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THE CHEMISTRY OF Δ^4-OXAZOLINES 1. NUCLEOPHILIC ADDITIONS TO FORM SUBSTITUTED FURANS

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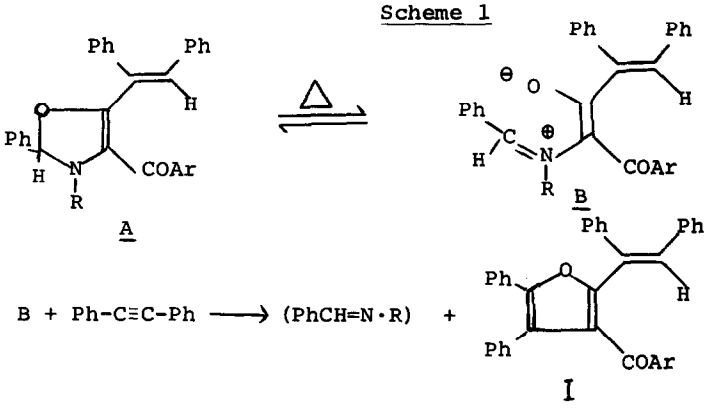
We recently reported a new synthesis of some Δ^4-oxazolines (A) by the addition of azomethine ylids (derived from thermal cleavage of acylaziridines) to diphenylcyclopropenone (DPP)[2] These novel heterocycles exhibit thermochromism and photochromism which was attributed to ring-chain isomerisation to a labile new azomethine ylid (B). We wish to report a series of nucleophilic additions of a novel nature which serve to confirm the equilibrium in scheme 1 and provide a

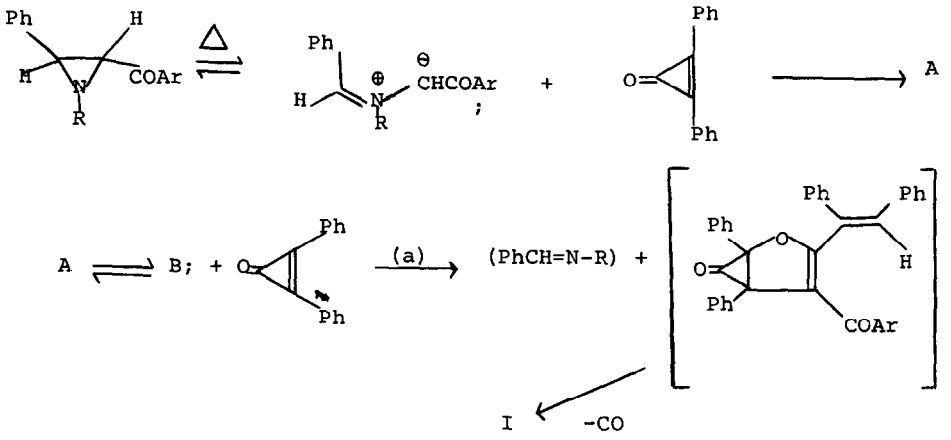
Scheme 1



route to new substituted furans, as exemplified in scheme 1 for diphenylacetylene. Treatment of 0.20 g of A(Ar=Ph,R=C_6H_{11}) with 0.1 g of diphenylacetylene in 25 ml of refluxing toluene for 18 hrs., followed by chromatographic separation on alumina afforded the furan I, 0.145 g, (74% yield) m.p. 195-6° (see table 1).

Furans of type I are also observed as by-products in the high temperature reaction of an acyl aziridine with DPP with loss of carbon monoxide envisaged as follows in scheme (2)

Scheme 2



Treatment of 0.1 g of A(Ar=Ph R=C_6H_{11}) with 0.1 g of DPP in 10 ml of refluxing toluene for 18 hrs, then chromatography on alumina afforded the furan I, 0.060 g, m.p. 192-4°. The alternative mechanism involving loss of carbon monoxide from the DPP prior to cycloaddition is considered unlikely since the possibility of thermal decarbonylation of DPP to diphenylacetylene under the reaction conditions was discounted by a separate control reaction. The benzaldehyde portion of the imine by-product was isolated and identified as the 2,4-dinitrophenylhydrazone. The attack by the oxygen of B on the carbon-carbon double bond of DPP in step (a) is to be contrasted with the reaction of pyridinium ylids[4] with DPP where attack occurs at the carbonyl carbon of DPP with the formation of α-pyrones.

Addition of DPP to acylaziridines via the azomethine ylid therefore involves competing 1:1 and 2:1 reactions to form A and I respectively. Higher reaction temperatures (i.e. refluxing toluene rather than benzene) as expected favour the formation of I.

The Δ^4-oxazolines react with other electrophilic species to form various

Table 1

Properties of Substituted Furans and 2,3-Dihydrofurans [a]

Structure	Ar	m.p.	% yield	Infrared C=O($CHCl_3$)	Nuclear Magnetic Resonance $\delta^{CHCl_3}_{TMS}$ [b] Aryl protons	Vinyl protons	Furan ring	Tolyl CH_3 and ester	Mass Spectrum Parent Peak Calcd.	Meas.
I	Ph	195-6°	74	1695	7.2(25H)m	7.99(1H)s			502.1933	502.1935
I	p-Tolyl	186-7°	70.5	1693	7.2(24H)m	8.05(1H)s		2.35(3H)s	516.2089	516.2089
II	p-Tolyl	112-3°	57	1695 1730	7.4(14H)m	7.9(1H)s		2.37(3H)s 1.13-6(6H)t 4.16(4H)q	508.1886	508.1875
II	Ph	114-5°	54	1700	7.55(15H)m	7.96(1H)		1.11-6(6H)t 4.17(4H)q	494.1729	494.1716
III	Ph	73-4°	48.5	1690 1730	7.55(14H)m	8.05(1H)		2.70(3H)s 3.62(3H)s	422.1518	422.1528
IV	Ph	179-80°	59	1690 1730	7.45(20H)m	8.15(1H)		3.47(3H)s	484.1675	484.1678
V	Ph	222-4°	65.5	1695 1725	7.4(21H)m		4.05(1H)d [c] J=9.2Hz 4.16(1H)d		497.1627	497.1621
V	p-Tolyl	155-8°	64.5	1705 1720	7.6(20H)m		4.09(1H)d [c] J=9.25Hz 4.22(1H)d	2.38(3H)s	511.1784	511.1783

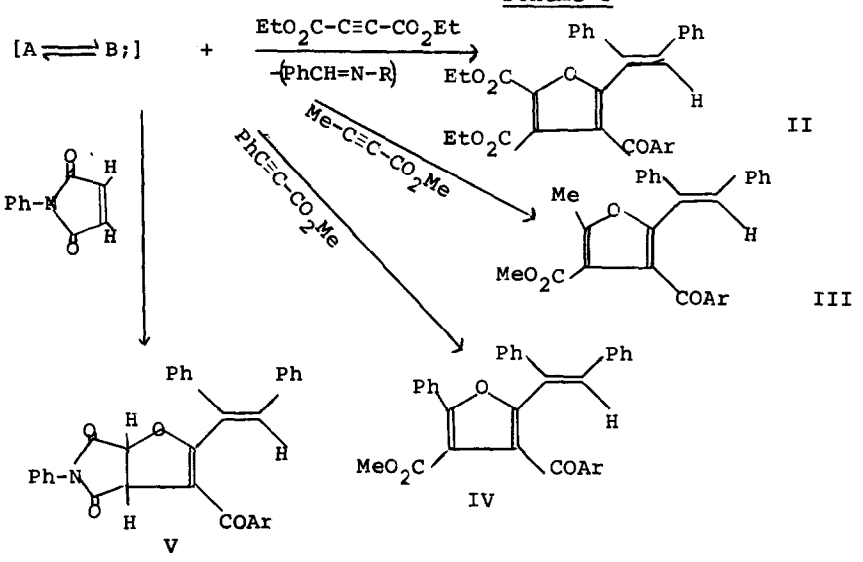
a. Satisfactory analytical data and/or parent mass peak measurement on all new compounds

b. Abbreviations: m=multiplet; s=singlet; d=doublet; t=triplet; q=quartet.

c. Assigned cis stereochemistry to ring junction (see reference 3).

substituted furans and dihydrofurans in fair yields as summarised in scheme 3 and table 1.

Scheme 3



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