4,4,5,5-Tetramethyl-2-aryl-2-oxazolines (Va,b). A mixture of 0.40 g (1.7 mmole) of aziridine IIIa in 10 ml of 96% sulfuric acid was heated at 100° for 15 min, after which the acid was neutralized with aqueous carbonate solution, and the oxazoline was extracted with chloroform. The extracts were dried with magnesium sulfate and vacuum evaporated. Recrystallization of the residue from hexane gave 0.32 g (82%) of oxazoline Va with mp 56.5-57°. IR spectrum (CCl_4): 1645 and 1075 cm^{-1}. UV spectrum, λ_{max} (log ε): 248 (4.52, in hexane); 250 nm (4.42, in ethanol). PMR spectrum (CCl_4): δ1.26 s, 1.41 s, 7.39 d, and 7.73 d (J = 8.5 Hz). Found: C 66.0; H 7.2; N 5.8%. $C_{13}H_{16}ClNO$. Calculated: C 65.7; H 6.8; N 5.9%.

Oxazoline Vb, with mp 83.5-84° (from hexane), was similarly obtained in 90% yield. IR spectrum (CCl_4): 1645 and 1063 cm^{-1}. UV spectrum, λ_{max} (log ε): 242 (4.54, in hexane) and 239 nm (4.52, in ethanol). PMR spectrum (CCl_4): δ 1.28 s, 1.41 s, 7.35, 7.58, and 7.83. Found: C 57.3; H 5.8; N 5.0%. $C_{13}H_{15}Cl_2NO$. Calculated: C 57.3; H 5.6; N 5.1%.

Aniline (an equimolar amount with respect to isocyanate IVa) was added to the products of photolysis of azide Ia in olefin II, and the precipitate was separated. The highly volatile compounds were removed in the vacuo from a portion of the solution containing, according to the PMR spectral data, 1.26 mmole of aziridine IIIa, and 7 ml of concentrated sulfuric acid was added dropwise with ice cooling to the residue. After 2 h, the mixture was worked up by the method described above to give, after vacuum distillation, 190 mg (64%) of oxazoline Va with mp 50-50.5° and bp 92-93° (10 mm).

LITERATURE CITED

1. Y. Hayashi and D. Swern, J. Am. Chem. Soc., 95, 5205 (1973).
2. V. P. Semenov, A. N. Studenikov, A. D. Bespalov, and K. A. Ogloblin, Zh. Org. Khim., 9, 1760 (1973).

ELECTROPHILIC SUBSTITUTION OF ACETAMIDO- AND ACETOXYBENZO-1,4-DIOXANES

V. K. Daukshas, G. V. Purvanetskas,
L. Z. Balyavichyus, É. B. Udrenaite,
and V. L. Gineitite

UDC 547.841;543.422.25.4

The products of acylation, bromination, and nitration of 5- and 6-acetamido- and 5- and 6-acetoxybenzo-1,4-dioxanes were established. It is shown on the basis of calculations by the self-consistent field (SCF) MO LCAO method that the directions of the electrophilic substitution reactions of these derivatives and of benzo-1,4-dioxane correspond to the π-electron population of the AO of the carbon atoms of the aromatic ring stipulated by the boundary occupied MO.

Substitution of acetamido- and acetoxybenzo-1,4-dioxanes and subsequent removal of the N- or O-acetyl substituents may serve as a method for the synthesis of new amino and hydroxy derivatives of this series, which are of interest for the preparation of physiologically active substances [1]. However, this synthetic method has not yet been developed sufficiently.

We have established that the reaction of 5-acetamidobenzo-1,4-dioxane (I) with acetyl or butyryl chlorides in the presence of $AlCl_3$ in carbon disulfide gives three acyl derivatives (II-IV or V-VII), whereas reaction in nitrobenzene gives practically only isomers III or VI, which are the products of thermodynamic control. The products of kinetic control (II, IV or V, VII) are converted to isomers III or VI when they are heated with $AlCl_3$ in nitrobenzene. Addition and reverse splitting out of substituents consequently occur at higher rates in the ring 6 and 8 positions than in the 7 position.

V. Kapsukas Vilnius State University, Vilnius 232734. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 467-473, April, 1977. Original article submitted April 14, 1976.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C (solvent)	Found, %			Empirical formula	Calc., %			UV spectrum		IR spectrum, cm^{-1}		PMR spectrum^a, δ, ppm
		C	H	N		C	H	N	λ_{max}, nm	lg ε	ν_{NH}	ν_{CO}	
II	150—151,5 (ethyl acetate)	61,1	5,6	5,8	$C_{12}H_{13}NO_4$	61,3	5,6	5,9	232 279	4,40 3,83	3300	1680	6,62 (d 8-H) 7,12 (d 7-H)
III	134—135,5 (benzene)	60,9	5,5	5,9	$C_{12}H_{13}NO_4$	61,3	5,6	5,9	243 284	4,40 3,98	3350	1690	7,22 (d 8-H) 7,83 (d 6-H)
IV	150,5—151,5 (methyl acetate)	61,2	5,3	5,8	$C_{12}H_{13}NO_4$	61,3	5,6	5,9	288	4,31	3360	1670	7,15 (d 6-H) 7,38 (d 7-H)
V	(Vitrifies)	63,7	6,5	5,6	$C_{14}H_{17}NO_4$	63,9	6,5	5,3	231 279	4,32 4,01	3330	1695	6,65 (d 8-H) 7,06 (d 7-H)
VI	108—109 (ethyl acetate)	63,7	6,6	5,6	$C_{14}H_{17}NO_4$	63,9	6,5	5,3	240 284	4,64 3,16	3420	1690	7,25 (d 8-H) 7,81 (d 6-H)
VII	118—119 (dipropyl ether)	63,8	6,5	5,2	$C_{14}H_{17}NO_4$	63,9	6,5	5,3	218 287	4,53 4,36	3325	1680	7,09 (d 6-H) 7,35 (d 7-H)
VIII	113,5—114,5 (isopropyl alcohol)	62,3	5,9	7,2	$C_{10}H_{11}NO_3$	62,2	5,7	7,2	237 285 354	4,51 4,12 3,66	3350	1650	6,80 (d 8-H) 7,40 (d 7-H)
IX	151—151,5 (isopropyl alcohol)	62,1	6,0	7,2	$C_{10}H_{11}NO_3$	62,2	5,7	7,2	232 294	4,22 3,86	3480 3400	1675	7,39 (d Ar-H) 7,45 (d Ar-H)
X	143,5—144,5 (isopropyl alcohol)	62,4	5,8	7,0	$C_{10}H_{11}NO_3$	62,2	5,7	7,2	249 321	4,18 4,34	3485 3355	1655	6,72 (d 6-H) 7,15 (d 7-H)
XII	129,5—130,5 (isopropyl alcohol)	61,5	5,4	—	$C_{10}H_{10}O_4$	61,8	5,2	—	222 291	4,33 4,01	3460 3360^b	1675	6,92 (s Ar-H)
XIV	156,5—157,5 (ether)	44,3	3,9	5,0	$C_{10}H_{10}BrNO_3$^{c}	44,1	3,7	5,1	217 256	4,64 4,32	3340	1680	6,79 (d Ar-H) 6,87 (d Ar-H)
XV	76,5—77,5 (pentane)	41,8	3,7	5,9	$C_8H_8BrNO_2$	41,8	3,5	6,1	215	4,70	3400	—	6,54 (d 6-H) 6,87 (d 7-H)
XXV	199,5—200,5 (ethanol)	61,2	5,5	5,8	$C_{12}H_{13}NO_4$	61,3	5,6	5,9	255 282 345	4,45 4,05 3,72	3225	1645	7,41 (s 5-H)
XXIX	85,5—86 (ethanol)	43,8	3,4	—	$C_{10}H_9BrO_4$^{d}	44,0	3,3	—	292	3,61	—	1715 1785	7,55 (s 8-H) 6,39 (s 5-H)
XXX	105—106 (ethanol)	50,0	3,9	5,8	$C_{10}H_9NO_6$	50,2	3,8	5,9	216 246 289 330	4,05 3,93 3,87 shoulder	—	1780	6,80 (s 8-H) 6,41 (s 5-H) 7,45 (s 8-H)
XXXII	221—222^e (water)	57,1	5,1	6,5	$C_{10}H_{11}NO_4$	57,4	5,3	6,7	236 300	3,97 4,37	3370 3240^b	1690	7,18 (s Ar-H)^f
XXXIII	283—285^e (methanol—water)	60,8	6,3	6,0	$C_{12}H_{15}NO_4$	60,8	6,4	5,9	218 303	4,25 4,21	3340 3250^b	1700	7,20 (s Ar-H)

---

[a] Chemical shifts: 0.58–0.61 (t, CH_3), 2.04–2.07 (s, $OCOCH_3$), 2.05–2.10 (s, $NCOCH_3$), 2.27–2.37 (s, $ArCOCH_3$), 2.65–2.70 (t, $ArCOCH_2$), 3.98–4.05 ppm (s, OCH_2CH_2O). The spin–spin coupling constants (J) of the aromatic protons of II, IV, V, VII, VIII, X, XIV, and XV are 8–9 Hz, as compared with 2–3 Hz for III, VI, and IX. [b] ν_{OH}. [c] Found: Br 29.4%. Calculated: Br 29.4%. [d] Found: Br 29.3%. Calculated: Br 29.3%. [e] With decomposition. [f] In deuteropyridine: 7.25 (d, 4-H) and 8.28 ppm (d, 5-H), J = 9 Hz.

TABLE 2. Calculated and Experimental Data on the Absorption

Compound	Calc. (within the PPP approximation)		Expt.	
	ΔE, eV	f	λ_{max}, eV	ε_{max}
I′	4,47; 5,11; 5,79; 6,05; 6,65	0,002; 0,364; 0,507; 0,653; 0,166	4,40; 5,02; 5,79;	2000; 8500; 26900;
I″	4,38; 4,97; 5,62; 5,89; 6,33	0,022; 0,179; 0,286; 0,864; 0,455	—*; 6,46	—; shoulder
XIX′	4,66; 5,64; 5,96; 6,09; 6,41	0,016; 0,047; 0,130; 0,131; 0,948	4,54; —; —;	2000; —; —;
XIX″	4,65; 5,60; 5,72; 6,11; 6,36	0,017; 0,038; 0,067; 0,196; 0,864	—; 6,17	—; 74600
XXIV′	4,38; 4,92; 5,97; 6,15; 6,57	0,074; 0,426; 0,477; 0,636; 0,555	4,25; 4,92; 5,82;	4300; 12300; 28800;
XXIV″	4,39; 4,91; 5,73; 6,16; 6,51	0,028; 0,538; 0,272; 0,354; 0,494	—; 6,39	—; shoulder
XXVIII′	4,46; 4,89; 5,67; 5,96; 6,46	0,062; 0,133; 0,049; 0,370; 0,858	4,38; —; 5,37;	3200; —; shoulder
XXVIII″	4,48; 4,90; 5,51; 5,72; 6,38	0,019; 0,227; 0,097; 0,008; 0,807	5,64; 6,14	shoulder 35300
XXXI	4,60; 5,58; 6,43; 6,56; 7,89	0,023; 0,122; 1,103; 0,817; 0,160	4,46; 5,60; 6,20; —; —	2900; 6500; 40000; —; —

---

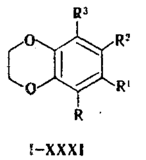
*The band is not visible.

TABLE 3. Results of the Calculation of the Structures of Molecules of the Compounds within the PPP or CNDO/2 Approximations

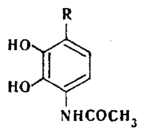
Calculated characteristics	Compound	Carbon atoms							Oxygen atoms			Nitrogen atom or ester oxygen atom
		5	6	7	8	angular		carbonyl	1	4	carbonyl	
						At 5-C	At 8-C					
AO π-electron population stipulated by the boundary occupied MO	I′	0,409	0,162	0,108	0,444	0,211	0,029	0,003	0,017	0,085	0,237	0,284
	I″	0,293	0,001	0,310	0,136	0,496	0,080	0,006	0,047	0,331	0,135	0,166
	XIX′	0,006	0,358	0,312	0,019	0,419	0,436	0,001	0,241	0,207	0,001	0,001
	XIX″	0,014	0,330	0,317	0,015	0,429	0,423	0,001	0,238	0,234	0,001	0,001
	XXIV′	0,034	0,331	0,269	0,061	0,219	0,436	0,008	0,219	0,103	0,140	0,179
	XXIV″	0,031	0,320	0,269	0,074	0,205	0,446	0,007	0,226	0,107	0,140	0,175
	XXVIII′	0,002	0,356	0,287	0,045	0,318	0,449	0,003	0,248	0,167	0,035	0,093
	XXVIII″	0,001	0,328	0,292	0,053	0,309	0,461	0,003	0,255	0,181	0,032	0,086
	XXXI	0,020	0,304	0,304	0,020	0,424	0,424	—	0,244	0,244	—	—
π-Electron charge on the atom	I′	−0,033	−0,030	+0,002	−0,042	−0,064	−0,006	+0,240	+0,064	+0,046	−0,486	+0,311
	I″	−0,038	−0,061	−0,008	−0,042	−0,034	−0,002	+0,242	+0,068	+0,058	−0,496	+0,316
	XIX′	−0,049	−0,005	−0,004	−0,017	−0,016	−0,010	+0,294	+0,048	+0,047	−0,424	+0,137
	XIX″	−0,049	−0,014	−0,008	−0,017	−0,007	−0,007	+0,294	+0,049	+0,049	−0,426	+0,138
	XXIV′	−0,085	−0,024	−0,031	−0,023	−0,014	−0,030	+0,235	+0,068	+0,069	−0,489	+0,325
	XXIV″	−0,049	−0,025	−0,067	−0,031	−0,006	−0,031	+0,235	+0,068	+0,072	−0,488	+0,323
	XXVIII′	−0,070	−0,029	−0,013	−0,026	−0,018	−0,025	+0,284	+0,068	+0,068	−0,416	+0,177
	XXVIII″	−0,030	−0,030	−0,051	−0,036	−0,010	−0,026	+0,286	+0,068	+0,071	−0,419	+0,177
	XXXI	−0,035	−0,016	−0,016	−0,035	−0,018	−0,018	—	+0,069	+0,069	—	—
Total charge on the atom	XXXI	−0,032	−0,001	−0,001	−0,032	+0,128	+0,128	—	−0,218	−0,218	—	—

Substituted pyrocatechins XXXII and XXXIII, which are evidently formed by dealkylation of IV and VII, were also isolated among the products of acylation of I in carbon disulfide. A mixture of IV and X was obtained by alkylation of derivative XXXII with 1,2-dibromoethane.

Compounds II-IV are hydrolyzed by hydrochloric acid to amines VIII-X. The latter are converted through their diazonium salts to hydroxy derivatives XI-XIII. Isomers XI and XIII are known [2], and the XII structure was therefore assigned to the their isomer. The structures of butyryl derivatives V-VIII and XXXIII were established by comparison of their UV and PMR spectra with the spectra of the acetyl analogs.



I-XXXI



XXXII, XXXIII

I R=NHCOCH$_3$, R^1=R^2=R^3=H; II R=NHCOCH$_3$, R^1=COCH$_3$, R^2=R^3=H; III R=NHCOCH$_3$, R^1=R^3=H, R^2=COCH$_3$; IV R=NHCOCH$_3$, R^1=R^2=H, R^3=COCH$_3$; V R=NHCOCH$_3$, R^1=COC$_3$H$_7$, R^2=R^3=H; VI R=NHCOCH$_3$, R^1=R^3=H, R^2=COC$_3$H$_7$; VII R=NHCOCH$_3$, R^1=R^2=H, R^3=COC$_3$H$_7$; VIII R=NH$_2$, R^1=COCH$_3$, R^2=R^3=H; IX R=NH$_2$, R^1=R^3=H, R^2=COCH$_3$; X R=NH$_2$, R^1=R^2=H, R^3=COCH$_3$; XI R=OH, R^1=COCH$_3$, R^2=R^3=H; XII R=OH, R^1=R^3=H, R^2=COCH$_3$; XIII R=OH, R^1=R^2=H, R^3=COCH$_3$; XIV R=NHCOCH$_3$, R^1=R^2=H, R^3=Br; XV R=NH$_2$, R^1=R^2=H, R^3=Br; XVI R=OH, R^1=R^2=H, R^3=Br; XVII R=NHCOCH$_3$, R^1=NO$_2$, R^2=R^3=H; XVIII R=NHCOCH$_3$, R^1=R^3=H, R^2=NO$_2$; XIX R=OCOCH$_3$, R^1=R^2=R^3=H; XX R=OCOCH$_3$, R^1=Br, R^2=R^3=H; XXI R=OCOCH$_3$, R^1=R^2=H, R^3=Br; XXII R=OCOCH$_3$, R^1=NO$_2$, R^2=R^3=H; XXIII R=OCOCH$_3$, R^1=R^3=H, R^2=NO$_2$; XXIV R=R^2=R^3=H, R^1=NHCOCH$_3$; XXV R=R^3=H, R^1=NHCOCH$_3$, R^2=COCH$_3$; XXVI R=R^3=H; R^1=NHCOCH$_3$, R^2=Br; XXVII R=R^3=H, R^1=NHCOCH$_3$, R^2=NO$_2$; XXVIII R=R^2=R^3=H, R^1=OCOCH$_3$; XXIX R=R^3=H, R^1=OCOCH$_3$, R^2=Br; XXX R=R^3=H, R^1=OCOCH$_3$, R^2=NO$_2$; XXXI R=R^1=R^2=R^3=H; XXXII R=COCH$_3$; XXXIII R=COC$_3$H$_7$

The reaction of I with bromine in CCl_4 gives only XIV, which is hydrolyzable to amine XV. The latter is converted through its diazonium salt to hydroxy derivative XVI, methylation of which leads to the known 5-bromo-8-methoxybenzo-1,4-dioxane [3].

A mixture of isomers XVII and XVIII in a ratio of 1:5, which have been synthesized by other methods [4, 5], is formed in the nitration of I with acetyl nitrate in acetic anhydride.

The bromination and nitration of 5-acetoxybenzo-1,4-dioxane (XIX) are described in [6]. We obtained more specific information to the effect that isomers XX and XXI are formed in a ratio of 5.4:1 in bromination and isomers XXII and XXIII are formed in a ratio of 3.7:1 in nitration.

The bromination and nitration of XXIV and XXVIII give 7-substituted derivatives XXVI, XXVII and XXIX, XXX, and the amounts of the other isomers do not exceed 3% of the amount of the principal reaction product.

The reaction of XXIV with acetyl chloride in the presence of $AlCl_3$ in carbon disulfide gives XXV, whereas the reaction in nitrobenzene gives a complex mixture of substances containing a small amount of this derivative.

Compounds XXVI and XXVII have been described [4, 7]. The structures of derivatives XXV, XXIX, and XXX are confirmed by the presence in their PMR spectra of two unsplit singlets of aromatic protons (Table 1).

In order to ascertain the reasons for the observed orientation of the substituents we calculated the electronic structures of the molecules of I, XIX, XXIV, and XXVIII by the self-consistent field (SCF) MO LCAO method within the Pariser–Parr–Pople (PPP) π-electron approximation and of the benzo-1,4-dioxane (XXXI) molecule with allowance also for all of the valence electrons [complete neglect of differential overlap (CNDO/2)]. Data on the geometry of the molecules of the benzo-1,4-dioxane series are not available, and the average bond lengths and valence angles were therefore, adopted [8]. The orientation of the acetamido and acetoxy substituents (in the form of planes) was examined in two conformations: with the CO group directed to the aromatic ring side (I', XIX', XXIV', and XXVIII') and to the heteroring side (I'', XIX'', XXIV'', and XXVIII'').

According to the NMR spectral data, XXXI exists in a half-chair conformation [9], and we adopted the same conformation for its 6-substituted derivatives (XXIV, XXVIII). The angles of rotation of the oxygen atoms in the 1 and 4 positions of the heteroring about the $C_{Ar}-O$ bond ($\varphi_1 = \varphi_2 = 23°$ for the half-chair conformation) were calculated from a CNDO/2 program. The angles of rotation of the nitrogen atom in XXIV of the ester oxygen atom in XXVII (φ_3) are zero degrees.

The calculated (PPP method) energies of the electronic transitions (ΔE) and the oscillator forces (f) of XXIV, XXVIII, and XXXI are in agreement with the experimentally determined λ_{max} and ε_{max} values of the absorption bands (Table 2).

Agreement between the calculated and experimental characteristics of the UV spectra of I and XIX is observed at φ_1, φ_2, and φ_3 angles of, respectively, 30, 40, and 20, and 43.5, 43.5, and 70°. This indicates the existence of I in a distorted boat conformation (the 1-O, 2-C, and 3-C atoms of the heteroring are coplanar with the angular carbon atom adjacent to the 4-O atom, and the latter and a second angular C atom are found under and above the plane), whereas XIX exist in boat conformation. Because of the low degree of informative character of the UV spectrum, the φ_i angles of XIX were established only approximately. The reason for the small φ_3 angle in the I molecule as compared with XIX may be the relatively large positive charge on the nitrogen atom (Table 3), which reduces its van der Waals radius, and also the greater length of the $C_{Ar}-N$ bond as compared with the $C_{Ar}-N$ bond as compared with the $C_{Ar}-O$ bond.

The data from the calculations (Table 3) show that the directions of the electrophilic substitution reactions of I, XIX, XXIV, and XXVIII are not determined by the charges on the carbon atoms of the aromatic ring but by the π-electron population of the atomic orbitals of these atoms stipulated by the boundary occupied molecular orbital. The latter factor is considered to be the deciding factor when the charges on the atoms are small [10]. The same also holds true for XXXI, since 6-substituted derivatives are formed in its substitution reactions [1]. Another factor that hinders substitution of benzo-1,4-dioxane derivatives in the 5 and 8 positions may be the necessity for an increase in angles φ_1 and φ_2 on conversion of the molecules of the reaction products to conformations of the boat type from half-chain conformations. The incorporation of a bromo substituent only in the 8 position of the ring of I can be explained by steric hindrance of the 6 position. The increased sensitivity of bromine as a reagent to steric effects has been noted [11]. The 6 position in the XIX molecule is probably hindered by the 5-substituent to a lesser degree. The possible reason for the primary formation of 6-substituted derivatives in the nitration of I and XIX is the ability of nitrating agents to add first to the acetamido or acetoxy groups and only subsequently to migrate to the closest ring position [11] (conformations I' and XIX'). The similar formation of 7-substituted derivatives may be the contribution of the less likely I'' and XIX'' conformations.

In the calculations within the PPP approximation hyperconjugation effects were not taken into account, the parameters in [12] were adopted, and the $\beta_{C_{Ar}-N}$ and β_{CO-N} resonance integrals were -2.82 and -3.03 eV. The φ_i angles were determined more precisely by multiplication of the resonance integrals by cos φ_i. The parameters in [13] were adopted for the calculations within the CNDO/2 approximation.

EXPERIMENTAL

The UV spectra of ethanol solutions of the compounds were recorded with Spektromom 202 (Table 1) or SF-16 (Table 2) spectrophotometers. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of CF_3COOH solutions were recorded with a BS 487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The isomer ratios were determined with an LKhM-8MD chromatograph with a 3-m long column; the stationary phase was 9% silicone rubber on Chromosorb W-AW, the carrier gas was helium, and the column temperature was 200-250°.

Acylation. A) A 24-g (0.18 mole) sample of anhydrous $AlCl_3$ was added at 5° to a solution of 9.7 g (0.05 mole) of I [14] and 0.15 mole of acetyl or butyryl chloride in 40 ml of CS_2, and the mixture was stirred and refluxed for 6 h, after which it was poured over ice. The precipitate was removed by filtration to give 1.1 g (11%) of XXXII or 1.6 g (14%) of XXXIII. The filtrate was extracted with $CHCl_3$, and the extract was concentrated (the ratio of isomers II, III, and IV was 1:1.6:0, and the ratio of isomers V, VI, and VII was 1:5.3:8.4) and passed through activity II Al_2O_3 [elution with benzene–acetone (2:1)]. The solvent was removed from the fraction with R_f 0.3-0.6 by distillation, and the residue was crystallized. The acetyl derivatives were crystallized from ethyl acetate to give 1.6 g (13%) of isomer II. The filtrate was evaporated, and the residue was crystallized from benzene to give 4.6 g (38%) of isomer III. The butyryl derivative was crystallized from dipropyl ether to give, initially, 3.2 g (24%) of isomer VII and, subsequently, 2.1 g (16%) of isomer VI. The filtrate was evaporated, and the residue was recrystallized from hexane to give 0.3 g (2%) of isomer V. Compound XXIV was acetylated similarly, and XXV was obtained in 85% yield.

B) Acylation in nitrobenzene was carried out at 60° for 6 h, and the products were isolated as in method A. Compounds III, IV, VI, and XXV were obtained in 56, 4, 58, and 8% yields, respectively.

Isomerization of II and IV. A solution of 0.35 g (1.5 mmole) of II or IV, 0.63 g (5 mmole) of anhydrous $AlCl_3$, and 0.23 g (3 mmole) of acetyl chloride in 4 ml of nitrobenzene was saturated with HCl, after which it was stirred at 50° for 6 h. It was then poured over ice, and the aqueous mixture was extracted with $CHCl_3$. The extract was investigated with a chromatograph. A mixture of isomers II with III (1:1) was obtained from II, and a mixture of III with IV (1:10) was obtained from IV.

Alkylation of XXXII. A 19.5-g (0.1 mole) sample of dibromoethane was added at 50° to a mixture of 4 g (0.02 mole) of XXXII, 3 g (0.03 mole) of K_2CO_3, and 40 ml of ethylene glycol, after which 5 g (0.05 mole) of K_2CO_3 was added at 130°, and the mixture was refluxed for 2 h. It was then poured into water, and the aqueous mixture was extracted with $CHCl_3$. The solvent was removed by distillation, and the resulting 3.9 g of a mixture of IV and X was hydrolyzed with HCl. The mixture was made alkaline and worked up to give 2.2 g (60% of X.

Hydrolysis of II-IV. A 0.015-mole sample of II-IV was refluxed with 70 ml of dilute HCl (1:1), after which the mixture was made alkaline. Amines VIII-X were obtained in ~ 90% yields. Compound XIV was similarly hydrolyzed, and XV was obtained in 93% yield.

Synthesis of XI-XIII. A solution of 0.9 g (0.013 mole) of $NaNO_2$ in 2 ml of water was added at 0° to a solution of 0.013 mole of VIII-X in 8 ml of dilute HCl (1:1). After 30 min, a solution of 2.1 g (0.013 mole) of $NaBF_4$ in 5 ml of water was added, and the mixture was stirred at 0° for 1 h. The precipitated diazonium tetrafluoroborates were removed by filtration. The crude compounds were obtained in 80-90% yields, and their IR spectra contained bands at 1075 (B-F) and 2250 cm^{-1} ($C\equiv N$). A 3.4-mmole sample of the tetrafluoroborate and 0.47 g (3.4 mmole) of Cu_2O were added to a solution of 216 g (0.9 mole) of $Cu(NO_3)_2$ in 360 ml of water, and the mixture was stirred at 20° until nitrogen evolution ceased. It was extracted with $CHCl_3$, and the extract was washed with 0.5% NaOH solution. The alkaline layer was acidified with HCl and extracted with CH_2Cl_2. The CH_2Cl_2 was removed by distillation. Workup gave 0.5 g (76%) of XI, 0.48 g (73%) of XII, and 0.55 g (80%) of XIII. Compound XV was converted to XVI by a similar method, and the crude product was obtained in 64% yield [6]. A mixture of 0.5 g (2 mmole) of XVI, 0.38 g (3 mmole) of dimethyl sulfate, 0.12 g (3 mmole) of NaOH, and 2 ml of water was refluxed for 5 h, after which it was worked up to give 0.37 g (70%) of the methyl ester [3].

Bromination. Bromination was carried out in CCl_4 with an equimolar amount of bromine at 10° (I and XXIV [15]) or 55° (XIX [2] and XXVIII [16]). Compounds XIV, XXVI, and XXIX were obtained in 86, 91, and 95% yields, and a mixture of XX and XXI was obtained in 82% yield.

Nitration. A mixture of 14 ml of acetic anhydride and 0.55 ml (15 mmole) of 99% HNO_3 was maintained at 25° for 30 min, after which it was added dropwise at 0° to a solution of 1.93 g (10 mmole) of I in 10 ml of acetic anhydride, and the mixture was stirred at 0° for 3 h. It was then poured into water, and the aqueous mixture was stirred at 40° for 20 min. It was then filtered to give 2.05 g (86%) of a mixture of nitro derivatives, which was refluxed with 10 ml of ethanol to dissolve isomer XVII [1.1 g (54%)]. Crystallization of the residue from acetone gave 0.2 g (10%) of isomer XVIII. Compound XXIV was nitrated similarly, and XXVII was obtained in 91% yield. Compounds XIX and XXVIII were nitrated at 10°, and a mixture of isomers XXII and XXIII was obtained in 93% yield; XXX was obtained in 88% yield.

The characteristics of the compounds that were synthesized for the first time are presented in Table 1.

LITERATURE CITED

1. V. K. Daukshas and É. B. Udrenaite, Khim. Geterotisikl. Soedin., No. 9, 1155 (1975).
2. V. K. Daukshas, B. A. Puodzhyunaite, and L. É. Mazhuolite, Zh. Org. Khim., 2, 301 (1966).
3. V. K. Daukshas, G. V. Purvanetskas, and G. B. Shebeka, Nauch. Tr. Vyssh. Uchebn. Zaved. Lit. SSR, Ser. Khim., 16, 153 (1974).
4. P. M. Heertjes, A. A. Nijman-Knape, H. Talsma, and N. J. Faason, J. Chem. Soc., No. 4, 1313 (1955).
5. P. M. Heertjes, A. A. Knape, and H. Talsma, J. Chem. Soc., No. 6, 1868 (1954).
6. V. K. Daukshas, and G. V. Purvanetskas, Nauch. Tr. Vyssh. Uchebn. Zaved. Lit. SSR, Ser. Khim., 16, 171 (1974).
7. P. M. Heertjes, A. A. Knape, H. Talsma, and P. Andriese, J. Chem. Soc., No. 1, 18 (1954).
8. Chemist's Handbook [in Russian], Vol. 1, Khimiya, Leningrad (1971), p. 352.
9. M. J. Cook, A. R. Katritzky, and M. J. Sewell, J. Chem. Soc., B, No. 6, 1207 (1970).
10. K. Fukui and H. Fujimoto, Bull. Chem. Soc. Jpn., 42, 3399 (1969).
11. D. E. Pearson and C. A. Buehler, Synthesis, No. 9, 455 (1971).
12. L. Z. Balyavichyus, V. A. Urba, L. N. Kidalova, A. B. Bolotin, and E. I. Shifrovich, Lit. Fiz. Sbornik, 15, 763 (1975).
13. J. A. Pople and G. A. Segal, J. Chem. Phys., 43, 136 (1965).
14. V. K. Daukshas and É. B. Udrenaite, Nauchn. Tr. Vyssh. Uchebn. Zaved. Lit. SSR, Ser. Khim., 18, 98 (1976).
15. P. M. Heertjes and L. Revallier, Rec. Trav. Chim., 69, 262 (1950).
16. V. K. Daukshas, I. A. Dembinskene, and Ya. B. Vitkunaite, Zh. Org. Khim., 5, 481 (1969).