

REACTION OF ARYLMETHYLENEMALONALDEHYDES WITH SOME NUCLEOPHILES

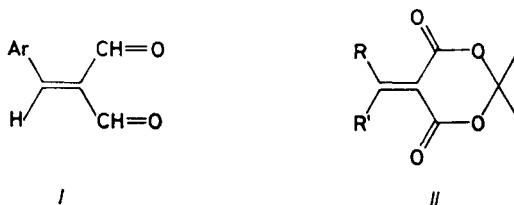
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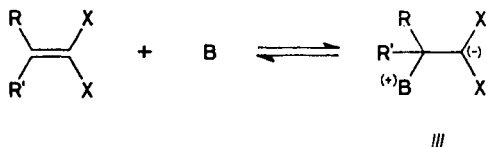
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Reaction of arylmethylenemalonaldehydes with tributylphosphine and tertiary amines affords compounds of dipolar structure whereas reaction with primary and secondary amines leads to 1,4-addition products. Salts of nucleophilic inorganic anions add to arylmethylenemalonaldehydes under formation of salts of substituted malonaldehydes.

Arylmethylenemalonaldehydes¹⁻³ *I* can be regarded as the so-called organic Lewis acids⁴ characterized by the presence of a C=C double bond, activated in the position 1 by two geminal strongly electron-accepting groups capable of electron delocalization. Compounds of this type, mainly derivatives of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum acids) *II*, have been studied in detail by Polanski and his co-workers⁴.



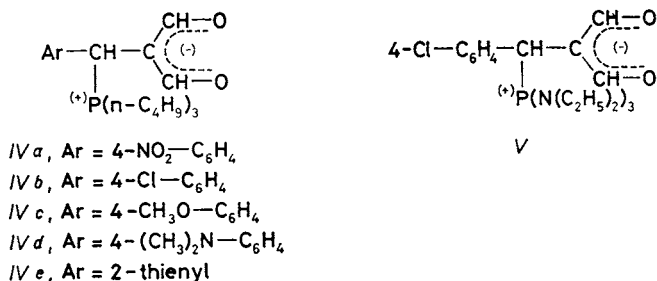
The electron-acceptor character of organic Lewis acids manifests itself particularly in their reaction with nucleophiles. One of the characteristic transformations of these compounds is the formation of dipolar structures on addition of tertiary bases⁵ (Scheme 1).



SCHEME 1

A similar reactivity could also be assumed in the case of arylmethylenemalon-aldehydes. Some reactions typical for organic Lewis acids, *e.g.* their reaction with water and alcohols, have been observed with arylmethylenemalon-aldehydes already earlier^{2,6}. In this communication we describe reactions of arylmethylenemalon-aldehydes with phosphines, primary, secondary and tertiary amines, and potassium salts of nucleophilic inorganic anions. The substituents on the benzene nucleus were chosen so as to represent both electron acceptors (Ar = 4-NO₂-phenyl, 4-Cl-phenyl) and electron donors (Ar = 4-CH₃O-phenyl, 4-(CH₃)₂N-phenyl). Thienylidene derivatives were also included as representatives of heteroaromatic methylenemalon-aldehydes.

As expected, arylmethylenemalon-aldehydes reacted with tributylphosphine to give dipolar products *IV*. The structure of these compounds follows unequivocally from



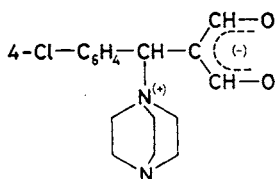
the spectral parameters. Their ¹H NMR spectra exhibit one signal for both formyl protons (δ = 8.63–8.92) and a doublet due to the Ar-CH-P⁺ proton at δ = 4.62–5.02 (²J(¹H, ³¹P) = 15.5–17.0) depending on the substituent on the aromatic nucleus. Ultraviolet spectra display an absorption band at λ = 270 nm, characteristic of a malonaldehyde anion. Similarly to tributylphosphine, tris(diethylamino)-phosphine reacted smoothly with 4-chlorophenylmethylenemalon-aldehyde to give the dipolar adduct *V*. No reaction of arylmethylenemalon-aldehydes with triphenyl-phosphine was observed.

According to the literature data^{7,8}, the reaction of organic Lewis acids with tertiary phosphines is to a considerable extent reverse. Thus, *e.g.* in dilute solutions, adducts of substituted phenylmethylenemalononitriles with tributylphosphine are almost completely dissociated into their components even in the presence of strongly activating substituents such as nitro group in position 4 of the benzene nucleus⁷. With our compounds, we observed partial dissociation only in the case of 4-di-methylamino group. This fact shows unequivocally that arylmethylenemalon-aldehydes belong to strong organic Lewis acids such as 5-arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-diones which do not undergo any reverse dissociation. This conclusion agrees with the results of pK_a measurements. The pK_a values⁹ for 4-chloro-

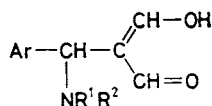
phenylmethylene- and 4-methoxyphenylmethylenemalonaldehyde in water are 4.59 and 4.91, respectively; the values are comparable with those for 5-arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-diones². (According to a recent study, using the stopped-flow method, phenylmethylenemalonaldehyde is even somewhat stronger organic Lewis acid than the corresponding derivative of 2,2-dimethyl-1,3-dioxane-4,6-dione⁶.)

The reaction of 4-chlorophenylmethylenemalonaldehyde with tertiary amines was studied using 1,4-diazabicyclo[2,2,2]octane which had been suitable also with substituted 5-methylene-2,2-dimethyl-1,3-dioxane-4,6-diones⁵. As expected, also in this case the reaction afforded the dipolar adduct VI. However, the adduct was unstable, hygroscopic and retained nonstoichiometric amount of solvent that could not be removed even by prolonged drying *in vacuo*. Similarly to the parent aldehyde, the adduct forms yellow solutions indicating a great extent of dissociation to the starting components.

The position of the equilibrium depends considerably on solvent polarity and can be followed by NMR spectroscopy. Proton NMR spectrum of the adduct VI in C^2HCl_3 exhibits one signal of both protons at $\delta = 9.88$; this value is not too different from those of formyl proton signals for the starting 4-chlorophenylmethylenemalonaldehyde ($\delta = 10.18$ d, 1 H ($J = 0.5$); 10.02 s, 1 H). Also the Ar—CH proton signal is shifted only slightly (from $\delta 8.03$ to 7.60). This evidence indicates an almost complete dissociation of the adduct VI. On the other hand, the spectrum measured in $(C^2H_3)_2$.SO shows that in this strongly polar medium the adduct predominates. The formyl protons appear as a singlet at $\delta = 8.92$, the CH protons as a singlet at $\delta = 5.75$, the values being similar to those for the adduct of 4-chlorophenylmethylenemalonaldehyde with tributylphosphine ($\delta = 8.90$ and 4.89). An attempted preparation of analogous adduct with triethylamine was unsuccessful.



VI

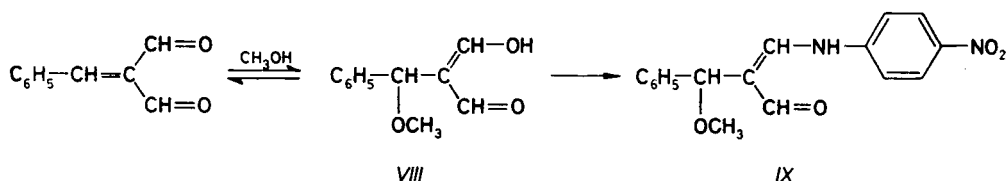


- VII a, Ar = 4-Cl-C₆H₄; R¹, R² = (CH₂)₂O(CH₂)₂
 VII b, Ar = 4-CH₃O-C₆H₄; R¹, R² = (CH₂)₂O(CH₂)₂
 VII c, Ar = 2-thienyl; R¹, R² = (CH₂)₂O(CH₂)₂
 VII d, Ar = 4-Cl-C₆H₄; R¹, R² = CH₃
 VII e, Ar = 4-CH₃O-C₆H₄; R¹, R² = CH₃
 VII f, Ar = 3-thienyl; R¹ = (CH₃)₃C; R² = H
 VII g, Ar = 3-thienyl; R¹ = 4-NO₂ C₆H₄; R² = H

Primary and secondary amines react easily with arylmethylenemalonaldehydes to give substituted malonaldehydes VII as 1,4-addition products. This reaction is reverse and in dilute solutions the adducts are significantly dissociated into the

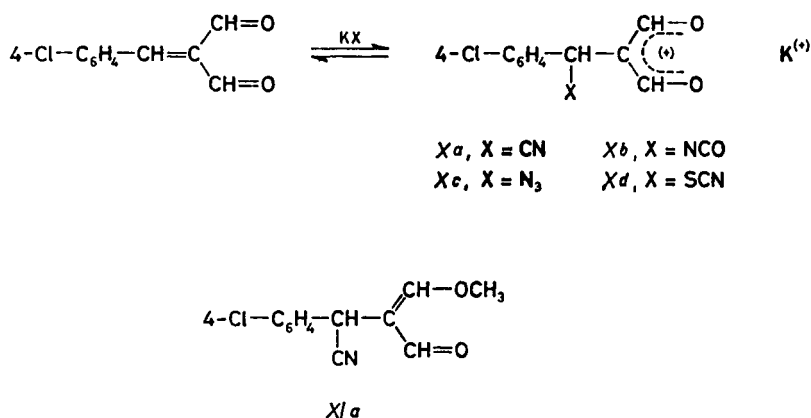
starting components. Thus, *e.g.* UV spectrum of the adduct *VIIa* in cyclohexane ($c = 5 \cdot 10^{-5} \text{ mol l}^{-1}$) shows an about 32% dissociation. On acidification, the adduct *VII* liberated the starting dialdehyde in almost quantitative yield.

Reichardt¹⁰ described formation of aminoacrolein *IX* by reaction of phenylmethylenealdehyde with 4-nitroaniline in methanol. In this case methanol was added primarily and the formed adduct *VIII* reacted with 4-nitroaniline under formation of the final product *IX* (Scheme 2). However, reaction of 3-thienylmethylenealdehyde with 4-nitroaniline in tert-butyl alcohol, which does not react with methylenemalonaldehydes, led to the product *VIIg*.



SCHEME 2

On treatment with inorganic salts of some nucleophilic anions (CN^- , NCO^- , N_3^-), solutions of 4-chlorophenylmethylenealdehyde in *N,N*-dimethylformamide lose their original characteristic yellow colour, indicating addition of the anion to the double bond in the starting dialdehyde (Scheme 3). Actually, this type of addition was confirmed by isolation of the methoxyacrolein derivative *XIa* from the reaction with KCN followed by alkylation.



SCHEME 3

When the reaction with potassium salts of the mentioned anions was carried out in tert-butyl alcohol, the salts *X* precipitated as white solids, strongly contaminated with the starting inorganic salt and the solvent. Since attempts to purify the salts *A* by crystallization or reprecipitation were unsuccessful, they could not be characterized by elemental analysis. However, ^1H NMR spectra of these compounds in $(\text{C}^2\text{H}_3)_2\text{SO}$ confirmed unequivocally the structure *X*. They exhibit a characteristic two-proton signal of malonaldehyde anion in the region $\delta = 8.25-8.33$ and a one-proton signal of the $\text{CH}-\text{X}$ group at $\delta = 6.41$ (*Xa*), 5.49 (*Xb*), 5.47 (*Xc*) or 5.47 (*Xd*). Whereas 4-chlorophenylmethylenemalonalddehyde did not react with KSCN in *N,N*-dimethylformamide, the reaction mixture in tert-butyl alcohol gradually deposited the salt *Xd*, the reaction equilibrium being favourably influenced by its insolubility.

The equilibrium character of the reaction of arylmethylenemalonalddehydes with inorganic salts can be demonstrated by reaction of 4-methoxyphenylmethylenemalonalddehyde with excess of potassium azide in an aqueous solution. The dialdehyde dissolved easily to form a yellow solution, although in pure water it was practically insoluble. Extraction of this solution with benzene afforded almost quantitatively the free dialdehyde.

Quite recently, a similar addition of KCN to 2-arylidene-1,3-diketones has been described and utilized in the synthesis of heterocyclic compounds¹¹.

Our findings confirm the expected high reactivity of the $\text{C}=\text{C}$ double bond in methylenemalonalddehydes towards nucleophilic reagents, comparable with other organic Lewis acids, e.g. 2,2-dimethyl-1,3-dioxane-4,6-dione. However, if the nucleophilic species contains a mobile hydrogen atom (primary and secondary amines), this atom is transferred during the reaction to the oxygen atom of the malonaldehyde grouping to form a malonaldehyde derivative. Also addition reactions of arylmethylenemalonalddehydes with inorganic salts, leading to salts of substituted malonaldehydes *X*, reflect high activation of the $\text{C}=\text{C}$ double bond.

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried over phosphorus pentoxide at $25^\circ\text{C}/25\text{ Pa}$ for 24 h. Infrared spectra were recorded on a Zeiss UR 20 spectrometer, ^1H NMR spectra on Tesla B 467 (60 MHz) and Varian XL 200 (200 MHz) instruments. UV spectra were obtained with a Specord UV VIS spectrometer, mass spectra with an AEI MS-902 instrument.

Adducts with Tributylphosphine *IV*

Tributylphosphine (0.3 ml) was added to the arylmethylenemalonalddehyde (1 mmol) in benzene (2 ml) or dichloromethane (used for *IVa* and *IVd*, sparingly soluble in benzene). The solution warmed spontaneously and its yellow colour rapidly disappeared. After standing for several minutes, light petroleum was added until the turbidity persisted. The mixture was warmed to get

a clear solution and allowed to crystallize at room temperature. The separated product was collected on filter, washed with light petroleum and crystallized from benzene–light petroleum. Yields, melting points, analytical and spectral data are given in Tables I–IV. Mass spectra of these compounds exhibited no molecular ions but only ions corresponding to tributylphosphine and the dialdehydes.

Adduct V

Tris(diethylamino)phosphine (0.258 g; 1.04 mmol) was added to a solution of 4-chlorophenylmethylenemalonaldehyde (0.195 g; 1 mmol) in toluene (2 ml). The mixture warmed spontaneously and the yellow colour rapidly disappeared. After cooling with ice, the crystallized product was collected and washed with cold toluene; yield 0.367 g (83%), m.p. 98–103°C. An analytical sample was obtained by crystallization from toluene. For $C_{22}H_{37}ClN_3O_2P$ (442.0) calculated: 8.02% Cl, 9.51% N, 7.01% P; found: 8.17% Cl, 9.58% N, 7.50% P. 1H NMR (C^2HCl_3): 8.85 s, 2 H (–CHO); 7.05–7.57 m, 4 H (aromatic H); 5.53 d, 1 H (CH–P, $^2J(PH) = 22$); 2.82 to 3.48 m, 12 H (N–CH₂CH₃); 1.12 t, 18 H (N–CH₂CH₃, $^3J(CH_2, CH_3) = 7$). IR spectrum (KBr), cm^{-1} : 2 718 (C–H in CH=O); 1 632 m, 1 565 s, br (C=C and C=O); 1 493 m, 1 590 m, sh (C–C arom.).

Adduct of 4-Chlorophenylmethylenemalonaldehyde with 1,4-Bicyclo[2,2,2]octane VI

A solution of 1,4-diazabicyclo[2,2,2]octane (0.112 g) in ether (2 ml) was added to a solution of 4-chlorophenylmethylenemalonaldehyde (0.195 g; 1 mmol) in ether (5 ml). The precipitate was filtered and washed with ether under exclusion of moisture to give 0.212 g (69%) of white product,

TABLE I
Adducts IV

Compound	Yield, % (m.p., °C)	Formula (mol. wt.)	Calculated/found	
			% P	% X
IVa	92 (152–154)	$C_{22}H_{34}NO_4P$ (407.5)	7.62	3.44 ^a
			7.92	3.52
IVb	98 (153–154.5)	$C_{22}H_{34}ClO_2P$ (396.9)	7.82	8.95 ^b
			7.46	8.87
IVc	91.6 (136–137)	$C_{23}H_{37}O_3P$ (392.5)	7.92	—
			7.75	—
IVd	93.2 (124–126)	$C_{24}H_{40}NO_2P$ (405.6)	7.65	3.46 ^a
			7.60	3.44
IVe	97.8 (85–87)	$C_{20}H_{33}O_2PS$ (368.5)	8.42	8.70 ^c
			8.29	9.23

^a X = N; ^b X = Cl; ^c X = S.

TABLE II
Proton NMR spectra of adducts *IV* (60 MHz, C²HCl₃)

Compound	CH—O	P ⁽⁺⁾ —CH	H-arom.	(n-C ₄ H ₉) ₃
<i>IVa</i>	8.92 s, 2 H	5.02 d, 1 H ² J(PH) = 17	7.55—7.85 m, 2 H 8.00—8.30 m, 2 H	0.58—2.62 m, 27 H
<i>IVb</i>	8.90 s, 2 H	4.89 d, 1 H ² J(PH) = 16.3	7.27—7.52 m, 4 H	0.68—2.67 m, 27 H
<i>IVc</i>	8.90 s, 2 H	4.85 d, 1 H ² J(PH) = 16	6.67—6.98 m, 2 H 7.28—7.57 m, 2 H	0.63—2.57 m, 27 H
<i>IVd</i> ^a	8.63 s, 2 H	4.62 d, 1 H ² J(PH) = 16.5	6.42—6.73 m, 2 H 7.05—7.35 m, 2 H	0.50—2.50 m, 27 H
<i>IVe</i>	8.90 s, 1 H	5.31 d, 1 H ² J(PH) = 15.5	6.82—7.45 m, 3 H	0.57—2.57 m, 27 H

^a (C²H₃)₂SO.

TABLE III
Infrared spectra of adducts *IV* (KBr, cm⁻¹)

Compound	vC—H) in CH—O	v(O=CH=C=CH=O)
<i>IVa</i>	2 732 w, 2 802 w	1 629 w, br, 1 565 s, 1 558 s, sh
<i>IVb</i>	2 743 m, 2 780 w, 2 813 w	1 622 m, 1 575 vs, sh, 1 565 vs, 1 558 vs, sh
<i>IVc</i>	2 747 m, br, 2 780 vw, 2 815 vw	1 611 m, 1 566 vs, 1 557 s, sh
<i>IVd</i>	2 730 w, br	1 612 m, 1 567 s, 1 557 s, sh
<i>IVe</i>	2 726 w, 2 789 w	1 628 w, 1 565 s, 1 557 s, sh

TABLE IV
Ultraviolet spectra of adducts *IV* in cyclohexane

Compound	λ _{max} , nm	ε	Reverse dissociation, %
<i>IVa</i>	270	19 500	0
<i>IVc</i>	273	22 070	0
<i>IVd</i>	269	36 360	27.6

(c = 5 · 10⁻⁵ mol l⁻¹)

m.p. 39–43°C, which liquefied rapidly on exposure to air. Its ^1H NMR spectrum contained strong signals of ether which could not be removed even on prolonged drying *in vacuo* (oil pump). Similarly, the reaction in benzene afforded a product, containing benzene. ^1H NMR spectrum (C^2HCl_3): 9.88 s, 2 H ($-\text{CHO}$); 7.60 s, 1 H (CH); 7.34–7.80 m, 4 H (aromatic H); 2.85 s, 12 H (1,4-diazabicyclooctane); ^1H NMR spectrum ($\text{C}^2\text{H}_3)_2\text{SO}$: 8.92 s, 2 H (CHO); 5.75 s, 1 H (CH); 7.83–8.13 m, 2 H (aromatic H); 7.30–7.58 m, 2 H (aromatic H); 3.00 s, 12 H (1,4-diazabicyclooctane).

Adducts of Arylmethylenemalondehydes with Amines VIIa–f

The arylmethylenemalondehyde (1 mmol) was dissolved in dry ether (10 ml; solubility of the 2-thienyl derivative was increased by adding 2 ml of dichloromethane) and the amine (1 mmol; dimethylamine as a 3.3 mol l^{-1} solution in ether) was added. The precipitated product was washed with ether and dried. Yields, melting points, analytical and spectral data are given in Tables V–VII. UV spectrum of VIIa (cyclohexane): $\lambda_{\text{max}} = 230 \text{ nm}$; 245 nm, sh. From the absorption ($D = 0.28$) at λ_{max} of 4-chlorophenylmethylenemalondehyde (308 nm, $\epsilon = 18\,300$), 32.6% dissociation was calculated at concentration $4.7 \cdot 10^{-5} \text{ mol l}^{-1}$.

Recovery of 4-chlorophenylmethylenemalondehyde: The adduct VIIa (0.430 g; 1.53 mmol) was stirred with dilute (1:5) hydrochloric acid (25 ml) and dichloromethane (15 ml). After 20 min the organic layer was separated and the aqueous one extracted twice with dichloromethane

TABLE V
Adducts VII

Compound	Yield, % (m.p., °C)	Formula (mol. wt.)	Calculated/found			
			% C	% H	U N	% X
VIIa	86.9 (96–100)	$\text{C}_{14}\text{H}_{16}\text{ClNO}_3$ (281.7)	59.78	5.69	4.98	12.61 ^a
			60.14	5.80	4.94	12.39
VIIb	89.2 (76–79)	$\text{C}_{15}\text{H}_{19}\text{NO}_4$ (277.3)	64.97	6.91	5.05	—
			64.51	6.88	4.87	—
VIIc	84.2 (82–87)	$\text{C}_{12}\text{H}_{15}\text{NO}_3\text{S}$ (253.3)	56.99	5.94	5.54	12.63 ^b
			56.98	6.01	5.30	12.47
VIId	93.6 (114–117.5)	$\text{C}_{12}\text{H}_{14}\text{ClNO}_2$ (239.7)	60.20	5.84	5.84	14.82 ^a
			60.30	5.85	5.59	15.03
VIIe	85.2 (105–108.5)	$\text{C}_{13}\text{H}_{17}\text{NO}_3$ (235.3)	66.36	7.28	5.95	—
			66.09	7.24	5.78	—
VIIf	92.0 (83–84.5)	$\text{C}_{12}\text{H}_{17}\text{NO}_2\text{S}$ (239.4)	60.21	7.16	5.85	13.39 ^b
			60.45	7.15	5.71	12.93
VIIg	35.0 (150.5–155)	$\text{C}_{14}\text{H}_{12}\text{NO}_4\text{S}$ (304.4)	57.25	3.97	9.20	10.53 ^b
			57.30	4.09	9.32	9.83

^a X = Cl; ^b X = S.

TABLE VI
 ^1H NMR spectra of adducts VII (60 MHz, C^2HCl_3)

Compound	OH	CH=O	Ar	N-CH	NR_1R_2
VIIa	11.78 bs, 1 H	8.45 s, 2 H	7.25–7.45 m, 4 H	4.60 s, 1 H	3.90 t (5.0), 4 H; 2.61 bs, 4 H
VIIb	10.95 bs, 1 H	8.55 s, 2 H	6.73–6.97 m, 2 H, 7.23–7.47 m, 2 H OCH ₃ : 3.74 s, 3 H	4.65 s, 1 H	3.58–3.92 m, 4 H; 2.63 bs, 4 H
VIIc	8.55 bs, 1 H	8.35 s, 2 H	6.89–7.55 m, 3 H	5.10 bs, 1 H	3.76 t (5.0), 4 H; 2.65 bs, 4 H
VIIId	6.92 bs, 1 H	8.74 s, 2 H	7.16–7.45 m, 4 H	4.88 s, 1 H	2.67 bs, 6 H
VIIe	8.37 bs, 1 H	8.79 s, 2 H	6.73–6.96 m, 2 H, 7.3g–7.63 m, 2 H OCH ₃ : 3.75 s, 3 H	4.90 s, 1 H	2.65 bs, 6 H
VIIIf ^a	9.24 vbrs, 1 H	8.54 s, 2 H	7.13–7.25 m, 1 H, 7.53–7.64 m, 2 H	5.20 s, 1 H	1.25 s, 9 H
VIIIg ^b	—	9.33 bs, 2 H	7.15 dd (1, 4; 4.9), 1 H 7.42 dd (1.2; 1.2; 2.9), 1 H 7.55 dd (2.9; 4.9), 1 H	5.96 bd, 1 H	7.55 m, 2 H; 8.25 m, 2 H NH: 7.69 bd, 1 H

^a (C^2H_3)₂SO, 100 MHz; ^b (C^2H_3)₂SO, 200 MHz.

(15 ml). The combined extracts were dried over magnesium sulfate and the solvent was evaporated to give 0.286 g (96%) of chromatographically pure 4-chlorophenylmethylenemalonalddehyde.

Reaction of 3-Thienylidenemalonalddehyde with 4-Nitroaniline in Tert-butyl Alcohol

4-Nitroaniline (0.138 g; 1 mmol) was dissolved at 60°C in tert-butyl alcohol (3 ml) and 3-thienylidenemalonalddehyde (0.166 g; 1 mmol) was added with stirring. The stirred solution was allowed to cool and the product *VIIg* was collected on filter and washed with tert-butyl alcohol. The yield, melting point and spectral data are given in Tables V—VII.

Adducts of Inorganic Salts with 4-Chlorophenylmethylenemalonalddehyde *X*

A mixture of 4-chlorophenylmethylenemalonalddehyde (1 mmol), the corresponding potassium salt (1 mmol) and tert-butyl alcohol (2 ml) was stirred until the yellow coloration disappeared (several hours). Dry ether (5 ml) was added, the product was filtered, washed several times with ether with exclusion of moisture and dried *in vacuo*. Yields and melting points: *Xa*, 42%, 220°C (decomp.), *Xb*, 51%, 215°C (decomp.); *Xc*, 38%, 230°C (decomp.); *Xd*, 45%, 190–216°C. The ¹H NMR spectra are given in Table VIII.

TABLE VII
Infrared spectra of adducts *VII* (Nujol, cm⁻¹)

Compound	$\nu(\text{CH})$ in $\text{CH}=\text{O}$	$\nu(\text{C}=\text{C}-\text{C}=\text{C})$	$\nu(\text{OH})$ (chelate)
<i>VIIa</i>	2 730 w	1 670 m, 1 567 s	2 600–3 100
<i>VIIb</i>	2 725 w	1 620 w, 1 561 m	2 600–3 100
<i>VIIc</i>	2 722	1 627 m, 1 567 vs	2 600–3 100
<i>VII d</i>	—	1 619 m, 1 565 s	center about 2 900
<i>VIIe</i>	—	1 624 w, 1 561 s	center about 2 900
<i>VII f</i>	—	1 615 w, br, sh, 1 556 s	—
<i>VII g</i>	—	1 660 m, 1 584 s, br	—

TABLE VIII
Proton NMR spectra of adducts *X* (200 MHz, (C²H₃)₂SO)

Compound	CH—O	H-arom.	CH—X
<i>Xa</i>	8.33 bI, 2 H	7.16 m, 2 H; 7.05 m, 2 H	6.41 bs, 1 H
<i>Xb</i>	8.29 bs, 2 H	7.19 m, 2 H; 7.06 m, 2 H	5.49 bs, 1 H
<i>Xc</i>	8.25 bs, 2 H	7.18 m, 2 H; 7.04 m, 2 H	5.47 bs, 1 H
<i>Xd</i>	8.33 bs, 2 H	7.18 m, 2 H; 7.05 m, 2 H	5.47 bs, 1 H

Methoxyacrolein XI

A mixture of 4-chlorophenylmethylenemalonalddehyde (1 mmol) and potassium cyanide (1 mmol) was stirred at room temperature in dimethylformamide (2 ml). After disappearance of the yellow colour (several minutes), methyl iodide (0.1 ml) was added. The mixture was stirred for 2 h and partitioned between ether and 1% aqueous potassium carbonate. The ethereal layer was washed with 1% potassium carbonate solution and dried over solid potassium carbonate. Evaporation gave 0.142 g (60%) of the product which was practically pure according to TLC. Crystallization from light petroleum-ethyl acetate afforded an analytical sample, m.p. 80–81.5°C. For $C_{12}H_{10}ClNO_2$ (235.7) calculated: 61.16% C, 4.28% H, 15.04% Cl, 5.94% N; found: 61.33% C, 4.23% H, 15.06% Cl, 6.06% N. 1H NMR spectrum (C^2HCl_3): 9.23 d, 1 H (CHO, $J = 0.3$ Hz); 7.09 s, 1 H (CH—OCH₃); 5.6–7.39 m, 4 H (aromatic H); 5.24 d, 1 H (—CH—CN, $J = 0.3$ Hz); 4.08 s, 3 H (OCH₃). IR spectrum ($CHCl_3$), cm^{-1} : 2 745 w (CH in CH=O); 2 832 w, sh ($\nu_s(CH_3)$ in OCH₃); 2 250 w (C≡N); 1 695 w, sh, 1 678 m, 1 648 s, 1 633 m, sh (C=O and C—C).

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