N-Methyl-1,2,3,4-tetrahydropyrido[2,3-c]coumarin Methiodide (VI). A 0.24-g (10 mmole) sample of sodium hydride was added to a solution of 1.3 g (6.4 mmole) of pyridocoumarin V in 10 ml of dimethylformamide at 20°C, and the mixture was allowed to stand for 20 min. Methyl iodide (6 ml) was then added, and the mixture was heated at 40-42°C for 4 h. It was then cooled to 0°C, and the resulting precipitate was removed by filtration, washed with water, and dried to give 0.76 g (33%) of methiodide VI with mp 168-170°C (from alcohol). IR spectrum: 1700 (lactone $C=O$) and 1605 cm^{-1} ($C=C$). UV spectrum, λ_{max} (log ε): 280 (3.98) and 316 nm (3.73). Found: C 47.4; H 4.7; I 35.4; N 3.9%. $C_{14}H_{16}INO_2$. Calculated: C 47.1; H 4.5; I 35.5; N 3.9%.

1-Oxo-1H-2,3,4,5-tetrahydrobenzofuro[2,3-c]azepine (I). A solution of 1 g (4.5 mmole) of IX in 10 ml of trifluoroacetic acid was maintained at 20°C for 3 days, after which it was vacuum evaporated to dryness, and the residue was crystallized from alcohol to give 0.88 g (95%) of benzofuroazepine I with mp 244-246°C. IR spectrum: 3205 (NH) and 1645 cm^{-1} (amide $C=O$). UV spectrum λ_{max} (log ε): 279 nm (3.73). Found: C 72.2; H 5.6; N 7.0%. $C_{12}H_{11}NO_2$. Calculated: C 71.6; H 5.5; N 7.0%.

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N-ALKYLATION OF 1,4-DIHYDROPYRIDINE-3,5-DICARBOXYLIC ACID ESTERS

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UDC 547.827:542.953

Alkylation of the anions of 1,4-dihydropyridines (1,4-DHP) formed by treatment of sodium hydride in aprotic solvents gave 1-alkyl(up to C_6H_{13})-3,5-bis(ethoxycarbonyl)- and 1-alkyl-3,5-bis(aryloxycarbonyl)-1,4-DHP. The presence of a substituent in the 4 position increases the reactivity of the 1,4-DHP anion in the alkylation reaction. The absorption maximum in the UV spectra of the 1,4-DHP anion is shifted ~100 nm bathochromically as compared with the neutral molecule. The long-wave absorption maximum in the UV spectra of 1-alkyl-1,4-DHP is shifted hypsochromically as compared with the 1-unsubstituted compounds; this is explained by steric hindrance of the conjugation of the $C=O$ groups with the π-electron system of the ring. The introduction of an alkyl group at the nitrogen atom facilitates the electrical oxidation of 1,4-DHP.

1,4-Dihydropyridines (1,4-DHP) [1] have become important as antioxidants [2] and coronary-dilating [3] and hypotensive agents [4]. Less study has been devoted to 1-substituted 1,4-DHP, although as closer analogs of the redox enzyme NADH they may be of special interest.

Of the known methods for the preparation of 1-alkyl-1,4-DHP-3,5-dicarboxylic acid esters, the alkylation of 1,4-DHP anions is of greatest promise [5, 6]. The acid properties of 1,4-DHP-3,5-dicarboxylic acid esters (I) are weakly expressed, and a strongly alkaline agent such as sodium hydride is therefore necessary for the formation of anion II, and polar aprotic solvents promote the reactions [5-9].

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0009-3122/78/1411-1226\$07.50

TABLE 1. 1-Alkyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Esters (III)

Compound	R	R^1	R^2	X	Reaction condition[a] time, h	Reaction condition[a] temp., °C	mp, °C	Found, % C	Found, % H	Found, % N	Empirical formula	Calc., % C	Calc., % H	Calc., % N	Yield, %
IIIa	CH_3	C_2H_5	H	p-$CH_3C_6H_4SO_3$	1	20	85–86[b]								83
IIIb	C_2H_5	C_2H_5	H	I	1	20	62–63	63,8	8,4	4,9	$C_{15}H_{23}NO_4$	64.0	8,2	5,0	54
IIIc	n-C_3H_7	C_2H_5	H	p-$CH_3C_6H_4SO_3$	1	100	63–64	65,5	8,2	4,9	$C_{16}H_{25}NO_4$	65,1	8,5	4,7	58
IIId	C_2H_5	C_2H_5	CH_3	I	1	20	69	65,0	8,4	4,8	$C_{16}H_{25}NO_4$	65,1	8,5	4,7	67; 28[c]
IIIe	n-C_5H_{11}	C_2H_5	CH_3	Br	3	100	88–90	67,4	9,5	4,3	$C_{19}H_{31}NO_4$	67,6	9,3	4,2	65
IIIf	n-C_3H_7	C_2H_5	C_6H_5	I	2	100	92–93	71,6	8,0	3,5	$C_{22}H_{29}NO_4$	71,1	7,9	3,8	75
IIIg	n-C_4H_9	C_2H_5	C_6H_5	I	3	100	91–93	71,8	8,2	3,7	$C_{23}H_{31}NO_4$	71,7	8,1	3,6	62
IIIh	n-C_5H_{11}	C_2H_5	C_6H_5	Br	3	100	94–95	72,2	8,4	3,4	$C_{24}H_{33}NO_4$	72,2	8,3	3,5	73
IIIi	n-C_6H_{13}	C_2H_5	C_6H_5	I	3	100	56–58	72,7	8,7	3,4	$C_{25}H_{35}NO_4$	72,6	8,5	3,4	45[d]
IIIj	i-C_4H_9	C_2H_5	C_6H_5	Br	3	100	87–89	72,0	7,8	3,4	$C_{23}H_{31}NO_4$	71,7	8,1	3,6	35[d]
IIIk	n-C_4H_9	C_2H_5	$C_6H_4OCH_3$-p	I	3	100	79–81	69,3	8,0	3,5	$C_{24}H_{33}NO_5$	69,4	8,0	3,4	64
IIIl	n-C_5H_{11}	C_2H_5	$C_6H_4OCH_3$-p	Br	3	100	63–64	69,7	8,5	3,3	$C_{25}H_{35}NO_5$	69.9	8,3	3,3	68
IIIm	CH_3	C_2H_5	C_6H_4Br-m	I	1	20	108–109	57,0	5,8	3,3	$C_{20}H_{24}BrNO_4$[e]	56,9	5,7	3,3	64[c]
IIIn	CH_3	C_2H_5	C_6H_4Br-p	I	2	20	132–133	56,8	5,8	3,3	$C_{20}H_{24}BrNO_4$[f]	56,9	5,7	3,3	51[c]
IIIo	C_2H_5	C_2H_5	C_6H_4Br-p	I	1	20	79–81	57,9	5,9	3,1	$C_{21}H_{26}BrNO_4$[g]	57,8	6,0	3,2	46[c]
IIIp	C_2H_5	C_2H_5	$C_6H_4NO_2$-p	I	1	20	88	62,4	6,7	7,3	$C_{21}H_{26}N_2O_6$	62,7	6,5	7.0	55
IIIq	CH_3	C_6H_5	H	I	2	20	102–103	72,6	6,0	3,7	$C_{22}H_{21}NO_4$	72,7	5,8	3,9	76
IIIr	C_2H_5	C_6H_5	H	I	2	20	127–128	73,1	6,1	3,7	$C_{23}H_{23}NO_4$	73,2	6,1	3,7	81
IIIs	CH_3	$C_6H_4CH_3$-p	H	I	2	20	160–161	73,5	6,2	3,5	$C_{24}H_{25}NO_4$	73,6	6,4	3,6	79
IIIt	C_2H_5	$C_6H_4CH_3$-p	H	I	2	20	158	73.8	6,7	3,4	$C_{25}H_{27}NO_4$	74,0	6,7	3,5	87
IIIu	CH_3	$C_6H_4OCH_3$-p	H	I	2	20	128–130	68,0	6,0	3,2	$C_{24}H_{25}NO_6$	68,1	6,0	3,3	70
IIIv	C_2H_5	$C_6H_4OCH_3$-p	H	I	2	20	148–149	68,4	6,3	3,1	$C_{25}H_{27}NO_6$	68,6	6,2	3,2	82
IIIw	CH_3	$C_6H_4OCH_3$-m	H	I	2	20	111	67,9	6,3	3,3	$C_{24}H_{27}NO_6$	68,1	6,0	3.3	66

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a) In anhydrous hempa, except for specially indicated cases. b) According to the data in [7], this compound had mp 84-85°C and was obtained in 65% yield (X = I). c) In anhydrous tetrahydrofuran. d) Column chromatography on neutral activity II (Brockmann classification) Al_2O_3 with elution by chloroform–hexane–acetone (9:7:1) was used for the isolation. e) Found: Br 19.0%. Calculated: Br 18.9%. f) Found: Br 18.2%. Calculated: Br 18.9%. g) Found: Br 17.8%. Calculated: Br 18.3%.

TABLE 2. Spectra of 2,6-Dimethyl-3,5-bis-(ethoxycarbonyl)-1,4-DHP Anions (II, $R^1 = C_2H_5$) at 350-800 nm[a]

R^2	λ_{max}, nm (lg ε)	R^2	λ_{max}, nm (lg ε)
H	481 (3,83)[b]	$C_6H_4OCH_3$-*p*	453 (3,76)
CH_3	454 (3,79)[c]	$C_6H_4N(CH_3)_2$-*p*	454 (3,72)
C_6H_5	455 (3,78)	$C_6H_4NO_2$-*m*	454 (3,76)

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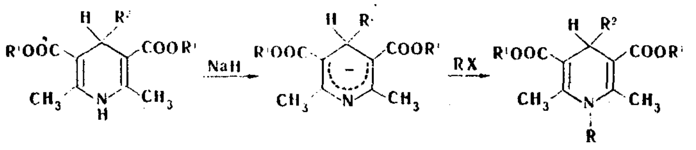
a) The arithmetic mean is presented. b) According to the data in [7], this value is 469 (4.05). c) According to the data in [7], this value is 441 (4.20).

Up until now no systematic study has been made of the effect of substituents (particularly a substituent in the 4 position) on the reactivities of 1,4-DHP (I) in alkylation reactions and of the possibility of the use of the method for the synthesis of 1-alkyl-3,5-bis(alkoxycarbonyl)1,4-DHP (III) with an alkyl chain longer than ethyl. 1-Alkyl derivatives of 3,5-bis(aryloxycarbonyl)-1,4-DHP were unknown.

In the present research we have obtained 1,4-DHP (III) with alkyl groups up to hexyl inclusively and have synthesized 1-alkyl-3,5-bis(aryloxycarbonyl)-1,4-DHP (IIIq-w) for the first time.



I II III a-w

III a $R=CH_3$, $R^1=C_2H_5$, $R^2=H$; b $R=R^1=C_2H_5$, $R^2=H$; c $R=n\text{-}C_3H_7$, $R^1=C_2H_5$, $R^2=H$; d $R=R^1=C_2H_5$, $R^2=CH_3$; e $R=n\text{-}C_5H_{11}$, $R^1=C_2H_5$, $R^2=CH_3$; f $R=n\text{-}C_3H_7$, $R^1=C_2H_5$, $R^2=C_6H_5$; g $R=n\text{-}C_4H_9$, $R^1=C_2H_5$, $R^2=C_6H_5$; h $R=n\text{-}C_5H_{11}$, $R^1=C_2H_5$, $R^2=C_6H_5$; i $R=n\text{-}C_6H_{13}$, $R^1=C_2H_5$, $R^2=C_6H_5$; j $R=i\text{-}C_4H_9$, $R^1=C_2H_5$, $R^2=C_6H_5$; k $R=n\text{-}C_4H_9$, $R^1=C_2H_5$, $R^2=C_6H_4OCH_3\text{-}p$; *l* $R=n\text{-}C_5H_{11}$, $R^1=C_2H_5$, $R^2=C_6H_4OCH_3\text{-}p$; m $R=CH_3$, $R^1=C_2H_5$, $R^2=C_6H_4Br\text{-}m$; n $R=CH_3$, $R^1=C_2H_5$, $R^2=C_6H_4Br\text{-}p$; o $R=R^1=C_2H_5$, $R^2=C_6H_4Br\text{-}p$; p $R=R^1=C_2H_5$, $R^2=C_6H_4NO_2\text{-}p$; q $R=CH_3$, $R^1=C_6H_5$, $R^2=H$; r $R=C_2H_5$, $R^1=C_6H_5$, $R^2=H$; s $R=CH_3$, $R^1=C_6H_4CH_3\text{-}p$, $R^2=H$; t $R=C_2H_5$, $R^1=C_6H_4CH_3\text{-}p$, $R^2=H$; u $R=CH_3$, $R^1=C_6H_4OCH_3\text{-}p$, $R^2=H$; v $R=C_2H_5$, $R^1=C_6H_4OCH_3\text{-}p$, $R^2=H$; w $R=CH_3$, $R^1=C_6H_4OCH_3\text{-}m$, $R^2=H$

The reaction was carried out by the successive action of sodium hydride and alkyl halides or p-toluenesulfonic acid esters on solutions of 1,4-DHP (I). The use of the sulfonic acid esters increases the yields of III by ~10%. An increase in the size of the alkyl group of the alkylating agent requires more severe conditions, namely, an increase in the polarity of the solvent and an increase in the temperature (Table 1). We were unable to obtain 1,4-DHP III (R = iso-C_3H_7, $R^1 = C_2H_5$, and $R^2 = C_6H_5$), and IIIj was formed in only 35% yield because of steric reasons [9].

In the case of 4-unsubstituted 1,4-DHP the yields of 1-alkyl derivatives III are lower than in the case of 4-substituted derivatives III, and an alkyl chain longer than n-propyl cannot be introduced. The steric effect of a substituent in the 4 position on the conjugation of substituents in the 3 and 5 positions with the dihydropyridine ring has already been noted [7, 11]. Analysis of the UV spectra of anions II showed that the same interrelationship also holds for dihydropyridine anions (Table 2). The conjugation of the substituents in the 3 and 5 positions with the dihydropyridine ring of 4-unsubstituted anions of 1,4-DHP II is expressed more strongly, and the negative charge on the nitrogen atom is therefore lower than in the case of the 4-substituted compounds regardless of the electronic character of the substituent in the 4 position, and a decrease in the reactivity is observed.

The introduction of a 1-methyl substituent in 1,4-DHP III gives rise in the UV spectrum to a hypsochromic shift of the long-wave maximum that is most characteristic for the 1,4-DHP system (Table 3); this is counter to the electron-donor character of the substituent. It is known that the introduction of alkyl groups at the nitrogen atom in β-aminovinylcarbonyl systems shifts the absorption maximum bathochromically (~10 nm) [16]. Consequently, the reason for the shift in our case must be sought in steric factors, which hinder conjugation of the C=O groups with the π-electron system of the ring [7]. The greatest shift in the series of

TABLE 3. UV and IR Absorption Spectra of 1-Alkyl-1,4-DHP III

Compound	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1} (% absorption)
IIIb	232 (4,31), 267 (4,13), 360 (3,95)	1692 (82), 1630 (73), 1570 (70)
IIIc	233 (4,29), 268 (4,15), 358 (3,92)	1690 (90), 1630 (82), 1572 (81)
IIId	235 (4,11), 263 (3,94), 351 (3,83)	1695 (71), 1632 (58), 1572 (52)
IIIe	235 (3,91), 264 (3,85), 351 (3,73)	1685 (88), 1625 (73), 1567 (72)
IIIf	205 (4,24), 243 (4,20), 353 (3,81)	1685 (78), 1630 (64), 1570 (66)
IIIg	205 (4,19), 243 (4,17), 350 (3,78)	1690 (80), 1635 (54), 1570 (48)
IIIh	205 (4,19), 243 (4,17), 349 (3,75)	1688 (82), 1630 (53), 1570 (51)
IIIi	205 (4,16), 243 (4,15), 348 (3,73)	1690 (87), 1630 (76), 1570 (72)
IIIj	205 (4,33), 240 (4,19), 344 (3,76)	1695 (78), 1635 (67), 1570 (70)
IIIk	202 (4,31), 226 (4,20), 257[a] (4,06), 284[a] (3,42), 349 (3,73)	1690 (84), 1630 (73), 1567 (74)
IIIl	202 (4,28), 227 (4,17), 259[a] (4,00), 284[a] (3,34), 348 (3,70)	1687 (74), 1625 (62), 1572 (70)
IIIm	203 (4,35), 242 (4,05), 355 (3,64)	1690 (75), 1635 (53), 1575 (57)
IIIn	203 (4,35), 223 (4,26), 244 (4,30), 353 (3,86)	1695 (65), 1668 (75), 1630 (56), 1575 (45)
IIIo	203 (4,34), 222 (4,25), 244 (4,28), 351 (3,81)	1690 (79), 1650 (50), 1582 (64)
IIIp	202 (4,49), 241 (4,20), 265[a] (4,03), 330[a] (3,64)	1685 (76), 1635 (61), 1570 (59)
IIIq	204 (4,35), 240 (4,26), 264[a] (4,09), 367 (3,89)	1700 (74), 1645 (60), 1625 (66), 1602 (73), 1575 (80)
IIIr	204 (4,31), 240 (4,20), 265[a] (4,07), 374 (3,85)	1712 (68), 1640 (64), 1582 (54)
IIIs	205 (4,26), 218[a] (4,21), 239 (4,14), 267 (4,04), 368 (3,78)	1715 (66), 1675 (48), 1635 (57), 1578 (38)
IIIt	206 (4,36), 218[a] (4,25), 239 (4,26), 266 (4,16), 372 (3,89)	1712 (70), 1638 (63), 1580 (55)
IIIu	203 (4,33), 225 (4,37), 238[a] (4,28), 268 (4,18), 367 (3,90)	1715 (72), 1640 (70), 1612 (55), 1582 (58)
IIIv	203 (4,31), 225 (4,33), 238[a] (4,21) 268 (4,13), 376 (3,82)	1712 (65), 1640 (63), 1578 (57)
IIIw	202 (4,20), 221 (4,19), 238[a] (3,97), 272 (3,88), 367 (3,58)	1705 (84), 1640 (72), 1605 (78), 1575 (75)

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a) Shoulder. Long-wave maxima in the UV spectra of known compounds I and III [R, R^1, R^2, λ, nm (literature λ_{max})]: H, C_2H_5, H, 373 (373 [12], 375 [13, 14]); CH_3, C_2H_5, H, 359 (355 [13]); H, C_2H_5, CH_3, 356 (350 [13]); CH_3, C_2H_5, CH_3, 352 (348 [13]); H, C_2H_5, C_6H_5, 360 (355 [13]); CH_3, C_2H_5, C_6H_5, 354 (355 [13]); H, C_2H_5, $C_6H_4OCH_3$-p, 359 (357 [14]); H, C_2H_5, C_6H_4Br-m (362 [15]); H, C_2H_5, C_6H_4Br-p (360 [15]); H, C_6H_5, H (384 [10]); H, $C_6H_4CH_3$-p, H (386 [10]); H, $C_6H_4OCH_3$-p, H (384 [10]); H, $C_6H_4OCH_3$-m, H (386 [10]). IR spectra in $CHCl_3$ [R, R^1, R^2, cm^{-1} (% absorption)]: H, C_2H_5, H, 1692 (95), 1625 (76); CH_3, C_2H_5, H, 1680 (93), 1645 (72), 1582 (76); H, C_2H_5, C_6H_5, 1692 (95), 1620 (68); CH_3, C_2H_5, C_6H_5, 1682 (93), 1640 (65), 1580 (68); H, C_6H_5, H, 1710 (91), 1660 (69), 1625 (78); CH_3, C_6H_5, H, 1702 (88), 1643 (74), 1612 (54), 1598 (56), 1580 (68).

ethyl esters III is observed in the case of 4-unsubstituted 1,4-DHP (14 nm); this effect is considerably smaller (3-8 nm) in the case of 4-substituted 1,4-DHP, in which conjugation is already partially disrupted. An increase in the length of the alkyl group gives rise to a small increase in the hyposchromic shift. Of all of the aryl esters III, the shift is a maximum for the 1-methyl derivatives (17-19 nm); it is somewhat smaller (10-14 nm) for III (R = C_2H_5).

The steric character of this phenomenon is confirmed by a comparison of the effect of 1 substitution in 1,4-DHP series that contain 3,5-ester and 3,5-cyano groups. In the latter series, in view of the small volume of the cyano group the steric effect of the adjacent substituents is smaller, and the introduction of a 1-alkyl substituent leads to a bathochromic shift of the maximum in the UV spectra in conformity with the electron-donor character of the substituent [7, 17].

The UV-spectral data are in agreement with the conclusions from an analysis of the Stuart—Brigleb models of the molecules. Free rotation of the ester groups about the C—C bond in the 3 and 5 positions is possible in the case of 1,4-unsubstituted I (R^1 = C_2H_5, R^2 = H), and conjugation of the C=O groups with the π-electron system of the ring consequently may be maximal. The introduction of a substituent (CH_3 or C_6H_5) in the 4 position

TABLE 4. Peak (E_p) and Half-Wave ($E_{1/2}$) Potentials in the Electrochemical Oxidation of 2,6-Dimethyl-3,5-bis(ethoxycarbonyl)-1,4-DHP (I and III, $R^1 = C_2H_5$)

R^2	R					
	H	CH_3	C_2H_5	n-C_3H_7	n-C_4H_9	n-C_5H_{11}
H	0,90[a]; 0,85[20]	0,88; 0,83				
CH_3	1,00; 0,92	0,92; 0,88[b]	0,92; 0,88			1,04; 1,01
C_6H_5	1,07; 1,02[19]	1,03; 0,95	1,04; 0,95	1,06; 1,02	1,05; 0,98	1,05; 1,03
$C_6H_4CH_3$-p	1,08; 1,00[19]	0,94; 0,90	0,96; 0,88		1,03; 0,96	1,03; 0,98
C_6H_4Br-p	1,11; 1,05[15]	1,00; 0,92	1,03; 0,94			
$C_6H_4NO_2$-p	1,22: 1,17[15]	1,08; 0,98				
$C_6H_4NO_2$-m	1,21; 1,13[15]	1,12; 1,03				
$C_6H_4NO_2$-o	1,11; 1,06[15]	1,01; 0,95				

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a) For each compound the first number is E_p, and the second number is $E_{1/2}$ (in volts). b) According to the data in [21], $E_{1/2}$ = 0.85 V (0.1 M $LiClO_4$ in 50% acetonitrile).

hinders free rotation, which becomes impossible for both ester groups simultaneously. Substituents in the 1 position, which fix the 2,6-methyl groups in such a way that it also hinders rotation of the ester groups, hinder the possibility of conjugation to an even greater extent.

Thus inhibition of conjugation in the case of introduction of a 1-alkyl group is more substantial in this case than the effect of the electronic character of the incorporated alkyl groups.

Three characteristic bands are observed in the IR spectra of 1-alkyl-1,4-DHP III in Nujol (Table 3) at 1560-1720 cm^{-1}. It seems likely that the high-frequency bands (~1690-1710 cm^{-1}) is due to C=O stretching vibrations [10 12]. The second band (~1630 cm^{-1}) evidently cannot be assigned to the vibrations of individual bonds; this band is due to vibrations associated with the entire system of conjugated bonds [18].

The origin of the third band (~1570 cm^{-1}), which is not present in the spectra of 1-unsubstituted 1,4-DHP but does appear in the spectra of 1-substituted 1,4-DHP [18], is not at all clear. In contrast to the spectra of 1-unsubstituted 1,4-DHP [10, 12, 18], the high-frequency band is the more intense of the first two bands. The spectra of III in chloroform do not differ substantially from the spectra of III in Nujol, whereas changes are observed in the spectra of 1-unsubstituted 1,4-DHP in chloroform: the high-frequency band also becomes more intense (Table 3; see also [18]).

The electrochemical oxidation (EO) of 1-alkyl-1,4-DHP III on a rotating platinum microanode in acetonitrile was studied (Table 4). The incorporation of an alkyl group at the nitrogen atom facilitates the electrochemical oxidation of 1,4-DHP; this is evidently associated with the electron-donor effect of the alkyl group. The 1-methyl derivatives are oxidized most easily, but the difference in the EO potentials between them and the corresponding I [15, 19, 20] in the case of different substituents in the 4 position ranges from 0.02 V, which is within the limits of the error in the measurements, to 0.15 V. The EO potentials increase as the substituent in the 1 position becomes longer. It may be assumed that in this case steric hindrance to the approach of a molecule to the electrode begins to prevail over the electronic character of the substituent. The effect of substituents in the 4 position on the EO potentials does not differ from the regularities observed in the 1-unsubstituted series [15].

We thank Academician of the Academy of Sciences of the Latvian SSR Ya. P. Stradyn' for his discussion of the EO data and I. V. Dipan for recording the IR spectra.

EXPERIMENTAL

The IR spectra of Nujol suspensions and $2.5 \cdot 10^{-2}$ M solutions of the compounds in $CHCl_3$ were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in alcohol were recorded with a Specord UV-vis spectrophotometer. The 1,4-DHP anions (II) were prepared for UV recording by the following method. A 0.60-g sample of sodium hydride was added in a nitrogen atmosphere to 30 ml of freshly distilled anhydrous dimethyl sulfoxide (DMSO), and the mixture was heated at 70°C for 1 h. It was then cooled and filtered through a No. 1 glass filter. A 1-ml sample of this solution was added to 1 ml of a $5 \cdot 10^{-4}$ M solution of 1,4-DHP in DMSO, and the overall volume was brought up to 10 ml. The spectra were recorded immediately after preparation of the samples in tightly sealed cuvettes (Table 2).

Dihydropyridines I ($R^1 = C_2H_5$) were obtained via the Hantzsch reaction by known methods [1], and 1,4-DHP I (R^1 = aryl) were obtained by the method in [10]. The known 1,4-DHP III were synthesized by our general method. The experimental electrical oxidation conditions were presented in [19].

N-Alkylation of 2,6-Dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Esters. Sodium hydride [0.14 g (6 mmole) in the preparation of 1-methyl and ethyl derivatives, and 0.18 g (7.5 mmole) in the case of 1-propyl and longer substituents] was added to a solution of 5 mmole of 1,4-DHP in 30 ml of anhydrous hempa (or tetrahydrofuran), as a result of which a vigorous reaction with hydrogen evolution was observed, and strongly colored (from orange to dark-brown) anion II, which gives characteristic green fluorescence, was formed. At the end of hydrogen evolution, the alkylating agent (10 mmole in the case of methyl or ethyl derivatives, and 15 mmole for all of the remaining derivatives) was added in the course of 30 min, and the mixture was warmed to the necessary temperature and maintained at that temperature for the indicated time (Table 1). It was then poured into 300 ml of 5% NH_4Cl, and the mixture was allowed to stand overnight. The semisolid alkylated compound was separated and crystallized from 80% alcohol.

The reaction with 4-unsubstituted 1,4-DHP was carried out in a nitrogen atmosphere.

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