MICHAEL REACTION OF METHYLENEMALONALDEHYDES: SYNTHETIC APPROACH TO 4*H*-PYRAN-5-CARBOXALDEHYDES AND 2-AMINO-4*H*-PYRAN-5-CARBOXALDEHYDES

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Base-catalyzed addition of β-dicarbonyl compounds to methylenemalonaldehydes led to tetracarbonyl compounds *II* which were dehydrated in an acid medium to 4*H*-pyran-5-carboxaldehydes *III*. In the addition of compounds containing a nitrile group, the primarily formed addition products were immediately cyclized to give directly 2-amino-4*H*-pyran-5-carboxaldehydes *V*.

Michael reaction still represents an important method of C—C bond formation[1-4]. Methylenemalonaldehydes *I* proved to be very reactive in many reactions with nucleophilic reagents[5,6] and are thus ideal compounds for this reaction type. The products – substituted malonaldehydes – are suitable starting compounds for synthesis of numerous heterocyclic derivatives.

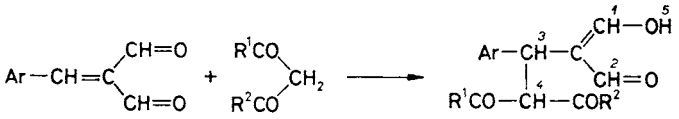
We studied Michael reaction of methylenemalonaldehydes using the following series of C-acids: β-dicarbonyl compounds such as diethyl malonate, ethyl acetoacetate, 2,4-pentanedione and 5,5-dimethyl-1,3-cyclohexanedione, cyano compounds such as malononitrile and methyl cyanoacetate, and nitromethane as the representative of nitro compounds.

The base-catalyzed reaction of arylmethylenemalonaldehydes with β-dicarbonyl compounds resulted in substituted malonaldehydes *II* (Scheme 1; Table I).

The rate of this reaction depends strongly on the solvent (Table II). In a solvent of low polarity such as benzene, the reaction leads to an equilibrium which can be proven by dissociation of the isolated product in the presence of a catalyst. Transition to more polar solvents shifts the equilibrium completely to the product side and increases the reaction rate. We ascribe this effect to an enhanced solvation of the product.

The effect of the catalyst was followed using the reaction of 3-thienylidenemalonaldehyde with 2,4-pentanedione in tert-butyl alcohol in the presence of 1 mole % of a catalyst (triethylamine, potassium tert-butoxide or potassium fluoride). Whereas

the activity of the former two catalysts is roughly the same, potassium fluoride is somewhat less effective (Table III). As found already earlier[7], reactions of this type can also be catalyzed with acetylacetonates of transition metals.

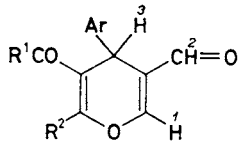


I *II*

a, Ar = 4-CH_3O—C_6H_4; $R^1 = R^2 = OC_2H_5$
b, Ar = 4-Cl—C_6H_4; $R^1 = CH_3$; $R^2 = OC_2H_5$
c, Ar = 4-CH_3O—C_6H_4; $R^1 = CH_3$; $R^2 = OC_2H_5$
d, Ar = 3-thienyl; $R^1 = CH_3$; $R^2 = OC_2H_5$
e, Ar = 4-Cl—C_6H_4; $R^1 = R^2 = CH_3$
f, Ar = 3-thienyl; $R^1 = R^2 = CH_3$

SCHEME 1

On the basis of these experiments we carried out the preparative reactions in tert-butyl alcohol with triethylamine as catalyst and obtained malonaldehydes *II* in 60–87% yields. In most cases the products were isolated in the crystalline state, except those derived from 5,5-dimethyl-1,3-cyclohexandione which were not characterized and directly converted into the corresponding pyran derivatives *III*.



III

a, Ar = 4-Cl—C_6H_4; $R^1 = R^2 = CH_3$
b, Ar = 4-CH_3O—C_6H_4; $R^1 = R^2 = CH_3$
c, Ar = 3-thienyl; $R^1 = R^2 = CH_3$
d, Ar = 4-Cl—C_6H_4; $R^1,R^2 = —CH_2—C(CH_3)_2—CH_2—$
e, Ar = 3-thienyl; $R^1,R^2 = —CH_2—C(CH_3)_2—CH_2—$
f, Ar = 4-Cl—C_6H_4; $R^1 = OC_2H_5$; $R^2 = CH_3$
g, Ar = 4-CH_3O—C_6H_4; $R^1 = OC_2H_5$; $R^2 = CH_3$
h, Ar = 3-thienyl; $R^1 = OC_2H_5$; $R^2 = CH_3$

TABLE I

Malonaldehydes *II*, pyrans *III*, and aminopyrans *V*

Compound	Yield, % (m.p., °C) (b.p., °C/Pa)	Formula (mol. wt.)[a]	Calculated/found			
			% C	% H	% N	% X
IIa	78·5 (126·5–127)	$C_{18}H_{22}O_7$ (350·4)	61·71 61·55	6·33 6·49	— —	— —
IIb	76·6 (127–132·5)	$C_{16}H_{17}ClO_5$ (324·8)	59·17 59·16	5·28 5·42	— —	10·92[b] 11·01[b]
IIc	66·9 (112·5–115)	$C_{17}H_{20}O_6$ (320·3)	63·64 63·90	6·29 6·40	— —	— —
IId	82·3 (125–130·5)	$C_{14}H_{16}O_5S$ (296·3)	56·74 57·16	5·44 5·65	— —	10·82[c] 10·71[c]
IIe	78·6 (129–135)	$C_{15}H_{15}ClO_4$ (294·7)	61·13 61·13	5·13 5·34	— —	12·03[b] 11·86[b]
IIf	87·1 (144–147)	$C_{13}H_{14}O_4S$ (266·3)	58·63 58·60	5·30 5·35	— —	12·04[c] 12·05[c]
IIIa	67·6[d] (150/0·25)	$C_{15}H_{13}ClO_3$ (276·7)	65·11 65·16	4·73 4·59	— —	12·81[b] 13·00[b]
IIIb	73·5[d] (95·5–97·5) (150/0·25)	$C_{16}H_{16}O_4$ (272·3)	70·58 70·93	5·92 5·64	— —	— —
IIIc	86[e,f] (68–72) (150/0·25)	$C_{13}H_{12}O_3S$ (248·3)	62·88 62·56	4·87 4·98	— —	12·91[c] 12·52[c]
IIId	66·5[d,g] (131·5–134)	$C_{18}H_{17}ClO_3$ (316·8)	68·25 67·96	5·41 5·54	— —	11·19[b] 11·30[b]
IIIe	71 (158–160·5)	$C_{16}H_{16}O_3S$ (288·4)	66·64 66·88	5·59 5·74	— —	11·11[c] 11·09[c]
IIIf	94·1[e,f] (150–155/0·25)	$C_{16}H_{15}ClO_4$ (306·8)	62·65 62·24	4·93 5·27	— —	11·56[b] 11·46[b]
IIIg	92·5 (92·5–95) (160/0·25)	$C_{17}H_{18}O_5$ (302·3)	67·54 67·67	6·00 6·28	— —	— —
IIIh	75[e] (54–55)	$C_{14}H_{14}O_4S$ (278·3)	60·42 60·37	5·07 4·87	— —	11·52[c] 11·06[c]
Va	42·7 (168–169)	$C_{13}H_9ClN_2O_2$ (260·7)	59·90 59·41	3·48 3·48	10·74 10·66	13·60[b] 13·77[b]
Vb	42·1 (180·5–186·5)	$C_{14}H_{12}N_2O_3$ (256·3)	65·62 65·55	4·72 4·77	10·93 10·95	— —

TABLE I
(*Continued*)

Compound	Yield, % (m.p., °C) (b.p., °C/Pa)	Formula (mol. wt.)[a]	Calculated/found			
			% C	% H	% N	% X
Vc	49·3 (177·5–180·5)	$C_{11}H_8N_2O_2S$ (232·3)	56·89 56·55	3·47 3·50	12·06 12·12	13·80[c] 13·71[c]
Vd	38·8 (185–188)	$C_{11}H_8Cl_2N_2O_2$ (271·1)	48·74 49·14	2·97 3·04	10·33 10·59	26·15[b] 25·98[b]
Ve	52·9 (138–140)	$C_{14}H_{12}ClNO_4$ (293·7)	57·25 57·02	4·12 4·07	4·77 4·54	12·07[b] 11·82[b]
Vf	60·3 (123–126)	$C_{12}H_{11}NO_4S$ (265·3)	54·33 54·31	4·18 4·17	5·28 5·17	12·08[c] 12·07[c]

[a] Confirmed by mass spectrometry; [b] % Cl; [c] % S; [d] without isolation of *II*; [e] from *II*; [f] after chromatography; [g] after crystallization from n-hexane–ethyl acetate.

Proton NMR spectra of the addition products, measured in hexadeuteriodimethyl sulfoxide (Table IV), are compatible with the structure *II*: they exhibit characteristic broad two-proton signal of the malonaldehyde system in the region of $\delta = 8{\cdot}19$ to 8·26 (H-1, H-2) and one-proton signals of the CH-groups at $\delta = 4{\cdot}50-5{\cdot}26$ (H-3) and $\delta = 4{\cdot}50-5{\cdot}18$ (H-4). The adduct from ethyl acetoacetate consisted of an about 1 : 1 mixture of two diastereoisomers. Spectra obtained in deuteriochloroform were much more complex and indicated the presence of several forms as a result

TABLE II
Effect of solvent on rate of reaction of 3-thienylidenemalonaldehyde with 2,4-pentanedione (catalyzed with 1 mole % of triethylamine)

Solvent	Conversion, %			
	5 min	15 min	30 min	60 min
Benzene	3	12	14	15
Dioxane	9	17	20	20
Acetonitrile	20	24	27	32
Dimethylformamide	35	46	55	65
Tert-butyl alcohol	52	70	82	93
Dimethyl sulfoxide	68	84	94	99

TABLE III

Effect of catalyst (1 mole %) on rate of reaction of 3-thienylidenemalonaldehyde with 2,4-pentanedione in tert-butyl alcohol

Catalyst	Conversion, %			
	5 min	15 min	30 min	60 min
KF	30	50	83	94
$(C_2H_5)_3N$	52	70	82	93
$(CH_3)_3COK$	48	70	83	93

TABLE IV

Proton NMR chemical shifts for compounds *IIa*—*IIf* in hexadeuteriodimethyl sulfoxide (at 200 MHz)

Substance	H-1	H-2	H-3	H-4	*J*(3, 4)
IIa[a]	8·19 bs	8·19 bs	4·70 d	4·50 d	12·4
IIb[b,c]	8·25 bs	8·25 bs	4·50 bs	4·88 bs	*d*
	8·25 bs	8·25 bs	4·57 d	4·99 d	12·3
IIc[b,e]	8·20 bs	8·20 bs	4·55 d	4·93 bd	12·3
	8·20 bs	8·20 bs	4·48 bs	4·83 bs	*d*
IId[b,f]	8·24 bs	8·24 bs	4·67 bd	4·82 bd	12·4
	8·24 bs	8·24 bs	4·70 bd	4·91 bd	12·4
IIe[g]	8·23 bs	8·23 bs	4·55 bs	5·26 bs	*d*
IIe[h,i]	8·26 bs	8·26 bs	4·52 d	5·25 bs	10·6
IIf[j]	8·23 bs	8·23 bs	4·72 bd	5·18 bs	12·0

[a] 7·29 bs, 4 H (arom.), 3·36 s (OCH_3), CH_2 — 3·90 q (3 × 7·0), 4·05 q (3 × 7·0), CH_3 — 0·93 t (2 × 7·0), 1·11 t (2 × 7·0); [b] mixture of diastereoisomers; [c] 7·28 m, 4 H (arom.), 7·78 m, 4 H (arom.), CH_2 — 3·92 q (3 × 7·1), CH_3 — 0·97 t (2 × 7·1), CH_3CO — 2·06 s, 6 H, CH_2 — 3·45 q (3 × 7·1), 4·05 q (3 × 7·1), CH_3 — 1·06 t (2 × 7·1), 1·12 t (2 × 7·1); [d] value not determined; [e] 6·78 m, 4 H, 7·21 m, 4 H (arom.), CH_3O — 3·70 s, 6 H, CH_2 — 3·90 q (3 × 7·0), 3·91 q (3 × 7·1), 4·05 q (3 × 7·0), 4·06 q (3 × 7·1), CH_3 — 0·98 t (2 × 7·0), 0·98 t (2 × 7·1), 1·14 t (2 × 7·0), 1·19 t (2 × 7·1), CH_3CO — 1·98 bs, 1·99 bs; [f] 6·95 bd (1·1, 4·9), 1 H, 6·97 dd (1·3, 4·9), 1 H, 7·13 bdd (1·1, 2·9), 1 H, 7·18 ddd (0·4, 1·3, 2·9), 1 H, 7·35 dd (2·9, 4·9), 1 H, 7·35 dd (2·9, 4·9), 1 H (2-thienyl), CH_2 — 3·95 q (3 × 7·1), CH_3 — 0·99 t (2 × 7·1), CH_3CO — 2·06 bs; CH_2 — 3·44 q (3 × 7·1), 4·04 q (3 × 7·1), CH_3 1·06 t (2 × 7·1), 1·11 t (2 × 7·1), CH_3CO — 2·06 bs; [g] 7·26 bs, 4 H (arom.), CH_3CO — 2·00 s, 6 H; [h] 7·27 bs, 4 H (arom.), CH_3CO — 2·00 s; [i] at 70°C; [j] 6·96 bd (1·0, 4·9), 7·16 dd (1·0, 2·9), 7·36 dd (2·9, 4·3) (2-thienyl), CH_3CO — 2·01 bs, 6 H.

of enolization and hydrogen bond formation. IR spectra of the adducts *II* are given in Table V.

Malonaldehydes *II* (except *IIa*) were easily dehydrated in an acidic medium to give pyrans *III*, similarly as described by Reichardt[8] for the adduct of sodium salt of malonaldehyde with phenylmethylenemalonaldehyde. This reaction represents

TABLE V

Infrared spectra of malonaldehydes *II* (Nujol, cm^{-1})

Compound	HO—CH=C(R¹)—CH=O				R¹CO	R²CO
	ν(O—H)	ν(C—H)	ν(C=C)	ν(C=O)	ν(C=O)	ν(C=O)
IIa	2 490 w, vbr	—	1 556 m, br 1 538 m, sh		1 556 m	
IIb	3 326 m	2 765 w	1 626 s	1 659 m	1 659 m	1 736 m
IIc	3 316 m	2 763 w	1 622 s	1 658 m	1 658 m	1 736 m
IId	3 315 s	2 761 w	1 617 s	1 658 s	1 658 s	1 734 s
IIe	3 248 s, vbr	—	1 617 s	1 657 s	1 708 m	
IIf	3 110 s, vbr	2 747 m	1 640 s, br	1 656 s, sh	1 729 s, 1 692 m	

TABLE VI

Proton NMR parameters of compounds *IIIa*—*IIIh* in deuteriochloroform (60 MHz)

Compound	H-1	H-2	H-3	arom.
IIIa[a]	7·17—7·30 m	9·31 s	4·89 s	7·17—7·30 m
IIIb[b]	7·19 s	9·32 s	4·68 s	6·67—7·30 m
IIIc[c]	7·18 s	9·37 s	4·89 s	6·88—7·30 m
IIId[d]	7·35 s	9·33 s	4·67 s	7·11—7·30 m
IIIe[e]	7·33 s	9·38 s	4·88 s	6·90—7·25 m
IIIf[f]	7·10—7·42 m	9·32 s	4·72 s	7·10—7·42 m
IIIg[g]	7·10—7·30 m	9·32 s	4·71 s	7·10—7·30 m
IIIh[h]	7·23 s	9·38 s	4·90 s	6·85—7·32 m

[a] CH_3CO — 2·35 s, CH_3 — 2·11 s; [b] OCH_3 — 3·73 s, CH_3CO — 2·34 s, CH_3 — 2·11 s; [c] CH_3CO — 2·37 s, CH_3 — 2·15 s; [d] CH_2 — 2·49 s, 2·20 s, CH_3 — 1·03 s, 1·10 s; [e] CH_2 — 2·48 s, 2·25 s, CH_3 — 1·03 s, 1·10 s; [f] OCH_2CH_3 — 4·02 q (3 × 7·5), 1·14 t (2 × 7·5), CH_3CO — 2·42 s; [g] OCH_3 — 3·42 s, OCH_2CH_3 — 4·03 q (3 × 7·5), 1·16 t (2 × 7·5); [h] OCH_2CH_3 — 4·10 q (3 × 7·5), 1·17 t (2 × 7·5).

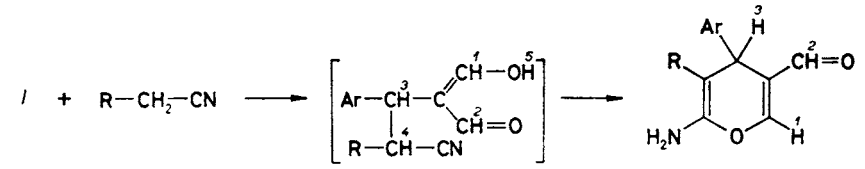
a novel synthetic approach to substituted 4*H*-pyran-5-carboxaldehydes which are obtained in 66–94% yields (Table I). The products *III* are oils, crystallizing only with difficulty. The only exception are compounds derived from 5,5-dimethyl-1,3-cyclohexanedione which crystallize very well. Their ^{1}H NMR and IR spectra are given in Tables VI and VII.

Whereas the reaction of arylmethylenemalonaldehydes with dicarbonyl compounds stopped at the stage of malonaldehydes *II*, we were not able to isolate analogous products in the reaction with cyano derivatives. During the reaction the primarily formed malonaldehydes *IV* cyclized to give aminopyrans *V*, isolated as the final products in 39–60% yields (Scheme 2; Table I). An analogous cyclization reaction has been observed already earlier[9–12].

Proton NMR spectra of aminopyrans *V*, taken in a mixture of hexadeuteriodimethyl sulfoxide and deuteriochloroform (Table VIII) show that of both tautomeric forms *V* and *VI* only the former is present. The spectra exhibit a sharp two-proton signal of the NH_2 group which disappears on addition of deuterium oxide. Its position is strongly solvent-dependent. In hexadeuteriodimethyl sulfoxide this signal

TABLE VII
Infrared spectra of compounds *IIIa*–*IIIh*

Compound	—CH=O		R^1CO—	ν(C=C)	$\delta_s(CH_3)$
	ν(C—H)	ν(C=O)	ν(C=O)		
IIIa	2 743 w 2 834 w	1 693 s	1 680 m, sh	1 665 m, sh 1 596 m	1 382 w
IIIb	2 745 w	1 693 s	1 680 m, sh	1 661 w, sh 1 588 m, sh	1 382 w
IIIc	2 741 w 2 833 w	1 692 s	1 680 s, sh	1 664 m, sh 1 594 m	1 383 w
IIId	2 737 w 2 830 w	1 687 s	1 678 s, sh	1 660 m, sh 1 618 m	1 368 m 1 393 w
IIIe	2 738 w 2 831 w	1 687 s	1 678 s, sh	1 660 m, sh 1 618 m	1 368 m 1 391 w
IIIf	2 741 w 2 834 w	1 687 m	1 711 m	1 634 w, sh 1 622 m	1 383 w
IIIg	2 741 w	1 688 s	1 710 s	1 633 m, sh 1 621 m	1 383 m
IIIh	2 740 w 2 831 w	1 684 s	1 709 s	1 633 m, sh 1 622 s	1 371 m 1 383 m



IV *V*

a, Ar = 4-Cl—C_6H_4; R = CN
b, Ar = 4-CH_3O—C_6H_4; R = CN
c, Ar = 3-thienyl; R = CN
d, Ar = Cl_2C=CH—CH=CH; R = CN
e, Ar = 4-Cl—C_6H_4; R = $COOCH_3$
f, Ar = 3-thienyl; R = $COOCH_3$

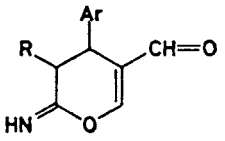
SCHEME 2

appears in the region of aromatic protons (δ = 7·00–7·50) whereas in deuteriochloroform it is shifted downfield (to $\delta \sim 6$) where there is no overlap with other signals. Because of solubility problems, we employed a mixture of both solvents. Chemical shifts of the pyran proton signals (H-1, H-3) in *V* correspond to those found for the pyrans *III*; the same was observed with the formyl proton signals. Also IR spectra confirm presence of the amino group (Table IX).

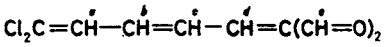
TABLE VIII
Proton NMR parameters of compounds *Va*–*Vf* (60 MHz)

Compound	H-1	H-2	H-3	arom.	NH_2
Va[a]	7·91 s	9·32 s	4·22 s	7·70–7·50 m	
Va[b]	7·17–7·57 m	9·33 s	4·37 s	7·17–7·57 m	6·08 bs
Vb[a,c]	7·85 s	9·33 s	4·15 s	6·72–7·28 m	
Vb[b,c]	7·35 s	9·35 s	4·32 s	6·73–7·33 m	6·10 bs
Vc[a]	7·83 s	9·37 s	4·33 s	6·82–7·57 m	
Vd[b,e]	7·78 s	9·44 s	3·86 dd	—	4·51 bs
Ve[d,f]	7·15–7·28 m	9·31 s	4·66 s	7·15–7·28 m	6·26 bs
Vf[d,g]	7·15 s	9·35 s	4·83 s	6·85–7·23 m	6·27 bs

[a] In hexadeuteriodimethyl sulfoxide; [b] in deuteriochloroform–hexadeuteriodimethyl sulfoxide; [c] OCH_3 — 3·72 s; [d] in deuteriochloroform; [e] measured at 200 MHz in deuteriochloroform–hexadeuteriobenzene (4 : 1); side chain protons: 6·71 dd (0·7, 10·3), 1 H, 6·25 ddd (0·9, 10·4, 15·0), 1 H, 5·83 ddd (0·7, 7·6, 15·0), 1 H; [f] OCH_3 — 3·56 s; [g] OCH_3 — 3·62 s.



VI

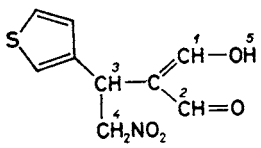


VII

The intermediate *IV* can be detected *e.g.* by thin-layer chromatography, however, attempted isolation by crystallization or chromatography resulted in cyclization. The intermediate *IV* is stabilized in a strongly polar medium such as hexadeuteriodimethyl sulfoxide in which its cyclization is very slow. We utilized this behaviour for ^{1}H NMR characterization of the primary addition product from malononitrile and 3-thienylidenemalonaldehyde. The spectrum exhibited a two-proton signal of formyl protons at $\delta = 8{\cdot}52$ (H-1, H-2), one-proton signals of the CH-groups at $\delta = 4{\cdot}57$ (H-3) and $\delta = 5{\cdot}77$ (H-4) with coupling constant $J(3, 4) = 12$ Hz and confirmed thus unequivocally the structure *IV*.

In the reaction of polyenylidenemalonaldehyde *VII* two types of products can be expected: products of 1,4- and 1,6-addition (1,8-addition is not probable because of the presence of two bulky chlorine atoms). It is known[13] that both addition types are possible, the 1,6-addition being preferred in the cited case[13]. For this reason, we followed the reaction of this dialdehyde with malononitrile in a mixture of hexadeuteriodimethyl sulfoxide and hexadeuteriobenzene by ^{1}H NMR spectroscopy (hexadeuteriobenzene was added to separate the olefinic proton signals). Signals of the starting compounds slowly disappeared and the NMR spectrum detected formation of only one product, 1,4-adduct, which was very slowly converted into the aminopyran *Vd*.

Similarly to β-dicarbonyl compounds, also nitromethane reacts with arylmethylenemalonaldehydes in tert-butyl alcohol in the presence of triethylamine as catalyst. Thus, 3-thienylmethylenemalonaldehyde afforded the substituted malonaldehyde *VIII* in 60% yield.



VIII

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried over phosphorus pentoxide at 25°C and 25 Pa for 24 h. Infrared spectra were recorded on a Zeiss UR-20

spectrometer, ^{1}H NMR spectra were measured on Tesla BS 467 (60 MHz), Tesla BS 497 (100 MHz) and Varian XL-200 (200 MHz) instruments. Ultraviolet spectra were obtained with a Specord UV VIS spectrometer, mass spectra with an AEI MS-902 instrument. High-performance liquid chromatography (HPLC) was carried out on a Pye Unicam instrument (PU 4 003 pump, PU 4 025 detector), detection at 254 nm, column 100 × 4·6 mm packed with LiChrosorb Si 100 (10 μm), mobile phase hexane–ethyl acetate 7 : 3.

TABLE IX

Infrared spectra of compounds *Va*–*Vf* in chloroform (cm^{-1})

Compound	—CH=O		ν(C=C)	ν(NH_2)	Others
	ν(C—H)	ν(C=O)			
Va	2 745 w 2 840 w	1 682 s 1 695 m, sh	1 634 m	3 506 w 3 406 m	2 202 m[a]
Vb	2 741 w	1 682 m 1 693 w, sh	1 632 w	3 503 w 3 403 w δ(*cis*): 1 660 m, sh	2 204 w[a]
Vc	2 744 w	1 681 m 1 695 w, sh	1 645 m 1 600 m	3 408 m 3 332 m 3 298 m, sh 3 251 m 3 213 m 3 185 m δ(*cis*): 1 665 s	2 207 w, sh[a] 2 193 m[a]
Vd	2 760 vw 2 855 w	1 673 m	1 633 m 1 598 w 1 588 w, sh	3 328 m, sh 3 252 w 3 210 w	2 202 w[a] 2 185 vw, sh[a] 981[b]
Ve	2 743 w 2 840 w	1 695 s 1 680 s	1 617 w	3 489 m 3 333 w δ(*cis*): 1 662 w, sh	1 713 w, sh[c]
Vf	2 740 w 2 833 w	1 694 s 1 680 s, sh	1 617 m	3 489 m 3 332 w, br δ(*cis*): 1 662 w, sh	1 714 m, sh[c]

[a] ν(C—N); [b] ν(C—H) in $Cl_2C{=}CH{-}CH{=}CH{-}$; [c] ν(C=O) in CO_2CH_3.

Compounds *II*

Triethylamine (several drops) was added to a solution of the arylmethylenemalonaldehyde (2 mmol) and the β-dicarbonyl compound (2·2 mmol) in tert-butyl alcohol (4 ml) and the mixture was set aside at room temperature until the starting dialdehyde disappeared (several hours). The reaction was monitored by TLC or by disappearance of the yellow colour of the starting dialdehyde. In the reaction with diethyl malonate the mixture was heated to 80°C for 5 h. The solvent was evaporated *in vacuo*, the residue codistilled with benzene and crystallized from ethyl acetate–n-hexane. The product of reaction with diethyl malonate was isolated by chromatography on silica gel (light petroleum–ethyl acetate 1 : 1) and then crystallized. The yields, melting points, elemental analyses and spectral data are given in Tables I, IV and V.

Pyrans *III*

A) A mixture of the malonaldehyde *II* (2 mmol), *p*-toluenesulfonic acid (30 mg), and benzene (4 ml) was refluxed for 1 h. Most of the benzene was distilled off, another portion of benzene (4 ml) was added and the procedure was repeated. The residue was diluted with dichloromethane, filtered through a small amount of silica gel, the solvent was evaporated and the product distilled or crystallized. For yields and physical and spectral properties of the products see Tables I, VI, and VII.

B) After reaction of the arylmethylenemalonaldehyde with the β-dicarbonyl compound (see preparation of *II*) the mixture was evaporated and twice codistilled with benzene. Further procedure was the same as described under *A*).

Kinetic Measurements

To a solution of 3-thienylidenemalonaldehyde (83 mg; 0·5 mmol) and 4-nitrotoluene (internal standard, about 8 mg) in the given solvent (2 ml) was added 2,5-pentanedione (1 ml of 1 mol l^{-1} solution) in the same solvent. After determination (HPLC) of the dialdehyde : standard ratio, a solution of the catalyst in the same solvent (1 ml, concentration $5 . 10^{-3}$ mol l^{-1}) was added and the decrease in the dialdehyde concentration was followed by HPLC.

2-Aminopyrans *V*

The arylmethylenemalonaldehyde (2 mmol) was dissolved in tert-butyl alcohol (4 ml). Malononitrile or methyl cyanoacetate (2·2 mmol) was added, followed by a trace of triethylamine. After standing overnight, the solvent was evaporated, the residue twice codistilled with benzene, dissolved in dichloromethane and filtered through silica gel. The solvent was evaporated and the residue crystallized from ethyl acetate–hexane. The yields, physical properties and analytical and spectral data are given in Tables I, VIII, and IX.

Identification of Primary Reaction Product with Malononitrile

4-Chlorophenylmethylenemalonaldehyde (20 mg; 0·10 mmol) and malononitrile (7 mg; 0·11 mmol) were dissolved in hexadeuteriodimethyl sulfoxide (0·3 ml). After standing for 10 min, ^{1}H NMR spectrum corresponded to structure *IVa*: 8·52 s, 2 H (H-1, H-2); 7·35—7·50 m, 4 H (arom.); 5·77 d, 1 H (H-4, $J(3, 4) = 12$); 4·57 d, 1 H (H-3, $J(3, 4) = 12$).

Reaction of *VII* with Malononitrile

Compound *VII* (20·5 mg; 0·1 mmol) and malononitrile (7 mg; 0·108 mmol) in an NMR tube

were dissolved in a mixture of hexadeuteriodimethyl sulfoxide and hexadeuteriobenzene (4 : 1). ^{1}H NMR spectrum showed a slow disappearance of the starting compounds and formation of a single product: 6·75 d, 1 H (H_a, $J(H_a, H_b)$ = 10·0); 6·42 ddd, 1 H (H_b, $J(H_a, H_b)$ = 10·0; $J(H_b, H_c)$ = 15·1; $J(H_b, H_d)$ = 0·7); 6·18 dd, 1 H (H_c, $J(H_c, H_d)$ = 8·8; $J(H_b, H_c)$ = 15·1); 5·32 d, 1 H ($CH(CN)_2$, $J(CH(CN)_2, H_d)$ = 10·8); 4·18 dd, 1 H (H_d, $J(H_c, H_d)$ = 8·8; $J(CH(CN)_2, H_d)$ = 10·8); 8·59 bs, 2 H (H_e). On standing (2 days), this product was converted into the 2-aminopyran *Vd*.

Addition of Nitromethane

A mixture of 3-thienylidenemalonaldehyde (1·0 g; 6·02 mmol), nitromethane (3 ml; 18·5 mmol), tert-butyl alcohol (9 ml), and triethylamine (1 drop) was set aside at room temperature for 2 days. The solvents were evaporated *in vacuo* and the residue was chromatographed on silica gel in light petroleum–ethyl acetate (1 : 2), affording 0·812 g (60%) of *VIII*. ^{1}H NMR spectrum (in hexadeuteriodimethyl sulfoxide): 8·40 bs, 2 H (H-1); 4·77 t, 1 H (H-2, J(H-2, H-3) = 8·1); 5·11 d, 2 H (H-3, J(H-2, H-3) = 8·1); 7·40 m, 1 H, 7·24 m, 1 H and 7·00 m, 1 H (thiophene). IR spectrum (KBr), cm^{-1}: 2 550 m, vv, br (O—H); 1 629 s (C=O); 1 570 s, br, 1 381 s (NO_2). For $C_9H_9NO_4S$ (227·2) calculated: 47·57% C, 5·30% H, 6·16% N. 14·11% S; found: 47·32% C, 5·35% H, 6·05% N, 14·17% S.

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