

## SYNTHESIS OF POLYENYLIDENEMALONALDEHYDES

Ludmila A. YANOVSKAYA<sup>a</sup>, Galya V. KRYSHAL<sup>a</sup>, Dalimil DVOŘÁK<sup>b</sup>  
 Vladimír KRÁL<sup>b</sup> and Zdeněk ARNOLD<sup>b</sup>

<sup>a</sup> Zelinski Institute of Organic Chemistry,

Academy of Sciences of USSR, Moscow, USSR and

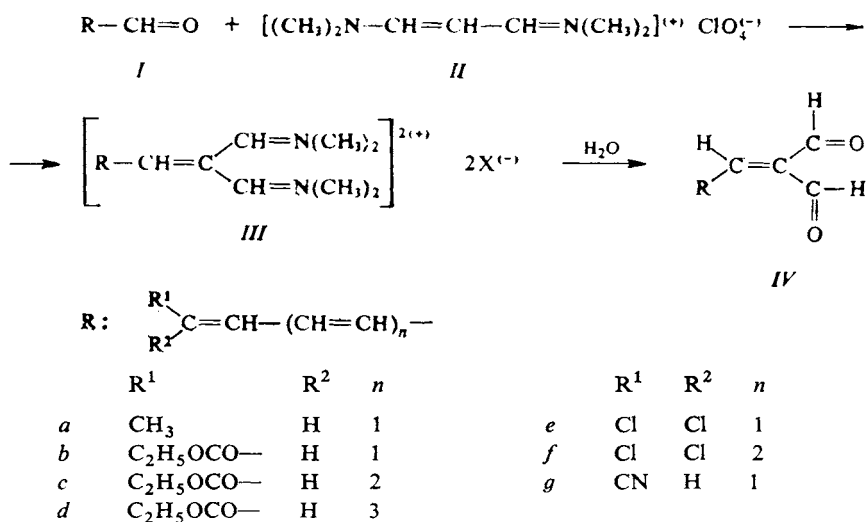
<sup>b</sup> Institute of Organic Chemistry and Biochemistry,

Czechoslovak Academy of Sciences, 166 10 Prague 6, Czechoslovakia

Received October 5th, 1984

Condensation of polyenals *I*, where substituents R<sup>1</sup> and R<sup>2</sup> are CH<sub>3</sub>, H, C<sub>2</sub>H<sub>5</sub>OCO, Cl or CN, with 1,3-bis(dimethylamino)trimethinium perchlorate (*II*), followed by hydrolysis of the intermediate *III*, afforded polyenylidenemalonaldehydes *IV*. Properties and spatial arrangement of these products are briefly discussed.

Recently, we developed a synthetic approach to benzylidenemalonaldehydes and related compounds<sup>1-4</sup> consisting in condensation of aromatic aldehydes with the 1,3-bis(dimethylamino)trimethinium salt *II* (Scheme 1) and subsequent hydrolysis. The remarkable reactivity<sup>2,5</sup> of these hitherto inaccessible unsaturated dialdehydes<sup>3</sup> prompted us to apply this method to the aliphatic series.



SCHEME I

Alkylidenemalonaldehydes have not been described as yet, although Tietze who studied<sup>6,7</sup> cycloadditions of *in situ* arising 2-alkylidene-1,3-dicarbonyl compounds with olefinic components obtained in one case<sup>8</sup> a product which was probably formed *via* an alkylidenemalonaldehyde arising by reaction of sodium salt of malonaldehyde with the corresponding aliphatic aldehyde. Reichardt<sup>9</sup> prepared tetraethyl acetals of several alkylidenemalonaldehydes by Wittig reaction but their hydrolysis has never been described.

It has been found that neither saturated aldehydes nor conjugated aldehydes with one double bond condense with the trimethinium salt *I*; contrariwise, aldehydes whose carbonyl is conjugated at least with two double bonds afford the corresponding polyenylidenemalonaldehydes *IVa–IVg* in satisfactory to good yields. In addition

TABLE I

Preparation, yields, melting (boiling) points and elemental analyses of polyenylidenemalonaldehydes *IV*

Compound <sup>a</sup> (ref.)	Method catalyst <sup>b,c</sup>	Yield %	M.p., °C b.p., °C/Pa	Formula mol.wt.	Calculated/Found		
					% C	% H	% X
<i>IVa</i> <sup>11</sup>	<i>B</i>	43.1	75–80/25 <sup>d</sup>	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub> (150.2)	71.98	6.71	—
	0.2 <sup>b</sup>				72.08	6.78	—
<i>IVb</i> <sup>12</sup>	<i>A</i>	59.6	95–98 <sup>e</sup>	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub> (208.2)	63.45	5.81	—
	0.2 <sup>b</sup>	44.0	—	—	63.09	5.76	—
	<i>A</i> <sup>f</sup>				—	—	—
0.3 <sup>c</sup>	—	—	—	—	—	—	
<i>IVc</i> <sup>12</sup>	<i>A</i>	74	103–106.5 <sup>g</sup>	C <sub>13</sub> H <sub>14</sub> O <sub>4</sub> (234.3)	66.66	6.02	—
	0.14 <sup>b</sup>				66.88	6.02	—
<i>IVd</i> <sup>13</sup>	<i>A</i>	51	126–129.5 <sup>g</sup>	C <sub>15</sub> H <sub>16</sub> O <sub>4</sub> (260.3)	69.22	6.20	—
	0.1 <sup>b</sup>				68.83	6.13	—
<i>IVe</i> <sup>14</sup>	<i>A</i>	92	87–89.5 <sup>h</sup>	C <sub>8</sub> H <sub>6</sub> O <sub>2</sub> Cl <sub>2</sub> (205.0)	46.86	2.96	34.58 <sup>i</sup>
	0.5 <sup>b</sup>				47.00	3.01	34.56
<i>IVf</i> <sup>15</sup>	<i>A</i>	71	130–134 <sup>e</sup>	C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> Cl <sub>2</sub> (231.1)	51.97	3.49	30.69 <sup>i</sup>
	0.14 <sup>b</sup>				51.72	3.62	30.43
<i>IVg</i> <sup>16</sup>	<i>A</i> <sup>f</sup>	25	83–87 <sup>j</sup>	C <sub>9</sub> H <sub>7</sub> NO <sub>2</sub> (161.2)	67.08	4.38	8.69 <sup>k</sup>
					66.78	4.18	8.61

<sup>a</sup> Reference to the starting polyenal; <sup>b</sup> BF<sub>3</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, ml/mmol; <sup>c</sup> anhydrous ZnCl<sub>2</sub>, g/mmol, added without cooling, after dissolution the mixture again cooled; <sup>d</sup> bath temperature; <sup>e</sup> from tetrachloromethane; <sup>f</sup> from the acetal; <sup>g</sup> from ethyl acetate; <sup>h</sup> sublimed; <sup>i</sup> % Cl; <sup>j</sup> from cyclohexane–benzene; <sup>k</sup> % N.

to 2,4-hexadienal, a series of aldehydes with two to four conjugated double bonds, substituted with chlorine, ethoxycarbonyl or nitrile groups, was investigated (Scheme 1). In two cases the reaction was performed with the corresponding acetal (*Ib*, *Ig*) instead of the aldehyde. Here the lower yield may be outweighed by the better accessibility and higher stability of the acetals than of the corresponding polyenals. The condensation was carried out in acetic anhydride or in a 1 : 1 mixture of acetic anhydride and acetic acid with boron trifluoride etherate or zinc chloride as catalysts (Table I). The crude intermediate *III* was hydrolyzed, the product extracted with an appropriate solvent and purified by distillation, sublimation or crystallization. The dialdehydes *IV* are yellow to red, mostly crystalline compounds, stable in refrigerator for several months. Their analytical and spectral data are in complete accord with the assumed structure (Tables I–IV).  $^1\text{H}$  NMR Spectra of the polyenyldene-malonaldehydes *IV* show characteristic splitting of the low-field ( $\delta > 10$ ) aldehyde proton signal due to the coupling across four bonds with the  $\text{R}-\text{CH}=\text{}$  proton, the coupling constant being about 2 Hz. On the basis of this signal the dialdehyde part of the molecule is assigned a conformational arrangement (Scheme 1) similar

TABLE II  
 $^1\text{H}$  NMR Spectra of dialdehydes *IV*

Compound	$\text{CH}=\text{O}$	Olefinic protons	Other signals
<i>IVa</i>	10.25 d (1 H, $J = 2$ Hz) 9.77 s (1 H)	6.25–7.8 m (5 H)	1.93 d (3 H, $J = 5$ Hz; $\text{CH}_3$ )
<i>IVb</i>	10.25 d (1 H, $J = 2$ Hz) 9.81 s (1 H)	6.8–8.1 m (4 H) 6.23 d (1 H, $J = 14.5$ Hz) = $\text{CH}\cdot\text{COOC}_2\text{H}_5$	4.25 q (2 H, $J = 7$ Hz; $\text{CH}_2\text{CH}_3$ ) 1.30 t (3 H, $J = 7$ Hz; $\text{CH}_2\text{CH}_3$ )
<i>IVc</i>	10.24 d (1 H, $J = 2$ Hz) 9.79 s (1 H)	6.6–7.9 m (6 H) 6.06 d (1 H, $J = 14.5$ Hz) = $\text{CH}-\text{COOC}_2\text{H}_5$	4.21 q (2 H, $J = 7$ Hz; $\text{CH}_2\text{CH}_3$ ) 1.29 t (3 H, $J = 7$ Hz; $\text{CH}_2\text{CH}_3$ )
<i>IVd</i>	10.26 d (1 H, $J = 2$ Hz) 9.82 s (1 H)	6.45–8.0 m (8 H) 5.98 d (1 H, $J = 15.5$ Hz) = $\text{CH}-\text{COOC}_2\text{H}_5$	4.21 q (2 H, $J = 7$ Hz; $\text{CH}_2\text{CH}_3$ ) 1.32 t (3 H, $J = 7$ Hz; $\text{CH}_2\text{CH}_3$ )
<i>IVe</i>	10.22 d (1 H, $J = 2$ Hz) 9.77 s (1 H)	6.60–8.0 m (4 H)	—
<i>IVf</i>	10.20 d (1 H, $J = 2$ Hz) 9.77 s (1 H)	6.7–8.0 m (6 H)	—
<i>IVg</i>	10.24 d (1 H, $J = 2$ Hz) 9.85 s (1 H)	6.7–8.2 m (4 H) 5.5–5.9 m (1 H = $\text{CH}\cdot\text{CN}$ )	—

TABLE III  
IR Spectra of dialdehydes *IV* ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ )

Compound	$\text{CH}=\text{O}$	$\text{C}=\text{O}$	$\text{C}=\text{C}$
<i>IVa</i>	2 730 w, 2 755 w 2 783 w, 2 833 w, sh	1 680 s 1 694 s, sh	1 635 m 1 589 vs 1 563 s
<i>IVb</i>	2 750 vw, vbr 2 836 w, sh	1 712 s (ester) 1 685 s (ald.)	1 626 m 1 595 s 1 565 w
<i>IVc</i>	2 733 2 759 2 785 vw	1 680 s 1 697 s, br 1 708 s, sh, br	1 624 s 1 602 m 1 580 s 1 554 m
<i>IVd</i>	2 738 w	1 679 s 1 695 s	1 623 m, 1 603 s 1 589 s, 1 567 s 1 556 s, sh 1 538 m, sh
<i>IVe</i>	2 730 w, 2 755 w 2 840 w, sh, 2 870 w	1 682 vs 1 697 s, sh	1 589 vs, 1 559 m, sh 1 549 s
<i>IVf</i>	2 734 w, 2 758 w 2 783 w, 2 839 w, sh	1 681 vs 1 693 s, sh	1 606 m, 1 591 m, sh 1 575 s, sh, 1 566 vs 1 557 s, sh, 1 539 m, sh
<i>IVg</i>	2 750 vw, vbr 2 840 w, sh	1 688 s 1 697 s, sh	1 597 m 1 559 w $\nu(\text{C}\equiv\text{N})$ 2 223 w

TABLE IV  
UV Spectra of dialdehydes *IV* in acetonitrile, nm ( $\epsilon \cdot 10^{-3}$ )

Compound	
<i>IVb</i>	227 (7·16); 310 sh (35·13); 321 (44·16); 336 sh (36·31)
<i>IVc</i>	248 (3·33); 321 sh (45·76); 337·5 (71·63); 352 (71·50)
<i>IVd</i>	274·5 (5·81); 346 sh (55·03); 358·5 (88·35); 368 (88·60)
<i>IVe</i>	235 (4·12); 310 sh (30·75); 325 (35·87); 350 (29·21)
<i>IVf</i>	244·5 (3·94); 320 sh (38·28); 339 (60·04); 349 (59·17)

to the arrangement found by us previously for 3-phenyl-2-propenylidenemalonaldehyde and some other compounds<sup>4,10</sup>.

## EXPERIMENTAL

The melting points were determined on a Kofler block, the analytical samples were dried over phosphorus pentoxide at 25°C/25 Pa. The IR spectra were measured on a Zeiss UR 20 spectrometer, <sup>1</sup>H NMR spectra on a Tesla B 46 (60 MHz) spectrometer in deuteriochloroform (tetramethylsilane as internal standard), UV spectra on a Unicam SP 8000 spectrometer. The starting aldehydes *I* were prepared by known methods<sup>11-16</sup>.

### Preparation of Polyenylidenemalonaldehydes

To a stirred, ice-cooled solution of 1,3-bis(dimethylamino)trimethinium perchlorate (5 mmol) in acetic anhydride (20 ml; method *A*) or in a 1 : 1 mixture of acetic anhydride and acetic acid (method *B*; see ref.<sup>4</sup>) the catalyst (Table I) was added. After portionwise addition of the aldehyde *I* (5.2 mmol), the mixture was stirred for 1 h at 0°C and set aside overnight at room temperature. The product was precipitated with ether (200 ml), washed with ether (3 × 100 ml) and hydrolyzed by stirring with water (150 ml) and a suitable solvent (50 ml; benzene or benzene-dichloromethane 5 : 2). After 1 h the organic layer was separated, replaced by fresh solvent (50 ml) and stirred for 1/2 h. The organic layer was again separated, the aqueous one extracted with benzene (2 × 50 ml), the combined extracts were dried over anhydrous magnesium sulfate, filtered through a small amount of silica gel and evaporated. The crude product was purified by distillation, sublimation or crystallization (Table I).

## 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. Dvořák D., Arnold Z.: Tetrahedron Lett. 23, 4401 (1982).
6. Tietze L.-F., Kiedrowski G., Harms K., Clegg W., Sheldrick G.: Angew. Chem. 92, 130 (1980).
7. Tietze L.-F., Kiedrowski G., Berger B.: Angew. Chem. 94, 222 (1982).
8. Tietze L.-F., Glösenkamp K.-H., Holla W.: Angew. Chem. 94, 793 (1982).
9. Reichardt C., Pressler W., Würthwein E.-U.: Angew. Chem. 88, 88 (1976).
10. Král V., Laatikainen R., Arnold Z.: Tetrahedron, in press.
11. Nazarov I. N., Nazarova I. I., Torgov I. V.: Dokl. Akad. Nauk SSSR 122, 82 (1958).
12. Janovskaja L. A., Stěpanova R. N., Kogan G. A., Kučerov V. F.: Izv. Akad. Nauk SSSR, Ser. Khim. 1963, 857.
13. Kovalev B. G., Mamšurin A. A., Dormibontova N. P.: Zh. Org. Khim. 1966, 1584.
14. Julia M., Bauchaudon J.: Compt. Rend. 253, 1111 (1961).
15. Julia M., Bullot J.: Compt. Rend. 249, 129 (1959).
16. Janovskaja L. A., Kovalev B. G., Kučerov V. F.: Izv. Akad. Nauk SSSR, Ser. Khim. 1965, 684.

Translated by M. Tichý.