SYNTHESIS OF AMINALS AND AMINALACETALS OF α-SUBSTITUTED β-DIMETHYLAMINOACROLEIN

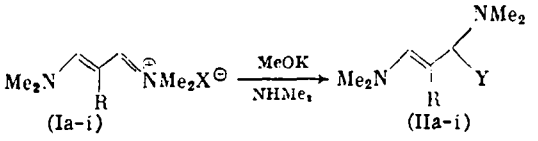
Zh. A. Krasnaya, T. S. Stytsenko,
and V. S. Bogdanov

UDC 542.91:547.447.5

Aminals and aminalacetals of conjugated ω-dimethylaminoaldehydes are convenient reagents for synthesis of various types of aminopolyenes, since they condense extremely easily and without catalysts with ketones, β-diketones, and CH-acids at the active methyl or methylene group [1, 2].

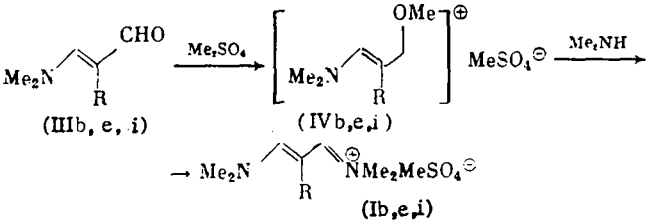
For the first time $Me_2N-CH=CH-CH(NMe_2)_2$ (IIa) was obtained from the trimethine salt (Ia) and $NaNMe_2$ [3]. We modified the method for obtaining this aminal and synthesized the previously unknown $Me_2N-(CH=CH)_n-CH(Y)(NMe_2)$, where n = 2-4 and Y = OMe, NMe_2 [4]. We synthesized the first aminalacetals (IIb, c) and aminals (IId) of α-substituted β-dimethylaminoacroleins from salts of (Ib-d) [5-7].

It is known that (IIb-d) easily form γ-substituted δ-dimethylaminodienones, which reversibly isomerize to 2-dimethylamino-2H-pyrans, thereby causing solvato-, thermo-, and photochromism in these compounds [5, 7]. In this paper the synthesis of aminals and aminalacetals of various α-substituted β-dimethylaminoacroleins (IIb-i) is described



R, X (Table 1), R, Y (Table 2).

The starting trimethine salts (Table 1), except for (Ib, e, i) were obtained by aminoformylation of vinyl esters, acids, enamines, and acetals with the aminoformylating complex prepared from $POCl_3$ and DMF. Salts (Ib, e, i) were obtained by the action of Me_2NH in CH_2Cl_2 on adducts (IVb, e, i) which were formed from aldehydes (IIIb, e, i) and dimethyl sulfate



R = Me(IIIb), (IVb), (Ib); R = i-Pr(IIIe), (IVe), (Ie); R = F(IIIi), (IVi), (Ii).

Aldehydes (IIIb, e, i) were isolated upon aminoformylation of the corresponding substrates by treatment with saturated K_2CO_3 solution followed by heating (15 min, 80-90°C) until disappearance according to the UV spectrum of the reaction products with λ_{max} of 320-325 nm and appearance of λ_{max} of 295-300 nm.

The UV spectra of salts (Ia-k) (Table 1) indicate that for meso substituted trimethine salts the Ferster–Dewar–Nott rule holds, in that upon introduction into an odd position of the polymethine chain (counting the nitrogen atom) of an electron donating substituent a bath-

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 106-111, January, 1988. Original article submitted July 9, 1986.

0568-5230/88/3701-0096$12.50

TABLE 1. Trimethine Salts Me_2N / \ $\overset{\oplus}{N}Me_2\overset{\ominus}{X}$ (Ia–i), R

Compound	R	X	Starting reagent	Yield, %	Mp, °C	λmax, nm, EtOH
(Ia) [4]	H	ClO_4	CH_2=CHOBu	70	120–121	312
(Ib) [10]	Me	$MeSO_4$	MeCH=CHOEt	67	*	324
(Ic) [11]	Ph	ClO_4	$PhCH_2COOH$	79	193–194	322
(Id) [11]	Cl	ClO_4	$ClCH_2COOH$	40	123–124	327
(Ie) [10]	*i*-Pr	$MeSO_4$	*i*-PrCH=CHOEt	40	*	360
(If) [12]	CN	ClO_4	Me_2NCH=CHCN	80	141–143	305
(Ig) [13]	NMe_2	ClO_4	Me_2NCH=$CHNMe_2$	67	122–123	310
(Ih) [13]	OEt	ClO_4	$Me_2NCH_2CH(OEt)_2$	67	119–121	327
(Ii) [14]	F	$MeSO_3$	FCH_2COONa	37	*	328

*Polycrystalline mass.

TABLE 2. Yields, Reaction Conditions, and Constants of Me_2N–CH=C(R)–CH(NMe_2)(Y) (IIa–i)

Compound	R	Yields, %	Ratio of aminal* (Y = NMe_2) and aminalacetal (Y = OMe)	Bp, °C (p, mm Hg)	n_D^{20}	Reaction conditions, Temp., °C (time, h)
(IIa)	H	70	9 : 1	75–80(10)	1.4750	65–70(2.5)
(IIb)	Me	65	9 : 1	77–80(7)	1.4752	75–78(1)
(IIc)	Ph	68	2 : 3	82–83(0.3)	1.5410	75–78(2)
(IId)	Cl	66	9 : 1	92–93(7)	1.4930	30–35(1) 45–50(0.2)
(IIe)	*i*-Pr	39	1 : 4	75–80(7)	1.4355	20(2.5)
(IIf)	CN**	90	9 : 1	90–95(0.35)		20(1)
(IIg)	NMe_2	67	0 : 1	80–82(10)	1.4720	75–78(2)
(IIh)	OEt	68	3 : 1	102–105(10)	1.4620	45–50(1)
(IIi)	F	65	9 : 1	70–72(10)	1.4610	45–50(0.5)

*Established from NMR spectrum (Table 3).
**Mp 62-75°C (Mp is not sharp because of aminalacetal impurity).

ochromic shift of the absorption maximum is observed, and introduction into this position of an electron accepting substituent leads to a hypsochromic shift [8, 9].

Reaction of salts (Ia-i) with MeOK in benzene with addition of 2 moles of $HNMe_2$ gives good yields of a mixture of aminals and aminalacetals (IIa-i) containing primarily in most cases the more reactive aminal (Table 2).

The structure of (IIa-i) was proved by ^1H and ^{13}C NMR spectra (Table 3). Aminal (IIh) according to ^1H and ^{13}C NMR spectra is a mixture of E and Z isomers in a ratio of 1:1. Freshly prepared alcohol solutions of (IIb-i) have UV absorption maxima (λ_{max}) corresponding to tne λ_{max} of salts (Ib-i). This indicates that compounds (IIb-i) in alcohol solution undergo transformations analogous to those found earlier for (IIa) [2].

Salts (Ia-i), which have OR^1 as counterion, unlike salt solutions, quickly transform into aldehydes (IIIa-i).

This transformation is observed by disappearance in the UV spectrum of the λ_{max} of salt (I) and appearance of the λ_{max} of aldehyde (III). Aldehydes (III) were obtained by aminoformylation either as the main product (IIIb, e, i) or as a byproduct (IIIc, d, f-h) in isolation of the corresponding trimethine salts. (Formula, top of page, following Tables 3 and 4.)

The structures of (IIIb-i) were confirmed by ^1H and ^{13}C NMR spectra (Table 4).

TABLE 3. ^1H and ^{13}C Spectra of $Me_2^aNCH=C^b(R)-CH^d(Y)-NMe_2^c$ (IIa-i)

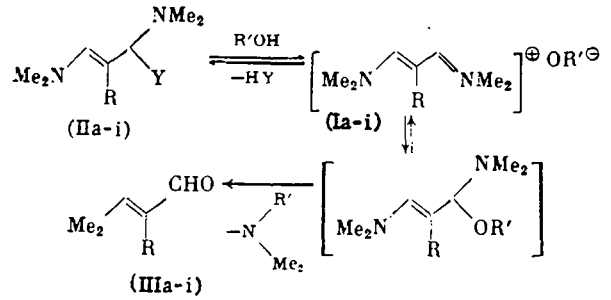
Compound	R	Y	NMR spectrum, δ, ppm from TMS: NMe_2 a	NMe_2 e	OMe	H_d	H_b	Solvent	^{13}C NMR spectrum, δ, ppm from TMS ($J_{^{13}C\,^1H}$, Hz): NMe_2	C_b	C_c	C_d	OMe	Solvent, 20% of weight of (II)
(IIa)[a]	H	NMe_2	2.57	2.10	–	2.62	5.87	Without solvent	40,57 (134,3)	142,6 (161,1)	92,94 (151,4)	88,74 (136,7)		
									41,09 (136,7)					C_6D_6
		OMe	2.57	2.24	3,17	3,92	6,02		40,39 (134,3)	144,08	94,69	97,61	54,52	
									39,24 (134,3)		(153,8)	(148,9)	(141,6)	
(IIb)[b]	Me	NMe_2	2,39	2,03		2,94	5,34	The same	41,25 (135)	140,01	114,12	91,44		C_6D_6
									40,09 (135)	(156,3)		(136,7)		
		OMe	2.43	2,09	3,07	3.47	5,54		44,33 (135)	142,00	115,39	101.97	55,22	
									44,68 (135)	(148,9)		(146,5)	(139,2)	
(IIc)[c]	Ph	NMe_2	2.41	2,31		2.55	6,03	C_6D_6	45,33 (135)	141,03	109,13	103,25	57.24	C_6D_{12}
		OMe	2,41	2,31	3,2	4,18	6,18		41,28 (133)	(162,8)		(149,8)	(139.6)	
(IId)	Cl	NMe_2	2.72	2,04		2.78	5.78	Without solvent						
		OMe	2.78	2,18	3,15	3,85	5,98							
(IIe)[d]	i-Pr	NMe_2	2.36	2,15		2;8	5,40	The same						
		OMe	2.33	2,18	3,05	4,0	5,45							
(IIf)[e]	CN	NMe_2	2,58	2,16		2,6	6,03	C_6D_6	41,60 (136,9)	150,69	70,38	89,81		
									41,15 (133,2)	(161,8)		(139,6)		C_6D_6
		OMe	2,55	2,21	3,1	3,98	6.20		39,24	150,06	73.90	97,27	55.77	
										(163,7)				
(IIg)[f]	NMe_2							Without solvent						
		OMe	2,65	2,31	3,15	3,98	5,16							
(IIh)[g]	OEt	NMe_2	2.45	2,36		4.19	5,09	C_6D_6	47,64 and	126,68				
									41,49 (132)	(162,8)	151,84			
			2.40	2,2		2,78	4,79		43,99 and	120,66				
									41,28 (132)	(158,7)	134,72			C_6D_6
		OMe	2,57	2,36	3,23	4,04	5,38		43,24 and	127,19			55,59	
									39,55 (132)	(162,8)	131,46		(140)	
(IIi)[h]	F	NMe_2	2,64	2,21		2,3	4,87		43,16, 43,07,	122,57	137,7	87,1		
									41,24 (133,5)	(162,8)		(135,0)		C_6D_6
		OMe	2,5	2,12	3,24	4,03	5,12	C_6D_6	39,21, 42,92	120,77		94,71		
									(133,5)	(162,8)				

[a]In (IIa), Y = NMe_2: chemical shift (CS) of H_c 3.9 in (IIa), Y = OMe: H_c 4.03 $J_{b,c}$ = 13, $J_{c,d}$ = 7 Hz. [b]CS of Me 1.53. [c]CS of Ph 7.0-7.6, ^{13}C NMR spectrum of aminalacetal is shown which was obtained by [6]. [d]CS of i-Pr 1.03 m. [e]CS of CN 121.27 (d 10.2, d 4.6), [f]CS of NMe_2 at C_c 2.48; [g]CS of OEt: CH_2 3.38 and 3.89, CH_3 in the region of 1.0-1.25. [h]In (IIi), Y = NMe: J_{H_bF} = 32, $J_{NMe_2,F}$ = 1.8; in (IIi), Y = OMe: J_{H_bF} = 32.6, J_{H_dF} = 9.5 Hz.

TABLE 4. Constants and UV, ^1H and ^{13}C NMR Data of $Me_2^aNCH^b\overset{|}{\underset{R}{C}}{}^c\text{-CHO}$ (IIIa-i)

Compound	R	Bp, °C (p, mm Hg)	n_D^{20}	λ_{max}, nm of C_2H_5OH	NMR spectrum, δ, ppm from TMS in $CDCl_3$			^{13}C NMR spectrum, δ, ppm from TMS ($J_{^{13}C,^1H}$, Hz)				Solvent
					NMe_2	H_b	CHO	NMe_2	C_b	C_c	CHO	
(IIIa)[a]	H	70–72 (0,3)	1,5480	287	2,85 and 2,96	7,11	8,97	37,6 and 44,2	160,1	101,2	187,6	CCl_4
(IIIb)[b,c]	Me	72–74 (0,35)		295	3,08	6,51	8,78	42,8	168,4 160,0	108,4	191,2 190,2	$CDCl_3$
(IIIc)[d]	Ph	122–125 (0,25)	1,6310	295	2,76	6,8	9,1	42,98 (130)	157,54 (163)	114,57	188,68 (166,5)	$CDCl_3$
(IIId)[e]	Cl	100–102 (0,23)	–	298	3,3	7,16	8,93					
(IIIe)[f]	*i*-Pr	90–92 (0,3)	1,5320	290	3,09	6,42	8,80	42,3 (137,8)	158,18 (160)	117,64 (21,3)	190,05 (162,8)	$CDCl_3$
(IIIf)[g,h]	CN			289	3,32 and 3,43	7,7	9,02	39,4 (142,4) 48,0 (144,4)	163,8 (168,4)	85,8	189,4 (172,0)	CD_3OD
(IIIg)[h,i]	NMe_2	65–67 (0,3)	1,5450	290	3,18	6,33	8,7					
(IIIh)[k]	OEt	88–90 (0,5)	1,5490	295	3,15	6,33	8,55					
(IIIi)[l]	F	92–94 (0,4)	1,5770	300	3,12 and 3,13	6,3	8,45	41,36 and 41,18	142,3 (165,4)	138,8	176,73 (170,9)	$CDCl_3$

[a] CS of H_c 4.95, $J_{b,c}$ = 13, $J_{H_c,CHO}$ = 8 Hz. [b] Mp 39-40°C. [c] CS of Me 1.85 ppm (PMR) and 6.2 and 8.6 ppm (^{13}C NMR). [d] CS of Ph 7.1-7.25 (PMR), 126.16, 127.24, 130.77, and 134.30 (^{13}C NMR). [e] Mp 40-43°C. [f] CS of i-Pr 1.2 ppm (PMR), 23.84 (d, 124.0) and 20.03 (q, 125.8) (^{13}C NMR). [g] Mp 141-142°C. [h] CS of CN 117.5 ppm. [i] CS of NMe_2 2.61 ppm. [k] CS of EtO 1.23 and 3.86 ppm. [l] J_{H_bF} = 27, $J_{CHO,F}$ = 20 (PMR), $J_{C_c,F}$ = 231.9, J_{C_c,H_b} = 36.0, J_{C_cCHO} = 11.0, $J_{CHO,F}$ = 14.0, J_{HCO,H_b} = 3.05 Hz.



EXPERIMENTAL

UV spectra were measured on a Specord UV VIS instrument and ^1H NMR spectra were obtained on a Bruker-250 instrument with working frequency for ^1H nuclei of 250 MHz. ^{13}C NMR spectra were obtained under pulse conditions on a Bruker-250 spectrometer with working frequency of 62.89 MHz. The internal standard was TMS.

Trimethine salts (Ia-i) and aldehydes (IIIb, e, i) were obtained based on methods shown in Table 1; changes introduced in the methods are described above.

General Method for Obtaining (IIa-i). To MeOK, obtained from 3.9 g (0.1 mole) of K dispersed in 50 ml abs. benzene and 4 ml abs. MeOH in 70 ml abs. benzene, cooled to 10°C, 13 ml Me_2NH (0.2 mole) in 13 ml abs. benzene and trimethine salt (0.1 mole) were added. After standing (time and temperature shown in Table 2) the mixture was cooled and the precipitate of inorganic salt was separated and washed with abs. benzene. The benzene solution was evaporated and the residue distilled under vacuum. The yields and constants of (IIa-i) are shown in Table 2.

Isolation of Aldehydes (IIIc, d, f, g, h). The mother liquor after separation of trimethine salt (I) was evaporated under vacuum. The residue was shaken with an equal volume of saturated K_2CO_3 for ~5 min. The organic layer was passed through a column of Al_2O_3 (height ~5-7 cm), dried with K_2CO_3, and evaporated. The residue was distilled under vacuum. Constants of (IIIc, d, f, g, h) are shown in Table 4.

CONCLUSIONS

Aminals and aminalacetals of α-substituted β-dimethylaminoacrolein were synthesized by the action of potassium methylate on meso-substituted trimethine salts in the presence of dimethylamine.

LITERATURE CITED

1. Zh. A. Krasnaya, T. S. Stytsenko, E. P. Prokof'ev, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 595 (1976).
2. Zh. A. Krasnaya and T. S. Stytsenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1060 (1981), 855 (1983).
3. H. Bredereck, F. Effenberger, D. Zeyfang, and K. A. Hirsch, Chem. Ber., 101, 4036 (1968).
4. Zh. A. Krasnaya and T. S. Stytsenko, Izv. Akad. Nauk SSSR, Ser. Khim., 850 (1983).
5. Zh. A. Krasnaya, E. P. Prokof'ev, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 123 (1978).
6. Zh. A. Krasnaya and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 1064 (1980).
7. Zh. A. Krasnaya, T. S. Stytsenko, V. S. Bogdanov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1075 (1985).
8. M. J. S. Dewar, J. Chem. Soc., 2329 (1950).
9. E. B. Khott, Chem. Soc., 1024 (1951).
10. S. M. Makin, O. A. Shavrygina, M. I. Berezhnaya, and T. P. Kolobova, Zh. Org. Khim., 8, 1394 (1972).
11. Ch. Jutz, R. Kircheechner, and H. Seidel, Chem. Ber., 102, 2301 (1969).
12. J. Kučera and Z. Arnold, Collect. Czech. Chem. Communs., 32, 1704 (1967).
13. Z. Arnold, Collect. Czech. Chem. Communs., 38, 1168 (1973).
14. C. Reichardt and K. Halbriffer, Liebigs, Ann. Chem., 737, 99 (1970).