SUBSTITUTED METHYLENEMALONALDEHYDES: CONDENSATION OF DIALDEHYDES WITH 1,3-BIS(DIMETHYLAMINO)TRIMETHINIUM PERCHLORATE

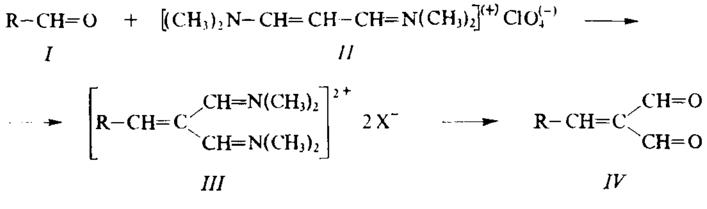
Ludmila A. YANOVSKAYA[a], Galya V. KRYSHTAL[a], Dalimil DVOŘÁK[b], Vladimír KRÁL[b] and Zdeněk ARNOLD[b]

[a] *Zelinsky Institute of Organic Chemistry,*
Academy of Sciences of the USSR, Moscow, USSR and
[b] *Institute of Organic Chemistry and Biochemistry,*
Czechoslovak Academy of Sciences, 166 10 Prague 6, Czechoslovakia

Received December 27th, 1984

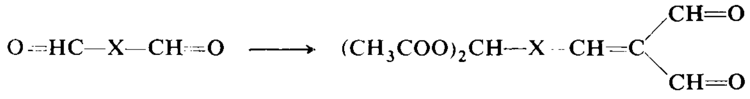
Selected unsaturated, aromatic, and heterocyclic dialdehydes reacted with 1,3-bis(dimethylamino)-trimethinium perchlorate in acetic anhydride in the presence of acid. One of the aldehyde group participated in the condensation, whereas the other was transformed into the diacetate. The obobtained substituted methylenemalonaldehydes were characterized by their ^{1}H NMR, IR, and mass spectra.

Recently, we have described[1,2] a simple synthesis of the so far unknown substituted methylenemalonaldehydes *IV*, consisting in condensation of aldehydes *I* with 1,3-bis-(dimethylamino)trimethinium perchlorate *II*. In acetic anhydride, in the presence of an acid, the reaction proceeds *via* a bis-iminium salt *III* which is hydrolyzed to give the unsaturated dialdehyde *IV*. A detailed study has revealed that reaction according to this scheme takes place with aromatic[3], heteroaromatic[4], and aliphatic unsaturated aldehydes[5], whereas experiments with aliphatic aldehydes and ketones of various types have been unsuccessful (Scheme 1).



SCHEME 1

This communication describes an attempted extension of the mentioned condensation with the aim to prepare more complex polyaldehydes. As starting compounds we selected three types of dialdehydes: unsaturated aliphatic dialdehydes (*Va*, *Vb*), dialdehydes of the benzene series (*Vc* – *Ve*), and one heteroaromatic dialdehyde (*Vf*) (Scheme 2).



$$O{=}HC{-}X{-}CH{=}O \longrightarrow (CH_3COO)_2CH{-}X{-}CH{=}C(CH{=}O)_2$$

V *VI*

a, X = —(CH=CH)$_2$—
b, X = —(CH=CH)$_3$—
c, X = 1,2-phenylen
d, X = 1,3-phenylen
e, X = 1,4-phenylen
f, X = 3,4-furylen

SCHEME 2

In all the studied cases we obtained products resulting from condensation of one aldehyde group whereas the second one was converted into the diacetate (Table I).

TABLE I

Melting points, mass spectra and elemental analyses of the methylenemalonaldehydes *VI*

VI	M.p., °C	Formula mol.wt.	*m/e*	Calculated/Found % C	Calculated/Found % H
a	79–82·5	$C_{13}H_{14}O_6$ (266)	266	58·65 58·26	5·26 5·21
b	93·5–98·5	$C_{15}H_{16}O_6$ (292)	292	61·64 61·99	5·48 5·49
c	–	$C_{15}H_{14}O_6$ (290)	230 ($M^+ - CH_3COOH$)	62·07 62·52	4·83 5·02
d	69–72·5	$C_{15}H_{14}O_6$ (290)	230 ($M^+ - CH_3COOH$)	62·07 62·22	4·83 5·08
e	79–83·5	$C_{15}H_{14}O_6$ (290)	290[a] 230 ($M^+ - CH_3COOH$)	62·07 62·15	4·83 4·92
f	105–108	$C_{13}H_{12}O_7$ (280)	280	55·70 56·15	4·28 4·29

[a] Negligible.

The isolated compounds can be thus classified as derivatives of conjugated unsaturated trialdehydes, containing the methylenemalonaldehyde structural unit.

In most cases, the yields were relatively high and the crude products were chromatographically almost pure. However, further purification was combined with considerable losses. Except *VIc*, the obtained products were yellow crystalline substances which were stored unchanged for several weeks in a refrigerator. The spectral data were in complete agreement with the given structure (Tables II–IV). No molecular ions were observed in the mass spectra of *VIc* and *VId* (and only a negligible one for *VIe*); instead, the spectra contained fragments arising by loss of acetic acid from the molecule.

TABLE II

Ultraviolet spectra of methylenemalonaldehydes *VI* in acetonitrile (nm, $\varepsilon \,.\, 10^{-3}$)

VIa	279 sh (17·56), 302 br (32·43)
VIb	235 (5·60), 310·5 sh (33·78), 328·5 (56·71), 341·5 (58·65)
VIc	230, 289 (9·05)
VId	209, 225, 295·5 (13·10)
VIe	222, 298·5 (18·28)

TABLE III

^{1}H NMR spectral data for methylenemalonaldehydes *VI* in C^2HCl_3

VI	—CH=O	—CH=C(CH=O)$_2$	CH(OCOCH$_3$)$_2$	Aromatic protons	(CH$_3$COO)$_2$CH
a	10·26 (d, 1 H)[a] 9·82 (s, 1 H)	6·0—7·88 (m, 6 H)		—	2·13 (s, 6 H)
b	10·22 (d, 1 H)[a] 9·77 (s, 1 H)	5·67—7·97 (m, 8 H)		—	2·12 (s, 6 H)
c	10·10 (s, 1 H) 9·94 (s, 1 H)	8·73 (s, 1 H)	7·70 (s, 1 H)	7·23—7·68 (m, 4 H)	2·08 (s, 6 H)
d	10·18 (s, 1 H) 10·06 (s, 1 H)	8·14 (s, 1 H)	7·35—7·81 (m, 5 H)		2·15 (s, 6 H)
e	10·18 (s, 1 H) 10·05 (s, 1 H)	8·15 (s, 1 H)	7·56—7·76 (m, 5 H)		2·16 (s, 6 H)
f	10·22 (d, 1 H)[a] 9·88 (s, 1 H)	8·99 (s, 1 H)	7·69—7·89 (m, 3 H)		2·12 (s, 6 H)

[a] $J = 2$ Hz.

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried over phosphorus pentoxide at 25°C/25 Pa for 24 h. Infrared spectra were taken on a Zeiss UR 20 spectrometer, ^{1}H NMR spectra on a Tesla B 467 (60 MHz) instrument, UV spectra on a Unicam SP 8000 spectrometer and mass spectra on an AEI MS-902 spectrometer.

Preparation of Methylenemalonaldehydes *VI*

VIa: The aldehyde *Va* (0·220 g; 2 mmol) was added to an ice-cooled solution of the trimethinium salt (0·453 g; 2 mmol) and freshly fused zinc chloride (0·3 g) in acetic anhydride (5 ml). The ice-cooled mixture was stirred for 1 h, left aside overnight at room temperature, and mixed with an excess of ether. The precipitated oil was twice washed with ether and decomposed by stirring with water (50 ml) and benzene (25 ml). After 1 h, the benzene layer was separated, replaced by another portion of benzene (25 ml) and stirred for 30 min. The organic layer was separated and the aqueous one extracted with (benzene 25 ml). The combined benzene solutions were dried over magnesium sulfate and filtered through a small amount of silica gel. Evaporation *in vacuo* afforded 0·230 g (43·2%) of product, melting at 76–81°C. An analytical sample was obtained by crystallization from ethyl acetate–light petroleum.

VIb: This compound was obtained in the same way as described for *VIa*; the crude product (62%) was purified by crystallization from ethyl acetate.

VId: Perchloric acid (70%; 0·5 ml), followed by the aldehyde *Vd* (1·00 g; 7·5 mmol), was gradually added to a stirred ice-cooled solution of the trimethinium salt (1·13 g; 5 mmol) in acetic anhydride (15 ml). The ice-cooled mixture was stirred for 1 h and then set aside overnight at room temperature. Further work up was the same as described for *VIa* except that the mixture was hydrolyzed with dilute hydrochloric acid (20 : 1) instead of water and the product was extracted

TABLE IV
Infrared spectral data for methylenemalonaldehydes *VI* ($CHCl_3$), cm^{-1}

VI	ν(CH=O)	ν(C=O(–CH=O))	ν(C=O(CH_3COO))	ν(C=C)
a	2 700	1 697 m, sh 1 682 s	1 766 s, br	1 596 s 1 569 m 1 556 w, sh
b	—	1 695 m, sh 1 680 s	1 765 s	1 580 s 1 557 m
c	2 740 vw, sh	1 685 m 1 702 m 1 715 w, sh	1 765 s	1 633 w
d	2 740 w	1 692 m	1 768 s	1 634 w
e	2 700–2 800 vw	1 683 s 1 703 m, sh	1 765 s	1 602 m

with a benzene–dichloromethane mixture (5 : 2). Yield 0·98 g (68%) of crude product which was purified by crystallization from ethyl acetate–light petroleum.

VIc: Obtained in 80% yield as described for *VId*. The compound was not obtained in the crystalline state but only as an oil. Since it decomposed on attempted distillation, the analytical sample was obtained under sublimation conditions at 90–100°C/25 Pa.

VIe: Obtained in the same manner as *VId*. To increase the solubility, acetic anhydride was diluted with a threefold amount of nitromethane and the reaction mixture was stirred for 48 h. The crude product, obtained in 80% yield, was crystallized from ethyl acetate–light petroleum.

VIf: To an ice-cooled solution of the trimethinium salt (0·453 g; 2 mmol) in a mixture of acetic anhydride (2·5 ml) and acetic acid (2·5 ml) was added boron trifluoride etherate (0·5 ml) followed by 3,4-diformylfuran (*Vf*; 0·124 g; 1 mmol). After standing overnight, the mixture was processed as described for *VIa*, affording 0·160 g (57%) of a crude product which was purified by sublimation.

REFERENCES

1. Arnold Z., Král V.: Czech. Appl. 8429–80 (1980).
2. Arnold Z., Král V., Dvořák D.: Tetrahedron Lett. *23*, 1725 (1982).
3. Arnold Z., Král V., Dvořák D.: This Journal *49*, 2602 (1984).
4. Arnold Z., Dvořák D., Král V.: This Journal *49*, 2613 (1984).
5. Yanovskaya L. A., Kryshtal G. V., Dvořák D., Král V., Arnold Z.: This Journal, *50*, 1300 (1985).

Translated by M. Tichý.