SYNTHESIS OF BENZYLIDENEMALONALDEHYDES

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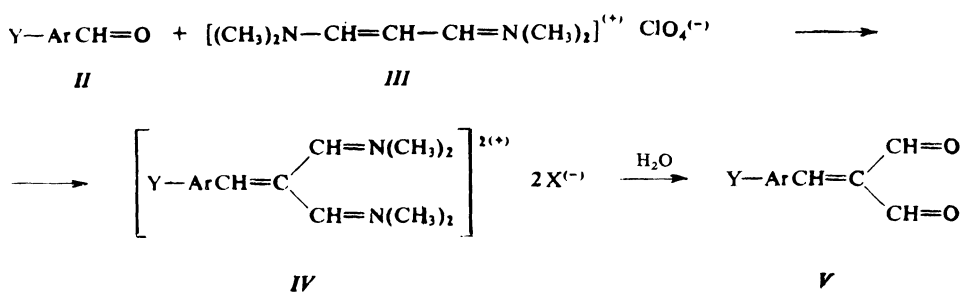A general two-step synthesis of benzylidenemalonaldehydes (*V*), based on condensation of substituted benzaldehydes with 1,3-bis(dimethylamino)trimethinium perchlorate, is described. The course of this reaction, character of the intermediate and spectral characteristics of the products are discussed. The obtained dialdehydes are classified as new organic Lewis acids.

The chemistry of unsaturated dialdehydes $R-CH=C(CH=O)_2$ (*I*) has been so far almost unexplored. As an exception we may mention 2,2,2-trichloroethoxycarbonyl-methylenemalonaldehyde (*Ia*) which was used successfully by Woodward[1] as one of the key intermediates in the cephalosporin C synthesis; however, even in this case the mentioned compound was not isolated. Moreover, the synthetic method used — an aldolisation reaction of a glyoxylic acid ester with malonaldehyde, followed by dehydration — is not suitable for obtaining compounds *I* with simpler carbon moieties[2]. Although tetraacetals of some alkylidenemalonaldehydes were prepared by Reichardt[2], their conversion into free dialdehydes has never been described. Formally, also dimethylaminomethylenemalonaldehyde[3] (*Ib*) and several other compounds prepared in this[4] or other laboratories[5-7], can be regarded as compounds of the type *I*, however, character of their substituents R (either marked electron donors or complex heterocyclic system) *a priori* makes these compounds different from those described in this paper.

$$R-CH=C(CH=O)_2$$
$$I$$

$$a, \ R = CCl_3CH_2OCO$$
$$b, \ R = (CH_3)_2N$$
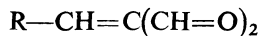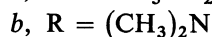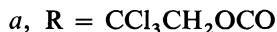
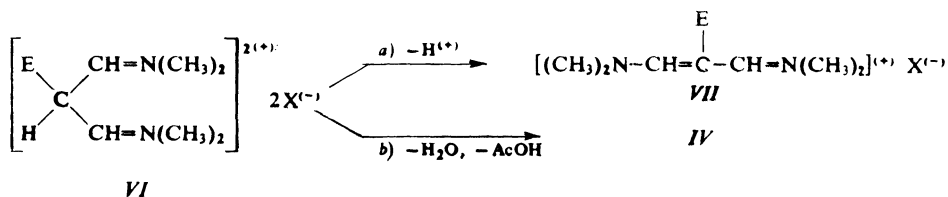We describe now the synthetic approach to the hitherto inaccessible benzylidene-malonaldehydes (*V*), utilizing our previous experience concerning the reactivity of polymethinium salts towards electrophilic reagents[8]. We found[9,10] that aromatic aldehydes *II* and a malonaldehyde derivative, 1,3-bis(dimethylamino)trimethinium perchlorate (*III*), reacted in the presence of a dehydration reagent and an acid to give

an intermediate of the assumed structure IV whose hydrolysis afforded the dialdehydes V (Scheme 1).

$$Y-ArCH=O \ + \ [(CH_3)_2N-CH=CH-CH=N(CH_3)_2]^{(+)} \ ClO_4^{(-)} \longrightarrow$$

$$\quad II \qquad\qquad\qquad\qquad III$$

$$\longrightarrow \left[Y-ArCH=C \begin{array}{c} CH=N(CH_3)_2 \\ \\ CH=N(CH_3)_2 \end{array} \right]^{2(+)} \ 2X^{(-)} \quad \xrightarrow{H_2O} \quad Y-ArCH=C \begin{array}{c} CH=O \\ \\ CH=O \end{array}$$

$$\qquad\qquad\qquad IV \qquad\qquad\qquad\qquad\qquad\qquad V$$

SCHEME 1

Our assumed course of this condensation agrees with many known acid-catalyzed electrophilic substitutions of trimethinium salts[3,8,11,12] (Scheme 2). The trimethinium salt is attacked in its central position by the electrophile under formation of the bis-iminium salt VI. In the hitherto described reactions, e.g. acid-catalyzed deuteriation[12], nitration[8] or formylation[3], the intermediate VI is stabilized by loss of proton under regeneration of the conjugated trimethinium system VII (pathway a). Presum-

$$\left[\begin{array}{c} E \\ \diagdown \\ H \diagup \end{array} C \begin{array}{c} CH=N(CH_3)_2 \\ \\ CH=N(CH_3)_2 \end{array} \right]^{2(+)} \ 2X^{(-)}$$

$$VI$$

$$a) -H^{(+)} \longrightarrow [(CH_3)_2N-CH=\overset{\overset{\displaystyle E}{|}}{C}-CH=N(CH_3)_2]^{(+)} \ X^{(-)}$$
$$VII$$

$$b) -H_2O, \ -AcOH \longrightarrow \qquad IV$$

E: $a)$ $^2H^{(+)}.NO_2^{(+)}$, $[(CH_3)_2N=CH-Cl]^{(+)}$; $b)$ Ar—CH—OH$^{(+)}$, Ar—CH=OBF$_3$, Ar——CH—OAc$^{(+)}$

SCHEME 2

ably, in the reaction described in this communication, as the electrophile serves the protonated aldehyde or its adduct with Lewis acid, or still more probably, the acylated species Ar—CH=OCOCH$_3^{(+)}$, if the condensation is carried out in acetic anhydride. The intermediate VI can be stabilized by vicinal olefin-forming elimination, yielding thus the salt IV (pathway b).

The found method was applied to a series of benzaldehydes containing substituents of various character, including both marked electron acceptors and donors (Table I). Acetic anhydride proved to be the best reaction medium and dehydration agent as well; optimum yields can in most cases be obtained with perchloric

TABLE I

Preparation of benzylidenemalonaldehydes V

Compound	Y method	Reaction time, h yield, %	M.p., °C b.p., °C/Pa	Formula (mol.wt.)	Calculated/Found % C	% H	% X
Va	2-NO$_2$	48	94—95·5[a]	$C_{10}H_7NO_4$	58·54	3·44	6·83[b]
	B	12·3		(205·2)	58·51	3·34	6·72[b]
Vb	3-NO$_2$	48	92—94[a]	$C_{10}H_7NO_4$	58·54	3·44	6·83[b]
	B	19·5		(205·2)	58·72	3·41	6·51[b]
Vc	4-NO$_2$	72	130—131·5[c]	$C_{10}H_7NO_4$	58·54	3·44	6·83[b]
	B	21		(205·2)	58·44	3·42	6·76[b]
Vd	2-Cl	48	75—76·5[a]	$C_{10}H_7ClO_2$	61·69	3·60	18·25[d]
	B	58·1		(194·6)	62·10	3·62	17·97[d]
Ve	3-Cl	48	20[e]	$C_{10}H_7ClO_2$	61·69	3·60	18·25[d]
	B	49·1	115—125/25	(194·6)	61·66	3·68	17·75[d]
Vf	4-Cl	48	73—74·5[a]	$C_{10}H_7ClO_2$	61·69	3·60	18·25[d]
	B	54		(194·6)	61·51	3·60	18·07[d]
Vg	3-Br	24	39—41·5[a]	$C_{10}H_7BrO_2$	50·29	2·93	33·47[f]
	B	41·8	120/25	(239·1)	50·34	2·99	33·83[f]
Vh	4-Br	48	92—94·5[a]	$C_{10}H_7BrO_2$	50·29	2·93	33·47[f]
	B	65·3		(239·1)	50·47	3·14	33·60
Vi	4-COOC$_2$H$_5$	24	64—66[h]	$C_{13}H_{12}O_4$	67·23	5·21	—
	B[g]	60		(232·2)	67·09	5·28	—
Vj	4-COOH	i	184—185	$C_{11}H_8O_4$	64·71	3·95	—
	i	93		(204·3)	64·80	3·98	—
Vk	H	24	100/25	$C_{10}H_8O_2$	74·99	5·03	—
	B[g]	66		(160·2)	74·59	5·00	—
Vl	2-CH$_3$O	48	34—36·5[e]	$C_{11}H_{10}O_3$	69·46	5·30	—
	A	57·9	115—125/25	(190·2)	69·23	5·28	—
Vm	3-CH$_3$O	20	25—26	$C_{11}H_{10}O_3$	69·46	5·30	—
	A	18·1	110—115/25	(190·2)	69·24	5·21	—
Vn	4-CH$_3$O	20	39—41[k]	$C_{11}H_{10}O_3$	69·46	5·30	—
	A	61		(190·2)	69·21	5·21	—
Vo	3,4-(CH$_3$O)$_2$	48	117—118[h]	$C_{12}H_{12}O_4$	65·45	5·49	—
	A	85·1		(220·2)	65·38	5·47	—
Vp	3,4-O-CH$_2$-O-	20	93—94[a]	$C_{11}H_8O_4$	64·71	3·95	—
	A	49·0		(204·2)	65·12	3·77	—
Vr	3,4,5-(CH$_3$O)$_3$	48	105—107[h]	$C_{13}H_{14}O_5$	62·39	5·64	—
	A	80·9		(250·3)	62·49	5·58	—

TABLE I

(Continued)

Compound	Y method	Reaction time, h yield, %	M.p., °C b.p., °C/Pa	Formula (mol.wt.)	% C	% H	% X
Vs	2,4,6-$(CH_3)_3$	7 days	40—43.5^e	$C_{13}H_{14}O_2$	77.20	6.98	—
	A	12.0	95/25	(202.3)	77.01	6.83	—
Vt	4-$NHCOCH_3$	16	155—157.5^m	$C_{12}H_{11}NO_3$	66.35	5.10	6.45^b
	A^l	23		(217.2)	66.87	5.10	6.44^b
Vu	4-$N(CH_3)_2$	72	119—121.5^a	$C_{12}H_{13}NO_2$	70.92	6.45	6.89^b
	A^n	47		(203.2)	70.86	6.32	6.92
Vv	4-$OCOCH_3$	24	59—61^h	$C_{12}H_{10}O_4$	66.05	4.62	—
	A	64.2		(218.2)	66.01	4.57	—
Vy	4-OH		176—177^h	$C_{10}H_8O_3$	68.18	4.58	—
	o	95		(176.2)	68.22	4.40	—
Vz	2-OH	24	159—160^h	$C_{10}H_8O_3$	68.18	5.58	—
	A	74		(176.2)	68.21	5.53	—

^{a} Crystallized from CCl_4; ^{b} % N; ^{c} from ethyl acetate–CCl_4 (1 : 1); ^{d} % Cl; ^{e} product was distilled; ^{f} % Br; ^{g} hydrolyzed with water; ^{h} sublimed product; ^{i} prepared by hydrolysis of Vi with 0.1M-NaOH for 1 h and acidification with 5% HCl; ^{j} from acetone; ^{k} from diethyl ether; ^{l} extracted with dichloromethane; ^{m} from ethyl acetate; ^{n} hydrolysis with 10% sodium acetate; ^{o} prepared by dissolution of derivative Vv in 0.1M-NaOH and acidification with 5% HCl.

acid or Lewis acids such as zinc chloride, boron trifluoride etherate or titanium tetrachloride. The reaction can be performed also in polyphosphoric acid and in pivaloyl chloride, yet the processing of the reaction mixture is usually more difficult. The intermediates IV are usually moisture-sensitive and therefore in standard preparations of the dialdehydes V the intermediates IV were precipitated and washed with ether, further purification being omitted; only in a few cases their structure was proved by analysis and spectra[13].

The intermediates IV are usually smoothly hydrolyzed. With derivatives containing electronegative substituents, it was advantageous to use dilute acid: although the hydrolysis was slower, the retro-aldolisation, observed in some cases, was suppressed. On the other hand, derivatives with markedly electropositive substituents are hydrolyzed better at higher pH (e.g. in the presence of an alkali metal acetate).

The obtained products V (Table I) are distillable liquids or solids which were purified by crystallization or sublimation. Their colour varies from pale yellow to red and they are of only limited stability at room temperature; they can be, however,

stored for several months at $-20°C$. The compounds are partly oxidized with air oxygen, particularly the liquids of which the most sensitive are *meta*-halogeno derivatives.

The unsubstituted (liquid) benzylidenemalonaldehyde or its solution in a non-polar solvent (*e.g.* tetrachloromethane) deposits in the course of several days a crystalline dimer which can be isolated and crystallized. Distillation *in vacuo* or heating in a solvent recovers practically quantitatively the monomer so that transformation to the dimer and its decomposition can be used as a purification operation. When this paper was in preparation, Reichardt described[14] formation of benzylidenemalonaldehyde in the attempted oxidation of cycloheptatrienylmalonaldehyde with silver salts; the same author observed also the dimerization and determined structure of the dimer by X-ray diffraction. It is noteworthy that the dimerization seems to be limited only to the unsubstituted benzylidenemalonaldehyde.

The structure of the dialdehydes *V* was confirmed by their ^{1}H NMR and IR spectra (Table II and III). The ^{1}H NMR spectra exhibit two signals of two different aldehyde groups, the more deshielded proton signal in the spectra of some derivatives being weakly splitted by coupling across four bonds with the methine proton at the double bond. Another characteristic signal is due to the methine proton ArCH= whose position $(\delta = 7.78 - 8.76)$ agrees with the assumed marked electronegativity of this group. Moreover, in comparable series (*e.g.* 4-substituted derivatives) its chemical shift reflects the expected effect of electroaffinity of the substituents. The anomalous spectrum of the *ortho*-hydroxy derivative *Vz* can be satisfactorily explained by an intramolecular hemiacetal bond as shown in formula *VIII*.
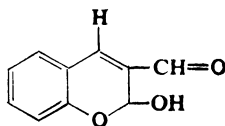
VIII

The question of spatial arrangement of the dialdehydes *V* will be analyzed separately; we can *a priori* say that neither of the possible conformers can be completely planar because of a steric interaction between the nucleus and one of the formyl groups. The complex shape of carbonyl bands in the IR spectra (Table III) can be interpreted as a manifestation of conformational inhomogeneity of the studied molecules.

The dramatic solvent-dependence of UV spectra (Fig. 1) ranks benzylidenemalonaldehydes among compounds, classified by Polansky[15] as organic Lewis acids. According to this author, this class comprizes such compounds in which two electronegative substituents on one double bond carbon atom polarize the double bond

TABLE II

Chemical shifts and multiplicities of ^{1}H NMR signals of benzylidenemalonaldehydes V in C^2HCl_3

Com-pound	CH=O	—CH=	Ar	Other signals
Va	10·08 s, 1 H 9·94 s, 1 H	8·52 s, 1 H	7·33—8·45 m, 4 H	—
Vb	10·20 s, 1 H 10·04 s, 1 H	8·08 s, 1 H	7·50—8·62 m, 4 H	—
Vc	10·18 d, 1 H $J = 0·5$ Hz 10·07 s, 1 H	8·12 bs, 1 H	8·37 m, 2 H 7·77 m, 2 H	—
Vd	10·08 s, 1 H 10·04 s, 1 H	8·42 s, 1 H	7·30—7·70 m, 4 H	—
Ve	10·17 s, 1 H 10·03 s, 1 H	8·08 s, 1 H	7·23—7·65 m, 4 H	—
Vf	10·18 d, 1 H $J = 0·5$ Hz 10·02 s, 1 H	8·03 bs, 1 H	7·63 m, 2 H 7·45 m, 2 H	—
Vg	10·17 s, 1 H 10·03 s, 1 H	8·06 s, 1 H	7·28—7·83 m, 4 H	—
Vh	10·17 s, 1 H 10·00 s, 1 H	8·03 s, 1 H	7·37—7·80 m, 4 H	—
Vi	10·17 s, 1 H 10·06 s, 1 H	8·22 s, 1 H	8·19 m, 2 H 7·68 m, 2 H	4·43 q, 2 H, $J = 7$ Hz CH_3CH_2 1·40 t, 3 H, $J = 7$ Hz CH_3CH_2
Vk	10·18 s, 1 H 10·05 s, 1 H	8·17 s, 1 H	7·58 m, 5 H	—
Vl	10·08 s, 1 H 10·03 s, 1 H	8·45 s, 1 H	6·80—7·77 m, 4 H	3·90 s, 3 H, —OCH$_3$
Vm	10·16 s, 1 H 10·02 s, 1 H	8·12 s, 1 H	6·95—7·58 m, 4 H	3·83 s, 3 H, —OCH$_3$
Vn	10·21 d, 1 H $J = 0·5$ Hz 9·97 s 1 H	7·96 bs, 1 H	7·75 m, 2 H 7·15 m, 2 H	3·88 s, 3 H, —OCH$_3$
Vo	10·23 s, 1 H 9·95 s, 1 H	7·90 s, 1 H	6·90—7·57 m, 3 H	3·97 s, 3 H, —OCH$_3$ 3·94 s, 3 H, —OCH$_3$
Vp	10·10 s, 1 H 9·86 s, 1 H	7·80 s, 1 H	6·73—7·35 m, 3 H	6·02 s, 2 H, CH$_2$
Vr	10·23 bs, 1 H 9·96 bs, 1 H	7·93 s, 1 H	7·27 s, 1 H 7·02 s, 1 H	3·93 s, 3 H, —OCH$_3$ 3·90 s, 6 H, —OCH$_3$

TABLE II

(*Continued*)

Com-pound	CH=O	—CH=	Ar	Other signals
Vs	10·52 s, 1 H 10·12 s, 1 H	8·76 s, 1 H	6·88 s, 2 H	2·24 s, 3 H, —CH$_3$ 2·12 s, 6 H, —CH$_3$
Vt[a]	10·02 s, 1 H 9·44 s, 1 H	7·95 s, 1 H	7·72 s, 4 H	10·32 br, 1 H, NH 2·03 s, 3 H, —COCH$_3$
Vu	10·20 d, 1 H $J = 0·9$ Hz 9·90 s, 1 H	7·78 bs, 1 H	7·88 m, 2 H 6·70 m, 2 H	3·12 s, 6 H, —N(CH$_3$)$_2$
Vv	10·17 s, 1 H 10·00 s, 1 H	8·07 s, 1 H	7·68 m, 2 H 7·25 m, 2 H	2·33 s, 1 H, COCH$_3$
Vy	10·17 s, 1 H 9·92 s, 1 H	7·92 s, 1 H	7·65 m, 2 H 6·92 m, 2 H	—
Vz	9·65 s, 1 H	6·55—7·57 m	6 H, Ar—CH=	6·35 s, 1 H, CH—OH

[a] Measured in hexadeuteriodimethyl sulfoxide.

to such an extent that the second carbon atom represents a strongly electron-deficient center. This then accepts the free electron pair of a base, *e.g.* an anion, whose negative charge is transferred to the neighbouring carbon atom where it is delocalized by the electronegative group. Most detailed investigations in this direction were done on benzylidene derivatives of cyclic systems such as 5,5-dimethyl-1,3-cyclohexanedione, 1,3-indanone and particularly the so-called Meldrum acids (2,2-dimethyl-1,3-dioxane-4,6-dione) which are as acidic as carboxylic acids[15].
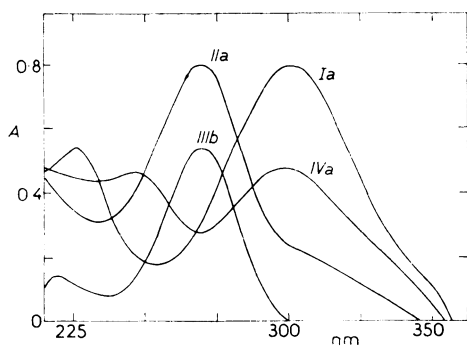

FIG. 1

Dependence of UV spectrum of benzylidenemalonaldehyde (*Vk*) on the character of solvent *I* CH$_3$CN; *II* H$_2$O; *III* 0·1M-NaOH; *IV* 0·1M-HCl *a*: $c = 5·47 . 10^{-5}$ mol$^-$ l^{-1}; *b*: $c = 2·19 . 10^{-5}$ mol$^-$ l^{-1}

TABLE III

IR Spectra of benzylidenemalonaldehydes V (CHCl$_3$), cm^{-1}

Com-pound	v(C—H(CH=O))	v(C=O)	v(C=O)	v Ring
Va	2 725 vw, sh 2 850 vw, sh	1 747 w 1 693 s	1 618 w, sh	1 600 m 1 574 m
Vb	2 728 vw 2 850 w, sh	1 742 w, sh 1 692 s	1 634 w, sh	1 607 w 1 576 w
Vc	2 723 vw 2 780 vw	1 743 w, sh 1 709 s 1 693 vs	1 596 m	1 613 m 1 495 w
Vd	2 723 vw 2 850 vw, sh	1 747 w 1 685 s	sh on 1 603	1 603 m 1 568 w 996 w
Vf	2 725 vw 2 780 vw	1 743 m, sh 1 703 s, sh 1 681 vs	1 591 vs	1 600 s, sh 1 565 m 1 492 m
Vg	2 733 vw 2 848 vw, sh	1 748 w 1 716 m, sh 1 703 m, sh 1 684 s	1 632 w	1 599 m 1 564 w 1 475 w
Vh	2 730 vw 2 850 vw, sh	1 745 w, sh 1 716 m, sh 1 706 m, sh 1 684 s	1 637 w	1 600 m 1 585 s 1 487 m
Vi	—	1 686 s (aldehyde) 1 714 (ester)	1 603 m, 1 559 w	
Vj	—	1 730 w, sh (dimer COOH) 1 703 m (aldehyde)	1 606 w, 1 579 w	
Vk	2 741	1 680 s 1 692 s, sh 1 754 m	1 633 m	1 601 m 1 575 m 1 496 w
Vl	2 726 vw 2 780 vw 2 871 w	1 747 w, sh 1 713 m, sh 1 692 s, sh	1 598 s, 1 589 s, sh 1 575 m, sh, 1 485 s 999 w	
Vm	2 748 vw, br	1 750 w, sh, br 1 715 m, sh 1 698 m, sh 1 681 s	1 633 m	1 598 s 1 581 m, sh 1 491 m, sh

TABLE III
(*Continued*)

Com-pound	ν(C—H(CH=O))	ν(C=O)	ν(C=C)	ν Ring
Vn	2 726	1 742 w, sh 1 693 s, sh 1 678 vs	1 604 s, 1 582 vs, 1 569 s, sh 1 558 s, sh, 1 515 s	
Vo	2 730 w	1 743 w, sh 1 716 m, sh 1 697 s, sh 1 680 s	1 600 m, sh, 1 586 s, 1 573 m, 1 518 s, 1 506 m, sh, 1 441 m, 1 000 w	
Vp	2 725 vw	1 745 w, sh, br 1 716 m, sh 1 697 m, sh 1 680 s	1 619 w	1 579 s 1 506 m 1 490 s
Vr	2 848 m	1 715 m, sh 1 697 s, sh 1 680 s	1 592 s, sh, 1 578 s, 1 505 s	
Vs	2 748 vw	1 748 w 1 715 m, sh 1 702 s, sh 1 691 s 1 680 s, sh		1 603 m 1 571 w, sh 999 w
Vt	—	+ amide I 1 714 m 1 706 m 1 682 m	1 581 m, br	1 503 m, sh
Vu	2 752 w	1 748 w, sh 1 690 m, sh 1 665 s	1 556 vs	1 609 vs 1 497 s, sh 1 522 vs
Vv	—	1 769 s (ester) 1 683 s (aldehyde) 1 699 s, sh	1 597 s, 1 581 m, sh	
Vy	—	1 690 w	1 606 m, 1 591 m, 1 579 sh, w	
Vz	2 830 w	1 681	1 634 w, 1 609 m, 1 573 w	

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The solvent-dependence of UV spectra of compounds V can be explained by inter-
action of their molecules with protic aolvents (Scheme 3). The UV-maximum in apro-
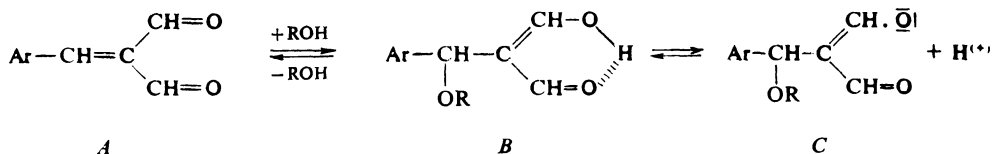
SCHEME 3

tic acetonitrile $(302$ nm$)$ is undoubtedly due to the conjugated system of the unsaturat-
ed dialdehyde (A). On the other hand, in water or ethanol the solvent adds to the
substrate and the arising species B undergoes dissociation to an anion (C), since the
same maximum $(270$ nm$)$ occurs also in 0.1M-NaOH. If the dissociation of the form B
is suppressed (as *e.g.* in 0.1M-HCl) the spectrum exhibits a maximum of lower inten-
sity at 302 nm and another one at about 245 nm but no band at 270 nm.

Our considerations derived from the UV spectra of compounds V have been
confirmed and extended by the ^{1}H NMR spectrum of 4-chlorobenzylidenemalonal-
dehyde (Vf) in 0.5M-NaO^{2}H in ^{2}H$_2$O. Under these conditions the formyl protons
appear as a single signal $(\delta = 8.32$ as compared with two signals at $\delta = 10.18$ and $\delta =$
$= 10.02$ in deuteriochloroform) whereas the methine proton signal occurs at $\delta = 5.88$
(instead of at $\delta = 8.03$ in deuteriochloroform). Both these base-induced changes are
fully consistent with an anion of the type C (Scheme 3).

EXPERIMENTAL

The melting points were determined on a Kofler block. Analytical samples were dried over phos-
phorus pentoxide at $25°$C/27 Pa for 24 h. ^{1}H NMR Spectra were taken on Varian HA-100
(100 MHz) and Tesla BS 467 (60 MHz) instruments in deuteriochloroform with tetramethyl-
silane as internal standard. IR Spectra were measured on a Zeiss UR 20, UV spectra on a Unicam
SP 8000 spectrometer.

Preparation of Benzylidenemalonaldehydes

A) Freshly fused and ground zinc chloride (5 g) was added to a stirred solution of 1,3-bis-
(dimethylamino)trimethinium perchlorate[16,17] (4.52 g; 20 mmol) in acetic anhydride (50 ml).
The stirring was continued until all dissolved, the solution was cooled and the aromatic aldehyde
(22 mmol) was slowly added. The solution was stirred for 1 h with ice-cooling and then set aside
at room temperature for the time specified in Table I. The product was precipitated, washed with
an excess of dry ether and hydrolyzed by stirring with a mixture of water (300 ml) and benzene
(100 ml). After the solids had dissolved, the mixture was stirred for 1 h, the organic layer was
separated and the aqueous one was extracted twice with benzene. The combined extracts were
dried over anhydrous magnesium sulfate and filtered through a thin layer of silica gel to remove
polar impurities. The solvent was evaporated and the residue crystallized from a suitable solvent
or distilled (Table I).

B) To an ice-cooled solution of the trimethinium salt in acetic anhydride (same as in the procedure *A*) 70% perchloric acid (5 ml) was added under stirring. The further work-up procedure was the same as described under *A*. The intermediate was hydrolyzed with dilute hydrochloric acid (1 : 20; about 500 ml) in the presence of a benzene–dichloromethane mixture (5 : 2; 100 ml). After the solids had dissolved, the mixture was stirred for 15—20 min and then processed as described in the experiment *A*. 3-Chloro- and 3-bromobenzylidenemalonaldehyde are extremely sensitive to air oxygen.

REFERENCES

1. Woodward R. B., Heusler K., Gosteli J., Naegeli P., Oppolzer W., Ramage R., Ranganathan S., Vorbrüggen H.: J. Amer. Chem. Soc. *88*, 852 (1966).
2. Reichardt C., Pressler W.: Angew. Chem. *88*, 88 (1976).
3. Arnold Z., Žemlička J.: This Journal *25*, 1318 (1960).
4. Arnold Z., Holý A.: This Journal *28*, 869 (1963).
5. Čiernik J.: This Journal *37*, 2273 (1972).
6. Reynolds G. A., VanAllen J. A.: J. Org. Chem. *34*, 2736 (1969).
7. Dressler J., Bodendorf K.: Arch. Pharm. (Weinheim) *303*, 4811 (1970).
8. Kučera J., Arnold Z.: This Journal *32*, 1704 (1967).
9. Arnold Z., Král V.: Czech. Appl. 8429—80; Czech. 217376 (1982).
10. Arnold Z., Král V., Dvořák D.: Tetrahedron Lett. *23*, 1725 (1982).
11. Lloyd D., McNab H.: Angew. Chem. *88*, 496 (1976).
12. Scheibe G., Jutz C., Seiffert W., Grosse D.: Angew. Chem. *76*, 270 (1964).
13. Arnold Z., Dvořák D., Král V.: This Journal, in press.
14. Reichardt C., Yun K.-Y.: Tetrahedron Lett. *23*, 3136 (1982).
15. Polansky O. E., Schuster P., Wessely F.: Tetrahedron *1966*, Suppl. 8, Part II, 463.
16. Malhotra S. S., Whiting M. C.: J. Chem. Soc. *1960*, 3812.
17. Arnold Z., Holý A.: This Journal *30*, 47 (1965).

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