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CYCLOADDITION REACTIONS OF ARYLMETHYLENEMALONALDEHYDES: AN APPROACH TO 4-ARYL-3,4-DIHYDRO-2H-PYRAN-5-CARBOXALDEHYDES

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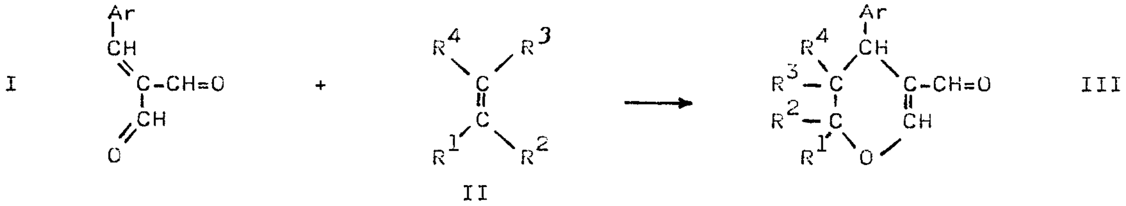
Abstract: The reaction of arylmethylenemalonaldehydes I with various types of olefins afforded a series of 4-aryl-3,4-dihydro-2H-pyran-5-carboxaldehydes III.

Exploring chemistry of arylmethylenemalonaldehydes I, readily accessible by the method recently developed in our Laboratory[1], we have ascertained a very pronounced reactivity of these compounds in cycloaddition reactions[2]. Playing here the role of a 4π- or 2π-component the dialdehydes I afford numerous new compounds, including hitherto undescribed structural types of heterocyclic and carbocyclic series.

As an example of synthetic potentialities of the studied additions we report in this paper the synthesis of a family of 4-aryl-3,4-dihydro-2H-pyran-5-carboxaldehydes III. Table 1 shows that the double bond character of the 2π-component used here (II) can vary from that of simple olefins to highly activated ketene acetals[4]. In most cases the reaction proceeds readily, simply by mixing both components in an inert solvent[5,6]. The reaction with olefins, requiring somewhat higher temperature, can be facilitated advantageously by acid catalysis[7]. Interestingly, the reaction of the dialdehyde I (Ar=p-ClC$_6$H$_4$) with cyclopentadiene afforded also the dihydropyran derivative IIId[9]. As far as the effect of substitution in dialdehydes I is concerned electronegative substituents enhance the reaction rate[10].



Scheme 1

The dihydropyran aldehydes III represent a new family of compounds, which are of a considerable preparative and theoretical interest. Full account of our work will be published in Collection of the Czechoslovak Chemical Communications.

Table 1 4-Aryl-3,4-dihydro-2H-pyran-5-carboxaldehydes III

III	R^1	R^2	R^3	R^4	Ar	Catalyst	Yield(%)	M.p. (B.p.)°C
a	Me	Me	H	H	4-Cl-Ph	ZnI_2	56.0	(140/0.2)
b	Ph	Ph	H	H	4-MeO-Ph	ZnI_2	67.5	121.5-124
c	Ph	Ph	H	H	2-thienyl	ZnI_2	50.0	165-166
d	H	$-CH=CH-CH_2-$		H	4-Cl-Ph	-	40.0^x	133-136
e	EtO	H	H	H	4-Cl-Ph	-	92.0^y	(135/0.2)
f	EtO	H	H	H	4-MeO-Ph	-	86.3^y	(130-135/0.2)
g	Mph^z	H	Me	Me	4-MeO-Ph	-	83.8^x	135-138
h	Mph^z	H	Me	Me	2-thienyl	-	49.0^x	139-141
i	MeO	MeO	H	H	4-MeO-Ph	-	91.6	(155-160/0.2)
j	MeS	MeS	H	H	2-thienyl	-	83.9	88.5-91

[x] One of possible isomers; [y] mixture of isomers; [z] morpholino.

REFERENCES AND NOTES

1. Z. Arnold, V. Král, D. Dvořák: Tetrahedron Lett. 23, 1725 (1982).
2. High reactivity in cycloadditions was recently found also by Polansky[3] with 2-benzylidene-1,3-indandione and some other 1,1-dicarbonyl ethylenes.
3. J. Bitter, J. Leitich, H. Partale, O.E. Polansky, W. Riemer, U. Ritter-Thomas, B. Schlamann, B. Stilkerieg: Chem. Ber. 113, 1020 (1980).
4. Other types of multiple bonds were also found to react. Thus addition of nitrosobenzene to dialdehydes I gives products presumably related in structure to aldehydes III. Further work on these lines is in progress.
5. We observed only slight solvent effect ($k_{CH_3CN}/k_{cyclohexane}$ equals approx. 3 for IIIe) in accord with the idea of an, in principle, concerted process.
6. As an example we mixed 2-thienylmethylenemalonaldehyde (0.166 g; 1 mmol) and $CH_2=C(SCH_3)_2$ (0.123 g; 1.025 mmol) in benzene (4 ml). After standing overnight the solvent was removed and the residue was treated with ether (0.5 ml) at 0°C. The separated product IIIj (0.24 g; 83.9%; m.p. 86-90.5°C) was crystallized from cyclohexane. M.p. 88.5-91°C. UV spectrum (EtOH), nm ($\varepsilon.10^{-3}$): λ_{max} 242 (19.6); sh 254 (18.5). ^{1}H-NMR spectrum 60 MHz ($CDCl_3$), δ: 9.3 (s, 1H, -CHO); 7.28 (d, ^4J = 2.5 Hz, 1H, -O-CH); 6.85-7.25 (m, 3H, thienyl); 4.10-4.67 (m, 1H, Ar-CH); 2.27-2.88 (m, 2H, $-CH_2-$); 2.22 (s, 3H, CH_3S-); 2.15 (s, 3H, CH_3S-). IR spectrum (CCl_4), cm^{-1} : 2727w, 2833w (C-H in CH=O); 1693s (C=O); 1631s (C=C); 2933w, 1435m, 1315w, 1021m, 963w (C-H in $S-CH_3$).
7. While acid catalysis is well documented in Diels-Alder reaction, in case of unsaturated carbonyl compounds it has not been unequivocally ascertained[8].
8. G. Desimoni, G. Tacconi: Chem. Rev. 75, 651 (1975).
9. By contrast, in the reaction of aldehydes I with butadiene or 2,3-dimethylbutadiene the role of the 4π-component is taken over by 1,3-dienes, the cyclic 1,1-dicarboxaldehydes being the main reaction products.
10. This dependence can be understood to reflect the acidity of dialdehydes I, looked upon as organic Lewis acids (see[1,3]).

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