2. It was found for the new radical that linear relationships exist between the HFC constants of the phosphorus nucleus and the temperature and the E_T parameter of the solvents.

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CONDENSATION OF MONOETHANOLAMINE VINYL ETHER WITH ALICYCLIC KETONES

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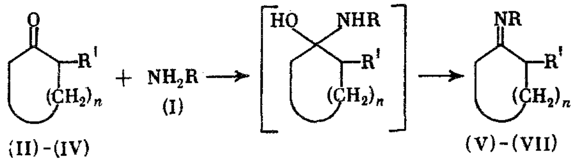
Previously [1] we described the condensation of monoethanolamine vinyl ether (I) with benzaldehydes and 2-furaldehyde. The condensation of (I) with various alicyclic ketones (II)-(IV) was studied in the present paper.

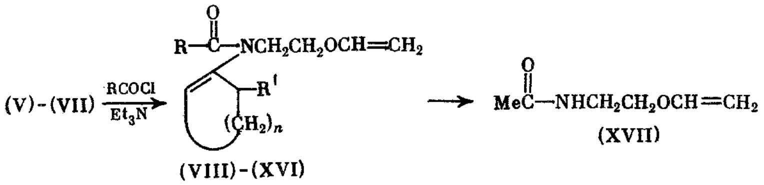
The reaction of (I) with ketones (II)-(IV) in benzene gave the new Schiff bases (V)-(VII), which contain the vinyl ether fragments, in 76-89% yield



$R = CH_2CH_2OCH{=}CH_2$ (I), (V)–(VII); $R' = H$ (III), (IV), (VI), (VII), Me (II), (V); $n = 2$ (IV), (VII), $n = 3$ (II), (III), (V), (VI)

Products (V)-(VII) are clear, colorless liquids with a characteristic odor, which are easily vacuum-distilled. In acid medium they hydrolyze to the starting compounds. The purity and structure of (V)-(VII) were confirmed by GLC, the elemental analysis data, and the IR spectra.

Together with using (I) to obtain Schiff bases, we checked the possibility of using (V)-(VII) to synthesize new polyfunctional vinyl monomers. As the result of reacting them with the acetyl, propionyl, and butyryl halides in the presence of Et_3N we obtain some new vinyl ethers of cycloalkenyl β-hydroxyethyl amides, and specifically (VIII)-(XVI).



R = Me (VIII), (XI), (XIV), Et (IX), (XII), (XV), Pr (X), (XIII), (XVI)

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TABLE 1. Physicochemical Characteristics of Synthesized Compounds

Compound	Yield, %	bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Found/calculated				Empirical formula
					MR	C, %	H, %	N, %	
(V)	81	105–107 (3,5)	1,4770	0,9317	54,84 / 54,79	73,23 / 72,92	10,54 / 10,49	7,55 / 7,73	$C_{11}H_{19}NO$
(VI)	89	123–125 (4)	1,4850	0,9570	50,10 / 50,14	71,67 / 71,85	9,79 / 10,18	8,02 / 8,38	$C_{10}H_{17}NO$
(VII)	76	93–94 (4)	1,4810	0,9567	45,44 / 45,50	70,85 / 71,24	9,84 / 9,80	8,72 / 9,15	$C_9H_{15}NO$
(VIII)	60	136–138 (2,5)	1,4880	0,9999	64,36 / 65,01	70,35 / 69,95	9,54 / 9,41	6,28 / 6,27	$C_{13}H_{21}NO_2$
(IX)	55	135–136 (2)	1,4895	0,9930	68,73 / 69,65	70,70 / 70,88	9,83 / 9,70	5,60 / 5,90	$C_{14}H_{23}NO_2$
(X)	52	151–152 (2,5)	1,4860	0,9799	73,51 / 74,31	71,66 / 71,71	9,99 / 9,96	5,48 / 5,57	$C_{15}H_{25}NO_2$
(XI)	61	136–138 (2,5)	1,4940	1,0205	59,78 / 60,24	68,67 / 68,89	8,82 / 9,09	6,69 / 6,69	$C_{12}H_{19}NO_2$
(XII)	56	126–127 (1,5)	1,4930	1,0095	64,22 / 64,88	69,73 / 69,95	9,32 / 9,46	6.20 / 6,27	$C_{13}H_{21}NO_2$
(XIII)	49	132–134 (1,5)	1,4910	1,0001	68,73 / 69,53	70,54 / 70,88	9,59 / 9,71	6,21 / 5,89	$C_{14}H_{23}NO_2$
(XIV)	53	126–127 (2,5)	1,4960	1,0302	55,28 / 56,71	67,58 / 67,69	8,97 / 8,71	7,10 / 7,17	$C_{11}H_{17}NO_2$
(XV)	57	118–119 (2)	1,4920	1,0109	59,98 / 61,35	68,40 / 68,89	8,70 / 9,09	7.03 / 6,69	$C_{12}H_{19}NO_2$
(XVI)	48	135–136 (2,5)	1,4900	0,9964	64,69 / 65,99	69,82 / 69,95	9,40 / 9,41	6,16 / 6,27	$C_{13}H_{21}NO_2$

Apparently, the same as in the case of N-(cycloalkylidene)alkylamines, the reaction includes electrophilic attack on the Schiff base: 1) of the N atom; 2) of the C atom with the cleavage of an α-H atom; 3) of the azomethine bond as a whole [2, 3].

The IR spectra of (VIII)-(XVI) contain a strong absorption band at 1660-1635 cm^{-1} (tertiary amide) and absorption bands of the vinyloxy group. The acetyl derivative (XVII), isolated by the hydrolytic cleavage of amide (XI), proved to be identical with the previously described [4] sample.

EXPERIMENTAL

The GLC was run on a Chrom-3 chromatograph, using a helium stream, a 300 × 0.3 cm stainless steel column packed with 15% poly(ethylene glycol adipate) deposited on Celite-503, and a katharometer as the detector. The IR spectra were recorded on a UR-20 spectrometer as a thin layer of the substance. The characteristics of the synthesized compounds are given in Table 1.

N-(Cyclohexylidene)-β-hydroxyethylamine vinyl ether (VI). A mixture of 9.8 g of freshly distilled cyclohexanone and 9.57 g of vinyl ether (I) in 60 ml of abs. C_6H_6 was heated in a flask, equipped with a water separator, until the liberation of water ceased. After distilling off the solvent we obtained 14.8 g (89%) of (VI). Compounds (V) and (VII) were obtained in a similar manner.

N-(Cyclohexen-1-yl)-β-hydroxyethylacetamide vinyl ether (XI). With vigorous stirring, to 12.3 g of acetyl bromide in 70 ml of abs. C_6H_6 at 0-5° was added dropwise 16.7 g of vinyl ether (VI), followed after 30 min by the slow addition of 10.1 g of Et_3N. After the reaction mixture had warmed up spontaneously to ∿20° the $Et_3N{\cdot}HCl$ precipitate was filtered, the filtrate was washed with water and dried over $MgSO_4$, and the solvent was distilled off. Vacuum-distillation of the residue gave 12.7 g (61%) of (XI).

Amides (VIII)-(XVI) were obtained in a similar manner.

Hydrolysis of (XI). A mixture of 3.0 g of (XI) and 10 ml of 12% HCl solution was heated for 3 h at 40°. After treating with potash the mixture was extracted with ether, the extract was washed in succession with 3% HCl solution, 5% NaOH solution, and water, dried over $MgSO_4$, and the solvent was distilled off. Vacuum-distillation of the residue gave 0.71 g of (XVII), bp 100-102° (3 mm); n_D^{30} 4648 (see [4]).

CONCLUSIONS

Schiff bases that contain vinyl ether fragments were synthesized by the condensation of monoethanolamine vinyl ether with cyclohexanone, 2-methylcyclohexanone, and cyclopentanone. Their reaction with carboxylic acid halides in the presence of triethylamine gives the vinyl ethers of cycloalkenyl hydroxyethyl amides.

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THERMAL REACTIONS OF AZULENES WITH MALONIC, DIPHENYLACETIC, AND HALOACETIC ACIDS

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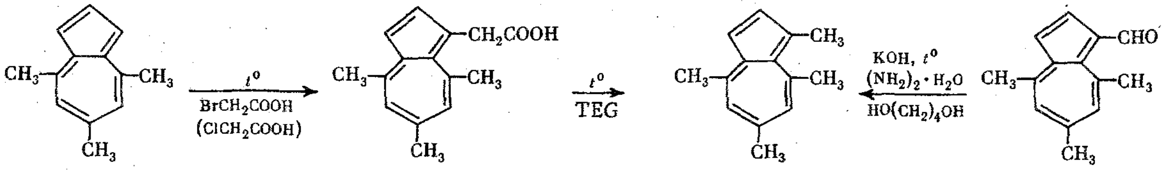
We found that the short heating at reflux of azulene with either diphenylacetic or malonic acid, without a catalyst, leads to the formation of mixtures of the corresponding 1-mono- and 1,3-diacylazulenes in respective yields of 55 and 1 or 22 and 5%. The acylation of 4,6,8-trimethylazulene (TMA) proceeds with the predominant formation of the 2-acyl derivatives (together with appreciable amounts of the 1-acyl-TMA in the reaction with malonic acid). The structure of the 1-acetyl derivatives of azulene and TMA (and also of 1,3-diacetylazulene) was proved by comparing their constants (melting point, R_f, and λ_{max}) with the data given in [1-3]. For the 2-acyl derivatives of TMA and all of the obtained ω,ω-diphenylacetylazulenes, after chromatographic purification, we determined the elemental composition and studied the UV and PMR spectra, which confirmed their structure. The thermal isomerization of the 1-acyl derivatives of TMA gives (to be sure, in lower yields) the above indicated 2-acyl derivatives, which can be considered as proof equivalent to counter synthesis, since similar 1—2 isomerization has been well studied [4-9].

The alkylation of azulene and its homologs under Friedel—Crafts conditions is directed to either the 1 or 3 position of the azulene ring, but because of the great sensitivity of azulenes to catalytic transformations [10, 11] these reactions always proceed to give low yields. For example, benzyl chloride under these conditions forms 1-benzylazulene in a total yield of 5.6% [11]. Alkyl halides give lower yields [1, 12]. The radical benzylation of azulene is also described [13].

It was shown by us that heating TMA with monobromo (or chloro-)acetic acid is accompanied by alkylation of the azulene ring in the 1 position, in which connection 4,6,8-trimethylazulenyl-1-acetic acid is formed in 30% yield.



(I) (II) (III)

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