SYNTHESIS OF N-VINYLOXYETHYLATED AMIDES AND UREAS

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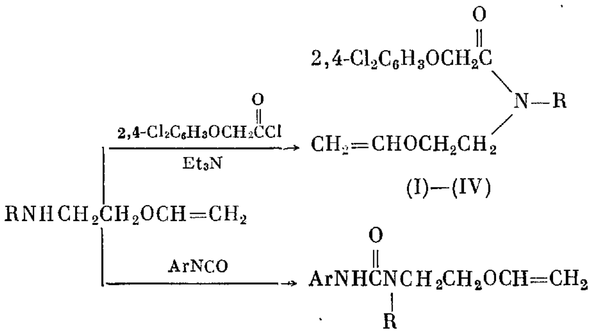
UDC 542.91:547.398.1:547.496.3

Halo-containing aryloxycarboxylic and benzoic acids and their derivatives, especially their amides, and urea derivatives have broad use in agriculture as efficient herbicides [1-7]. The preparation of amides and urea derivatives, containing vinyl ether fragments, is of considerable interest for expanding the assortment of physiologically active, including phytotoxic, vinyl monomers and obtaining from them biologically active polymeric products with a prolonged action. The purpose of the present paper is to determine whether N-vinyloxyethylated amides and ureas can be obtained by starting with the readily available vinyl ethers of amino and ketimino alcohols and acylating agents.

By reacting the vinyl ethers of monoethanolamine and N-benzylethanolamines, obtained by the reduction of the N-vinyloxyethylated Schiff bases of aromatic aldehydes with $NaBH_4$ [8], with 2,4-dichlorophenoxyacetyl chloride, phenyl isocyanate, and o-chlorophenyl isocyanate, we synthesized for the first time, in high yields, the amides (I)-(IV) and ureas (V)-(XI), which contain vinyl ether fragments.

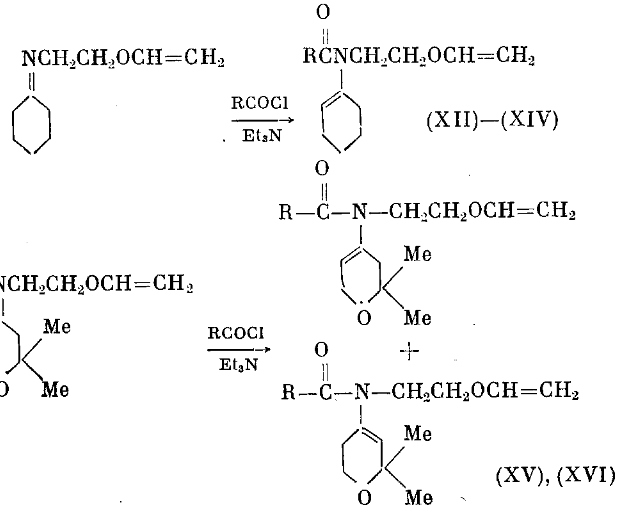


(I)—(IV)

(V)—(XI)

$R = H$ (I), (V), (VI); $C_6H_5CH_2$ (II), (VII); $4\text{-}Me_2NC_6H_4CH_2$ (III), (VIII), (IX); $4\text{-}MeOC_6H_4CH_2$ (IV), (X); CH=CH—CH=C—CH_2 (XI) $Ar = C_6H_5$ (V), (VII), (VIII), (X), (XI); $2\text{-}ClC_6H_4$ (VI), (IX).

The IR spectra of (I)-(XI) have bands in the regions 1210-1215, 1620-1670, and 3120-3130 cm^{-1}, which are characteristic for oxyvinyl and amide groups.



(XII)—(XIV)

(XV), (XVI)

$R = 2\text{-}ClC_6H_4$ (XII), (XV); $4\text{-}ClC_6H_4$ (XIII), (XVI); $2,4\text{-}Cl_2C_6H_3OCH_2$ (XIV).

Chemical and Metallurgical Institute of the Academy of Sciences of the Kazak SSR, Karaganda. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1893-1896, August, 1981. Original article submitted November 26, 1980.

0568-5230/81/3008-1560$07.50

TABLE 1. Properties of N-Vinyloxyethylated Amides and Ureas (I)-(XVI)

Compound	Yield, %	mp or bp (p, mm)	$\frac{\text{Found}}{\text{Calculated}}$, %				Empirical formula
			C	H	N	Cl	
(I)	62	80–81	48,80 49,66	4,51 4,48	4,90 4,83	23,81 24,48	$C_{12}H_{13}Cl_2NO_3$
(II)	73	73–74	59,57 60,00	5,51 5,00	4,05 3,68	18,13 18,68	$C_{19}H_{19}Cl_2NO_3$
(III)	69	84–85	59,20 59,57	5,70 5,67	6,69 6,62	17,00 16,78	$C_{21}H_{24}Cl_2N_2O_3$
(IV)	64	81–82	58,57 58,54	5,32 5,12	3,65 3,41	16,57 17,32	$C_{20}H_{21}Cl_2NO_4$
(V)	98	97–98	63,44 64,08	7,02 6,80	13,83 13,59	–	$C_{11}H_{14}N_2O_2$
(VI)	96	92–93	54,60 54,88	5,70 5,41	11,65 11,64	13,76 14,76	$C_{11}H_{13}ClN_2O_2$
(VII)	89	88–89	73,01 72,97	6,44 6,76	9,49 9,46	–	$C_{18}H_{20}N_2O_2$
(VIII)	95	104–105	70,08 70,80	7,44 7,37	12,64 12,39	–	$C_{20}H_{23}N_3O_2$
(IX)	93	63–64	64,40 64,25	5,80 6,42	11,20 11,24	10,00 9,50	$C_{20}H_{24}ClN_3O_2$
(X)	91	84–85	70,97 69,94	6,51 6,75	8,67 8,59	–	$C_{19}H_{22}N_2O_3$
(XI)	93	63–64	66,85 67,13	6,17 6,29	10,21 9,79	–	$C_{16}H_{18}N_2O_3$
(XII) [a]	81	165–167 (1,5)	66,79 66,78	6,31 6,54	4,92 4,58	11,08 11,62	$C_{17}H_{20}ClNO_2$
(XIII) [b]	83	154–155 (1,0)	66,62 66,78	6,71 6,54	4,73 4,58	11,17 11,62	$C_{17}H_{20}ClNO_2$
(XIV)	61	78–79	59,20 58,38	5,90 5,68	3,70 3,78	18,49 19,19	$C_{18}H_{21}Cl_2NO_3$
(XV) [c]	74	172–173 (1,5)	64,13 64,38	6,70 6,56	4,79 4,17	10,09 10,58	$C_{18}H_{22}ClNO_3$
(XVI) [d]	78	161–162 (1,0)	64,90 64,38	6,38 6,56	4,64 4,17	10,68 10,58	$C_{18}H_{22}ClNO_3$

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[a] n^{20}_D 1,5482, d^{20}_4 1,1510.

[b] n^{20}_D 1,5552, d^{20}_4 1,1544.

[c] n^{20}_D 1,5390, d^{20}_4 1,1682.

[d] n^{20}_D 1,5450, d^{20}_4 1,1706.

As was shown by us previously [9], the reaction of the N-vinyloxyethylated Schiff bases of carbonyl compounds that have H atoms on the α,α' C atoms with acyl halides is regioselective and leads to the formation of the N-acylation products. The use of the acid chlorides of the o-chlorobenzoic, p-chlorobenzoic, and 2,4-dichlorophenoxyacetic acids as the acylating agents in the reaction with 2-vinyloxy-N-cyclohexylideneethylamine and 4-[(2-vinyloxyethyl)-imino]-2,2-dimethyltetrahydropyran, obtained as was described in [10], led to the N-vinyloxyethylated amides of the cyclohexene (XII)-(XIV) and dihydropyran series (XV) and (XVI) as shown on previous page.

Compounds (XII), (XIII), (XV), and (XVI) are viscous oils that easily distill in vacuo. In the PMR spectra, besides the signals of the protons of the aromatic ring and vinyloxyethyl group, are present the signals of the vinyl protons of the cyclohexene and dihydropyran rings in the 5.2-5.6 ppm region. By determining the ratios of the integral intensities of the signals of the vinyl protons on the C^3 and C^5 atoms of the pyran ring it was established that compounds (XV) and (XVI) represent a mixture of isomers that differ in the position of the double bond.

In the initial tests on sugar beet, carried out in the All-Union Scientific Research Institute of Chemical Agents for Plant Protection, amide (XIV) displayed herbicidal activity. Based on the data of testing the phytotoxic activity by the method of Yu. A. Shcheglov and Ya. Yu. Starosel'skii under laboratory, vegetative, and field conditions,* compounds (I), (II), (IV), (IX), (VI), and (XI), at a concentration of 10 kg/hectare, exhibit herbicidal activity toward dicotyledonous plants.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument, and the PMR spectra were recorded on a Tesla BS0487C spectrometer (80 MHz, internal standard = HMDS).

N-(2-Vinyloxyethyl)-2,4-dichlorophenoxyacetamide (I). With cooling and stirring, to a mixture of 4.8 ml (0.05 mole) of monoethanolamine vinyl ether and 5.06 g (0.05 mole) of Et_3N in 50 ml of abs. benzene were slowly added dropwise 12.0 g (0.05 mole) of 2,4-dichlorophenoxyacetyl chloride in 30 ml of benzene. Then the mixture was stirred for 30 min at 40-45°C, cooled, and filtered. After removing the benzene on a rotor evaporator we obtained 8.99 g (62%) of (I) as white scales with mp 80-81°.

The other vinyl ethers of the 2,4-dichlorophenoxyacetamido alcohols (II)-(IV) were obtained in a similar manner (Table 1).

N-(4-Dimethylamino)benzyl-N-(2-vinyloxy)ethyl-N'-phenylurea (VIII). With vigorous stirring, to 11.5 g (0.052 mole) of N-(2-vinyloxy)ethyl-N-(4-dimethylamino)benzylamine in 30 ml of abs. benzene were slowly added dropwise 5.95 g (0.05 mole) of phenyl isocyanate. Then the mixture was stirred for 30 min at 50-60°. After the usual workup we obtained 16.2 g (95.6%) of (VIII) with mp 104-105°.

The (V)-(XI) derivatives were obtained under analogous conditions (see Table 1).

N-(1-Cyclohexene-1-yl)-N-(2-vinyloxyethyl)-o-chlorobenzamide (XII). With stirring and cooling with a water–ice mixture, to a mixture of 8.7 ml (0.05 mole) of 2-vinyloxy-N-cyclohexylideneethylamine and 5.05 g (0.05 mole) of Et_3N in 60 ml of abs. benzene were slowly added dropwise 8.7 g (0.05 mole) of o-chlorobenzoyl chloride. After the usual workup and vacuum distillation we obtained 12.27 g (81%) of (XII), bp 165-167° (1.5 mm).

The other vinyl ethers of N-acylamino alcohols of the cycloalkene and dihydropyran series, (XIII)-(XVI), were obtained under the above described conditions (see Table 1).

CONCLUSIONS

N-Vinyloxyethylated amides were synthesized by reacting the vinyl ethers of amino and ketimino alcohols with the acid chlorides of the 2,4-dichlorophenoxyacetic, o-, and p-chlorobenzoic acids, while the previously unknown N-vinyloxyethylated derivatives of ureas were obtained from the vinyl ethers of amino alcohols and aryl isocyanates.

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CHROMIUM ARENEACETYLENIC CHELATE COMPLEXES

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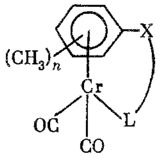
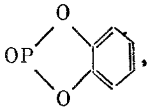
UDC 542.91:541.49:547.1'13:546.765

As a continuation of synthesizing arene chelate complexes (I) [1-5] we obtained the previously unknown areneacetylenic chelate complexes (IIIb-e) ($L=C\equiv CCH_3$).

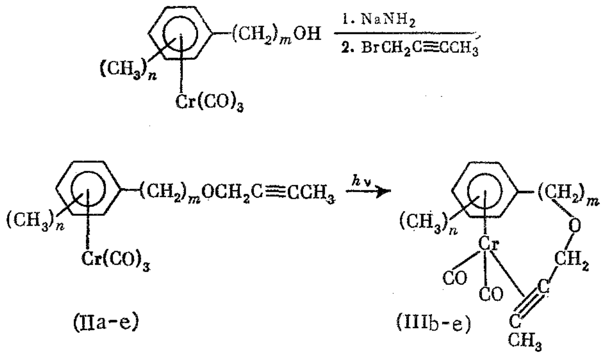


(I)

$L = CH = CH_2$, $OPPh_2$, $OP(OPh)_2$, , OPF_2; X = bridge, composed of $(CH_2)_m$ or various combinations of CH_2 and O.

For this purpose we synthesized the arenechromium tricarbonyl complexes (IIa-e). To insert the methylacetylenic group in the side chain of the arene ligand, the arenechromium tricarbonyl complexes with phenol [6] or with hydroxyalkylarenes [2, 3] were treated in succession with $NaNH_2$ and 1-bromo-2-butyne in either dimethoxyethane or diglyme.

Intramolecular π coordination of the acetylenic ligand to give chelates (IIIb-e) occurs when the arenechromium tricarbonyl complexes (II), containing a methylacetylenic grouping in either the γ, δ, or ε position of the side chain (m = 1-3), are irradiated with UV light.



(IIa-e) (IIIb-e)

$n = 0$, $m = 0$ (a); $n = 2\,[3,5\text{-}(CH_3)_2]$, $m = 1$ (b); $n = 2\,[3,5\text{-}(CH_3)_2]$, $m = 2$ (c); $n = 3\,[2,4,6\text{-}(CH_3)_3]$, $m = 2$ (d); $n = 3\,[2,4,6\text{-}(CH_3)_3]$, $m = 3$ (e).

In contrast to the chromium areneolefinic chelates (I) [1], stable (III) chelates are formed in the case of the 3- and 4-atom bridges (m = 1, 2), connecting the arene and acetylenic ligands, and not of the 2- and 3-atom bridges, like for (I) ($L=C\text{-}CH_2$). Complex (IIIe) (5-atom bridge) is also formed, but is less stable than (IIIb-d). It should be mentioned that for the areneolefinic chelates (I) ($L=CH=CH_2$) a corresponding decrease in the stability was observed [1] beginning with the 4-atom bridge, whereas chelate (III) with a 2-atom bridge is not formed at all, while the UV irradiation of (IIa) leads to a

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0568-5230/81/3008-1563$07.50