ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 4, pp. 574–577. © Pleiades Publishing, Inc., 2006.
Original Russian Text © M.O. Manukyan, A.V. Babakhanyan, G.A. Panosyan, S.T. Kocharyan, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 4, pp. 604–607.

Cyclodimerization of 3,2-Stevens Rearrangement Products of 1,9-Bisammonium Salts Containing a 5-Oxanonane-2,7-diyne-1,9-diyl Group

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Received January 13, 2005

Abstract — 1,9-Bisdimethylammonium salts containing a 5-oxanonane-2,7-diyne-1,9-diyl along with alkoxycarbonylalkyl group, undergo double 3,2-Stevens rearrangement under the action of corresponding sodium alcoholates to form allene diamino esters whose prototropic isomerization under the action of dilute HCl gives rise to diketo diesters. The latter undergo 1,4-alcohol elimination under the reaction conditions and yield diene keto esters that cyclodimerize into cyclohexene derivatives. The bisammonium salt with a cyanomethyl group rearranges to form an allene dinitrile, which isomerizes into a diene compound.
DOI: 10.1134/S107036320604013X

According to published data, ammonium salts comprising an alkoxycarbonylmethyl and a propargyl groups, under the action of sodium alcoholates in diethyl ether or benzene undergo 3,2-Stevens rearrangement to form diene amino esters [1]. It is also known that structurally related ammonium salts with a 4-alkoxy-2-butynyl group under the action of sodium alcoholates form 3,2-Stevens rearrangement products whose protoropic isomerization and hydrolysis under the action of dilute HCl gives rise to 3-alkoxy-2-oxo-3-pentenoic acids. The latter eliminate alcohol under the reaction conditions, yielding diene keto esters that cyclodimerize into cyclohexene derivatives [2].

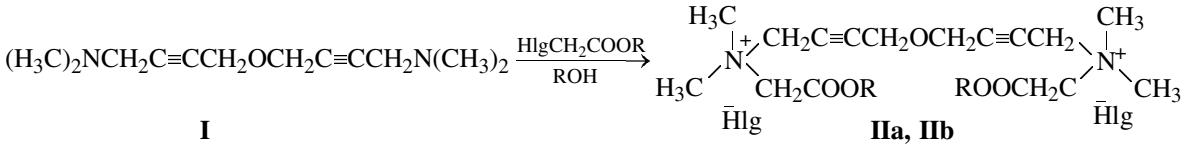
Of particular interest was to study the Stevens rearrangement of bisammonium salts containing, along with alkoxycarbonylmethyl, a common 5-oxanonane-2,7-diyne-1,9-diyl group. The presence of this group in the starting salt makes possible double Stevens rearrangement with formation of various intermediates that present interest in terms of various transformations, including cyclodimerization [2]. Our research showed that the starting bisammonium salts under successive treatment with basic and acidic agents behave similarly to monoammonium salts. The final reaction products are the same cyclohexene derivatives as those obtained previously by cyclodimerization of the intermediate diene keto esters [2] (Table 1).

Salt **VIII** containing a cyanomethyl group rearranges in a similar way. In view of the fact that highly unsaturated diamines **IVa**, **IVb**, and **IX** are impossible to distill, they were purified by column chromatography. Therewith, almost pure diamines were obtained. According to ^{1}H and ^{13}C NMR data, diene aminonitrile **XI** exists as four isomers, the three of which have *Z,Z*, *E,E*, and *E,Z* configurations. As to the fourth isomer, its existence is hardly imaginable. Probably, exists due to the presence of two competing conjugations, rendering the bond between the 3- and 4-C atoms partiallly double-bond character; as a result, free rotation about this bond is hindered.

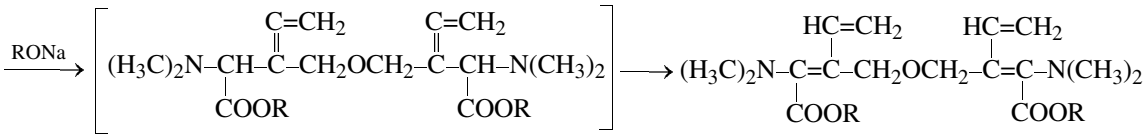
The similar behavior of mono- and bisammonium salts in this reaction makes it an interesting object for study. A principal characteristic feature of the Diels–Alder reaction with keto esters **VIa** and **VIb** is that it occurs in mild conditions and requires no heating which is most frequently required in diene syntheses.

According to published data [3], the 1,4-alcohol elimination from compounds **Va** and **Vb** gives rise to *cis*-diene keto esters **VIa** and **VIb**, since the *trans*-diene components are known not to be involved in diene syntheses.

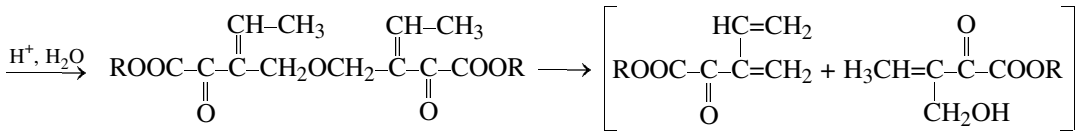
The structure of the resulting compounds was proved by the ^{1}H and IR spectra, and their purity was checked by GLC. The structure of the products was



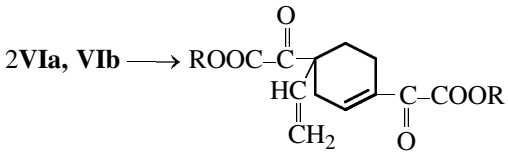
I **IIa, IIb**



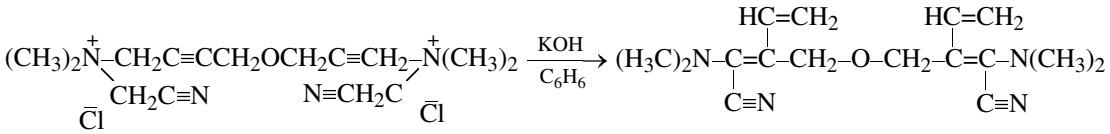
IIIa, IIIb **IVa, IVb**



Va, Vb **VIa, VIb**



VIIa, VIIb



VIII **IX**

R = CH_3 (**a**), C_2H_5 (**b**); Hlg = Br (**a**), Cl (**b**).

also studied by ^{13}C NMR spectroscopy, as well as COSY, DEPT, HMQC, and NOESY which allowed us to assign the ^1H and ^{13}C NMR spectra. In particular, the ^{13}C NMR spectrum contains four signals, two of which belong to the carbonyl group and two, to the ester group (Table 2).

Table 1. Yields, constants, and elemental analyses of compounds **IIa, IIb, IVa, IVb, VIIa, VIIb, VIII**, and **IX**

Comp. no.	Yield, %	Found, %				Formula	Calculated, %			
		C	H	N	Hlg		C	H	N	Hlg
IIa [a]	97	–	–	5.28	33.11	$C_{18}H_{30}Br_2N_2O_5$	–	–	5.78	33.06
IIb [a]	95	–	–	5.68	16.07	$C_{20}H_{34}Cl_2N_2O_5$	–	–	6.18	15.67
IVa [b]	32	60.73	7.53	7.41	–	$C_{18}H_{28}N_2O_5$	61.36	7.95	7.95	–
IVb [b]	29	62.72	7.92	6.82	–	$C_{20}H_{32}N_2O_5$	63.16	8.42	7.37	–
VIIa [c]	25	59.45	5.23	–	–	$C_{14}H_{16}O_6$	60.00	5.71	–	–
VIIb [c]	21	61.74	6.77	–	–	$C_{16}H_{20}O_6$	62.34	6.49	–	–
VIIIa	98	–	–	7.34	20.15	$C_{16}H_{24}Cl_2N_4O$	–	–	7.79	19.78
IXb	37	67.63	8.09	19.13	–	$C_{16}H_{22}N_4O$	67.13	7.69	19.58	–

[a] Hygroscopic. [b] Undergo tarring when distilled; R_f for **IVa, IVb**, and **IX** are 0.81, 0.71, and 0.77, respectively. [c] Compound **VIIa**: bp 185–188°C (2 mm Hg.), n_D^{20} 1.5040; compound **VIIb**: bp 188–191°C (1 mm Hg), n_D^{20} 1.4967.

Table 2. IR and ^1H and ^{13}C NMR spectra of compounds **IIa, IIb, IVa, IVb, VIIa, VIIb, VIII**, and **IX**

Comp. no.	IR spectrum, cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)
IIa	1075, 1230, 1725 (COO, O), 2240 (C≡C)	3.41 s (12H, NCH_3), 3.82 s (6H, OCH_3), 4.60 s (4H, $NCH_2C{\equiv}C$), 4.75 s (4H, OCH_2), 4.83 s (4H, NCH_2COO)
IIb	1075, 1225, 1730 (COO, O), 2240 (C≡C)	1.38 t (6H, CH_3CH_2, *J* 7.1), 2.44 s (12H, NCH_3), 3.43 s (4H, $NCH_2C{\equiv}C$), 4.30 q (4H, CH_3CH_2, *J* 7.2), 4.41 s (4H, OCH_2), 4.84 s (4H, NCH_2COO)
IVa	920, 990, 1620, 1630, 3090(C=C), 1075, 1230, 1725 (COO)	2.42 s (12H, NCH_3), 3.35 s (6H, OCH_3), 3.78 s (4H, OCH_2), 4.90–5.45 m (4 H, CH_2=), 6.28–6.42 m (2H, CH=)
IVb	920, 990, 1620, 1630, 3095 (C=C), 1070, 1235, 1725 (COO)	1.05 t (6H, CH_3CH_2, *J* 7.2), 2.32 s (12H, NCH_3), 3.44 q (4H, OCH_2CH_3, *J* 7.2), 3.76 s (4H, OCH_2), 4.80–5.42 m (4H, CH_2=), 6.20–6.37 m (2H, CH=)
VIIa [a]	920, 990, 1630, 1645, 3025, 3090 (C=CH, $CH{=}CH_2$), 1070, 1145, 1250, 1725 (COO), 1680 (C=O)	2.04 d.d.d (1H, *J* 13.5, 7.2 and 6.1, CH_2) and 2.21 d.m (1H, *J* 13.5, CH_2), 2.30–2.37 m (2H, CH_2), 2.62 d.m (1H, *J* 19.9, CH_2) and 2.89 d.m (1H, *J* 19.9, CH_2), 3.83 s (3H, OCH_3), 3.88 s (3H, OCH_3), 5.19 d (1H, *J* 17.6, $=CH_2$) and 5.34 d (1H, *J* 10.7, $=CH_2$), 5.92 d.d (1H, *J* 7.6 and 10.7, =CH), 7.01 t.t (1H, *J* 4.1 and 1.8, =CH)
VIIb	920, 990, 1630, 1645, 3020, 3090 (C=CH, $CH{=}CH_2$), 1075, 1140, 1250, 1725 (COO), 1680 (C=O)	1.34 t (3H, *J* 7.1, OCH_2CH_3), 1.37 t (3H, *J* 7.1, OCH_2CH_3), 2.03 d.d.d (1H, *J* 13.5 and 6.1, CH_2) and 2.19 m (1H, CH_2), 2.30–2.376 m (2H, CH_2), 2.60 d. m (1H, *J* 19.9, CH_2) and 2.89 d.m (1H, *J* 19.9, CH_2), 4.28 q (2H, OCH_2CH_3), 4.33 q (2H, *J* 7.1, OCH_2CH_3), 5.18 d (1H, *J* 17.5, $=CH_2$) and 5.33 d (1H, *J* 10.7, $=CH_2$), 5.92 d.d (1H, *J* 17.6 and 10.7, =CH), 6.99 t. t (1H, *J* 4.2 and 1.9, =CH)
VIII	2225 (C≡C), 2250 (C≡N), 1070, 1150, 1225 (COC)	3.37 s (12H, NCH_3), 4.44 s (4H, OCH_2), 4.83 s (4H, $CH_2C{\equiv}C$), 5.22 s (4H, $CH_2C{\equiv}N$)
IX [b]	920, 990, 1615, 1630, 3020, 3095 (C=C), 1070, 1140, 1220 (COC), 2205 (C≡N)	2.63, 2.61, 2.61, and 2.60 s (12H, NCH_3), 4.36, 4.33, 4.33, and 4.06 s (4H, OCH_2), 5.40 and 5.40 d.d (2H, CH_2=, *J* 11.0, 1.4), 5.69 and 5.65 d. d (2H, CH_2=, *J* 17.8, 1.4), 6.67 and 6.77 d.d (0.7H, CH=, *J* 17.1, 11.0), 6.83 and 6.83 d.d (1.3H, CH=, *J* 17.8, 11.2)

[a] ^{13}C NMR spectrum, δ_C, ppm: 19.80 (CH_2), 28.20 (CH_2), 32.50 (CH_2), 51.55 (C), 52.54 (OCH_3), 52.61 (OCH_3), 118.98 ($=CH_2$), 135.16 (=C), 136.98 (=CH), 145.08 (=CH), 162.33 (COO), 186.48 (CO), 194.77 (CO). [b] ^{13}C NMR spectrum, δ_C, ppm: 43.38, 43.80 (NCH_3), 62.93, 63.30, 66.60, 67.49 (OCH_2), 112.19, 112.34, 112.68, 112.74 (C≡N), 118.94, 119.26, 119.34, 119.77 (CH_2=), 126.34, 126.43, 126.80, 126.84 (*C*=CN), 130.09, 130.28, 132.11, 132.17 (CH=), 135.46, 135.67, 137.27, 138.24 (=CN).

EXPERIMENTAL

The IR spectra were measured on UR-20 and Specord IR-75 instruments in mineral oil or in thin film. The ^1H NMR spectra were obtained on a Varian Mercury-300 spectrometer (300.075 MHz for ^1H and 75.46 MHz for ^{13}C) in DMSO-d_6–CCl_4, 1 : 3, and $CDCl_3$ at 303 K; internal reference TMS.

Gas chromatography was performed on an LKhM-80 instrument, thermal conductivity detector, oven temperature 50–220°C (16 deg min^{-1}), 2000 × 3 mm, 10% Apiezon-L on Inerton-AW (0.20–0.25 mm), carrier gas helium, rate 60 ml min^{-1}.

Thin-layer chromatography was performed on Silufol UV-254 plates in benzene–hexane, 2 : 1; development in iodine vapor. Preparative separation was performed by column chromatography on silica gel (L 40/100).

Ammonium salts IIa, IIb, and VIII. A mixture of 0.02 mol of 4,4'-oxybis[(but-2-ynyl)dimethylamine] (**I**) prepared by the Mannich reaction [4], and 0.04 mol of alkyl monobromo(chloro)acetate or chloroacetonitrile in 7 ml of absolute methanol or ethanol was allowed to stand at room temperature for 2–3 days (in the case of chlorides, the reaction mixture was heated for 2–3 h at 40–45°C). The resulting salt was washed with absolute diethyl ether and dried in a dessicator over $CaCl_2$.

Rearrangement of ammonium salts IIa, IIb, and VIII. *a*. To 0.016 mol of salt **IIa** or **IIb** in 10 ml of absolute diethyl ether, 0.048 mol of sodium alkoxide (obtained from 0.048 mol of sodium and 8–10 ml of

methanol or ethanol) and 3 drops of corresponding alcohol were added. With salt **VIII**, potassium hydroxide in benzene was used as the basic reagent. The reaction mixture was intermittently stirred and ground. After heat release was complete, the mixture was refluxed for 20 min, after which diethyl ether and water were added. The ethereal layer was separated, and the aqueous layer was extracted with two portions of diethyl ether. The combined extracts were dried with magnesium sulfate. The ether was removed by distillation to obtain 2.9, 3.2, and 3.3 g of compounds **IVa**, **IVb**, and **IX**, respectively, that were purified by column chromatography to obtain 1.8, 1.74, and 1.7 g of individual compounds **IVa**, **IVb**, and **IX**.

b. Rearrangement of salts **IIa** and **IIb** was performed in a similar way. The only difference was that the combined ethereal extracts were treated with 1.5 N HCl. The ethereal layer was separated, and the residue was treated with two portions of diethyl ether. The combined ethereal extracts were dried with magnesium sulfate and distilled.

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