 123.90, 126.42, 130.45, 132.06, 132.71 and 140.85 (10C), 161.34 (C=O ester), 163.78 (C=O ester), 191.45 (C=O) ppm. IR (KBr) (ν_{max}/cm^{-1}): 3437 (NH), 1705 and 1633 (C=O). Anal. Calcd for $C_{15}H_{11}NO_6$: C, 59.80; H, 3.68; N, 4.65. Found: C, 59.88; H, 3.75; N, 4.70%. MS (*m/z*, %): 301 (M, 11).

*Diethyl 9-oxo-1,9-dihydro-2-oxa-1-aza-fluorene-3,4-dicarboxylate (**3b**)*

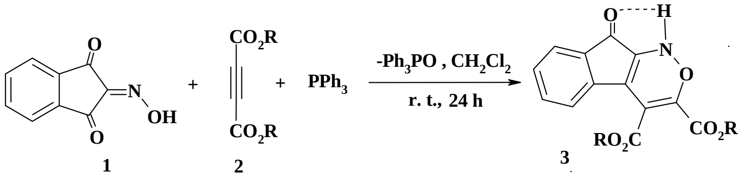
White powder, yield: 75%, m.p. 84–87 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 and 1.31 (6H, 2t, $^3J_{HH}$ =7 Hz, $2CH_3$), 4.17–4.79 (4H, m, $2OCH_2$), 7.28-7.49 (4H, m, 4CH aromatic). 13.97 (1H, br s, NH)ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.91 and 14.53 ($2CH_3$), 62.11 and 63.06 ($2OCH_2$), 110.89, 119.78, 121.28, 122.08, 124.25, 126.50, 130.51, 132.13, 132.64 and 140.80 (10C), 161.18 (C=O ester), 163.82 (C=O ester), 191.27 (C=O) ppm. IR (KBr) (ν_{max}/cm^{-1}): 3442 (NH), 1708 and 1640 (C=O). Anal. Calcd for $C_{17}H_{15}NO_6$: C, 62.00; H, 4.59; N, 4.25. Found: C, 62.45; H, 4.50; N, 4.20%. MS (*m/z*, %): 329 (M, 5).

*Di-t-butyl 9-oxo-1,9-dihydro-2-oxa-1-aza-fluorene-3,4-dicarboxylate (**3c**)*

White powder, yield: 66%, m.p. 80–82 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 and 1.45 (18H, 2s, $6CH_3$), 7.23-7.64 (4H, m, 4CH aromatic). 13.93 (1H, br s, NH)ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 28.57 and 28.73 ($6CH_3$ of t-butyl groups), 81.80 and 87.46 (2C of *t*-butyl groups), 110.88, 119.82, 121.44, 122.25, 123.83, 126.53, 130.40, 132.13, 132.83 and 140.77 (10C), 161.30 (C=O ester), 163.64 (C=O ester), 191.28 (C=O) ppm. IR (KBr) (ν_{max}/cm^{-1}): 3446 (NH), 1712 and 1639 (C=O). Anal. Calcd for $C_{21}H_{23}NO_6$: C, 65.44; H, 6.02; N, 3.63. Found: C, 65.40; H, 6.10; N, 3.55%. MS (*m/z*, %): 385 (M, 8).

Results and Discussion

Reaction of indan-1,2,3-trione 2-oxime **1** with acetylenic ester **2** in the presence of triphenylphosphine affords dialkyl 9-oxo-1,9-dihydro-2-oxa-1-aza-fluorene-3,4-dicarboxylate **3** in good yield (Scheme 1).



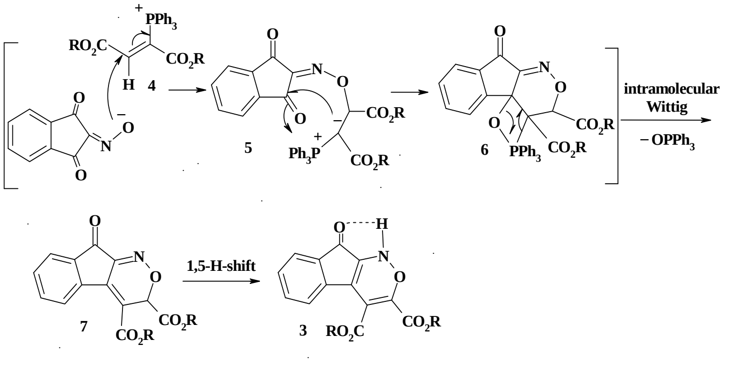
3	R	%yield* of **3**
a	Methyl	78
b	Ethyl	75
c	t-Butyl	66
	* Isolated yields	

Scheme 1. Condensation of acetylenic esters and indan-1,2,3-trione 2-oxime in the presence of triphenylphosphine

The structures of compounds (**3a–c**) were deduced from their elemental analyses and their IR, ^{1}H NMR, ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* values. The ^{1}H NMR spectrum of compound **3a** exhibited two single sharp lines readily recognised as arising from methoxy (δ=3.78 and 3.90 ppm). Aromatic protons resonate between 7.23 and 7.51 ppm as multiplets. The ^{1}H NMR spectrum of compound **3a** exhibited a D_2O-exchangable broad signal at 14.02 ppm for NH proton, indicating extensive intramolecular hydrogen-bond formation[18].

The ^{13}C NMR spectrum of compound **3a** showed 15 distinct signals in agreement with the proposed structure. The IR spectrum of compound **3a** also supported the suggested structure, strong absorption band was observed at 3437 cm^{-1} for the NH group. Strong absorption bands were observed at 1705 and 1633 cm^{-1} for C=O groups. The mass spectrum of compound **3a** showed the molecular ion peak at 301.

On the basis of the well established chemistry of trivalent phosphorus nucleophiles[19–24], it is reasonable to assume that compound **3** result from initial addition of triphenylphosphine to the acetylenic ester and concomitant protonation of the 1:1 adduct, followed by attack of oxygen of the anion of indan-1,2,3-trione 2-oxime to vinyltriphenylphosphonium cation **4** to generate yilid **5**, which undergoes an intramolecular Wittig reaction to produce triphenylphosphine oxide and **7**, which is a tautomer of **3** (Scheme 2).



Scheme 2. Suggested mechanism for formation of compound **3**

Conclusion

We report a three-component reaction between indan-1,2,3-trione 2-oxime and acetylenic esters with triphenylphosphine, to produce dialkyl 9-oxo-1,9-dihydro-2-oxa-1-aza-fluorene-3,4-dicarboxylate in good yields. This one-pot method is simple and effective under mild conditions and carries the advantage that not only is the reaction performed under neutral conditions but also that the substances can be mixed without any activation nor modification.

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