Tetrahedron Letters,Vol.23,No.6,pp 603-606,1982 0040-4039/82/060603-04$03.00/0
Printed in Great Britain

6-ALKOXY-3,4-DIHYDRO-2H-PYRANS FROM SUBSTITUTED α,β-UNSATURATED ESTERS

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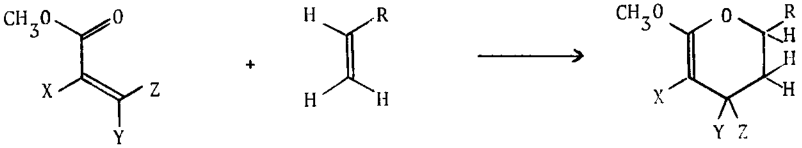
Abstract: Cycloaddition reactions of substituted α,β-unsaturated esters with various electron-rich olefins lead to 6-alkoxy-3,4-dihydro-2H-pyrans.

Dihydropyran formation by thermal cycloaddition reaction of α,β-unsaturated aldehydes or ketones, behaving as heterodienes, are well known.[1] However, until recently, reactions of unsaturated esters with electron-rich olefins have been reported to yield only cyclobutane derivatives.[2-7] We present here results indicating that 6-alkoxy-3,4-dihydropyrans are formed in reactions of various electron-rich alkenes (R=OAlk, Salk, Aryl, ...) with methyl acrylates substituted with one additional electron-withdrawing group in the α-position. Here the formation of the dihydropyran ring is promoted by push-pull resonance stabilization of the ketene acetal moiety.



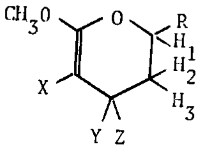
The results are summarized in Table I. The reactions were generally carried out in ~1M solutions in the indicated solvents. Free-radical inhibitors were used in reactions of trisubstituted olefins with styrenes to prevent copolymerization.[7,8]

The identification of these heterocyclic adducts follows from the spectroscopic data (Table II) consistent with literature analogues.[1,9] The most diagnostic feature in the NMR spectrum is the H_1 absorption split by two three-bond couplings.[10] In the IR spectrum the conjugated C=C absorption at 1640-1680 cm^{-1} was also diagnostic.

The reactions are not entirely unprecedented [12,13]: 6-alkoxy-3,4-dihydro-2H-pyrans have been suggested in the dimerizations of various acrylates.[14-16] Amice and Conia first proposed such an intermediate in the cycloaddition of ketene acetal with methyl acrylate.[17] 5-Alkylidene Meldrum's acid derivatives and vinyl ethers yield analogous heteroadducts.[18] Finally, the results reported here are nicely paralleled by the cycloaddition reactions of diethyl azodicarboxylate with electron-rich olefins in which labile 6-alkoxy-dihydrooxazines were found.[19-20]

Chemical properties of the new dihydropyrans as well as further experimental work clarifying the mechanism of these cycloadditions will be reported on shortly.

Table I



Reactants[a]				Conditions (b)		Dihydropyran	
X	Y	Z	R	Temp.(C°)	Solvent	N°	Yield(%)(c)
CN	H	H	$OCH_2CH(CH_3)_2$	25	C_6H_6	1	62
CN	CN	H	OC_6H_5	25	$CDCl_3$	2	(56)
CN	CO_2CH_3	H	$OCH_2CH(CH_3)_2$	25	$CDCl_3$	3	(75)
CN	CO_2CH_3	H	$C_6H_4OCH_3$(p)	25	CH_3CN	4	51
CO_2CH_3	CO_2CH_3	H	$C_6H_4OCH_3$(p)	70	None	5	30
CO_2CH_3	CO_2CH_3	H	SCH_3	25	None	6	47 (d)
CO_2CH_3	CO_2CH_3	H	$OCH_2CH(CH_3)_2$	25	$CDCl_3$	7	(70)
CN	CO_2CH_3	CN	C_6H_5	70	CH_3CN	8	(23)(e)
CN	CO_2CH_3	CN	$C_6H_4CH_3$(p)	70	CH_3CN	9	(40)
CN	CO_2CH_3	CN	$C_6H_4OCH_3$(p)	70	CH_3CN	10	(43)
CN	CO_2CH_3	CN	$OCH_2CH(CH_3)_3$	70	CH_3CN	11	34

[a] Styrenes and vinyl ethers, commercially available, were distilled before use. Tri- and tetra-substituted electron-poor olefins were synthesized according to published procedures.[4,8,11]

[b] Reactions were followed by NMR: reaction times varied from minutes to a few hours.

[c] Yields are for pure isolated products (pyrans 2-11 obtained as a mixture of stereoisomers) except those reported between brackets which have been calculated by NMR. Because of their thermal instability, elementary analysis were difficult to carry out for these adducts; however, correct analytical data have been obtained in several cases.

[d] Reassigned structure from reference 4.

[e] A 20% yield of copolymer[11] was isolated in this reaction.

Table II

Spectral Data of 6-Alkoxy-3,4-Dihydro-2H-Pyrans 1-11

Compound N°	Characteristic NMR data ($CDCl_3$, TMS)						I.R.
	Chemical Shift (δ)				Coupling Constant (Hz)		$\nu_{c=c}$ (cm^{-1})
	Y	R	H_1	H_2,H_3,Z	$^3J_{H_1,H_2}$	$^3J_{H_1,H_3}$	
1	1.6-2.5	3.3(O-CH_2) 1.6(CH) 0.95(CH_3)	5.2	1.6-2.5	3	3	1680
2	--	6.9-7.2	5.9	2-2.2	2	2	1640
3	3.8	3.3(OCH_2) 1.6(CH) 0.95(CH_3)	5.2	1.9-2.8	2	2	1640
4	4.4	6.8-7.5	5.1	2.08-2.4 3.8	4	8	1660
5	3.5	3.8(OCH_3) 6.8-7.4(ring)	5.2	2.2	4	10	1660
6	3.55	2.3	5.4	2.1	5	7	1670
7	3.62	3.3(OCH_2) 1.8(CH) 0.95(CH_3)	5.25	2.0-2.1	4	5	1670
8	3.8	7.45	5.4	2.2-2.7	2	7	1650
9	3.9	2.35(CH_3) 7.25-7.6(ring)	5.35	2.55-2.85	2	7	1640
10	3.9	3.85(OCH_3)	5.3	2.3-2.8	3	8	1650
11	3.9	3.5 (OCH_2) 1.8 (CH) 0.95 (CH_3)	5.5	2.3-2.6	2	5	1670

Acknowledgments

We thank the National Science Foundation, Grant DMR-78-09290, the U. S. Army Research Office, Grant DAAG-29-77-G0231, the Government of Iraq, and the Sonatrach Corp. of Algeria for support, and Dr. J. M. McIntyre of Tennessee Eastman Co. for a gift of methyl α-cyanoacrylate.

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(Received in USA 11 May 1981)