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THERMOLYSIS OF PHENOXYACETYL-CYANOMETHYLENETRIPHENYLPHOSPHORANES-TANDEM INTRAMOLECULAR WITTIG AND CLAISEN REARRANGEMENT REACTIONS

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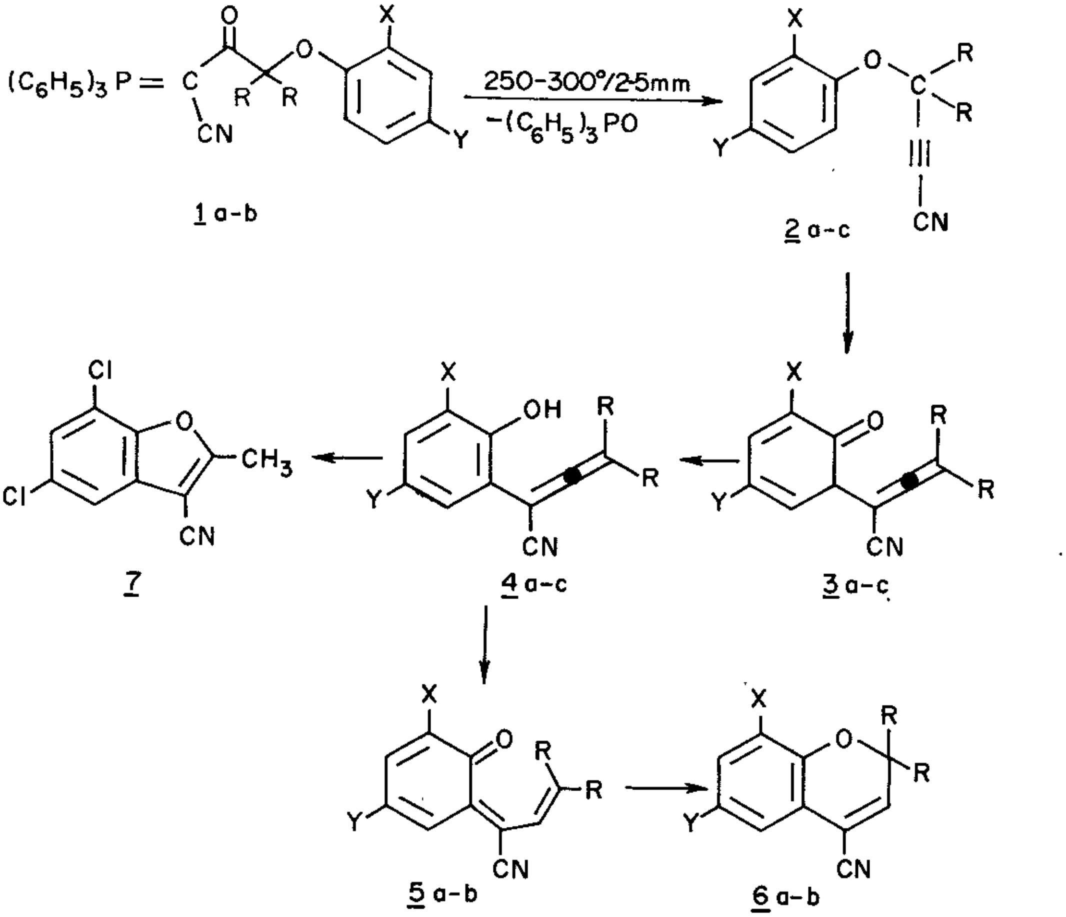
Abstract - Thermolysis of acyl-cyanomethylenetriphenylphosphorane containing aryloxyacetyl moiety in the acyl group results in tandem intramolecular Wittig and Claisen rearrangement reaction. The orthoallenylphenol intermediates formed cyclise to give a 2H-chromene or a benzofuran depending on substituents.

The Claisen rearrangement of aryl propargly ethers offers a general route for the preparation of 2H-chromenes[1]. In some cases and particularly in polar solvents or in presence of a base the ortho-allenyl phenol intermediates cyclise to give benzofurans[2-6]. In general the ethers are obtained from phenol and propargyl halide[7]. We have made use of the intramolecular Wittig reaction[8] of substituted acyl-triphenylphosphoranes for the synthesis of propynenitriles[9]. We expected that application of this method for the synthesis of aryl propargyl ethers, which under the conditions might show 3,3-sigmatropic and other accompanying reactions will provide a single step synthesis for 2H-chromene. We report the utility of this combination with three examples.

The ylides 1a-c [(a) X=Y=R=H; (b) X=H, Y=Cl, R=CH_3; (c) X=Y=Cl, R=H)] were prepared from cyanomethylene triphenylphosphorane and the corresponding phenoxyacetylchloride via transylidation reaction following a previously reported procedure[9]. Thermolysis of 1a-c was carried out at 2-5 mm in a short path vacuum distillation apparatus immersed in woods metal bath maintained at 250-300°C. The distillate contains the products 2 and 6 or 7 contaminated with triphenyl phosphine oxide. At higher temperatures, the formation of the corresponding phenol was also observed. Pure compounds 2 and 6 or 7 were isolated by column chromatography over SiO_2 and eluting with hexane and progressively increasing the polarity by addition of ethyl acetate and characterised by spectral data[10] 1a gave 2a (30%) and 6a (2%), 1b gave 2b (5%) and 6b (87%); 1c gave 7c (26%).

It was well established that 2H-chromenes are formed from ortho-allenyl phenols via a 1,5-H shift to form an ortho-quinone monomethide intermediate of type 5 followed by a 6π-electron electrocyclic reaction[11]. Under the conditions employed the propargyl ether 2a and 2b derived from 1a and 1b respectively follow the above pathway whereas 2c containing a chlorine in ortho position shows deviation in that it gives a benzofuran derivative 7 in place of 2H-chromene. The instances where the ortho-allenyl phenol cyclises to give a benzofuran are those when the medium is highly polar or contains a base to generate a phenolate anion[2-5,11]. It was also reported that the electron donar and attracting groups favour the formation of 6-and 5-membered rings respectively[6]. In the intermediates 4a-c the electrophilicity of allenic carbon is enhanced by the α,β-unsaturated nitrile system. This should have favoured the benzofuran formation[12] by a nucleophilic addition on allenic carbon in ortho-allenyl phenol 4 but in practice, this is not the case always. In the case of 4c, the 1,5-H shift may have been prevented by intramolecular hydrogen bond formation between the phenolic OH and chlorine. Such an effect has been observed in pyrimidine series[13] and may explain the difference in the behaviour of compound 4c from others. Not all the propargylic ethers 2a-c formed under our experimental conditions rearrange completely. The highest yield of rearranged product is obtained in case of 2b. This may be due to the effect of gem dimethyl group in 2b which is known to enhance the ease of Claisen rearrangement[14]. We will report elsewhere the findings of our investigations currently in progress on the pyrrolysis of different substituted phosphoranes of type 1 under optimized conditions.



a) X=Y=R=H; b) X=H, Y=Cl, R=CH_3; c) X=Y=Cl; R=H

Scheme 1

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10. Compound 6a: Oily liquid; high resolution mass: found m/e 157.0520, calcd. for $C_{10}H_7NO$ 157.0527; IR($CHCl_3$):ν_{CN} 2239 cm^{-1}; ^{1}HNMR($CDCl_3$,δppm) 4.89 (d,2H,J=4Hz), 6.53 (t,1H,J=4Hz), 6.77-7.25 (unresolved, 4H): Compound 6b:m.p:59°; mass spectrum: m/e 219, isotope peak at m/e 221; IR($CHCl_3$):ν_{CN} 2236 cm^{-1}; ^{1}HNMR($CDCl_3$): 1.47(s,6H), 6.4(s,1H), 6.74(d,1H,J=9Hz), 7.15(q,1H, J_{ortho} =9Hz, J_{meta} = 2Hz), 7.27 (d,1H,J=2Hz); ^{13}CNMR($CDCl_3$):27.3(q), 77(s), 109.7(s), 115((s), 118.2(s), 119(d), 124.9(d), 126.8(s), 131.4(d), 144.1(d), 151(s). Compound 7: m.p.: 149-150°; mass spectrum: m/e at 225, isotope peaks at m/e 227 and 229; IR(KBr):ν_{CN} 2238 cm^{-1}; ^{1}HNMR($CDCl_3$): 2.71(s,3H), 7.31(d,1H,J=2Hz), 7.44(d,1H,J=2Hz); ^{13}CNMR ($CDCl_3$): 14(q), 92.1(s), 111.8(s), 117.7(s) overlapping with 117.7(d), 125.8(d), 128.2(s), 130.6(s), 148.1(s), 166.8(s).
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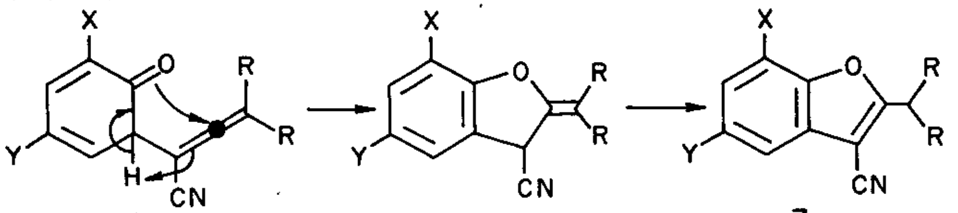
12. An alternative to the dienone-phenol prototropy given in scheme 1 would be a single step aromatization and cyclisation shown below. This is akin to the type of cyclisation observed in the flash vacuum pyrolysis of phenyl propargyl ether to give indanone (B.H. Al-Sader and D.M. Al-Fekri, J. Org. Chem., 1978, 43, 3626).



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This mechanism has not been taken into consideration by any investigator so far as viable for benzofuran formation.

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