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SYNTHESIS OF 1,4,5,6-TETRAHYDROPYRIDINE DERIVATIVES STARTING FROM trans-3-CHLORO-1,3-ALKADIEN-5-ONES

G. G. Melikyan, K. A. Atanesyan,
G. Kh. Aslanyan, M. R. Tirakyan,
L. A. Khachatryan, and Sh. O. Badanyan

UDC 547.385.2'821'822.07:543.422

A method has been developed for the synthesis of 3-carbethoxy-2-methyl-6-(oxoalkylidene)-1,4,5,6-tetrahydropyridines by reaction of trans-3-chloro-1,3-alkadien-5-ones with ethyl aminocrotonate. It is shown that the corresponding vinylacetylanic ketones are intermediate products of the reactions.

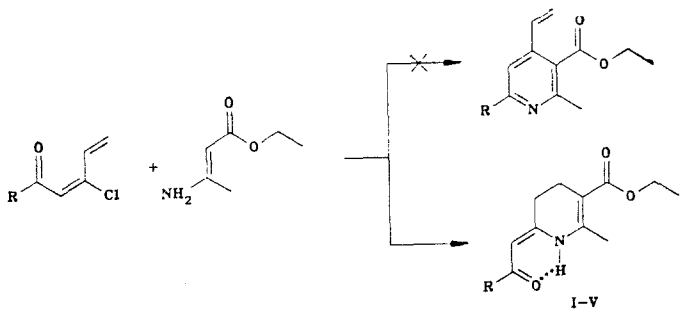
β-Chlorovinyl ketones are reagents for C-, N-, O-, P-, and S-ketovinylation [2]. In particular, reaction of β-chlorovinyl ketones with ethyl aminocrotonate gives ethyl esters of 2-methyl-6-alkylnicotinic acid [3].

With a view to developing a method for the synthesis of nitrogen-containing heterocyclic compounds, it was of interest to react vinyl-substituted derivatives of β-chlorovinyl ketones — trans-3-chloro-1,3-alkadien-5-ones — in an analogous manner. The reactions were conducted without a solvent at 100°C with a molar ratio of dienone—ethyl aminocrotonate of 1:2.5. It turned out that the reaction products were not ethyl 4-vinyl-2-methyl-6-alkylnicotinates but 3-carbethoxy-2-methyl-6-(2-oxoalkylidene)-1,4,5,6-tetrahydropyridines.

β-Chlorovinyl ketones react with ethyl aminocrotonate through the chlorovinyl and carbonyl groups [3]. In the case of trans-3-chloro-1,3-alkadien-5-ones, as is evident from the structure of compounds I-V, the chlorovinyl and terminal vinyl groups participate in the reaction.

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375094.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 497-500, April, 1987. Original article submitted June 5, 1985; revision submitted May 7, 1986.

 0009-3122/87/2304-0414$12.50



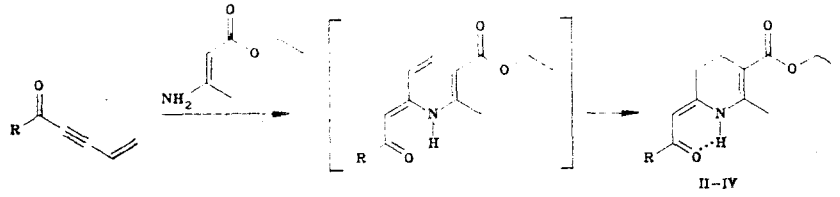
I–V

I R=CH_3, II R=C_2H_5, III R=C_3H_7, IV R=i-C_3H_7, V R=C_4H_9

It is known from the literature [4] that the signal from the NH proton in the PMR spectra of the trans-isomers of β-aminovinyl ketones occurs at 5.00-6.75 ppm while in the cis-isomers it occurs at 9.70-14.0 ppm. In compounds I-V the signals from the NH protons appear at 11.3-11.5 ppm so that it can be concluded that they exist in a cis-chelated form. This is in agreement with the available data concerning the shift of the configurational equilibrium in the direction of the cis-isomer [5] in the case of nitrous derivatives of β-diketones.

The structure of compounds I-V indicates that in the reaction process there is a change in geometry of the $C_{(3)}$—$C_{(4)}$ double bond. The cis configuration of the acetyl and vinyl groups in the initial trans-3-chloro-1,3-alkadien-5-ones changes to trans in the reaction products. The fact that the geometry of the double bond has changed makes it possible to suggest that initially there is an apparent dehydrochlorination of trans-3-chloro-1,3-alkadien-5-ones when treated with ethyl aminocrotonate acting as a base to give vinylacetylenic ketones, which then undergo an additive cyclization reaction via the multiple bonds with a second molecule of ethyl aminocrotonate.

In order to confirm this proposal, the reaction of vinylacetylenic ketones with ethyl aminocrotonate was carried out under similar conditions with a ratio of reagents of 1:1. As expected, 1,4,5,6-tetrahydropyridine derivatives II-IV were obtained as a result of the reactions. It is possible that initially there is trans-addition of ethyl aminocrotonate to the triple bond of the vinylacetylenic ketone to give the corresponding intermediate, which is converted to compounds II-IV as a result of intramolecular cyclization.



II–IV

EXPERIMENTAL

PMR spectra in CCl_4 were obtained on a Perkin—Elmer R12B (60 MHz) spectrometer, with TMS as internal standard. ^{13}C NMR spectra were recorded on a Bruker WH-90 instrument (22.63 MHz) without suppression and with complete suppression of spin-spin coupling. IR spectra were re-

TABLE 1. Constants of Compounds I-V

Compound	bp, °C (mm Hg)	n_D^{20}	TLC*, R_f	Empirical formula	M·	Yield, % †
I	127 (1)	1,5660	0,34	$C_{12}H_{17}NO_3$	223	45
II	147 (1)	1,5684	—	$C_{13}H_{19}NO_3$	237	42 (50)
III	166 (1)	1,5606	0,42	$C_{14}H_{21}NO_3$	251	43 (44)
IV	160 (1)	1,5503	0,45	$C_{14}H_{21}NO_3$	251	58 (60)
V	186 (2) [T_{mp} 37]	(n_D^{38} 1,5501)	0,46	$C_{15}H_{23}NO_3$	265	47

*Eluent hexane—ether (1:1).

†Yields of the reactions of vinylacetylenic ketones with ethyl aminocrotonate are given in brackets.

TABLE 2. Spectral Characteristics of 1,4,5,6-Tetrahydropyridine Derivatives I-V

Compound	IR spectrum, cm^{-1}			PMR spectrum, ppm
	C=C	C=O	$COOC_2H_5$	
I*	1575	1633	1695	1,22 (3H, t, CH_3); 2,0 (3H, s, CH_3); 2,3 (3H, s, 2-CH_3); 2,41 (4H, s, 4-CH_2, 5-CH_2); 4,13 (2H, q, OCH_2); 5,13 (1H, s, CH); 11,40 (1H, broad. s, NH); $J_{CH_3-CH_2}$ =7,3 Hz
II	1575	1625	1690	1,0 (3H, t, CH_3); 1,2 (3H, t, CH_3); 2,23 (2H, q, CH_2CO); 2,3 (3H, s, 2-CH_3); 2,4 (4H, s, 4-CH_2, 5-CH_2); 4,08 (2H, q, OCH_2); 5,04 (1H, s, CH); 11,33 (1H, broad. s, NH); $J_{CH_3-CH_2}$=6,6 (OC_2H_5), $J_{CH_3-CH_2}$=7,1 Hz
III	1573	1626	1693	0,87 (3H, broken t, CH_3), 1,22 (3H, t, CH_3); 2,21 (2H, t, CH_2CO); 2,3 (3H, s, 2-CH_3); 2,4 (4H, s, 4-CH_2, 5-CH_2); 4,1 (2H, q, OCH_2); 5,06 (1H, s, CH); 11,48 (1H, broad. s, NH); $J_{CH_3-CH_2}$=7,3(OC_2H_5), $J_{CH_3(CH_2)-CH_2}$=6,9 Hz
IV	1575	1625	1690	1,0 (6H, d, $2CH_3$); 1,21 (3H, t, CH_3); 2,3 (3H, s, 2-CH_3); 2,4 (4H, s, 4-CH_2, 5-CH_2); 4,1 (2H, q, OCH_2); 5,08 (1H, s, CH); 11,52 (1H, broad s, NH); $J_{CH_3-CH(CH_2)}$=6,8 Hz
V	1586	1635	1700	0,86 (3H, broken t, CH_3); 1,21 (3H, t, CH_3); 1,0—1,75 (4H, m, $2CH_2$); 2,3 (3H, s, 2-CH_3); 2,4 (4H, s, 4-CH_2, 5-CH_2); 4,08 (2H, q, OCH_2); 5,02 (1H, s, CH); 11,45 (1H, broad. s, NH); $J_{CH_3-CH_2}$=6,8 Hz (OC_2H_5)

*^{13}C NMR spectrum ($CDCl_3$): 14.2 (q, $GOOCH_2CH_3$), 19.3 ,q, 2—CH_3), 20.0; 27.4 (t, C_4, t, C_5), 29.5 (q, $\underline{CH_3}CO$), 59.6 (t, $COO\underline{CH_2}CH_3$), 98.2 (d, CH), 103.9 (s, C_3), 144.9; 154.6 (s, C_2, s, C_6), 167.1 (s, $\underline{COOC_2H_5}$), 198.2 m. d (s, $CH_3\underline{CO}$).

corded in CCl_4 on a UR-10 instrument, mass spectra were recorded on a MX-1303 spectrometer with electron ionization energy of 30 eV. TLC analysis was carried out on Silufol UV-254 plates with development under UV light.

trans-3-Chloro-1,3-alkadien-5-ones were obtained according to the method in [6], vinylacetylenic ketones according to the method in [7], and ethyl aminocrotonate according to the method in [8]. Constants and spectral characteristics of 3-carbethoxy-2-methyl-6-(2-oxoalkylidene)-1,4,5,6-tetrahydropyridines (I-V) are given in Tables 1 and 2.

Reaction of trans-3-Chloro-1,3-alkadien-5-ones with Ethyl Aminocrotonate. A mixture of 0.02 mole of trans-3-chloro-1,3-alkadien-5-one and 0.05 mole of ethyl aminocrotonate was heated for 1h at 100°C (reaction monitored by TLC). After cooling to 20°C, the reaction mixture was saturated with K_2CO_3, agitated for 10 min, and extracted with ether (4 × 20 ml). The ether solution was washed with water and dried over Na_2SO_4. The ether was evaporated and the residue distilled. Samples of compounds I-V for analysis were isolated by preparative TLC on plates (20 × 20 cm) with Al_2O_3 (Brockmann activity II) as sorbent in the system hexane—ether (2:1).

Reaction of Vinylacetylenic Ketones with Ethyl Aminocrotonate. A mixture of 0.02 mole of vinylacetylenic ketone and 0.02 mole of ethyl aminocrotonate was heated for 1 h at 100°C. The reaction mixture was distilled. Samples of compounds II-IV for analysis were obtained by preparative TLC under the conditions given above.

trans-3-Chloro-1,3-heptadien-5-one. $CH_3CH_2COCH_D{=}CClCH_C{=}CH_AH_B$, bp 63-64°C (3 mm), n_D^{20} 1.5170, yield 57%. PMR spectrum: 1.01 (3H, t, CH_3); 2.42 (2H, q, CH_2); 5.60 (1H, d. d. d, A-H, J_{AC} = 10.6, J_{AB} = J_{AD} = 1.6 Hz); 5.98 (1H, split d, B-H, J_{BC} = 17.0 Hz); 6.4 (1H, m, D-H); 7.76 m. d. (1H, d. d, C-H). IR spectrum: 1556, 1607 (C=C-C=C), 1681 cm^{-1} (C=O). Found, %: C 58.1, H 6.3. C_7H_9ClO. Calculated, %: C 58.1, H 6.2.

trans-3-Chloro-1,3-Octadien-5-one. $CH_3CH_2CH_2COCH_D{=}CClCH_C{=}CH_AH_B$, bp 51°C (1 mm), n_D^{20} 1.5073, yield 47%. PMR spectrum: 0.86 (3H, t, CH_3); 1.57 (2H, sextet, CH_2); 2.38 (2H, t, CH_2); $J_{CH_3-CH_2}$ = 6.6 Hz); 5.60 (1H, d. d. d, A-H, J_{AC} = 10.7, J_{AB} = J_{AD} = 1.7 Hz); 5.97 (1H, d. d. d, B-H, J_{BC} = 16.8, J_{BD} = 0.7 Hz); 6.39 (1H, m, D-H); 7.77 m. d. (1H, d. d. d, C-H, J_{CD} = 0.7 Hz). IR spectrum: 1550, 1600 (C=C-C=C), 1680 cm^{-1} (C=O). Found, %: C 60.6, H 7.2. $C_8H_{11}ClO$. Calculated, %: C 60.9, H 6.9.

trans-3-Chloro-6-methyl-1,3-heptadien-5-one. $(CH_3)_2CHCOCH_D{=}CClCH_C{=}CH_AH_B$, bp 47°C (1 mm), n_D^{20} 1.5086, yield 48%. PMR spectrum: 1.05 (6H, d, $2CH_3$); 2.58 (1H, septet, CH); 5.63 (1H, d. d. d, A-H, J_{AC} = 10.0, J_{AB} = J_{AD} = 1.3 Hz); 6.0 (1H, split d, B-H, J_{BC} = 15.8 Hz); 6.47 (1H, m, D-H), 7.78 m. d. (1H, d. d, C-H). IR spectrum: 1555, 1608 (C=C-C=C), 1685 cm^{-1} (C=O). Found, %: C 60.5, H 6.5. $C_8H_{11}ClO$. Calculated, %: C 60.9, H 6.9.

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STABLE N-ACYL PYRIDINIUM AND BENZPYRIDINIUM SALTS AS ALKYLATING AGENTS

A. I. Kostin, A. K. Sheinkman, and A. S. Savchenko

UDC 547.821.3.07:543.87:541.127

The reaction of acyl chlorides with pyridinium bases and antimony pentachloride yields stable N-acyl salts that are efficient acylating agents. The kinetics of the reaction of N-acyl-pyridinium salts with p-nitroaniline was studied, and the reactivities of acylpyridinium cations and the ion pairs were determined.

The nucleophilic mechanism of acylation catalyzed by pyridinium salts assumes the intermediate formation of N-acylpyridinium salts as the active acylating agents [1]. But until now there have been no quantitative data to characterize the acylating capability of most such salts; this is evidently due to their extreme sensitivity to traces of moisture which makes it very laborious to work with them. The exceptions are the relatively stable N-acyl salts of 4-N,N-dimethylaminopyridine, the acylating capability of which has been studied [2].

A communication has recently appeared on the synthesis of N-acetyl-, propionyl-, and benzylpyridinium hexafluoroantimonates by acylation of pyridine with solutions of carboxonium salts in SO_2 [3]. N-nitro- and N-nitrosopyridinium fluoroborates have been synthesized analogously [4]. Detailed syntheses of stable N-acyl imidazole salts have been described [5].

We have obtained stable N-acyl pyridinium (Ia-c), quinolinium (IIa-c), isoquinolinium (III), and acridinium (IVb, c) salts and have studied their acylating capability. These salts were synthesized as described in [6], by the successive addition to acyl halide solution of equivalent amounts of pyridinium base and antimony pentachloride at −50°C. The compounds thus obtained are shown in Table 1.

In the IR spectrum of the synthesized substance a strong absorption band is observed in the region 1780-1815 cm^{-1} of the vibrational valency of the carbonyl group of an acyl residue. The position of this band indicates the linkage of the acyl residue with the quarternary nitrogen atom.

Donetsk State University, Donetsk 340055.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 501-504, April, 1987. Original article submitted April 25, 1985; revision submitted May 5, 1986.

0009-3122/87/2304-0417$12.50