Pergamon

Tetrahedron Letters, Vol. 37, No. 7, pp. 1097-1100, 1996

0040-4039/96 $15.00 + 0.00

0040-4039(95)02314-3

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

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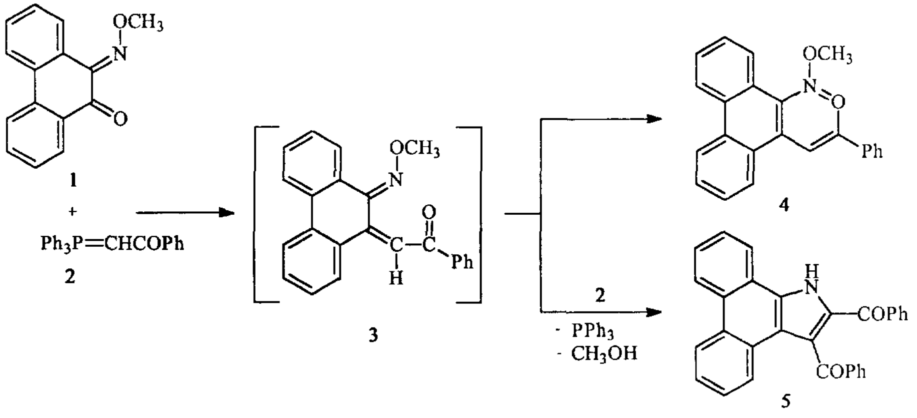
Abstract: *1-Methoxy-1H-phenanthro[9,10-c][1,2]oxazine 4 prepared from the reaction of 10-(methoxyimino)phenanthren-9-one 1 with benzoylmethylene(triphenyl)phosphorane 2, reacts thermally with dienophiles 6, 9a,b to give the triphenylene-o-dicarboxylic derivatives 8, 11a,b in high yield.*

Recently we investigated[1-5] 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" reaction[1] 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 dienes[5].

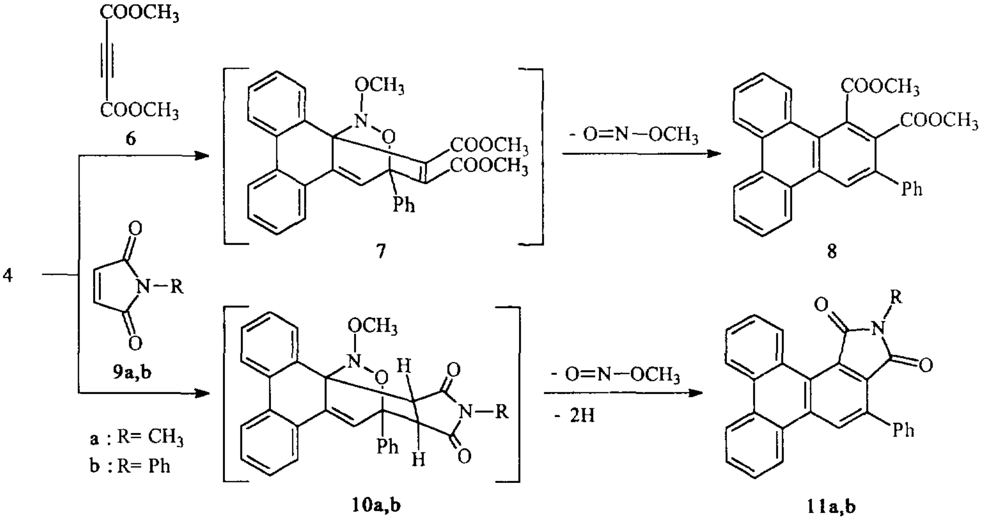
The work detailed here involves the reaction of monooxime **1** with benzoylmethylene(triphenyl)phosphorane **2** and the reactions of the main product, 1-methoxy-1H-phenanthro[9,10-c][1,2]oxazine **4**, with some dienophiles, as it is depicted in Schemes 1 and 2.

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 known[7] 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.



Scheme 1

When **4** and two equivalents of DMAD **6** were heated in benzene at reflux for 5 days dimethyl 3-phenyltriphenylene-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-1,2-dicarboxylic acid N-methylimide **11a**[6] was isolated in 90% yield. Similarly from the reactin of **9b** the N-phenylimide **11b**[6] was isolated in 83% yield after refluxing in xylene for 38h. Both MS and NMR spectra[6] 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-phenyl-triphenylene derivatives.

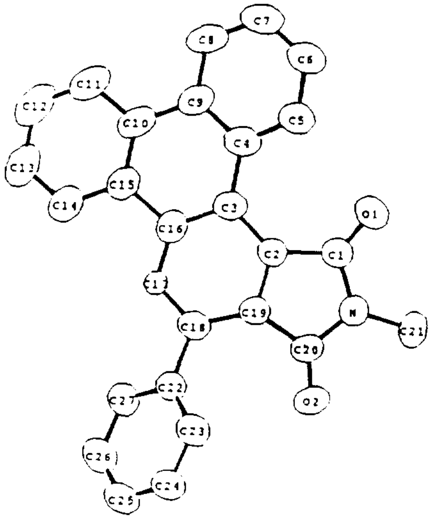


Figure 1

Acknowledgement We thank Boutaris and Son Co. for financial support to A.T.

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

Compound **4**: mp. 158-160 °C ; ^{1}H NMR ($CDCl_3$) 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 ; ν_{max} 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) 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; ν_{max} 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) 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; ν_{max} 1770, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) 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; ν_{max} 1770, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) 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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(*Received in UK* 17 *October* 1995; *revised* 5 *December* 1995; *accepted* 7 *December* 1995)