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Synthesis of 1-Methoxy-1H-phenanthro[9,10-c][1,2]oxazine and its Transformation to Triphenylene-o-dicarboxylic Derivatives

Demetrios N. Nicolaides^{*}, Raed Wajih Awad, Georgios K. Papageorgiou and Julia Stephanidou-Stephanatou

Laboratory of Organic Chemistry, Aristotelian University of Thessaloniki, 450 06 Thessaloniki, Greece

Aristides Terzis and Catherine P. Raptopoulou

X-Ray Laboratory, NCR "Demokritos" Athens, Greece

Abstract: 1-Methoxy-1H-phenanthro[9,10-c][1,2]oxazine 4 prepared from the reaction of 10-(methoxyimino)phenanthren-9-one 1 with benzoylmethylene(triphenyl)phosphorane 2, reacts thermally with dienophiles 6, 9a,b to give the triphenylene-o-dicarboxylic derivatives 8, 11a,b in high yield.

Recently we investigated¹⁻⁵ reactions of phosphorus ylides with *o*-quinone monoximes. The final products obtained depend on the nature of the above reactants. Wittig olefination products were formed either as stable compounds^{1,3,5} or as intermediates^{1,4}, which were further transformed to stable fused heterocyclic derivatives. However, in some cases "Wittig type" reaction¹ of the oximino group or participation^{2,4} of the 1,4-oxaza-1,3-diene system leading to formation of oxazole derivatives were observed. The stable Wittig olefination products were used as dienes⁵.

The work detailed here involves the reaction of monooxime 1 with benzoylmethylene(triphenyl)phosphorane 2 and the reactions of the main product, 1-methoxy-1H-phenanthro[9,10-c][1,2]oxazine 4, with some dienophiles, as it is depicted in Schemes 1 and 2.

Treatment of monoxime 1 with two equivalents of phosphorus ylide 2 in boiling benzene for 4 days gave, after separation by column chromatography, the title compound 4^6 (17%), 2,3-dibenzoyl-1H-dibenzo[e,g]indole 5^6 (12%) (Scheme 1) and the known⁷ 2-phenylphenanthro[9,10-b]furan (2%). The formation of the isolated products 4 and 5 can be explained through an initial Wittig olefination of 1 leading to the intermediate 3. Further electrocyclization of the (Z-)benzoylmethylidene derivative 3 can account for the formation of 4, whereas by Michael addition of a second ylide species 2 to 3, followed by subsequent triphenylphosphine and methanol elimination compound 5 can be formed.





When 4 and two equivalents of DMAD 6 were heated in benzene at reflux for 5 days dimethyl 3phenyltriphenylene-1,2-dicarboxylate 8 was isolated in 58% yield, obviously through an initial Diels-Alder cycloadition of dienophile 6 to 4, leading to the formation of the intermediate 7 from which by further elimination of nitrous methyl ester and rearomatization of the polycyclic system, 8 was formed (Scheme 2). The possibility of an initial elimination of the nitrous ester followed by addition of the dienophile 6 was excluded because in a control experiment compound 4 remained unchanged after refluxing in xylene for 2 days.



Scheme 2

By refluxing 4 and two equivalents of N-methylmaleimide 9a in xylene for 1 day 3-phenyltriphenylene-1,2dicarboxylic acid N-methylimide 11a⁶ was isolated in 90% yield. Similarly from the reactin of 9b the Nphenylimide 11b⁶ was isolated in 83% yield after refluxing in xylene for 38h. Both MS and NMR spectra⁶ of the products favour structure 11 instead of the expected 1,2-dihydro-derivatives. The structure of compound 11a was unequivocally established by X-ray crystallography^{8,9} (Figure 1).

In conclusion, the easily prepared phenanthro-oxazine 4 acts as diene precursor for the forma-tion of 3-phenyltriphenylene derivatives.



Figure 1

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References and Notes

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6. Selected data for 4,5,8 and 11

Compound 4: mp. 158-160 °C ; ¹H NMR (CDCl₃) δ 3.64 (s, 3H), 6.27 (s, 1H), 7.52-7.70 (m, 7H), 8.15-8.18 (m, 2H), 8.44-8.47 (m, 1H), 8.62-8.68(m, 2H) and 8.89-8.92 (m, 1H); MS *m/z* 339 (M⁺, 100%), 324(9), 308(52), 296(52), 165(17). Compound 5: mp. 199-201 °C ; v_{max} 1660 cm⁻¹; ¹H NMR (CDCl₃) δ 7.29-7.62 (m, 7H), 7.64-7.86 (m, 4H), 7.88-8.17 (m, 3H), 8.20-8.39 (m, 3H), 8.20-8.39 (m, 1H), and 8.42-8.87 (m, 4H); MS *m/z* 425 (M⁺, 100%), 397(14), 369 (12), 348(11), 320(18). Compound 8: mp. 182-184 °C; v_{max} 1720 cm⁻¹; ¹H NMR (CDCl₃) δ 3.78 (s, 3H), 4.05 (s, 3H), 7.37-7.88 (m, 8H), 8.08-8.27 (m, 2H), 8.40-8.78 (m, 2H), 9.18-9.52 (m, 2H); MS *m/z* 420 (M⁺, 100%), 405(65),390(23), 361(6), 346(10), 302(13). Compound 11a: mp. 229-230°C; v_{max} 1770, 1700 cm⁻¹; ¹H NMR (CDCl₃) δ 3.00 (s, 3H), 7.39-7.90 (m, 8H), 7.96-8.30 (m, 2H), 8.34-8.71 (m, 2H), and 9.06-9.50 (m, 2H); MS *m/z* 387 (M⁺, 100%), 331(25), 294(21), 218(22), 164(11). Compound 11b: mp. 261-263 °C; v_{max} 1770, 1710 cm⁻¹; ¹H NMR (CDCl₃) δ 7.39-8.00 (m, 11H), 8.05-8.25 (m, 2H), 8.43-8.62 (m, 2H), and 9.21-9.53 (m, 2H); MS *m/z* 449 (M⁺, 100%), 420(48), 303(10), 225(14).

All compounds gave correct elemental analysis.

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