INTRAMOLECULAR CYCLIZATION OF PROPARGYL ARYLCARBAMATES

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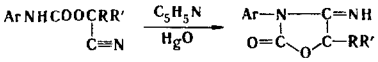
UDC 547.787.1+632.938

It was found that the products of intramolecular cyclization of alkynyl arylcarbamates have an oxazolidine structure.

We have previously shown that when α-cyanoalkyl esters of arylcarbamic acids are heated in the presence of pyridine or red mercuric oxide they undergo intramolecular cyclization to give oxazolidine derivatives [1]:

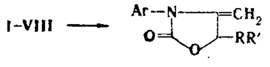


We have synthesized I-VIII, which contain a $C{\equiv}C$ triple bond in place of the $C{\equiv}N$ triple bond, by reaction of aryl isocyanates with alkynyl alcohols, as described in an American patent [2].

$$ArN{=}C{=}O + HOCRR'C{\equiv}CR'' \longrightarrow ArNHCOORR'C{\equiv}CR''$$

I-VIII

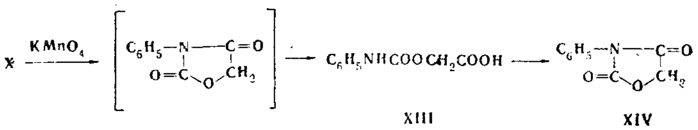
In pyridine at high temperatures these alkynyl carbamates (I-VIII) are cyclized to 2-oxo-3-aryl-4-methylideneoxazolidines or their 5,5'-dimethyl derivatives:



IX-XII

Inasmuch as the literature contains contradictory data regarding the six- [3] or five-link [4] structure of the condensation products, in the present paper we present new arguments in favor of oxazolidine structure of IX-XII. Absorption bands characteristic for $C{\equiv}C$ and $\equiv CH$ groups (2100, 3300 cm^{-1}) are absent in the IR spectra of these compounds, but bands corresponding to the absorption of an exocyclic $C{=}CH_2$ group [5] at 1635 and 1630 cm^{-1} and corresponding to the absorption of the $C{=}O$ groups of the oxazolidine ring [6] at 1730 and 1690 cm^{-1} appear.

In addition, the presence of an oxazolidine ring in the heterocyclization products was confirmed by some of their transformations. The product of intramolecular cyclization of propynyl N-phenylcarbamate was used as the object of the investigation. The previously described carboxymethyl N-phenylcarbamate (XIII), which is converted to 3-phenyloxazolidine-2,4-dione (XIV) on heating [7], was obtained by oxidative degradation of this product:



XIII XIV

However, the formation of XIII might have been represented as occurring not only from a five-membered ring but also from a six-membered ring.

Armenian Agricultural Institute, Yerevan. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1477-1480, November, 1974. Original article submitted June 12, 1972; revision submitted March 18, 1974.

TABLE 1. Ar-NHCOOCRR'C≡CR"

Compound	Ar	R	R′	R″	mp, °C	Empirical formula	R_f	Found, %				Calculated, %				Yield, %
								C	H	Cl	N	C	H	Cl	N	
I	C_6H_5	CH_3	CH_3	H	97–98*	$C_{12}H_{13}NO_2$	0,54	70,6	6,0	—	6,8	70,9	6,4	—	6,9	95
II	C_6H_5	H	H	H	63–64 †	$C_{10}H_9NO_2$	0,38	68,1	5,4	—	8,0	68,6	5,1	—	8,0	99
III	C_6H_5	CH_3	CH_3	$CH{=}CH_2$	98–99	$C_{14}H_{15}NO_2$	0,56	73,0	6,8	—	6,4	73,4	6,6	—	6,1	70
IV	C_6H_5	H	H	CH_3	68–69	$C_{11}H_{11}NO_2$	0,63	69,4	6,0	—	7,7	69,8	5,8	—	7,4	81
V	p-ClC_6H_4	CH_3	CH_3	H	116–117	$C_{12}H_{12}NO_2Cl$	0,60	60,9	5,3	14,4	5,6	60,6	5,0	20,0	5,9	66
VI	p-ClC_6H_4	H	H	H	126–128	$C_{10}H_8NO_2Cl$	0,58	57,8	4,2	16,6	7,0	57,3	3,8	16,9	6,7	89
VII	p-ClC_6H_4	CH_3	CH_3	$CH{=}CH_2$	107–109	$C_{14}H_{14}NO_2Cl$	0,72	63,3	5,8	13,3	4,8	63,7	5,3	13,5	5,3	60
VIII	p-ClC_6H_4	H	H	CH_3	121–123	$C_{11}H_{10}NO_2Cl$	0,58	58,8	4,9	15,6	6,0	59,0	4,4	15,9	6,3	80

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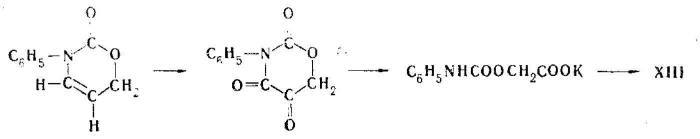
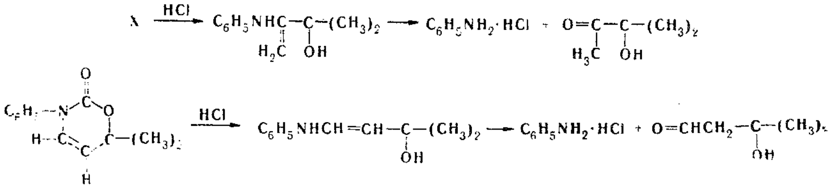
* Mp 103.2-103.5° [2], 98-99° [4].

† Mp 62.4-62.7° [2].



The choice between these two schemes could be made only if we were able to isolate the intermediate 3-phenyloxazolidine-2,4-dione, the formation of which would confirm the presence of a five-membered ring. However, the isolation of this compound under the conditions of the oxidation reaction does not seem possible. The assumption that the intermediate 3-phenyloxazolidine-2,4-dione is cleaved to carboxymethyl N-phenylcarbamate under the influence of the potassium hydroxide liberated during the oxidation by potassium permanganate was confirmed. We have previously shown that the hydrochloride of 2-oxo-3-phenyl-4-iminooxazolidine is extremely unstable in aqueous media and undergoes hydrolysis to give 3-phenyloxazolidine-2,4-dione [1], which, as demonstrated by our special experiments, is actually converted completely to carboxymethyl N-phenylcarbamate under the influence of dilute potassium hydroxide solution at room temperature.

Data obtained during the acid hydrolysis of the starting heterocycles constitute evidence in favor of the five-membered ring. It was shown that most of the compounds obtained are resinified under the influence of concentrated hydrochloric acid. An exception to this is the product of heterocyclization of α,α-dimethylpropynyl N-phenylcarbamate, the acid hydrolysis of which gave aniline hydrochloride. The formation of the latter could again be represented by two schemes, which, however, should lead to the preparation of different carbonyl compounds.



The carbonyl compound formed was identified in the form of the dinitrophenylhydrazone. If the starting compound is an oxazolidine derivative, one should have expected the formation of 3-methyl-3-hydroxy-2-butanone, the dinitrophenylhydrazone of which is described in [8] and melts at 139-140°. The dinitrophenylhydrazone that we isolated does not depress the melting point of an authentic sample of 3-methyl-3-hydroxy-2-butanone dinitrophenylhydrazone.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The individuality of the substances was monitored by thin-layer chromatography (TLC) on activity II Al_2O_3 in an acetone–hexane system (20 : 80 or 15 : 85), and the chromatograms were developed with a 0.5% solution of $AgNO_3$ and in UV light.

Alkynyl Esters of Arylcarbamic Acids (I-VIII, Table 1). One to two drops of pyridine were added with stirring and cooling with ice water to a mixture of 20 mmole of aryl isocyanate and 22 mmole of alkynylcarbinol, and the mixture was allowed to stand overnight at room temperature. The reaction product was recrystallized from octane.

TABLE 2. Oxazolidines

Compound	Ar	R	R′	mp, °C	Empirical formula	R_f	Found, %			Calc., %			Yield, %
							C	H	N	C	H	N	
IX	C_6H_5	CH_3	CH_3	124—125*	$C_{12}H_{13}NO_2$	0,69	71,3	6,1	7,2	70,9	6,4	6,9	94
X	C_6H_5	H	H	89—90†	$C_{10}H_9NO_2$	0,68	68,9	4,9	8,2	68,6	5,1	8,0	86
XI	*p*-ClC_6H_4	CH_3	CH_3	127—128	$C_{12}H_{12}NO_2Cl$	0,34	60,3	5,0	6,2	60,6	5,0	5,9	95
XII	*p*-ClC_6H_4	H	H	117—118	$C_{10}H_8NO_2Cl$	0,57	56,9	4,1	6,2	57,3	3,8	6,7	98

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* Mp 131.5-132° [2], 94-95° [4] (the difference between the melting points is apparently explained by the fact that the authors isolated the alkynyl carbamate rather than the cyclic product).

† Mp 97.5-98° [2].

3-Aryl-4-methylene-5,5-alkyl(dialkyl)oxazolidin-2-one (IX-XII, Table 2). A 0.025-g sample of pyridine or triethylamine was added to 5 mmole of the alkynyl arylcarbamate, and the mixture was heated on an oil bath at a temperature 10-20° higher than the melting point of the starting material for 4-8 h. The products obtained were recrystallized from octane.

Carboxymethyl Carbamate (XIII). A) Finely ground potassium permanganate (4.5 g) was added in portions with vigorous stirring in the course of 5 h to a cooled (to 5-8°) mixture of 3 g of X in 40 ml of water. The next day, the mixture was stirred for 2 h, after which it was filtered, and the filtrate was washed repeatedly with hot water. The aqueous solution was evaporated to dryness, and the residue was acidified with dilute (1 : 1) hydrochloric acid (3-4 ml). The acidic mixture was extracted with ether, the ether was removed at room temperature, and the residue was recrystallized from water. The yield of ester XIII with mp 140° was 1.2 g (36%). Found, %: N 7.23. $C_9H_9O_4$. Calculated, %: N 7.18. Heating of the latter at 140-160° for 0.5-1 h gave 3-phenyloxazolidine-2,4-dione with mp 124-126°. No melting-point depression was observed for a mixture of this product with a genuine sample.

B) A 0.17-g (0.1 mole) sample of 3-phenyloxazolidine-2,4-dione was added to a solution of 0.056 g (0.1 mole) of potassium hydroxide in 5 ml of water, and the resulting solution was acidified with hydrochloric acid, and the newly generated crystals were removed by filtration to give 0.15 g (80%) of a product with mp 140-141°.

Hydrolysis of 3-Phenyl-4-methylene-5,5-dimethyloxazolidin-2-one (IX). A mixture of 1 g (5 mmole) of 3-phenyl-4-methylene-5,5-dimethyloxazolidin-2-one, 10 ml of concentrated hydrochloric acid, and 2.5 ml of water was refluxed until the oxazolidinone had dissolved completely. The water was removed from the resulting solution and the residue was washed repeatedly with ether. The mixture was filtered to give (96%) of aniline hydrochloride with mp 189-191°. The ether was removed from the filtrate, and the residue was dissolved in ethanol to give 3-methyl-3-hydroxy-2-butanone, which was isolated in the form of the 2,4-dinitrophenylhydrazone with mp 139-140° [7].

LITERATURE CITED

1. V. V. Doblatyan and É. N. Ambartsumyan, Arm. Khim. Zh., 23, 173 (1970).
2. US Patent No. 2844590 (1958); Chem. Abstr., 53, 2255 (1970).
3. S. L. Shapiro, W. Bandurco, and L. Freedman, J. Org. Chem., 26, 3710 (1961).
4. P. R. Easton, D. R. Casady, and R. D. Dillard, J. Org. Chem., 27, 2927 (1962).
5. K. Nakanishi, Infrared Spectra and Structure of Organic Compounds [Russian translation], Mir, Moscow (1965), p. 28.
6. A. J. Speziale and L. R. Smith, J. Org. Chem., 27, 3742 (1962).
7. M. E. Lablinc, Comptes Rend., 127, 66 (1968); Beilstein, 12, 340.
8. C. R. Matsoyan, G. A. Chukhadzhyan, and S. A. Vartanyan, Zh. Obshch. Khim., 30, 1202 (1960).